J. Org. Chem. **1990**, *55*, 2601-2609

Ab Initio Transition Structures for Hydroborations of Alkenes, Allenes, and Alkynes by Borane, Diborane, Methylborane, Methylfluoroborane, and Dimethylborane

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Received August 14, 1989

The transition structures for the hydroborations of ethylene, propene, *cis*-2-butene, *trans*-2-butene, isobutene, acetylene, 2-butyne, allene, methylallene, and ethylallene by borane, ethylene and propene by methylborane, ethylene by methylfluoroborane and dimethylborane, and ethylene by diborane have been located with ab initio molecular orbital calculations and the 3-21G basis set. The parent reactions of borane with ethylene and acetylene have also been studied at higher theoretical levels. Substituent effects on the stabilities of complexes and on the activation energies are in accord with experimental data.

Introduction

The hydroboration of alkenes[1] has been widely utilized in organic synthesis, most recently to extraordinary advantage in asymmetric synthesis.[2] The details of the mechanism are still of interest. Brown's group studied the kinetics of the reaction of alkenes with the disiamylborane dimer in THF.[3] They found that the hydroboration exhibited second-order kinetics, first-order both in alkene and disiamylborane. It was suggested the mechanism of the reaction involves a direct attack of alkenes on the borane dimer as the rate-determining step followed by a fast addition of the newly released borane monomer to the remaining alkenes. This mechanism was considered to be generally applicable to all dialkylborane dimers.

Twenty years later, Brown measured the kinetics of hydroboration of alkenes with the 9-BBN dimer as well as the disiamylborane dimer in a variety of solvents at 25 °C by a more convenient quantitative IR procedure.[4] In these and other cases, three-halves-order kinetics was observed. These new data led Brown to conclude that the reaction proceeds by an equilibrium dissociation of the borane dimer, followed by a slow reaction of the alkene with the monomer.

Studies with many alkenes have shown that the hydroboration reaction is both regioselective and stereoselective. Usually, the boron atom becomes bonded primarily to the less substituted carbon atom of the alkenes and acetylenes in a cis fashion, corresponding to anti-Markovnokoff addition.[1a,4] This has been explained on the basis of both steric and electronic effects. Experimental evidence such as entropy data (−27 eu),[5,6] isotope effect ($k_H/k_D = 1.18$),[7] and a weakly negative ρ value (−0.5)[8] for substituents on styrene implicates the transition state is early, that there is some development of positive charge at the transition state, and that the B–H bond is significantly broken in the rate-determining step. The boron is attacked by the most nucleophilic end of the multiple bond, which is the least substituted terminus. Steric factors also favor addition of the boron atom to the less substituted end of the multiple bond.

The regioselectivity not only depends upon the substitution of the borane or the alkene, but also upon the presence of electron-donating or electron-withdrawing groups on the alkenes.[9] For example, a CH_3O substituent on styrene increases the amount of anti-Markownikoff product, while an NO_2 substituent decreases the amount of anti-Markownikoff product. The effects of substituents on the double bond of alkenes on rates with 9-BBN were also examined by Nelson.[10] It was found that the relative rates of hydroboration of these alkenes are well correlated with the MNDO calculated HOMO energy level of the alkenes. The higher the HOMO energy of the alkenes, the faster the reaction proceeds. This can be accounted for by the enhanced interaction of HOMO of alkenes and LUMO of boranes when they are brought close together.[11-14] The influence of the substitution upon the regioselectivity was also demonstrated. The formation of the B–C bond occurs predominantly at the position where the atomic orbital coefficient in the alkene HOMO is largest.

In order to explain the observed regiochemistry and stereochemistry as well as substituent effects, Brown proposed that the hydroboration involves a four-center transition state with the B–H bond polarized.[9a,b] According to Brown's postulate, the borane acts both as an electrophile with olefins donating electrons to the empty p orbital of boron and as a nucleophile with the borane hydrogen donating electrons back to the olefins. On the other hand, Streitwieser has suggested the hydroboration proceeds

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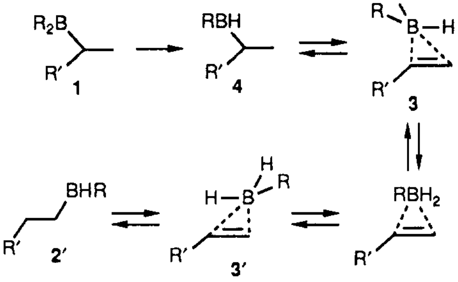
through an intermediate triangular π-complex followed by a three-center-like transition state.[15] Arguments against this mechanism were raised by Pasto and Kang on the ground of kinetic isotope effects.[16]

The absolute rate of the reaction of borane with ethylene in the gas phase was determined by Fehlner.[5] The barrier for the overall reaction was estimated to be 2 ± 3 kcal/mol. A variety of theoretical calculations with both ab initio and semiempirical techniques have been carried out for the reaction of borane with ethylene in gas phase. Divergent results were obtained. The CNDO/2 result of Dasgupta[12] and the MNDO study of Dewar and Mckee[13] supported the π-complex mechanism, finding an overall barrier of 7.6 kcal/mol for the forward reaction. The ab initio study by Morokuma[17] and Houk[18a,19,20] and the PRDDO study by Lipscomb[14] favored the four-center transition structure, giving an activation energy of 5.6–11.7 kcal/mol. In each case, a weakly bound π-complex of borane and ethylene prior to the transition state was found.

As a closely related issue, the mechanism of alkylborane rearrangements is thought to be similar to that of hydroboration. Brown first proposed that the hydroboration rearrangement proceeds by the elimination of an alkylborane and its subsequent addition to another carbon atom of the newly formed olefin.[1a–c,21] The main evidence for this conclusion comes from the observation that alkylboranes intermolecularly exchange alkyl groups with free alkenes when a mixture of high-boiling olefins and the alkylboranes derived from low-boiling olefins is heated.[12,22] However, the rate of transalkylation is dependent upon the concentration and the nature of the high-boiling olefins,[23] which should not be the case if the elimination of alkylboranes is the rate-determining step. Also, the elimination–addition mechanism does not explain the role of compounds with B–H bonds, which accelerate the isomerization of alkylboranes.[23] Furthermore, it was reported recently that the rearrangement of *cis*-1,2-dimethylcyclohexylborane[22] and *cis*-1,2-dimethylcyclopentylborane[24] is highly stereoselective, indicating that there are no "free" olefins.

