

HYDROBORATION - KINETICS AND MECHANISM

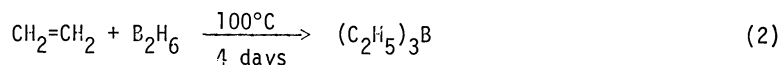
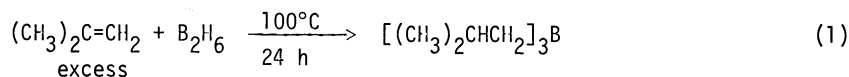
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Abstract - The kinetics of hydroboration of alkenes with several dialkylborane dimers have been studied extensively. The reaction of alkenes with disiamylborane dimer displays second-order kinetics, first-order in the dimer and first-order in the alkene. (9-BBN)₂, on the other hand, reacts by a prior dissociation of the dimer, followed by the reaction of the monomer with the alkene. Borinane dimer also reacts by the dissociation mechanism. By following the kinetics of the reactions of alkenes, alkynes, aldehydes and ketones, alcohols and amines with (9-BBN)₂, a spectrum of mechanistic pathways has been revealed: comprising a direct attack of the substrate on the 9-BBN dimer (Mechanism 1), a slow dissociation of the dimer, followed by a fast attack of the substrate on the monomer (Mechanism 2), and an equilibrium dissociation of the dimer, followed by a slow reaction of the monomer with the substrate (Mechanism 3). The actual mechanism that a given substrate follows is dependent on the nucleophilicity of the substrate. Thus with less hindered amines, we observe Mechanism 1; more hindered amines give Mechanism 2; reactive alkenes give Mechanism 2; less reactive alkenes give Mechanism 3. This unraveling of the full spectrum of mechanisms permits a clearer understanding of the reaction of borane derivatives. A systematic study of the hydroboration characteristics of representative 9-BBN-Lewis base complexes reveals that the complex dissociates prior to hydroboration. The results provide a rational explanation for the marked catalytic effect of ether solvents on the hydroboration reaction. Dihaloborane-methyl sulfide complexes also hydroborate alkenes by the dissociation mechanism. These studies point to a general trend in the mechanism of hydroboration.

INTRODUCTION

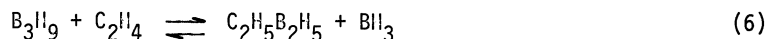
The reaction of diborane with alkenes in the gas phase was first reported by Hurd in 1948 (Ref. 1). Whatley and Pease (Ref. 2) studied the kinetics of hydroboration of ethylene with



diborane at 154°C by following the rate of pressure drop. The rate equation (Eqn. 3) was

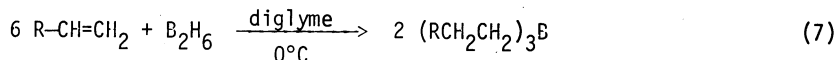
$$-\frac{dp}{dt} = \frac{k[\text{B}_2\text{H}_6]^{3/2}}{1-2.0\left(\frac{[\text{B}_2\text{H}_6]}{[\text{C}_2\text{H}_4]}\right)} \quad (3)$$

complex. A mechanism was proposed involving the reaction of B₃H₉ with ethylene (Eqns. 4, 5 and 6).



The slowness of the reaction in the gas phase discouraged organic chemists from using this reaction.

In 1956, Brown and Subba Rao (Ref. 3) discovered that the addition of >B-H onto >C=C< bonds occurs with great ease in ether solvents (Eqn. 7). This development made organoboranes



easily available and the organoboranes thus produced have been utilized in organic synthesis very effectively (Ref. 4). Hydroboration is very slow in hydrocarbon solvents (Ref. 5).

However, mechanistic studies of the reaction have lagged far behind the synthetic applications. This may be attributed to several reasons. The hydroboration of alkenes with BH_3 in ether solvents is very fast (Ref. 3) ($t_{1/2} \sim$ one minute) and is highly complex in nature. It involves three consecutive addition reactions (Eqns. 8-10),

addition reactions:



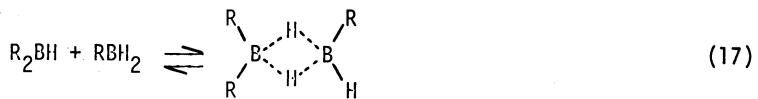
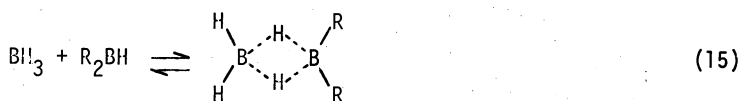
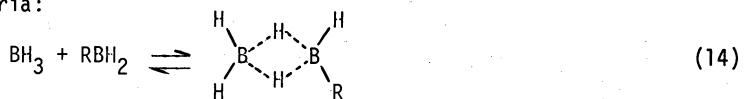
three redistribution processes (Eqns. 11-13)

redistribution reactions:



and five monomer-dimer equilibria (Eqns. 14-18) (Ref. 6).

monomer-dimer equilibria:

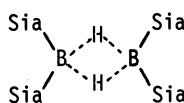
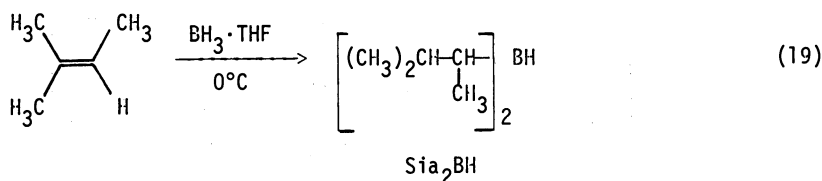


Consequently, the kinetics of the hydroboration reaction could not be studied.

In an attempt to simplify the situation, we decided to study the kinetics of hydroboration of alkenes with dialkylborane dimers.

KINETICS OF HYDROBORATION OF ALKENES WITH DISIAMYLBORANE DIMER

Disiamylborane can be conveniently prepared by the reaction of $\text{BH}_3 \cdot \text{THF}$ with 2-methyl-2-butene (Eqn. 19) (Ref. 7). It exists predominantly as a dimer (**1**) (Ref. 8) and hydroborates

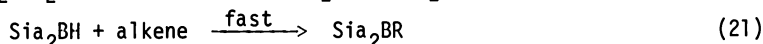
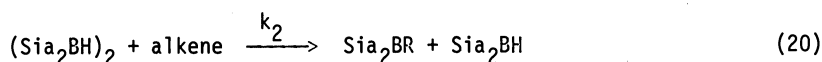


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alkenes at convenient rates at 0°C. For us, this was the first attractive candidate for studying the kinetics of hydroboration. Consequently, we determined the rates of the reaction of disiamylborane dimer with representative alkenes in THF at 0°C (Ref. 9). The experimental procedure involved quenching aliquots of reaction mixtures into methanol at required time intervals and analyzing the residual alkene by gas chromatography.

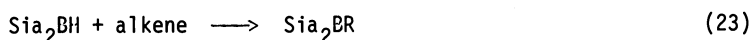
A priori, there are two distinct mechanistic possibilities for the hydroboration of alkenes with disiamylborane dimer:

1. Direct-attack mechanism



The direct-attack mechanism predicts a second-order reaction, first-order in (Sia₂BH)₂ and first-order in the alkene.

2. Dissociation mechanism



The reaction will exhibit first-order kinetics when the dissociation step (Eqn. 22) is rate-determining and three-halves-order kinetics when the hydroboration step (Eqn. 23) is rate-determining.

The reaction of a typical alkene, cyclopentene, with disiamylborane dimer displayed second-order kinetics, first-order in the alkene and first-order in the dimer. The plot of $[(1/b-2x)-1/b]$ vs. time was linear* (Fig. 1).

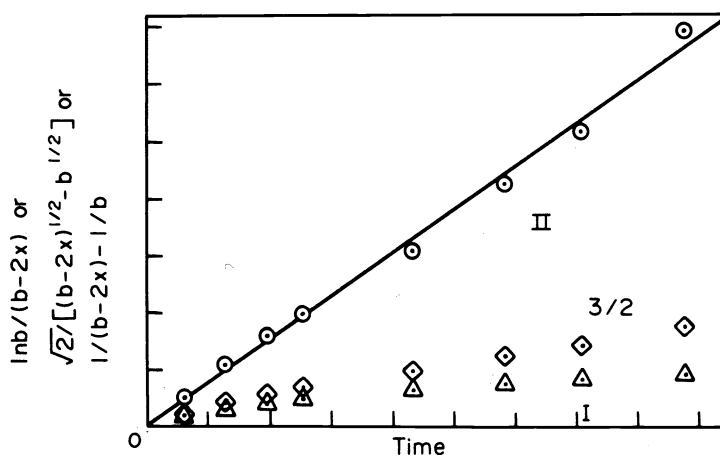



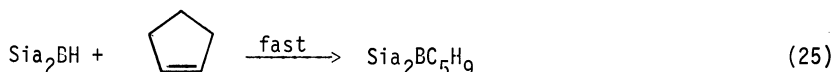
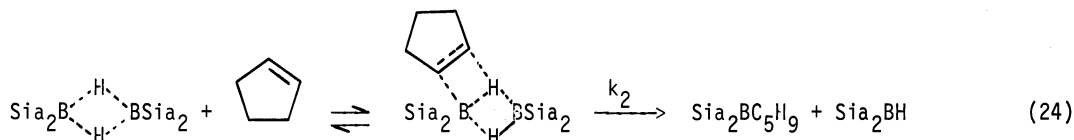
Fig. 1. Rate plot for the reaction of cyclopentene with (Sia₂BH)₂ in THF at 0°C.

* The second-order kinetic expression is $k = 1/t[1/b-2x - 1/b]$ where b is the initial concentration and $b-2x$, the concentration at time t , of the alkene.

Changing the initial concentration of the reactants did not alter the second-order rate constants significantly:

Initial Conc., <i>M</i>		$10^4 k_2$
	$(\text{Sia}_2\text{BH})_2$	$\text{M}^{-1}\text{s}^{-1}$
0.400	0.200	14.2
0.200	0.200	14.6
0.200	0.100	13.2

The second-order kinetics supports the direct attack mechanism for the hydroboration of cyclopentene with $(\text{Sia}_2\text{BH})_2$ (Eqns. 24 and 25).



The second-order rate constants for the hydroboration of a number of alkenes with $(\text{Sia}_2\text{BH})_2$ were also determined (Ref. 9).

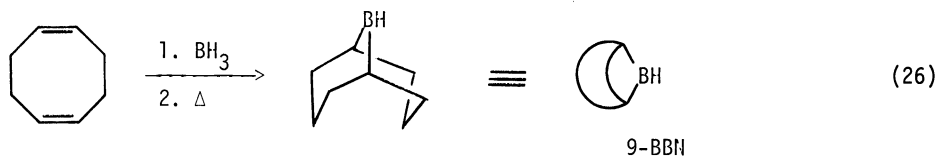
In the course of our work, we identified some problems associated with the disiamylborane kinetics:

- 1) Disiamylborane is not stable above 0°C.
- 2) It is a mixture of four diastereomers (Ref. 8). We are not certain as to how this will affect its kinetic behavior.
- 3) The quenching method employed for the kinetic study is rather tedious.

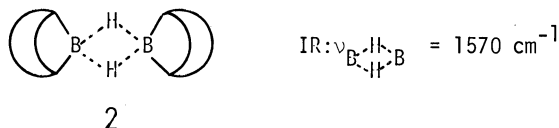
As a result, we decided to study the kinetics of hydroboration with other R_2BH reagents free of these complications by more convenient, more precise techniques.

