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Alkylation of dimethylaminobis(trifluoromethyl)borane by 1-alkenes

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Abstract

Dimethylaminobis(trifluoromethyl)borane, $(\text{CF}_3)_2\text{BNMe}_2$ (**A**), undergoes B-alkylation on treatment with 1-alkenes of the general formula $(\text{R}^1\text{CH}_2)(\text{R}^2)\text{C}=\text{CH}_2$ to yield triorganoboron adducts $\text{Me}_2(\text{H})\text{N}-\text{B}(\text{CF}_3)_2\text{CH}_2(\text{R}^2)\text{C}=\text{CHR}^1$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$ (**I**); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_2(\text{CF}_3)_2\text{B}-\text{NHMe}_2$ (**II**); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Et}$ (**III**); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_2(^t\text{Bu})$ (**IV**); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$ (**V**); $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}=\text{CMe}_2$ (**VI**); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$ (**VII**); $\text{R}^1 = ^n\text{Pr}$, $\text{R}^2 = \text{H}$ (**VIII**); $\text{R}^1 = ^i\text{Pr}$, $\text{R}^2 = \text{H}$ (**IX**)). In contrast, monosubstituted ethene derivatives $(\text{R}^2)\text{CH}=\text{CH}_2$ ($\text{R} = ^s\text{Bu}$, Ph , Mes , Me_3Si , Et_3Si) react with **A** to form the corresponding methylmethyleneimine boron adducts $\text{H}_2\text{C}=\text{N}(\text{Me})-\text{B}(\text{CF}_3)_2\text{CH}_2\text{CH}_2\text{R}^2$ (**X**, **XII–XV**).

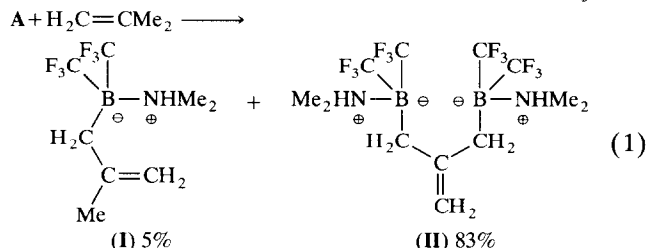
With $(^t\text{Bu})(\text{Me})\text{C}=\text{CH}_2$, **A** undergoes both types of reaction, yielding a 1/4 mixture of $\text{Me}_2(\text{H})\text{N}-\text{B}(\text{CF}_3)_2\text{CH}_2(^t\text{Bu})\text{C}=\text{CH}_2$ (**XIa**) and $\text{H}_2\text{C}=\text{N}(\text{Me})-\text{B}(\text{CF}_3)_2\text{CH}_2\text{CH}(\text{Me})(^t\text{Bu})$ (**XIb**). Whereas **I–IX** and **XIa** are formed by an ene-type reaction, **X** and **XIb–XV** result from a shift of a hydride from the dimethylamino group to the alkylating substituent. The novel boranes have been characterized by elemental analysis and multinuclear NMR, IR and mass spectroscopy.

1. Introduction

Bis(trifluoromethyl)dimethylaminoborane, $(\text{CF}_3)_2\text{BNMe}_2$ (**A**), contains a BN multiple bond that exhibits a reactivity which differs considerably from that of other aminoboranes. Thus **A** has been shown to undergo readily [2 + 4] cycloaddition reactions with suitable dienes [1] and ene reactions with nitriles, RCH_2CN , and carbonyl compounds of the general formula $\text{R}^2\text{C}(\text{O})\text{CH}_2\text{R}^1$ [2]. In these reactions, which are depicted in Scheme 1, a boron–carbon bond is formed, and both the boron and the nitrogen atom undergo an increase in coordination number from three to four. An alternative reaction pathway involving a hydride shift from the dimethylamino group to the alkylating substituent was found when **A** was treated with substrates lacking a suitable hydrogen atom for the quaternation of the nitrogen atom (see Scheme 1) [3]. This ambivalent behaviour of the highly reactive BN multiple bond in **A** prompted us to investigate the reaction of **A** with 1-alkenes of the formula $(\text{R}^1\text{CH}_2)(\text{R}^2)\text{C}=\text{CH}_2$ (R^1 , $\text{R}^2 = \text{H}$, alkyl, aryl) and $(\text{R}^2)\text{HC}=\text{CH}_2$ ($\text{R}^2 = \text{alkyl}$) in a systematic fashion, and the results of this investigation are presented below.

