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B–C bond formation by ene-type reactions of dimethylaminobis(trifluoromethyl)borane with nitriles and carbonyl compounds. Crystal structure of $(NCCH_2)(CF_3)_2B \cdot NHMe_2$ *

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Abstract

Dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (A), reacts with nitriles $RCH_2{-}C{\equiv}N|$ to yield triorganoboron adducts $(|N{\equiv}C{-}CHR)(CF_3)_2B \cdot NHMe_2$ (R = H (I), Cl (II), Me (III) and Et (IV)). Analogously carbonyl compounds of the general formula $R^2{-}C(O){-}CH_2R^1$ form the respective complexes $(R^2{-}C(O){-}CHR^1)(CF_3)_2B \cdot NHMe_2$: $R^1 = H$, $R^2 = {}^tBu$ (V), $R^1 = H$, $R^2 = Ph$ (VI), $R^1 = H$, $R^2 = C{=}CH{-}CH{=}C(Me){-}O$ (VII), $R^1 = H$, $R^2 = Me$ (VIII), $R^1 = H$, $R^2 = CH{=}CMe_2$ (IX), $R^1 = H$, $R^2 = OMe$ (X), $R^1 = H$, $R^2 = O^tBu$ (XI), $R^1 = H$, $R^2 = OSiMe_3$ (XII), $R^1 = H$, $R^2 = OC(Me){=}CH_2$ (XIII), $R^1 = H$, $R^2 = OCH_2CH{=}CH_2$ (XIV), $R^1 = H$, $R^2 = NMe_2$ (XV), $R^1 = Me$, $R^2 = NMe_2$ (XVI), $R^1 = H$, $R^2 = NEt_2$ (XVII), $R^1 = Cl$, $R^2 = OEt$ (XVIII), $R^1 = Me$, $R^2 = OMe$ (XIX), $R^1 = Et$, $R^2 = OMe$ (XX), $R^1 = C(O)OMe$, $R^2 = OMe$ (XXI), $R^1 = C(O)O^tBu$, $R^2 = O^tBu$ (XXII), R^1, $R^2 = CH_2OCH_2$ (XXIII). Their identities have been confirmed by multinuclear NMR, IR, and mass spectroscopy. The crystal and molecular structure of I has been determined by an X-ray diffraction study. Individual molecules are linked to form infinite chains through hydrogen bonding. The B–C (1.627(3) Å $(B{-}CF_3)$ and 1.629(4) Å $(B{-}CH_2CN)$) and B–N bond lengths (1.600(3) Å) are normal.

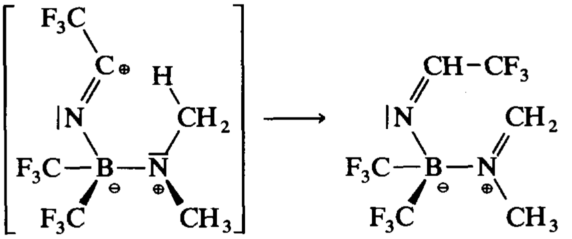
1. Introduction

The multiple boron–nitrogen bonding in aminobis(trifluoromethyl)boranes has important consequences for the structures and reactivities of these compounds. Thus the structures of $(CF_3)_2BNMe_2$ (A) [1] and $(CF_3)_2BN(^iPr)_2$ [2] are characterized by short B–N separations and coplanarity of the bonds extending from the boron and nitrogen atoms.

Furthermore, these aminoboranes resemble olefins in their reactions with 1,3-dienes, [2 + 4] cycloadducts being formed [3]. They also combine with isocyanates and isothiocyanates to yield [2 + 2] cycloaddition products [4]. The latter products as well as those obtained by reaction with polar 1,3-dienes demonstrate the electrophilic nature of the boron atom; that is, the central linkage of the aminoboranes is polarized $\overset{\delta+\,\delta-}{B{=}N}$.

The polar nature of this bond was also indicated by reactions involving hydroboration by A of some alkynes, alkenes, ketones and nitriles. In these reactions the nucleophilic substrates apparently coordinate to the boron atom before they abstract a hydride from the dimethylamino group [5]. The proposed reaction sequence is illustrated in eqns. (1) and (2) for a nitrile and ketone, respectively.

$$|N{\equiv}CCF_3 + (CF_3)_2B{-}\overline{N}(CH_3)_2 \longrightarrow$$



(1)

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* Dedicated to Professor Ulrich Wannagat on the occasion of his 70th birthday.

