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REVIEW

Trifluoromethyl-substituted Aminoboranes and Amine Boranes Revealing Alkene and Alkane Chemistry

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CONTENTS

1 INTRODUCTION

Donor-free boranes with pentafluorophenyl (C_6F_5—) or perfluorovinyl ($F_2C{=}CF$—) groups bonded to boron are stable and well-characterized compounds.[1–3] In contrast, perfluoroalkyl derivaties, e.g. $(R_f)_3B$ ($R = CF_3$, C_2F_5, . . .), are still unknown in spite of considerable efforts made in the past towards their synthesis. Owing to the extraordinary electronic properties of an R_f group, species like $(CF_3)_3B$ should be extremely strong Lewis acids. At the same time, the B—C bond should possess only little polarity.

Two routes of decomposition, known as α- and β-elimination, are responsible for the inherent instability of perfluoroalkylboranes.

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(1) *α-Elimination*: A CF_3 group bonded to a three-coordinate boron atom is amenable to exothermic elimination of difluorocarbene with formation of a thermodynamically favored B—F bond (eqn [1]).

$$F_3C{-}B\langle \rightarrow F_2C + F{-}B\langle \quad [1]$$

The reverse reaction, i.e. the insertion of CF_2 into the B—F bond of BF_3, has not been observed,[4] although CH_2 (generated from diazomethane) inserts into a B—F bond to give fairly stable $FCH_2{-}BF_2$[5] (Eqn [2]).

$$BF_3 + N_2CH_2 \rightarrow FCH_2{-}BF_2 + N_2 \quad [2]$$

The thermal stability decreases considerably in the series $FCH_2{-}BF_2 > F_2CH{-}BF_2 > F_3C{-}BF_2$. While $F_2CH{-}BF_2$ is in fact unknown, the synthesis of $F_3C{-}BF_2$ has been reported,[6,7] although its characterization is in our opinion ambiguous.

(2) *β-Elimination*: Alkyl groups carrying a fluorine atom in the *β*-position were found to be readily split off. Thus, $Me_2B{-}CHMe{-}CF_3$ decomposes slowly at room temperature with formation of Me_2BF and $Me{-}CH{=}CF_2$ according to Eqn [3].[8]

$$Me_2B{-}CHMe{-}CF_3 \rightarrow Me_2BF + Me{-}CH{=}CF_2 \quad [3]$$

To our knowledge only two perfluoroalkyl derivatives of three-coordinate boron, $nC_3F_7B(NMe_2)_2$ and $nC_3F_7BO_2C_6H_4$ had been reported and fully characterized[9] prior to our studies outlined in the present review. The surprising stability of these two perfluoropropyl species can be ascribed to the presence of two ligands capable of additional *π*-donation to boron, thereby considerably decreasing its electron deficiency.

Perfluoroalkyl derivatives of tetracoordinated boron behave in an entirely different fashion. Borates like $[CF_3BF_3]^-$, first reported by Chambers *et al.* in 1960,[10–12] are surprisingly stable. The transformation of fluoroalkyl derivatives of tricoordinate boron into tetracoordinate species is therefore expected to be an important driving force in trifluoromethylboron chemistry.

Over the last 15 years we have systematically studied the synthesis, reactivity and structures of mono-, bis- and tris-(trifluoromethyl)boron compounds. We have been able to assess specific effects for which the $F_3C{-}B$ bond is responsible. This bond is less polar than C—B bonds are in general, because of the withdrawal of electron density from carbon by the fluorine atoms. At the same time it is weak due to repulsion of two positively charged atoms (**1**).[17] Its modest polarity makes the $B{-}CF_3$ bond resistant towards nucleophilic attack. Furthermore, the steric demand of an R_f with respect to an n-alkyl group shields the boron atom efficiently. Moreover, the large overall electronegativity of a CF_3 group, which may be compared with that of Cl,[14] enhances the electron deficiency of the boron atom.

$$\overset{\delta+}{C}{-}\overset{\delta+}{B}$$

1

Thus, the aminotrifluoromethylboranes on which this review is focused constitute a novel family of compounds whose properties are unprecedented in boron chemistry. These will be outlined in the following sections, and perspectives for applications will be given.

2 PREPARATION OF TRIFLUOROMETHYL BORON COMPOUNDS

With the exception of the $[CF_3BF_3]^-$ and $[(CF_3)_2BF_2]^-$ anions, trifluoromethylboron compounds were unavailable until nucleophilic trifluoromethylation with $P(NEt_2)_3/CF_3Br$ ('Ruppert's reagent')[15] or $(Me_2N)_2C{=}C(NMe_2)_2/CF_3I$[16] was discovered. Anyway, even with these efficient reagents, the entry into CF_3B chemistry is only of limited scope.

2.1 BX_3 and Me_3SnCF_3

The reaction of BF_3 with Me_3SnCF_3 in CCl_4 was first studied by Chambers *et al.*[10] It furnished the surprisingly stable salt $[Me_3Sn][CF_3BF_3]$, from which the potassium salt $K[CF_3BF_3]$ was obtained by action of KF/H_2O (Scheme 1). When BF_3 is reacted with an excess of Me_3SnCF_3 at 60 °C, a second CF_3 group is transferred onto boron according to Scheme 2.[17,18] Apparently a third

$$BF_3 + Me_3SnCF_3 \rightarrow$$

$$[Me_3Sn][CF_3BF_3] \xrightarrow{+KF} Me_3SnF + K[CF_3BF_3]$$

Scheme 1

$$[Me_3Sn][CF_3BF_3] \rightarrow$$

$$Me_3SnF + \{CF_3BF_2\} + Me_3SnCF_3 \rightarrow$$

$$[Me_3Sn][(CF_3)_2BF_2]$$

$$[Me_3Sn][(CF_3)_2BF_2] + KF \rightarrow$$

$$Me_3SnF + K[(CF_3)_2BF_2]$$

Scheme 2

CF_3 group cannot be attached to boron in this way. Either the Lewis acidity of Me_3Sn^+ is too weak for abstraction of F^- from $[(CF_3)_2BF_2]^-$, or intermediate $(CF_3)_2BF$ is too unstable, the reagent Me_3SnCF_3 in general only being capable of transferring CF_3 groups to rather strong Lewis acids. The structure of $Cs[(CF_3)_2BF_2]$ has been determined by X-ray diffraction (Fig. 1).

With the even stronger Lewis acids BCl_3 and BBr_3, Me_3SnCF_3 reacts explosively even at $-20\,°C$. When the reaction is carried out at $-90\,°C$ in pentane solution employing a large excess of Me_3SnCF_3, the initially colorless precipitate, consisting of $[Me_3Sn][CF_3BX_3]$, decomposes upon warming to -70 to $-40\,°C$ to form $[(CF_3)_2BF_2]^-$ and $[CF_3BF_3]^-$. The decomposition channels of these primary reaction products have been studied[19] and are displayed in the sequence of reactions shown in Scheme 3.

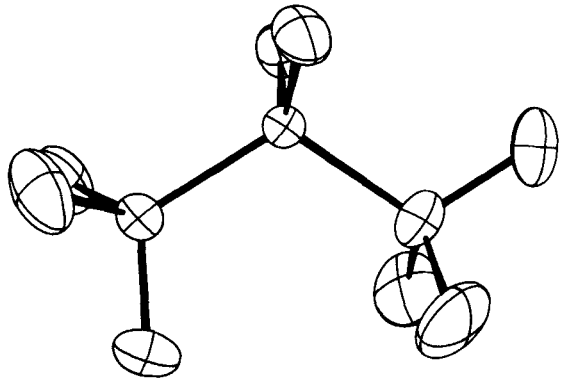


Figure 1 The anion of $Cs[(CF_3)_2BF_2]$ contains CF_3 groups which are staggered and eclipsed with respect to the other bonds formed by the boron atom.

$$BX_3 + Me_3SnCF_3 \rightarrow [Me_3Sn][CF_3BX_3]$$

$$[Me_3Sn][CF_3BX_3] \rightarrow Me_3SnX + \{CF_3BX_2\}$$

$$\rightarrow CF_2 + FBX_2$$

$$FBX_2 + Me_3SnCF_3 \rightarrow Me_3SnX + \{CF_3BFX\}$$

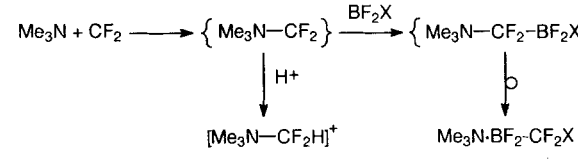
$$\rightarrow CF_2 + F_2BX$$

$$F_2BX + Me_3SnCF_3 \rightarrow Me_3SnX + \{CF_3BF_2\}$$

$$\{CF_3BF_2\} + Me_3SnCF_3 \rightarrow [Me_3Sn][(CF_3)_2BF_2]$$

Scheme 3

The pathways along which these initially formed reaction products decompose in the presence of trimethylamine have been further investigated. NMe_3 was expected to trap CF_3BF_2, which is supposed to be an intermediate.[19] Under these modified reaction conditions a complex mixture of products was obtained which not only contained the expected amine adduct $CF_3BF_2 \cdot NMe_3$ but also $CF_2XBF_2 \cdot NMe_3$ (X = Cl, Br). Furthermore, anions with CF_2X groups, i.e. $[(CF_3)(CF_2X)BF_2]^-$, $[(CF_2X)_2BF_2]^-$ and $[(CF_2X)BF_3]^-$, were obtained as well as $[(CF_3)_2BF_2]^-$ and $[CF_3BF_3]^-$ in combination with the cation $[Me_3N{-}CF_2H]^+$. Obviously difluorocarbene has been trapped both by CF_3BF_2 and by NMe_3, the latter yielding the ylide $Me_3N{-}CF_2$ according to Scheme 4.



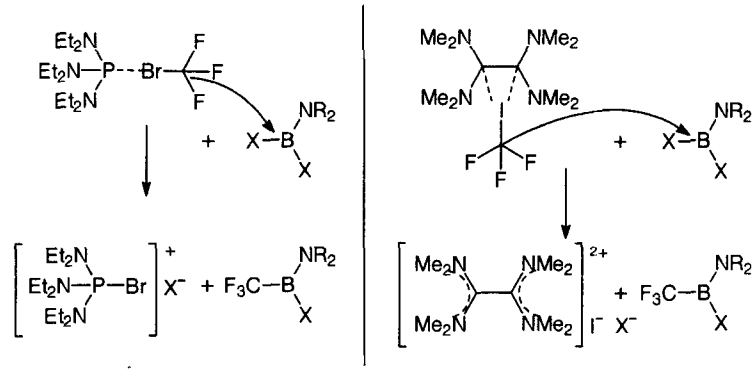
Scheme 4

This ylide can either capture a proton to yield $[Me_3N{-}CF_2H]^+$, or insert into the B—X bond of BF_2X.

Attempts were also made to react Me_3SnCF_3 with Me_2BBr, $MeBF_2$, B_2H_6 and other boranes; however, no trifluoromethyl boron derivatives could be isolated.

2.2 Trifluoromethylation with $P(NEt_2)_3/CF_3Br$ or $(Me_2N)_2C{=}C(NMe_2)_2/CF_3I$

Chlorine or bromine atoms in an aminohalogenoborane may be substituted by a CF_3 group supplied by either of the reagent combinations $P(NEt_2)/CF_3Br$ ('Ruppert's reagent')[15] or $(Me_2N)_2C{=}C(NMe_2)_2/CF_3I$ in polar aprotic



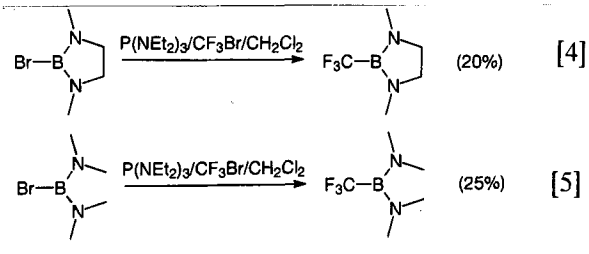
Scheme 5. Trifluoromethylation of boron by $P(NEt_2)_3/CF_3Br$ or $(Me_2N)_2C{=}C(NMe_2)_2/CF_3I$.

solvents.[16] Plausible mechanisms of the two reaction pathways are displayed in Scheme 5.

The reaction of $P(NEt_2)_3$ with CF_3Br is initiated by nucleophilic attack of $P(NEt_2)_3$ on the positively polarized bromine. This weakens the bromine–carbon bond, the carbanion attacks the borane, and the halogen, which is a better leaving group than CF_3^-, is replaced. The reaction of $(Me_2N)_2C{=}C(NMe_2)_2$ with CF_3I takes a similar pathway. Here a deep red charge-transfer complex is formed which acts as trifluoromethylating agent. Both reactions are sensitive to the choice of the solvent, only the polar aprotic solvents CH_2Cl_2 or tetramethylene sulfone being suited. Due to the basicity of $P(NEt_2)_3$ and $(Me_2N)_2{=}C(NMe_2)_2$ only poorly Lewis acidic substrates can be trifluoromethylated. Strong acids like BCl_3 will form complexes with $P(NEt_2)_3$, or react with $(Me_2N)_2C{=}C(NMe_2)_2$ in an irreversible fashion. Thus either of these routes is useless. Likewise, dichloro- or dibromoaminoboranes disposing over moderately electron withdrawing N-bonded groups (e.g. Ph) withstand attempts of trifluoromethylation by these reagents.

2.2.1 $CF_3B(NR_2)_2$

Diaminobromoboranes, $BrB(NR_2)_2$, can be trifluoromethylated in CH_2Cl_2 solution according to



Eqns [4] and [5]. The two trifluoromethylboranes shown have been obtained in 20 and 25% yield, respectively.[20]

Both species are thermally stable at room temperature but decompose slowly under elimination of difluorocarbene when heated to 140 °C.

2.2.2 $(CF_3)_2BNR_2$ and $[(CF_3)_3BNR_2]^-$

The trifluoromethylation of Cl_2BNR_2 (R = Me, Et, iPr) in CH_2Cl_2 is nonselective as long as less than three equivalents of trifluoromethylating agent are employed. Otherwise tris(trifluoromethyl)borates, $[(CF_3)_3BNR_2]^-$, are formed according to Scheme 6 in yields which depend on the nature of the ligands (R) attached to nitrogen.