2. Results

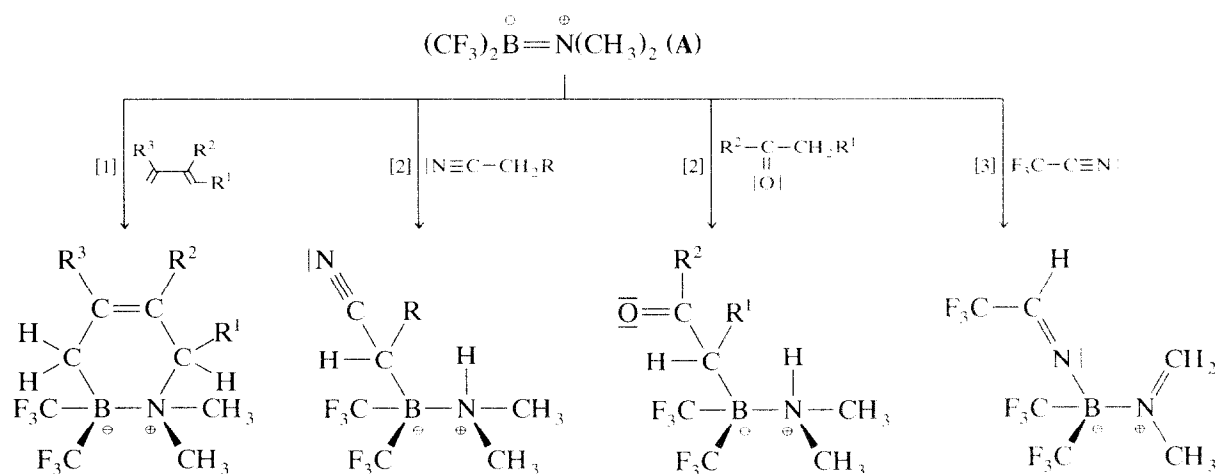
Isobutylene is known to undergo ene reactions with silaneimines [4]. We have found that it reacts similarly with **A** even at -10°C . Under these conditions a 5:83 mixture of the 1:1 adduct **I** and the 1:2 product **II** is obtained according to eqn. (1). The high yield of **II** indicates that **I** reacts faster with **A** than isobutylene.



The formation of both species is shown in the upper part of Scheme 2.

2-Ethyl-1-butene, $\text{Et}_2\text{C}=\text{CH}_2$, reacts analogously at 0°C to give the *E*-isomer **III**, and 2,4,4-trimethyl-1-pentene, $(^t\text{BuCH}_2)(\text{Me})\text{C}=\text{CH}_2$, yields **IV**, the proton being abstracted almost exclusively from the 2-methyl group. Compound **V** is formed analogously from **A** and methylstyrene, $(\text{Ph})(\text{Me})\text{C}=\text{CH}_2$. Alkenes with a β -carbon atom bearing a hydrogen atom and an alkyl group (i.e. $\text{H}_2\text{C}=\text{CHCH}_2\text{R}^1$) react less readily, and reaction times of to 4 days at temperatures of 50°C are