Several alternative mechanisms have been proposed to interpret these observations. Mikhailov suggested that the transalkylation starts with the formation of a π-complex involving the vacant orbital of boron and the π-orbital of the C=C double bond, followed by the replacement of one olefin by another via a six-membered transition state.[23] Secondly, Williams proposed an isomerization mechanism which takes the catalytic action of compounds with B–H bonds into account.[25] According to this mechanism, the alkylborane is converted to the less substituted alkylborane 1 by loss of an alkene. This secondary borane rearranges via the intermediate 3 and 4 to the alkylborane 2. Recently, Rickborn and Field viewed the mechanism of alkylborane rearrangement as an intramolecular process,[22,24] which involves an intermediate olefin–boron π-complex. Rickborn also proposed that the suggested π-complex is different from the one in hydroboration. The reasons are that the rate of hydroboration is significantly enhanced by ethereal solvents such as THF, while THF solvent has a relatively small effect on the rate of the rearrangement and no detectable effect on the stereochemistry. Moreover, the rearrangement process is known to be accelerated by the compounds with B–H bonds, while no such "catalytic" effect has been observed for the hydroboration.



Overall, it is generally accepted that the mechanism of the simplest hydroboration of ethylene with borane in the gas phase involves π-complex formation followed by a four-center transition state. There is a very low barrier for the reaction in the gas phase.[5] For diborane and simple alkyldiboranes, the question of whether monomers or dimers are involved in the rate-determining step in solution is not fully resolved. Brown proposed that the unsolved monomer formed from sterically hindered diboranes attacks alkenes, and the source of activation lies in the energy required to dissociate the dimer or uncomplex the solvent.[26] Clark and Schleyer proposed that the solvated monomer attacks alkenes, and that the activation energy comes from the energy required to displace the solvent by alkenes.[27] Full understanding of the mechanism of hydroboration and the nature of the transition state requires an extensive study of geometries and energies of the intermediates and transition structures involved in reactions of substituted alkenes and boranes.

We have performed an ab initio molecular orbital study of the parent reaction and many substituted versions, as well as reactions of several acetylenes. Understanding of small model systems explored at the ab initio level provides information for the development of empirical force fields, and this has provided results which have been used for the calculation of large systems.

Results and Discussion

Calculations were performed with Pople's GAUSSIAN 82 or 86 programs.[28] Geometry optimizations were performed with the RHF/3-21G basis set for all the systems studied. For the reaction of BH_3 with ethylene, the geometries were

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Table I. Bond Lengths (Å), Angles (deg), Activation Energies, and Complex Formation Energies (kcal/mol) for the Reaction of Borane with Ethylene at RHF/3-21G, RHF/4-31G, RHF/6-31G, and MP2/3-21G Levels**

method/basis set	C1–C2	C1–B3	C2–B3	B3–H4	C2–H4	∠BCC2	∠BCC1	E_a or E_c[a]
				Transition Structures				
RHF/3-21G	1.403	1.764	1.914	1.269	1.688	73.4	62.0	8.6
RHF/4-31G	1.397	1.754	1.905	1.261	1.692	73.4	61.9	11.7
RHF/6-31G**	1.384	1.776	1.876	1.242	1.718	71.6	63.9	6.6
MP2/3-21G	1.425	1.757	1.876	1.271	1.675	71.4	62.6	-6.9
				Complexes				
RHF/3-21G	1.325	2.620	2.603	1.190	2.666	74.6	76.0	-5.3
RHF/4-31G	1.322	2.855	2.838	1.184	2.869	75.9	77.3	-3.0
RHF/6-31G**	1.322	2.894	2.893	1.189	2.958	76.7	76.9	-2.5
MP2/3-21G	1.359	2.278	2.279	1.202	2.961	72.7	72.6	-12.6

	total energy, au	
method/basis set	**TS-1**	**Complex-1**
RHF/3-21G	-103.82455	-103.84665
RHF/4-31G	-104.25278	-104.27621
RHF/6-31G**	-104.42124	-104.43576
MP2/3-21G	-104.08577	-104.09484

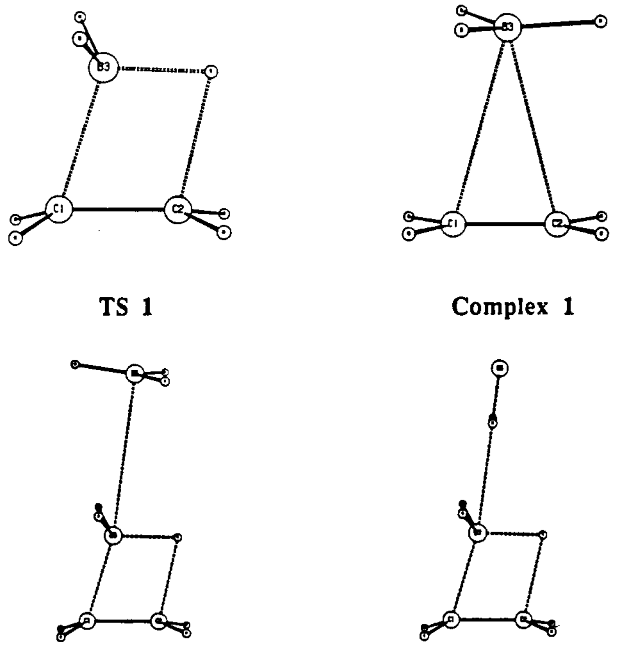
[a] E_a for transition structures and E_c for complexes.

further optimized at MP2/3-21G, RHF/6-31G**, and MP2/6-31G* levels. The transition structures for the reactions of borane with ethylene and acetylene were found to have only one imaginary vibrational frequency from a normal coordinate analysis. Frequencies were not calculated for the other transition structures.

The Reaction of Borane with Ethylene. There are extensive theoretical studies of the nature of the transition state in hydroboration reaction of borane with ethylene. Dasgupta initially studied the reaction with the CNDO/2 method.[12] He examined the energies of optimized four-center and three-center complexes for the ethylene–borane reaction and found that the three-center complex is more stable than the four-center one by 50 kcal/mol. He regarded the three-center complex as the transition state. Dewar carried out MNDO calculations on the potential surface and found a π-complex intermediate separated by two transition structures.[13] One leads from the π-complex to reactants and the other leads to the product. The formation of the π-complex was the rate-determining step for the overall reaction. An activation energy of 7.6 kcal/mol was calculated for this reaction.

