by the pK_a of the coordinated ligand and will correlate with K_{eq}. It is known that K_{eq} correlates very well with the basicity of nonhindered pyridines,[2] which is entirely consistent with these observations.

In 1966 Hoard suggested[24] that the alteration in the coordination geometry of protoheme on binding dioxygen was the probable starting point for a mechanism to account for the cooperative nature of reversible oxygenation in hemoglobin. There has been a great deal of interest in the systematic study of the conformation of the first-row transition-metal metalloporphyrins with the goal of understanding the electronic and structural contributions to the equilibrium geometries.[3,4] Zn(II), being an end member of the series (d^{10}), has received considerable attention.

The early expectation was that Zn(II) would be too large to fit into the central hole of the porphinato ligand.[25] Crystal structures of several five-coordinate Zn(II) porphyrins found the Zn(II) some 0.3 Å out of the mean plane of the porphyrin ring.[25-28] Solution NMR studies also found the Zn(II) displaced some 0.3 Å from the mean plane of the porphyrin ring.[5] In 1978 Scheidt and co-workers[29] reported the structure of a bis(toluene)solvate of (tetraphenylporphinato)zinc(II) in which the Zn(II) ion is centered in the central hole of the core, with somewhat compressed Zn–N bonds.

If the geometry with the Zn(II) centered in the central hole of the core is indeed an energy minimum in solution, then the k_2 for the binding of L to ZnTPP should be lower than the diffusion-controlled rate limit by an amount reflecting the activation energy required to move the Zn(II) out of the plane. Since k_1 appears to be at or near the diffusion-controlled limit, given the steric restrictions of the system, we suggest that the equilibrium solution conformation for ZnTPP has the Zn(II) displaced out of the plane by an amount close to that found in five-coordinate complexes.

The idea that the Zn(II) is displaced from the plane of the porphyrin ring in ZnTPP in solution is supported by published ^{15}N NMR studies.[30] On binding an extraplanar pyridine to ZnTPP the porphyrin ^{15}N resonance shifts to low field, with the magnitude of the shift linearly dependent on the pK value of the substituted pyridine. The chemical shift of the 3-cyanopyridine complex is only 0.17 ppm to low field from the uncomplexed porphyrin, and the maximum observed shift is only 2.2 ppm.

The Zn–N bond length reported in the planar ZnTPP is 2.036 Å while the average Zn–n bond length in four nonplanar five-coordinate ZnTP–L systems is 2.070 Å. If there were a substantial change in the Zn–porphyrin geometry in going from ZnTPP to ZnTPP–L in solution, we would expect a larger porphyrin ^{15}N chemical shift change.

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Registry No. ZnTPP-py, 24389-79-5; ZnTPP-*N*-MeIm, 67820-10-4; py, 110-86-1; *N*-MeIm, 616-47-7.

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Molecular Addition Compounds. 9. Effect of Structure on the Reactivities of Representative Borane–Amine Complexes in Typical Reactions Such as Hydrolysis, Hydroboration, and Reduction[1]

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A number of borane–amine complexes with widely different structural features in the amine portion was prepared and their reactivities toward typical B–H reactions, such as hydrolysis, hydroboration of 1-octene, and reduction of cyclohexanone, were studied. BH_3–amine complexes containing an *N*-phenyl group are hydrolyzed by neutral hydroxylic solvents, while others require a strong acid medium for the hydrolysis. In hydroboration, BH_3–*N*-phenylamine complexes react rapidly with 1-octene in THF at 25 °C, while all other types require refluxing THF or toluene for reaction. Again, BH_3–*N*-phenylamine complexes reduce cyclohexanone in THF at 25 °C at reasonable rates, while others require acetic acid solvent or mineral or Lewis acids to achieve the desired reduction. Thus, among such borane–amine addition compounds, the BH_3–*N*-phenylamines emerge as unique hydroborating and reducing agents. The results of the present study provide insights into the mechanisms of the hydroboration and reduction reactions. The rates of hydroboration of alkenes with BH_3–amine complexes are inversely related to the stability of the adduct, arguing for a prior dissociation of the adduct, followed by the reaction of BH_3 with the alkene. The reduction of cyclohexanone with BH_3–amine complex in THF proceeds by an analogous dissociation mechanism. In acetic acid or in the presence of mineral or Lewis acids, a bimolecular attack of the BH_3–amine complex on the protonated carbonyl group has been considered to be the most viable mechanistic pathway. However, this does not account for the effect of acids on hydrolytic behavior. Consequently, caution is urged in considering possible interpretation of the acid-enhanced reactions of amine–boranes.

Subsequent to the initial report by Köster[3] that alkenes can be hydroborated by borane–triethylamine complexes, the hydroborating ability of several other BH_3–amine complexes, such as with pyridine,[4] trimethylamine,[5] and *tert*-butylamine,[4]

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Table I. Melting Points and Solubilities of Borane–Amine Complexes

amine	mp,[a] °C	solubility[a] H_2O	CH_3OH	THF	diglyme	cyclohexane	benzene
trimethylamine	93.5–94.5 (94–94.5)	SS	VS	VS	S	SS	S
triethylamine	−4 (−4)	SS	VS	VS	VS	VS	VS
pyridine	10–11 (10–11)	SS	VS	VS	VS	SS	VS
2-picoline	49–50 (50–51)	SS	VS	VS	VS	SS	VS
2,6-lutidine	110–112 (110–111)	VSS	VS	VS	VS	SS	VS
morpholine	93–95 (92–95)	VS	VS	VS	VS	SS	S
N-methylmorpholine	42.5–43.5	S	S	S	S	SS	S
N-ethylmorpholine	−10 to −8	S	VS	VS	VS	S	VS
N-phenylmorpholine	97–99	reacts	reacts	VS	VS	S	VS
DABCO[b,c]	>270	I	SS	SS	SS	VSS	SS
TMEDA[b,c]	179–179.5	I	SS	SS	SS	VSS	SS
N,N'-dimethylpiperazine[b,c]	175–177	I	SS	S	S	I	S
N,N-dimethylaniline	34–35 (35)	reacts	reacts	VS	VS	S	VS
N,N-diethylaniline	−30 to −27	reacts	reacts	VS	VS	S	VS
piperidine	81–83	SS	VS	VS	VS	SS	VS
N-methylpiperidine	−6 to −4	SS	VS	VS	VS	SS	VS
2-(diethylamino)ethanol[d]	−42 to −40	VS	VS	VS	VS	I	VS
2-(dimethylamino)ethanol[d]	11–12.5	VS	VS	VS	VS	I	VS

