ADDITION COMPOUNDS OF BORON TRIFLUORIDE, BORANES AND ALANE WITH *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE AND TRIETHYLENEDIAMINE

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Abstract - This review summarizes the studies conducted in the Richard B. Wetherill Laboratory on the synthesis of addition compounds of boron trifluoride, boranes and alane with *N,N,N',N'*-tetramethylethylenediamine and the heterocycle, triethylenediamine. The applications of such addition compounds are also briefly discussed.

INTRODUCTION

Amine-boranes represent the largest number of known boron-nitrogen compounds. The first amine-borane to be reported was trimethylamine-borane ($Me_3N{\cdot}BH_3$), prepared by the fast, direct reaction of diborane with trimethylamine.[2] Since then, numerous amine complexes of borane have emerged and their application to organic synthesis has been examined.[3] The properties of amine-boranes are markedly dependent upon the substituents on boron and nitrogen.[4] In recent years a number of partially substituted boranes has been prepared and found to be highly useful reagents.[5] With few exceptions, the preparation and chemistry of the corresponding amine complexes remained relatively unexplored until recently. Recent studies in this laboratory have resulted in a simple procedure for the preparation of triethylamine-monoalkylborane adducts ($Et_3N{\cdot}BH_2R$) starting from triethylamine-thexylborane ($Et_3N{\cdot}BH_2Thx$)[6] and have led to the discovery of promising new applications for these derivatives. The triethylamine component could be removed from these adducts by treatment with either $THF{\cdot}BH_3$[7] or $Et_2O{\cdot}BF_3$[8] to produce the free monoalkylborane for reduction and hydroboration applications. However, this procedure suffers from certain difficulties. Both $Et_3N{\cdot}BH_3$ and $Et_3N{\cdot}BF_3$ are highly soluble in the usual tetrahydrofuran (THF) medium, making them difficult to separate from the desired product.[7,8] This problem can be circumvented in part by changing to a pentane (n-C_5H_{12}) solution from which $Et_3N{\cdot}BF_3$ can be precipitated at -50°C.[8] Furthermore, the $Et_3N{\cdot}BH_2R$ adducts are liquids of uncertain purity, which cannot be purified readily.[6,9]

One of the intriguing problems in borane chemistry has been the relative instability of many of the borane reagents.[5] For example, thexylborane ($ThxBH_2$), dicyclohexylborane (Chx_2BH), disiamylborane (Sia_2BH) and diisopinocampheylborane (Ipc_2BH) all possess limited stability upon

storage.[10-13] Consequently, they must be synthesized and used shortly thereafter. Hence, it appeared highly desirable to develop stable crystalline derivatives which could be stored either neat or in solution for extended periods of time and then conveniently converted to the free borane as and when needed. A series of experiments were carried out in our laboratory to explore the possibility of utilizing *N,N,N',N'*-tetramethylethylenediamine (TMED) and the heterocycle, triethylenediamine (TED), as stabilizing addendum for organoboranes. This review concerns itself with the preparation of the addition compounds of boron trifluoride, borane, alane, dialkylboranes and monoalkylboranes with TMED and TED, with particular emphasis on work conducted in our laboratories. The application of these addition compounds are also mentioned.

ADDITION COMPOUNDS OF TMED AND TED WITH BORON TRIFLUORIDE, BORON AND ALANE

Over the years, various workers have carried out experiments involving addition compounds of TMED and TED with boron trifluoride (BF_3), borane (BH_3) and alane (AlH_3).[14-19] These adducts are highly insoluble in the usual organic solvents (THF, Et_2O, $CHCl_3$, *n*-C_5H_{12} and C_6H_6). During the course of our work, it became desirable to achieve a convenient precipitation of BF_3, BH_3 and AlH_3 from ether solvents. Surprisingly, no work had been reported previously on the precipitation of the above Lewis acids from their solutions in ether solvents using TMED or TED. Our primary objective was to establish conditions for the precipitation of BF_3, BH_3 and AlH_3 from Et_2O and THF. Consequently, we were interested both in the stoichiometry of the reaction between the above Lewis acids with the difunctional Lewis bases, TMED and TED, and in the solubility of the products. Generally, a monofunctional Lewis acid can react with a difunctional Lewis base to afford either the mono adduct or the bis adduct, depending upon the nature of the acid and base involved and the particular solvent used for the reaction.[14,20]