Ab initio calculations by Lipscomb, Schleyer, and Morokuma at several levels show that the formation of the π-complex prior to the transition state is exothermic. The transition state is higher in energy than the reactants by 5.6–11.7 kcal/mol and is a four-center structure.[14,17,27] Since it is known by the flow reactor technique study of Fehlner that the parent reaction proceeds in the gas phase with little or no activation energy,[5] the ab initio calculations at low levels must overestimate the reaction energy barrier. Although inclusion of polarization functions and CI lowers the calculated barrier, the calculated activation energy is still much higher than the experimental estimate of 2 ± 3 kcal/mol.[5]

We have obtained a transition structure and a complex at the RHF/6-31G** level. This is comparable to the published[17,18] RHF/4-31G and RHF/3-21G surfaces on which a π-complex intermediate was found.[13] We could not find a MP2/6-31G* complex or transition structure. They most likely do not exist.



TS 1 **Complex 1**

Diborane **Water-borane**

Figure 1. 3-21G transition structure and complex for hydroboration of ethylene with BH_3 and transition structures for hydroboration of ethylene with diborane and with the borane–water complex.

The geometrical parameters of the transition structures located at various levels of theory are summarized in Table I and shown as **TS**-1 and **Complex**-1 in Figure 1. At all levels, the π-complex is more stable than the reactants. The transition structure is a four-center one. Larger basis sets give a slightly more advanced, or later, transition structure, while introduction of correlation energy corrections via second-order Moller-Plesset (MP2) perturbation theory results in an earlier transition structure. Overall, the positions of the transition structure and the π-complex are relatively insensitive to the level of theory used, and the 3-21G geometry is close to the most accurate one.

However, there are substantial changes in energetics at different computational levels, as shown in Table I. It is interesting to note that the 4-31G energies are higher than the 3-21G ones by 2.3 kcal/mol for the complex and 3.1 kcal/mol for the transition state. Inclusion of polarization functions (6-31G**) lowers the activation energy but destabilizes the complex as compared to the RHF/3-21G level. Introduction of correlation energy corrections (MP2/3-21G) causes the reaction to have a negative activation energy. This calculation was performed only after MP2/6-31G* calculations failed. The differences in energy

Table II. Summary of the Transition Structure and Complex Search for the Ethylene + Borane Reaction at the MP2/6-31G* Level[a]

	Search for the Transition Structure					
C2–H4	1.717	1.737	1.800	1.900	2.000	2.300
C1–B3	1.698	1.730	1.761	1.809	1.854	2.010
E_{rel}	−14.6	−14.5	−14.3	−14.1	−14.0	−12.0
	Search for the Complex					
C2–H4	2.266	2.234	2.091	2.074	1.980	
C1–B3	2.266	2.133	1.943	2.089	1.895	
E_{rel}	−10.0	−10.9	−11.4	−12.0	−13.2	

[a] C2-H4 distances were fixed. Energies are relative to the reactants (kcal/mol).

Table III. MP2/6-31G* and MP4/6-311G* Single-Point Calculation on RHF/3-21G Geometry[a]

	MP2/6-31G*				MP3/6-311G*		
	R	C	TS		R	C	Ts
ΔH	0.0	−16.0	−21.7	ΔH	0.0	−4.0	−11.0
ΔG	0.0	−7.2	−11.2	ΔG	0.0	−1.1	−0.5
	MP2/6-311G*				MP4/6-311G*		
	R	C	TS		R	C	TS
ΔH	0.0	−6.6	−14.1	ΔH	0.0	−3.4	−9.8
ΔG	0.0	+1.3	−3.6	ΔG	0.0	−1.9	+1.0

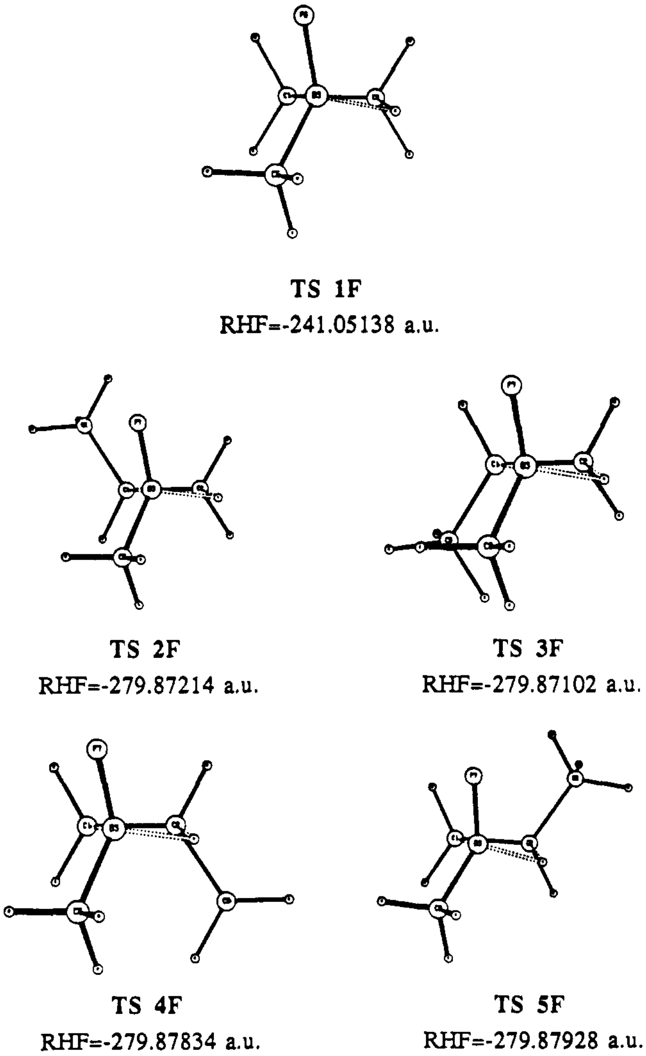
[a] The free energies (kcal/mol) for reactants, complex, and transition state are obtained by combining the enthalpy with the RHF/3-21G entropy at 25 °C.

between the transition state and the complex at 3-21G, 6-31G**, and MP2/3-21G are 13.9, 9.1, and 5.7 kcal/mol, respectively. This suggests that the complex and the transition structure might disappear with higher level calculations.