[a] Values in parentheses were reported earlier. [b] Bis adduct of BH_3 with diamine. [c] The adduct is very soluble in pyridine. [d] The –OH group also reacts competitively. When an amine:BH_3 ratio of 3:4 is employed, the borate esters of BH_3–amine adducts are obtained cleanly. Hydrolysis with water provides the BH_3–amine adduct. [e] Abbreviations: I, insoluble (<0.1 g/100 mL of solvent); SS, slightly soluble (0.1–1.0 g/100 mL of solvent); VSS, very slightly soluble; S, soluble (1.0–3.0 g/100 mL of solvent); VS, very soluble (3.0–25 g/100 mL of solvent).

were investigated under various reaction conditions.[4-8] The subject has been reviewed recently.[9,10] The reduction of carbonyl compounds has also been studied extensively.[9,10] Aldehydes and ketones,[11-16] acid chlorides,[17] etc. have been reduced effectively.

Years ago we initiated a study on the effect of structure of the amine on the reactivity of BH_3–amine complexes toward typical B–H reactions, such as hydrolysis, hydroboration of alkenes, and reduction of ketones. It was thought that such a systematic study might help, not only in developing the scope of these molecular addition compounds in synthetically useful transformations, such as hydroboration and reduction, but also in understanding the mechanisms of these reactions. We report the details of that study in this paper.

Results

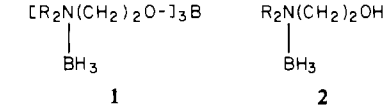
Preparation of Borane–Amine Complexes. The borane–amine complexes were prepared from BH_3·THF and the amine, either in a high-vacuum apparatus or in a round-bottom flask, by employing the usual bench-top techniques, especially when large amounts of the adducts were needed. In the case of monobasic amines, an amine:borane ratio of 1:1 was employed, while for dibasic amines, it was 1:2. The physical constants and solubility are given in Table I. None of the compounds showed significant dissociation at room temperature, and all are stable to dry air. In contrast to the other derivatives, the BH_3–*N*-phenylamine complexes are moisture sensitive.

Table II. Times[a] for Total Hydrolysis of BH_3–Amine Complexes at 25 °C

amine	time for total hydrolysis: 50% aqueous diglyme	1.0 M HCl in 50% aqueous diglyme	1.0 M HCl in 50% aqueous ethylene glycol
N-phenylmorpholine	2	3	
N,N-diethylaniline	30	30	
N,N-dimethylaniline	50	50	
pyridine		30	4
2,6-lutidine		50	6
2-picoline		105	7
piperidine			10
morpholine			120
2-(diethylamino)ethanol			180
2-(dimethylamino)ethanol			300
triethylamine			390
N-methylpiperidine			600[b]
trimethylamine			1000[b]
N-ethylmorpholine			6720
N-methylmorpholine			6720[c]
TMEDA[d]			no reacn
DABCO[d]			no reacn
N,N'-dimethylpiperazine[d]			no reacn

[a] Time in minutes. [b] Extrapolated. [c] Two-thirds of theoretical amount of H_2. [d] Bis adduct of BH_3 with the amine.

While attempting to prepare the BH_3 adducts of 2-(dimethylamino)- and 2-(diethylamino)ethanols, we noted that, concurrently with complexation, partial alcoholysis of the BH_3 by the –OH group also occurred. By using a BH_3:alcohol ratio of 4:3, the corresponding esters (**1**) were prepared. Hydrolysis provided the adducts with the free –OH group (**2**).



1 **2**

The bis adducts of BH_3 with dibasic amines, such as *N,N*-dimethylpiperazine, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and 1,4-diazabicyclooctane (DABCO), were the only ones that could be obtained, irrespective of whether a 1:1

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Table III. Hydroboration of 1-Octene by BH_3–*N*-Phenylamine Complexes in THF at 25 °C[a]

amine	amt of 1-octene, mmol	time, h	amt of 1-octene reduced, mmol	amt of H_2 evolved, mmol	total % of hydride utilized
N-phenylmorpholine	25	0	20		
		1	25	1	96
N,N-diethylaniline	25	0	17		
		1	22		
		2	25	0.6	95
N,N-dimethylaniline	25	0	8.3		
		1	17		
		2	19		
		4	22		
		6	23.2		
		8	24		
		1[b]	25	0.2	94

[a] Amount of BH_3–amine in all cases is 9.16 mmol. [b] 1 h at 50 °C.

or a 2:1 amine:BH_3 ratio was employed.

The effects of structure on the reactivity of the various BH_3–amine complexes toward typical B–H reactions, such as hydrolysis, hydroboration of 1-octene, and reduction of cyclohexanone, were then studied.

Hydrolysis of BH_3–Amine Complexes. Hydrolysis of the BH_3–amine complexes was first studied in 50% aqueous diglyme by monitoring the volume of H_2 evolved. Complexes containing the *N*-phenyl groups, borane–*N*-phenylmorpholine, borane–*N,N*-diethylaniline, and borane–*N,N*-dimethylaniline, were hydrolyzed rapidly in the order indicated (Table II). With all other borane–amine complexes, there was no H_2 evolution, even after 12 h at 25 °C. Consequently, these reactions were followed in 1 M HCl in 50% aqueous diglyme. For those cases where this reaction was inconveniently slow, the reaction was then followed in 1 M HCl in 50% aqueous ethylene glycol (Table II).

It may be noted that BH_3–*N*-phenylamine complexes are hydrolyzed much faster than the others. The order of reactivity among the BH_3–*N*-phenylamine complexes seems to be explicable in terms of the strength of the base and, consequently, the stability of the adduct formed. The weaker the adduct, the more easily it is hydrolyzed. This explanation does not apply to the acid hydrolysis (Table II), which does not seem to depend on the stability of the adduct.