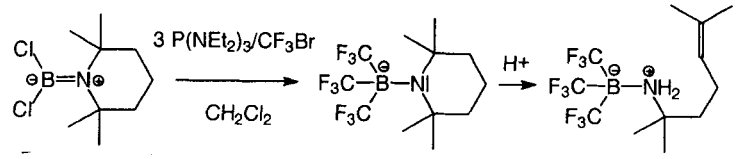
$$Cl_2BNR^1R^2 \xrightarrow{3\,P(NEt_2)_3/CF_3Br} [(CF_3)_3BNR^1R^2]^- \xrightarrow{H^+} (CF_3)_3B\cdot NHR^1R^2$$

Scheme 6

The amine boranes $(CF_3)_3B\cdot NHR^1R^2$ collected in Table 1 were obtained by treating the respective anions $[(CF_3)_3BNR^1R^2]^-$ with concentrated hydrochloric acid. Yields up to 75% were obtained

Table 1 Diorganylamine tris(trifluoromethyl)boranes $(CF_3)_3B\cdot NHR^1R^2$ (Refs 21, 22)

R^1		R^2
Me		Me
Et		Et
	$(CH_2)_5$	
	$(CH_2)_6$	
cyclo-C_6H_{11}		cyclo-C_6H_{11}
Me		CH_2Ph
Me		tBu



Scheme 7

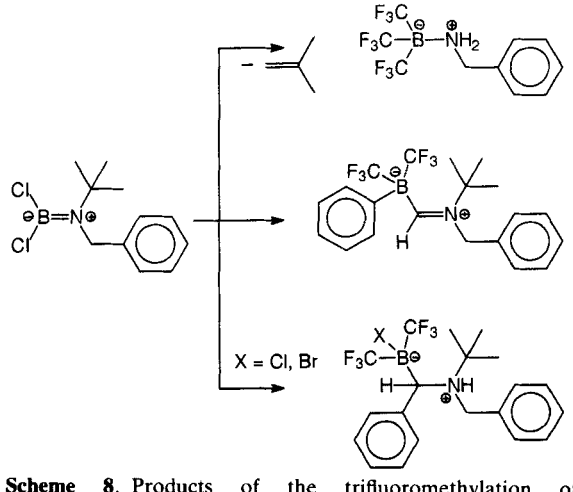
for $R^1 = R^2 = Et$, while the yield was only 1% for $R^1 = Me$, $R^2 = CH_2Ph$. About 1% of ethylamine tris(trifluoromethyl)borane, $(CF_3)_3B \cdot NH_2Et$, has been isolated as a by-product in the synthesis of $(CF_3)_3B \cdot NHEt_2$.[21]

Concomitant with the trifluoromethylation of tetramethylpiperidinodichloroborane according to Scheme 7 the tetramethylpiperidine ring is opened in a Hofmann-type fashion and the primary amine adduct is obtained.[22]

As depicted in Scheme 8, the trifluoromethylation of $Cl_2BN(tBu)CH_2Ph$ is accompanied by the formation of several unexpected products. During work-up, isobutylene is eliminated and benzylamine tris(tifluoromethyl)borane is formed in *ca* 9% yield. Although the formation of the other products $(Ph(CF_3)_2B—CH=N(tBu)CH_2Ph$ (*ca* 1%) and $X(CF_3)_2B—CHPh—NH(tBu)CH_2Ph$ (X = Cl, Br; *ca*. 4%) cannot be explained unambiguously, their identity and constitution are indisputable from the results of a single-crystal X-ray examination of $Ph(CF_3)_2B—CH=N(tBu)CH_2Ph$ and NMR spectra.[22]

Likewise, crystal and molecular structures of $(CF_3)_3B \cdot NHEt_2$, $(CF_3)_3B \cdot NH_2Et$[21] and $(CF_3)_3B \cdot NH(CH_2)_6$[22] have been determined.

The trifluoromethylation of Br_2BNEt_2 with two equivalents of Ruppert's reagent in CH_2Cl_2 yields



Scheme 8. Products of the trifluoromethylation of $Cl_2BN(tBu)CH_2Ph$.

a mixture of products whose distribution roughly corresponds to Eqn [6].

$$Br_2BNEt_2 \xrightarrow{2\,P(NEt_2)_3/CF_3Br/CH_2Cl_2} 0.05\,Br_2BNEt_2 + 0.15\,(CF_3)BrBNEt_2 + 0.42(CF_3)_2BNEt_2 + 0.38\,(CF_3)_3BNEt_2^- \quad [6]$$

Due to losses upon work-up, the actual yield of $(CF_3)_2BNR_2$ was not higher than 17% for R = Me (**2**), 20% for R = Et (**3**) and 35% for R = iPr (**4**).[23] The yield of **2**, for example, is considerably increased when the trifluoromethylation is carried out in tetramethylene sulfone as solvent. This forms a weak complex with **2** but neither with Cl_2BNMe_2 nor $(CF_3)ClBNMe_2$. That weak interaction suppresses transfer of a third CF_3 group and thus almost no $[(CF_3)_3BNMe_2]^-$ is formed. Furthermore, the high boiling point of tetramethylene sulfone facilitates considerably the isolation of **2** by fractional distillation. Altogether the yield of **2** has been increased thereby from 17% to 55–60%.

The molecular and crystal structure of **4**, which is a solid at room temperature, m.p. 44 °C, has been determined by a single-crystal X-ray investigation,[23] while the geometry of **2** has been obtained from a gas-phase electron diffraction study.[13]

2.2.3 $(CF_3)RBNR_2$

In contrast, no suitable conditions have yet been found to selectively prepare $(CF_3)ClBNR_2$ and its derivatives $(CF_3)RBNMe_2$ (R = alkyl).[24] The trifluoromethylation of Cl_2BNMe_2 with 1.1 equivalents of the reagent $P(NEt_2)_3/CF_3Br$ in tetramethylene sulfone takes place roughly with the stoichiometry given in eqn [7].

$$Cl_2BNMe_2 + 1.1\,P(NEt_2)_3/CF_3Br \rightarrow 1.1\,[BrP(NEt_2)_3]^+Cl^- + 0.3Cl_2BNMe_2 + 0.3\,(CF_3)ClBNMe_2 + 0.4(CF_3)_2BNMe_2 \quad [7]$$

Not more than 30% of $(CF_3)ClBNMe_2$ can be obtained because considerable amounts of

unreacted starting material Cl_2BNMe_2 and **2** are present as well. Work-up losses reduce the overall yield of $(CF_3)ClBNMe_2$ to ca 10–12%.

Chlorine in $(CF_3)ClBNMe_2$ can be replaced by an ethyl or isopropyl group using Grignard reagents at −30 °C according to Eqn [8].

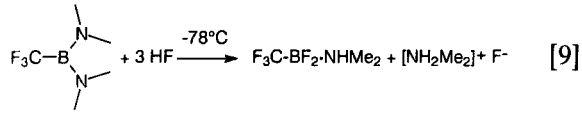
$$(CF_3)ClBNMe_2 + RMgBr \xrightarrow[R=Et,\ iPr]{-30\,^\circ C/ether} (CF_3)RBNMe_2 + MgBrCl \quad [8]$$

Although the trifluoromethylation of $BrEtBNMe_2$ with one equivalent of $P(NEt_2)_3/CF_3Br$ in tetramethylene sulfone furnishes the desired product $(CF_3)EtBNMe_2$, concomitantly plenty of the doubly trifluoromethylated by-product $[BrP(NEt_2)_3]^+[(CF_3)_2EtBNMe_2]^-$ is formed. Again work-up losses diminish the overall yield of $(CF_3)EtBNMe_2$ to 12%. In conclusion, mono(trifluoromethyl)aminoboranes cannot be synthesized as conveniently on a large scale as the aminoboranes $(CF_3)_2BNR^1R^2$ can by direct trifluoromethylation in tetramethylene sulfone. It is therefore not surprising that the chemistry of the former compounds has not been studied in great detail.

3 REACTIONS OF $CF_3B(NR_2)_2$

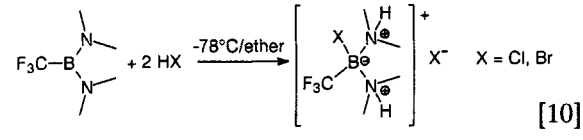
3.1 Reactions with HX (X = F, Cl, Br)

$CF_3B(NMe_2)_2$ reacts at a temperature between −78 °C and 20 °C with three equivalents of anhydrous HF to give quantitatively the dimethylamine adduct of trifluoromethyldifluoroborane according to Eqn [9].[25]



[9]

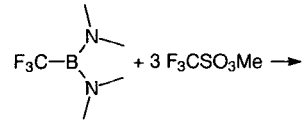
In contrast, HCl and HBr do not cleave a B—N bond under similar conditions but form exclusively the respective boronium salts according to Eqn [10].[25]



[10]

3.2 Reaction with F_3CSO_3Me

The strong methylating agent F_3CSO_3Me resembles HF. Reacted in a 3:1 ratio with $CF_3B(NMe_2)_2$ it yields the trimethylamine adduct of the unknown free Lewis acid trifluoromethylbis(trifluoromethylsulfonyl)borane Eqn [11].



$$F_3C(F_3CSO_3)_2B{\cdot}NMe_3 + [Me_4N]^+[SO_3CF_3]^- \quad [11]$$

4 REACTIONS OF $CF_3(R)BNR_2$ AND $(CF_3)_2BNR_2$

4.1 Reactions with protic molecules HX (X = F, Cl, Br, OH, etc.)

The trifluoromethyl-substituted aminoboranes so far known, i.e. $(CF_3)ClBNMe_2$, $(CF_3)iPrBNMe_2$, $(CF_3)EtBNMe_2$, $(CF_3)_2BNMe_2$ (**2**), $(CF_3)_2BNEt_2$ (**3**), $(CF_3)_2BN(iPr)_2$ (**4**) and $(CF_3)_2BNMetBu$, are expected to readily add molecules with an acidic proton across their B=N double bond under appropriate conditions. However, not all of these numerous possible combinations have been actually tested. The reactions shown in Eqns [12] and [13] have been studied, and the products appropriately characterized.

$$(CF_3)_2BNR_2 + HX \rightarrow (CF_3)_2XB{\cdot}NHR_2 \quad [12]$$

R = Me; X = F, Cl, Br, OH, $CH_3C(=O)O$, CN
R = Et; X = F, Cl, Br, OH
R = iPr; X = F, Cl, Br

$$(CF_3)XBNR_2 + HX \rightarrow (CF_3)X_2B{\cdot}NHR_2 \quad [13]$$

R = Me; X = Cl
R = Et; X = Cl, Br

The thermal stability as well as the chemical stability of the amine boranes obtained is higher when two CF_3 groups rather than one are attached to boron. These amine boranes are remarkably resistant to acids. Thus $(CF_3)Cl_2B{\cdot}NHMe_2$, for example, withstands HCl/ether at 60 °C, but the B—Cl and B—Br bonds are readily hydrolyzed under alkaline conditions.

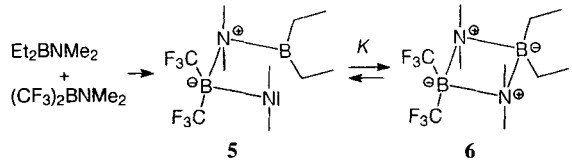
The structures of $(CF_3)_2FB \cdot NHMe_2$ and $(CF_3)_2(HO)B \cdot NHMe_2$ have been examined by X-ray diffraction.[25]

4.2 Cycloaddition reactions

Unlike aminoboranes in general, the above-mentioned trifluoromethyl-substituted aminoboranes are stable to homo-[2 + 2] cyclodimerization. However, $(CF_3)ClBNMe_2$ and Cl_2BNMe_2 slowly hetero-dimerize to yield the stable four-membered ring

$$(CF_3)ClB\overline{—NMe_2—BCl_2—}NMe_2.^{24}$$

Compound **2** combines with Et_2BNMe_2 (and also with Me_2BNMe_2) at room temperature to form a head-to-tail dimer (**5**). This dimer is in equilibrium with the four-membered heterocycle (**6**) according to Scheme 9. The equilibrium constant $K = [\mathbf{5}]/[\mathbf{6}]$ has been determined in $CDCl_3$ solution by ^{19}F NMR spectroscopy in the temperature range 293–320 K.[24] From the equations $\Delta G = -RT \ln K$ and $\Delta G = \Delta H - T\Delta S$, ΔH and ΔS were calculated: $\Delta H = 78 \pm 10$ kJ mol^{-1} and $\Delta S = 260 \pm 20$ J K^{-1} mol^{-1}. Although **5** in equilibrium with **6** is stable at room temperature in C_6D_6 solution when stored in a sealed tube, addition of species which react irreversibly with **2** decomposes the heterodimers.

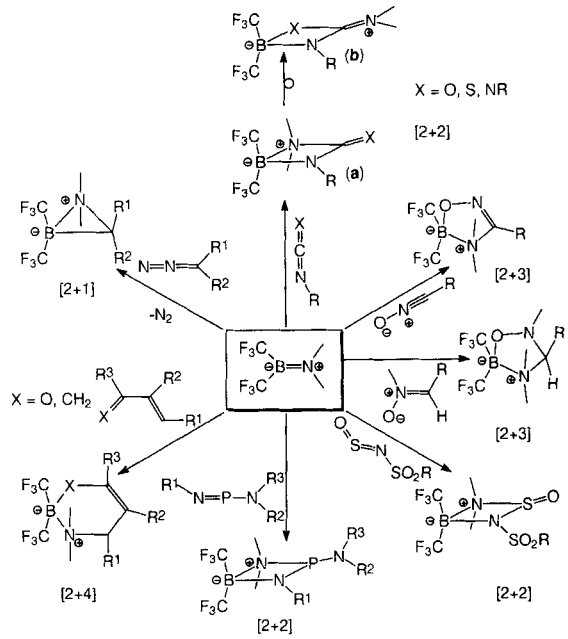


5 **6**

Scheme 9

The B=N double bond of aminoboranes with only one CF_3 group attached to boron is considerably less reactive than that of bis(trifluoromethyl) derivatives. The most reactive species known so far is **2**. It undergoes a variety of reactions which are unprecedented in aminoborane chemistry. Usually its addition reactions proceed smoothly at or below room temperature in a nonpolar solvent, or with neat compounds, yields in general being high and work-up easy. In the following sections we outline cycloaddition reactions of **2**. Analogous reactions of **3** and $(CF_3)RBNMe_2$ (R = Cl, Et, and iPr), as far as they are known, will be discussed as well.

Cycloaddition reactions that **2** undergoes with various substrates containing double-bond systems are summarized in Scheme 10. These may be of [2 + 1], [2 + 2], [2 + 3] and [2 + 4] types.



Scheme 10. Cycloaddition reactions of $(CF_3)_2BNMe_2$ (**2**).

4.2.1 [2 + 1] cycloaddition reactions

Diazoalkanes $R^1R^2CN_2$ react with **2** with elimination of N_2 in a formal [2 + 1] cycloaddition reaction to yield quantitatively novel azoniaboratacyclopropanes, $(CF_3)_2\overline{B—NMe_2—}CR^1R^2$.[26,27] The intermediacy of five-membered heterocycles can be excluded because elimination of nitrogen and the color change of the reaction mixture occur simultaneously. Up to now the azoniaboratacyclopropanes

$$(CF_3)_2\overline{B—NMe_2—}CR^1R^2$$

with R^1 and R^2 as listed in Table 2 have been reported. It seems that the reaction is of general applicability when R^1 and R^2 = H, alkyl and phenyl.

