# Theoretical Study of the $BH_3$-Catalyzed Hetero Diels–Alder Reaction between Ethylene and Nitrosoethylene

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*Received September 16, 1994 (Revised Manuscript Received March 13, 1995®)*

The geometries of *cis-* and *trans*-nitrosoethylene and their *O-* and *N*-borane complexes were optimized with the RHF/6-31G* and MP2/6-31G* theoretical models and the transition states and products with RHF/6-31G*. The energy was evaluated up to the MP3/6-31G*//RHF/6-31G* level on all species involved in the reaction. The stability of the geometric isomers of nitrosoethylene and their borane complexes were considered on the basis of their total energies and by comparing the bond orders. The reactivity was discussed in terms of the activation barriers. The bond orders and the charge transferred from ethylene to the nitrosoethylene moiety in the transition states were also used to rationalize the reactivity. It was shown that the reaction is an inverse electron demand Diels–Alder cycloaddition and that borane has a profound influence as a catalyst. Since the predicted activation energies are relatively low, the borane-catalyzed reaction should be experimentally feasible.

## Introduction

Pericyclic reactions[1] have secured an immutable and well-deserved stature in the minds and hands of chemists. The most popular of them all is the Diels–Alder reaction.[2] The introduction of heterodienes has extended the synthetic versatility of cycloaddition reactions by allowing rapid access to various heterocycles.[3]

Of the many compounds that can undergo cycloaddition reactions, nitrosoethylene compounds lead to valuable heterocyclic compounds with an NO bond in the cycle.[4] Although these compounds are able to act either as heterodienes or as nitroso dienophiles, their reactivity is critically dependent on their structure and presence of a catalyst. Nitrosoethylene compounds are generally unstable and are generated in situ by base-promoted elimination of α-haloximes. Some of the cycloadducts that can undergo reversible cycloaddition reaction can be stabilized by further cycloaddition reaction, for example with thebaine.[5] Similarly nitroalkenes have been shown to be very powerful dienes in combination with Lewis acids for hetero Diels–Alder reactions.[6]

## Methodology

Gaussian 92[7] was employed to fully optimize the geometries without any symmetry constraints at the restricted Hartree-Fock (HF)[8] level with the standard basis sets, 3-21G* and 6-31G*. The reactants and their complexes with the catalyst were optimized up to MP2/6-31G*. Electron correlation was incorporated by applying second- and third-order Möller–Plesset (MP2 and MP3) theory for energy evaluation on the RHF/6-31G* geometries, keeping the core electrons frozen (FC).[9] Analytic vibrational frequencies were obtained up to the HF/6-31G* level to determine the number of imaginary frequencies for the stationary points (minima have zero and transition structures have one imaginary frequency). The normal coordinates of the imaginary vectors of the transition structures were carefully examined and indicate that the movements point in the direction of the formation or breaking of the new bond corresponding to the forward or backward reaction, respectively.

## Results and Discussion

Although the all-carbon Diels–Alder reactions have been theoretically studied extensively,[10] there are fewer reports that involve heteroatoms.[11] Semiempirical and low level ab initio calculations have been reported for the conformations and stability of nitrosoethylene.[12] Here we report the Diels–Alder reactions with nitrosoethylene at a much higher theoretical level.

The geometries of the reactants generated at MP2/6-31G* level are presented in Figure 1. Two possible

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® Abstract published in *Advance ACS Abstracts,* May 1, 1995.