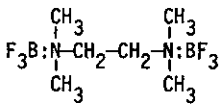
Boron Trifluoride - The reaction between $Et_2O{\cdot}BF_3$ and TMED proceeds directly to the formation of 1:2 complex (Eq. 1), with no evidence for the formation of the intermediate 1:1 complex.[14]

$$\text{TMED} + 2\ Et_2O{\cdot}BF_3 \xrightarrow[25°C]{\text{THF}} \text{TMED}{\cdot}2\ BF_3\downarrow \qquad (1)$$

The 1:2 adduct precipitates completely at 25°C. Any excess TMED over the 1:2 stoichiometry remains unreacted. Thus, the addition of $Et_2O{\cdot}BF_3$ to an equimolar amount of TMED in THF precipitates precisely half of the amine as the adduct with half of the amine remaining in solution (Eq 2).

$$\text{TMED} + Et_2O{\cdot}BF_3 \xrightarrow[25°C]{\text{THF}} 0.5\ \text{TMED}{\cdot}2\ BF_3\downarrow + 0.5\ \text{TMED} \qquad (2)$$

Identical results were obtained in Et_2O. The same results were realized with reverse addition. Elemental analysis and ^1H NMR spectrum indicated that the 1:2 adduct could be represented either as the symmetrical bis adduct (1) or as the boronium tetrafluoroborate (2). The ^{11}B NMR spectrum



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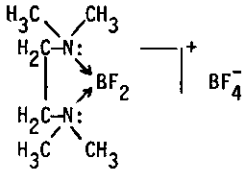


(2)

displayed a sharp quartet (J_{BF} = 14.7 Hz). This unambiguously supports structure (1) for the 1:2 adduct. Triethylenediamine reacts with $Et_2O{\cdot}BF_3$ in Et_2O and THF according to equations 3 and 4

$$TED + 2\ Et_2O{\cdot}BF_3 \xrightarrow[25°C]{Et_2O} TED{\cdot}2\ BF_3\downarrow \qquad (3)$$

$$TED + Et_2O{\cdot}BF_3 \xrightarrow[25°C]{THF} TED{\cdot}BF_3\downarrow \qquad (4)$$

respectively. The adducts precipitate completely from Et_2O and THF at 25°C. Both mono and bis adducts were prepared earlier by different routes.[15,21] This fast, complete reaction of boron trifluoride with TMED or TED to form highly insoluble adducts provides a convenient means to remove TMED, TED or BF_3 from ether solvents, such as Et_2O or THF.

Borane - Irrespective of the mode of addition and the quantity of the reactants, both TMED and TED react instantaneously with borane methyl sulfide ($Me_2S{\cdot}BH_3$) in THF to precipitate the bis adduct (Eqs 5 and 6).

$$TMED + 2\ Me_2S{\cdot}BH_3 \xrightarrow[25°C]{THF} TMED{\cdot}2\ BH_3\downarrow \qquad (5)$$

$$TED + 2\ Me_2S{\cdot}BH_3 \xrightarrow[25°C]{THF} TED{\cdot}2\ BH_3\downarrow \qquad (6)$$

Similar results were obtained in Et_2O. On heating a 1:1 mixture of $TED{\cdot}2\ BH_3$ and TED to 160°C, a clear melt is obtained, which on cooling, crystallizes to give the mono adduct, $TED{\cdot}BH_3$. This development was utilized in the selective precipitation of borane from a solution containing a mixture of organoboranes.[22] This method was also used in the generation of monoalkylboranes (RBH_2) from their amine adducts.[23]

Alane - The addition compounds of TMED and TED with alane (AlH_3) were conventionally synthesized by reacting the hydrochloride or hydrobromide of the Lewis bases with lithium aluminum hydride (Eqs 7 and 8).[18,19]

$$TMED{\cdot}2\ HCl + 2\ LiAlH_4 \xrightarrow{TMED} 2\ TMED{\cdot}AlH_3 + 2\ LiCl + H_2\uparrow \qquad (7)$$

$$TED{\cdot}HBr + LiAlH_4 \xrightarrow{Et_2O} TED{\cdot}AlH_3 + LiBr + H_2\uparrow \qquad (8)$$