The three-membered ring structure has been confirmed by X-ray investigations of

$$(CF_3)_2\overline{B—NMe_2—}C(CH_2Ph)SiMe_3$$

and

$$(CF_3)_2\overline{B—NMe_2—}CPh_2$$

Table 2 Azoniaboratacyclopropanes

$(CF_3)_2\overline{B—NMe_2—CR^1R^2}$

R^1	R^2	Ref.
H	H	26
H	$SiMe_3$	
$CH_2C_6H_5$	$SiMe_3$	
Ph	Ph	27
	$H_4C_6—C_6H_4$	
H	Ph	
H	*o*-, *m*-, *p*-FC_6H_4	
H	C_6F_5	
CH_3	EtOC(=O)	
H	tBu	

(Fig. 2). The diazomethane components quoted in Table 2 reacted in fact as clean carbene sources. CF_3SiF_3 is known to eliminate CF_2 thermally under mild conditions. The difluorocarbene thus generated did not form a three-membered ring with **2**, but the noncyclic isomer $(CF_3)_2FB—FC{=}NMe_2$ (Scheme 11).[27]

$$(CF_3)_2BNMe_2 \xrightarrow[-SiF_4]{CF_3SiF_3} \{(CF_3)_2\overline{B—NMe_2—CF_2}\}$$

$$\rightarrow (CF_3)_2FB—FC{=}NMe_2$$

Scheme 11

Although a three-membered ring may be an intemediate at low temperature, this could not be detected because the final product is formed so

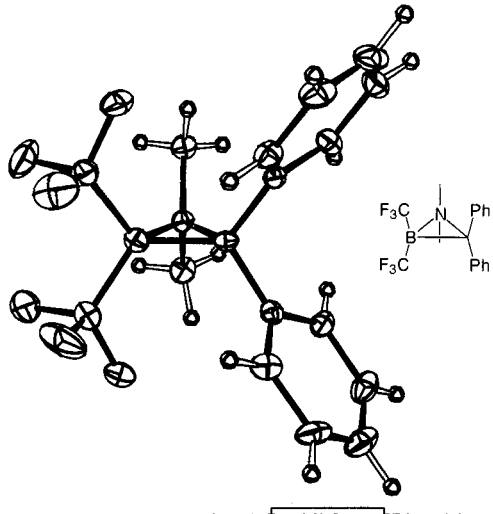


Figure 2 The structure of $(CF_3)_2\overline{B—NMe_2—CPh_2}$ with nearly equidistant endocyclic B—N, B—C and N—C bond lengths of 1.573(8), 1.586(8) and 1.556(6) Å, respectively.

readily. Generally the noncyclic isomer is thermodynamically more stable than the corresponding three-membered ring for R^1, $R^2 = F$ or other electronegative substituents. It should be further mentioned that certain diazocarbonyl compounds, e.g. ethyl diazoacetate, react in an ene-type fashion with **2** with preservation of the diazo group; see below.[26]

4.2.2 [2+2] Cycloaddition reactions

4.2.2.1 With isocyanates, isothiocyanates and carbodiimides

[2+2] Cycloaddition reactions were found to occur when **2** was combined with isocyanates, isothiocyanates and carbodiimides RN=C=X, disposing of cumulated double bonds (Scheme 10). At low temperature the N=C bond adds directly to the B=N double bond, and four-membered rings of type (**a**),

$$(CF_3)_2\overline{B—NMe_2—C(=X)—NR},$$

are obtained when X = S or O.[28]

At or above room temperature isomerization of several species listed in Table 3 to type (**b**) heterocycles

$$(CF_3)_2\overline{B—X—C(=NMe_2)—NR}$$

takes place. Isomerization products that have been characterized are displayed in Table 4.[7-8]

The ease of isomerization is determined both by the strength of the C=X double bond relative to the B—X single bond and by the bulkiness of the substituent R. Isothiocyanates having weak C=S double bonds therefore exert a higher tendency to undergo such a rearrangement than isocyanates with strong C=O bonds. Sterically

Table 3 Type (**a**) products $(CF_3)_2\overline{B—NMe_2—C(=X)—NR}$ of [2+2] cycloaddition reactions of **2** with isocyanates and isothiocyanates (Ref. 28)

R	X
Me	O
tBu	O
Ph	O
CF_3	O
Me	S
Et	S
tBu	S
Ph	S
p-FC_6H_4	S

Table 4 Type (**b**) [2 + 2] cycloaddition products

$(CF_3)_2\overline{B—X—C(=NMe_2)—N}R$

formed with isocyanates, isothiocyanates and carbodiimides (Refs 27, 28)

R	X
Me	O
Me	S
Et	S
tBu	S
Ph	S
p-FC_6H_4	S
iPr	NiPr
C_6H_{11}	NC_6H_{11}

demanding substituents R prevent a favorable coplanar arrangement of the C=NMe_2 group in type (**b**) compounds. Therefore no such isomer could be obtained with R = tBu.

The structures of

$(CF_3)_2\overline{B—NMe_2—C(=X)—N}$-tBu (X = O, S)

and

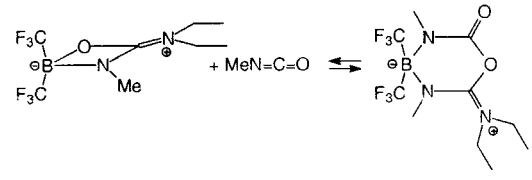
$(CF_3)_2\overline{B—S—C(=NMe_2)—N}Ph$

have been determined by X-ray investigations (Fig. 3).

The carbodiimides (iPr)N=C=N(iPr) and cyclo-C_6H_{11}—N=C=N—cyclo-C_6H_{11} react at elevated temperature with **2** to form type (**b**) compounds (Table 4). On the other hand, **3** and MeN=C=O at room temperature give the type (**b**) derivative in a straightforward fashion. This is capable of reversibly incorporating one more MeN=C=O (Eqn. [14], to form the six-membered heterocycle

$(CF_3)_2\overline{B—NMe—C(=NEt_2)—O—C(=O)—N}Me.$

Its structure has also been determined by an X-ray investigation.[28]



[14]

Likewise, $(CF_3)ClBNMe_2$ also undergoes a [2 + 2] cycloaddition reaction with tBuN=C=O to yield the four-membered type (**a**) heterocycle

$(CF_3)Cl\overline{B—NMe_2—C(=O)—N}$-tBu.[24]

4.2.2.2 With N-sulfinylsulfonamides

The reaction of **2** with N=S double bonds of *N*-sulfinylimides X—N=S=O requires electron-withdrawing substituents X to proceed specifically according to a [2 + 2] cycloaddition mechanism. Simple *N*-sulfinylimines such as Me—N=S=O give no stable products at all. Generally S=O groups do not exert sufficient reactivity towards the B=N bond; for example SO_2 gave no stable product with **2**. On the contrary, F_3CCH_2—N=S=O undergoes an ene-type reaction to yield the dimethylamine adduct $(F_3C—HC=N—S(=O))(CF_3)_2B \cdot NHMe_2$ (Eqn [15].

$$F_3CCH_2—N=S=O + (CF_3)_2BNMe_2 \rightarrow (F_3C—HC=N—S(=O))(CF_3)_2B \cdot NHMe_2 \quad [15]$$

N-sulfinylsulfonamides (X = RSO_2) with R = Me, Pr, Ph, *p*-Tol were found to react readily with **2** to form novel four-membered heterocycles

$(CF_3)_2\overline{B—NMe_2—S(=O)—N}—SO_2R$

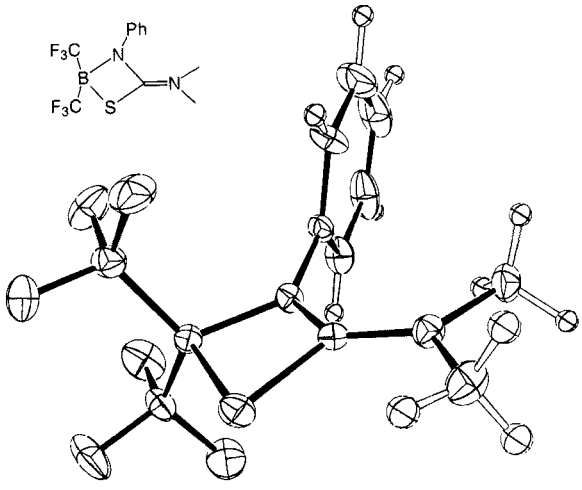


Figure 3 A view of $(CF_3)_2\overline{B—S—C(=NMe_2)—N}Ph$ showing the roughly planar four-membered ring and its coplanarity with its exocyclic NC_2 substituent.

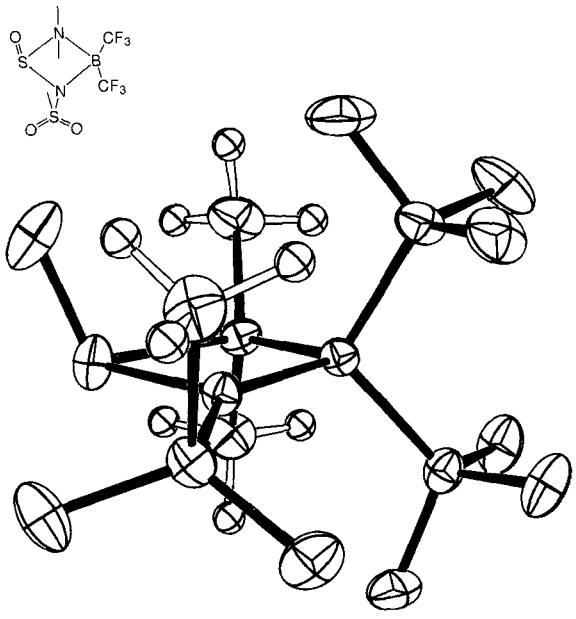


Figure 4 The structure of

$$(CF_3)_2\overline{B—NM_2—S(=O)—N}—SO_2$$

Me exhibits a planar four-membered ring despite the pyramidality of the ring sulfur atom.

according to Scheme 10. The structure of

$$(CF_3)_2\overline{B—NMe_2—S(=O)—N}—SO_2Me$$

has been determined by an X-ray investigation (Fig. 4).[29]

4.2.2.3 With aminoiminophosphines

Th N=P double bond in aminoiminophosphines of the general formula $R^1N{=}P{-}NR^2R^3$ is also one of the systems found hitherto that reacted readily with **2** and yielded the respective four-membered heterocycles

$$(CF_3)_2\overline{B—NMe_2—P(NR^2R^3)—NR^1}.$$

Prepared examples with different substituents R^1, R^2, R^3 are set out in Table 5. To our knowledge, these make up the first B—N—P—N four-membered heterocycles with single bonds. The structure of one example of these 1-aza-3-azonia-2-borata-4-phosphacyclobutane derivatives (R^1, R^2 = tBu, R^3 = $SiMe_3$) has been determined (Fig. 5).[29]

All compounds were shown to be air-stable, volatile solids which can be handled without particular precautions.

Table 5 [2 + 2] Cycloadducts

$$(CF_3)_2\overline{B—NMe_2—P(NR^2R^3)—NR^1}$$

of **2** with aminoiminophosphines (Ref. 29)

R^1	R^2	R^3
$SiMe_3$	$SiMe_3$	$SiMe_3$
tBu	tBu	$SiMe_3$
$SiMe_3$	iPr	iPr
$SiMe_3$	TMP[a]	

[a] Tetramethylpiperidino.

4.2.3 [2+3] Cycloaddition reactions

Compound **2** reacts with nitrile oxides, which are typical 1,3-dipolar reactants R—C=N—O, to yield the respective [2 + 3] cycloaddition products

$$(CF_3)_2\overline{B—NMe_2—RC{=}N—O}$$

(R = mesityl (Mes), Ph, *p*-ClPh; tBu, iPr). These novel five-membered heterocycles are air-stable solids at room temperature. The structure of one typical example, R = tBu, has been determined (Fig. 6).[29]

Combining **2** and nitrones RHC=N(Me)—O furnishes analogously five-membered heterocycles of the general constitution

$$(CF_3)_2\overline{B—NMe_2—RHC—NMe—O},$$

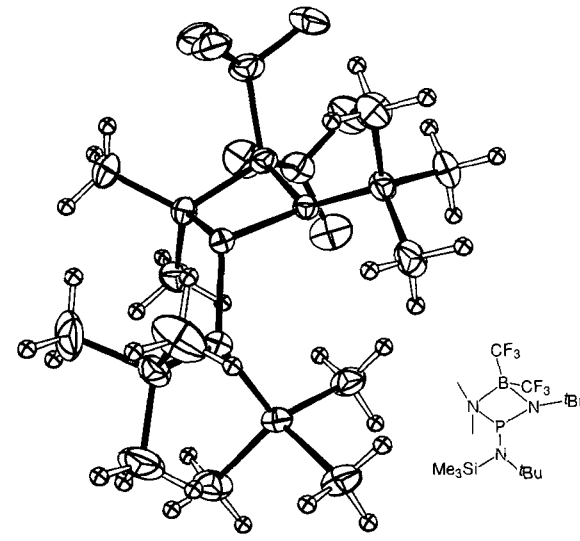


Figure 5 The structure of

$$(CF_3)_2\overline{B—NMe_2—P(N\text{-}tBuSiMe_3—N\text{-}tBu}$$

possesses a four-membered ring, which is folded by 26.8(5)° about its transannular N···N tieline.

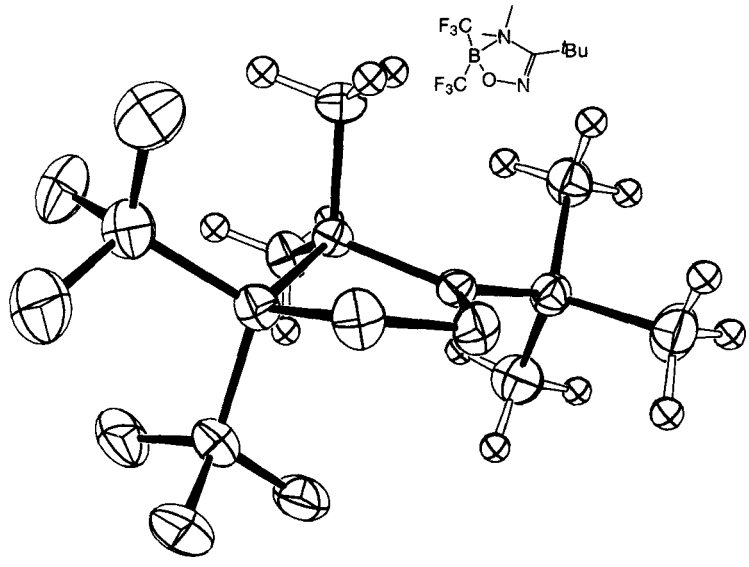


Figure 6 The structure of $(CF_3)_2\overline{B—NMe_2—tBuC=N—O}$, showing the envelope form of the five-membered ring.

with R = Ph, *p*-ClPh, tBu and iPr. These [2 + 3] cycloadducts are thermally less stable than the above-mentioned analogues obtained from nitrile oxides. However,

$$(CF_3)_2\overline{B—NMe_2—PhHC—NMe—O}$$

is a stable compound. This is in contrast to unstable

$$(CH_3)_2\overline{B—NMe_2—PhHC—NMe—O},$$

which has been identified only by NMR spectroscopy and found to be in equilibrium with its educts[30] (Eqn. [16]).

$$(CH_3)_2BNMe_2 + PhHC{=}N(Me){—}O \rightleftarrows (CH_3)_2\overline{B—NMe_2—PhHC—NMe—O} \quad [16]$$

4.2.4 [2+4] Cycloaddition reactions

Dialkylaminobis(trifluoromethyl)boranes react smoothly with a wide variety of 1,3-dienes and *β*-unsaturated carbonyl compounds of general formula

$$X{=}CR^3{—}CR^2{=}CR^1H$$

to yield six-membered heterocycles

$$(CF_3)\overline{B—NR_2—CHR^1—CR^2{=}CR^3—X}$$

by a [2+4] cycloaddition mechanism (Scheme 10).[31] Table 6 sets out the products which were characterized, with X = O and CH_2, and R^1, R^2 and R^3 as given in the Table.