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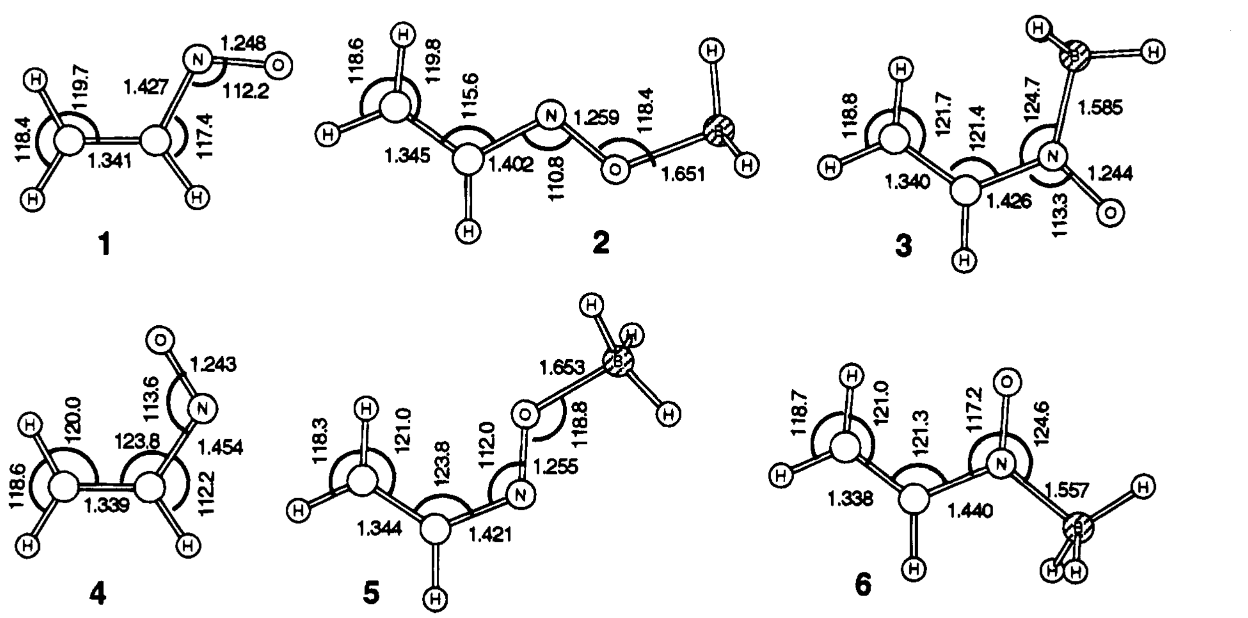

**Figure 1.** Geometries of the reactants optimized at the MP2/6-31G* level.

**Table 1. Energy Gain (kcal/mol) for Borane Complexation of Isomers 1 and 2**

| complex | $\Delta E_a$[a] | $\Delta E_b$[b] | $\Delta E_c$[c] |
|---|---|---|---|
| **2** | 14.87 | 5.12 | 15.69 |
| **3** | 21.08 | 13.21 | 29.03 |
| **5** | 14.61 | 4.73 | 14.71 |
| **6** | 22.79 | 16.62 | 32.83 |

[a] $\Delta E_a$ = RHF/3-21G//RHF/3-21G. [b] $\Delta E_b$ = RHF/6-31G*//RHF/6-31G*. [c] $\Delta E_c$ = MP2/6-31G*//MP2/6-31G*.

geometric isomers of nitrosoethylene were considered, *cis* and *trans*. In both isomers **1** and **4**, as expected, all atoms are coplanar enabling maximum possible molecular orbital overlap of the atomic p-orbitals. Borane can form at least two more complexes for each isomer, forming either NB or OB donor–acceptor bonds (Figure 1). For example, in complex **2** the heavy atoms attached to the NO double bond either can be in the more stable transoid or can form a less stable cisoid isomer.

The energy gain for the borane complexation of the two geometrical isomers **1** and **2** are given in Table 1. The most stable is the *N*-borane complex with *cis*-nitrosoethylene **6**, with a complexation energy of 32.8 kcal/mol at the MP2/6-31G* level. In the case of the oxygen complexes, there is a small preference of the *trans* over the *cis* isomer.