KINETICS OF HYDROBORATION WITH 9-BORABICYCLO[3.3.1]NONANE DIMER

9-Borabicyclo[3.3.1]nonane, 9-BBN, is easily prepared in a high state of purity by the cyclic hydroboration of 1,5-cyclopentadiene with BH_3 (Eqn. 26) (Ref. 10).



It exists as a stable dimer (2) in the solid state and in solution in noncomplexing solvents.



Its stability at ambient temperatures encouraged us to study the kinetics of hydroboration at 25°C (Ref. 11). In the beginning, we studied the kinetics using the quenching method (Ref. 11). As we pointed out earlier, the quenching method is tedious. However, we then discovered that the reaction could be continuously followed by monitoring the B-H-B stretching absorption of 9-BBN dimer by using a quantitative IR spectrometer (Ref. 12). This provided a more convenient, more precise kinetic procedure. Much of the results presented in this lecture utilize this technique.

The hydroboration of a reactive alkene, such as cyclopentene, with $(9\text{-BBN})_2$ in CCl_4 at 25°C, followed first-order kinetics, first-order in $(9\text{-BBN})_2$ (Fig. 2).

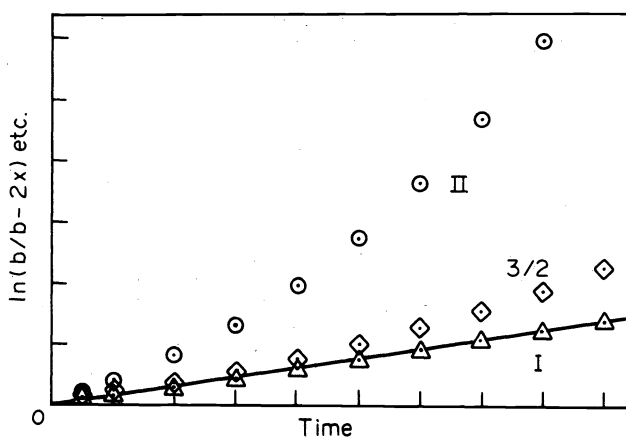




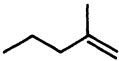




Fig. 2. Rate plot for the reaction of cyclopentene with $(9\text{-BBN})_2$ in CCl_4 at 25°C .

The first-order rate constant is independent of the initial concentrations of the reactants.

Initial Concn., M		$10^4 k_1$, s^{-1}
	$(9\text{-BBN})_2$	
0.400	0.200	1.54
0.400	0.100	1.58
0.200	0.100	1.58

The hydroboration of several other alkenes exhibited first-order kinetics. Moreover, the same kinetic order was observed in several other solvents as well. The reaction is significantly faster in THF:

Alkene	$10^4 k_1$, s^{-1}				
	CCl_4	THF			Et_2O
	1.54	13.9	1.51	2.05	2.83
	1.46	13.7	1.51	1.99	2.81
	1.45	14.0	1.48	2.02	2.80
	1.54	11.8	1.46	2.06	2.77

A discussion of the solvent effect is deferred to a later section of this lecture.

In contrast to the behavior of reactive alkenes, less reactive alkenes, such as cyclohexene, react with $(9\text{-BBN})_2$ by three-halves-order kinetics, first-order in the alkene and one-half-order in $(9\text{-BBN})_2$ (Fig. 3).

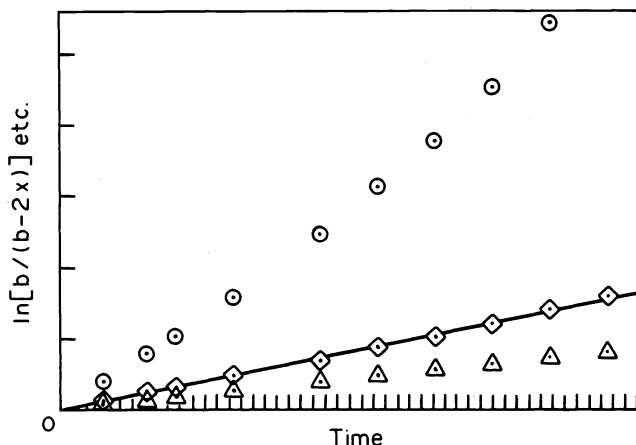



Fig. 3. Rate plot for the reaction of cyclohexene with $(9\text{-BBN})_2$ in CCl_4 at 25°C .

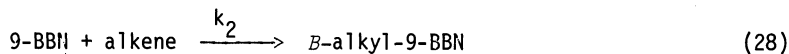
Changing the initial concentrations of either cyclohexene or $(9\text{-BBN})_2$ did not alter the three-halves-order rate constant significantly:

Initial Concn., M		$10^4 k_{3/2}$
	$(9\text{-BBN})_2$	$M^{-1/2} s^{-1}$
0.400	0.200	0.323
0.400	0.100	0.324
0.200	0.100	0.345

Alkenes, such as *cis*-3-hexene and 2-methyl-2-butene, displayed intermediate kinetics. Their rate data did not fit into the integrated rate expressions for either first- or three-halves-order (in the usual solvent CCl_4 at 25°C):

Initial Concn., M		$10^4 k_1$	$10^4 k_{3/2}$	$10^4 k_2$
<i>cis</i> -3-Hexene	$(9\text{-BBN})_2$	s^{-1}	$M^{-1/2} s^{-1}$	$M^{-1} s^{-1}$
0.400	0.200	1.07	1.73	5.78
0.400	0.100	1.45	1.08	4.75
0.200	0.100	0.925	2.07	9.45

These results are markedly different from those on disiamylborane and are explicable in terms of the dissociation mechanism (Eqns. 27 and 28).



The rate expression can be derived by using the steady-state approximation on the 9-BBN intermediate (Eqn. 29) (Ref. 11).

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2] \left(\frac{1/2 k_2[\text{alkene}]}{k_{-1}[9\text{-BBN}] + 1/2 k_2[\text{alkene}]} \right) \quad (29)$$

With highly reactive alkenes,

$$1/2 k_2[\text{alkene}] \gg k_{-1}[9\text{-BBN}]$$

the rate equation simplifies to a first-order kinetic expression (Eqn. 30).

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2] \quad (30)$$

On the other hand, with less reactive alkenes, such as cyclohexene, the hydroboration step is slow,

$$1/2 k_2[\text{alkene}] \ll k_{-1}[9\text{-BBN}]$$

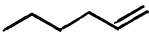
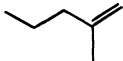


and the rate equation simplifies to the three-halves-order kinetic expression (Eqn. 31)

$$-\frac{d[(9\text{-BBN})_2]}{dt} = k_{3/2}[(9\text{-BBN})_2]^{1/2}[\text{alkene}] \quad (31)$$




where $k_{3/2} = 1/2(k_1/k_{-1})^{1/2}k_2$.

When $1/2 k_2[\text{alkene}] \approx k_{-1}[9\text{-BBN}]$, neither the first- nor the three-halves-order rate expression is satisfactory, and intermediate kinetics are displayed (e.g., *cis*-3-hexene and 2-methyl-2-butene).

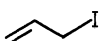
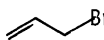
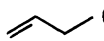
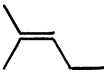
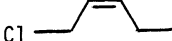
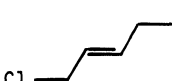
A simple way to test the kinetic results would be to determine the relative reactivities of alkenes toward $(9\text{-BBN})_2$ by an independent procedure and to compare them with the relative reactivities indicated by the kinetic data. As expected for the proposed mechanism, the relative reactivities of reactive alkenes determined by the competition method (Ref. 13) differed significantly from each other, even though the first-order rate constants are practically the same. The comparisons are made for data in CCl_4 at 25°C .

Alkene	Relative Reactivity	$10^4 k_1, \text{s}^{-1}$
	1.00	1.54
	1.96	1.46
	0.233	1.45
	0.072	1.54

In the case of less reactive alkenes which follow the three-halves-order kinetics, the proposed mechanism requires that the relative reactivities parallel those calculated from the three-halves-order rate constants, since the relative reactivities are the ratios of the k_2 's (Eqn. 31). In fact, this is the case.

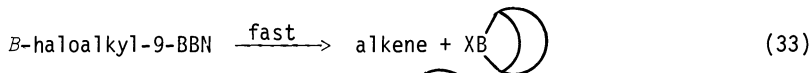
Alkene	Relative Reactivity	$10^4 k_{3/2} \text{M}^{-1/2} \text{s}^{-1}$
	1.00	0.323
	0.159	0.051
	0.088	0.020

The study was later extended to several haloalkenes (Ref. 14). The behavior was similar to that of the alkenes:

Haloalkene	$10^4 k_1 a_s^{-1}$	$10^4 k_{3/2} a_M^{-1/2} s^{-1}$
	1.63	
	1.57	
	1.55	
		intermediate
		0.161
		0.024

^aIn CCl_4 at 25°C.



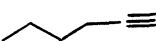
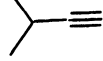
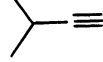
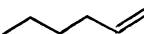
In the case of certain haloalkenes, the initial addition product is the *B*-haloalkyl-9-BBN derivatives. These rapidly eliminate *B*-chloro-9-BBN to form alkenes which are rapidly hydroborated by 9-BBN to form the *B*-alkyl-9-BBN derivatives. These were actually the observed products (Ref. 14). The observance of first-order and three-halves-order kinetic behavior indicates that these latter two steps are rapid and do not enter into the rate equation (Eqn. 29). The mechanism can now be depicted (Eqns. 27, 32-34).



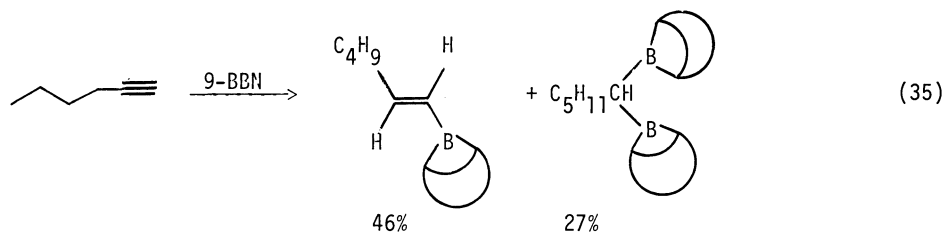
We were very much intrigued by the apparently different results that we had realized with $(\text{Sia}_2\text{BH})_2$ and $(9\text{-BBN})_2$. Since our major aim was to understand the mechanism of the hydroboration reaction as a whole, we decided to resolve the differences in the behavior of $(\text{Sia}_2\text{BH})_2$ and $(9\text{-BBN})_2$ in two ways--one, to study the mechanisms of the reactions of substrates of progressively increasing nucleophilicities with $(9\text{-BBN})_2$ and two, to study the mechanism of hydroboration with yet another R_2BH reagent, also without the special problems afforded by $(\text{Sia}_2\text{BH})_2$.