When Et_2O is used as the solvent, the hydrochloride cannot be used. The by-product, which is insoluble in Et_2O, will precipitate along with the desired product. In the precipitation reaction, TMED and AlH_3 afforded either the mono adduct or the bis adduct, depending upon the solvent used for the reaction.[24] In diethyl ether (Et_2O), TMED precipitated AlH_3 as TMED·2 AlH_3 (Eq 9).

$$\text{TMED} + 2\ AlH_3 \xrightarrow{Et_2O} \text{TMED}\cdot 2\ AlH_3\downarrow \qquad (9)$$

On the other hand, TMED precipitated AlH_3 as TMED·AlH_3 in THF (Eq 10). However, the precipita-

$$\text{TMED} + AlH_3 \xrightarrow[25°C]{\text{THF}} \text{TMED}\cdot AlH_3 \qquad (10)$$

tion of the mono adduct from THF is incomplete. TED precipitated AlH_3 as the 1:1 complex irrespective of the solvent used (Eq 11). In both Et_2O and THF, the precipitation of the adduct proceeds

$$\text{TED} + AlH_3 \xrightarrow[25°C]{\text{THF or } Et_2O} \text{TED}\cdot AlH_3\downarrow \qquad (11)$$

quantitatively. TED·2 AlH_3 is not formed in THF, even in the presence of two molar equivalents of AlH_3.

This precipitation reaction was recently utilized in the successful synthesis of lithium trialkylborohydrides (LiR_3BH).[25] Recently the reaction of lithium aluminum hydride with representative trialkylboranes, as a potential route to lithium trialkylborohydrides, was investigated. Trialkylboranes with primary alkyl groups reacted with lithium aluminum hydride according to equation 12.

$$LiAlH_4 + R_3B \xrightarrow[25°C,0.25\ h]{\text{THF}} LiR_2BH_2 + RAlH_2 \qquad (12)$$

Trialkylboranes having secondary alkyl groups behaved differently. They afforded a mixture of dialkylborohydrides and trialkylborohydrides. Examination of the above reaction at -78°C established that the reaction proceeds with the initial formation of the desired trialkylborohydride (Eq 13), followed by a transfer of the alkyl group (Eq 14).

$$LiAlH_4 + R_3B \xrightarrow[-78°C]{\text{THF}} LiR_3BH + AlH_3 \qquad (13)$$

$$LiR_3BH + AlH_3 \xrightarrow[25°C]{\text{THF}} LiR_2BH_2 + RAlH_2 \qquad (14)$$

This study indicated that a new synthesis of LiR_3BH might be achieved if the aluminum hydride could be removed as soon as formed so as to avoid the fast subsequent reaction. The observation that TED rapidly and quantitatively precipitates aluminum hydride as TED·AlH_3 from Et_2O was utilized. Accordingly, lithium aluminum hydride was reacted with trialkylboranes in Et_2O in the presence of the heterocyclic amine, TED, to give the corresponding lithium trialkylborohydrides.

Aluminum hydride precipitated out of solution as TED·AlH_3, leaving pure product in solution. The data on the addition compounds of boron trifluoride, borane and alane with TMED and TED are summarized in Table I.

TABLE I

Summary of Data on Addition Compounds of Boron Trifluoride, Borane and Alane with *N,N,N',N'*-Tetramethylethylenediamine and Triethylenediamine

	TMED		TED	
Lewis Acid	1:1[a]	1:2[b]	1:1[a]	1:2[b]
	mp, °C		mp, °C	
BF_3	—	210-212[c]	199-201[d]	> 300[c]
BH_3	-3 to -1[e]	184-185[c,d]	168-170[e]	> 300[c,d]
AlH_3	140-143[f]	95-99[c]	280-282[c,d]	—

[a]1:1 = TMED·MX_3 or TED·MX_3. [b]1:2 = TMED·2 MX_3 or TED·2 MX_3. [c]Complete precipitation at 25°C from Et_2O. [d]Complete precipitation at 25°C from THF. [e]Does not precipitate in this form. TED·BH_3 was prepared by melting together TED and TED·2 BH_3. TMED·BH_3 has been prepared previously by a corresponding procedure.[32] [f]Incomplete precipitation at 25°C from THF.