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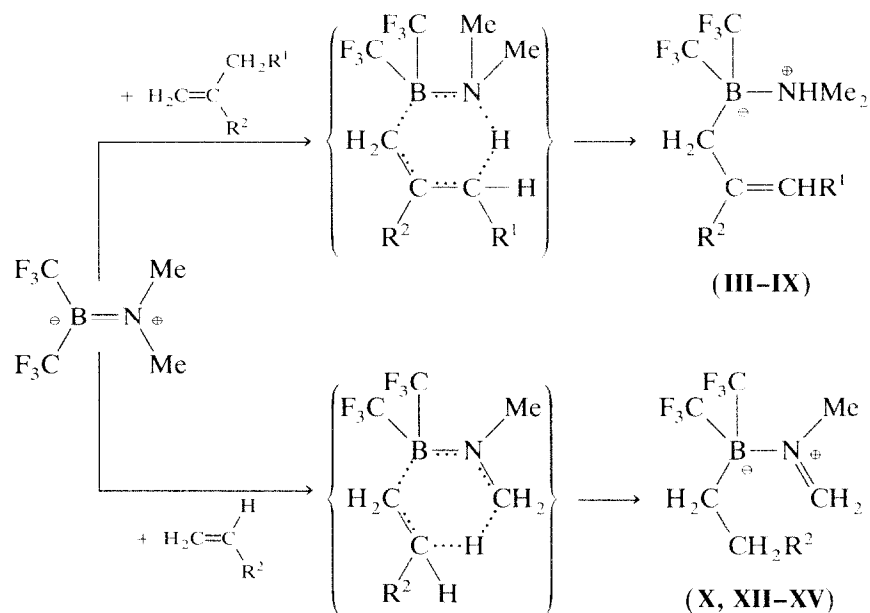


Scheme 1.

required to produce substantial yields of **VII–IX**. Bulky substituents attached to the β -carbon atom of 1-alkenes, as *e.g.* in $\text{H}_2\text{C}=\text{CHCHMeEt}$, prevent formation of the transition state required for a shift of the H proton to nitrogen. In this case a different type of reaction (which was observed previously when **A** was treated with alkynes, nitriles or carbonyl compounds [3]) is favoured as shown in Scheme 2 (lower part). This alternative pathway involves transfer of a hydride from an N-methyl group to an olefinic carbon atom, as is

shown by the formation of **X**. The hydride shift pathway takes place whenever there are no available hydrogens α to the double bond, *e.g.* in $\text{H}_2\text{C}=\text{CHR}^2$, $\text{R}^2 = \text{Ph}$ (**XII**), **Mes** (**XIII**), Me_3Si (**XIV**), and Et_3Si (**XV**). The reaction of **A** with $\text{CH}_3=\text{CH}(\text{tBu})$ has already been reported [3].

The reaction of $\text{H}_2\text{C}=\text{C}(\text{CH}_3)(\text{tBu})$ with **A** is an interesting borderline case since significant amounts of both the ene and hydride shift products are formed, in a total yield of 75% (eqn. (2)).



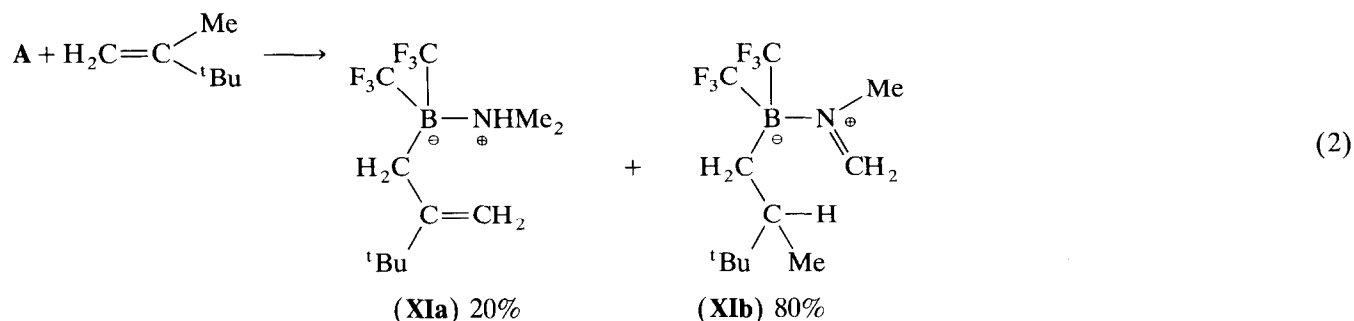
	R^1	R^2	%
III	Me	Et	92
IV	H	$\text{CH}_2(\text{tBu})$	83
V	H	Ph	90
VI	H	$\text{CH}=\text{CMe}_2$	40
VII	Ph	H	79
VIII	^nPr	H	60
IX	^iPr	H	68
X		^tBu	57
XII		Ph	12
XIII		Mes	19
XIV		SiMe_3	89
XV		SiEt_3	81

Scheme 2.

