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# Theoretical Study of Substituent Effects on the Lewis Acid−Base Property of Aminoboranes

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The reactivity of aminoboranes has been studied theoretically. We have derived the unoccupied reactive orbitals localized on the boron p$\pi$ atomic orbital and the occupied reactive orbitals localized on the nitrogen lone-pair orbital in these compounds. The Lewis acidity of the boron center and the Lewis basicity of the nitrogen center have been estimated, by which the effect of substituents on the reactivity of aminoboranes is systematically examined. The results show that the substituent effects in aminoboranes are somewhat different from those in other boranes and amines owing to the p$\pi$−p$\pi$ conjugation. The experimentally observed reactivity trend in [2 + 2] cycloaddition reactions has been found to be understood in terms of local characteristics of aminoboranes as a Lewis acid and as a Lewis base. This view has been suggested to be applicable to other types of reactions of aminoboranes.

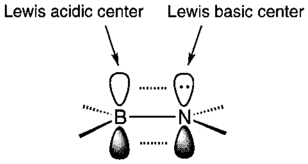
## Introduction

The nature of the B−N bond in aminoboranes, which shows similarity to the C−C double bond in alkenes in steric conformation, has been of considerable interest for many years.[1] A number of experimental and theoretical studies have been performed to quantify the $\pi$-bonding strength in these compounds.[2−12] It is now well-established that the B−N bond in aminoboranes has a double-bond character brought about by back-donation of the nitrogen lone pair of electrons to the boron p$\pi$ orbital, although the strength of conjugation is weaker in aminoboranes compared with that in alkenes.[13] Despite the isoelectronic and isosteric character of aminoboranes with alkenes, the reactivity of the B═N bond is not necessarily similar to that of C═C bonds. For example, aminoboranes readily form dimeric compounds,[14] while the [2 + 2] cycloaddition reaction does not occur thermally in alkenes. The reactivity of aminoboranes varies markedly, depending on the substituents. This has been made use of in syntheses.[15,16]

Two other aspects that make the understanding of reactivity in aminoboranes attractive and important should be emphasized here. First, unlike alkenes, a Lewis acidic center and a Lewis basic center coexist in aminoboranes (Scheme 1).

In performing asymmetric synthesis, catalysts having more than one active site have been paid much attention.[17,18] Thus, theoretical methods for evaluating the local activity of a reaction center in these compounds will be of great use in exploring the way of achieving a better enantioselectivity. Aminoboranes may be considered here to be the smallest molecular model having two active sites in a molecule. Second, the reactivity of tricoordinate boron compounds is known to be affected by the p$\pi$−p$\pi$ conjugation.[19,20] The electron-accepting level of boron is mainly determined by the electron-donating or -withdrawing power of a substituent through a $\sigma$-bond. The p$\pi$−p$\pi$ conjugation should be another significant factor that determines the reactivity of the boron center. These two factors may also be of importance in determining the reactivity of the nitrogen center. Since the two centers are located adjacent to each other in aminoboranes, the conjugation will affect both the Lewis acidity and the Lewis basicity of the active sites.

**SCHEME 1**



Unfortunately, only a few studies have been carried out theoretically to investigate the reactivity of aminoboranes,[21,22] and accordingly, little is known from a quantum chemical point of view about the chemical activities of these compounds. Gilbert has recently performed B3LYP calculations on the [2 + 2] dimerization reaction and the [4 + 2] cycloaddition reaction of aminoboranes.[21] He showed that the calculated structural and energetic data agreed well with the experimental results and interpreted qualitatively the reactivity trends in terms of steric and electronic factors.

In this paper, we examine systematically the reactivity of aminoboranes by applying an orbital interaction scheme that takes local characteristics of chemical reactions explicitly into account. The procedure permits us to evaluate the Lewis acidity of the boron center and the Lewis basicity of the nitrogen center in aminoboranes in a chemically graspable form. We analyze the substituent effects on the reactivity of several aminoboranes, and then discuss the electronic mechanism by which the reactivity varies depending on the substituent groups introduced. Two types of [2 + 2] cycloaddition reactions of aminoboranes, the cycloaddition reaction with isocyanic acid, and the dimerization reaction are studied, and the experimentally observed trends are compared with theoretically estimated activation energies.