Indeed the best calculations performed, with polarization functions and correlation energy corrections (MP2/6-31G*), predict that there is no complex and no transition structure. Table II summarizes the search for the complex and the transition structure at this level. The whole geometry was optimized with the constraint of only the C_2–H_4 bond. The energy decreases steadily as ethylene approaches BH_3. The calculated energy of the complex is higher than that of the TS, and attempted optimization of the complex with MP2/6-31G* gives the product directly. These results are reminiscent of our calculations on the reactions of halocarbenes with alkenes,[18b] where complexes found at the RHF level of theory disappear with inclusion of correlation energy. There is no complex and no activation barrier at the best level we used.

The conclusion for the parent reaction will also hold for the reaction of borane with substituted alkenes. Nevertheless, there will be some similarity between the maximum calculated at the RHF level and the transition state, which will be a free energy maximum.[18b] MP4/6-311G* single-point calculation on the RHF/3-21G geometries of reaction of borane with ethylene combined with entropy consideration indicates that the complex is stabilized by 1.9 kcal/mol, and the barrier relative to the reactants is 1.0 kcal/mol on the free energy surface (Table III). On the other hand, as described below, dialkylboranes will always have significant positive activation energies. For that reason, we continue to compare RHF transition states of various reactions to see how substituents alter the geometries and enthalpies of the transition states.

The Reaction of Methylfluoroborane with Ethylene and Propene. Haloboranes are stronger Lewis acids than borane itself, primarily because the attached halogens withdraw electrons from boron when they are complexed to Lewis bases.[29] It might be expected that monohaloborane, dihaloborane and alkylhaloborane would be powerful hydroboration agents. However, they often strongly coordinate with basic solvents such as diethyl ether or THF and, as a consequence, react slowly in the hydroboration reaction.[30] The regioselectivity of attack on alkenes for haloboranes is greater than that of borane and is roughly comparable to that of dialkylboranes.[29,31] Although hydroborations with haloboranes have been heavily studied and used for synthetic purposes, the reaction mechanism has attracted little attention. In order to understand the nature of the transition structure involved in this reaction, we have performed ab initio calculations using methylfluoroborane as a model agent.



TS 1F
RHF=-241.05138 a.u.

TS 2F
RHF=-279.87214 a.u.

TS 3F
RHF=-279.87102 a.u.

TS 4F
RHF=-279.87834 a.u.

TS 5F
RHF=-279.87928 a.u.

Figure 2. Transition structures for hydroboration of ethylene and propene with methylfluoroborane.

The transition structures of hydroborations of methylfluoroborane with ethylene and propene were located with the 3-21G basis set. The activation energies and geometrical parameters are summarized in Table IV. Figure 2 is a top view of those transition structures looking along the forming B–C bond. The four-center transition state is still found. However, the BH bond is rotated about 10° away from being parallel to the C–C bond.

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Table IV. Geometries (Å and deg) and Activation Energies for the Reactions of Methylfluoroborane with Ethylene and Propene (3-21G)

TS	C1=C2	C1-B3	C2-B3	B3-H4	C2-H4	∠BCC2	∠BCC1	E_a
1F	1.401	1.768	1.942	1.278	1.689	74.6	61.4	27.5
2F	1.407	1.760	1.930	1.283	1.669	74.2	63.4	29.0
3F	1.405	1.764	1.926	1.281	1.679	73.9	61.6	29.7
4F	1.407	1.753	1.968	1.277	1.691	76.1	59.9	25.1
5F	1.410	1.749	1.964	1.280	1.696	76.1	59.8	24.5

The forming B–C bond length (1.76 Å) is shorter than that for hydroboration of dimethylborane (see later), but the activation energy is higher by about 7.0 kcal/mol. The p orbitals of fluorine and boron are similar in energy so that the overlap between them stabilizes the reagent but destabilizes the transition structure.

For the reaction of methylfluoroborane with propene, there are four transition structures which lead to the formation of two regioisomers and two stereoisomers. **TS-2F** and **TS-5F** differ in energy by 4.5 kcal/mol, which is larger than that of borane with propene (3.7 kcal/mol), indicating the methylfluoroborane is more regioselective than borane. **TS-2F**, **TS-3F** and **TS-4F**, **TS-5F** differ in energy by 0.7 and 0.6 kcal/mol, respectively, favoring the conformation with the propene methyl group cis to the fluorine atom.

The Reaction of Diborane with Ethylene. There are two possible mechanisms for the reaction of diborane (B_2H_6) with ethylene. One involves the dissociation of diborane into monomeric BH_3, followed by the addition of BH_3 on the double bond of ethylene. Alternatively, diborane may attack ethylene directly to form ethylborane plus BH_3, with BH_3 associated to some extent in the transition state. Diborane reacts with alkenes very slowly in the gas phase[32] or in hydrocarbon solvents, while the reaction rate is greatly accelerated in ether solvents.[1a,b]

Based upon kinetic studies, it has been proposed that reaction of diborane with ethylene occurs via the prior dissociation mechanism in the gas phase.[32a] In ether solvent, diborane is in equilibrium with the H_3B–ether complex,[33] which undergoes fast hydroboration with alkenes.[34,35] Pasto and co-workers have shown that the reaction of H_3B–THF with 2,3-dimethyl-2-butene exhibits second-order kinetics.[15] They concluded that the H_3B–THF complex reacts directly with the alkene. Brown, on the other hand, proposed that the H_3B–THF complex dissociates into free BH_3, which subsequently undergoes fast hydroboration.[34] Ab initio model theoretical studies support the notion that H_3B–THF attacks alkenes directly, but also support Brown's contention that the solvent molecule is virtually unbound to the four-centered transition state.[27] The facile reactivity of borane–ether complex was attributed to the fact that the ether solvent displaced during the reaction is a better leaving group than BH_3.