**Table 2. Bond Orders[14] for the Isomers of Nitrosoethylene and Their Borane Complexes Calculated at the MP2/6-31G* Level[a]**

| | bond | | | | | |
|---|---|---|---|---|---|---|
| compd | CC | CN | NO | OB | NB | BV |
| A **1** | 1.843 | 0.966 | 1.717 | | | |
| B | 1.987 | 1.203 | 2.176 | | | |
| A **2** | 1.774 | 1.011 | 1.580 | 0.340 | | 3.286 |
| B | 1.917 | 1.262 | 1.951 | 0.666 | | 3.678 |
| A **3** | 1.829 | 0.921 | 1.699 | | 0.534 | 3.450 |
| B | 1.964 | 1.124 | 2.085 | | 0.859 | 3.867 |
| A **4** | 1.870 | 0.944 | 1.745 | | | |
| B | 2.009 | 1.175 | 2.191 | | | |
| A **5** | 1.805 | 0.978 | 1.610 | 0.332 | | 3.280 |
| B | 1.944 | 1.230 | 1.993 | 0.663 | | 3.675 |
| A **6** | 1.844 | 0.924 | 1.689 | | 0.588 | 3.484 |
| B | 1.984 | 1.093 | 2.102 | | 0.909 | 3.895 |

[a] A = Mülliken bond orders; BV = boron valence; B = Löwdin bond orders.

The stability of the borane complexes can be rationalized in terms of their bond orders[13] (Table 2). Since the degree of conjugation determines the molecular energy, the bond orders can give a qualitative information on both conjugation and energy of the molecule. The CN single bond of nitrosoethylene is located between the CC and NO double bonds. The CN bond orders for the *trans* isomer **1** are 0.022 and 0.028 higher than for the *cis* isomer **2**. Since there are no sterically large groups in nitrosoethylene, it is reasonable to assume that all energetic differences between the isomers are electronic. Higher conjugation is present in isomer **1** than in **4** and consequently, on the basis of the bond orders, it is predicted to be more stable. In the borane complexes **2**, **3**, **5**, and **6**, the bond orders of both the CC and the CN bonds decrease, in the case of oxygen complex **2** the CN bond orders slightly increase, while in the nitrogen

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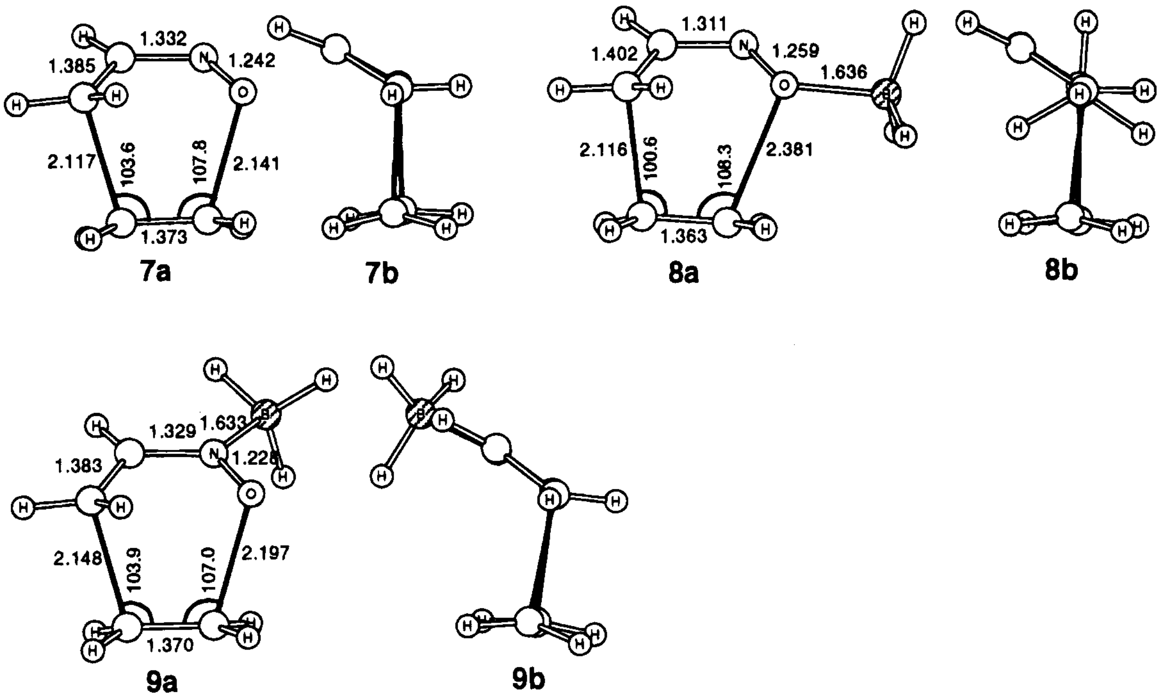