The bis adducts of BH_3 with *N,N'*-dimethylpiperazine, TMEDA, and DABCO are not hydrolyzed at all under these conditions. This may be due to an exceptionally low solubility of these adducts in this solvent system.[18]

Hydroboration of 1-Octene. The reactivities of the various BH_3–amine complexes toward hydroboration of 1-octene were determined in THF at 25 °C. In all cases the ratio of 1-octene to the complex was maintained at 3:1. In addition, a 10% excess of the BH_3–amine adduct was utilized.

It was observed that the three BH_3–*N*-phenylamine complexes, namely, borane–*N*-phenylmorpholine, borane–*N,N*-diethylamine, and borane–*N,N*-dimethylamine, hydroborate 1-octene at fast rates, in the order indicated (Table III). The other BH_3–amine adducts did not show any evidence of hydroboration, even after 2 h at 25 °C. Hence, in these cases, the reactions were studied in refluxing THF (Table IV). To study the effect of temperature on this reaction, the hydroboration of 1-octene was studied in refluxing toluene as well (Table IV). As expected, the hydroboration proceeds much faster in refluxing toluene. Consequently, for hydroboration utilizing BH_3–amine complexes, refluxing toluene is more convenient.

As observed in hydrolysis, the BH_3–*N*-phenylamine complexes are much more reactive for hydroboration than the other BH_3–amine complexes. The order of reactivity among the BH_3–amine complexes is closely related to its stability. BH_3–*N*-phenylamine complexes are rendered less stable by the weakly basic nature of these amines due to the steric and electronic effects of the phenyl group. Consequently, they are more reactive. With other complexes also, it can be noted that decreasing the stability of the adduct by either steric or electronic factors results in a rate increase. For example, borane–*N*-ethylmorpholine reacts with 1-octene much faster than does borane–triethylamine. (The reason is obviously the weaker basic nature of *N*-ethylmorpholine due to the electron-withdrawing effect of the oxygen.) Borane–2,6-lutidine hydroborates 1-octene faster than does borane–pyridine, the rate difference being caused by the steric effect of the methyl groups in 2,6-lutidine. Thus the reactivities of the various BH_3–amine complexes toward hydroboration are explicable in terms of the stability of the adduct.

The behavior of the bis adducts of BH_3 with the diamines (Tables IV and V) in hydroboration is worth mentioning. In THF at 25 °C, none of these adducts show any reaction. In refluxing THF, the bis adduct of BH_3 with *N,N'*-dimethylpiperazine is completely soluble. The first 50% of the reaction is over in 2 h. Further reaction is very slow. $2BH_3$·TMEDA and $2BH_3$·DABCO are not soluble in THF, and hence they react only very slowly. In refluxing toluene, both bis(borane)–*N,N'*-dimethylpiperazine and $2BH_3$·TMEDA react swiftly (1 h) up to the first 50%, further reaction being slow. $2BH_3$·DABCO is not soluble, even in refluxing toluene, and hence, its reaction with 1-octene is slow, even in refluxing toluene.

Reduction of Cyclohexanone. Reactivities of the BH_3–amine complexes in the reduction of cyclohexanone were then studied. First, the reactions were carried out in THF at 25 °C. The ratio of cyclohexanone to BH_3–amine was kept at 3:1; in addition, a 10% excess of the BH_3–amine adduct was maintained. As observed in the hydrolysis and hydroboration reactions, borane–*N*-phenylmorpholine, borane–*N,N*-diethylaniline, and borane–*N,N*-dimethylaniline react at reasonable rates with cyclohexanone in the order given (Table VI). In all three cases, the reaction goes to 67% completion with further reaction being very slow. It must be noted that a similar behavior has been observed in the reduction of ketones by diborane with the reaction becoming quite slow at the $(RO)_2BH$ stage.[19]

The other BH_3–amine complexes are highly inert toward cyclohexanone in THF at 25 °C. For example, there is no reaction between borane–pyridine (or BH_3·NMe_3) and cyclohexanone over a period of 38 h at 25 °C. Consequently, we studied the reaction of BH_3–amine complexes with cyclohexanone in glacial acetic acid at 25 °C on the basis of the report that BH_3·NMe_3 reduced ketones in glacial acetic acid with little loss of active hydride[20] (Table VII). BH_3–*N*-phenylamine complexes are swiftly hydrolyzed by HOAc and hence could not be included in this study. In marked contrast to the reduction in THF wherein the reaction goes only to 67% completion in HOAc solvent, the reaction proceeds to near completion in many cases, suggesting that the acid plays a very

(18) We were initially surprised at the extreme inertness of these bis adducts toward acid hydrolysis. We even thought they might have a structure close to that of the diammoniate of diborane (Schultz, D. R.; Parry, R. W. *J. Am. Chem. Soc.* **1958**, *80*, 8). However, the IR spectral analysis did not show any peak at ~2220 cm^{-1}, which is characteristic of BH_4^-. Hence, these bis adducts arise as a result of symmetrical cleavage of B_2H_6. Their chemical inertness seems to arise from their high crystal lattice energy, their low solubility, and possibly other factors.

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Table IV. Hydroboration of 1-Octene by BH_3-Amine Complexes in Refluxing Tetrahydrofuran at 69 °C

amine	amt of BH_3-amine, mmol	amt of 1-octene, mmol	amt of 1-octene reduced, mmol				amt of H_2 evolved, mmol		total % hydride utilized
			2 h	4 h	6 h	20 h	in reacn[a]	on hydrolysis	
2,6-lutidine	9.16	25	25				1.1	0.45	97
N-ethylmorpholine	9.16	24	13.2	15.5	17.8	22.5		3.1	93
2-(diethylamino)ethanol[b]	9.16	25	9.3		14.0	19.3	0.8	3.62	90
2-picoline	9.16	25	8	10	11.5	17.5	1.35	8.0	98
N-methylmorpholine	9.16	25	6	9.4	10	17.5	2.0	5.0	90
pyridine	9.16	25	6.25	8.5	10	17.5	1.35	7.9	97
triethylamine	9.16	25	6.5	8.5	10	16.5	1.2	8.1	94
2-(dimethylamino)ethanol[b]	9.16	25	6.5	8	9	13	1.6	13.1	101
trimethylamine	9.16	25	0.75	2	3.5	10.7	1.2	11.7	87
N-methylpiperidine	9.16	25	2	3	4.5	9.5	2.0	15.0	96
morpholine	9.16	25	0	0	0	0	3.2	22.6	94.5
piperidine	9.16	25	0	0	0	0	0.8	22.5	96
N,N'-dimethylpiperazine[c]	4.58	25	12.5	12.5		14			
TMEDA[c]	4.58	25	2.5	3.75	7	13			
DABCO[c]	4.58	25	0	0	1.25	4.75			

[a] BH_3-secondary amine complexes have a tendency to lose H_2. For example, $BH_3 \cdot Me_2NH$ loses H_2 at 0 °C (McCoy, R. E.; Bauer, S. H. *J. Am. Chem. Soc.* 1956, *78*, 2061). Under our conditions, the BH_3-secondary amine complexes that we have used do not lose much H_2 during the reaction. [b] The -OH group protected as borate ester by employing 33% excess BH_3. [c] Bis adduct of BH_3 with the diamine.