## Computational Method

Geometry optimizations were carried out at the B3LYP/6-31G* level[23,24,25] by applying the Gaussian 98 program.[26] The exchange potential in B3LYP was the three-parameter hybrid functional of Becke,[23] and the correction potential was that of Lee, Yang, and Parr.[24] The B3LYP functional has been shown

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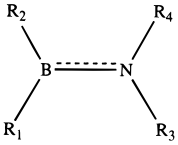
**SCHEME 2**



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| **1** | H | H | H | H |
| **2** | Me | H | H | H |
| **3** | Me | Me | H | H |
| **4** | H | H | Me | H |
| **5** | H | H | Me | Me |
| **6** | Cl | Cl | Me | Me |
| **7** | $CF_3$ | $CF_3$ | Me | Me |

to perform well for prediction of activation energies as well as geometries.[27] All of the optimized structures were verified to be the ground or transition states by vibrational frequency calculations at this level. Single-point B3LYP/6-31+G** calculations were carried out to estimate the activation energies. The calculated energies were corrected by zero-point energies scaled by a factor of 0.9804.[28] The Lewis acidity and basicity were estimated by using the molecular orbitals (MOs) with the 6-31G* basis set.[25]

## Results and Discussion

We have investigated several substituted aminoboranes. The species studied are shown below (Scheme 2). The [2 + 2] cycloaddition is one of the simplest chemical reactions that aminoboranes undergo. We focus our attention on this type of reaction to clarify the basic aspects of the electronic structure in aminoboranes to determine their reactivity.

**Reactive Orbitals.** Chemical interactions are local by nature; therefore, molecular orbitals which participate actively in chemical reactions should be localized well on the reaction center. Let us call these orbitals *reactive orbitals*. We have already presented the formulation of the theory in detail in our previous papers,[29] and therefore we just briefly describe the method used herein. In obtaining the reactive orbitals for a variety of molecules, we have to define at first common reference orbital functions $\delta_r$ for the Lewis acidic center and $\delta_s$ for the Lewis basic center that are most suited for representing the bond formation with the attacking reagent. Once the reference functions are defined, these can be written in the form of a linear combination of the occupied MOs $\phi_i$ ($i = 1, 2, ..., m$) and the unoccupied MOs $\phi_j$ ($j = m+1, m+2, ..., M$) of an aminoborane molecule. The unoccupied orbital that is localized to the maximum extent on $\delta_r$ of the acidic or electron-accepting center $r$ is given by

$$\phi_{\mathrm{unoc}}(\delta_r) = (\sum_{j=m+1}^{M} d_{j,r}\phi_j)/(\sum_{j=m+1}^{M} d_{j,r}{}^2)^{1/2} \tag{1}$$

where $d_{j,r}$ is the coefficient of $\delta_r$ expanded in the linear combination of the canonical MOs. Similarly, the occupied orbital that has the maximum amplitude on $\delta_s$ of the basic or electron-donating center $s$ is given by

$$\phi_{\mathrm{oc}}(\delta_s) = (\sum_{i=1}^{m} d_{i,s}\phi_i)/(\sum_{i=1}^{m} d_{i,s}{}^2)^{1/2} \tag{2}$$

For the purpose of determining the reference functions, $\delta_r$ and $\delta_s$, in aminoboranes, we have calculated the interaction frontier orbitals[30] with the 6-31G* basis set for the dimer of aminoborane, or cyclodiborazane. The geometry of this complex has been optimized at the B3LYP/6-31G* level of theory. The interaction orbital of an aminoborane fragment that plays the electron-acceptor part and that of the other aminoborane fragment that plays the electron-donor part have been derived by representing first the wave function of the dimer in terms of the electron configurations of the two aminoborane fragments[31] and then by applying a pair of unitary transformations of the canonical MOs within the unoccupied MO subspace of one $H_2B{=}NH_2$ molecule and within the occupied MO subspace of the other $H_2B{=}NH_2$ molecule. As a consequence, we have obtained a pair of fragment orbitals that represents $B{\leftarrow}N$ electron delocalization in the dimer system. The interaction frontier orbitals derived in this way are shown in Figure 1.

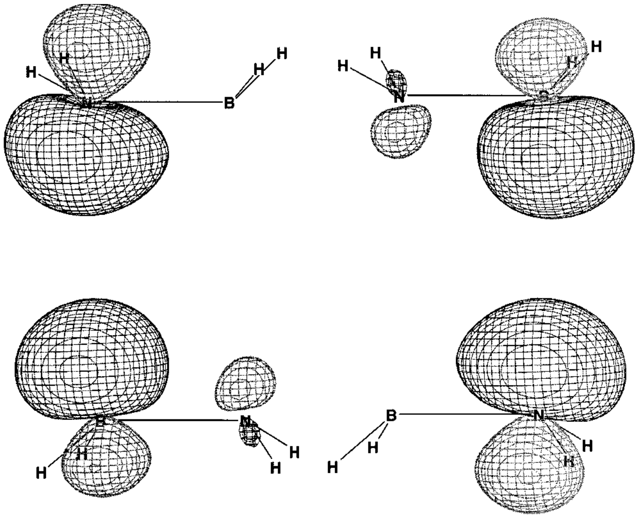


**Figure 1.** Unoccupied and occupied interaction frontier orbitals of **1** taking part in electron delocalization from the monomer located above to the monomer located below (left) and from the latter to the former (right) in the dimer. They were obtained by carrying out unitary transformations of the MOs of the two fragments to represent orbital interactions in terms of pairs of fragment orbitals.