Steric hindrance by bulky substituents, above all by R^1, limits the scope of this cycloaddition reaction. Expectedly the reactivity of **2** is significantly higher than that of **3**, which did not enter into cycloaddition with acetylcyclohexene. Moreover, $(CF_3)_2$BNMe-tBu did not undergo any [2+4] cycloaddtion at all.[32]

Even **2** could only be added to those dienes whose terminal carbon atoms were monosubsti-

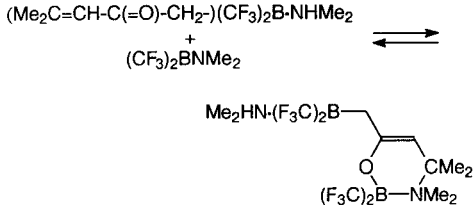
Table 6 [2+4] Cycloaddition products

$(CF_3)_2\overline{B—NR_2—CHR^1—CR^2{=}CR^3—X}$

obtained from **2** (R = Me) and **3** (R = Et), (Ref. 31)

Reactant	R^1	R^2	R^3	X
2	H	Me	Me	CH_2
2	H	H	Me	CH_2
2	Me	H	Me	CH_2
2	H	H	Me	O
2	H	Me	OMe	O
2	Me	Me	H	O
2	OMe	H	Me	O
2	$(CH_2)_4$		Me	O
3	H	Me	Me	CH_2
3	H	H	Me	CH_2
3	H	H	Me	O

tuted. Otherwise, no stable six-membered rings could be obtained. For instance, 2-methyl-2-penten-4-one did not form the expected cycloadduct but underwent an ene-type reaction and yielded the dimethylamine borane ($Me_2C{=}CH{-}C(=O){-}CH_2{-}$)$(CF_3)_2B\cdot NHMe_2$. This combines reversibly with a further molecule of **2** and a six-membered ring is formed according to Eqn. [17]. Attempts to isolate this latter 1:2 adduct by sublimation *in vacuo* reversed its formation by means of a retro-Diels–Alder-type reaction.



[17]

All [2+4] cycloaddition products that were studied are air-stable, volatile solids, only those containing a B—O bond being slowly hydrolyzed by water. The molecular and crystal structures of

$$\overline{(CF_3)_2B{-}NR_2{-}CH_2{-}CMe{=}CMe{-}CH_2}$$

(R = Me, Et)

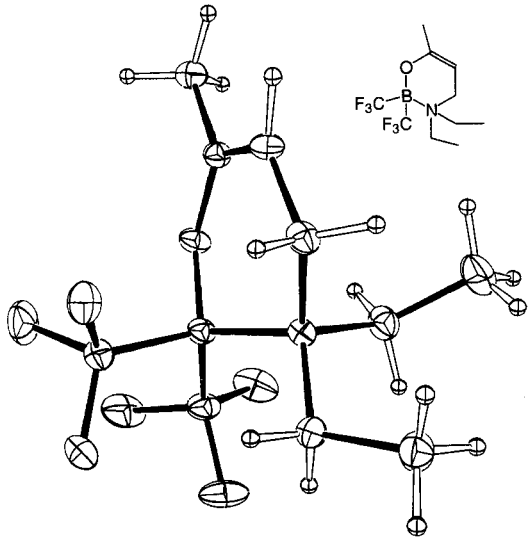


Figure 7 The structure of

$$\overline{(CF_3)_2B{-}NEt_2{-}CH_2{-}CH{=}CMe{-}O}$$

contains a six-membered ring in a conformation which lies between canonical half-chair and half-boat forms.

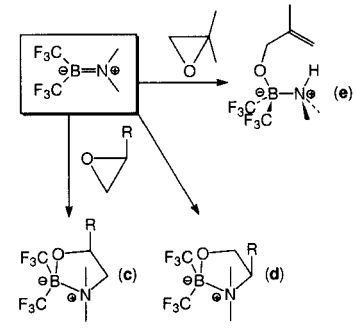
and

$$\overline{(CF_3)_2B{-}NEt_2{-}CH_2{-}CH{=}CMe{-}O}$$

have been determined by X-ray investigations. Figure 7 gives an example.[31]

4.3 Epoxide ring-opening reactions

Compound **2** exhibits high reactivity towards epoxides. Reactions which have been studied are displayed in Scheme 12.[33]



Scheme 12. Reactions of $(CF_3)_2BNMe_2$ (**2**) with epoxides.

Monosubstituted epoxides

$$\overline{O{-}CH_2{-}CHR}$$

react readily with **2** at low temperature to form 1-oxa-2-azonia-3-boratacyclopentanes. These are summarized in Table 7. The reaction follows a pathway leading to **c**, where the R group is close to the oxygen, almost independently of the electronic properties of the substituent R, e.g. Me in comparison with CF_3. For R = Ph, two different pathways are followed which give a 1:3 mixture of isomers **c** and **d**. Upon heating, **c** is quantitati-

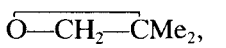
Table 7 1-Oxa-2-azonia-3-boratacyclopentanes $\overline{O{-}CH_2{-}CHR}$ (Ref. 33)

R	Product type
CH_3	**c**
CH_2F	**c**
CF_3	**c**
C_2H_5	**c**
$CH_2C_6H_5$	**c**
C_6H_5	**c**/**d** ≈ 1/3

Table 8 Reactants $(X)CR^2CH_2R^1$ and products of ene-type or hydride-transfer reactions with **2** (Refs 34–39)

Reactant	X	R^1	R^2	Reaction	Type of product
Nitrile	N≡	H, Me, . . .	—	Ene	**g**
Nitrile	N≡	—	CF_3	Hydride	
Ketone	O=	H, Me, . . .	Me, CF_3, tBu, . . .	Ene	**f/g**
Ester	O=	H, Me,	OR	Ene	**g**
Amide	O=	H, Me	Nr_2	Ene	**g**
Thioketone	S=	H	tBu	Hydride/Ene	**f**
Thio-ester	S=	H, Me	OR	Ene	**g**
Dithio-ester	S=	H, Me, . . .	SR	Ene	**g**
Thio-amide	S=	H, Me, . . .	NR_2	Ene	**g**
Alkene	H_2C=	H, Me, . . .	Alkyl, Ph, . . .	Ene	**f**
Alkene	H_2C=	Alkyl	H	Ene	**f**
Alkyne	H-C≡	Alkyl	—	Hydride/Ene	**f**
Alkyne	H-C≡	—	Ph, tBu, . . .	Hydride	

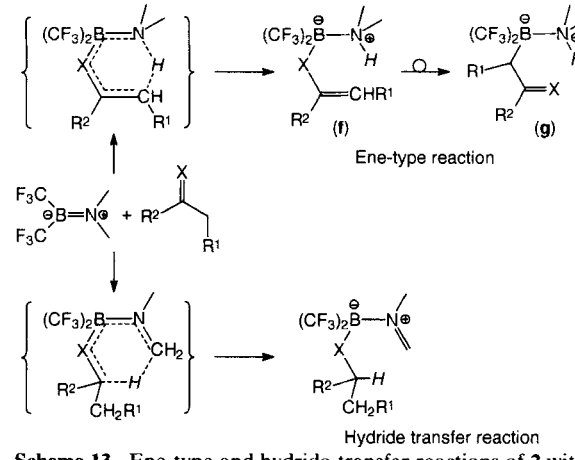
vely converted to isomer **d**. On the contrary,



which might be expected to form a five-membered ring of type **d**, reacts indeed in an ene-type reaction to give a noncyclic derivative **e** (Scheme 12). Obviously any of the five-membered rings **c** or **d** would be sterically overcrowded, with two vicinal CF_3 and four Me groups being close.

4.4 Ene-type and hydride-transfer reactions

The analogy of dimethylaminobis(trifluoromethyl)borane, **2** to olefins that was evident from the above-mentioned cycloaddition reactions is further substantiated by ene-type reactions or/and hydride-transfer reactions.[34–39] Such reactions which **2** undergoes with a variety of compounds are displayed in Scheme 13. The general formula $(X)CR^2CH_2R^1$, where X is connected to C by either a double or triple bond, includes many types of reactants. These are presented in Table 8. Depending on the substituents X, R^1 and R^2, either ene-type or hydride-transfer reactions take place, but there are also some borderline cases where both reactions proceed competitively.[39] Moreover, there are two varieties of ene-type reaction products, **f** and **g**. We assume that products **g** emerge from a rearrangement of intermediate species of type **f**.



Scheme 13. Ene-type and hydride-transfer reactions of **2** with $(X)CR^2CH_2R^1$.

Scheme 13 is discussed in some detail below.

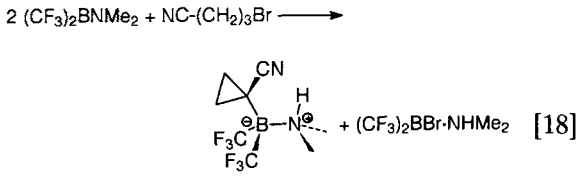
4.4.1 Ene-type reactions

4.4.1.1 Nitriles

Acetonitrile is known to form a Lewis acid–base adduct with a wide variety of boranes, the N-atom being coordinated to boron. No such simple adduct formation occurs with **2**. Indeed, nitriles of the general formula $NC—CH_2R^1$ readily undergo ene-type reactions to form the respective dimethylamine boranes $(NC—CHR^1)(CF_3)_2B \cdot NHMe_2$ (R^1 = H, Cl, Me, Et, $(CH_2)_3Cl$, $(CH_2)_{4,5,6}Br$) of type **g** (Scheme 13).

However, $NC(CH_2)_3Br$ reacts differently: with two equivalents of **2** it yields a novel species with a 1-cyanocyclopropane ring attached to boron (Eqn [18]),[34] whose structure is shown in Fig. 8.

Reaction [18], in which **2** furthermore acts as an HBr acceptor, underscores the tendency of bis-(trifluoromethyl)aminoboranes to strive for four-fold coordination.



[18]

Also, the less reactive species $CF_3(R)BNMe_2$ (R = Et; iPr) combine smoothly with CH_3CN in an ene-type reaction and give isolable products in high yields according to Eqn [19].[24]

$$CF_3(R)BNMe_2 + CH_3CN \rightarrow CF_3(R)(NC{-}CH_2)B \cdot NHMe_2 \quad [19]$$

While **2** reacts rapidly also with long-chain α-nitriles, $CF_3(Et)BNMe_2$ and $CF_3(iPr)BNMe_2$ combine only with acetonitrile and the reaction time amounts to days, rather than minutes as found in the case mentioned earlier.

The molecular and crystal structures of

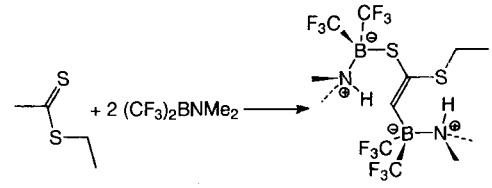
$$(\overline{CH_2CH_2C}{-}CN)(CF_3)_2B \cdot NHMe_2,$$

$(NC{-}CH_2)(CF_3)_2B \cdot NHMe_2$ and $CF_3(Et)(NC{-}CH_2)B \cdot NHMe_2$ have been determined by X-ray diffraction studies.[24, 34, 35]

4.4.1.2 Carbonyl compounds

Many carbonyl and thiocarbonyl compounds of the general formula $R^1CH_2{-}C(=X){-}R^2$ with X, R^1 and R^2 as listed in Table 9 also undergo ene-type reactions with **2** according to Scheme 13.

Methyl ketones, carboxylic esters, dialkylamides and dialkylthioamides in general *C*-alkylate boron and give products of type **g**. Of the carbonyl derivatives so far tested, only $CF_3C(=O)Me$, $EtSC(=S)Me$ and $EtSC(=S)Et$ form the respective enol and thioenol derivatives of type **f**. $EtSC(=S)Me$ under appropriate conditions adds two equivalents of **2** according to Eqn [20].



[20]

4.4.1.3 Ethyl diazoacetate

That ethyl diazoacetate behaves differently from other diazomethane derivatives has already been mentioned in Section 4.2.[26] Instead, at −120 °C it forms a borylated ethyl diazoacetate quantitatively, in another ene-type reaction, Eqn [21].

$$(CF_3)_2BNMe_2 + N_2CHCO_2Et \xrightarrow{-120\,^\circ C/\text{ether}} (EtO_2CCN_2)(CF_3)_2B \cdot NHMe_2 \quad [21]$$

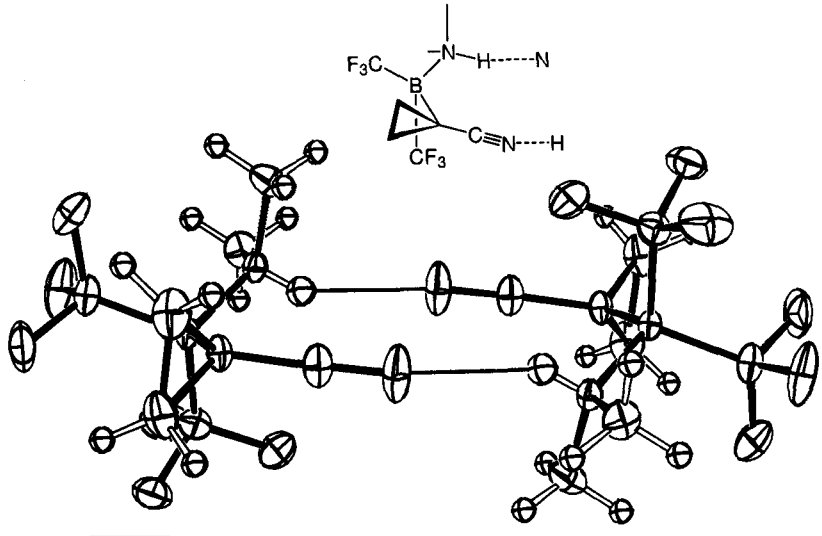


Figure 8 The structure of $(\overline{CH_2CH_2C}{-}CN)(CF_3)_2B \cdot NHMe_2$ showing the centrosymmetric hydrogen-bonded dimers found in the crystal.