KINETICS OF HYDROBORATION OF ALKYNES WITH $(9\text{-BBN})_2$

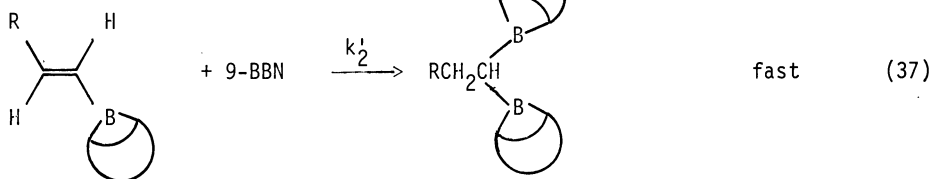
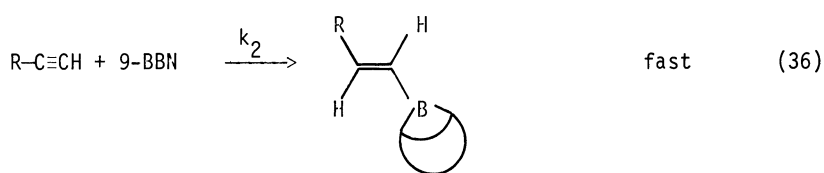
Several reactive alkynes, such as 1-hexyne, 3-methyl-1-butyne, *etc.*, exhibited first-order kinetics in their reaction with $(9\text{-BBN})_2$ at 25°C (Ref. 15).

Alkyne	$10^4 k_1, s^{-1}$			
	THF	CCl_4		
	14.1	1.52	1.48	1.98
	14.0			
	13.9			
	13.9	1.54	1.51	2.05

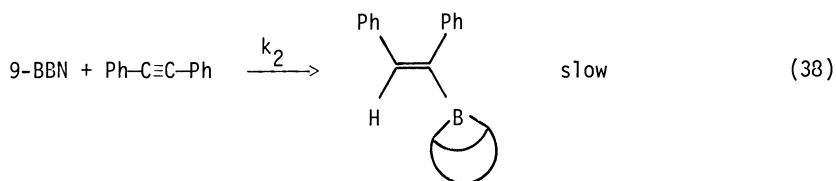
The first-order rate constants are in close agreement with those for the hydroboration of reactive alkenes. The data clearly indicate that the reaction involves the rate-determining dissociation of 9-BBN dimer, followed by a fast reaction of the alkyne with the monomer. In the case of terminal alkynes, the initial product of hydroboration, namely, the *B*-alkenyl-9-BBN, reacts further with the 9-BBN to form the 1,1-dibora compounds (Eqn. 35).




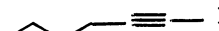

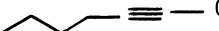


This additional step serves only as a way to deplete the 9-BBN monomer concentration, making the dissociation of $(9\text{-BBN})_2$ more rate-determining in nature. Hence, the mechanism of hydroboration of reactive alkynes may be presented as:



Like the less reactive alkenes, the hydroboration of 1,2-diphenylethyne with $(9\text{-BBN})_2$ follows three-halves-order kinetics ($k_3/2 = 1.3 \times 10^{-6} \text{M}^{-1/2} \text{s}^{-1}$), indicating that the reaction involves an equilibrium dissociation of the dimer, followed by a slow reaction of the monomer with the alkyne (Eqns. 27 and 38). No dihydroboration is observed.

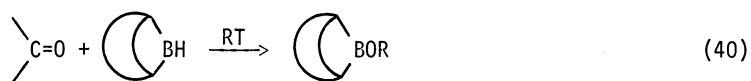
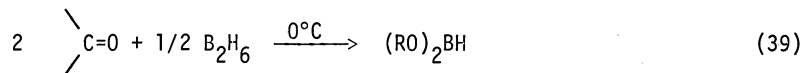


Our studies on the kinetics of hydroboration of 1-haloalkynes also indicate the operation of the dissociation mechanism (Ref. 16):

Haloalkyne	$10^4 k_1 s^{-1}$ in CCl_4 at $25^\circ C$	$10^4 k_{3/2} M^{-1/2} s^{-1}$ in CCl_4 at $25^\circ C$
	1.54	
 I		intermediate
 Br		intermediate
 Cl		0.651
Ph-  -Br		0.149
Ph-  -Cl		0.057

KINETICS OF THE REDUCTION OF ALDEHYDES AND KETONES WITH $(9-BBN)_2$

Aldehydes and ketones are reduced by borane reagents with great facility (Refs. 17-19).



In an attempt to study the effect of increasing nucleophilicity of the substrate on the mechanism of reaction with $(9-BBN)_2$, we followed the kinetics of the reduction of a number of aldehydes and ketones with $(9-BBN)_2$ in THF at $25^\circ C$, and in some cases, in CCl_4 and cyclohexane (Ref. 20). Like reactive alkenes and alkynes, hexanal reacts with $(9-BBN)_2$, exhibiting first-order kinetics (Fig. 4).

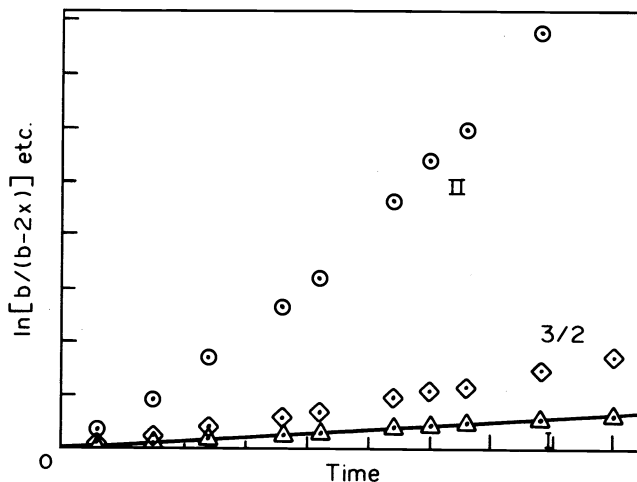



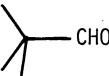
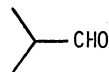
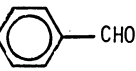
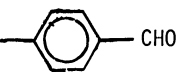
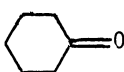


Fig. 4. Rate plot for the reaction of hexanal with $(9-BBN)_2$ in CCl_4 at $25^\circ C$.

The first-order rate constants in THF, CCl_4 and cyclohexane agree very well with those for the hydroboration of reactive alkenes and alkynes.

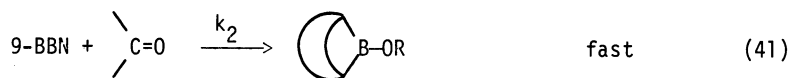
Solvent	$10^4 k_1, s^{-1}$
THF	14.2
CCl_4	1.42
cyclohexane	1.41

Many other aldehydes and reactive ketones, such as cyclohexanone, also exhibit first-order kinetics.

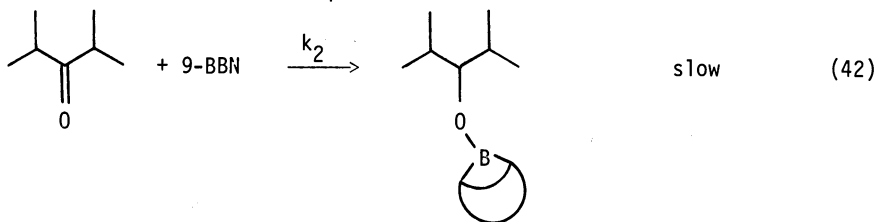
Aldehyde or Ketone	$10^4 k_1, ^a \text{ s}^{-1}$	Relative Reactivity by the Competition Method ^a
	14.2	100
	12.8	
	13.2	
	11.7	62
	12.4	
	13.7	87
	13.1	142
	14.4	25.5

^aIn THF at 25°C.

The mechanism of the reduction of aldehydes and reactive ketones, like hydroboration, must clearly involve a rate-determining dissociation of $(9\text{-BBN})_2$, followed by a fast reaction of the monomer with the carbonyl compound (Eqns. 27 and 41).



The reduction of 2,4-dimethyl-3-pentanone, on the other hand, followed three-halves-order kinetics ($k_3/2 = 0.98 \times 10^{-5} \text{ M}^{-1/2} \text{ s}^{-1}$), indicating an equilibrium dissociation of the dimer, followed by a slow reaction of the monomer with the ketone (Eqns. 27 and 42).

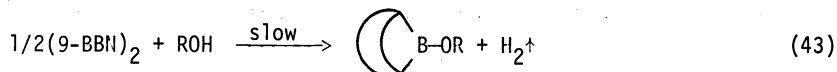


Several ketones showed intermediate kinetic behavior (Ref. 20). Thus, the mechanism of the reduction of aldehydes and ketones with $(9\text{-BBN})_2$ is very similar to that of the hydroboration of alkenes and alkynes.

Our next substrate of interest was alcohol.

KINETICS OF PROTONOLYSIS OF (9-BBN)₂ WITH ALCOHOLS

(9-BBN)₂ is protonolyzed by alcohols and phenols at convenient rates (Ref. 18). The reaction can be conveniently monitored by measuring the volume of evolved H₂ as a function of time (Ref. 18) (Eqn. 43). We determined the rates of protonolysis of (9-BBN)₂ with repre-

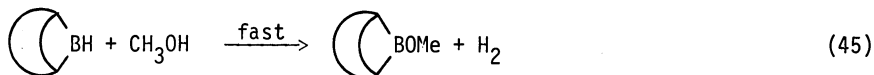
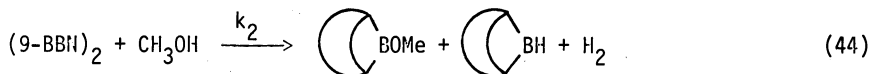


sentative alcohols in CCl₄ and THF (Ref. 20).

In CCl₄, the protonolysis of (9-BBN)₂ with hindered alcohols, such as *tert*-butyl alcohol, proceeded by first-order kinetics. Increasing the concentration of *tert*-butyl alcohol did not alter the first-order rate constant significantly.

Initial Concn., M		10 ⁴ k ₁ , s ⁻¹
(9-BBN) ₂	<i>tert</i> -BuOH	
0.200	0.800	1.53
0.100	1.50	1.60
0.100	2.00	1.57

This indicates that the reaction involves the rate-determining dissociation of the dimer, followed by a fast reaction of the monomer with the alcohol. With less hindered alcohols, the situation was different. The reaction of methanol with (9-BBN)₂ in CCl₄ at 25°C proceeded faster than that of *tert*-butyl alcohol and failed to obey the integrated rate expressions of either first- or second-order. This may be due to a competition between the direct-attack mechanism (Eqns. 44 and 45) and the dissociation mechanism (Eqns. 27 and 45). The



rate expression in such a case may be derived as follows:

$$\text{For the dissociation pathway: } -\frac{d[(9\text{-BBN})_2]}{dt} = k_1[(9\text{-BBN})_2]$$

$$\text{For the dimer-attack pathway: } -\frac{d[(9\text{-BBN})_2]}{dt} = k_2[\text{CH}_3\text{OH}][(9\text{-BBN})_2]$$

$$\text{For the overall process: } -\frac{d[(9\text{-BBN})_2]}{dt} = (k_1 + k_2[\text{CH}_3\text{OH}])(9\text{-BBN})_2 \quad (46)$$

This equation eludes simple methods of integration. However, we could evaluate k₁ and k₂ by the following method.

When the reaction is done in the presence of excess methanol, first-order kinetics are displayed. The observed rate constant k_{obs} is a composite of k₁ and k₂ (Eqn. 47).

$$k_{\text{obs}} = k_1 + k_2[\text{CH}_3\text{OH}] \quad (47)$$

We determined the value of k_{obs} at several different CH₃OH concentrations and plotted k_{obs} vs. [CH₃OH]. The plot was linear with slope (k₂) equal to 7.0 × 10⁻⁵M⁻¹s⁻¹ and intercept (k₁) 1.45 × 10⁻⁴s⁻¹. Similar plots were established for ethanol and isopropyl alcohol (Fig. 5).