ADDITION COMPOUNDS OF TMED AND TED WITH DIALKYL AND MONOALKYLBORANES

Dialkylboranes - The possibility of utilizing either TMED or TED to precipitate quantitatively BF_3, BH_3 or AlH_3 from ether solvents made the TMED and TED adducts of dialkylboranes and monoalkylboranes of considerable interest. Accordingly, the possibility of utilizing TMED or TED as a stabilizing addendum for dialkylboranes and monoalkylboranes was explored. The dialkylboranes, Chx_2BH, Sia_2BH and Ipc_2BH were selected for the study. Unfortunately, our attempts to stabilize these dialkylboranes with TMED were unfruitful. The adducts appear to be dissociated, so that the dialkylboranes undergo the usual redistribution reactions. Presumably, the dissociation is the result of conflicting steric requirement of the dialkylboranes and the tertiary amine.

Diisopinocampheylborane (Ipc_2BH) reacts with TMED with the displacement of α-pinene, providing the TMED addition compound of monoisopinocampheylborane ($IpcBH_2$, Eq 15). If one-half equivalent

$$Ipc_2BH + TMED \xrightarrow[25°C]{neat} TMED\cdot BH_2Ipc + \alpha\text{-pinene} \qquad (15)$$

of TMED is used, the bis adduct of $IpcBH_2$ is obtained (Eq 16).[26] Both the mono and the bis adducts

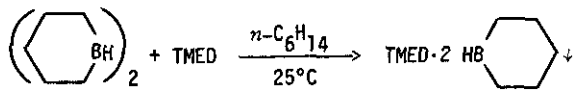
$$2\ Ipc_2BH + TMED \xrightarrow[34°C,0.5\ h]{Et_2O} TMED\cdot 2\ BH_2Ipc + 2\ \alpha\text{-pinene} \qquad (16)$$

are crystalline, air-stable compounds. An unexpected development was the discovery that the bis adduct of TMED with $IpcBH_2$ separates in much higher optical purity than the α-pinene used to synthesize Ipc_2BH. Reaction of the adduct with $Et_2O{\cdot}BF_3$ precipitates TMED as $TMED{\cdot}2\ BF_3$, leaving the optically pure chiral hydroborating agent, $IpcBH_2$, in solution.[27] The mono and the bis adducts can also be prepared according to equations 17 and 18 respectively.[14]

$$Et_3N{\cdot}BH_2Ipc + TMED \xrightarrow[25°C,1\ h]{neat} TMED{\cdot}BH_2Ipc + Et_3N \qquad (17)$$

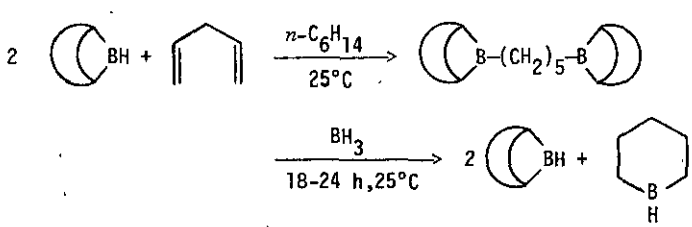
$$2\ TMED{\cdot}BH_2Ipc + 2\ Et_2O{\cdot}BF_3 \xrightarrow[25°C,0.5\ h]{THF} TMED{\cdot}2\ BH_2Ipc + TMED{\cdot}2\ BF_3\downarrow \qquad (18)$$

Recently the reaction of heterocyclic dialkylboranes, borinane and 9-borabicyclo[3.3.1]nonane, (9-BBN), with various amines was compared using an infrared technique.[28] A special objective of the study was to determine whether it was possible to complex preferentially one of the dialkylboranes with a suitable amine and effect a separation of the two reagents from their mixtures. It was found that both borinane and 9-BBN form complexes with TMED and TED, but there was a vast difference in the rate of reaction. In *n*-hexane (n-C_6H_{14}) solution, 9-BBN takes several hours for complete reaction. In contrast, borinane reacts practically instantaneously. The nature of the complex between borinane and TMED varies with the reaction solvent. In *n*-hexane, even in the presence of excess TMED, only the bis adduct is formed (Eq 19).