**Figure 2.** Transition structures of ethylene addition to nitrosoethylene and its borane complexes.

complex **6** they slightly decrease. It is quite reasonable to expect that bond orders of the two double bonds will increase in the borane complexes because a new donor–acceptor bond is formed. In the oxygen complexes **2** and **5**, the double and single bonds are alternating increasing the bond orders of the single bonds and decreasing the bond orders of the double bonds, a characteristic of conjugated systems. However, in the nitrogen complexes, the boron atom is not conjugated with the CC double bond, and consequently, the bond order for CN decreases compared to the uncomplexed nitrosoethylene. The bond order for the NB bond is higher than that for the OB bond, indicating higher stability of the nitrogen complex. Furthermore, in the oxygen complexes a stronger bond is formed with the *trans* isomer **1**, while in the nitrogen complexes it is with the *cis* isomer **2** (Table 2).

Transition state theory,[15] despite some fundamental objections to its validity, has been successfully used for the calculation of activation barriers and prediction of mechanisms of reactions. The geometries of the RHF/6-31G* transition structures and products are presented in Figures 2 and 3, respectively. All transition states are for the concerted but not necessarily synchronous mechanism of the reaction. The classification of synchronicity of the reaction can be obtained on the basis of bond orders of the newly formed bonds. As expected, all transition structures are asynchronous since the reacting diene is asymmetric. In the course of the reaction, two different bonds are being formed: a carbon–oxygen and a carbon–nitrogen bond. In such cases, since the asymmetricity of the transition structure based on bond distances can be misleading, it should be viewed in terms of the bond orders. By comparison of the differences of the bond orders for the uncatalyzed cycloaddition reactions, it can be concluded that transition structure **8** is the most asymmetric, while transition structure **1** is the most synchronous (Table 3). The same conclusion can be anticipated on the basis of chemical intuition. The less polar reactants should form products through more synchronous transition state, and the more polarized reactive centers will go through more asynchronous transition structures as is the case with **8**.

The total energies of the species involved in borane-catalyzed ethylene addition to nitrosoethylene and the corresponding activation barriers calculated with different theoretical models are presented in Tables 4 and 5. Since the activation barriers are not experimentally known for this reaction, they are compared to the available results from the ethylene addition to butadiene. Usually the calculated total energy of a transition structure is compared with the total energy of the separated reactants to obtain the activation barrier. When the reactants can form a stable complex, it is reasonable to calculate the activation energy by comparing the total energies of the reactant complex and the transition structures. Also, when the reactants have more geometric isomers, the calculation of the activation energy is done with the most stable isomers. Nevertheless, all mentioned combinations of activation energies have been considered and are presented in Table 5. As expected the more stable *trans* isomers of nitrosoethylene and nitrosoethylene borane complexes, have a higher activation energy than the *cis* isomers. Furthermore, the stability of the nitrosoethylene borane complexes relative to the separated components give rise to negative activation energies when it is calculated from the total energies of the separated species. The borane-catalyzed reaction has a lower activation barrier than the uncatalyzed reaction, indicating that the reaction is with an inverse electron demand. Even a simple comparison of the frontier orbitals[16] shows that the reaction is HOMO dienophile- and LUMO diene-controlled (Table 6). Borane as a catalyst has a profound influence on the reactivity of the system by decreasing the electronic