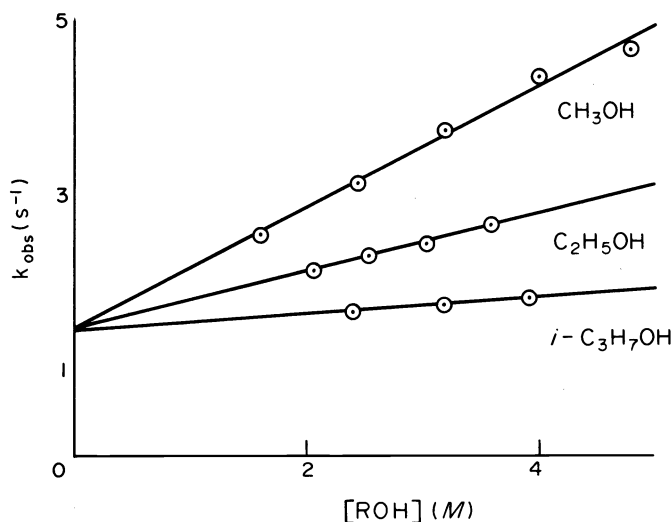


Fig. 5. Plot of k_{obs} vs. $[\text{ROH}]$ for the protonolysis of $(9\text{-BBN})_2$ in CCl_4 at 25°C , $[(9\text{-BBN})_2] = 0.200\text{ M}$.

A comparison of the plot data will indicate that the k_1 values are essentially the same for all three alcohols and agree well with the first-order rate constant for the hydroboration of reactive alkenes and alkynes and the reduction of aldehydes.

Plot of k_{obs} vs. $[\text{ROH}]$

ROH	$10^4 k_1 \text{ s}^{-1}$	$10^5 k_2 \text{ M}^{-1} \text{ s}^{-1}$
CH_3OH	1.45	7.0
$\text{C}_2\text{H}_5\text{OH}$	1.44	3.3
$i\text{-C}_3\text{H}_7\text{OH}$	1.42	1.0

The decreasing k_2 values from methanol to isopropyl alcohol are also expected on the basis of steric effects.

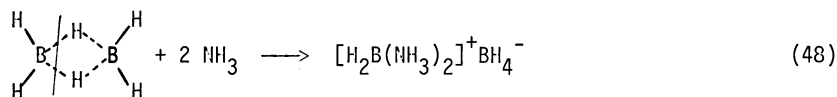
In THF, the reaction exhibits first-order kinetics in the case of hindered as well as unhindered alcohols, indicating that the dissociation mechanism operates (Refs. 18 and 20).

Alcohol	$10^4 k_1 \text{ s}^{-1}$, at 25°C
methanol	15.4
1-hexanol	14.1
<i>tert</i> -butyl alcohol	14.2
2,3-dimethyl-2-butanol	15.2
tri- <i>n</i> -octylcarbinol	14.0
2,2,4-trimethyl-3-pentanol	15.0

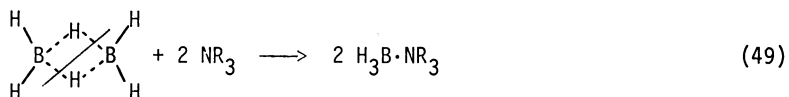
Thus with alcohols which are better nucleophiles than aldehydes and ketones, the first kinetic evidence for the direct-attack mechanism has been observed. Our next logical extension was to study the kinetics of complexation of $(9\text{-BBN})_2$ with amines.

KINETICS OF COMPLEXATION OF $(9\text{-BBN})_2$ WITH AMINES

The reaction of amines with boranes has been studied in detail. Ammonia reacts with diborane, cleaving the $\text{B} \cdots \text{H} \cdots \text{B}$ unsymmetrically (Ref. 22) (Eqn. 48).

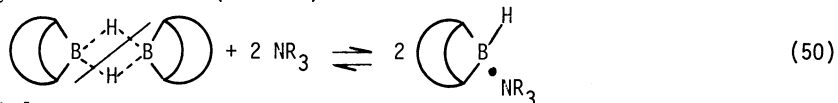


On the other hand, primary, secondary and tertiary amines react with diborane to form monomeric amine-boranes, indicating a symmetrical cleavage (Eqn. 49) (Ref. 23).



R = alkyl and H

The reaction of $(9\text{-BBN})_2$ with amines is reversible and leads to monomeric 9-BBN-amine adducts, suggesting a symmetrical cleavage (Eqn. 50). The reaction proceeds to completion with unhindered and moderately hindered amines (Ref. 24).



R = H and alkyl

We determined the rates of complexation of $(9\text{-BBN})_2$ with representative amines by the IR procedure in cyclohexane at 25°C (Ref. 25). The reaction of pyridine with $(9\text{-BBN})_2$ was very much faster than the dissociation of $(9\text{-BBN})_2$ under the same conditions. The rate data fit into the second-order kinetic expression very well (Fig. 6). Doubling the concentration

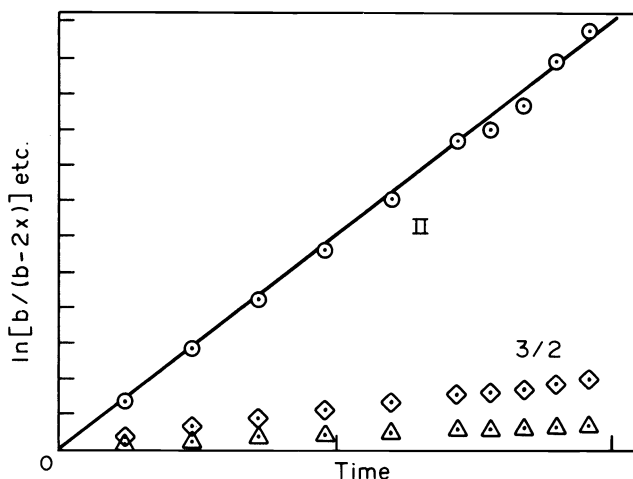


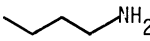
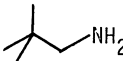

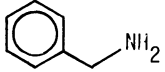
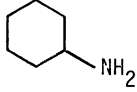
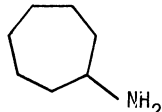


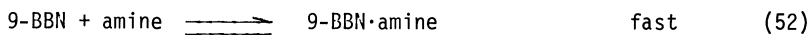
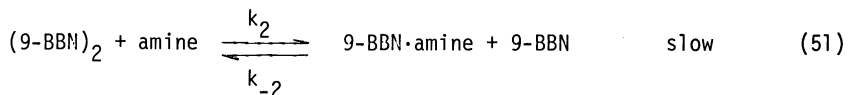
Fig. 6. Rate plot for the reaction of pyridine with $(9\text{-BBN})_2$ in cyclohexane at 25°C.

of pyridine did not affect the second-order rate constant significantly.

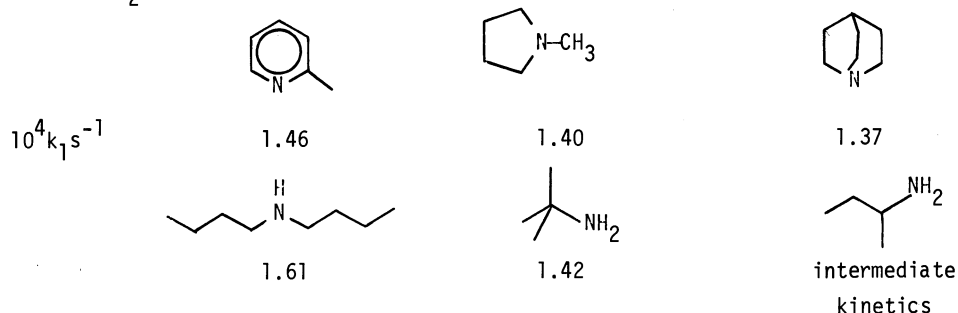
Several other unhindered amines also exhibited second-order kinetics:

				
	H	H		
$10^2 k_2 \text{M}^{-1} \text{s}^{-1}$	27.5	5.63	1.73	1.40
				
	N	NH ₂	NH ₂	NH ₂
$10^2 k_2 \text{M}^{-1} \text{s}^{-1}$	1.20	0.95	0.51	0.45

The second-order kinetics clearly require that these amines react with $(9\text{-BBN})_2$ by a direct-attack mechanism (Eqns. 51 and 52).

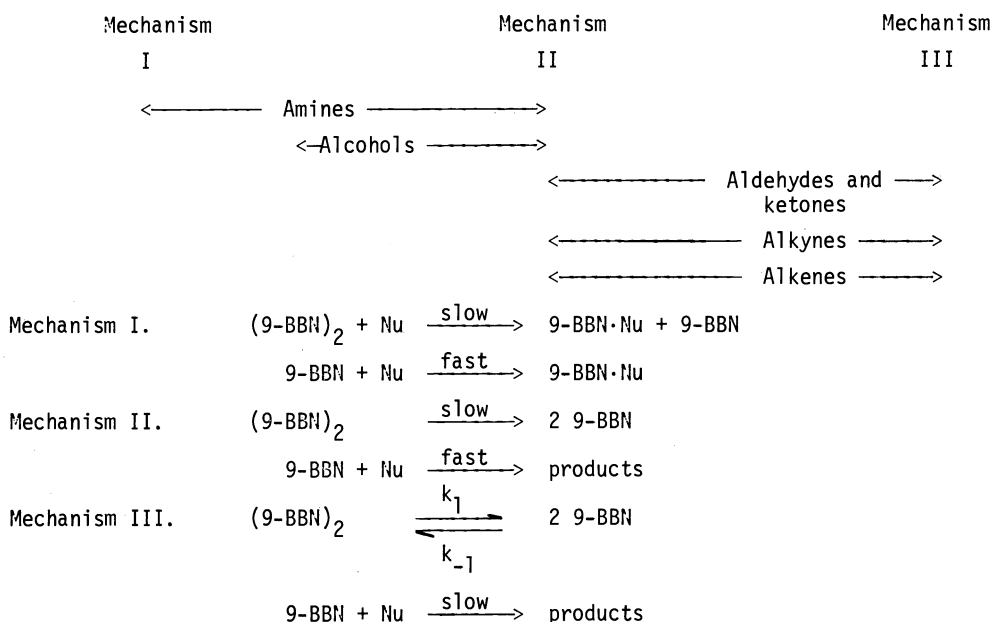


More hindered amines, such as 2-methylpyridine, exhibited first-order kinetics, first-order in $(9\text{-BBN})_2$.



The first-order rate constants are independent of the amine and are in close agreement with those obtained in the earlier studies. Obviously, with more hindered amines, the dissociation mechanism is operating wherein the dissociation of $(9\text{-BBN})_2$ is rate-determining (Eqns. 27 and 52).

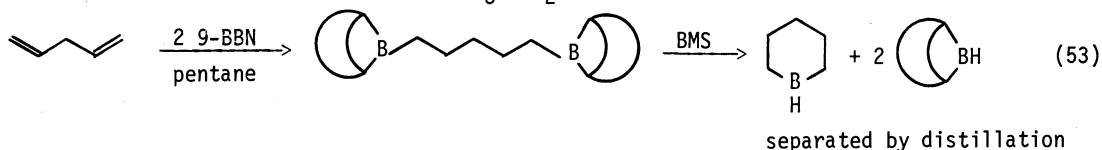
The above detailed investigation of the reactions of nucleophiles with $(9\text{-BBN})_2$ has revealed a unique spectrum of mechanisms.