Table 9 Ene-type reactions of **2** with $R^1CH_2—C(=X)—R^2$ (Refs 35, 36)

R^1	R^2	X	Type of product
H	t-Bu	O	**g**
H	CF_3	O	**g**
H	Ph	O	**g**
H	$\overline{C=CH—CH=CMe—O}$	O	**g**
H	Me	O	**g**
H	$CH=CMe_2$	O	**g**
H	OMe	O	**g**
H	OtBu	O	**g**
H	$OSiMe_3$	O	**g**
H	$OC(Me)=CH_2$	O	**g**
H	$OCH_2CH=CH_2$	O	**g**
H	NMe_2	O	**g**
Me	NMe_2	O	**g**
H	NEt_2	O	**g**
Cl	OEt	O	**g**
Me	OMe	O	**g**
Et	OMe	O	**g**
C(=O)OMe	OMe	O	**g**
C(=O)OtBu	OtBu	O	**g**
$—CH_2—$	$—OCH_2—$	O	**g**
H	NMe_2	S	**g**
Me	NMe_2	S	**g**
H	OEt	S	**g**
Me	OEt	S	**g**
H	SEt	S	**f**
Me	SEt	S	**f**

The structures of $(EtO_2CCN_2)(CF_3)_2B \cdot NHMe_2$[26] (Fig. 9) and $(tBuC(=O)CH_2)(CF_3)_2B \cdot NHMe_2$[40] have been determined.

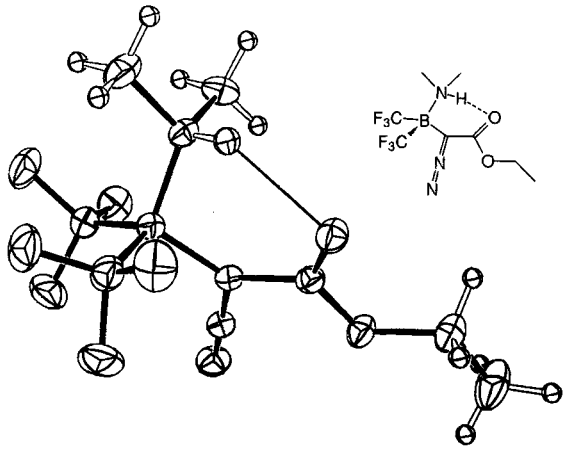


Figure 9 In $(EtO_2CCN_2)(CF_3)_2B \cdot NHMe_2$ N—H···O hydrogen bonding leads to six-membered ring formation.

Table 10 Ene-type reaction products $(R^1CH=CR^2—CH_2)(CF_3)_2B \cdot NHMe_2$ obtained from **2** and alkenes $R^1CH_2—C(=CH_2)—R^2$ (Ref. 39)

R^1	R^2
Me	Et
H	CH_2tBu
H	Ph
H	$CH=CMe_2$
Ph	H
nPr	H
iPr	H

4.4.1.4 Alkenes

α-Olefins of the general formula $R^1CH_2—C(=CH_2)—R^2$ with R^1 and R^2 as displayed in Table 10 react analogously to the related carbonyl compounds $R^1CH_2—C(=O)—R^2$ in forming *B*-alkylated products of type **g** (Scheme 13). Isobutene ($R^1 = H$, $R^2 = Me$) is an exception: even when in excess it adds not just one equivalent of **2** but the addition is carried on to a diborylated species according to Eqn [22].[39]

$$(CF_3)_2BNMe_2 + H_2C=CMe_2 \rightarrow$$

$$(Me—C(=CH_2)—CH_2)(CF_3)_2B \cdot NHMe_2$$

(5%)

$$H_2C=C[(CH_2)(CF_3)_2B \cdot NHMe_2]_2$$

(83%) [22]

4.4.2 Hydride-transfer reactions

Alkynes $H—C\equiv C—R^2$, with R^2 = Ph, *p*-Tol, tBu and

$$—\overline{C=CH—(CH_2)_3—CH_2},$$

and alkenes $H_2C=CR^2H$, with hydrogen in place of a CH_2R^1 group and R^2 = sBu, Ph, Mes, $SiMe_3$ and $SiEt_3$, react exclusively via the the hydride-transfer route to yield the corresponding methylmethyleneimine-stabilized adducts (*trans*-$R^2—CH=CH)(CF_3)_2B \cdot N(=CH_2)Me$ and

$(R^2CH_2CH_2)(CF_3)_2B \cdot N(=CH_2)Me$ (Scheme 13).[37,38] Similarly, nitriles and ketones lacking α-hydrogen atoms, e.g. CF_3CN, $(CF_3)_2C(=O)$ and $(CF_3)C(=O)Ph$, readily undergo a hydride-transfer reaction to yield the methylmethyleneimine borane derivatives $R(CF_3)_2B \cdot N(=CH_2)Me$ [$R = CF_3—HC=N$, $(CF_3)_2HC—O$ and $(CF_3)(Ph)HC—O$.

Methylmethyleneimine-coordinated trifluoromethylboranes are thermally less stable than amine boranes and tend to decompose vigorously when heated to 90 °C and above.

4.4.3 Borderline cases

Among the alkynes and alkenes there are some borderline cases where both reaction pathways are important. For example, alkynes —C—H—C≡C—CH_2R^1, with R^1 = nPr and nBu, yield *ca* 7:3 mixtures of (*trans*-$R^1H_2C—CH=CH)(CF_3)_2B \cdot N(=CH_2)Me$, resulting from the hydride-transfer reaction, and $(R^1HC=C=CH)(CF_3)_2B \cdot NHMe_2$, products of an ene-type reaction.

A similar mixture of products,

$$(\overline{CH_2(CH_2)_4}CH—CH=CH)(CF_3)_2B \cdot N(=CH_2)Me$$

and

$$(\overline{CH_2(CH_2)_4}C=C=CH)(CF_3)_2B \cdot NHMe_2,$$

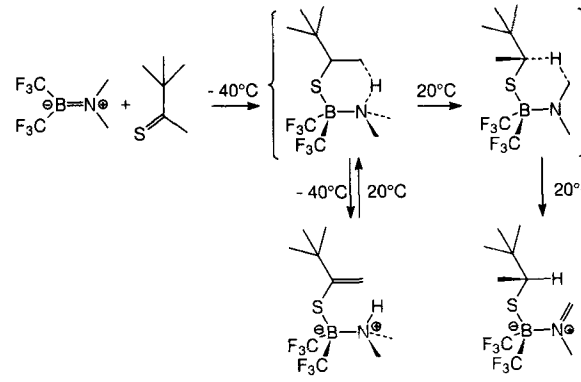
was obtained when

$$\overline{CH_2(CH_2)_4}CH—C\equiv CH$$

(having only one hydrogen in a position suitable for an ene-type reaction) was employed as the alkyne component.

For $R^2 = SiMe_3$ the competition of two simultaneous reactions produces a 6:4 mixture of (*trans*-$Me_3Si—CH=CH)(CF_3)_2B \cdot N(=CH_2)Me$ (which is formed by hydride transfer) and $(Me_3Si—C\equiv C)(CF_3)_2B \cdot NHMe_2$ (resulting from C—H addition across the B=N double bond of **2**).[38]

The reaction of $(CF_3)_2BNMe_2$ with $H_2C=C(CH_3)(tBu)$ is an interesting borderline case since significant amounts both of ene-type, $(tBu—C(=CH_2)—CH_2)(CF_3)_2B \cdot NHMe_2$ (20%), and hydride-transfer product, $(tBu)(Me)CH—CH_2)(CF_3)_2B \cdot N(=CH_2)Me$ (80%), are formed.



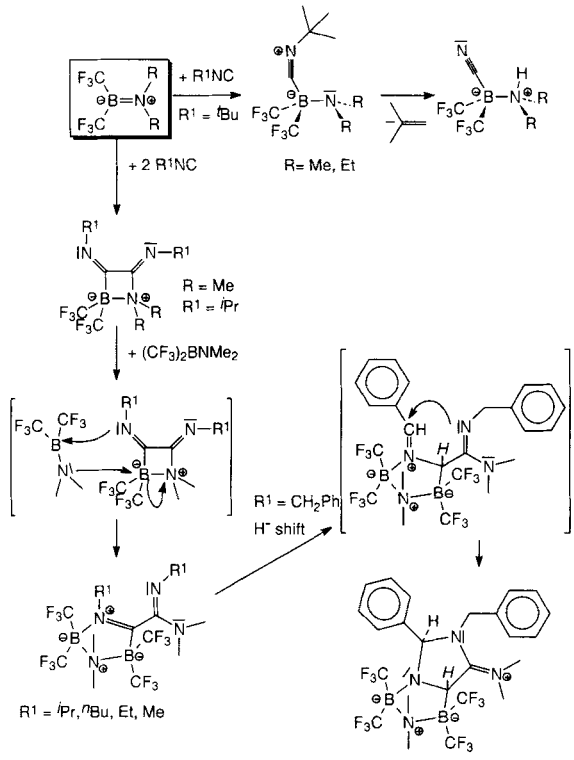
Scheme 14. t-Butyl methyl thioketone and $(CF_3)_2BNMe_2$.

t-Butyl methyl thioketone reacts with **2** in an even more complicated fashion, as is depicted in Scheme 14. When the reaction was carried out at −40 °C, the type **f** product resulting from an ene-type reaction was obtained as a crystalline material. Upon warming a solution of this species in CH_2Cl_2 to ambient temperature, a rearrangement was initiated that led to a product whose structure is in agreement with the hydride-transfer process. This rearrangement was monitored by ^1H NMR spectroscopy in the temperature interval 308–318 K. First-order kinetics were revealed, with an activation energy E_a of 112 ± 19 kJ mol^{-1} K^{-1}.[36]

4.5 Reactions with isocyanides

Reactions of **2** and **3** with isocyanides $R^1—N\equiv C$ are summarized in Scheme 15.[41] Depending on whether **2** or **3** was employed, and the nature of R^1, different pathways of addition reactions were found. tBu—N≡C forms colorless solids with **2** and **3** at −20 °C in pentane solution. These were shown to be the respective 1:1 adducts, with the lone pair of the isocyanide coordinated to the boron atom. When such solutions were warmed to 20 °C, isobutene was rapidly evolved. The respective dimethylamine and diethylamine adducts of bis(trifluoromethyl)cyanoborane, $NC(CF_3)_2B \cdot NHMe_2$ and $NC(CF_3)_2B \cdot NHEt_2$, were formed quantitatively. The formation of these cyanoborane derivatives may be regarded as a 'boron version' of the hydrocyanation of β-unsaturated ketones promoted by $TiCl_4$.[42] The structure of $NC(CF_3)_2B \cdot NHMe_2$ has been determined by an X-ray investigation.[41]

Less bulky isopropyl isocyanide is not susceptible to propene elimination, and so it also forms



Scheme 15. Reactions of **2** and **3** with isocyanides.

an adduct at low temperature with **2**; upon warming to ambient temperature, this adduct decomposes to a black tarry material. Careful work-up of this residue by sublimation afforded two species in proportions which depended on the reaction conditions. Thus a reaction time of 1 h at ambient temperature furnished mainly the four-membered ring

$$(CF_3)_2\overline{B—NMe_2—C(=N\text{-}iPr)—C(=N\text{-}iPr)}.$$

This was contaminated with the five-membered heterocycle

$$(CF_3)_2\overline{B—NMe_2—B(CF_3)_2—N\text{-}iPr=C—C(NMe_2)=N\text{-}iPr};$$

however, after two weeks at 25 °C, mainly the latter was isolated in low overall yield (Scheme 15).

Employing the less bulky n-alkyl isocyanides nBu—N≡C, Et—N≡C and Me—N≡C, the respective analogous five-membered heterocycles were obtained directly. Their formation can be regarded as a formal [2+3] cycloaddition reaction between an intermediate four-membered heterocycle and **2** (Scheme 15). One of these species,

$$(CF_3)_2\overline{B—NMe_2—B(CF_3)_2—NEt=C—C(NMe_2)=CNEt},$$

was studied by X-ray diffraction.[41]

Benzyl isocyanide carries the reaction with **2** even further: a novel bicyclic species,

$$(CF_3)_2\overline{B—NMe_2—B(CF_3)_2—CH—C(=NMe_2)—N(CH_2Ph)—CH(Ph)—N},$$

whose constitution has also been revealed by an X-ray crystallographic investigation, was formed (Fig. 10). We assume initial formation of a five-membered heterocycle analogous to that with $R^1 = Et$. In a successive step (Scheme 15) a hydride H^- from the benzylic carbon moves to the electronically poor B—C=N ring carbon atom. The strongly different polarity of these carbon atoms is presumably the driving force for this hydride transfer. This hydride migration may well be assisted by a nucleophilic attack of the

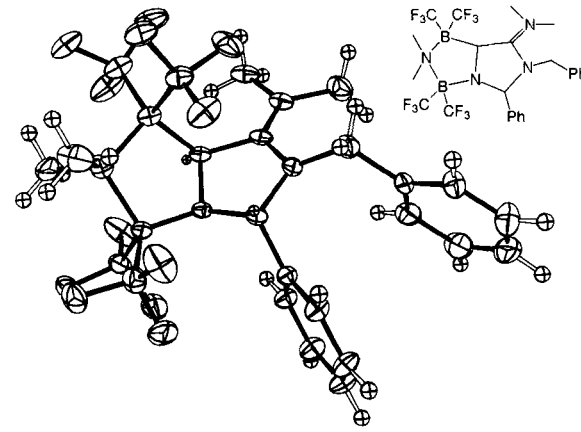


Figure 10 The structure of

$(CF_3)_2$

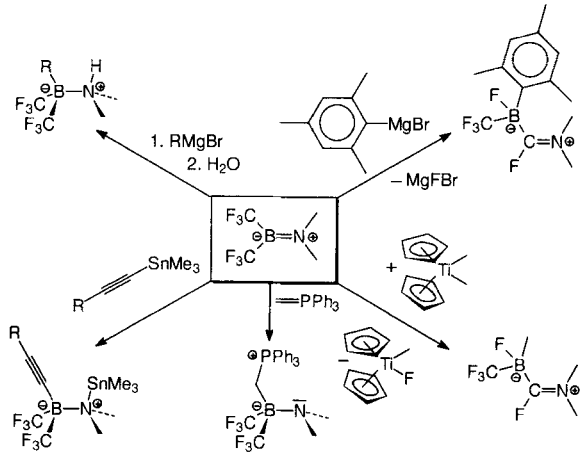
$B—NMe_2—B(CF_3)_2—\overline{CH—C(=NMe_2)—N(CH_2Ph)—CH(Ph)—N}$

contains B—N bonds involving tertiary and quaternary nitrogen atoms, the former being more than 0.1 Å shorter than the latter, presumably due to a hyperconjugative $N(p_\pi) \rightarrow B$ interaction.

$NCH_2C_6H_5$ nitrogen on the benzylic carbon, which finally closes the second ring.

4.6 Reactions with carbanions

Reactions of **2** with carbanions, as present in organometallic reagents, are summarized in Scheme 16.



Scheme 16. Reactions of **2** with carbanions.

Compound **2** reacts with a wide variety of Grignard reagents RMgBr at −78 °C in ether to yield, after hydrolysis, the dimethylamine boranes $(CF_3)_2RB \cdot NHMe_2$ (R = Me, Et, iPr, Ph, *p*-ClPh, *p*-Tol, *o*-Tol, —C≡CH).[34] It was impossible to link the bulky tBu group to boron either with organomagnesium or organolithium reagents. While the *o*-tolyl group is easily attached to boron, MesMgBr under similar reaction conditions selectively abstracted fluoride from one of the CF_3 groups. The structure of $(CF_3)(Mes)FB—FC{=}NMe_2$ thereby formed was confirmed by an X-ray investigation (Fig. 11).