The major components of the unoccupied interaction frontier orbital have been shown to be the s and $p_z$ atomic orbitals (AOs) of the boron atom, where the $z$-axis has been taken along the B−N bond. The difference in Lewis acidity of aminoboranes may be discussed in a planar monomeric form, and we assume here that the p$\pi$-type AO function having an extension perpendicular to the molecular plane plays the major role. Thus, we have taken the $p_z$ AO components of the boron in the unoccupied interaction frontier orbital as the reference orbital for the Lewis acidic center. On the other hand, the occupied interaction frontier orbital has been accounted for dominantly by the s and $p_z$ AOs of the nitrogen atom. The s functions do not need to be considered here for the above-mentioned reason. Thus, we have taken the $p_z$ AO components of the nitrogen in the occupied interaction frontier orbital as the reference orbital for the Lewis basic center. The unoccupied reactive orbital $\phi_{\mathrm{unoc}}(\delta_r)$ and the occupied reactive orbital $\phi_{\mathrm{oc}}(\delta_s)$ of **1** obtained by using $\delta_r$ and $\delta_s$ determined above are presented in Figure 2. The former is seen to be localized on the boron, and the latter is localized on the nitrogen. It is interesting to note, however, that the reactive orbitals obtained in this manner are delocalized to some extent over the adjacent atom, suggesting that the $B{\leftarrow}N$ $\pi$ back-donation should have an influence on the reactivity. One may find that the reactive orbitals derived by projection of the reference functions onto the MOs of aminoborane in an isolated state bear a close resemblance to the pair of interaction frontier

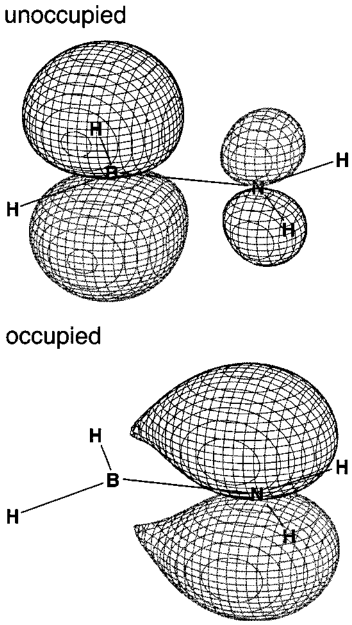


**Figure 2.** Unoccupied and occupied reactive orbitals of aminoborane **1** in a planar monomeric form. They were obtained by projecting the reference orbital functions $\delta_r$ and $\delta_s$ onto the RHF/6-31G* unoccupied and occupied MO subspaces of **1**, respectively.

orbitals that have been obtained from an analysis of the wave function for the cycloadduct of the reaction.

**Substituent Effects on the Lewis Acidity and Lewis Basicity.** The levels of the reactive orbitals localized on the Lewis acidic center $r$ and the Lewis basic center $s$ are estimated by

$$\lambda_{\mathrm{unoc}}(\delta_r) = \Big(\sum_{j=m+1}^{M} d_{j,r}{}^2 \epsilon_j\Big)\Big/\Big(\sum_{j=m+1}^{M} d_{j,r}{}^2\Big) \qquad (3)$$

and

$$\lambda_{\mathrm{oc}}(\delta_s) = \Big(\sum_{i=1}^{m} d_{i,s}{}^2 \epsilon_i\Big)\Big/\Big(\sum_{i=1}^{m} d_{i,s}{}^2\Big) \qquad (4)$$

where $\epsilon_j$ and $\epsilon_i$ signify the orbital energies of the component canonical MOs $\phi_j$ and $\phi_i$, respectively. By representing the denominators of the right-hand sides of eqs 2 and 3 by $(1 - a^2)^{1/2}$ and $b^2$, respectively, we obtain

$$\delta_r = a\phi_{\mathrm{oc}}(\delta_r) + (1 - a^2)^{1/2}\phi_{\mathrm{unoc}}(\delta_r) \qquad (5)$$

and

$$\delta_s = b\phi_{\mathrm{oc}}(\delta_s) + (1 - b^2)^{1/2}\phi_{\mathrm{unoc}}(\delta_s) \qquad (6)$$