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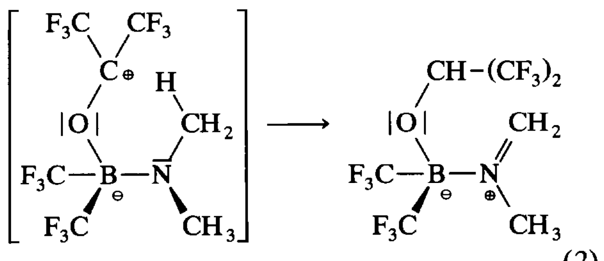
$\overline{\underline{O}}{=}C(CF_3)_2 + (CF_3)_2B{-}\overline{N}(CH_3)_2 \longrightarrow$



(2)

The reaction in eqn. (1) contrasts sharply with that of boron trihalides with acetonitrile, which yields classical Lewis acid/base complexes, $X_3\overset{\ominus}{B}{-}\overset{\oplus}{N}{\equiv}CCH_3$, at low temperature [6]. That the analogous acetonitrile complex, $(CF_3)_3\overset{\ominus}{B}{-}\overset{\oplus}{N}{\equiv}CCH_3$, which was recently obtained by dehydration of the acetamide adduct with P_4O_{10} [7], exhibits even greater thermal stability proves that CF_3 groups do not destabilize the boron–acetonitrile link. Thus we have extended our studies of the reaction of A with nitriles and carbonyls.

The substrates studied in the present work differ from those examined previously [5] in that hydrogen atoms are present in the α-position with respect to the functional group. This subtle difference changes the course of reaction with A, and we report below on observations which reveal the occurrence of a new type of reaction involving formation of a boron–carbon bond.

2. Reactions of $(CF_3)_2BNMe_2$ with nitriles

When CH_3CN was added to a solution of A in pentane, a solid separated that showed physical, chemical and spectroscopic properties which were not those expected for a Lewis acid/base complex. The precipitate had the composition of a 1:1 adduct, sublimed at 60°C and 10^{-1} torr, and was not sensitive towards air or moisture. The ^1H NMR spectrum confirmed the presence of a $NHMe_2$ group while the ^{13}C spectrum suggested that it contained a carbon atom directly bonded both to boron and to the cyano group. The only formulation in agreement with these observations is $(|N{\equiv}C{-}CH_2)(CF_3)_2B \cdot NHMe_2$ (**I**). The structure was later confirmed by a single crystal X-ray study (see later). Other nitriles carrying two α hydrogen atoms reacted analogously (eqn. (3)), and yields were almost quantitative.

$$|N{\equiv}C{-}CH_2R + \underset{\textbf{(A)}}{(CF_3)_2BNMe_2} \longrightarrow \underset{\textbf{(I–IV)}}{(|N{\equiv}C{-}CHR)(CF_3)_2B \cdot NHMe_2} \quad (3)$$

	I	II	III	IV
R	H	Cl	Me	Et
Yield (%)	88	80	86	91

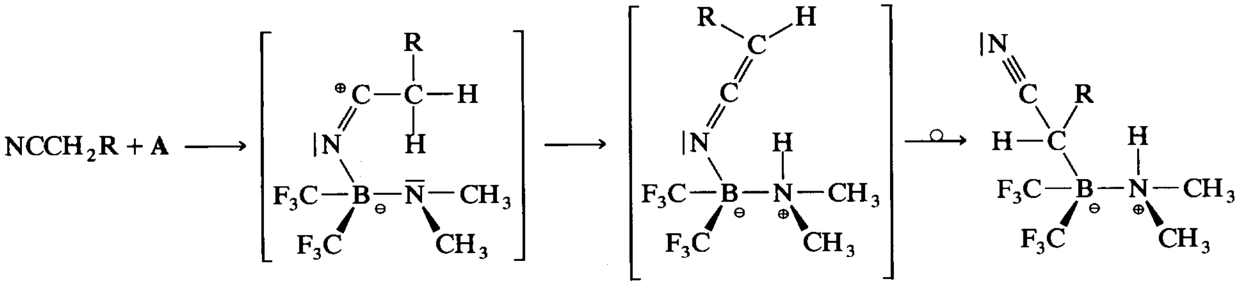
Whereas CH_2ClCN reacts with A in a selective fashion, $CHBr_2CN$ yields a tar-like material in which traces of $(|N{\equiv}C{-}CBr_2)(CF_3)_2B \cdot NHMe_2$ were detected by mass spectroscopy: *m/e*; 392(1%)$[M]^+$/273 (4%) $[M-C_2F_5]^+$/193 (7%) $[M-C_2F_5-Br]^+$/94 (100%) $[F_2BNH(CH_3)_2]^+$.