Analogously, Cp_2TiMe_2 (Cp = cyclopentadienyl) reacted with **2** by placing a methyl group on the boron atom and yielded $(CF_3)(Me)FB—FC{=}NMe_2$.[27]

The Wittig reagent $Ph_3P{=}CH_2$ adds to **2** according to Scheme 16 to form the Lewis acid-base adduct. Its constitution was confirmed by an X-ray investigation (Fig. 12).[29] This adduct is an air-stable, nonvolatile solid which dissociates into its constituents when heated *in vacuo* to *ca* 140 °C. This thermal stability is surprising in view of unsuccessful attempts to obtain an adduct with $Ph_3P{=}CHMe$. Although at −40 °C adduct formation was suggested by NMR spectra, attempts to isolate this species at room temperature failed,

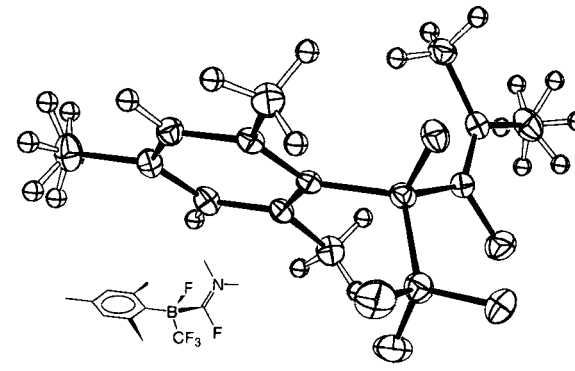


Figure 11 A sketch of $(CF_3)(Mes)FB—FC{=}NMe_2$ showing disorder of the two methyl groups; and emphasizing the planarity exerted by the imine double bond.

owing to dissociation into its components. This inability to coordinate may be ascribed to the steric demand exerted by the dimethylamino and the two CF_3 groups, which offers sufficient space to coordinate to boron only to a relatively small fourth ligand such as CH_2PPh_3.

While $SnMe_4$ (for example) does not react with **2**, the ethynylstannanes Ph—C≡C—$SnMe_3$ and Bu—C≡C—$SnMe_3$ add across the B=N double bond. After hydrolyses, $(Ph—C{\equiv}C)(CF_3)_2B \cdot NHMe_2$ and $(Bu—C{\equiv}C)(CF_3)_2B \cdot NHMe_2$, respectively, were obtained in good yield.[40]

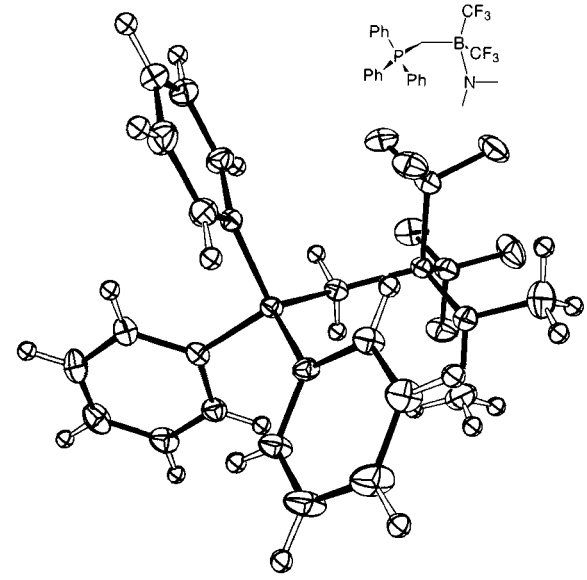
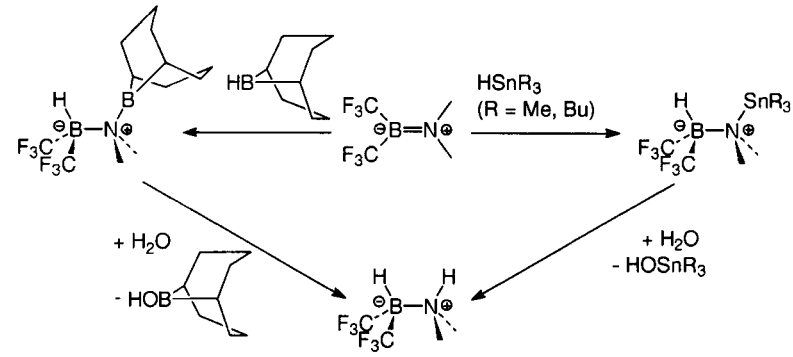


Figure 12 The structure of $Ph_3P—CH_2—(CF_3)_2B—NMe_2$ exhibits a slightly pyramidal BNC_2 fragment with a short B—N bond, 1.500(5) Å.



Scheme 17 Hydrogenation of **2**.

4.7 Hydrogenation of the boron–nitrogen bond

Compound **2** reacts with 9-borabicyclo[3.3.1]-nonane (9-BBN) in hexane solution in a straightforward fashion according to Scheme 17.[43] The N—B bond to the bicyclononane residue is readily cleaved upon treatment with water. Separation of $(CF_3)_2BH \cdot NHMe_2$ from HO-9-BBN, however, was found to be difficult because these two compounds possess similar volatility and solubility in various solvents. In order to circumvent this problem of separation, attempts were made to replace 9-BBN by $BH_3 \cdot NMe_3$ or catecholborane. While the former did not react at all, catecholborane attacked the CF_3 groups.

Therefore hydrostannation of **2** with R_3SnH (R = Me, Bu) was attempted. Both stannanes add quantitatively across the B=N double bond (Scheme 17). The Sn—N bond is rapidly cleaved by addition of water, and $(CF_3)_2BH \cdot NHMe_2$ is obtained. Separation of $(CF_3)_2BH \cdot NHMe_2$ from Bu_3SnOH is greatly facilitated by their almost complete immiscibility; therefore, Bu_3SnH is to be recommended.

The analogous diethylamine derivative, $(CF_3)_2BH \cdot NHEt_2$, however, is only accessible by hydrogenation of **3** using Me_3SnH.

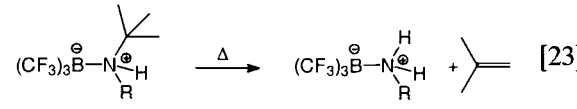
5 SUBSTITUTION AND CLEAVAGE REACTIONS

The preceding section was above all focused on addition reactions in which, at least in the first step, the aminotrifluoromethylborane fragment was retained. This section will deal with reactions directed towards modifications of aminotrifluoromethylboranes at the nitrogen and boron centers.

5.1 Modifications at nitrogen

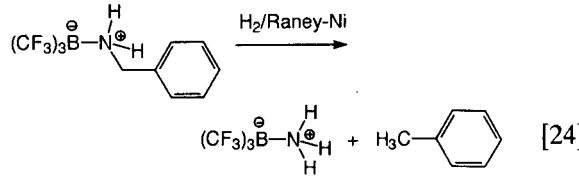
5.1.1 Removal of alkyl groups

N-Alkyl groups in amine trifluoromethylborane complexes show a similar chemical behaviour to ammonium cations. The tBuN group linked to tris(trifluoromethyl)borane is unstable and eliminates isobutene above *ca.* 40 °C to yield complexed primary amines according to Eqn [23].[22]



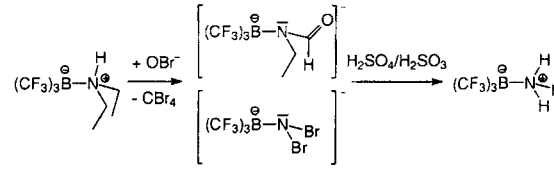
[23]

Likewise a benzyl group can be removed by catalytic hydrogenation with H_2/Raney nickel or with H_2/Pd–C according to Eqn [24].[44]



[24]

Complete oxidative cleavage of the two *N*-ethyl groups in $(CF_3)_3B \cdot NHEt_2$ is achieved by treatment with hypobromite (Br_2/KOH) under conditions similar to the haloform reaction (Scheme 18). Hereby the ammine adduct $(CF_3)_3B \cdot NH_3$ is accessible in high yield.[45] This had been obtained for the first time by subjecting $(CF_3)_3B \cdot NH(tBu)CH_2C_6H_5$ successively to the cleavage reactions of Eqns [23] and [24].[44]



Scheme 18

Surprisingly the N—B and B—C bonds are not affected by hypobromite. This is obviously due to the high steric demand of three CF_3 groups, which create a fluorosphere around boron. The fate of the ethyl groups is not yet fully clear. As by-products, CBr_4 and, when insufficient hypobromite was used, $(CF_3)_3B \cdot NH(C(=O)H)Et$ were obtained. Isolation of $(CF_3)_3B \cdot NH_3$ from the acidified aqueous solution can be achieved by extraction with ether.

The crystal and molecular structures of $(CF_3)_3B \cdot NH_3$ (Fig. 13) and the corresponding tetrahydrate $(CF_3)_3B \cdot NH_3 \cdot 4H_2O$, which is formed when the former is exposed to moist air, have been determined.[44,46]

The $CH_2{=}N$ group in adducts of $MeN{=}CH_2$ is hydrolyzed under alkaline conditions according to Eqn [25]. Thus methylamine–borane adducts are made accessible.[39,45]

$$(CF_3)_2R\overset{\ominus}{B}{-}N\overset{\oplus}{\diagdown\!\!\diagup} \xrightarrow[-\,OCH_2]{+\,H_2O} (CF_3)_2RB{-}\overset{\oplus}{N}\overset{H}{\diagdown\!\!\diagup}H \qquad [25]$$

5.1.2 Attachment of alkyl groups

Owing to the ammonium-type nature of the nitrogen in amine boranes, $(CF_3)_2RB \cdot NH_n(Me, Et)_{(3-n)}$ ($n = 1, 2, 3$; R = H, alkyl, aryl, CF_3, . . .) is easily deprotonated by alkali, e.g. KOH in ether.

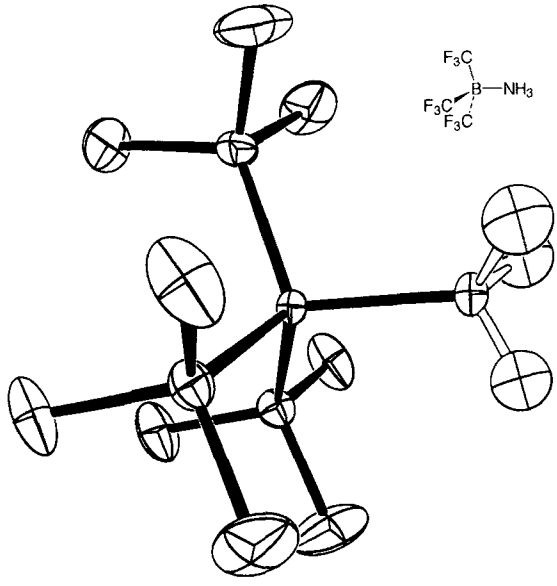


Figure 13 A sketch of $(CF_3)_3B \cdot NH_3$ showing the all-staggered orientation of the boron substituents.

In such anions $[(CF_3)_2RB \cdot NH_{(n-1)}(Me, Et)_{(3-n)}]^-$ the nitrogen is a nucleophile. The strength of its nucleophilic character depends on the steric and electronic demand of the R groups bonded to boron and the degree of substitution at nitrogen. Alkylation is therefore easily possible with alkyl chlorides, bromides and iodides, allyl bromide and other alkylating agents such as methyltrifluoromethylsulfonate. According to Eqn [26] the respective tris(trifluoromethyl)borane adducts of tertiary amines were obtained.[21]

$$[(CF_3)_3B{-}NR_2]^- + R^1 - X \rightarrow$$

$$(CF_3)_3B \cdot NR_2R^1 + X^- \qquad [26]$$

$X = I, CF_3SO_3, R^1 = Me$; $X = Br, R^1 = CH_2{=}CH{=}CH_2$

Similarly KOH in ether deprotonates the nitrogen in $(CF_3)_2HB \cdot NHMe_2$ to give ethereal solutions of the potassium salt $K[(CF_3)_2HB{-}NMe_2]$. This salt reacts with methyl iodide, benzyl chloride, allyl chloride and propargyl bromide according to Eqn [27] to yield the respective bis(trifluoromethyl)borane adducts.[43]

$$[(CF_3)_2HB{-}NMe_2]^- + R^1{-}X \rightarrow$$

$$(CF_3)_2HB \cdot NMe_2R^1 + X^- \qquad [27]$$

$X = I, R^1 = Me$; $X = Cl, R^1 = CH_2Ph$, $CH_2{=}CH{=}CH_2$; $X = Br, R^1 = CH_2C{\equiv}CH$

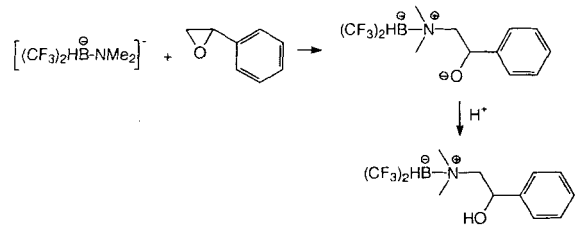
Compounds with a B—H bond are potential hydroboration reagents. However, the presence of two CF_3 groups attached to boron changes the character of the B—H bond dramatically. All attempts to use $(CF_3)_2HB \cdot NHMe_2$ for hydroboration of alkenes and alkynes failed. Likewise $(CF_3)_2HB \cdot NMe_2CH_2CH{=}CH_2$ and $(CF_3)_2HB \cdot NMe_2CH_2C{\equiv}CH$, which contain an olefinic and an acetylenic bond respectively, show no tendency to undergo intra- or inter-molecular hydroboration, even when heated to 100 °C for a week.

This failure is due to the strengthened B—N bond in amine bis(trifluoromethyl)boranes, since a requirement for hydroboration is that boron is in a tricoordinated state. Therefore the lack of reactivity in hydroboration is also a proof of the presence of a strong B—N bond.

The crystal and molecular structure of $(CF_3)_2HB \cdot NMe_2CH_2Ph$ has been determined.[43]

Nucleophilic attack of the nitrogen in

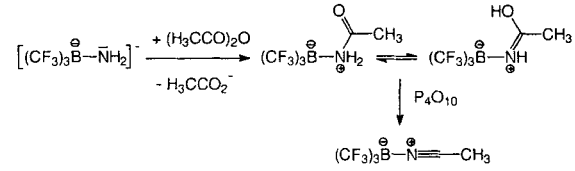
$[(CF_3)_2HB—NMe_2]^-$ opens the oxirane ring of styrene epoxide according to Scheme 19.[43]



Scheme 19

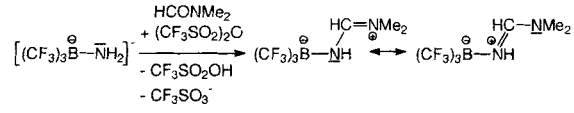
5.1.3 Attachment of acyl groups

Acylation of $(CF_3)_3B \cdot NH_3$ is achieved by reacting the potassium salt $K[(CF_3)_3B—NH_2]$ with $(MeCO)_2O$ according to Scheme 20. The acylated species exists as a mixture of tautomers. With P_4O_{10}, water is eliminated at elevated temperature and the acetonitrile adduct of tris(trifluoromethyl)borane is formed (Scheme 20).[44] $(F_3CCO)_2O$ and C_6F_5COCl react analogously to yield the respective acyl derivatives, $(CF_3)_3B \cdot NH_2COCF_3$ and $(CF_3)_3B \cdot NH_2COC_6F_5$. However, attempts to remove water with P_4O_{10} analogously to Scheme 20 were unsuccessful.