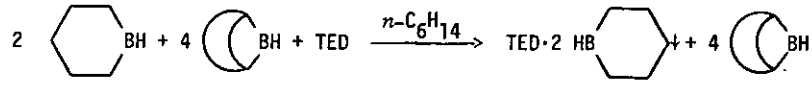
(19)

In THF and $CHCl_3$, both mono and bis adducts are formed according to the amount of TMED present. The bis adduct is sparingly soluble in *n*-hexane (85% precipitates from a 1 *M* solution at 0°C). However, with TED, borinane forms both mono and bis adducts in *n*-hexane. The bis adduct is practically insoluble at 25°C. An unpublished study with 9-BBN showed that in *n*-hexane it also formed only bis adduct with TMED and both mono and bis adducts with TED. The TMED adduct does not possess much air stability and undergoes oxidation readily. A recently reported improved synthesis of borinane starts with 9-BBN and 1,4-pentadiene (Eq 20).[29] In this synthesis, use of Et_3N was made in



(20)

separating borinane from 9-BBN. The low solubility and fast rate of complexation between borinane and TMED or TED has also been utilized to effect this separation (Eq 21).[30]



(21)

Monoalkylboranes - The versatile monoalkylborane, thexylborane ($ThxBH_2$), reacts directly with TMED or TED to form the 1:1 adduct (Eqs 22 and 23).

$$ThxBH_2 + TMED \xrightarrow[25°C]{neat} TMED{\cdot}BH_2Thx \qquad (22)$$

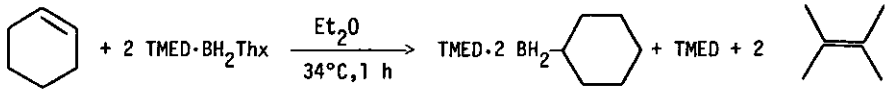
$$ThxBH_2 + TED \xrightarrow[25°C]{THF} TED{\cdot}BH_2Thx \qquad (23)$$

The 1:2 adduct could be prepared by combining 2 moles of $ThxBH_2$ with 1 mole of the amine (Eq 24).

$$2\ ThxBH_2 + TMED \xrightarrow[25°C]{neat} TMED{\cdot}2\ BH_2Thx \qquad (24)$$

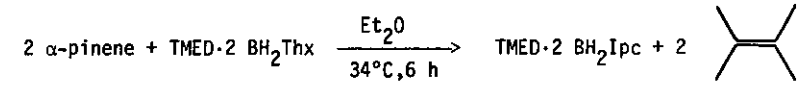
Both TMED·2 BH_2Thx and TED·BH_2Thx are crystalline compounds. However, TED·BH_2Thx exhibits more oxidative and hydrolytic stability than TMED·2 BH_2Thx. These addition compounds are used in the indirect synthesis of monoalkylboranes. In general, it is not possible to synthesize monoalkylboranes by the direct reaction of olefins with borane.

Hydroboration of olefins usually proceeds rapidly past the monoalkylborane stage to give either dialkylboranes or trialkylboranes. Thexylborane amine (TMED or TED) adducts react with olefins with facile displacement of tetramethylethylene and the formation of the corresponding monoalkylborane amine (TMED or TED) adducts in nearly quantitative yield. The 1:1 adduct, TMED·$ThxBH_2$, reacts with olefins, except α-pinene, to give the 1:2 adduct, TMED·2 BH_2R (Eq 25).



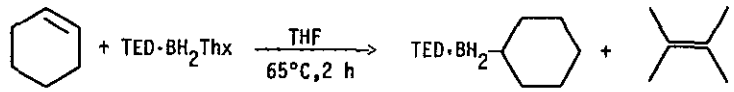
(25)

TMED·BH_2Thx reacts with α-pinene to give the 1:1 adduct, TMED·BH_2Ipc. The 1:2 adduct, TMED·2 BH_2Thx, reacts with olefins, including α-pinene, to give the 1:2 adduct, TMED·2 BH_2R (Eq 26).[31]



(26)

The reaction between TED·BH_2Thx and olefins needs a relatively more vigorous condition.[31] Thus, olefins react with TED·BH_2Thx in refluxing THF to form the corresponding monoalkylborane TED adducts (Eq 27).