We assume that reaction (3) proceeds in successive steps (Scheme 1). The first step involves boron–nitrogen complex formation in a process analogous to that in eqn. (1). This complexation leads to an increase in the acidity of the α-hydrogen atoms of the nitrile, and one of these protons is then transferred to the basic centre. In a final step the aza-allene derivative rearranges to yield the ene-type reaction product.

3. Reactions of $(CF_3)_2BNMe_2$ with carbonyl compounds

An analogous reaction was observed when A was treated with carbonyl compounds of the general formula $R^2{-}C(O){-}CH_2R^1$, with R^1 = H, Cl, alkyl and R^2 = alkyl, alkoxy and dialkylamino. Yields were almost quantitative. The reaction proceeds as suggested by Scheme 2, the first intermediate being the same as that proposed in eqn. (2).

The rearrangement of the enol intermediate of the above-mentioned carbonyl derivatives is too rapid to be



Scheme 1.

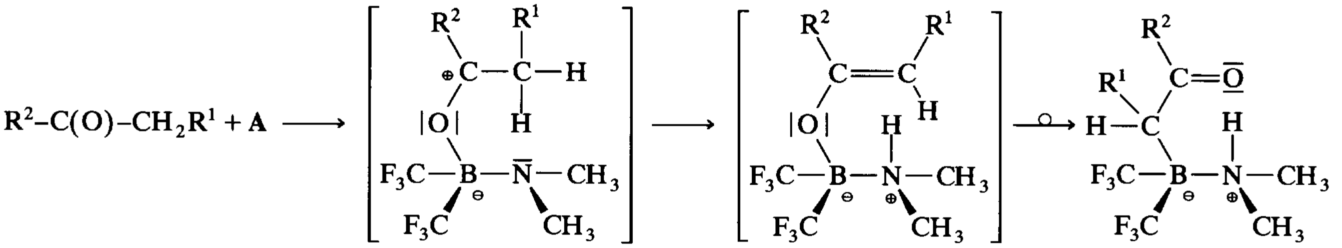
detected by NMR spectroscopy. With $Et_2C{=}O$, however, the rearrangement is inhibited, and the formation of the corresponding enol product, $(EtC(=CHMe)O)(CF_3)_2B \cdot NHMe_2$, is suggested by NMR spectra: ^{1}H: δ $C{=}CHCH_3$ 4.64 ppm, q; δ $C{=}CHCH_3$ 1.53 ppm, d; ^{13}C: δ $C{=}CHCH_3$ 153.7 ppm; δ $C{=}CHCH_3$ 98.6 ppm.

4. Properties and spectra

All the compounds **I–XXIII** are colourless solids, the melting points of which are listed in Table 1. They are not sensitive towards air or moisture and are soluble in polar organic solvents.

The ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **I–XXIII** were recorded. The data, which are set out in Table 1, are consistent with the proposed structures, and only a few comments are necessary. The NCH_3 and BCF_3 groups in **II, III, IV, XVI, XVIII, XIX, XX** and **XXIII** are magnetically non-equivalent and thus give rise to pairs of ^{1}H, ^{13}C and ^{19}F signals. However this splitting is not consistently observed for all three nuclei because of line broadening. The ^{1}H resonance of the NMe_2 group appears as a doublet with $^3J(HH)$ *ca.* 5.7 Hz, while the corresponding carbon atoms show a small $^4J(CF)$ coupling of 1.5–2.0 Hz. This small coupling is of high diagnostic value because the ^{13}C resonances of the CF_3 groups are hardly detectable. All other carbon atoms directly linked to boron give rise to broad signals.