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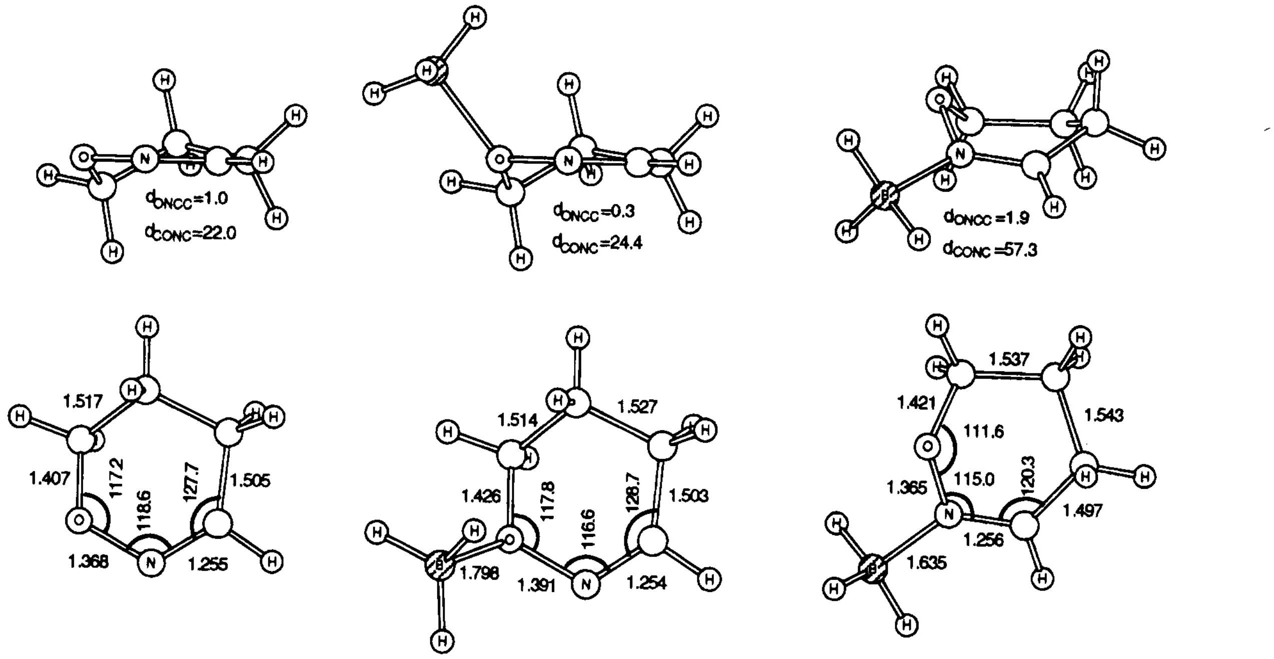

**11** **12** **13**

**Figure 3.** Geometries of products calculated with RHF/6-31G*.

**Table 3. The Bond Orders for the Transition Structures Calculated at the RHF/6-31G* Level**[a]

| TS | *a* | *b* | *a* − *b* | *a* + *b* | *c* |
|---|---|---|---|---|---|
| A **7** | 0.402 | 0.249 | 0.153 | 0.651 | |
| B | 0.430 | 0.303 | 0.127 | 0.733 | |
| A **8** | 0.390 | 0.129 | 0.261 | 0.519 | 0.393 |
| B | 0.415 | 0.162 | 0.253 | 0.577 | 0.704 |
| A **9** | 0.382 | 0.215 | 0.167 | 0.597 | 0.513 |
| B | 0.407 | 0.262 | 0.145 | 0.669 | 0.806 |

[a] A = Mülliken bond orders; B = Löwdin bond orders; a = the left new forming bond as presented in Figure 2; b = the right new forming bond as presented in Figure 3; c = bond order between boron and a heteroatom.

density on the diene and lowering its LUMO energy. From the activation energy evaluated with the highest theoretical model employed here (MP3/6-31G*//RHF/6-31G*), the most reactive combination of reactants is the one that produces transition structure **9** involving the *N*-borane complex. The reliability of this theoretical model has been demonstrated for a pericyclic reaction in the case of the ethylene addition to butadiene where the activation energy of 25.98 kcal/mol is in reasonable agreement with the experimental value (25.4 and 27.5 kcal).[17] All pericyclic reactions considered have considerably lower activation energy compared to the ethylene–butadiene addition. The reaction taking place through transition state **9** has 14.38 kcal/mol lower activation energy than the ethylene addition to butadiene, and it is reasonable to expect that it would be experimentally feasible at modest reaction conditions.