Recent kinetic studies in the gas phase have shown that diborane does not react with water at room temperature.[36] The reaction of borane with water to release hydrogen is also a very slow reaction. Wang and Jolly provide some evidence for the existence of borane–water complex.[37] Ab initio calculations at the HF/6-31G* level predict a 6 kcal/mol complexation energy between borane and water.[38] Gas-phase studies also indicate that the reaction of water with diborane occurs via prior dissociation of diborane.[39]

Borane reacts with alkenes with little or no activation energy.[5,36] Consequently, the rate-determining step must be the dissociation of diborane, unless there is a very strong assistance to dissociation. The entropy of dissociation should be favorable, while that for bimolecular association reaction is expected to be on the order of −25 to −45 eu (the entropy for the reaction of borane with ethylene obtained from 3-21G calculations is −35 eu), which amounts to a contribution to the free energy of activation of 8–14 kcal/mol at room temperature. Thus, for the direct reaction of diborane with ethylene to be favored, it must have an activation enthalpy which is 8–14 kcal/mol less than that of diborane dissociation. The dissociation energy of diborane in the gas phase has been determined to be of the order of 35–40 kcal/mol.[40] Recent ab initio molecular orbital calculations with large basis sets including electron correlation predict that the binding energy of diborane is approximately 40 kcal/mol,[41] while calculations at the Hartree–Fock level underestimate the binding energy by about half. We have undertaken a computational study of the reaction of diborane with ethylene in order to understand better the effect of the second borane upon the reaction energetics and the reaction transition-state geometry.

The transition structure for the reaction of diborane with ethylene was located with ab initio RHF calculations with the 3-21G basis set. First, we took the 3-21G transition structure of the borane plus ethylene reaction and optimized an associated BH_3 moiety. Then the constraints were released, and the structure was optimized to a saddle point. The structure is shown in Figure 1. The optimized saddle point was characterized by the calculation of vibrational frequencies. It has two imaginary vibrational frequenices, the larger one ($800i$ cm^{-1}) corresponding to the normal mode along the hydroboration pathway, while the other ($45i$ cm^{-1}) corresponds to a rotation mode of the second BH_3 moiety. The B–B distance in the transition structure is 3.2 Å, indicating that the second BH_3 is virtually free. This structure is only 1.8 kcal/mol lower in energy than the total energy of borane plus the transition structure of BH_3 with ethylene. The 1.8 kcal/mol stabilizing interaction is not particularly significant, since there will be some basis set superposition error at this level. This is not an authentic transition structure, since it has two negative force constants, but the smaller one is indicative of nearly free rotation of the displaced borane. We did not further

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Table V. Geometries (Å) and Activation Energies (kcal/mol) for the Diborane + Ethylene and Water Borane Complex + Ethylene Reactions at the 3-21G Level Compared to Those for the Borane + Ethylene Reaction

Reaction	C1=C2	C1-B3	B3-H4	C2-H4	B3-B5	B3-O5	E_a
$B_2H_6 + C_2H_4$	1.403	1.758	1.266	1.690	3.218		21.5
BH_3-$H_2O + C_2H_4$	1.378	1.720	1.232	1.900		3.224	30.2
$BH_3 + C_2H_4$	1.403	1.764	1.269	1.688			8.6

Table VI. Geometries (Å and deg), Activation Energies, and Complex Formation Energies (kcal/mol) for Hydroborations of Various Alkenes at the 3-21G Level

TS	C1-C2	C1-B3	C2-B3	C2-H4	B3-H4	∠BCC2	∠BCC1	E_a
1	1.403	1.764	1.914	1.688	1.269	73.4	62.0	8.6
2	1.408	1.752	1.931	1.682	1.266	74.4	60.9	7.1
3	1.408	1.753	1.902	1.668	1.273	73.1	61.8	10.7
4	1.414	1.744	1.950	1.682	1.263	75.4	60.0	5.6
5	1.399	1.782	1.935	1.690	1.273	73.9	62.2	15.5
6	1.397	1.800	1.959	1.690	1.278	74.4	62.2	20.3
7	1.404	1.781	1.925	1.673	1.275	73.3	62.4	18.6
8	1.413	1.742	1.919	1.667	1.270	74.1	60.8	9.1
9	1.416	1.742	1.922	1.667	1.269	74.2	60.7	8.7

complex	C1-C2	C1-B3	C2-B3	B3-H4	C2-H4	∠BCC2	∠BCC1	E_c
1	1.325	2.620	2.603	1.190	2.666	74.6	76.0	-5.3
2	1.328	2.498	2.581	1.191	2.645	78.3	71.4	-5.8
3	1.327	2.639	2.513	1.191	2.644	69.9	80.4	-5.8
4	1.331	2.457	2.613	1.191	2.620	81.4	68.4	-6.3
5	1.320	2.949	2.936	1.193	2.912	76.5	77.6	-3.0
6	1.317	3.329	3.237	1.196	3.168	74.6	82.9	-2.7
7	1.311	2.860	2.939	1.191	2.946	80.3	73.6	-3.1
8	1.329	2.551	2.526	1.190	2.620	73.8	75.8	-5.6
9	1.332	2.500	2.495	1.191	3.109	74.3	74.7	-6.3

optimize this structure, since the potential surface is so flat in this region. The activation energy calculated is 22 kcal/mol, 13 kcal/mol above that calculated for the BH_3–ethylene reaction. However, the energy of dissociation of diborane is much too low at the 3-21G level, and so an activation energy of 30–40 kcal/mol is expected for this process.

These calculations, like those carried out early on the reaction of the borane–water complex, predict that the corresponding solvent molecule or BH_3 is dissociated from the reacting borane in the transition state corresponding to the saddle point. This is compatible with both mechanisms proposed earlier, since the same transition state is obtained in either case. However, using the entropic considerations described earlier, even with wide ranges of uncertainty, the dissociation–combination mechanism should have $\Delta G^{\ddagger} \leq 30$ kcal/mol ($\Delta H^{\ddagger} = 35$–40 kcal/mol, $\Delta S^{\ddagger} = 0$–30 eu) for the first step and $\Delta G^{\ddagger} = 0$–10 kcal/mol ($\Delta H^{\ddagger} = 0$ to -10 kcal/mol, $\Delta S^{\ddagger} = -25$ to -45 eu) for the second step, while the single step process should have $\Delta G^{\ddagger} = 35$–45 kcal/mol ($\Delta H^{\ddagger} = 30$–40 kcal/mol, $\Delta S^{\ddagger} = -25$ to -45 eu). Based upon this estimate, the dissociation–combination process is likely the preferred one in the gas phase.

Table V compares the approximate transition structure of the reaction of diborane with ethylene to that of BH_3–H_2O complex with ethylene as described by Clark and Schleyer (Figure 1).[27] The geometry around the four-center locus of bonding changes is very similar in both cases to that for the parent reaction of borane monomer with ethylene. These calculations on the gas-phase reactions of borane monomers with alkenes should be reliable for modeling the stereoselectivity and regioselectivity in solution, where the mechanism of the reaction might be either of the two discussed above, but the transition structure will be about the same in either case.