Table V. Hydroboration of 1-Octene by BH_3-Amine Complexes in Toluene at 113 °C[c]

amine	amt of BH_3-amine, mmol	amt of 1-octene reacted, mmol										amt of H_2 evolved during reacn, mmol	amt of 1-octanol, mmol
		1 h	2 h	3 h	4 h	6 h	8 h	10 h	12 h	14 h	22 h		
2,6-lutidine	9.16	25										1	24.5
N-ethylmorpholine	9.16	21.7	23	24								1.2	23
2-(diethylamino)ethanol[a]	9.16	19	20.5	22								0.8	23.2
2-picoline	9.16	19	22.5	24								0.67	22.5
N-methylmorpholine	9.16	19.5	21	22.5	24							1.0	23
pyridine	9.16	16	21	22.5	24							1.2	22.5
triethylamine	9.16	16	19.5	21	22.2	22.5						1.5	23
2-(dimethylamino)ethanol[a]	9.16	11.2	13.2		16				22.5			1.6	22.8
morpholine	9.16	6	9.4	12.5		17.4			22.5			2.45	22.5
trimethylamine	9.16	5.2	8.5	10.8	12.1	15				20		0.8	20
N-methylpiperidine	9.16		8.3		12		15		16.2			0.5	15.5
piperidine	9.16		1.5		3		4.5	6	7.5		18.5	1.5	
N,N'-dimethylpiperazine[b]	4.58	15.5	18	19.3	20.5	21.5	21.5					2.0	21
TMEDA[b]	4.58	12.5	15	16.5	18	18.7	19					1.5	18
DABCO[b]	4.58	0	0	0	0	0.5	1		2.5			0.5	

[a] -OH group protected as the borate ester by employing 33% excess BH_3. [b] Bis adduct of BH_3 with the amine. [c] Amount of 1-octene in all cases is 25 mmol.

important role in this reduction reaction. To verify the role of acid in this reaction, the reduction of cyclohexanone with borane–2,6-lutidine was tried in ethyl acetate. In 2 h, no reaction was observed. This duration is sufficient to effect complete reduction in acetic acid solvent. The effect of various acids on the reaction of BH_3–amine complexes with cyclohexanone was investigated in THF at 25 °C (Table VIII). In all cases studied, the reaction was much faster in the presence of acid than in its absence, thus establishing the role of acid in enhancing the rate of reduction.

Discussion

The foregoing systematic study of the reactivity of BH_3–amine complexes toward hydroboration and reduction greatly helps in appreciating the possible scope of these reagents in synthetic chemistry. The BH_3–*N*-phenylamine complexes emerge as particularly valuable hydroborating agents and as convenient reducing agents in anhydrous media. The powerful role of acid in the reduction of ketones with BH_3–amine adducts permits greater variation in choosing the reaction conditions. Thus, reductions can be carried out in protic or aprotic solvents as well as in the presence of protic or Lewis acids.

The primary purpose of this study was not the mechanisms of the reactions but an understanding of the effect of structure of the amine on the reactivities of the BH_3–amine complexes.

Table VI. Reduction of Cyclohexanone by BH_3-*N*-Phenylamine Complexes in THF at 25 °C[a]

amine	time, h	amt of cyclohexanone reduced, mmol	amt of H_2 evolved on hydrolysis, mmol	amt of cyclohexanol, mmol
N-phenylmorpholine	0	14.3		
	3	16.0		
	5	16.7		
	7	16.7		
	24	18.3	5.95	18.7
N,N-diethylaniline	0	13.1		
	3	16.4		
	5	16.7		
	7	16.7		
	24	17.5	6.15	17.3
N,N-dimethylaniline	0	7.4		
	1	8.75		
	3	10.9		
	5	13.5		
	7	15.9		
	10	16.2		
	24	16.5	7.75	16.0

[a] Amount of BH_3-amine in all cases is 9.16 mmol and of cyclohexanone 25 mmol.

Table VII. Reduction of Cyclohexanone by BH_3-Amine Adducts in Glacial Acetic Acid at 25 °C[b]

amine	amt of BH_3-amine, mmol	amt of cyclohexanone reduced, mmol											amt of H_2 evolved, mmol	total % hydride utilized
		0 h	1 h	2 h	3 h	4 h	5 h	7 h	14 h	20 h	22 h	24 h		
2,6-lutidine	9.16	19.2	21.2	21.8									4.4	96
2-picoline	9.16	18.7	21.2	21.8	22.1	22.5			23.8				2.2	95
pyridine	9.16	18.7	21.2	21.8	22	22.5			23.5				1.25	90
piperidine	9.16	16.2	20	21.5			22.5			24			0.8	90
morpholine	9.16	16.7	19.2	20.8	21.5	21.8				23.8			1.65	93
2-(diethylamino)ethanol	9.16	12.5	16.7	18		19.5						21.3	3.6	90
2-(dimethylamino)ethanol	9.16	13	17.3	18.2		19					20.8		3.9	90
triethyamine	9.16	11.2	16.5				17.8				20		4.1	88
trimethylamine	9.16	11.2	16				17				19.5		1.65	80
N-methylpiperidine	9.16	12	15.5		16.7			18				20.5	1.65	81
N-methylmorpholine	9.16	6.5	12	15		17.1		18				19.3	5.1	90
N-ethylmorpholine	9.16	6.5		14.8		17		17.8				19	3.6	84
N,N'-dimethylpiperazine[a]	4.58	3.8	4.8		6.8		10	11			17.5		1.2	68
TMEDA[a]	4.58	2.3	5		7.8		10	13.3			19.6		5.5	90
DABCO[a]	4.58	1.5	2.3		5		5.8	7			15		1.4	60

[a] Bis adduct of BH_3 with the amine. [b] Amount of cyclohexanone in all cases is 25 mmol.

