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Alkylation of dimethylaminobis(trifluoromethyl)borane by 1-alkenes

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Abstract

Dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (**A**), undergoes B-alkylation on treatment with 1-alkenes of the general formula $(R^1CH_2)(R^2)C{=}CH_2$ to yield triorganoboron adducts $Me_2(H)N{-}B(CF_3)_2CH_2(R^2)C{=}CHR^1$ ($R^1 = H$, $R^2 = Me$ (**I**); $R^1 = H$, $R^2 = CH_2(CF_3)_2B{-}NHMe_2$ (**II**); $R^1 = Me$, $R^2 = Et$ (**III**); $R^1 = H$, $R^2 = CH_2(^tBu)$ (**IV**); $R^1 = H$, $R^2 = Ph$ (**V**); $R^1 = H$, $R^2 = CH{=}CMe_2$ (**VI**); $R^1 = Ph$, $R^2 = H$ (**VII**); $R^1 = {}^nPr$, $R^2 = H$ (**VIII**); $R^1 = {}^iPr$, $R^2 = H$ (**IX**)). In contrast, monosubstituted ethene derivatives $(R^2)CH{=}CH_2$ ($R = {}^sBu$, Ph, Mes, Me_3Si, Et_3Si) react with **A** to form the corresponding methylmethyleneimine boron adducts $H_2C{=}N(Me){-}B(CF_3)_2CH_2CH_2R^2$ (**X**, **XII–XV**).

With $(^tBu)(Me)C{=}CH_2$, **A** undergoes both types of reaction, yielding a 1/4 mixture of $Me_2(H)N{-}B(CF_3)_2CH_2(^tBu)C{=}CH_2$ (**XIa**) and $H_2C{=}N(Me){-}B(CF_3)_2CH_2CH(Me)(^tBu)$ (**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.

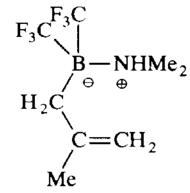
1. Introduction

Bis(trifluoromethyl)dimethylaminoborane, $(CF_3)_2BNMe_2$ (**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 $R^2C(O)CH_2R^1$ [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 $(R^1CH_2)(R^2)C{=}CH_2$ (R^1, $R^2 = H$, alkyl, aryl) and $(R^2)HC{=}CH_2$ ($R^2 =$ alkyl) in a systematic fashion, and the results of this investigation are presented below.

2. Results

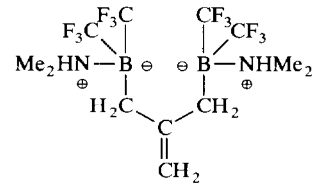
Isobutylene is known to undergo ene reactions with silaneimines [4]. We have found that it reacts similarly with **A** even at −10°C. Under these conditions a 5:83 mixture of the 1:1 adduct **I** and the 1:2 product **II** is obtained according to eqn. (1). The high yield of **II** indicates that **I**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

$$A + H_2C{=}CMe_2 \longrightarrow$$



(**I**) 5%

+



(**II**) 83%

(1)

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

2-Ethyl-1-butene, $Et_2C{=}CH_2$, reacts analogously at 0°C to give the *E*-isomer **III**, and 2,4,4-trimethyl-1-pentene, $(^tBuCH_2)(Me)C{=}CH_2$, yields **IV**, the proton being abstracted almost exclusively from the 2-methyl group. Compound **V** is formed analogously from **A** and methylstyrene, $(Ph)(Me)C{=}CH_2$. Alkenes with a *β*-carbon atom bearing a hydrogen atom and an alkyl group (i.e. $H_2C{=}CHCH_2R^1$) react less readily, and reaction times of to 4 days at temperatures of 50°C are