TABLE 1. NMR spectral data for compounds I–XIV (δ in ppm) ^a

	I	II	III	IV	V	VI	VII	VIII	IX	X	XIa	XIb	XII	XIII	XIV	XV
¹ H																
$\delta(\text{NCH}_3)$	2.80	2.80	2.78	2.81	2.71	2.79	2.75	2.76	2.76	3.66	2.75	3.78	3.63	3.74	3.65	3.67
$\delta(\text{BCH}_2)$	1.57	1.62	1.51	1.62	2.08	1.63	1.78	1.49	1.48	0.61	1.59	0.98	1.13	0.88	0.66	0.67
										0.71		1.04	1.17	0.91	0.70	0.70
$\delta(\text{=CCH}_3)$	1.75		1.62			1.80										
						1.83										
$\delta(\text{=CH}_n)$	4.61	4.59	5.01	4.60	5.07	4.78	6.40	5.38	5.38		4.72					
	4.64			4.79		4.95	6.45	5.52	5.47		4.96					
						5.68										
$\delta(\text{CCH}_2)$			2.07	1.98				1.36		1.0			2.60	2.58	0.22	0.24
								1.99		1.5			2.73	2.64	0.27	0.29
$\delta(\text{CCH}_3)$			1.04	0.92				0.89	0.98	0.86	0.86	0.73		2.29		0.94
										0.87		0.85		2.33		
$\delta(\text{CHC}_2)$									2.28	2.04		1.40				
$\delta(\text{SiCH}_n)$																
$\delta(\text{C}_6\text{H}_5)$					7.18		7.23						7.22		–0.01	0.53
					7.43		7.44						7.38	6.88		
$\delta(\text{N=CH}_2)$										7.66		7.71	7.59	7.71	7.62	7.65
										7.74		7.84	7.65	7.81	7.74	7.75
$\delta(\text{NH})$	~ 5.65	~ 5.60	~ 4.25	~ 5.57	~ 5.60	~ 4.35	~ 4.0	~ 3.95	~ 3.95		~ 4.0					
¹⁹ F																
$\delta(\text{CF}_3)$	–67.0	–61.9	–62.1	–61.8	–61.8	–62.0	–62.5	–62.5	–62.4	–64.7	–63.8	–61.6	–64.5	–64.5	–64.3	–64.5
												–65.7				
¹¹ B																
$\delta(\text{B})$	–8.0	–8.6	–8.5	–9.0	–8.1	–8.0	–8.5	–8.6	–8.8	–6.1	–	–5.6	–6.0	–5.8	–5.1	–5.3
¹³ C																
$\delta(\text{NCH}_3)$	38.9	40.8	40.1	41.4	40.9	40.3	39.7	39.7	39.8	48.2	40.0	48.6	48.1	48.4	48.1	48.2
$\delta(\text{BCH}_2)$	24.9	24.9	22.0	26.0	22.0	23.6	20.4	19.5	19.8	13.0	19.0	17.0	18.0	17.0	8.5	8.0
$\delta(\text{CCH}_3)$	25.0		13.1	31.0		19.4		13.5	22.7	11.3	26.9	16.3		20.7		7.4
			12.6			26.3		22.9		18.7		27.0		23.5		
$\delta(\text{CCH}_2)$			24.1	32.8				34.8		28.9		29.3	30.2	40.2		
										30.3						
$\delta(\text{SiCH}_n)$															9.0	2.8
															–2.3	3.0
$\delta(\text{CC}_3)$				52.1					31.1	37.0	29.4	34.0				
$\delta(\text{N=CH}_2)$										167.0		166.4	167.4	167.0	166.9	166.7
$\delta(\text{C=CH}_n)$	146.2	150.9	144.1	149.1	149.6	135.8					158.1					
						144.8										
$\delta(\text{C=CH}_n)$	110.9	108.5	116.4	113.2	113.9	113.0	125.6	127.7	124.6		105.9					
						127.8	129.9	131.6	139.0							
$\delta(\text{C}_6\text{H}_5)$					127.7		125.8						125.6	128.6		
					128.0		126.9						127.9	128.9		
					128.9		128.6						128.4	134.6		
					145.0		137.6						145.2	138.8		