It is evident from eqs 5 and 6 that $(1 - a^2)$ represents the vacancy of the Lewis acidic center $r$, while $b^2$ indicates the occupancy of the Lewis basic center $s$ by electrons. Thus, we can measure by $(1 - a^2)$ and $b^2$ how efficiently a reacting molecule can use its Lewis acidic center and Lewis basic center for interaction with an attacking reagent, respectively. Now, by applying the second-order perturbation scheme, we may define the *Lewis acidity* of the site $r$ and the *Lewis basicity* of the site $s$ as follows:[19,20]

$$\text{Lewis acidity} = \frac{\langle \delta_r | \phi_{\mathrm{unoc}}(\delta_r)\rangle^2 \gamma}{\lambda_{\mathrm{unoc}}(\delta_r)} = \frac{(1 - a^2)\gamma}{\lambda_{\mathrm{unoc}}(\delta_r)} \qquad (7)$$

$$\text{Lewis basicity} = -\frac{\langle \delta_s | \phi_{\mathrm{oc}}(\delta_s)\rangle^2 \gamma}{\lambda_{\mathrm{oc}}(\delta_s)} = \frac{-b^2\gamma}{\lambda_{\mathrm{oc}}(\delta_s)} \qquad (8)$$

where $\gamma$ is a constant having an energy unit. The calculated values of the Lewis acidity and basicity are summarized in Tables 1 and 2, respectively, with the elements that determine the acidity or basicity. In addition, the Mulliken and natural bond population analyses have been done.[32,33] The charges of B and N in aminoboranes calculated by these methods at the RHF/6-31G* level are shown in Table 3. The two methods show similar trends of charges in their orders.

The substituent effect of the methyl group can be analyzed by comparing the data for **1**, **2**, **3**, **4**, and **5**. The methyl group is generally known as an electron-donating group. When a borane molecule is substituted by methyl groups, the reactivity of the boron center will decrease. In fact, the B−N bond energy of $(\mathrm{Me})_3\mathrm{B{-}NH_3}$ is smaller than that of $\mathrm{H_3B{-}NH_3}$.[34] By comparing **1**, **2**, and **3** in Table 1, one finds that the calculated Lewis acidity values follow the expected order. Interestingly, however, the methyl groups on the boron center has the secondary effect of increasing the Lewis basicity of the remote nitrogen center as seen in Table 2, by shifting the electronic charge from the boron to the nitrogen. The positive charge on the boron is larger in **3** than in **1**, as shown in Table 3. The B−N bond has been shown to be strengthened when methyl groups are introduced to the nitrogen atom in borazane.[34,35] It is therefore anticipated that methyl groups attached to nitrogen increase the Lewis basicity of aminoboranes. It is surprising, however, that the order of calculated Lewis basicities of **1**, **4**, and **5** is opposite to the expectation, as demonstrated in Table 2. In addition, the methyl groups attached to the nitrogen atom reduce, although in a small margin, the Lewis acidity of the boron center. As the methyls are placed on the nitrogen, the electronic charge is delocalized through the p$\pi$−p$\pi$ conjugation to the boron, making the double bond stronger. As a result, the ability of nitrogen to act as a Lewis base toward another Lewis acid decreases.

We have also examined the effect of chloro groups. It is known that $\mathrm{BCl_3}$ forms a weaker Lewis acid−base complex with $\mathrm{NH_3}$, as compared with $\mathrm{BH_3}$. We have obtained the bond energies for $\mathrm{Cl_3B{-}NH_3}$ (95.8 kJ/mol), $\mathrm{HCl_2B{-}NH_3}$ (99.8 kJ/mol), $\mathrm{H_2ClB{-}NH_3}$ (106.6 kJ/mol), and $\mathrm{H_3B{-}NH_3}$ (113.4 kJ/mol) at the B3LYP/6-31G* level. The Lewis acidity of boron appears to be lowered by introducing chloro groups into the boron in these compounds. The electronegative −Cl group lowers the unoccupied reactive orbital level of the boron center, contrary to the methyl substituted case, but the reactive orbital is forced to be delocalized over the chloro substituents, as depicted by a smaller $(1 - a^2)$ value in **6** compared with those in others. Thus, **6** shows the acidity lower than **5**. The strength of B−N conjugation appears to remain much the same in **5** and in **6**, as the extent of localization of the occupied reactive orbital on the nitrogen, $b^2$, gives the same value, 0.94. These lead, on the other hand, to a much lower value of the Lewis basicity of the nitrogen in **6** compared with those in **1**−**5**.

Bürger and co-workers have extensively developed the chemistry of aminoboranes.[15] They observed the unusual reactivity in $(\mathrm{CF_3})_2\mathrm{B{=}NH_2}$ and showed that this aminoborane undergoes several kinds of pericyclic reactions. We have examined **7**. The Lewis acidity value for this compound has been estimated to be the largest of all, reflecting the extraordinary electron-withdrawing ability of the trifluoromethyl group. On the other hand, the Lewis basicity of **7** is the lowest. The $-\mathrm{CF_3}$ group is a very strong electron-withdrawing substituent,

**TABLE 1: Comparison of the Elements Determining the Lewis Acidity of the Boron Atom in Aminoboranes**

| species | $\lambda_{\mathrm{unoc}}$ (au) | $1 - a^2$ | Lewis acidity[a] |
|---|---|---|---|
| 1 | 0.332 | 0.785 | 2.365 |
| 2 | 0.348 | 0.758 | 2.176 |
| 3 | 0.362 | 0.737 | 2.038 |
| 4 | 0.336 | 0.774 | 2.304 |
| 5 | 0.336 | 0.769 | 2.288 |
| 6 | 0.289 | 0.655 | 2.262 |
| 7 | 0.270 | 0.709 | 2.629 |

[a] Calculated by eq 7, in which $\gamma$ is 1 au.