The reactivity can also be rationalized in terms of the bond orders in the transition structure. The energy of the transition state can be evaluated on the basis of Hammond's principle in cases when the energies of the reactants and the products are available.[18] The thermodynamic outcome of the reaction is presented in Table 6. The most exothermic reaction is the one with the *N*-complexed isomer. All calculations were done with the *cis*-nitrosoethylene in borane complexes. It has been pointed out that only similar compounds can be analyzed in this way.[13] In this respect only two of the transition structures **8** and **9** can be compared. On the basis of the bond orders, transition structure **9** is more advanced (Table 3, *a* + *b*) and consequently closer to the product **13** that has lower energy (Table 7). Therefore the prediction based on the bond orders is in agreement with the energy prediction.

Since the reaction is LUMO diene controlled, the transfer of charge from the diene to borane in their complex should increase the rate of the cycloaddition reaction. Comparison of both isomeric borane complexes shows that in the *cis* isomer there is a higher transfer of charge than in the *trans* isomer. This is to be expected since the *cis* isomer is less stable, and the reaction is predicted to be more feasible in the case of borane complex with nitrogen than with oxygen (Table 8).

It is also interesting to consider the charge transfer from the donor to the acceptor in the transition structures. The charge distribution on the dienophile moiety of the transition state is presented in Table 9. The largest transfer of charge occurs in **8**, and contrary to the calculated energy barrier, the most reactive species would be expected to be borane complex **5**. An apparent disadvantage of this line of thought is that it does not account for the steric interactions which can change the energy of the transition structure. Steric interactions in **8** between borane and ethylene moiety are stronger than in **9**.

It is interesting to determine the bond order of the heteroatom–boron bond in the product–borane complex and the influence of a borane complexation on the change of bond orders in the newly formed bonds. The structures

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**Table 4. Total Energies (au) of Reactants, Transition States, and Products for Borane-Catalyzed Ethylene Addition to Nitrosoethylene**[a]

| species | $E_a$ | $E_b$ | $E_c$ | $E_d$ | $E_e$ |
|---|---|---|---|---|---|
| $BH_3$ | −26.237 302 | −26.390 007 | −26.464 244 | −26.464 229 | −26.479 029 |
| Et | −77.600 988 | −78.031 718 | −78.285 028 | −78.284 340 | −78.305 356 |
| tBD | −154.059 46 | −154.919 65 | −155.422 66 | −155.422 66 | −155.455 65 |
| **1** | −205.50 0 27 | −206.677 37 | −207.265 50 | −207.259 05 | −207.274 27 |
| **2** | −231.761 27 | −233.075 54 | −233.754 75 | −233.746 88 | −233.773 43 |
| **3** | −231.771 17 | −233.088 42 | −233.776 01 | −233.767 77 | −233.793 62 |
| **4** | −205.496 59 | −206.670 53 | −207.259 44 | −207.253 12 | −207.268 04 |
| **5** | −231.757 18 | −233.068 08 | −233.747 13 | −233.739 14 | −233.765 84 |
| **6** | −231.770 21 | −233.087 03 | −233.776 00 | −233.768 03 | −233.793 05 |
| **7** | −283.064 88 | −284.648 36 | −285.533 34 | −285.529 05 | −285.547 18 |
| **8** | −309.339 82 | −311.062 82 |  | −312.023 41 | −312.056 80 |
| **9** | −309.348 74 | −311.074 83 |  | −312.052 03 | −312.080 49 |
| **10**[14] | −231.603 21 | −232.879 61 |  | −233.679 06 | −233.395 63 |
| **11** | −283.192 79 | −284.781 44 |  | −285.632 10 | −285.665 13 |
| **12** | −309.462 95 | −311.181 93 |  |  |  |
| **13** | −309.472 87 | −311.198 56 |  |  |  |

[a] $E_a$ = RHF/3-21G//RHF/3-21G; $E_b$ = RHF/6-31G*//RHF/6-31G*; $E_c$ = MP2/6-31G*//MP2/6-31G*; $E_d$ = MP2/6-31G*//RHF/6-31G*; $E_e$ = MP3/6-31G*//RHF/6-31G*.