^a I, II, IV and V in (CD₃)₂CO; III and VI–XV in CDCl₃; ¹H: 250.13 MHz, int. std. CHCl₃ = 7.27 ppm/CD₃COCD₂H = 2.05 ppm. ¹³C: 62.9 MHz, int. std. CDCl₃ = 77.0 ppm/(CD₃)₂CO = 29.8 ppm. ¹⁹F: 84.67 MHz, int. std. CFCI₃. ¹¹B: 25.52 MHz, ext. std. BF₃ · OEt₂.



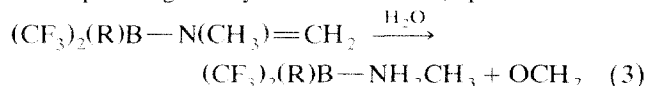
Although the requirements for an ene-type reaction are fulfilled, only *ca.* 20% of the corresponding reaction product **XIa** is produced and **XIb** is formed in 80% yields by the hydride shift pathway. We assume that steric crowding accounts for the preferred formation of **XIb**.

Ene reactions are known to follow a concerted reaction mechanism as depicted in Scheme 2. In the case of **A**, where an extremely polar B=N double bond reacts with an alkene, it is possible that the reaction is initiated by Lewis-acid/base adduct formation of the boron atom with the terminal =CH₂ group. The observation that CH₂=CH(CHClMe) does not react with **A** supports this suggestion, and indicates that only electron-rich 1-alkenes undergo reactions according to Scheme 2. Starting from such primary adducts both ene and hydride shift reactions proceed via different six-membered cyclic transition states. Though we cannot present any direct experimental evidence, *e.g.* low temperature NMR spectra, for the existence of such adducts, the identities of the by-products support this suggestion. When, for example, **A** and CH₂=CH^tBu were allowed to react on a 0.1 molar scale and the products subsequently hydrolyzed according to eqn. (3), we obtained not only ^tBuCH₂CH₂(CF₃)₂B-NH₂Me but also up to 4% of ^tBuCH₂CH₂(CF₃)₂B-NHMe₂. The formation of this by-product indicates that the hydride transfer is not absolutely restricted to a cyclic transition state as illustrated in Scheme 2, but may perhaps also proceed from a Lewis-acid/base adduct.

3. Properties and spectra

All the novel boranes are colourless solids or oily liquids. Compounds **I–IX**, which were obtained by an

ene-type reaction, are stable to air and moisture, while species **X** and **XIb–XV** containing a methylmethylenimine group readily undergo hydrolysis to give the corresponding methylamine adducts (eqn. (3)).



Traces of such hydrolysis products were detected in the NMR spectra whenever moisture was not rigorously excluded. Compounds **X** and **XIb–XV** are thermally less stable than **I–IX** and may *decompose vigorously* when heated to 90°C and above. The as yet unknown alkyl-bis(trifluoromethyl)boranes, (CF₃)₂BR, are unstable with respect to exothermal decomposition into the corresponding difluoroboranes, F₂BR, and difluorocarbene. This degradation pathway obviously becomes more important in complexes of borane with N(CH₃)=CH₂, which are more susceptible to thermal decomposition than are those of the basic secondary amine NH(CH₃)₂.

The ¹H, ¹⁹F, ¹¹B and ¹³C NMR spectra of **I–XV** were recorded. The NMR parameters, which are set out in Table 1, reveal some significant differences between the products formed by an ene-type reaction and those resulting from hydride shift (*e.g.* δ(¹¹B) 8–9 ppm *vs.* 5–6 ppm, respectively). Characteristic features of **X** and **XIb–XV** are the AB spin system of the N=CH₂ group in the ¹H NMR spectra, with δ 7.6–7.8 ppm, ²J_{HH} 10–11 Hz, and a resonance at 167 ppm in the ¹³C spectrum that is assigned to the N=CH₂ carbon atom.