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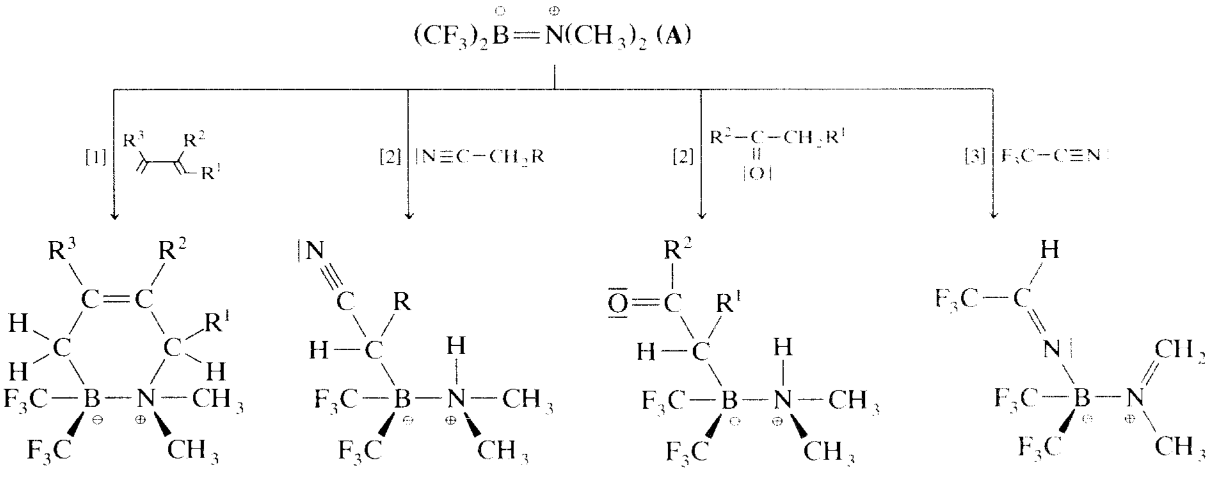
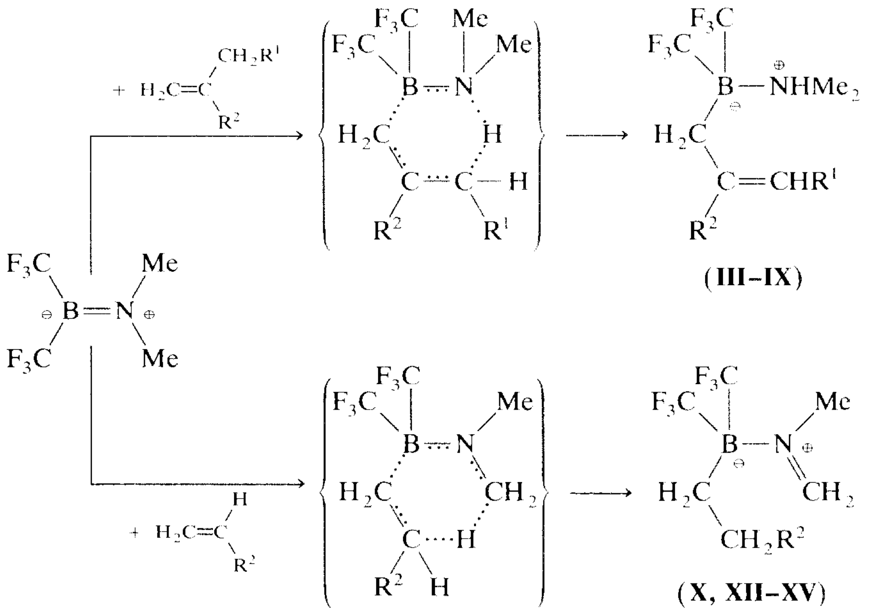


Scheme 1.

required to produce substantial yields of **VII–IX**. Bulky substituents attached to the β-carbon atom of 1-alkenes, as *e.g.* in H_2C=CHC*H*MeEt, 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 $H_2C=CHR^2$, R^2 = Ph (**XII**), Mes (**XIII**), Me_3Si (**XIV**), and Et_3Si (**XV**). The reaction of **A** with $CH_2=CH(^tBu)$ has already been reported [3].

The reaction of $H_2C=C(CH_3)(^tBu)$ 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)).