**TABLE 2: Comparison of the Elements Determining the Lewis Basicity of the Nitrogen Atom in Aminoboranes**

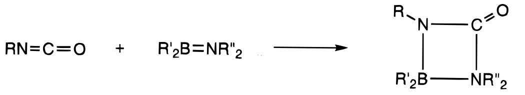
| species | $\lambda_{\mathrm{oc}}$ (au) | $b^2$ | Lewis basicity[a] |
|---|---|---|---|
| 1 | −0.432 | 0.950 | 2.200 |
| 2 | −0.425 | 0.954 | 2.243 |
| 3 | −0.420 | 0.957 | 2.276 |
| 4 | −0.454 | 0.945 | 2.079 |
| 5 | −0.477 | 0.940 | 1.969 |
| 6 | −0.512 | 0.940 | 1.836 |
| 7 | −0.527 | 0.925 | 1.755 |

[a] Calculated by eq 8, in which $\gamma$ is 1 au.

**TABLE 3: Mulliken and Natural Charges Calculated at the RHF/6-31G* Level of Theory**

| | Mulliken charge | | natural charge | |
|---|---|---|---|---|
| species | B | N | B | N |
| 1 | 0.270 | −0.862 | 0.551 | −1.137 |
| 2 | 0.466 | −0.891 | 0.767 | −1.140 |
| 3 | 0.666 | −0.917 | 0.998 | −1.149 |
| 4 | 0.251 | −0.687 | 0.546 | −0.948 |
| 5 | 0.243 | −0.520 | 0.550 | −0.778 |
| 6 | 0.463 | −0.562 | 0.788 | −0.835 |
| 7 | 0.469 | −0.588 | 0.781 | −0.765 |

**SCHEME 3**



and the boron atom becomes electron-deficient. Then, the p$\pi$−p$\pi$ conjugation is strengthened, as depicted by the smaller $b^2$ value for **7** compared with those for **5** and **6**, to shift the electronic charge from the nitrogen to the boron. The methyl groups attached to the nitrogen are not strong enough as electron-donating groups to counterbalance the decrease in electron population on the nitrogen, making the nitrogen a poor Lewis base toward another Lewis acid. Despite the high Lewis acidity, the positive charge on the boron is not large in **7** because of a strong p$\pi$−p$\pi$ conjugation. Hence, in the case of aminoboranes, electronic charge cannot predict properly the reactivity of the Lewis acidic center or the Lewis basic center.

**Cycloaddition Reactions of Aminoboranes.** [2 + 2] cycloaddition is a simple and typical reaction that aminoboranes undergo. Aminoborane **7** shows a remarkable reactivity toward [2 + 2] cycloaddition with isocyanates RN═C═O (Scheme 3).[15i] We have optimized the reactant and transition-state structures for the cycloaddition reaction of **7** with isocyanic acid (R = H). The geometries of the transition state and the cyclic product for **7** are drawn in Figure 3. As a whole, the theoretically determined structure agrees well with the experimentally observed one.[15i]

At the transition state, an extraordinary short distance between B of **7** and N of isocyanic acid can be found in Figure 3. We have also calculated the transition-state structures for all of the other aminoboranes. The calculated total energies are summarized in Table 4, and B···N and N···C bond lengths at the transition states are given in Table 5. Similar structural trends,