Table VIII. Effect of Acid on Reduction of Cyclohexanone by BH_3-Amine Complexes in THF at 25 °C[a]

amine	acid	amt of cyclohexanone reduced, mmol			amt of H_2 evolved, mmol	total % hydride utilized
		0 h	1 h	11 h		
2,6-lutidine	conc H_2SO_4	19.3	20.1		6.45	97
	HCl-THF	17.5	21		5.25	95
piperidine	conc H_2SO_4	22.2	23.8		3	98
	HCl-THF	22.5	23.8		2.7	96.5
trimethylamine	conc H_2SO_4	17.3	19.2	22.5	3.2	94
	HCl-THF	13.8	16.8		11.3	102
N-methylmorpholine	conc H_2SO_4	18.3	19.9	21.5	3.0	90
	HCl-THF	13.5	15.5		9.4	92

[a] Amount of BH_3-amine in all cases is 9.16 mmol, of cyclohexanone 25 mmol, and of acid 50 mmol.

However, it is of interest to consider the mechanistic pathway for the three reactions examined.

There appear to be five possible reaction pathways.

(A) Direct Attack. The BH_3–amine complex reacts directly with the reactive group:

$$RCH{=}X + H_3B{\cdot}NR_3 \rightarrow RCH_2{-}X{-}BH_2{\cdot}NR_3, \text{ etc.}$$

$$X = CH_2, O$$

(B) Prior Dissociation. The addition compound undergoes an initial dissociation to the free BH_3, followed by reaction of the borane with the reactive group:

$$H_3B{\cdot}NR_3 \rightleftharpoons H_3B + NR_3$$

$$RCH{=}X + H_3B \rightarrow RCH_2{-}X{-}BH_2, \text{ etc.}$$

$$X = CH_2, O$$

(C) Prior Dissociation in the Presence of Acidic Solvents or Media. Dissociation of the addition compound would be facilitated by reaction of the liberated amine with acid:

$$H_3B{\cdot}NR_3 \rightleftharpoons H_3B + NR_3$$

$$NR_3 + H^+ \rightleftharpoons R_3NH^+$$

$$RCH{=}X + BH_3 \rightarrow RCH_2XBH_2, \text{ etc.}$$

(D) Activation of the Reducible Group by Protonation, etc. The carbonyl group of aldehydes and ketones can be activated by coordination with protonic acids or Lewis acids, decreasing the electron density of the carbonyl carbon, making it more active toward attack by a hydride reagent:

$$RCHO + HA \rightleftharpoons RCH{=}\overset{+}{O}H \rightarrow R\overset{+}{C}HOH$$

$$R{-}\overset{+}{C}H{-}OH + H_3B{\cdot}NR_3 \rightarrow R{-}CH_2{-}OBH_2{\cdot}NR_3, \text{ etc.}$$

(E) Activation of the BH_3·(amine) Complex by Protonation or Association with Lewis Acids. Here the proton (or Lewis acid) could be associated in some manner with the BH_3 moiety, or it could be associated with the amine moiety. In either case, a greater reactivity of the borane moiety is postulated:

$$H_3B{\cdot}NR_3 + H^+ \rightleftharpoons H_3B{\cdot}NR_3^+ \text{ or } H_3B{\cdot}NR_3 + H^+ \rightleftharpoons H_3B{\cdot}NR_3{\cdots}H^+$$

This last case would differ from (C) in involving a direct attack by proton (or Lewis acid) on the amine moiety of the addition compound.

In the following pages, we present a discussion of our results and those available in the literature in light of these mechanistic possibilities.

Mechanism of Hydroboration of Alkenes with BH_3–Amine Complexes. Our data on the hydroboration of 1-octene with BH_3–amine complexes (Tables III–V) allow a rationalization of the mechanism in terms of the stability of the adduct. Any factor, steric or electronic, that decreases the stability of the adduct increases the rate of hydroboration. This behavior can be explained by the dissociation mechanism[21] (mechanism B):

$$BH_3{\cdot}NR^1R^2R^3 \rightleftharpoons BH_3 + R^1R^2R^3N$$

$$BH_3{\cdot}+ \text{ alkene} \rightarrow \text{product}$$

The weaker the complex, the easier it can dissociate, thus explaining the reactivity trend (Tables III–V).

These arguments, however, cannot rule out the operation of the direct-attack mechanism, mechanism A. Any factor that decreases the stability of the adduct may be expected, at least in principle, to increase the leaving tendency of the ligand

(21) For a recent review on the mechanism of hydroboration, see: Brown, H. C.; Chandrasekharan, J.; Wang, K. K. *Pure Appl. Chem.* **1983**, *55*, 1387.

Table IX. Effect of Adding Excess Lewis Base on the Rate of Hydroboration of Alkenes with BH_3–Lewis Base (LB) Complexes in Toluene[a,b]

alkene (amt, mmol)	BH_3·LB (amt, mmol)	molar equiv of LB added	temp, °C	$t_{1/2}$[c]
1-octene[d] (20)	BH_3·NEt_3[d] (6.67)	0	75	26 h
		1		54 h
		2		86 h
1-octene[d] (10)	BH_3·SMe_2[d] (3.33)	0	25	200 s
		1		325 s
		2		375 s
2,3-dimethyl-2-butene[e] (5)	BH_3·SMe_2[e] (5)	0	0	34 min
		1		52 min
		2		59 min

[a] Taken from ref 23. [b] The reactions were followed by monitoring the disappearance of the B-H absorption at ~4.0–4.3 μm in IR. [c] Time for the first 50% of the reaction. [d] In 20 mL of the solution. [e] In 25 mL of the solution.

in the bimolecular mechanism.[22] Recently, with a view to understanding the mechanism of hydroboration in general, we took a closer look at this reaction.[23] We thought that a rigorous means of distinguishing between the dissociation and the direct-attack mechanisms would be to study the effect of excess complexing agent on the hydroboration of 1-octene with BH_3–amine complex. The dissociation mechanism requires that the rate be repressed by the excess complexing agent, an outcome of the predissociation of the complex (mechanism B), while the direct-attack mechanism requires that there be no effect of excess complexing agent on the rate. In fact, the addition of 1 and 2 equiv of Et_3N significantly represses the rate of hydroboration of 1-octene with BH_3·NEt_3 in toluene at 75 °C (Table IX). We have observed that such a rate repression is applicable to almost all borane–Lewis base complexes we have studied.[23] Thus, it can now be conclusively stated that the hydroboration of alkenes with BH_3–amine complexes proceeds by the dissociation mechanism and not by the direct-attack one.