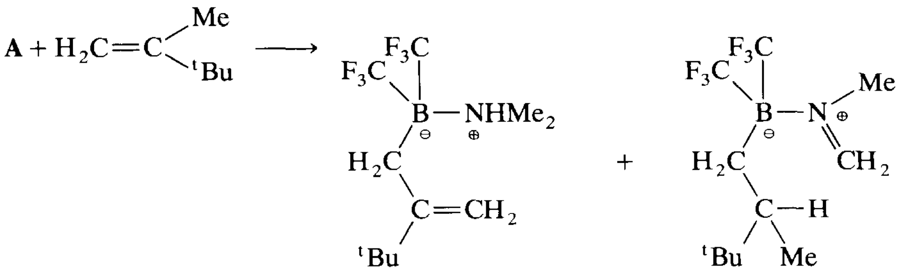
	R^1	R^2	%
III	Me	Et	92
IV	H	$CH_2{}^tBu$	83
V	H	Ph	90
VI	H	$CH=CMe_2$	40
VII	Ph	H	79
VIII	^nPr	H	60
IX	^iPr	H	68
X		^sBu	57
XII		Ph	12
XIII		Mes	19
XIV		$SiMe_3$	89
XV		$SiEt_3$	81

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																
$\delta(NCH_3)$	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
$\delta(BCH_2)$	1.57	1.62	1.51	1.62	2.08	1.63	1.78	1.49	1.48	0.61 0.71	1.59	0.98 1.04	1.13 1.17	0.88 0.91	0.66 0.70	0.67 0.70
$\delta(=CCH_3)$	1.75		1.62			1.80 1.83										
$\delta(=CH_n)$	4.61 4.64	4.59	5.01	4.60 4.79	5.07	4.78 4.95 5.68	6.40 6.45	5.38 5.52	5.38 5.47		4.72 4.96					
$\delta(CCH_2)$			2.07	1.98				1.36 1.99		1.0 1.5			2.60 2.73	2.58 2.64	0.22 0.27	0.24 0.29
$\delta(CCH_3)$			1.04	0.92				0.89	0.98	0.86 0.87	0.86	0.73 0.85		2.29 2.33		0.94
$\delta(CHC_2)$									2.28	2.04		1.40				
$\delta(SiCH_n)$															−0.01	0.53
$\delta(C_6H_5)$					7.18 7.43		7.23 7.44						7.22 7.38	6.88		
$\delta(N{=}CH_2)$										7.66 7.74		7.71 7.84	7.59 7.65	7.71 7.81	7.62 7.74	7.65 7.75
$\delta(NH)$	~5.65	~5.60	~4.25	~5.57	~5.60	~4.35	~4.0	~3.95	~3.95		~4.0					
^{19}F																
$\delta(CF_3)$	−67.0	−61.9	−62.1	−61.8	−61.8	−62.0	−62.5	−62.5	−62.4	−64.7	−63.8	−61.6 −65.7	−64.5	−64.5	−64.3	−64.5
^{11}B																
$\delta(B)$	−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																
$\delta(NCH_3)$	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
$\delta(BCH_2)$	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
$\delta(CCH_3)$	25.0		13.1 12.6	31.0		19.4 26.3		13.5 22.9	22.7	11.3 18.7	26.9	16.3 27.0		20.7 23.5		7.4
$\delta(CCH_2)$			24.1	32.8				34.8		28.9 30.3		29.3	30.2	40.2		
$\delta(SiCH_n)$															9.0 −2.3	2.8 3.0
$\delta(CC_3)$				52.1					31.1	37.0	29.4	34.0				
$\delta(N{=}CH_2)$										167.0		166.4	167.4	167.0	166.9	166.7
$\delta(C{=}CH_n)$	146.2	150.9	144.1	149.1	149.6	135.8 144.8					158.1					
$\delta(C{=}CH_n)$	110.9	108.5	116.4	113.2	113.9	113.0 127.8	125.6 129.9	127.7 131.6	124.6 139.0		105.9					
$\delta(C_6H_5)$					127.7 128.0 128.9 145.0		125.8 126.9 128.6 137.6						125.6 127.9 128.4 145.2	128.6 128.9 134.6 138.8		

[a] **I, II, IV** and **V** in $(CD_3)_2CO$; **III** and **VI–XV** in $CDCl_3$; ^{1}H: 250.13 MHz, int. std. $CHCl_3 = 7.27$ ppm/$CD_3COCD_2H = 2.05$ ppm. ^{13}C: 62.9 MHz, int. std. $CDCl_3 = 77.0$ ppm/$(CD_3)_2CO = 29.8$ ppm. ^{19}F: 84.67 MHz, int. std. $CFCl_3$. ^{11}B: 25.52 MHz, ext. std. $BF_3 \cdot OEt_2$.