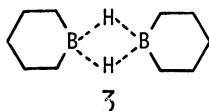
These studies of the reactions of $(9\text{-BBN})_2$ have clearly demonstrated that the hydroboration of alkenes with $(9\text{-BBN})_2$ proceeds by the dissociation mechanism. To verify whether this is representative of the general behavior of $R_2\text{BH}$ dimers in hydroboration reaction, the kinetics of hydroboration of representative alkenes with borinane dimer was undertaken.

KINETICS OF HYDROBORATION OF ALKENES WITH BORINANE DIMER

Borinane has been synthesized in the pure form by the hydroboration of 1,4-pentadiene with 9-BBN, followed by redistribution with $\text{BH}_3\cdot\text{SMe}_2$, BMS (Eqn. 53) (Ref. 26).



It exists as a dimer $\mathfrak{3}$ and shows an IR peak characteristic of the $\text{B}\cdots\text{H}\cdots\text{B}$ vibration at 1565



cm^{-1} (Ref. 27). Consequently, we undertook to determine the rates of hydroboration of representative alkenes with borinane dimer by using the quantitative IR method. Unfortunately, we encountered a major problem. With many alkenes, the rates were too fast to measure. However, we could satisfactorily measure the rates for many alkenes only by doing the reaction at 0°C in *n*-heptane, employing as low a concentration as would still permit reliable IR measurements (Ref. 28).

The reaction of cyclopentene with borinane dimer exhibits three-halves-order kinetics (Fig. 7).

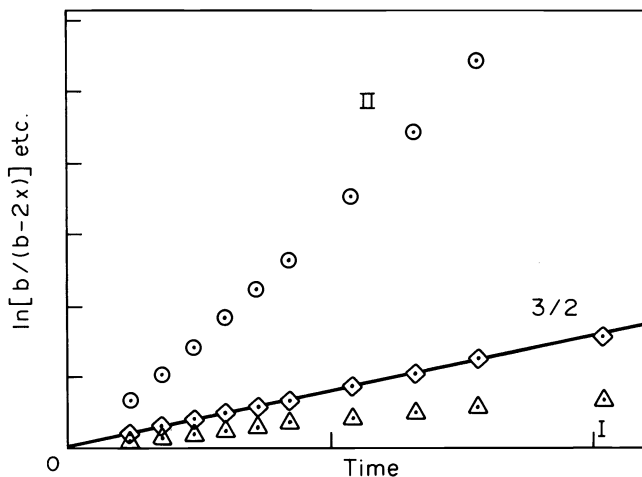

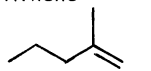
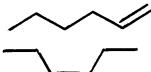

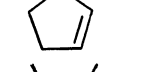
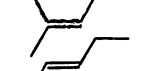
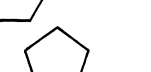
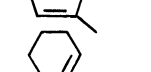




Fig. 7. Rate plot for the reaction of cyclopentene with borinane dimer in *n*-heptane at 0°C .

Changing the initial concentrations of the reactants did not alter the three-halves-order rate constants.

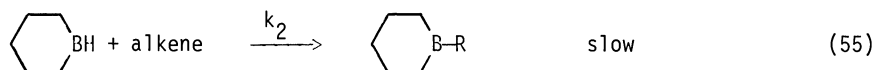
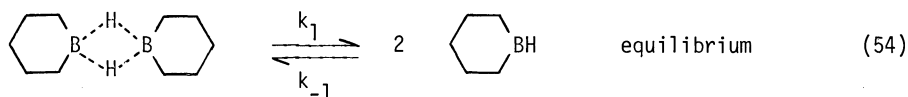
Initial Conc., <i>M</i>		$10^4 k_{3/2} \text{M}^{-1/2} \text{s}^{-1}$
	(Borinane) ₂	
0.200	0.100	15.4
0.200	0.050	15.1
0.100	0.050	16.0

The reaction of several other alkenes with borinane dimer displayed three-halves-order kinetics. The three-halves-order rate constants are parallel to the relative reactivities established by the competitive method, as expected for the dissociation mechanism.

Alkene	$10^4 k_{3/2} \text{M}^{-1/2} \text{s}^{-1}$	Relative Rate
		135
		100
	21.5	11.2
	15.6	5.4
	15.5	7.5
	12.3	5.0
	9.5	4.0
	3.43	1.5
	0.25	0.09

The rate constants for the terminal alkenes could not be obtained satisfactorily due to the very fast reaction ($t_{1/2} \sim 2.0$ min).

The observance of the three-halves-order kinetics for the various alkenes indicates that the dissociation mechanism operates:

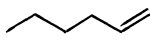

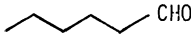




The similarity in the behavior of 9-BBN dimer and borinane dimer towards hydroboration strongly argues that the dissociation mechanism is the general pathway for the hydroboration of alkenes by R_2BH dimers. The reason for the markedly different behavior of Sia_2BH dimer is still not very clear. It may well be that the observed behavior is an artifact of the complexity of the reagent.

We have thus far been deferring a discussion of the effect of THF solvent on the rate of hydroboration of alkenes with $(9\text{-BBN})_2$. An understanding of this solvent effect has thrown light on the mechanism of hydroboration of alkenes with borane-Lewis base adducts.

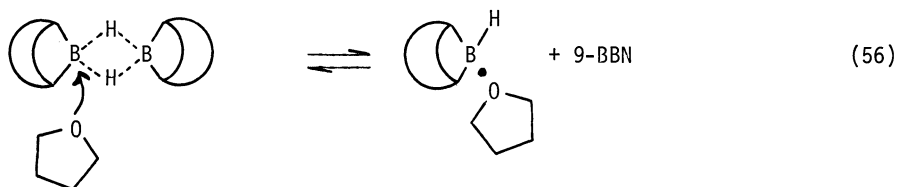
EFFECT OF THF SOLVENT ON THE RATE OF HYDROBORATION OF ALKENES WITH $(9\text{-BBN})_2$

The hydroboration of reactive alkenes with $(9\text{-BBN})_2$ proceeds significantly faster in THF than in noncomplexing solvents like CCl_4 . In fact, this rate acceleration is observed in all reactions of $(9\text{-BBN})_2$ which proceed by the rate-determining dissociation of the dimer.

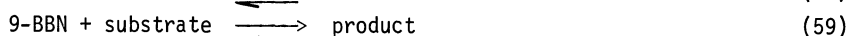
Nucleophile	$10^4 k_1 s^{-1}$	
	CCl_4	THF
	1.54	13.9
	1.52	15.1
 CHO	1.42	14.2
 OH	1.53	14.2
	1.46	14.1

This large rate acceleration (10 times) is not observed when the dimer-attack mechanism (Ref. 25) (Eqns. 51 and 52) or the rate-determining attack of 9-BBN monomer on the nucleophile (Ref. 16) is operative; a much smaller rate acceleration is observed.

The faster rate of dissociation of $(9\text{-BBN})_2$ in THF can be explained by proposing a direct attack of the THF molecule on the 9-BBN dimer (Eqns. 56 and 57) (Ref. 29).



We further propose that the 9-BBN·THF complex dissociates rapidly into 9-BBN, which then reacts with the substrate (Eqns. 58 and 59).

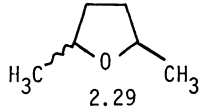


In other words, the THF molecules help in breaking up the bridging bonds of the 9-BBN dimer.

SUPPORT FOR THE PROPOSAL OF DIRECT ATTACK OF THF ON 9-BBN DIMER

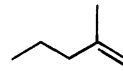
1. The reaction of pyrrolidine with $(9\text{-BBN})_2$ occurs by the direct attack of the base on the dimer (Ref. 25). THF, a Lewis base of comparable steric freedom, may also be capable of such an attack.

2. The rate acceleration that we observe for the hydroboration of reactive alkenes, such as 1-hexene, with $(9\text{-BBN})_2$ in THF is not observed in hindered ether solvents, such as diethyl ether or 2,5-dimethyltetrahydrofuran:

	CCl_4	THF	Et_2O	
$10^4 k_1 \text{s}^{-1}$ for 1-hexene	1.54	14.2	2.83	

With these hindered ethers, the direct attack on $(9\text{-BBN})_2$ becomes less probable on steric grounds.

3. The first-order rate constants for the hydroboration of 2-methyl-1-pentene were measured in CCl_4 -THF mixtures. The k_1 increases with increasing THF content, as expected for the direct attack proposal.

Volume Ratio	$10^4 k_1 \text{s}^{-1}$
CCl_4/THF	for 
4/1	2.94
2/1	3.69
1/1	5.23
1/2	7.75
1/4	9.86

The direct attack proposal requires that 9-BBN·THF be a reaction intermediate. Hence, we directed our attention toward its existence.

EVIDENCE FOR 9-BBN·THF

The hydroboration of a reactive alkene such as 2-methyl-1-pentene with $(9\text{-BBN})_2$ in THF exhibits a unique characteristic. When 0.200 *M* of 2-methyl-1-pentene is added to 0.100 *M* $(9\text{-BBN})_2$ in THF, there is an instantaneous initial disappearance of 16% of the alkene. The rest of the alkene disappears in the regular exponential fashion leading to the observed first-order rate constant. The rapid initial uptake of 16% of the alkene is attributed to the reaction of 9-BBN·THF with the alkene. Such a disappearance is not observed in other noncomplexing solvents. From this, it is possible to calculate the equilibrium constant for the formation of 9-BBN·THF complex from $(9\text{-BBN})_2$ and THF (Eqns. 60 and 61).



$$K = \frac{[\text{9-BBN}\cdot\text{THF}]^2}{[(9\text{-BBN})_2][\text{THF}]^2} = \frac{(0.100 \times 2 \times 0.16)^2}{(0.100 \times 0.84)(12.3)^2} = 8.05 \times 10^{-5} \text{M}^{-1} \quad (61)$$

The presence of 9-BBN·THF complex is also proved by the ^{11}B NMR spectrum of $(9\text{-BBN})_2$ in THF. In addition to the large peak due to 9-BBN dimer at δ 27.7 ppm (reference: $\text{BF}_3\cdot\text{OEt}_2$), a small doublet centered at 14.0 ppm is observed. This doublet corresponds to the 9-BBN·THF complex. The upfield shift corresponds to coordination of the boron atom to the THF molecule.

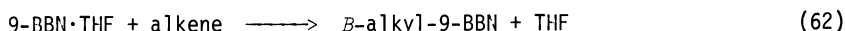
The IR spectrum of $(9\text{-BBN})_2$ in THF also indicates a small peak for the B-H stretching vibration at 2300 cm^{-1} , in addition to the large one for the B-H-B stretching at 1570 cm^{-1} . The reaction of 2-methyl-1-pentene with $(9\text{-BBN})_2$ was also followed by monitoring the 2300 cm^{-1} peak with the help of a quantitative IR spectrometer. When 2.5 mmol of 2-methyl-1-pentene were added to a solution of 2.5 mmol of $(9\text{-BBN})_2$ in THF (25 mL; 0.10 F), the peak at 2300 cm^{-1} disappeared immediately. It began to reappear after about 5 min and reached its maximum absorbance within 15 min. An additional 1.25 mmol was then added. The peak again disappeared immediately and reappeared, reaching its maximum absorbance 15 min later. The

immediate initial disappearance of the peak is due to a rapid reaction of 9-BBN·THF with the alkene. After all of the alkene has reacted (5 min), equilibrium begins to be reestablished between (9-BBN)₂ and THF. This 5-minute period is in good agreement with our previous observation that the half-life for the first-order reaction of (9-BBN)₂ with an alkene is about 8 min. The maximum absorbances of the peak that reappears are also in good agreement with that calculated from the equilibration constant *K* ($3.05 \times 10^{-5} M^{-1}$).