The EI mass spectral data are listed in Table 2. Compound **I** gives a $[M + H]^+$ fragment as well as other ions with $m/e > 234$ rather than a $[M]^+$ fragment. This indicates association of I in the vapour phase. A characteristic fragment from all compounds is the ion at m/e 94, $[F_2BNH(CH_3)_2]^+$, which is frequently the base peak. The $[M]^+$ peaks of **V–IX** show relative intensities of 3–10% while the fragmentation pattern is dominated by the alkyl group. The amide derivatives **XV–XVII** reveal quite intense $[M]^+$ peaks with 14–24% relative intensity. A diagnostic ion for



	R¹	R²	Yield (%)
V	H	ᵗBu	88
VI	H	Ph	94
VII	H	C=CH-CH=C(Me)-O	98
VIII	H	Me	71
IX	H	CH=CMe$_2$	82
X	H	OMe	90
XI	H	OᵗBu	81
XII	H	OSiMe$_3$	95
XIII	H	OC(Me)=CH$_2$	93
XIV	H	OCH$_2$CH=CH$_2$	90
XV	H	NMe$_2$	96
XVI	Me	NMe$_2$	98
XVII	H	NEt$_2$	89
XVIII	Cl	OEt	98
XIX	Me	OMe	94
XX	Et	OMe	92
XXI	C(O)OMe	OMe	97
XXII	C(O)OᵗBu	OᵗBu	93
XXIII	-CH$_2$-	-OCH$_2$-	99

Scheme 2.

TABLE 1. Physical properties and NMR spectral data for I–XXIII (δ in ppm)[a]

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX	XXI	XXII	XXIII
M.p.(°C)	144	142	125	119	75	96	135	83	86	45	130	125	77		94	71	71	81	48	66	79	67	137
^{1}H																							
$\delta(\mathrm{NC}H_3)$	2.88	2.93 3.00	2.88	2.88	2.74	2.83	2.84	2.76	2.79	2.78	2.78	2.77	2.74	2.75	2.65 2.86 3.01	2.65 2.79 2.88 3.06	2.69 3.32 3.38	2.89 2.96	2.78 2.81	2.80	2.85	2.83	2.76 2.84
$\delta(\mathrm{BC}H_n)$	1.74	4.58	2.22	2.04	1.96	2.49	2.26	2.01	1.97	1.79	1.71	1.80	1.87	1.84	1.65	1.95	1.70	4.10	2.00	1.79	3.45	3.21	2.13
$\delta(\mathrm{CC}H_3)$			1.30	1.12	1.13		2.39	2.24	1.91 2.11		1.43		1.88			1.23	1.05 1.15	1.30	1.21	0.94		1.42	
$\delta(=\mathrm{C}H)$							6.18 7.22		6.19				4.62 4.72	5.94 5.32 5.22									
$\delta(\mathrm{CC}H_2)$				1.52 1.65										4.56				4.22		1.54 1.85			2.48 2.35
$\delta(\mathrm{OC}H_3)$										3.62									3.70	3.71	3.69		4.31 4.42
$\delta(\mathrm{SiC}H_3)$												0.26											
$\delta(\mathrm{C}_6H_5)$						7.48 7.56 7.99								7.48 7.56 7.99									
$\delta(\mathrm{N}H)$	~6.6	~6.6	~6.4	~6.4	~7.2	~6.8	~6.7	~6.2	~6.8	~6.1	~6.4	~6.3	~5.6	~5.8	~8.0	~8.4	~8.3	~5.8	~6.5	~6.2	~7.0	~7.4	~6.5
^{19}F																							
$\delta(\mathrm{C}F_3)$	−63.2	−61.6 −62.5	−61.2 −61.8	−60.9 −61.6	−63.7	−63.2	−63.8	−63.4	−63.8	−63.5	−63.6	−63.5	−62.5	−63.0	−63.6	−59.0 −61.8	−62.6	−62.2	−61.9 −62.4	−61.6 −62.2	−62.6	−61.9	−61.4 −62.2
^{11}B																							
$\delta(B)$	−10.1	−9.2	−9.5	−9.1	−8.5	−8.2	−8.2	−8.8	−8.7	−8.4	−9.2	−8.5	−8.7	−8.7	−8.4	−8.7	−8.6	−8.4	−7.6	−7.5	−8.4	−8.3	−8.3