The EI mass spectral data are reported in Table 2. They confirm the proposed formulations, and allow a ready differentiation between ene-type and hydride shift reaction products. Thus, **I–IX**, have in common the base peak *m/e* 94 [F₂BNH(CH₃)₂]⁺ while **X** and

TABLE 2. EI mass spectral data (*m/e* relative intensity (%)) [fragment]⁺ for compounds **II–XV**

II	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 74 (9) [FBN(CH ₃) ₂] ⁺ / 44 (8) [C ₂ H ₆ N] ⁺ / 249 (4) [M] ⁺ (I) / 442 (1) [M] ⁺
III	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 55 (11) [C ₄ H ₇] ⁺ / 277 (8) [M] ⁺ / 84 (7) [C ₆ H ₁₂] ⁺ / 44 (5) [C ₂ H ₆ N] ⁺ / 74 (3) [FBN(CH ₃) ₂] ⁺ / 158 (1) [M - C ₂ F ₅] ⁺
IV	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 249 (31) [M - (CH ₃) ₂ C=CH ₂] ⁺ / 57 (25) [C(CH ₃) ₃] ⁺ / 290 (5) [M - CH ₃] ⁺ / 44 (3) [C ₂ H ₆ N] ⁺
V	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 311 (17) [M] ⁺ / 44 (11) [C ₂ H ₆ N] ⁺ / 118 (10) [C ₉ H ₁₀] ⁺ / 115 (6) [C ₉ H ₇] ⁺ / 117 (5) [C ₉ H ₈] ⁺
VI	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 55 (37) [C ₄ H ₇] ⁺ / 96 (22) [C ₇ H ₁₂] ⁺ / 69 (18) [C ₅ H ₉] ⁺ / 170 (12) [M - C ₂ F ₅] ⁺ / 274 (5) [M - CH ₃] ⁺ / 289 (2) [M] ⁺
VII	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 117 (70) [C ₉ H ₉] ⁺ / 311 (19) [M] ⁺ / 115 (14) [C ₉ H ₇] ⁺ / 118 (10) [C ₉ H ₁₀] ⁺ / 44 (10) [C ₂ H ₆ N] ⁺
VIII	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 44 (8) [C ₂ H ₆ N] ⁺ / 277 (8) [M] ⁺ / 158 (2) [M - C ₂ F ₅] ⁺ / 248 (1) [M - C ₂ H ₅] ⁺ / 235 (1) [M - C ₃ H ₆] ⁺
IX	94 (100) [F ₂ BNH(CH ₃) ₂] ⁺ / 69 (27) [C ₅ H ₉] ⁺ / 44 (11) [C ₂ H ₆ N] ⁺ / 277 (11) [M] ⁺ / 262 (10) [M - CH ₃] ⁺ / 158 (2) [M - C ₂ F ₅] ⁺
X	92 (100) [F ₂ B(N=CH ₂)CH ₃] ⁺ / 158 (9) [M - C ₂ F ₅] ⁺ / 277 (1) [M] ⁺
XIb	92 (100) [F ₂ B(N=CH ₂)CH ₃] ⁺ / 57 (60) [C(CH ₃) ₃] ⁺ / 234 (2) [M - C(CH ₃) ₃] ⁺ / 276 (1) [M - CH ₃] ⁺
XII	92 (100) [F ₂ B(N=CH ₂)CH ₃] ⁺ / 91 (65) [C ₇ H ₇] ⁺ / 77 (25) [C ₆ H ₅] ⁺ / 178 (24) [M - C ₂ F ₅] ⁺ / 228 (3) [M - CF ₃] ⁺ / 297 (1) [M] ⁺
XIII	92 (100) [F ₂ B(N=CH ₂)CH ₃] ⁺ / 133 (52) [C ₁₀ H ₁₃] ⁺ / 220 (20) [M - C ₂ F ₅] ⁺ / 119 (14) [C ₉ H ₁₁] ⁺ / 270 (6) [M - CF ₃] ⁺ / 339 (1) [M] ⁺
XIV	92 (100) [F ₂ B(N=CH ₂)CH ₃] ⁺ / 73 (33) [Si(CH ₃) ₃] ⁺ / 123 (24) [C ₃ H ₅ BF ₃ N] ⁺ / 173 (12) [C ₄ H ₅ BF ₃ N] ⁺ / 293 (1) [M] ⁺
XV	92 (100) [F ₂ B(N=CH ₂)CH ₃] ⁺ / 115 (8) [Si(C ₂ H ₅) ₃] ⁺ / 123 (8) [C ₃ H ₅ BF ₃ N] ⁺ / 173 (2) [C ₄ H ₅ BF ₃ N] ⁺