(XIa) 20% **(XIb)** 80%

(2)

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 $=CH_2$ group. The observation that $CH_2=CH(CHClMe)$ 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 $CH_2=CH^tBu$ were allowed to react on a 0.1 molar scale and the products subsequently hydrolyzed according to eqn. (3), we obtained not only $^tBuCH_2CH_2(CF_3)_2B-NH_2Me$ but also up to 4% of $^tBuCH_2CH_2(CF_3)_2B-NHMe_2$. 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 methylmethyleneimino group readily undergo hydrolysis to give the corresponding methylamine adducts (eqn. (3)).

$$(CF_3)_2(R)B-N(CH_3)=CH_2 \xrightarrow{H_2O} (CF_3)_2(R)B-NH_2CH_3 + OCH_2 \quad (3)$$

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, $(CF_3)_2BR$, are unstable with respect to exothermal decomposition into the corresponding difluoroboranes, F_2BR, and difluorocarbene. This degradation pathway obviously becomes more important in complexes of borane with $N(CH_3)=CH_2$, which are more susceptible to thermal decomposition than are those of the basic secondary amine $NH(CH_3)_2$.

The ^1H, ^{19}F, ^{11}B and ^{13}C 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.* $\delta(^{11}B)$ 8–9 ppm *vs.* 5–6 ppm, respectively). Characteristic features of **X** and **XIb–XV** are the AB spin system of the $N=CH_2$ 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 ^{13}C spectrum that is assigned to the $N=CH_2$ 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 $[F_2BNH(CH_3)_2]^+$ while **X** and

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

II	94 (100) $[F_2BNH(CH_3)_2]^+$/ 74 (9) $[FBN(CH_3)_2]^+$/ 44 (8) $[C_2H_6N]^+$/ 249 (4) $[M]^+$ (I)/ 442 (1) $[M]^+$
III	94 (100) $[F_2BNH(CH_3)_2]^+$/ 55 (11) $[C_4H_7]^+$/ 277 (8) $[M]^+$/ 84 (7) $[C_6H_{12}]^+$/ 44 (5) $[C_2H_6N]^+$/ 74 (3) $[FBN(CH_3)_2]^+$/ 158 (1) $[M - C_2F_5]^+$
IV	94 (100) $[F_2BNH(CH_3)_2]^+$/ 249 (31) $[M - (CH_3)_2C=CH_2]^+$/ 57 (25) $[C(CH_3)_3]^+$/ 290 (5) $[M - CH_3]^+$/ 44 (3) $[C_2H_6N]^+$
V	94 (100) $[F_2BNH(CH_3)_2]^+$/ 311 (17) $[M]^+$/ 44 (11) $[C_2H_6N]^+$/ 118 (10) $[C_9H_{10}]$/ 115 (6) $[C_9H_7]^+$/ 117 (5) $[C_9H_8]^+$
VI	94 (100) $[F_2BNH(CH_3)_2]^+$/ 55 (37) $[C_4H_7]^+$/ 96 (22) $[C_7H_{12}]^+$/ 69 (18) $[C_5H_9]^+$/ 170 (12) $[M - C_2F_5]^+$/ 274 (5) $[M - CH_3]^+$/ 289 (2) $[M]^+$
VII	94 (100) $[F_2BNH(CH_3)_2]^+$/ 117 (70) $[C_9H_9]^+$/ 311 (19) $[M]^+$/ 115 (14) $[C_9H_7]^+$/ 118 (10) $[C_9H_{10}]^+$/ 44 (10) $[C_2H_6N]^+$
VIII	94 (100) $[F_2BNH(CH_3)_2]^+$/ 44 (8) $[C_2H_6N]^+$/ 277 (8) $[M]^+$/ 158 (2) $[M - C_2F_5]^+$/ 248 (1) $[M - C_2H_5)^+$/ 235 (1) $[M - C_3H_6]^+$
IX	94 (100) $[F_2BNH(CH_3)_2]^+$/ 69 (27) $[C_5H_9]^+$/ 44 (11) $[C_2H_6N]^+$/ 277 (11) $[M]^+$/ 262 (10) $[M - CH_3]^+$/ 158 (2) $[M - C_2F_5]^+$
X	92 (100) $[F_2B(N=CH_2)CH_3]^+$/ 158 (9) $[M - C_2F_5]^+$/ 277 (1) $[M]^+$
XIb	92 (100) $[F_2B(N=CH_2)CH_3]^+$/ 57 (60) $[C(CH_3)_3]^+$/ 234 (2) $[M - C(CH_3)_3]^+$/ 276 (1) $[M - CH_3]^+$
XII	92 (100) $[F_2B(N=CH_2)CH_3]^+$/ 91 (65) $[C_7H_7]^+$/ 77 (25) $[C_6H_5]^+$/ 178 (24) $[M - C_2F_5]^+$/ 228 (3) $[M - CF_3]^+$/ 297 (1) $[M]^+$
XIII	92 (100) $[F_2B(N=CH_2)CH_3]^+$/ 133 (52) $[C_{10}H_{13}]^+$/ 220 (20) $[M - C_2F_5]^+$/ 119 (14) $[C_9H_{11}]^+$/ 270 (6) $[M - CF_3]^+$/ 339 (1) $[M]^+$
XIV	92 (100) $[F_2B(N=CH_2)CH_3]^+$/ 73 (33) $[Si(CH_3)_3]^+$/ 123 (24) $[C_3H_5BF_3N]^+$/ 173 (12) $[C_4H_5BF_5N]^+$/ 293 (1) $[M]^+$
XV	92 (100) $[F_2B(N=CH_2)CH_3]^+$/ 115 (8) $[Si(C_2H_5)_3]^+$/ 123 (8) $[C_3H_5BF_3N]^+$/ 173 (2) $[C_4H_5BF_5N]^+$