**Table 5. Activation Energies (kcal/mol) of Borane Catalyzed Ethylene Addition to Nitrosoethylene**[a]

| species | $\Delta E_a$ | $\Delta E_b$ | $\Delta E_c$ | $\Delta E_d$ | $\Delta E_e$ |
|---|---|---|---|---|---|
| A **7** | 22.83 | 38.11 | 10.79 | 9.00 | 20.70 (−5.28) |
| B **7** | 20.51 | 33.81 | 6.98 | 5.28 | 16.45 |
| C **8** | −0.79 | 22.76 |  | −9.91 | 1.16 |
| D **8** | −3.10 | 18.47 |  | −13.63 | −2.75 |
| E **8** | 14.08 | 27.88 |  | 4.90 | 13.79 (−12.19) |
| F **8** | 11.51 | 23.20 |  | 0.04 | 9.03 |
| C **9** | −6.38 | 15.22 |  | −27.87 | −13.70 |
| D **9** | −8.70 | 10.93 |  | −31.59 | −17.61 |
| E **9** | 14.70 | 28.47 |  | 0.05 | 11.60 (−14.38) |
| F **9** | 14.09 | 27.56 |  | −0.21 | 11.24 |
| **10**[14] | 32.46 | 41.15 |  | 12.98 | 25.98 (0.00) |

[a] $\Delta E_a$ = RHF/3-21G//RHF/3-21G; $\Delta E_b$ = RHF/6-31G*//RHF/6-31G*; $\Delta E_c$ = MP2/6-31G*//MP2/6-31G*; $\Delta E_d$ = MP2/6-31G*//RHF/6-31G*; $\Delta E_e$ = MP3/6-31G*//RHF/6-31G*; A = calculated with *trans* isomer **1**; B = calculated with *cis* isomer **4**; C = calculated with **1** and borane as reactants; D = calculated with **4** and borane as reactants; E = calculated with corresponding *trans* borane complex as a reactant; F = calculated with corresponding *cis* borane complex as a reactant.

**Table 6. Frontier Orbital Energies (eV) of the Reactants and Their Borane Complexes Calculated with RHF/6-31G*//MP2/6-31G***

| compound | HOMO | LUMO | $A^a$ | $B^a$ |
|---|---|---|---|---|
| ethylene | −0.374 40 | 0.183 93 |  |  |
| **1** | −0.397 04 | 0.076 38 | 0.580 97 | 0.450 78 |
| **2** | −0.416 04 | 0.029 04 | 0.599 97 | 0.403 44 |
| **3** | −0.427 03 | 0.028 35 | 0.610 96 | 0.402 75 |
| **4** | −0.395 63 | 0.066 51 | 0.579 56 | 0.440 91 |
| **5** | −0.418 21 | 0.020 58 | 0.602 14 | 0.394 98 |
| **6** | −0.427 74 | 0.021 57 | 0.611 67 | 0.395 97 |

[a] A = $LUMO_{dienophile}$ − $HOMO_{diene}$; B = $LUMO_{diene}$ − $HOMO_{dienophile}$.

**Table 7. Thermochemistry of the Reactions**

| products | $\Delta E_a{}^a$ | $\Delta E_b{}^a$ |
|---|---|---|
| **11** | −59.74 | −49.69 |
| **12** | −57.57 | −39.54 |
| **13** | −63.80 | −50.08 |

[a] $\Delta E_a$ = RHF/3-21G//RHF/3-21G; $\Delta E_b$ = RHF/6-31G*//RHF/6-31G*.