TABLE 3. Characteristic IR absorptions for compounds **II–XV** (cm^{-1})^a

	$\nu(\text{N–H})$	$\nu(\text{C=N})$	$\nu(\text{C=C})$	$\nu(\text{C–F})$
II	3185 m		1618 m	1085 vs
III	3280 w		1644 w	1085 vs
IV	3176 w		1620 w	1095 vs
V	3220 m		1630/1610/1573w	1085 vs
VII	3220 m		1640/1600 w	1094 vs
VIII	3220 m		1595 w	1095 vs
IX	3320 w		1593 w	1085 vs
X		1670 vw		1095 vs
XIa	3318 m		1595 w	1095 vs
XIb		1670 w		1095 vs
XII		1660 w	1600 w	1097 vs
XIV		1670 w		1105/1085 vs
XV		1669 w		1106/1083 vs

^a KBr discs, $\pm 2 \text{ cm}^{-1}$

XIb–XV give a base peak at m/e 92, $[\text{F}_2\text{B}(\text{CH}_3)\text{N}=\text{CH}_2]^+$. Peaks of the molecular ion $[\text{M}]^+$ are of low intensity except for **V** and **VII**, and in some cases were not detected at all.

Some diagnostic infrared wavenumbers assigned to $\nu(\text{N–H})$, $\nu(\text{C=N})$, $\nu(\text{C=C})$ and $\nu(\text{C–F})$ are quoted in Table 3.

4. Experimental details

The compounds discussed here have the following systematic names: bis(trifluoromethyl)(2-methyl-2-propenyl)borane-dimethylamine (**I**); 1,1-di[bis(trifluoromethyl)boryl-dimethylamine]methyl-ethylene (**II**); bis(trifluoromethyl)(*trans*-2-ethyl-2-butenyl)borane-dimethylamine (**III**); bis(trifluoromethyl)(2-neopentyl-2-propenyl)borane-dimethylamine (**IV**); bis(trifluoromethyl)(2-phenyl-2-propenyl)borane-dimethylamine (**V**); bis(trifluoromethyl)[2-(4-methyl-1,3-pentadienyl)-methyl]-borane-dimethyl-amine (**VI**); bis(trifluoromethyl)(*trans*-3-phenyl-2-propenyl)borane-dimethylamine (**VII**); bis(trifluoromethyl)(*trans*-2-hexenyl)borane-dimethylamine (**VIII**); bis(trifluoromethyl)(4-methyl-*trans*-2-pentenyl)borane-dimethylamine (**IX**); bis(trifluoromethyl)(3-methylpentyl)borane-methylmethyleneimine (**X**); bis(trifluoromethyl)(2-*t*-butyl-2-propenyl)borane-dimethylamine (**XIa**); bis(trifluoromethyl)(2,3,3-trimethylbutyl)borane-methylmethyleneimine (**XIb**); bis(trifluoromethyl)(2-phenylethyl)boranemethylmethyleneimine (**XII**); bis(trifluoromethyl)[2-(2,4,6-trimethylphenyl)-ethyl]borane-methylmethyleneimine (**XIII**); bis(trifluoromethyl)(2-trimethylsilylethyl)borane-methylmethyleneimine (**XIV**) and bis(trifluoromethyl)(2-triethylsilylethyl)borane-methylmethyleneimine (**XV**).