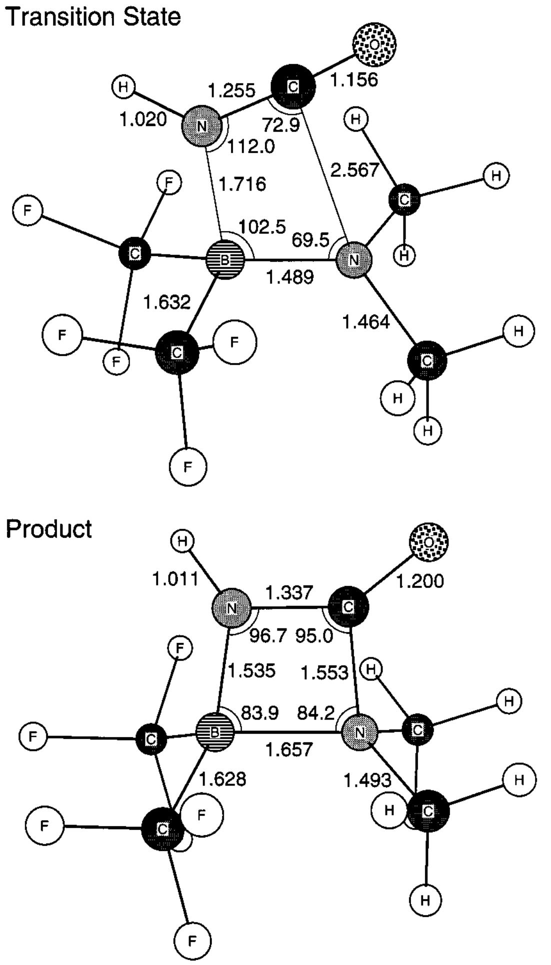


**Figure 3.** B3LYP/6-31G* optimized structures of the transition state and the cyclic product for the [2 + 2] cycloaddition reaction of **7** with isocyanic acid. The difference between the calculated values and the experimentally observed ones for the cycloaddition product of **7** with *tert*-butyl isocyanate have been shown to be < 0.03 Å in bond lengths and <2° in bond angles. See, ref 15i.

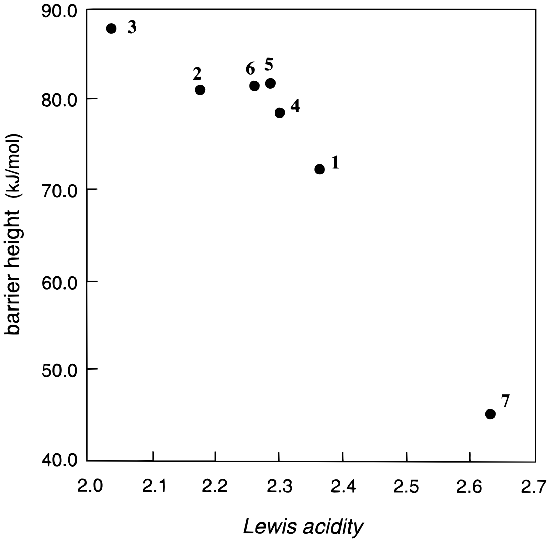


**Figure 4.** Relation between the calculated barrier heights for the [2 + 2] cycloaddition reaction of aminoboranes with isocyanic acid and the theoretically estimated Lewis acidity of the boron center.

**TABLE 4: Total Energies for the [2 + 2] Cycloaddition Reaction of Aminoboranes with Isocyanic Acid Calculated at the B3LYP/6-31+G**//B3LYP/6-31G* Level of Theory**[a]

| species | aminoborane[b] | isocyanic acid[b] | transition state[b] | barrier height[c,d] |
|---|---|---|---|---|
| 1 | −82.055 398 | −168.691 261 | −250.721 905 | 72.26 |
| | (−82.039 320) | (−168.677 510) | (−250.695 134) | (64.23) |
| 2 | −121.390 458 | | −290.053 002 | 81.11 |
| | (−121.368 695) | | (−290.021 106) | (71.61) |
| 3 | −160.723 711 | | −329.383 648 | 87.77 |
| | (−160.696 324) | | (−329.346 957) | (76.09) |
| 4 | −121.363 724 | | −290.026 967 | 78.61 |
| | (−121.348 171) | | (−290.000 715) | (70.59) |
| 5 | −160.673 313 | | −329.334 956 | 81.81 |
| | (−160.658 262) | | (−329.309 179) | (73.87) |
| 6 | −1079.964 291 | | −1248.625 811 | 81.67 |
| | (−1079.949 709) | | (−1248.600 330) | (74.18) |
| 7 | −834.795 999 | | −1003.471 473 | 45.32 |
| | (−834.735 401) | | (−1003.400 827) | (35.59) |

[a] Values calculated at the B3LYP/6-31G* level are shown in parentheses. [b] In au. [c] In kJ/mol. [d] Corrected by the zero-point energy scaled by a factor of 0.9804.

**TABLE 5: B···N and N···C Bond Lengths at the Transition State of the [2 + 2] Cycloaddition Reaction of Aminoboranes with Isocyanic Acid Calculated at the B3LYP/6-31G* Level of Theory**

| species | B···N[a] | N···C[a] |
|---|---|---|
| 1 | 1.786 | 2.421 |
| 2 | 1.856 | 2.356 |
| 3 | 1.991 | 2.220 |
| 4 | 1.833 | 2.414 |
| 5 | 1.874 | 2.377 |
| 6 | 1.751 | 2.560 |
| 7 | 1.716 | 2.567 |

[a] In Å.

that is, a short B···N bond and a long N···C bond, are found in all of the cases.