Scheme 20

On the other hand, $K[(CF_3)_3B—NH_2]$ reacted with dimethylformamide in the presence of $(F_3CSO_2)_2O$ with condensation (Scheme 21).



Scheme 21

The crystal and molecular structures of $(CF_3)_3B \cdot NH—CH=NMe_2$ have been determined.[44]

5.1.4 Cleavage of the boron–nitrogen bond

Compounds **2** and **3** add water at −78 °C across the B=N double bond with formation of the stable adducts $(CF_3)_2(HO)B \cdot NHR_2$ (Section 4.1). When such adducts are treated with alkali, e.g. KOH, the respective dialkylamine is liberated and the dihydroxyborate $K[(CF_3)_2B(OH)_2]$ is formed according to Eqn [28].[47]

$$(CF_3)_2(HO)B \cdot NHR_2 + KOH \rightarrow K[(CF_3)_2B(OH)_2] + HNR_2 \quad [28]$$
$$R = Me, Et$$

The potassium salt is stable at ambient temperature but may explode when heated to ≥72 °C. Concentrated hydrochloric acid decomposes an aqueous solution of this salt but in the presence of ether, $K[(CF_3)_2B(OH)_2]$ is transferred into the ethereal phase, presumably dissolving as an ether adduct (Scheme 22). Treatment of the ethereal phase with KHF_2 gives the novel fluorohydroxyborate $K[(CF_3)_2FBOH]$. This salt, m.p. 172 °C, is thermally more stable.[47]

$$K[(CF_3)_2B(OH)_2] \xrightarrow{Et_2O/HCl} \{(CF_3)_2BOH \cdot OEt_2\} \xrightarrow{KHF_2} K[(CF_3)_2FBOH]$$

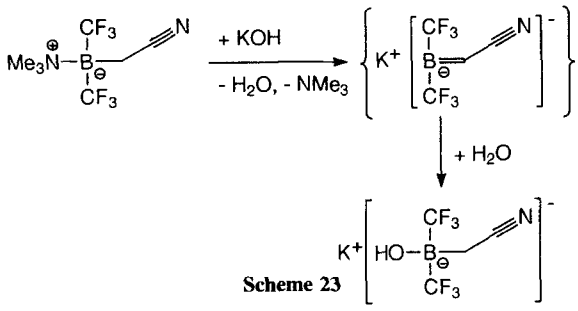
Scheme 22

In trimethylamine boranes of general formula $(CF_3)_2R^1B \cdot NMe_3$, salt formation as described in Section 5.1.2. is impossible. In the case of $R^1 = CH_2CN$, NMe_3 is smoothly replaced by OH^- upon treatment with powdered KOH in ether (Eqn [29]).[40]

$$(CF_3)_2(NCCH_2)B \cdot NMe_3 + KOH \rightarrow K[(CF_3)_2(NCCH_2)BOH] + NMe_3 \quad [29]$$

Little is known about the mechanism associated with this reaction. We assume that the elimination of NMe_3 from $(CF_3)_2(NCCH_2)B \cdot NMe_3$ is initiated by deprotonation of the CH_2 group, followed by elimination of NMe_3 and addition of water across the C=B double bond (Scheme 23). This assumption is supported by the general observation that only amine bis(trifluoromethyl)boranes with acidic CH groups α to boron undergo such elimination reactions. While $(CF_3)_2HB \cdot NMe_3$, for example, is stable to KOH/ether, $(CF_3)_2(BuC(=O)CH_2)B \cdot NMe_3$ immediately eliminates NMe_3. However, after work-up only $K[(CF_3)_2B(OH)_2]$ was obtained, with the $tBuC(=O)CH_2$ ligand disappearing according to Eqn [30].

$$(CF_3)_2(tBuC(=O)CH_2)B \cdot NMe_3 + KOH + H_2O \rightarrow K[(CF_3)_2B(OH)_2] + NMe_3 + tBuC(=O)CH_3 \quad [30]$$



Scheme 23

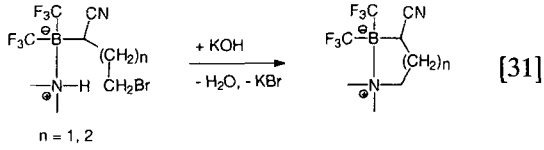
Presumably the $(CF_3)_2B—CH_2—C(=O)$-tBu intermediate is in equilibrium with its tautomer $(CF_3)_2B—O—C=CH_2(tBu)$, which is amenable to hydrolytic cleavage of the B—O bond.

The anion $[(CF_3)_2(NCCH_2)BOH]^-$ is remarkably stable in aqueous solution at pH 7–14, whereas rapid decomposition with elimination of HCF_3 takes place upon addition of concentrated hydrochloric acid.

5.2 Modification of $R(CF_3)_2B$ derivatives at boron

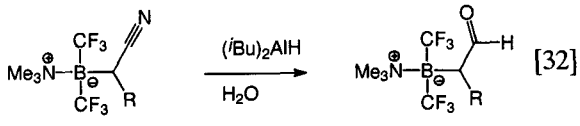
When the ligand R^1 carries a functional group in compounds of the constitution $(CF_3)_2R^1B \cdot NHMe_2$, then R^1 may be further modified without affecting the $B(CF_3)_2$ entity.

Ring closure with formation of five- and six-membered rings is observed upon treatment with KOH in ether (Eqn [31]).[34]



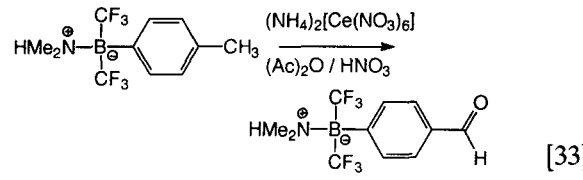
[31]

Nitrile groups in the β-position to boron can be reduced to aldehyde functions using $(iBu)_2AlH/CH_2Cl_2$ followed by hydrolysis of the intermediates according to Eqn [32].[34]

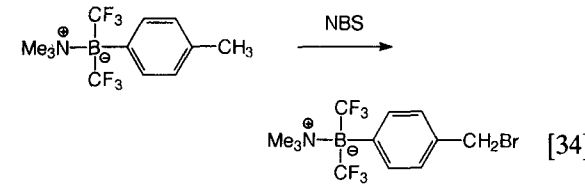


[32]

A *p*-tolyl group bonded to boron can be oxidized to an aldehyde using cerium(IV) nitrate (Eqn [33]), or brominated with *N*-bromosuccinimide (NBS) (Eqn [34]).



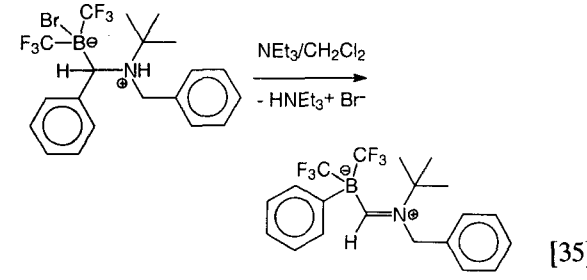
[33]



[34]

In both cases neither the B—C nor the B—N bond is attacked.[34]

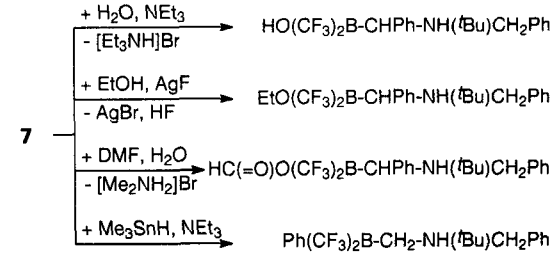
Dry NEt_3 eliminates HBr from $Br(CF_3)_2B—CHPh—NH(tBu)CH_2Ph$ and causes a skeletal rearrangement with 1,2-migration of a phenyl group from carbon to boron (Eqn [35]).[22]



[35]

To the contrary the bromine in the same educt $Br(CF_3)_2B—CHPh—NH(tBu)CH_2Ph$ (**7**) is substituted by a hydroxy or an ethoxy group using H_2O/NEt_3 or EtOH/AgF, respectively (Scheme 24). The constitution of $HO(CF_3)_2B—CHPh—NH(tBu)CH_2Ph$ has been confirmed by an X-ray investigation.[22]

Attempts to replace bromine by a CF_3 group using $Cd(CF_3)_2 \cdot DMF$, or by hydrogen with Me_3SnH, led to two unexpected species (Scheme 24). $Cd(CF_3)_2 \cdot DMF$ does not behave as a source for CF_3 groups that are capable of replacing Br.



Scheme 24. Reactivity of $Br(CF_3)_2B—CHPh—NH(tBu)CH_2Ph$ (**5**).

Instead it delivers a formiato group originating from the DMF ligand that is introduced more readily. In the presence of NEt_3 the above-mentioned rearrangement according to Eqn [34] took place, the rearranged product being capable of concomitant or successive hydrostannation of the C=N double bond by Me_3SnH.

5.3 Ring opening of azoniaboratacyclopropanes

Some reactions of azoniaboratacyclopropanes that involve fission of the B—N bond are displayed in Scheme 25.

Except for $R^1 = R^2 = Ph$ and for $R^1 = SiMe_3$, $R^2 = CH_2Ph$, all 1,1-dimethyl-2,2-bis(trifluoromethyl)azoniaboratacyclopropane derivatives

$$(CF_3)_2\overline{B—NMe_2—CR^1R^2}$$

reported in Table 2 (Section 4.2) react readily with H_2O with cleavage of the N—B bond to form $(CF_3)_2B(OH)—CR^1R^2—NHMe_2$. While for the two species mentioned as exceptions this N—B fission is kinetically hindered so that these compounds can be handled in moist air without precaution, all other species are hydrolyzed within minutes when dissolved in moist organic solvents. HCN reacts with

$$(CF_3)_2\overline{B—NMe_2—CHSiMe_3}$$

like a normal acid to yield $(CF_3)_2B(CN)—CH(SiMe_3)—NHMe_2$.

The crystal and molecular structures of $(CF_3)_2B(OH)—CHSiMe_3—NHMe_2$ have been determined by an X-ray investigation.[48]

Carbonyl compounds $R^3R^4C=O$ insert into the N—B bond of

$$(CF_3)_2\overline{B—NMe_2—CH_2}$$

and

$$(CF_3)_2\overline{B—NMe_2—CHSiMe_3}$$

to yield the novel heterocyclic 1-oxa-4-azonia-2-boratacyclopentanes

$$(CF_3)_2\overline{B—CR^1R^2—NMe_2—CR^3R^4O},$$

as reported in Table 11. The crystal and molecular structures of

$$(CF_3)_2\overline{B—CHSiMe_3—NMe_2—CMe_2O}$$

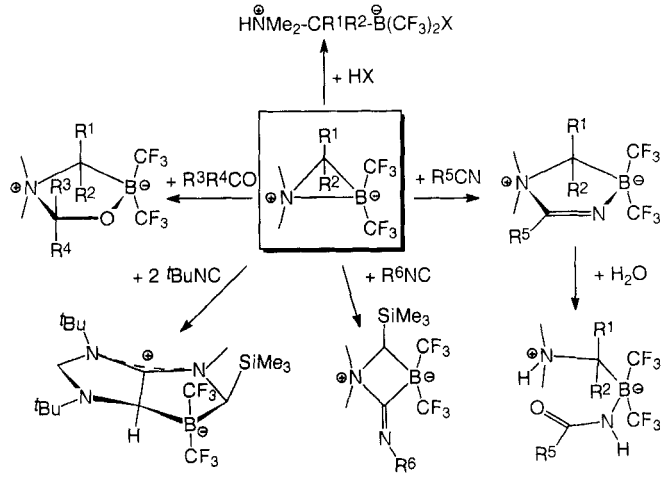
have been determined by an X-ray investigation.[48] Experiments employing different carbonyl derivatives, however, revealed that this ring expansion is restricted to ketones and aldehydes, while esters and amides do not undergo any similar reaction.

An analogous ring expansion reaction with formation of 1-aza-4-azonia-2-boratacyclopentenes

$$(CF_3)_2\overline{B—CR^1R^2—NMe_2—CR^5=N}$$

in high yields, as quoted in Table 12, is observed when the azoniaboratacyclopropane

$$(CF_3)_2\overline{B—NMe_2—CR^1R^2}$$



Scheme 25 Reactions of azoniaboratacyclopropanes.

Table 11 1-Oxa-4-azonia-2-boratacyclopentanes

$(CF_3)_2\overline{B—CR^1R^2—NMe_2—CR^3R^4O}$

(Ref. 48)

R^1	R^2	R^3	R^4
H	H	Et	Et
H	$SiMe_3$	H	Me
H	$SiMe_3$	Me	Me
H	$SiMe_3$	Et	Et
H	$SiMe_3$	Me	$CH{=}CMe_2$
H	$SiMe_3$	Me	$\overline{C{=}CMe(CH_2)_2CH_2}$

is treated wth nitriles R^5CN (Scheme 25). In the course of the reaction of

$$(CF_3)_2\overline{B—NMe_2—CHSiMe_3}$$

with $H_2C{=}CH—CH_2—CN$ the C=C double bond must have migrated, because the R^5 substituent has become *trans*-CH=CHMe in the isolated product.