The foregoing account has clearly established that 9-BBN·THF is a reactive intermediate. Our next step is to understand the mechanism of the reaction of 9-BBN·THF with the alkene.

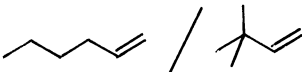

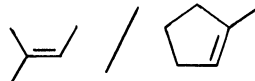
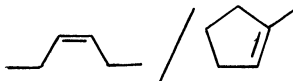

MECHANISM OF THE REACTION OF 9-BBN·THF WITH ALKENES

A priori, there are two mechanistic possibilities for hydroboration with 9-BBN·THF--the direct-attack mechanism (Eqn. 62), or the dissociation mechanism (Eqns. 58 and 59). Both



mechanisms will lead to the same first-order kinetics when THF is present in large excess.

The relative reactivities of some selected alkene pairs toward (9-BBN)₂ were determined in CCl₄ and in THF at 25°C by the competitive method.

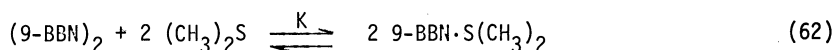
Alkene Pair	Relative Reactivity	
	CCl ₄	THF
	4.3	4.2
	0.31	0.31
	0.61	0.57
	0.36	0.37
	2.2	2.3

The identical relative reactivities in CCl₄ and THF indicate that the hydroborating species must be the same in both solvents. In CCl₄, we have established that the actual hydroborating species is 9-BBN monomer. Hence, in THF also the monomer must be the actual hydroborating agent. This favors the dissociation mechanism (Eqns. 58 and 59).

This raises an interesting problem. The fact is that the 16% of 9-BBN·THF complex present in 0.100 *M* (9-BBN)₂ in THF reacts with the reactive alkenes far faster than the dimer itself. This requires that the dissociation of the complex must proceed at a rate far greater than the dissociation of the dimer into the monomer. An explanation for this unique situation needs more understanding of the hydroboration characteristics of other 9-BBN·Lewis base adducts.

HYDROBORATION OF ALKENES WITH (9-BBN)₂ IN DIMETHYL SULFIDE

Just as in the case of (9-BBN)₂ in THF, part of (9-BBN)₂ exists as the complex in dimethyl sulfide. When 0.200 *M* 2-methyl-1-pentene is added to 0.100 *M* (9-BBN)₂ in dimethyl sulfide, there is a rapid initial uptake of 61% of the alkene. Following the initial uptake, exponential disappearance of the alkene is observed, leading to a first-order rate constant of $6.06 \times 10^{-4} s^{-1}$. The initial disappearance of alkene is due to its rapid reaction with the 9-BBN·SMe₂ adduct. Based on this, it is possible to calculate the equilibrium constant for the formation of 9-BBN·SMe₂ (Eqns. 62 and 63).



$$k = \frac{[9\text{-BBN}\cdot\text{S}(\text{CH}_3)_2]^2}{[(9\text{-BBN})_2][(\text{CH}_3)_2\text{S}]^2} = 2.1 \times 10^{-3}\text{M}^{-1} \quad (63)$$

HYDROBORATION OF ALKENES WITH 9-BBN-AMINE COMPLEXES

The hydroboration of 2-methyl-1-pentene with several 9-BBN-amine complexes were studied at 25°C. The 9-BBN-amine complexes were prepared by adding the stoichiometric quantities of the amine to the (9-BBN)₂ solution. The rate data are given in Fig. 8.

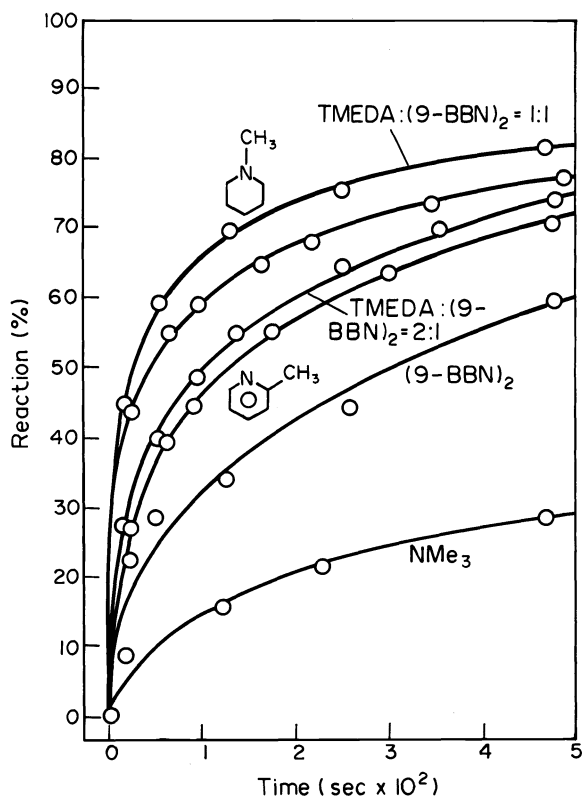


Fig. 8. Rates of hydroboration of 2-methyl-1-pentene with 9-BBN-amine complexes in THF at 25°C.

The hydroboration of 2-methyl-1-pentene with 9-BBN-NMe₃ is slower than that with (9-BBN)₂. On the other hand, several 9-BBN-amine adducts like 9-BBN-2-MePy, 9-BBN-*N*-methylpiperidine, 9-BBN-TMEDA react significantly faster than (9-BBN)₂ itself. The rate of hydroboration is inversely related to the stability of the adduct. In many of these cases, the 9-BBN-amine adduct is thermodynamically more stable (Ref. 24) than the dimer, yet it reacts faster than the dimer.

To verify whether 9-BBN-amine complexes hydroborate by the dissociation mechanism, we studied the effect of added Me₃N (50%) on the rate of hydroboration of 2-methyl-1-pentene with 9-BBN-NMe₃ (Fig. 9).

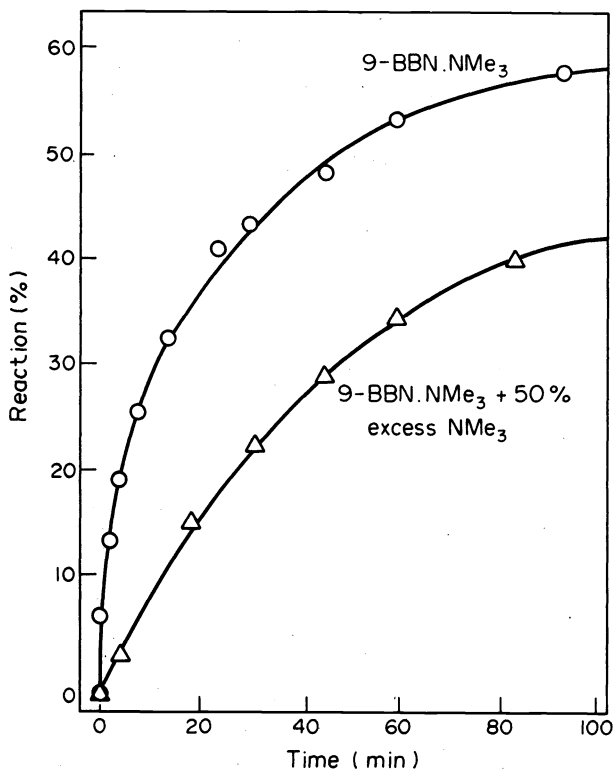


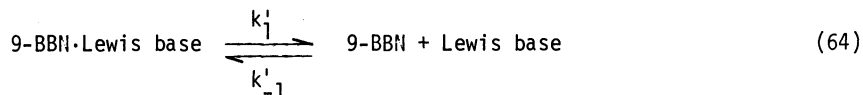
Fig. 9. Effect of Me_3N (0.5 eq) on the rate of hydroboration of 2-methyl-1-pentene with $9\text{-BBN}\cdot\text{NMe}_3$ in THF at 25°C .

A significant rate retardation was observed. This indicates that the dissociation mechanism operates.

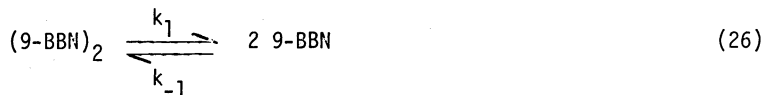
Now we have a complete picture of the whole situation. The identical relative reactivities of alkenes toward $(9\text{-BBN})_2$ in CCl_4 and in THF and the retardation by added NMe_3 of the rate of hydroboration of 2-methyl-1-pentene with $9\text{-BBN}\cdot\text{NMe}_3$ clearly indicate that the $9\text{-BBN}\cdot\text{Lewis base}$ complexes hydroborate alkenes by the dissociation mechanism. How can we explain why an addition compound, readily formed from the dimer by reaction with a suitable base, dissociates into monomer faster than the dimer itself?

THEORETICAL BASIS FOR THE ENHANCED REACTION OF CERTAIN $9\text{-BBN}\cdot\text{LEWIS BASE COMPLEXES}$

The discovery that certain $9\text{-BBN}\cdot\text{Lewis base}$ complexes which are thermodynamically more stable than $(9\text{-BBN})_2$ are more reactive towards 2-methyl-1-pentene than the dimer itself needs an explanation. The question is why



is faster than



in certain cases. At equilibrium between $(9\text{-BBN})_2$ and Lewis base,

$$\left(\frac{k_1}{k_{-1}}\right) / \left(\frac{k'_1}{k'_{-1}}\right)^2 = \frac{[9\text{-BBN}\cdot\text{Lewis base}]^2}{[(9\text{-BBN})_2][\text{Lewis base}]^2} = K \quad (65)$$

For the formation of > 90% of $9\text{-BBN}\cdot\text{Lewis base}$ complex in a solution of $0.200\ \text{M}$ $(9\text{-BBN})_2$ and $0.400\ \text{M}$ Lewis base,

$$K = 10^4\ \text{M}^{-1}.$$

By substituting $K = 10^4 M^{-1}$ into Eqn. 65, we arrive at a relationship between k_1 and k_{-1} for such relatively stable adducts (Eqn. 66).

$$k_1/k_{-1} = 10^{-2}(k_1/k_{-1})^{1/2} \quad (66)$$

†
 ΔG_{298}^\ddagger for the dissociation of $(9\text{-BBN})_2$ can be calculated from the known rate constant k_1 ($1.54 \times 10^{-4} s^{-1}$) by using the Eyring equation (22.6 kcal mol⁻¹). Therefore, the ground-state energy difference between $(9\text{-BBN})_2$ and two uncomplexed 9-BBN monomers must be slightly smaller than 22.6 kcal mol⁻¹. For simplicity, it is assumed to be 21.8 kcal mol⁻¹. This yields a value of 10^{-16} for k_1/k_{-1} . Substituting into Eqn. 66, we get $k_1/k_{-1} = 10^{-10}$. Therefore, ΔG_{298}^\ddagger for Eqn. 64 is only 13.6 kcal mol⁻¹. Thus, thermodynamically, the process $9\text{-BBN} \cdot \text{Lewis base} \rightarrow 9\text{-BBN} + \text{Lewis base}$ is more favorable than $(9\text{-BBN})_2 \rightarrow 2 \text{ 9-BBN}$ by 8.2 kcal mol⁻¹. Although one should use ΔG_{298}^\ddagger to compare the rates of these two processes, the ground-state energetics would certainly²⁹⁸ contribute to the faster rate of dissociation of the complex relative to the rate of dissociation of the dimer.