Mechanism of the Reduction of Cyclohexanone with BH_3–Amine Complexes. (a) In Neutral Solvents. Of the five mechanisms listed at the beginning of the Discussion, only mechanisms A and B apply for the reduction of ketones with BH_3–amine complexes, as in the case of hydroboration. In THF at 25 °C, only the BH_3–*N*-phenylamine complexes reduce cyclohexanone at reasonable rates. In these cases, the order of reactivity, borane–*N*-phenylmorpholine > borane–*N*,*N*-diethylaniline > borane–*N*,*N*-dimethylaniline, suggests that a dissociation mechanism similar to hydroboration might operate. Moreover, in these cases, there is a fast reaction to 67%, followed by further slow reaction. The same observation has been made in the reaction of ketones with diborane in THF as well, suggesting that a common intermediate, $BH_3 \rightarrow (RO)_2BH$, may be involved in these two cases. To further prove this point, we studied the order of reactivity of borane–*N*-phenylmorpholine toward the substrates alkene, ester, ketone, and acid chloride. We found the order alkene > ketone > ester > acid chloride (Table X). This indicates that the reaction rate increases with increasing electron density at the reaction center, a fact consistent with an electrophilic attack by the electron-deficient BH_3.

(b) In Acidic Solvents or in the Presence of Mineral or Lewis Acids. In the presence of mineral or Lewis acids, the mechanism of reduction of cyclohexanone becomes more difficult to unravel. At the outset, all mechanisms (A–E) appear to be strong candidates for consideration.

In acetic acid, the reactivity of BH_3–amine complexes toward cyclohexanone is not dependent on the stability of the adduct. Thus, less hindered BH_3–amine complexes, such as borane–piperidine, reduce cyclohexanone much faster than do more hindered ones, such as borane–triethylamine. Borane–morpholine, a complex which is very sluggish for hydroboration and reduction in THF, reduces cyclohexanone very rapidly in glacial acetic acid. These facts suggest that the mechanism of reduction in acetic acid may be drastically different from that in THF. This drastic change in the behavior in the presence of acids is also indicated by the following facts: (i) In neutral solvents, the reaction is fast only to 67% hydride uptake, while in acetic acid, the reaction goes cleanly to near completion in many cases. (ii) The reactivity of borane–2,6-lutidine toward the series alkene, ester, and ketone in acetic acid is in the order ketone > ester > alkene, indicating that the ease of reaction is inversely related to the electron density at the point of attack (Table XI). This is rationalizable in terms of a direct attack of the BH_3–amine complex on the substrate. (iii) Jones[24] has observed that essentially the same stereoselectivity is observed in the B_2H_6 and BH_3·NEt_3 reduction of 4-*tert*-butylcyclohexanone in the absence of acid. In both cases, 16% of *cis*-4-*tert*-butylcyclohexanol is observed. In the presence of acid (BF_3), the BH_3·NMe_3 reduction of 4-*tert*-butylcyclohexanone results in 46% of *cis*-4-*tert*-butylcyclohexanol; on the other hand, the isomer distribution for B_2H_6 reduction is unchanged in the presence of BF_3. The realization of greater amounts of axial alcohol in the presence of acid in the case of BH_3·NMe_3 reduction indicates a change in the species participating in the reduction. This also suggests that a direct attack of the amine complex may be involved in the presence of acid. In any case, it is very clear that the effect of acid on the reduction of ketones with BH_3–amine complexes cannot be accounted for in terms of a simple dissociation mechanism (mechanism B). To distinguish between mechanisms C, D, and E becomes more difficult. The faster reaction in the presence of acid can be explained by all three mechanisms. Mechanism C would predict a faster reaction in the presence of acid than in its absence, but identical selectivity in the presence or absence of acid. The different selectivities obtained probably indicate that mechanism C is not followed. However, this is the only observation presently available to discount mechanism C.

To distinguish between mechanisms D and E becomes more difficult. In acetic acid or aqueous acid solution, the kinetics of the reduction of acetone with borane–morpholine has been established to be second order, in comformity with a direct attack of the borane–morpholine complex on the carbonyl carbon. The rate acceleration by acid has been postulated to be due to the activation of the carbonyl group for attack by the hydridic agent by the conjugation of the acid (H^+ or HA or Lewis acid) with the carbonyl oxygen (mechanism D). The alternate possibility, mechanism E, is closely similar and has been postulated for the hydrolysis of BH_3–amine complexes (see next part). In our opinion, the intrinsic details of the mechanism of reduction of ketones with BH_3–amine complexes in the presence of acid solvents or acidic components are not yet understood completely and merit further attention.

Mechanism of Hydrolysis of BH_3–Amine Complexes. The hydrolysis of BH_3–*N*-phenylamine complexes occurs rapidly in neutral hydroxylic solvents. This behavior is similar to that observed in hydroboration and reduction in neutral solvents. Probably the mechanism involves the same free BH_3 species. The mechanism of acid hydrolysis of BH_3–amine complexes is significantly different. The order of reactivity in acid hy-

(22) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1983**, 606.
(23) Brown, H. C.; Chandrasekharan, J. *J. Am. Chem. Soc.* **1984**, *106*, 1863.
(24) Jones, W. M. *J. Am. Chem. Soc.* **1960**, *82*, 2528.

Table X. Reduction of Standard Series with Borane-*N*-Phenylmorpholine in THF at 25 °C[a]

series compd	amt of series compd reduced, mmol					amt of H_2 evolved on hydrolysis, mmol	total % hydride utilized
	0 h	1 h	2 h	3 h	14 h		
1-octene	18.7	24.6				1.8	93.5
acetone	7.5	13.5	15	15.8	17.7	7.6	92.5
ethyl acetate					4.2	16.5	92
acetyl chloride					2	22.1	95

[a] Amount of series compound in all cases is 25 mmol and of BH_3–amine 9.16 mmol.