Hydroborations of Methyl-Substituted Alkenes. Hydroborations of methyl-substituted alkenes have been studied by Dewar, using the MNDO technique.[13] The additions of borane to ethylene, propene, and isobutene as well as the addition of monomethylborane to ethylene were calculated to have two transition states: one leading to the formation of a loose π-complex, and the second leading from this complex to products. One of the transition states disappears for the addition of dimethylborane to ethylene. The regioselectivity of the additions was also considered. The calculated difference in energy between these two modes of addition is very small in gas phase, ranging from 0.2 to 0.8 kcal/mol. The predicted mode of addition of borane to propene is opposite to experimental observation in that boron is incorrectly predicted by MNDO to bond to the more substituted terminus.

We have studied the substituent effects in hydroboration both on transition states and π-complexes. First, we have obtained nine transition structures using the 3-21G basis set and gradient and second-derivative techniques. Then, we found an intermediate π-complex for each of these reactions by moving from the transiton structure toward the reactants. There are nine complexes corresponding to the nine transition structures. The geometries and energies of the transition structures and of the complexes are summarized in Table VI. Substituents have remarkably small effects on the transition-structure geometries. The forming CB bond varies only from 1.74 to 1.80 Å, while the forming CH bond length is 1.26–1.28 Å. The more substituted boranes have higher activation barriers and less fully formed CB and CH bonds. This indicates that steric effects cause the alkyl groups to be further apart in the transition structure.

TS-2 for the hydroboration of propene is more stable than **TS-3** by 3.6 kcal/mol. The predicted major isomer is consistent with the experimental data.

In the π-complexes, the substituents on the alkenes give complexes with relatively short C–B distances and stronger complexation. In contrast, substituents on the boron atoms tend to lengthen the complexing bond lengths, paralleling the destabilization of the π-complex. The complex leading to anti-Markovnikov addition is more compact than that leading to Markovnikov addition, probably due to the steric interaction between the alkene methyl group and the borane. The results indicate that the electronic effects induced by the electron-donating substituents are important, but steric effects cannot be neglected. For

Table VII. Geometries (Å and deg), Activation Energies, and Complex Formation Energies (kcal/mol) for the Reactions of Borane with Acetylene, Propyne, and 2-Butyne Calculated with the 3-21G Basis Set

TS	C1–C2	C1–B3	C2–B3	C2–H4	B3–H4	∠BCC2	∠BCC1	E_a
10	1.241	1.725	1.949	1.719	1.274	80.4	60.7	16.7
11	1.248	1.699	1.966	1.693	1.282	82.1	58.9	15.8
12	1.245	1.711	1.922	1.685	1.278	79.4	61.1	17.1
13	1.500	1.690	1.940	1.665	1.283	81.0	59.4	16.5
complex	C1–C2	C1–B3	C2–B3	C2–H4	B3–H4	∠BCC2	∠BCC1	E_c
10	1.190	2.809	2.832	2.874	1.189	79.9	76.8	−3.3
11	1.192	2.811	2.687	2.831	1.189	83.4	71.7	−3.9
12	1.192	2.838	2.697	2.805	1.189	75.4	79.3	−4.1
13	1.194	2.672	2.672	2.765	1.189	77.1	77.1	−4.4

Table VIII. Geometries (Å and deg), Activation Energies, and Complex Formation Energies (kcal/mol) for the Reactions of Borane with Acetylene at RHF/3-21G and MP2/6-31G* Levels

basis set	C1–C2	C1–B3	C2–B3	C2–H4	B3–H4	∠BCC2	∠BCC1	E_a
RHF/3-21G	1.241	1.725	1.949	1.719	1.274	80.4	60.7	16.7
MP2/6-31G*	1.250	1.707	1.813	1.717	1.241	73.8	65.3	−5.5

sterically hindered boranes, no complexes are expected to be formed, since electronic effects and steric effects operate in the same direction.

It can be seen from the table that methyl groups on boron increase the activation energies and destabilize the complexes, while placing the methyl groups on the double bonds of the alkenes decreases the activation energies and stabilizes the complexes. The anti-Markovnikov additions have lower activation energies than the Markovnikov, but the corresponding isomeric complexes have almost identical energies. The electrophilicity of the borane and nucleophilicity of the alkene account for these observations.

The complexes and the transition structures for the reactions of BH_3 with *cis*- and *trans*-2-butene were also located. It is observed experimentally that diisopinocampheylborane selectively hydroborates *cis*-2-hexene in the presence of the trans isomer. The reaction of diborane with alkenes is too fast to observe any selectivity.[42] The source of the selectivity with the sterically hindered alkene was attributed to the steric hindrance of the diisopinocampheylborane, but is not clear if the *cis*-alkene itself is intrinsically more reactive than the trans isomer. Our calculations indicate the addition of BH_3 to *cis*-2-butene is favored by 0.4 kcal/mol. One could argue that the preference originates from the release of steric interaction between the two methyl groups of *cis*-2-butene in the transition structure. However, this explanation is suspect, because the complex experiences very small changes in geometry as compared to the isolated alkenes, but shows an even greater difference in stability than the transition structures.

Hydroborations of Acetylene and Methyl-Substituted Alkynes. The complexation energies (E_c in Table VII) of these reactions are smaller than those of the corresponding alkene reactions by about 2 kcal/mol. This indicates that alkynes are poorer π-donors compared to alkenes, consistent with their higher ionization potentials. Methyl substituents increase the complexation energy, as expected. The geometries of the complexes are very similar. The triple bond carbons are only slightly bent. The slight shortening of the C–B distance with increasing substitution parallels the increasing complexation energy.

The calculated activation energies for these reactions are higher by 6–8 kcal/mol than those of corresponding alkene reactions. Although this is in qualitative agreement with the expectation based on the fact that HOMO energy of acetylene is lower than that of ethylene,[45] the difference is probably overestimated. As demonstrated in the case of the reaction of BH_3 with ethylene, the activation energy drops significantly upon inclusion of correlation energy corrections. Higher level calculations are necessary in order to predict the relative reactivities of corresponding alkenes and alkynes. Some experiments have indicated that the relative reactivities of alkenes and alkynes are quite dependent upon steric hindrance of both borane reagent and unsaturated system. Hydroborations of terminal alkynes with unhindered boranes give predominant double hydroboration products,[46,47] which indicates that double bonds are more reactive than triple bonds in these cases. Hydroborations stop at the first stage when hindered boranes or/and internal alkenes are involved.