In this type of reaction, the Lewis acidity of the boron center in aminoboranes should play the dominant role. The B···N transient bond is seen to become shorter when the Lewis acidity of the boron center becomes stronger. The unusually high reactivity of **7** toward cycloaddition with isocyanates is rationalized in this context. We have plotted in Figure 4 the barrier heights for the cycloaddition reaction with isocyanic acid against the Lewis acidity of boron estimated above. It can be seen that the barrier heights have a good correlation with the Lewis acidity. The barrier heights for the reaction of **2** and **3** are somewhat lower than those expected solely from the Lewis acidity, probably because the Lewis basicity of the nitrogen center is high in these compounds relative to those of others.

The N···C transient bond roughly becomes longer at the transition state, as the Lewis basicity of the nitrogen center becomes lower. Although the long N···C bond is ascribed in part to the repulsion between the lone pair of electrons on the nitrogen and the $\pi$ system of isocyanic acid, the long N···C distance in the reaction of **7** comes probably from the less effective electron delocalization. In the [4 + 2] cycloaddition reaction of aminoboranes with butadiene, similar structural trends were calculated by Gilbert.[21] He explained the longer N···C distance for **7** in the [4 + 2] Diels−Alder-like reaction by assuming that the lone pair of electrons in **7** was localized by electron-donating methyl groups on the nitrogen and was repelled by the carbon $\pi$ electrons. It is natural, however, to assume that the lone pair of electrons on the nitrogen is delocalized more strongly in **7** than in other aminoboranes. The present study has clarified that the Lewis basicity of the nitrogen center is extremely low in **7**. Thus, the longer N···C distance in **7** is ascribed to less effective electron delocalization from the nitrogen of **7** to the carbon of isocyanic acid.

**SCHEME 4**

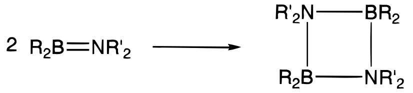
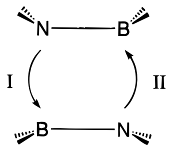


**TABLE 6: Total Energies for the [2 + 2] Cycloaddition Reaction between Two Aminoboranes Calculated at the B3LYP/6-31+G**//B3LYP/6-31G* Level of Theory**[a]

| reaction | monomeric form[b] | transition state[b] | barrier height[c,d] |
|---|---|---|---|
| **1 + 1** | −82.055 398 | −164.092 451 | 56.04 |
| | (−82.039 320) | (−164.064 619) | (44.69) |
| **2 + 2** (*trans*)[e] | −121.390 458 | −242.758 688 | 63.59 |
| | (−121.368 695) | (−242.720 112) | (50.59) |
| **2 + 2** (*cis*)[e] | −121.390 458 | −242.758 716 | 63.42 |
| | (−121.368 695) | (−242.720 148) | (50.40) |
| **3 + 3** | −160.723 711 | −321.422 228 | 70.90 |
| | (−160.696 324) | (−321.373 444) | (55.18) |
| **4 + 4** (*trans*)[e] | −121.363 724 | −242.705 888 | 62.68 |
| | (−121.348 171) | (−242.678 311) | (53.41) |
| **4 + 4** (*cis*)[e] | −121.363 724 | −242.705 927 | 62.96 |
| | (−121.348 171) | (−242.678 438) | (53.47) |
| **5 + 5** | −160.673 313 | −321.321 448 | 71.41 |
| | (−160.658 262) | (−321.293 556) | (65.61) |
| **6 + 6** | −1079.964 291 | −2159.888 121 | 109.59 |
| | (−1079.949 709) | (−2159.860 314) | (106.03) |
| **7 + 7** | −834.795 999 | −1669.548 358 | 119.72 |
| | (−834.735 401) | (−1669.445 697) | (71.06) |
| **3 + 5** | | −321.370 861 | 73.57 |
| | | (−321.332 976) | (61.61) |

[a] Values calculated at the B3LYP/6-31G* level are shown in parentheses. [b] In au. [c] In kJ/mol. [d] Corrected by the zero-point energy scaled by a factor of 0.9804. [e] Two ways of additions are possible owing to an asymmetrically attached substituent.

**SCHEME 5**



The [2 + 2] dimerization is a well-known reaction that aminoboranes undergo (Scheme 4). We have optimized the geometries of monomeric aminoboranes and the transition states for the dimerization reaction. The results of calculations are summarized in Table 6.