Table XI. Reduction of Standard Series with BH_3–Amine Complexes in Acetic Acid at 25 °C[b]

amine	series compd	amt of series compd reduced, mmol									amt of H_2 evolved, mmol	total % hydride[a] utilized
		0 h	1 h	2 h	3 h	4 h	6 h	16 h	20 h	22 h		
2,6-lutidine	acetone	10.2	11.5	12.3	13	13.5					13	97
									0		16	59
	ethyl acetate								0		16	59
	1-octene							0			15	54
piperidine	acetone	11.2	14.3	16.3			17.2			18.7	3.35	81
									0		4.5	16
	ethyl acetate								0		4.9	18
	1-octene								0		3.9	14
trimethylamine	acetone	1.5	3.5		5				11		7.4	67
									0		0	0
	ethyl acetate								0		0	0
	1-octene								0		0	0

[a] In all cases where all of the hydride is not used, acid hydrolysis, after reaction, gave a total hydride accounting of 90% or better.
[b] Amount of series compound in all cases is 25 mmol and of BH_3–amine 9.16 mmol.

drolysis is not dependent on the stability of the adduct, thus indicating that a simple dissociation mechanism is not involved.

Ryschkewitsch has observed that the acid hydrolysis of $BH_3{\cdot}NMe_3$ follows second-order kinetics, first order in the adduct and first order in acid.[25] Davis and co-workers have reported that $BH_3{\cdot}NMe_3$ undergoes a rapid exchange with D_2O in the presence of acid.[26] These facts indicate that in acid hydrolysis a direct attack of H^+ on the BH_3–amine complex is involved. There has been a considerable amount of work done on the site of attack of H^+ on the BH_3–amine complex.[27-29] Davis and co-workers, from their kinetic isotope effect studies, have concluded that the H^+ attacks the B–H bond of the ate complex.[27] In the acid hydrolysis of the closely related BH_4^- ions, Kreevoy and co-workers[29a] and Olah and co-workers[29b] have suggested that a pentacoordinate boron species may act either as the transition state or as an unstable intermediate. In any case, all of the results clearly indicate that the acid hydrolysis involves an attack of H^+ on the BH_3–amine complex. Our results on acid hydrolysis do not throw any light on the mechanistic details of the reaction. However, they are highly useful in deciding the time required to completely hydrolyze a given BH_3–amine complex. This information is required to develop a reliable method for quantitative analysis of the reagent based on hydride estimation,[30] a major objective of this exploratory study.

We wish to point out a major difference in the mechanisms often proposed for the acid-catalyzed reduction of ketones with BH_3–amine complexes and their acid hydrolysis. For the former reaction, mechanism D is proposed, and for the latter one, mechanism E. It may be quite possible that the mechanisms involved in these two closely related reactions are quite similar. As mentioned before, this question cannot be answered definitively at this time and merits further research.

Experimental Section

For vacuum line manipulations, a general-purpose, high-vacuum line, 10^{-6} torr, was used for measuring the volumes of gaseous compounds. The construction and technique have been described by Sanderson.[31] For the usual bench-top handling of air-sensitive compounds, standard procedures described in ref 30 were employed. GC analyses were carried out with an Aerograph instrument. THF solutions of 1-octene were analyzed on a 5-ft adiponitrile column; toluene solutions were analyzed on a 5-ft Ucon polar column. For cyclohexanone and cyclohexanol, 5-ft Carbowax 20 M and 1540 columns were respectively employed.

Materials. All amines except the 2-(dialkylamino)ethanols were dried over P_2O_5 and distilled under a N_2 atmosphere. The 2-(dialkylamino)ethanols were dried over K_2CO_3 and then distilled under a N_2 atmosphere. The alkenes and alkanes (internal standards) were obtained from Phillips Petroleum Co. and were used as such. The solvents were purified by drying over appropriate reagents reported in the literature and distilled under a N_2 atmosphere. A standard solution of hydrogen chloride in THF was prepared as reported in the literature.[32]

Vacuum Line Preparation of BH_3–Amine Complexes. The standard procedure was as follows. A weighed amount of amine, normally between 2 and 3 mmol, was placed into the reaction system of the vacuum line and thoroughly degassed. In the standard bulb was measured out an excess of diborane, and this was removed by liquid nitrogen to the reaction system. The liquid-nitrogen bath was removed and replaced by a −111 °C bath, then a −78 °C bath, and finally, an ice–water bath, 0 °C. The system was then stirred at 0 °C for 4–6 h. After this time, the system was cooled to −78 °C and unreacted diborane was removed to the standard bulb by liquid nitrogen. The amount of unreacted diborane was measured, and in all cases the theoretical amount of diborane had reacted with the amine.

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(30) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapter 9.
(31) Sanderson, R. T. "Vacuum Manipulations of Volatile Compounds"; Wiley: New York, 1948.
(32) Maxsom, R. N. *Inorg. Synth.* **1939**, *1*, 147.

This procedure was followed in all cases save for preparations with DABCO and *N*-phenylmorpholine. In these cases the solid amine was first dissolved in 6 mL of dry ether, thoroughly degassed, and then reacted as before.

Laboratory Bench Preparation of BH_3–Amine Complexes. The standard procedure was as follows. The equipment consisted of a 250-mL flask equipped with a pressure-equalized separatory funnel, a thermometer, an outlet tube closed to the atmosphere by stopcock, and a magnetic stirrer. The system was oven dried and assembled with a minimum exposure to air. It was then flamed out by Bunsen burner with dry nitrogen passing through the system. Into the flask under nitrogen was placed the theoretical amount of amine and freshly distilled tetrahydrofuran. The stirred system was cooled to 0 °C, and to it was added over 1 h a 20% excess of the theoretical diborane as standard solution in tetrahydrofuran. After complete addition, the system was stirred 1 h and then attached to a vacuum pump and trap through the outlet tube. Unreacted diborane and the solvent were removed to a −78 °C bath under vacuum. The trap, in all cases by hydrolysis of an aliquot, showed the presence of residual borane. The amine–borane product was transferred under dry nitrogen to a vacuum dessicator and dried overnight. After being dried, it was stored in a bottle under dry nitrogen until used.