The transition structure for the reaction of borane with acetylene was also located at MP2/6-31G* level. The geometry of the transition structure shows essentially no change from RHF/3-21G to MP2/6-31G* (Table VIII). The activation energy estimated at the MP4/6-311G* level using RHF/3-21G geometry is −2.8 kcal/mol.

Methyl substitution at the terminus to which hydride becomes attached reduces the activation energy by 0.9 kcal/mol, while a methyl group at the terminus where boron adds increases the activation energy by 0.4 kcal/mol. A 1.3 kcal/mol difference in energy between the anti-Markovnikov TS and the Markovnikov TS is compatible with the experimental observation of a 94:6 product ratio for propyne and other linear terminal alkynes.[44]

Methyl substituents have very little effect on the geometry of the transition structure. The forming B–C and H–C bond lengths in these transition structures are about same. Since a normal C–B bond is significantly longer than a normal C–H bond, the B–C bond formation in the transition structure is more advanced than the formation of the C–H bond. Correspondingly, the bending of alkyne moiety is more significant at the C_1 center than at the C_2 center in each of the transition structures.

A notable difference between these transition structures and the transiton structures for alkene reactions is the degree of steric crowding. The bending at the C_1 alkyne

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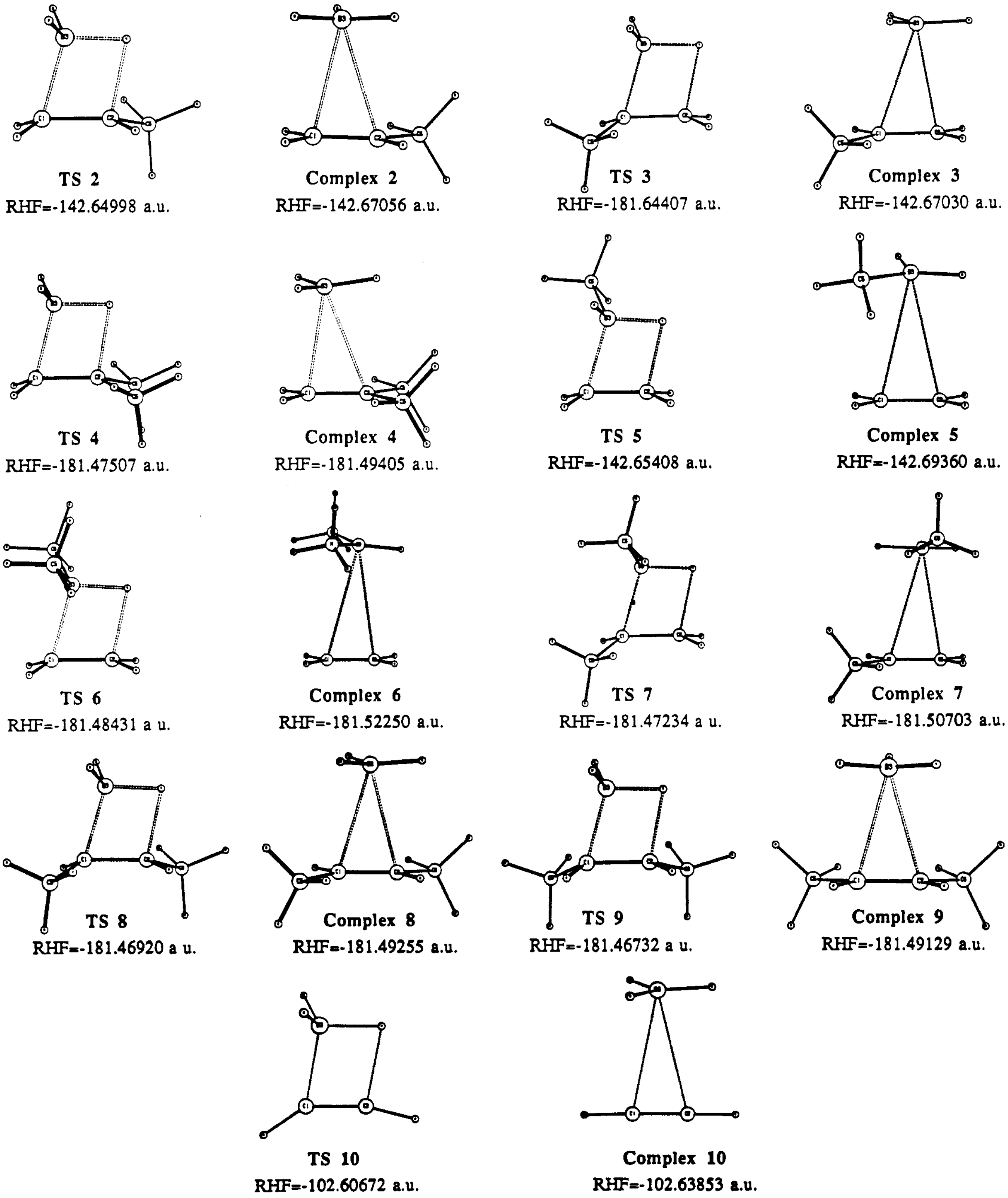

Figure 3. Transition structures for alkene hydroborations.

terminus is more significant in the alkyne transition structures than in alkene transition structures. The C_1 substituent in **TS-10–13** is staggered with respect to the borane substituents, while there is eclipsing in the alkene transition structures. Therefore, steric interactions are more important in the alkene transition structures. This influences the relative reactivities of alkenes and alkynes when the borane reagent is hindered or the unsaturated bond is internal.