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

	ν(N–H)	ν(C=N)	ν(C=C)	ν(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, ±2 cm^{-1}

XIb–XV give a base peak at *m/e* 92, $[F_2B(CH_3)\text{-}N{=}CH_2]^+$. Peaks of the molecular ion $[M]^+$ are of low intensity except for **V** and **VII**, and in some cases were not detected at all.

Some diagnostic infrared wavenumbers assigned to ν(N–H), ν(C=N), ν(C=C) and ν(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 $(CF_3)_2BNMe_2$ 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 $(CF_3)_2BNMe_2$ 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	$C_8H_{14}BF_6N$	38.21	5.60	46.20
		(38.60)	(5.67)	(45.80)
II	$C_{12}H_{20}B_2F_{12}N_2$	32.89	4.55	51.60
		(32.62)	(4.56)	(51.59)
III	$C_{10}H_{18}BF_6N$	43.18	6.49	40.63
		(43.35)	(6.55)	(41.15)
IV	$C_{12}H_{22}BF_6N$	46.67	7.06	37.01
		(47.24)	(7.27)	(37.36)
V	$C_{13}H_{16}BF_6N$	49.62	5.34	35.98
		(50.03)	(5.49)	(36.53)
VI	$C_{11}H_{18}BF_6N$	45.20	5.99	38.88
		(45.71)	(6.28)	(39.43)
VII	$C_{13}H_{16}BF_6N$	49.44	5.27	36.22
		(50.03)	(5.49)	(36.53)
VIII	$C_{10}H_{18}BF_6N$	42.98	6.33	40.39
		(43.35)	(6.55)	(41.15)
IX	$C_{10}H_{18}BF_6N$	43.57	6.61	41.40
		(43.35)	(6.55)	(41.15)
X	$C_{10}H_{18}BF_6N$	42.99	6.42	40.65
		(43.35)	(6.55)	(41.15)
XIa/b	$C_{11}H_{20}BF_6N$	45.10	6.87	38.61
		(45.39)	(6.93)	(39.16)
XII	$C_{12}H_{14}BF_6N$	47.67	4.94	37.38
		(48.36)	(5.07)	(38.25)
XIII	$C_{15}H_{20}BF_6N$	53.29	5.97	33.41
		(53.13)	(5.94)	(33.62)
XIV	$C_9H_{18}BF_6NSi$	36.80	6.13	38.69
		(36.89)	(6.19)	(38.90)
XV	$C_{12}H_{24}BF_6NSi$	42.79	7.12	33.76
		(43.01)	(7.22)	(34.02)

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