The free-energy diagram for the 9-BBN system is given in Fig. 10. At first sight, it might

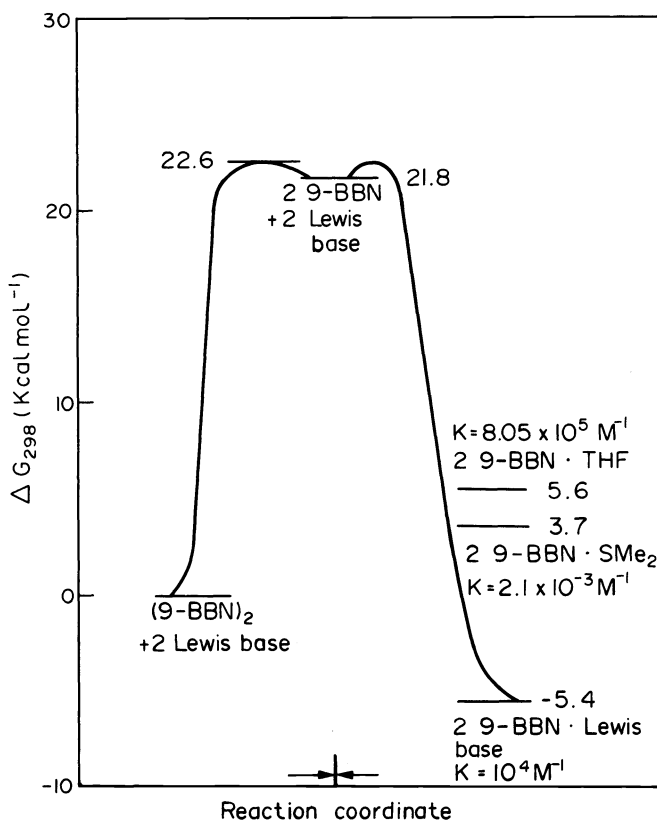


Fig. 10. Free-energy diagram for the 9-BBN system.

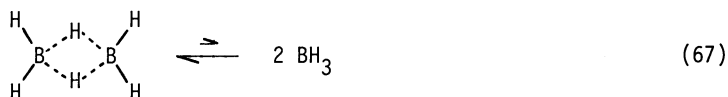
appear that the rate of dissociation of the complex to monomer must be slower than the rate of dissociation of dimer into monomer, since the complex can lie at a considerably lower level. For the particular example being considered now ($K = 10^4 M^{-1}$), the complex would be lower than the dimer in energy by 5.4 kcal mol⁻¹, leading to a dissociation energy of approximately 27.2 kcal mol⁻¹ ($21.8 + 5.4 \text{ kcal mol}^{-1}$). This appears to be considerably larger than the difference in energy between $(9\text{-BBN})_2$ and the monomer, 2 9-BBN: 21.8 kcal mol⁻¹. The apparent anomaly is resolved by noting that 27.2 kcal mol⁻¹ is really the difference in energy between two 9-BBN·Lewis bases and two 9-BBN monomers, plus two free Lewis bases. Therefore, the difference in the ground-state energies for dissociation of the 9-BBN·Lewis base complex into its components is really only one-half this quantity, 13.6 kcal mol⁻¹. This factor of two is the hidden nugget. For the dissociation of $(9\text{-BBN})_2$, two boron-bridge bonds are to be broken, while in a 9-BBN·Lewis base, only one bond has to be broken. We must, however, note that the relative rates of these two processes are dependent on the magnitude of K as well.

When $K \gg 10^4$, as in the case of pyridine and trimethylamine, the rate of hydroboration with 9-BBN·Lewis base is much less than that with $(9\text{-BBN})_2$. When $K \approx 10^4$, e.g., 2-methylpyridine, the rate of hydroboration with 9-BBN·Lewis base is faster than that with $(9\text{-BBN})_2$. When $K \ll 10^4$, e.g. THF, $(\text{CH}_3)_2\text{S}$, etc., the dimer exists in equilibrium with the Lewis base in solution and the 9-BBN·Lewis base complex reacts much faster than the dimer.

The dissociation mechanism for the hydroboration of alkenes with 9-BBN·Lewis base adducts appears to be very general and applicable to BH_3 ·Lewis base adducts as well.

MECHANISM OF HYDROBORATION WITH BH_3 ·LEWIS BASE COMPLEXES

Diborane hydroborates alkenes with exceptional difficulty in the gas phase. If the hydroboration involves the prior dissociation of B_2H_6 into BH_3 , this may be explained by the prohibitively large dissociation energy (35 kcal mol⁻¹) (Ref. 30) for the bridging bonds of diborane. (Eqns. 67 and 68).



The reaction is slow in hydrocarbon solvents (Ref. 5), but is strongly catalyzed by ether solvents (Ref. 3) and some other weak Lewis bases (Ref. 31). The rate of hydroboration with BH_3 ·amine complexes is a function of the stability of these adducts (Ref. 31), as we observed with 9-BBN·amine complexes. For example, BH_3 ·pyridine and BH_3 ·NMe₃ do not hydroborate alkenes at 25°C. On the other hand, *N*-phenylmorpholine· BH_3 and 2,6-dimethylpyridine· BH_3 hydroborate alkenes at 25°C with reasonable speed.

The ether solvents are very effective in bringing about the hydroboration. In diethyl ether and in diglyme, B_2H_6 exists in the dimeric form, but the hydroboration is fast. In THF, B_2H_6 exists as a loose complex, BH_3 ·THF, which is unstable above 0°C. In this solvent, the hydroboration is remarkably fast. Diborane forms a weak complex with dimethyl sulfide (Ref. 32). This adduct, BH_3 ·S(CH₃)₂, also hydroborates alkenes efficiently, but the rate is somewhat slower than that with BH_3 ·THF. Thus the rate of hydroboration is a sensitive function of the strength of the Lewis base. We consider that an explanation similar to the one given for the 9-BBN system should apply for the BH_3 system (Eqns. 69 and 70).

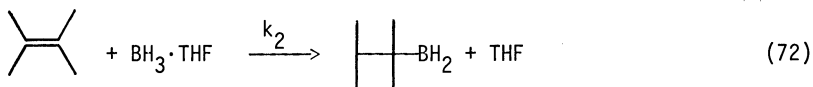
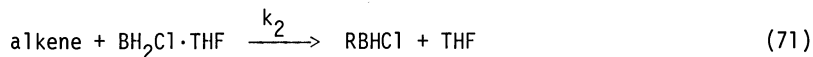


For ether solvents, $(\text{CH}_3)_2\text{S}$ and hindered amines,

$$\frac{k'_1}{k_{-1}} > \frac{k_1}{k_{-1}} .$$

A free-energy diagram similar to Fig. 10 can also be visualized.

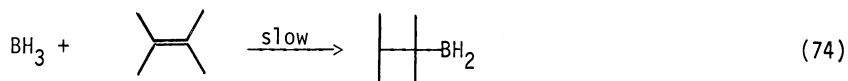
Pasto and coworkers (Refs. 33 and 34) studied the kinetics of hydroboration of alkenes with BH_2Cl ·THF (Eqn. 71) and of 2,3-dimethyl-2-butene with BH_3 ·THF (Eqn. 72).



Both reactions displayed second-order kinetics, first-order in the alkene and first-order in the hydroborating agent. On the basis of the magnitude of ΔS^\ddagger (-27 cal deg⁻¹mol⁻¹), Pasto has argued that the reaction of 2,3-dimethyl-2-butene with BH_3 ·THF proceeds by a direct attack of the alkene on BH_3 ·THF adduct.

Klein and coworkers (Ref. 35) studied the kinetics of hydroboration of substituted styrenes with $\text{BH}_3\cdot\text{THF}$ and found that the reaction exhibits second-order kinetics, first-order in $\text{BH}_3\cdot\text{THF}$ and first-order in the alkene. They also made an important observation. The reaction of an aged solution of *m*-methoxystyrene with $\text{BH}_3\cdot\text{THF}$ exhibits an induction period. They attributed this to the reaction of the reactive intermediate with an impurity present, probably peroxide. Only after all of the impurity had reacted did hydroboration occur. This clearly indicates that $\text{BH}_3\cdot\text{THF}$ is not the actual hydroborating species.

Our results and Klein's observations argue strongly for the dissociation mechanism for the hydroboration of alkenes with $\text{BH}_3\cdot\text{Lewis base complexes}$. Pasto's direct-attack proposal is based only on the ΔS^\ddagger value, since the same kinetic order will obtain both for the direct-attack mechanism (Eqn. 72) and the dissociation mechanism involving a prior dissociation of $\text{BH}_3\cdot\text{THF}$, followed by a slow reaction of BH_3 with the alkene (Eqns. 73 and 74) in THF solvent.

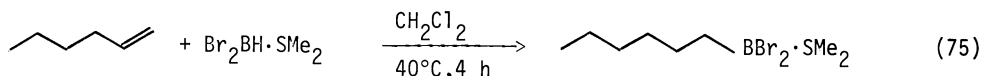


Over the years, arguments based on activation parameters alone have failed in conclusively proving reaction mechanisms.

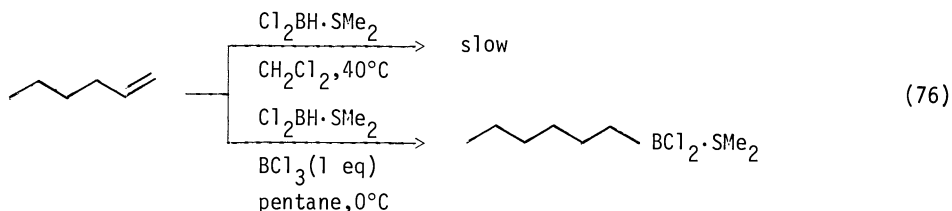
With a view to checking the generality of our proposal of a dissociation mechanism for the hydroboration of alkenes with borane-Lewis base adducts, we examined the hydroboration of 1-hexene with dibromoborane-methyl sulfide ($\text{Br}_2\text{BH}\cdot\text{SMe}_2$) in CH_2Cl_2 .

MECHANISM OF HYDROBORATION OF ALKENES WITH $\text{Br}_2\text{BH}\cdot\text{SMe}_2$

Dibromoborane-methyl sulfide (Ref. 36) hydroborates alkenes with reasonable ease (Eqn. 75) (Ref. 37).

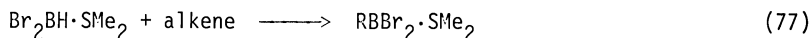


The corresponding dichloroborane-methyl sulfide, however, hydroborates alkenes at a much slower rate. In fact, it was necessary to add one molar equivalent of a Lewis acid, such as BCl_3 to achieve hydroboration at a satisfactory rate (Eqn. 76) (Ref. 37).