(27)

Comparison of the stability and the reactivity of the adducts of $ThxBH_2$ with TMED or TED indicates that TED forms a stronger complex with $ThxBH_2$ than TMED. Apparently the steric requirements of TED is less than that of TMED and hence TED is a stronger Lewis base than TMED. The addition compounds, TMED·2 BH_2R and TED·BH_2R, are air-stable and can be stored without special precaution for an appreciable amount of time without apparent change. The adducts are readily converted to the free RBH_2 by dissolving them in a suitable solvent and adding the appropriate quantity of $Et_2O{\cdot}BF_3$. A rapid precipitation of the amine-boron trifluoride complex occurs at room temperature (25°C). Simple filtration under nitrogen[5] provides the RBH_2 in solution (Eq 28).

$$\text{TMED}\cdot 2\ BH_2R + 2\ Et_2O{\cdot}BF_3 \xrightarrow[25°C,1\ h]{\text{THF}} 2\ RBH_2 + \text{TMED}\cdot 2\ BF_3\downarrow \qquad (28)$$

The TED·BH_2R adducts were recently used in the preparation of lithium monoalkylborohydrides ($LiRBH_3$).[31] Thus, TED·BH_2R reacts with lithium aluminum hydride at 65°C in THF to give the corresponding $LiRBH_3$ with concomitant precipitation of TED·AlH_3 (Eq 29). The data on the addition com-

$$\text{TED}\cdot BH_2R + LiAlH_4 \xrightarrow[65°C,2\ h]{\text{THF}} LiRBH_3 + \text{TED}\cdot AlH_3\downarrow \qquad (29)$$

pounds of dialkylboranes and monoalkylboranes with TMED and TED are summarized in Table II.

CONCLUSION

In recent years, various addition compounds of TMED and TED with boron trifluoride, boranes and alane were synthesized in the Richard B. Wetherill Laboratory under the supervision of Professor Herbert C. Brown. This review is aimed at assembling the data on these addition compounds so that it will be easier for the subsequent researcher to compare the 1:1 and 1:2 compounds of BF_3, BH_3, AlH_3, R_2BH and RBH_2 with TMED and TED. In this review, the stoichiometry and the completeness of the precipitation of BF_3, BH_3 and AlH_3 from Et_2O and THF utilizing TMED and TED as the precipitating agent have been discussed. The synthesis of addition compounds of TMED and TED with certain dialkylboranes is also presented. In addition, this review describes the method of preparation of TMED·2 BH_2R and TED·BH_2R--valuable means for stabilizing the monoalkylboranes. Various applications of these addition compounds are briefly mentioned in the appropriate places.

Acknowledgement - Financial support from the National Institutes of Health (GM 10937-19) in carrying out this work is gratefully acknowledged.

TABLE II

Summary of Data on Addition Compounds of Dialkylboranes and Monoalkylboranes with *N,N,N',N'*-Tetramethylethylenediamine and Triethylenediamine

Organoboranes	TMED 1:1[a]	TMED 1:2[b]	TED 1:1[a]	TED 1:2[b]
	mp, °C		mp, °C	
Dicyclohexylborane	*c*	*c*	—	—
Disiamylborane[d]	*c*	*c*	—	—
Diisopinocampheylborane	*e*	*f*	*e*	—
9-Borabicyclo[3.3.1]nonane	—	—	—	—
Borinane	*g*	142-144	183-187	232-234
3-Hexylborane	*h*	27-29	—	—
Cyclopentylborane	*h*	105-106	74-76	—
exo-Norbornylborane	*h*	118-119	140-141	—
Cyclohexylborane	*h*	100-101	109-111	—
Siamylborane[d]	*i*	90-92	70-72	—
trans-2-Methylcyclopentylborane	*h*	123-124	—	—
Isopinocampheylborane	113-115	140-141	126-127	—
Thexylborane	*i*	43-45	97-99	—

[a]1:1 = amine·BHR_2 or amine·BH_2R. [b]1:2 = amine·2 BHR or amine·2 BH_2R. [c]The adducts are dissociated and the dialkylboranes undergo redistribution reaction. [d]Siamyl ≡ 3-methyl-2-butyl. [e]Eliminates α-pinene affording amine·BH_2Ipc. [f]Eliminates α-pinene providing amine·2 BH_2Ipc. [g]Semisolid at 25°C. [h]Does not form TMED·BH_2R even in the presence of excess TMED. [i]Liquid at 25°C.

Dedication - This review is cordially dedicated to Professor Herbert C. Brown, Nobel Laureate, on the occasion of his 70th birthday and also in recognition of his contribution to chemistry.

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