Procedure for Hydrolysis of BH_3–Amine Complexes. The rates of reaction of amine–boranes were followed by hydrogen evolution. Weighed samples (3 mmol) of the amine–boranes were placed in 125-mL Erlenmeyer flasks equipped with a stirring bar. To this was added by pipette 7.5 mL of diglyme or ethylene glycol. The systems were stirred until all was dissolved. The flasks were then attached to a two-hole rubber stopper, which connected a 50-mL burette filled with the hydrolysis agent and a 250-mL inverted burette filled with water to collect evolved hydrogen. Water baths were placed around the systems and the temperatures controlled to 25 ± 1 °C. To the stirred solutions was added from the burette either 7.5 mL of water or 7.5 mL of 2.01 M hydrochloric acid. Time zero (0) was at start of addition. Initial concentrations were 1 M in acid and 0.2 M in BH_3–amine. The hydrogen evolved was passed through −78 °C baths to remove solvent vapors and then collected over water. The measured volume of gas was corrected for the amount of hydrolysis agent added, for temperature, and for vapor pressure of water to standard conditions to determine the amount of hydrolysis. This hydrogen evolution was followed at regular intervals until completion of reaction.

For hydrolyses with 12 M hydrochloric acid, no solvent was added. From the burette, 10 mL of the acid was delivered.

General Procedure for Hydroboration with BH_3–Amine Complexes. In the normal apparatus was placed 25 mmol of 1-octene (2.8 g) and 5 mmol of *n*-heptane (0.5 g) in 10 mL of either tetrahydrofuran or toluene. To the stirred solution was added over 30 min 9.16 mmol of the BH_3–amine complex (10% excess) in 18 mL of THF or toluene. Completion of addition time was designated as time zero (0). The system was kept at 25 ± 1 °C by use of a water bath. Samples were withdrawn at regular intervals and analyzed, and any gas evolution was followed on the flow meter. If reaction occurred at 25 °C, the system was followed. If, however, after 2 h there had been no reaction, a heating mantle was placed around the system and it was heated to reflux. Time zero (0) was at attainment of reflux. The reaction was followed as before.

This procedure was followed in all cases save with the diamine–bis(boranes). For these, the inverse method of addition was used, namely, 1-octene added to amine–borane. Excess amounts of the diamine–bis(boranes) (4.58 mmol, 10% excess) were used.

For reactions in THF, after the prescribed reaction time, the reaction mixture was cooled to 25 °C and then 10 mL of 12 M HCl was added to hydrolyze any residual hydride.

For reactions in toluene, after the prescribed reaction time, the systems were cooled to 25 °C and then oxidized. Oxidation was effected by addition of 2.5 mL of 6 N sodium hydroxide, followed by the addition, over 30 min, of 4 mL of 30% hydrogen peroxide. After oxidation and drying of the nonaqueous layer with K_2CO_3, the 1-octanol concentrations were determined by gas chromatography.

General Procedure for Reduction of Cyclohexanone by Amine–Boranes in Acetic Acid. In the usual apparatus was placed 25 mmol of cyclohexanone (2.46 g) and 5 mmol of *n*-decane (0.71 g) in 7.5 mL of acetic acid. The temperature was maintained at 25 ± 2 °C. To the flask was added over 30 min 9.16 mmol of BH_3–amine (10% excess) in 20 mL of acetic acid. This was followed in all cases, save with the diamine–boranes, in which case the inverse mode of addition was followed. Time zero (0) was at complete addition. The reaction was followed at regular intervals by gas chromatography and hydrogen evolution.

General Procedure for Reduction of Cyclohexanone by Phenylamine–Boranes in Tetrahydrofuran. In the usual apparatus was placed 25 mmol of cyclohexanone (2.46 g) and 5 mmol of *n*-dodecane in 7.5 mL of THF. The temperature was maintained at 25 ± 2 °C. To the flask was added over 30 min 9.16 mmol of phenylamine–borane (10% excess) in 20 mL of THF. Time zero (0) was at complete addition. The reaction was followed at regular intervals by gas chromatography. After total reaction time, 10 mL of ethylene glycol was added and the evolved hydrogen measured. The residual mixtures were then analyzed for cyclohexanol.

Effect of Various Acids on the Reduction of Cyclohexanone by Amine–Boranes in Tetrahydrofuran. In the normal apparatus was placed 25 mmol of cyclohexanone (2.46 g), 5 mmol of *n*-dodecane (0.85 g), and 9.16 mmol of the amine–borane (1.11, 0.906, 1.055, and 0.67 g respectively of 2,6-lutidine–, piperidine–, *N*-methylmorpholine–, and trimethylamine–boranes) in 10 mL of THF. To the above mixtures at 25 °C was added over 30 min either 29 mL of 1.78 M hydrogen chloride in THF (50 mmol) or 2.75 mL of concentrated sulfuric acid (50 mmol) dissolved in 29 mL of THF. After complete reaction, the cyclohexanol concentration was determined following hydrolysis with ethylene glycol.

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Registry No. DABCO·2BH_3, 15531-41-6; TMEDA·2BH_3, 5843-33-4; BH_3·SMe_2, 13292-87-0; H_2SO_4, 7664-93-9; HCl, 7647-01-0; trimethylamine·BH_3, 75-22-9; triethylamine·BH_3, 1722-26-5; pyridine·BH_3, 110-51-0; 2-picoline·BH_3, 3999-38-0; 2,6-lutidine·BH_3, 3999-42-6; morpholine·BH_3, 4856-95-5; *N*-methylmorpholine·BH_3, 15648-16-5; *N*-ethylmorpholine·BH_3, 88996-22-9; *N*-phenylmorpholine·BH_3, 84215-46-3; *N*,*N*′-dimethylpiperazine·2BH_3, 15531-21-2; *N*,*N*-dimethylaniline·BH_3, 1769-74-0; *N*,*N*-diethylaniline·BH_3, 13289-97-9; piperidine·BH_3, 4856-94-4; *N*-methylpiperidine·BH_3, 5275-41-2; 2-(diethylamino)ethanol·BH_3, 91128-41-5; 2-(dimethylamino)ethanol·BH_3, 82879-04-7; 1-octene, 111-66-0; cyclohexanone, 108-94-1; 2,3-dimethyl-2-butene, 563-79-1; acetone, 67-64-1; ethyl acetate, 141-78-6; acetyl chloride, 75-36-5.