**Table 8. Mülliken Charges with Hydrogens Summed on the Heavy Atoms of Nitrosoethylene and Its Borane Complexes Calculated at the MP2/6-31G* Level**

| compd | C1 | C2 | N | O | B |
|---|---|---|---|---|---|
| **1** | 0.083 | 0.216 | 0.050 | −0.349 |  |
| **2** | 0.136 | 0.225 | 0.115 | −0.354 | −0.123 |
| **3** | 0.156 | 0.236 | 0.073 | −0.259 | −0.206 |
| **4** | 0.117 | 0.168 | 0.059 | −0.344 |  |
| **5** | 0.189 | 0.195 | 0.125 | −0.347 | −0.163 |
| **6** | 0.151 | 0.250 | 0.126 | −0.301 | −0.226 |

**Table 9. Mülliken Charges on the Dienophile Moiety of the Transition Structures Calculated at the RHF/6-31G* Level**[a]

| TS | CT | C1 | C2 | N | O | B |
|---|---|---|---|---|---|---|
| **7** | 0.179 | 0.143 | 0.145 | 0.008 | −0.475 |  |
| **8** | 0.277 | 0.231 | 0.159 | 0.071 | −0.513 | −0.224 |
| **9** | 0.229 | 0.179 | 0.228 | 0.062 | −0.435 | −0.263 |

[a] CT = transferred charge from ethylene to the diene; atom numbering C1–C2–N–O as in nitrosoethylene.

**Table 10. Mülliken (Löwdin) Bond Orders**[14] **for Geometric Isomers of Nitrosoethylene and Their Borane Complexes Calculated by MP2/6-31G***

|  | newly formed bonds |  |  |  |
|---|---|---|---|---|
| compound[a] | CO | CC | OB | NB |
| A **11** | 0.822 | 0.966 |  |  |
| B | 1.100 | 1.070 |  |  |
| A **12** | 0.747 | 0.952 | 0.228 |  |
| B | 1.018 | 1.055 | 0.484 |  |
| A **13** | 0.788 | 0.952 |  | 0.491 |
| B | 1.069 | 1052 |  | 0.791 |

[a] A = Mülliken bond orders; B = Löwdin bond orders.

of the products and the product–borane complexes are presented in Figure 3. In complexes **12** and **13** (Table 10), both newly formed bonds have smaller bond orders in comparison with the non-complexed product **11**. Because oxygen is involved in both CO bonds between the two reactants' moieties of the product and BO bond of the complex **12** the bond order effect is the most profound. The CO bond order is decreased by 0.075 in comparison with 0.044 in complex **13**, as predicted on the basis of the electron distribution in compounds **11**–**13**. As in the case of the reactants complexes the bond order of BN is considerably higher than BO, indicating stronger borane complexation in structure **13**, as supported with energy gain by borane complexation (Table 11). Although absolute values of the energy gain vary with level and basis set of ab initio calculation, all of them predict that *N*-complexation should be at least several kcal/mol more stable than *O*-complexation, in full agreement with our study of the reactants' complexation discussed above and what is known of borane complexation.[19]

**Table 11. Energy Gain (kcal/mol) by Borane Complexation Of Product 11**[a]

| complex | $\Delta E_a$ | $\Delta E_b$ | $\Delta E_c$ | $\Delta E_d$ |
|---|---|---|---|---|
| **12** | 20.62 | 6.58 | | 0.00 |
| **13** | 26.84 | 17.01 | | 0.00 |

[a] $\Delta E_a$ = RHF/3-21G//RHF/3-21G; $\Delta E_b$ = RHF/6-31G*//RHF/6-31G*; $\Delta E_c$ = MP2/6-31G*//RHF/6-31G*; $\Delta E_c$ = MP3/6-31G*//RHF/6-31G*.

## Conclusion

All levels of applied ab initio calculations predict that the *trans*-nitrosoethylene isomer is more stable than the *cis* isomer, including their *O*- and *N*-borane complexes. The energy gain for the borane complex formation is considerable (15.71−32.83 kcal/mol evaluated at MP2/6-31G*//MP2/6-31G*), and the stability is higher for the *N*-borane complex. The bond order of the heteroatom−boron bond is in very good qualitative agreement with the energy stabilization by the complexation.

The activation energy barriers calculated at all employed theoretical models predict that borane is a strong catalyst with preferred *N*-complexation in the transition state. The bond orders and the charge transferred in the transition states show that the *O*-borane complex should be more reactive. In view of the experimental and calculated activation energies for the uncatalyzed and catalyzed reactions for the ethylene addition to butadiene, these reactions have considerably lower energy and should be experimentally feasible.

JO9415869

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