4.1. General procedure for **I–VI**, **XIa/b**, **XIV**, and **XV**

To a stirred solution of 12 mmol of alkene in 20 ml of dry pentane, 2.0 g (10.4 mmol) of $(\text{CF}_3)_2\text{BNMe}_2$ was added dropwise at 4°C . The mixture was allowed to warm to room temperature and stirring continued for 3 h. The solvent and other volatile by-products were removed *in vacuo* at ambient temperature and the residue was purified by sublimation or distillation *in vacuo* as appropriate. The more volatile compound **I**, m.p. 71°C , was separated from **II**, m.p. 114°C , by fractional sublimation.

4.2. General procedure for **VII–X**, **XII**, and **XIII**

A mixture of 2.0 g (10.4 mmol) of $(\text{CF}_3)_2\text{BNMe}_2$ and 30 of mmol alkene were sealed in a glass ampoule and heated to 50°C for 4–7 d. Unchanged starting materials and other volatile by-products were distilled off *in vacuo* at ambient temperature and **VII–X**, **XII** and **XIII** were obtained from the dark tarry residue by sublimation *in vacuo*.

For yields see text; for elemental analyses see Table 4.

TABLE 4. Elemental analyses

Compound	Formula	Analyses (Found (calc.) %)		
		C	H	F
I	$\text{C}_8\text{H}_{14}\text{BF}_6\text{N}$	38.21 (38.60)	5.60 (5.67)	46.20 (45.80)
II	$\text{C}_{12}\text{H}_{20}\text{B}_2\text{F}_{12}\text{N}_2$	32.89 (32.62)	4.55 (4.56)	51.60 (51.59)
III	$\text{C}_{10}\text{H}_{18}\text{BF}_6\text{N}$	43.18 (43.35)	6.49 (6.55)	40.63 (41.15)
IV	$\text{C}_{12}\text{H}_{22}\text{BF}_6\text{N}$	46.67 (47.24)	7.06 (7.27)	37.01 (37.36)
V	$\text{C}_{13}\text{H}_{16}\text{BF}_6\text{N}$	49.62 (50.03)	5.34 (5.49)	35.98 (36.53)
VI	$\text{C}_{11}\text{H}_{18}\text{BF}_6\text{N}$	45.20 (45.71)	5.99 (6.28)	38.88 (39.43)
VII	$\text{C}_{13}\text{H}_{16}\text{BF}_6\text{N}$	49.44 (50.03)	5.27 (5.49)	36.22 (36.53)
VIII	$\text{C}_{10}\text{H}_{18}\text{BF}_6\text{N}$	42.98 (43.35)	6.33 (6.55)	40.39 (41.15)
IX	$\text{C}_{10}\text{H}_{18}\text{BF}_6\text{N}$	43.57 (43.35)	6.61 (6.55)	41.40 (41.15)
X	$\text{C}_{10}\text{H}_{18}\text{BF}_6\text{N}$	42.99 (43.35)	6.42 (6.55)	40.65 (41.15)
XIa/b	$\text{C}_{11}\text{H}_{20}\text{BF}_6\text{N}$	45.10 (45.39)	6.87 (6.93)	38.61 (39.16)
XII	$\text{C}_{12}\text{H}_{14}\text{BF}_6\text{N}$	47.67 (48.36)	4.94 (5.07)	37.38 (38.25)
XIII	$\text{C}_{15}\text{H}_{20}\text{BF}_6\text{N}$	53.29 (53.13)	5.97 (5.94)	33.41 (33.62)
XIV	$\text{C}_9\text{H}_{18}\text{BF}_6\text{NSi}$	36.80 (36.89)	6.13 (6.19)	38.69 (38.90)
XV	$\text{C}_{12}\text{H}_{24}\text{BF}_6\text{NSi}$	42.79 (43.01)	7.12 (7.22)	33.76 (34.02)

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