The Hydroboration of Allenes. Hydroboration of allenes with borane is complicated, forming mixture of regioisomers and of mono- and dihydroboration products.[48] The reaction can be controlled by using less reactive 9-BBN or catecholborane to give monohydroboration products.[49] The regioselectivites of hydroboration of those

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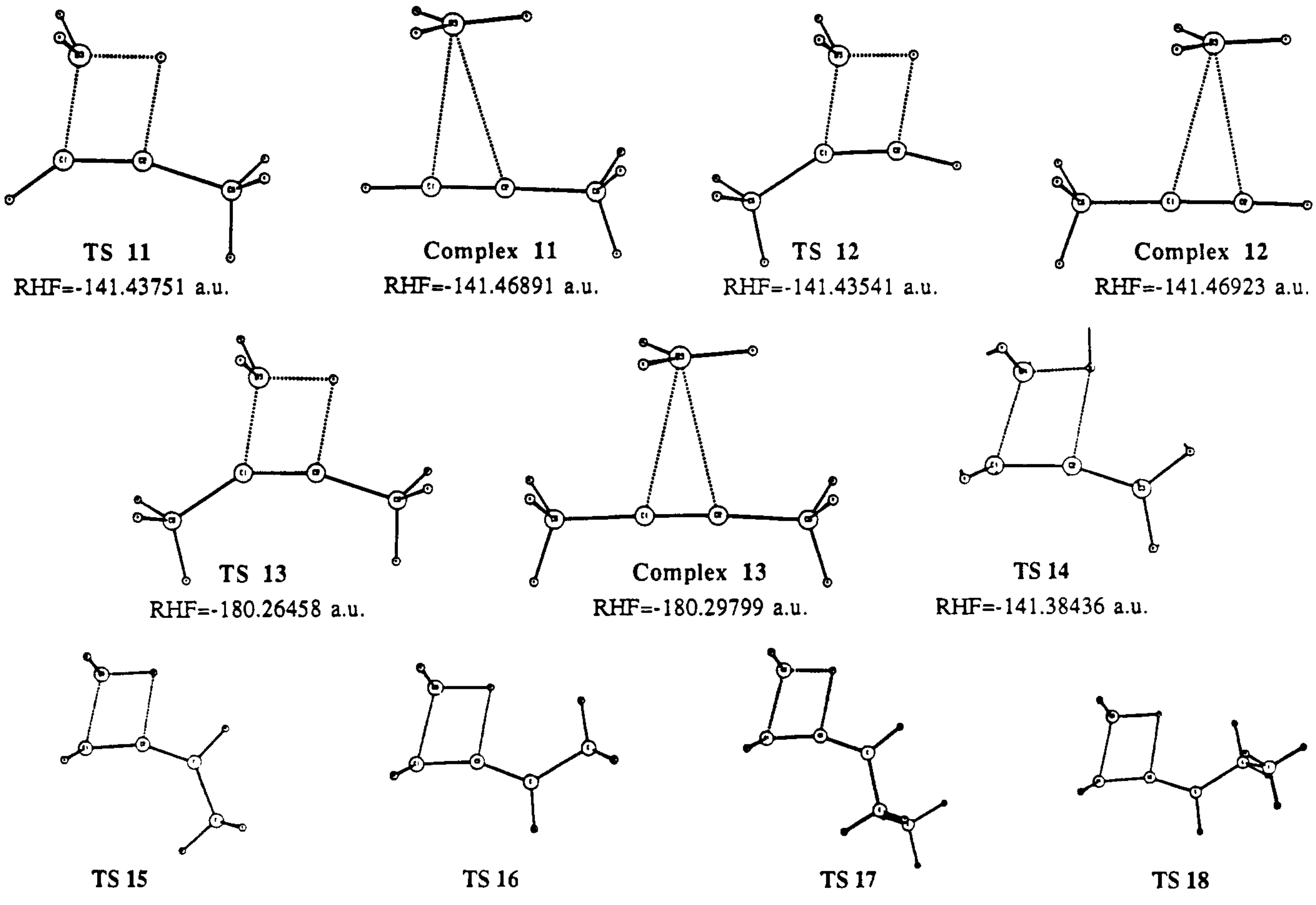
Table IX. Geometries (Å and deg) and Activation Energies for the Reactions of Borane with Allene, Methylallene, and Ethylallene Calculated with the 3-21G Basis Set

TS	C1-C2	C1-B3	C2-B3	B3-H4	C2-H4	∠BCC2	∠BCC1	E_a
14	1.374	1.780	1.913	1.255	1.691	73.4	63.1	11.8
15	1.374	1.783	1.913	1.253	1.695	73.3	63.2	10.3
16	1.373	1.786	1.922	1.250	1.720	73.7	63.1	10.4
17	1.375	1.781	1.915	1.254	1.695	73.4	63.1	10.2
18	1.373	1.784	1.924	1.250	1.720	73.8	62.9	10.3



TS 11 RHF=-141.43751 a.u.

Complex 11 RHF=-141.46891 a.u.

TS 12 RHF=-141.43541 a.u.

Complex 12 RHF=-141.46923 a.u.

TS 13 RHF=-180.26458 a.u.

Complex 13 RHF=-180.29799 a.u.

TS 14 RHF=-141.38436 a.u.

TS 15 RHF=-180.26242 a.u.

TS 16 RHF=-180.26228 a.u.

TS 17 RHF=-219.08211 a.u.

TS 18 RHF=-219.08193 a.u.

Figure 4. Transition structures for alkyne and allene hydroborations.

reagents with asymmetric allenes are very high. The *R* and *S* allenes can be resolved by reacting with chiral hydroborating reagents such as dipinanylborane.[50] The mechanism of this reaction has been considered to be similar to that of hydroboration with ethylene and acetylene.

The transition structures of hydroboration reactions of borane with allene, methylallene, and ethylallene were located with the 3-21G basis set. The bond lengths and bond angles (Table IX and Figure 4) resemble those of transition states of reactions of borane with ethylene and acetylene. The allene skeleton is bent to facilitate bond formation with borane. The activation energy is intermediate between those for ethylene and for acetylene. In the case of methylallene and ethylallene, two modes of addition of borane relative to the substituted group need to be considered. Namely, the borane can attach either from the side cis to the substituted group or anti to it. The energies of these two modes of additions are nearly the same, with the anti addition slightly favored.

Conclusion

For the reaction of borane with ethylene, the transition structure was located at various levels of theory, but disappears with inclusion of correlation energy corrections. The transition structure for the reaction of diborane with ethylene is essentially that of monoborane with ethylene with one borane moiety nearly dissociated. The diborane dissociation mechanism is favored for the gas-phase hydroboration by these calculations.

In the cases of propene and propyne, anti-Markovnikov transition structures are favored. Both electronic and steric effects contribute to the regioselectivity. The activation energies of alkyne reactions are higher than those of corresponding alkene reactions. The geometry of the transition structure changes only slightly upon alkyl substitution.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research.

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