We had thought that the hydroboration of alkenes with $\text{X}_2\text{BH}\cdot\text{SMe}_2$ would proceed through the dissociation mechanism. Indeed, addition of 1 molar equivalent of Me_2S significantly repressed the rate of hydroboration of 3-hexyne with $\text{Br}_2\text{BH}\cdot\text{SMe}_2$ (Fig. 11) (Ref. 38) at 0°C , supporting the dissociation mechanism. However, we were faced with a difficult problem in terms of the dissociation mechanism. BBr_3 is a stronger Lewis acid than BCl_3 (Ref. 39). Consequently, one would anticipate Br_2BH to be a stronger acid than Cl_2BH . Accordingly, $\text{Br}_2\text{BH}\cdot\text{SMe}_2$ should be more stable than $\text{Cl}_2\text{BH}\cdot\text{SMe}_2$, dissociating less easily than the latter. Thus, for a dissociation mechanism, $\text{Cl}_2\text{BH}\cdot\text{SMe}_2$ would be expected to be more reactive than $\text{Br}_2\text{BH}\cdot\text{SMe}_2$, contrary to observation. This raised grave doubts about the generality of the dissociation mechanism. This difficulty was examined by studying the kinetics of hydroboration of 1-hexene with $\text{Br}_2\text{BH}\cdot\text{SMe}_2$ in CH_2Cl_2 at 25°C , monitoring the disappearance of the B-H absorbance of the reagent at 2500 cm^{-1} with a quantitative IR spectrometer (Ref. 40).

A priori, there are two mechanistic possibilities, the direct-attack mechanism (Eqn. 77) and



the dissociation mechanism (Eqns. 78-80).

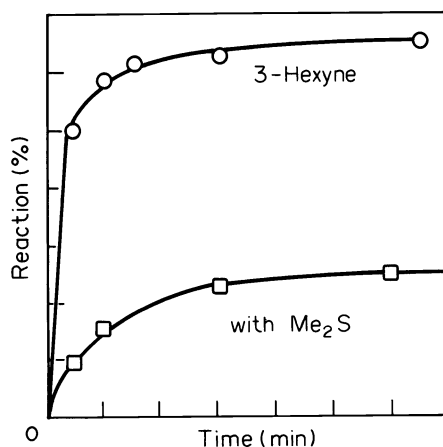
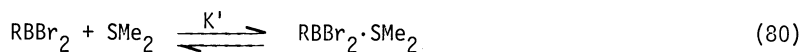
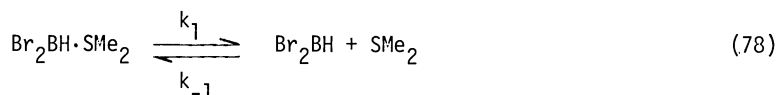


Fig. 11. Effect of Me_2S (1 eq) on the rate of hydroboration of 3-hexyne with $\text{Br}_2\text{BH}\cdot\text{SMe}_2$ in CH_2Cl_2 at 0°C .



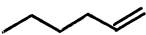

The direct-attack proposal requires second-order kinetic behavior, while the dissociation pathway should exhibit complex kinetic behavior (Eqn. 81).

$$-\frac{d[\text{Br}_2\text{BH}\cdot\text{SMe}_2]}{dt} = \frac{k_1 k_2 [\text{alkene}][\text{Br}_2\text{BH}\cdot\text{SMe}_2]}{k_{-1}(K')^{1/2}[\text{RBBr}_2\cdot\text{SMe}_2]^{1/2} + k_2[\text{alkene}]} \quad (81)$$

Our rate data revealed complex kinetic behavior. We obtained second-order rate constants exhibiting a significant downward drift with progress of the reaction. One possible explanation of this behavior was inhibition of the reaction by the product, $\text{RBBr}_2\cdot\text{SMe}_2$. Accordingly, we studied the effect of adding one molar equivalent of the product, $n\text{-hexylBBr}_2\cdot\text{SMe}_2$, on the rate of hydroboration of 1-hexene. We observed a significant rate retardation (Fig. 12).

This retardation can be readily accounted for by the dissociation mechanism. Since $\text{RBBr}_2\cdot\text{SMe}_2$ is a weaker complex than $\text{Br}_2\text{BH}\cdot\text{SMe}_2$, it can act as a source of a small concentration of Me_2S which will compete with the alkene for the intermediate, BHBr_2 . If this is so, addition of Me_2S should decrease the rate of hydroboration even more severely than that of $n\text{-hexylBBr}_2\cdot\text{SMe}_2$. Indeed, addition of one molar equivalent of Me_2S represses the rate of hydroboration of 1-hexene very severely. If the reaction proceeds by the direct-attack mechanism (Eqn. 77), the rate will be unaffected by the addition of Me_2S or the product.

It occurred to us that if the dissociation mechanism is correct, small quantities of an added Lewis acid, say BBr_3 , should catalyze the reaction by trapping the free Me_2S . In fact, 5 mol percent of BBr_3 catalyzes remarkably the hydroboration of 1-hexene with $\text{Br}_2\text{BH}\cdot\text{SMe}_2$ in CH_2Cl_2 :

Alkene	BBr_3 , mol %	Temp., $^\circ\text{C}$	Time for Completion
	—	25	8 h
	5	25	15 min
	—	40	> several days
	10	40	6 h

We find this BBr_3 catalysis to be extremely useful in the hydroboration of less reactive alkenes such as cyclohexene with $\text{Br}_2\text{BH}\cdot\text{SMe}_2$.

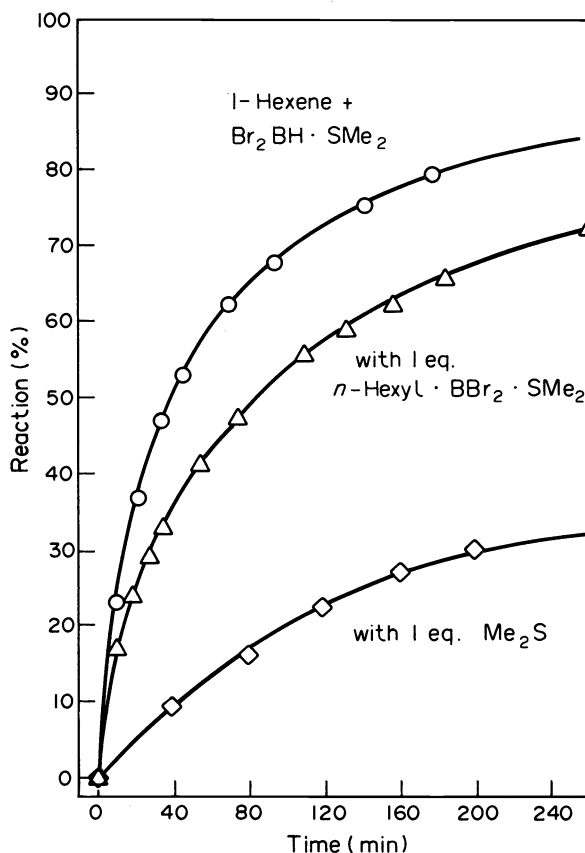


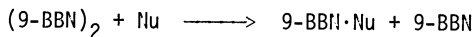
Fig. 12. Effects of *n*-hexylBBr₂·SMe₂ (1 eq) and Me₂S (1 eq) on the rate of hydroboration of 1-hexene with Br₂BH·SMe₂ in CH₂Cl₂ at 25°C.

This discovery clearly explains, in terms of the dissociation mechanism (Eqns. 78-80), why Br₂BH·SMe₂ is able to hydroborate alkenes much faster than Cl₂BH·SMe₂. RBCl₂·SMe₂ is a weaker complex than RBBBr₂·SMe₂ since RBCl₂ must be a weaker Lewis acid than RBBBr₂. As a result, RBCl₂·SMe₂ dissociates into RBCl₂ and Me₂S to a greater extent than does RBBBr₂·SMe₂ and thus has a larger rate-retarding effect on the reaction.

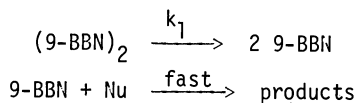
CONCLUSIONS

Our systematic studies on the reaction of (9-BBN)₂ with representative nucleophiles, such as alkenes, alkynes, aldehydes and ketones, alcohols and amines, have led to a complete understanding of the effect of the nucleophilicity of substrate on the mechanism of its reaction with (9-BBN)₂. A unique mechanistic spectrum for the reaction of (9-BBN)₂ with these representative nucleophiles (Nu) has been established:

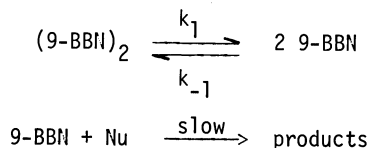
1. Second-order



2. First-order

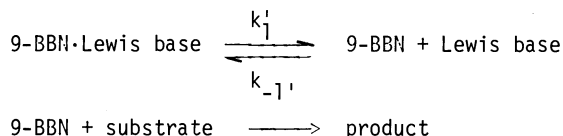


3. Three-halves-order



Amines, which are relatively strong nucleophiles, react by mechanisms 1 and 2. Alkenes, which are relatively weak nucleophiles, follow mechanisms 2 and 3.

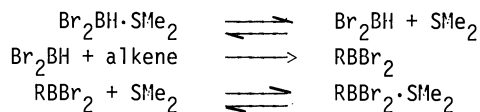
Our investigations of the effect of Lewis bases on the rate of hydroboration of alkenes with (9-BBN)₂ have established the mechanism for the hydroboration of alkenes with 9-BBN·Lewis base complexes. Very weak Lewis bases, such as diethyl ether and 2,5-dimethyltetrahydrofuran, have only a negligible effect on the rate of hydroboration of alkenes with (9-BBN)₂. Weak Lewis bases, such as THF, Me₂S and 2-methylpyridine, exert a marked accelerating influence on the rate of hydroboration. Strong Lewis bases, such as pyridine and trimethylamine, retard the reaction severely. The much faster rates achieved by certain 9-BBN·Lewis base adducts, as compared to those of the dimer itself, is nicely accounted for in terms of the dissociation mechanism:



With relatively weak Lewis bases, such as THF, 2-methylpyridine, *etc.* (relatively large values of k_1'/k_{-1}'), the rate of formation of monomer from the adduct is actually faster than that from the dimer. On the other hand, with relatively strong Lewis bases, such as pyridine and trimethylamine (relatively small values of k_1'/k_{-1}'), the rate of formation of monomer from the adduct becomes slower than that from the dimer. This is attributed to the ease of breaking a single B-Nu bond in the adduct as compared to the difficulty of breaking simultaneously two B-H bonds in the dimer.

The similarities in the influence of weak Lewis bases on the rates of hydroboration of alkenes with both (9-BBN)₂ and diborane make it possible to extrapolate our conclusions from the 9-BBN system to diborane. Thus we propose that the marked catalysis by Lewis bases, such as THF, Me₂S, *etc.*, of hydroboration by diborane can also be accounted for in terms of the dissociation mechanism.

Finally, our studies on the mechanism of hydroboration of 1-hexene with Br₂BH·SMe₂ indicate that the dissociation mechanism operates in this case as well, and resolves a long-standing apparent anomaly. We found that added Me₂S or the product of the reaction, RBBr₂·SMe₂, retards the hydroboration of 1-hexene with Br₂BH·SMe₂ significantly, indicating that the hydroboration involves a prior dissociation of the borane-Lewis base complex:



In conformity with the dissociation mechanism, substoichiometric quantities of a Lewis acid, say BBr₃, catalyze the reaction remarkably. This mechanism also explains why Br₂BH·SMe₂ is more reactive towards alkenes than Cl₂BH·SMe₂, even though it is more stable than the latter.

Thus the dissociation mechanism provides a simple explanation for many puzzling features about the hydroboration reaction that had appeared inexplicable in the past.

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