The reaction has been shown to take place in a concerted fashion (Scheme 5).[14] As we have seen in Scheme 5, the Lewis acidity of the boron and the Lewis basicity of the nitrogen that play key roles in the dimerization reaction are affected by substituents. Accordingly, the ease of dimerization is expected to be determined both by the acidity and by the basicity. The stabilization of the reacting system at the transition state brought about by electron delocalization as illustrated by I or by II in Scheme 5 is given in a second-order perturbation form by[29b]

$$\Delta E \cong -\frac{2(1-a^2)b^2h(\delta_r,\delta_s)^2}{\lambda_{\mathrm{unoc}}(\delta_r)-\lambda_{\mathrm{oc}}(\delta_s)} \qquad (9)$$

in which $h(\delta_r,\delta_s)$ is an integral representing the interaction between the unoccupied reactive orbital centered on the boron in one aminoborane molecule and the occupied reactive orbital centered on the nitrogen in the other aminoborane molecule. This integral is assumed to remain approximately the same in

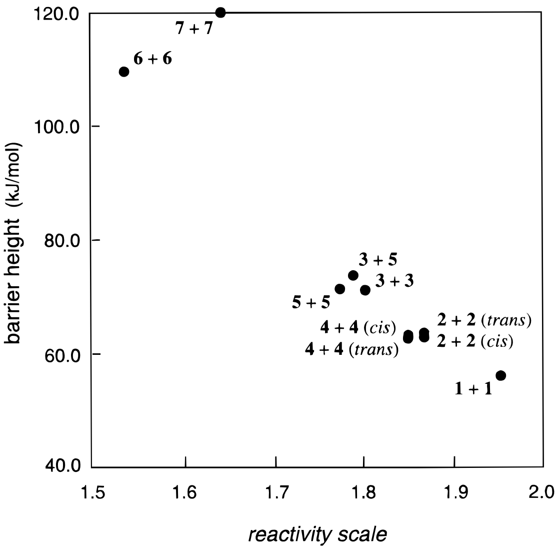


**Figure 5.** Relation between the barrier heights for the dimerization reactions of aminoboranes and the reactivity scale. The contributions from the two B···N interactions have been included.

magnitude for a given type of reaction, because we utilize here the reactive orbitals that have been localized well on the reaction sites. Then, we may employ a *reactivity scale* to measure the stabilization, as defined by

$$\text{reactivity scale} \cong \frac{(1 - a^2)b^2\gamma}{\lambda_{\text{unoc}}(\delta_r) - \lambda_{\text{oc}}(\delta_s)} \qquad (10)$$

where $\gamma$ is a constant having an energy unit. This scale takes a positive value, and the larger the scale is, the larger the stabilization should be. There are two acid−base interactions in the dimerization reactions, I and II in Scheme 5, and, accordingly, the scales for the two reaction sites are added.

Figure 5 shows the relation between the barrier height calculated at the B3LYP/6-31+G**//B3LYP/6-31G* level and the reactivity scale for the dimerization of aminoboranes. One finds a nice correlation between the barrier height and the reactivity scale estimated by eq 10. It is interesting to see that the reactivity of **7** toward dimerization is very low in agreement with the fact that no dimerization product has so far been reported for **7**. This may not have been imagined, considering the strong electron-withdrawing ability of trifluoromethyl groups and the electron-donating property of methyl groups. The present analysis shows that the methyl group is not strong enough in its electron-releasing ability to counterbalance the effect of trifluoromethyl groups on the nitrogen center. Thus, the high activation energy of **7** toward dimerization is attributed to an weak electron delocalization at the transition state. The barrier height for the addition of **3** with **5** is not necessarily high as compared with the dimerization of **3** or **5**. This signifies that steric effect does not play a crucial role in these reactions, except for the dimerization of aminoboranes having substituents both on the B and N centers, as in **7**.

## Conclusions

We have studied the reactivity of aminoboranes from the orbital interaction viewpoint, taking into account the local characteristics of chemical reactions. By deriving the unoccupied reactive orbital that shows the maximum localization on the boron p$\pi$ orbital and the occupied reactive orbital that is localized on the nitrogen lone-pair orbital in these compounds, the local nature of aminoboranes as a Lewis acid and as a Lewis base has been evaluated. The methyl group attached to the boron has been found to reduce the Lewis acidity of the boron center but to strengthen the basicity of the remote nitrogen center. Interestingly, the methyl group attached to the nitrogen reduces the Lewis basicity of the nitrogen center and, at the same time, weakens the Lewis acidity of the remote boron center. These relations arise from the p$\pi$−p$\pi$ conjugation between the lone pair of electrons on the nitrogen and the p$\pi$ orbital of the boron. The transition state for the [2 + 2] cycloaddition reaction of aminoboranes with isocyanic acid has also been calculated. In this reaction, the Lewis acidity of aminoboranes governs the reactivity. In contrast, the reactivity toward the [2 + 2] dimerization reaction has been found to be determined by the combination of the Lewis acidity of the boron center and the Lewis basicity of the nitrogen center. The unique reactivity of $(CF_3)_2B{=}NMe_2$ is explained clearly by considering its extraordinary high reactivity at the boron center and its extraordinary low reactivity at the nitrogen center among the aminoboranes examined in this study. The method used in this study will be of use in evaluating the reactivity of local sites in catalysts that possess many active centers.

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**Supporting Information Available:** Tables of total coordinates of atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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