The 1-aza-4-azonia-2-boratacyclopentene ring in

$$(CF_3)_2\overline{B—CR^1R^2—NMe_2—CR^5{=}N}$$

opens upon hydrolysis with formation of $(R^5C(O)NH)(CF_3)_2B—CR^1R^2—NHMe_2$. As an example the crystal and molecular structures of $(MeC(O)NH)(CF_3)_2B—CHSiMe_3—NHMe_2$ have been determined by an X-ray investigation.[48]

As Scheme 25 illustrates, the azoniaboratacyclopropane

$$(CF_3)_2\overline{B—NMe_2—CHSiMe_3}$$

combines with isocyanides R^6NC ($R^6 = p\text{-}TolSO_2CH_2$ and $R^6 = PhCH_2$) in a 1:1 ratio to give, by ring expansion, azoniaboratacyclobutane derivatives

Table 12 1-Aza-4-azonia-2-boratacyclopentanes

$(CF_3)_2\overline{B—CR^1R^2—NMe_2—CR^5{=}N}$

(Refs 27, 48)

R^1	R^2	R^5
H	H	CHClMe
H	$SiMe_3$	Me
H	$SiMe_3$	CHClMe
H	Ph	Me
	$H_4C_6—C_6H_4$	Me

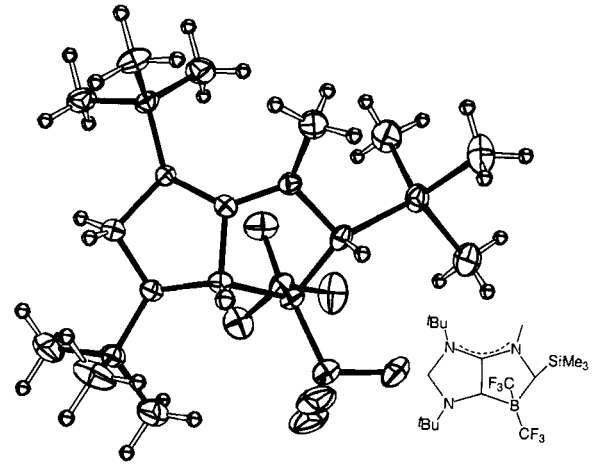


Figure 14 A view of

$(CF_3)_2\overline{B—CHSiMe_3—NMe—\overline{C—NtBu—CH_2—NtBu—CH}}$

from above the mean plane of the two puckered five-membered rings.

$$(CF_3)_2\overline{B—C(NR^6)—NMe_2—CHSiMe_3}.$$

Their constitution comprising a four-membered heterocyclic ring has been proved by an X-ray study.[49]

Surprisingly,

$$(CF_3)_2\overline{B—NMe_2—CHSiMe_3}$$

reacts with two equivalents of t-butyl isocyanide in a most complex fashion to form a novel diaza-azoniaboratabicyclo[3.3.0]octene species. The structure of this reaction product and the pathway of its formation were mostly doubtful until the result of an X-ray examination became available (Fig. 14).[49]

We now believe that the reaction of

$$(CF_3)_2\overline{B—NMe_2—CHSiMe_3}$$

with isocyanides starts with nucleophilic attack of the isocyano carbon atom on the boron atom and concomitant insertion into the B—N bond if formation of a four-membered ring is not strictly prevented. Though the primary step in the formation of the tBu derivative

$$(CF_3)_2\overline{B—CHSiMe_3—NMe—\overline{C—NtBu—CH_2—}\overline{\overline{NtBu—CH}}}$$

might be the same as for the other examples,

several consecutive rearrangements, and uptake of a second isocyanide molecule, are required. However, information on the intermediates involved is not available and therefore speculation about the mechanism is at present unwarranted.

6 SPECTROSCOPIC AND STRUCTURAL PROPERTIES

The trifluoromethylborane derivatives mentioned in the preceding sections have been characterized by several spectroscopic techniques, i.e. NMR, mass, infrared and Raman spectroscopies. Furthermore, gas-phase electron diffraction and single-crystal X-ray investigations have been performed, some results of which have been mentioned before. Here we will discuss some spectroscopic and structural aspects which are of general importance.

6.1 NMR spectra

All three nuclei of the B—CF_3 group can be studied by NMR spectroscopy. Of these, ^{19}F spectroscopy is most sensitive (abundance, $I=\frac{1}{2}$, gyromagnetic ratio) and hence most useful for routine analytical purposes.

6.1.1 ^{19}F NMR spectra

The ^{19}F resonance of a B—CF_3 fragment occurs in a relatively narrow range between −55 and −70 ppm relative to $CFCl_3$. For tricoordinate species this resonance is usually a broad singlet due to quadrupole broadening without discernible ^{11}B coupling. In tetracoordinated boron compounds the ^{19}F signal is often split into a 1:1:1:1 quartet revealing typically a $^2J_{FB}$ coupling constant of 25–30 Hz.

6.1.2 ^{13}C NMR spectra

^{13}C resonances of the CF_3 groups are hardly detectable due to quadrupole broadening by the ^{10}B and ^{11}B nuclei and furthermore the splitting caused by coupling to the fluorine atoms. Sharp lines are observed only in some tetracoordinated species: for example, in $K[(CF_3)_3BNHEt]$, $\delta=$ 130 ppm, $^1J_{CF}\simeq 315$ Hz, $^3J_{CF}\simeq 3.7$ Hz, $^1J_{CB}\simeq$ 71.5 Hz.[21] The carbon atoms of the B—NMe_n groups typically show a splitting due to coupling with the fluorine atoms of the CF_3 groups, with $^4J_{CF}=1$–2 Hz. This is of high diagnostic value.

6.1.3 ^{11}B NMR spectra

Replacement of Cl by trifluoromethyl groups does not shift the ^{11}B resonance: the chemical shift $\delta(^{11}B)$ of Cl_2BNMe_2, $(CF_3)ClBNMe_2$ and $(CF_3)_2BNMe_2$ remains close to 31 ppm. This is in sharp contrast to the effect exerted by alkyl groups: $\delta(^{11}B)$, $(CH_3)ClBNMe_2=38.5$ ppm, $(CH_3)_2BNMe_2=45.0$ ppm.[50] At first glance the effect by which a CF_3 group deshields a boron nucleus more than a methyl group is surprising. However the ^{11}B resonance in aminoboranes is governed both by σ- and π-effects of the ligands attached to boron. A Cl substituent is a weak π-donor, but stronger than CH_3 and CF_3. The CF_3 group attracts σ-electron density more than a CH_3 group but this makes boron better able to participate in the π-electron density offered by the nitrogen atom. This overcompensates the σ-effect and reinforces deshielding of the boron nucleus. A similar effect is observed for vinyl- and perfluorovinyl-boranes: $\delta(^{11}B)$, $(H_2C{=}CH)_3B=$ 56.4 ppm, $(F_2C{=}CF)_3B=46.1$ ppm.[3]

In amine boranes with tetracoordinated boron where π-donation is unimportant, fluorine effects, i.e. of CF_3 compared with CH_3, are smaller: $\delta(^{11}B)$, $(CF_3)_3B\cdot NH_3=-15.3$ ppm, $(CH_3)_3B\cdot NH_3=-8.7$ ppm.[44,50]

6.2 Fluorine effects on structures

The importance of fluorine effects on structures can be demonstrated by a comparison of the B—C and B—F bond lengths of $K[CH_3{-}BF_3]$[51] and its perfluorinated counterpart $K[CF_3{-}BF_3]$.[52] While the B—C bond is lengthened by 0.050(7) Å upon substitution by fluorine, the B—F bond is shortened by 0.033(7) Å. This can be interpreted as a result of different bond polarities arising from a variation of charges on the respective carbon and boron atoms.

Despite the considerable steric strain in $(CF_3)_3B$ adducts (the effective steric demand of a CF_3 group might be compared with that of an isopropyl group), these adducts are considerably more stable to dissociation than their $(CH_3)_3B$ analogues. B—N distances involving $(CF_3)_3B$ and a tetracoordinated nitrogen atom have been determined for several examples, 1.595(8) Å in $(CF_3)_3B\cdot NH_3$, 1.589(5) Å in $(CF_3)_3B\cdot NH_2Et$ and 1.596(8) Å in $(CF_3)_3B\cdot NHEt_2$.[44] Unfortunately

no such distance is available for NH_3, $EtNH_2$ or Et_2NH adducts of trimethylborane. However, the structure of the related complex $(CH_3)_3B \cdot NHMe_2$ has been investigated and the B—N bond length has been determined as 1.656(4) Å.[53] In spite of different amine ligands, this bond length might be compared with those mentioned above for tris(trifluoromethyl)borane adducts. The enhanced stability of amine trifluoromethylboranes correlates well with the observed B—N bond shortening of *ca* 0.06 Å.

A similar B—N bond shortening upon CH_3/CF_3 substitution is expected for a tricoordinated boron atom in aminoboranes. However, no (low-temperature) X-ray structure determination has yet been performed on **2**, whereas the structure of Me_2BNMe_2 at 110 K has been reported recently.[54] This latter species has a B=N bond length of 1.403(1) Å, which is in fact longer than that of compound **4**, 1.37(1) Å.[23] Electron diffraction studies of $CF_3B(NMe_2)_2$ and **2** have been performed in the gas phase;[13] B—N distances of 1.422(9) Å in $CF_3B(NMe_2)_2$ and 1.425(18) Å in **2** appear to be longer than in **4**, as far as comparison of solid and gas-phase structures is meaningful.

7. POTENTIAL APPLICATIONS OF TRIFLUOROMETHYLBORON DERIVATIVES

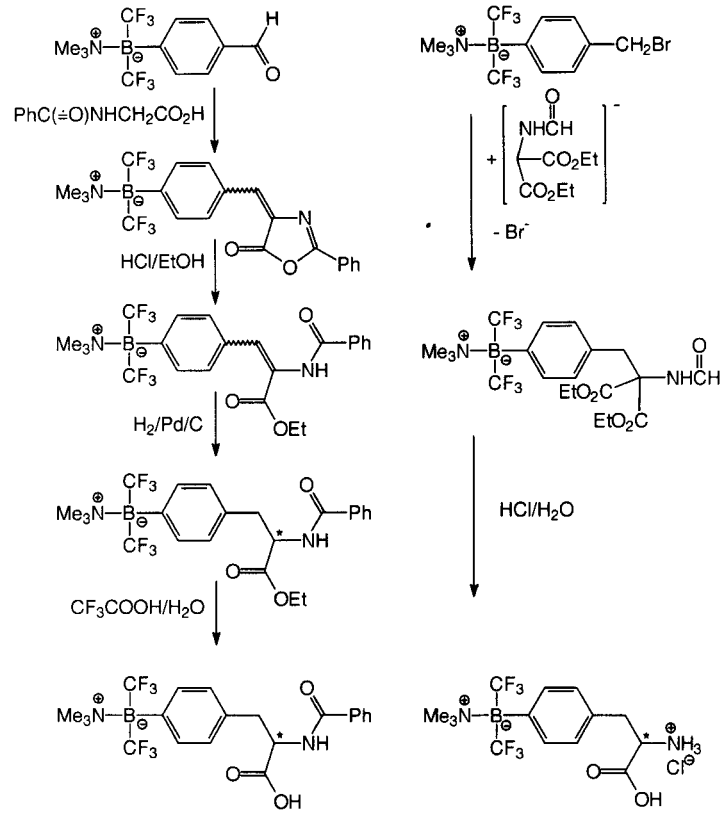
The chemistry of CF_3B derivatives as outlined in the present review is restricted to amino derivatives of tricoordinated boron, and to amine complexes and anions containing tetracoordinate boron. Rearrangement reactions with cleavage of the B—N bond and formation of stable molecules unambiguously prove that ligands other than nitrogen are capable of stabilizing CF_3B fragments. However, this question has not yet been approached systematically although there is evidence for reasonably stable trifluoromethylalkoxyboranes.[32]

Most of the interest in dialkylaminobis(trifluoromethyl)boranes $(CF_3)_2BNR_2$ results from their analogy to the isosteric alkenes $R_2C{=}CR'_2$, the electronically poor boron atom much resembling a carbocation. As this review underlines, this formal analogy, which cannot be verified experimentally for methylboron derivatives, is to a much broader extent validated by trifluoromethylboron derivatives. Although only reactions typical of olefins have been studied until now, unprecedented similarities have been found in spite of the limitations dictated by the steric effects imposed by the bulky ligands.

The major prospects for aminotrifluoromethylboranes are thus their inclusion as building blocks into organic molecules by replacement of CC units. Such isoelectronic CC/BN substitution may be desirable when one is striving to incorporate CF_3-group properties, or when for analytical, diagnostic or medical reasons a demand for boron is indicated. Interest in boron-containing amino-acids has increased since it has been shown that such compounds may be used in ^{10}B neutron capture therapy (BNCT). One candidate for treatment of melanomas which is presently under investigation is the phenylalanine derivative $(HO)_2B—C_6H_4—CH_2CH(NH_3)CO_2$.[55]

We have therefore set out to synthesize a related trifluoromethylboron-substituted species, $Me_3N—(CF_3)_2B—C_6H_4—CH_2CH(NH_3)CO_2$. Two classic routes for amino-acid synthesis were attempted, as displayed on the left- and right-hand sides of Scheme 26. Using the aldehyde reported in Section 5.2., an Erlenmeier synthesis using hippuric acid was undertaken. This led to the corresponding condensation product. The five-membered ring is cleaved and the C=C double bond catalytically hydrogenated. Treatment with trifluoroacetic acid furnished the amino-acid benzamide in an overall yield of *ca* 12%. Since cleavage of the amide seemed to be impeded, the alternative route displayed on the right-hand side of Scheme 26 was chosen. This is straightforward and leads directly to the hydrochloride of the desired racemic phenylalanine derivative, which has been obtained on a 10 g scale.[40]

While in the above-mentioned phenylalanine derivative the $(CF_3)_2B$ moiety is well separated from the amino carboxylic center, it is directly coordinated to the amino group in substituted amino-acids of the general formula $(CF_3)_2R^1B—NR^2R^3CHR^4COOH$. Depending on R^1–R^4, numerous possible *N*-borylated α-amino acids belong to this class of compounds. Three glycine derivatives ($R^4 = H$) with different extent of methyl substitution at nitrogen (R^2, $R^3 = H$, Me) and different R^1 groups (H, F_3C and $tBuCH_2CH_2$) attached to boron have been synthesized according to Eqns [36]–[38].[45] $(CF_3)_2HB \cdot NMe_2CH_2COOH$, $(CF_3)_3B \cdot$



Scheme 26 Synthesis of

$Me_3N{-}(CF_3)_2B{-}C_6H_4{-}CH_2CH(NHC(=O)Ph)CO_2H$ and $Me_3N{-}(CF_3)_2B{-}C_6H_4{-}CH_2CH(NH_3)CO_2$.

NH_2CH_2COOH and $(CF_3)_2(tBuCH_2CH_2)B \cdot NHMeCH_2COOH$.

$$[(CF_3)_2HB{-}NMe_2]^- + BrCH_2COOtBu \rightarrow (CF_3)_2HB \cdot NMe_2CH_2COOtBu + Br^- \quad [36]$$

$$[(CF_3)_3B{-}NH_2]^- + BrCH_2COOtBu + MeLi \rightarrow [(CF_3)_3B{-}NHCH_2COOtBu]^- + LiBr + CH_4 \quad [37]$$

$$[(CF_3)_2(tBuCH_2CH_2)B{-}NHMe]^- + BrCH_2COOtBu + MeLi \rightarrow [(CF_3)_2(tBuCH_2CH_2)B{-}NMeCH_2COOtBu]^- + LiBr + CH_4 \quad [38]$$

Since in $(CF_3)_3B \cdot NH_2CH_2COOtBu$ and $(CF_3)_2(tBuCH_2CH_2)B \cdot NHMeCH_2COOtBu$ the hydrogen atoms bonded to nitrogen are acidic, addition of MeLi is necessary to bring the alkylation reaction to completion. The free glycine derivatives were obtained by cleaving the t-butyl esters with trifluoroacetic acid.[45]

These successful syntheses have shown that the $(CF_3)_2BN$ group withstands, and allows, standard procedures required in chemical syntheses. This is essential and promising for any applications to follow.

Acknowledgments

The authors gratefully acknowledge the skill and enthusiasm of the PhD students whose names appear in the references. Professor D. J. Brauer is thanked for numerous X-ray investigations. The Ministerium für Wissenschaft und Forschung Nordrhein-Westfalen, the Deutsche Forschungsgemeinschaft and the Fonds der Chemie are thanked for financial support.

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