^{13}C																							
$\delta(NCH_3)$	40.9	40.8 41.3	41.0	40.8	39.6	39.8	39.9	39.8	39.7	39.9	39.8	39.7	40.8	40.8	35.2 38.0 39.1	35.8 38.1 41.3 41.8	39.8 41.1 43.7	40.9 41.3	40.3 39.7	39.9 40.4	41.1	40.9	40.0 40.7
$\delta(BCH_n)$	~ 2	~ 32	~ 11	~ 20	~ 22	~ 24	~ 24	~ 31	~ 30	~ 21	~ 22	~ 22	~ 22	~ 22	~ 17	~ 22	~ 19	~ 46	~ 28	~ 38	~ 42	~ 44	~ 28
$\delta(CCH_3)$			13.7	14.3	26.1		14.0	33.2	20.7 27.8		27.9		19.5			15.4	13.2 14.4	13.7	10.3	15.8		27.6	
$\delta(CCH_2)$				21.0										65.9				62.5		18.7			23.6
$\delta(CC_3)$					45.8						81.3											82.0	
$\delta(OCH_3)$										51.8									52.3	52.0	52.7		69.3
$\delta(SiC)$												−0.6											
$\delta(C{\equiv}N)$	120.6	118.9	124.0	123.2																			
$\delta(C{=}O)$					225.4	208.6	194.1	218.7	208.8	178.0	177.5	178.9	174.8	176.5	176.7	181.9	176.4	173.3	181.0	180.6	172.6	171.8	184.9
$\delta(C{=}CC)$							151.5 159.1		156.7				154.6	133.8									
$\delta(C{=}CH)$							109.4 122.0		126.2				102.6	118.2									
$\delta(C_6H_5)$						128.5 128.6 133.5 137.8																	

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[a] **I–IV** in $(CD_3)_2CO$; **V–XV** and **XVII–XXIIII** in $CDCl_3$; **XVI–XVII** in CD_3CN. ^1H: 250.13 MHz, int. std. $CHCl_3 = 7.27$ ppm/$CD_3COCD_2H = 2.05$ ppm/$CHD_2CN = 1.95$ ppm. ^{13}C: 62.9 MHz, int. std. $CDCl_3 = 77.0$ ppm/$(CD_3)_2CO = 29.8$ ppm/$CD_3CN = 1.30$ ppm. ^{19}F: 84.67 MHz, int. std. $CFCl_3$. ^{11}B: 25.52 MHz, ext. std. $BF_3 \cdot OEt_2$.

TABLE 2. EI mass spectral data for **I–XXIII**: $m/e(\%)$ [assignment]$^+$

I	94 (100) $[F_2BNH(CH_3)_2]^+$/74 (41) $[FBN(CH_3)_2]^+$/115 (32) $[M-C_2F_5]^+$/44 (20) $[C_2H_6N]^+$/35 (2) $[M+H]^+$
II	94 (100) $[F_2BNH(CH_3)_2]^+$/44 (16) $[C_2H_6N]^+$/149 (15) $[M-C_2F_5]^+$/74 (14) $[FBN(CH_3)_2]^+$
III	94 (100) $[F_2BNH(CH_3)_2]^+$/129 (14) $[M-C_2F_5]^+$/74 (13) $[FBN(CH_3)_2]^+$/44 (10) $[C_2H_6N]^+$
IV	94 (100) $[F_2BNH(CH_3)_2]^+$/247 (22) $[M-CH_3]^+$/44 (17) $[C_2H_6N]^+$/143 (13) $[M-C_2F_5]^+$
V	94 (100) $[F_2BNH(CH_3)_2]^+$/236 (93) $[M-C(CH_3)_3]^+$/57 (25) $[C(CH_3)_3]^+$/174 (6) $[M-C_2F_5]^+$/293 (3) $[M]^+$
VI	105 (100) $[C_6H_5CO]^+$/120 (25) $[C_6H_5COCH_3]^+$/94 (15) $[F_2BNH(CH_3)_2]^+$/77 (15) $[C_6H_5]^+$/194 (6) $[M-C_2F_5]^+$/313 (4) $[M]^+$
VII	124 (100) $[C_7H_8O_2]^+$/109 (60) $[C_6H_5O_2]^+$/92 (21) $[FBOHN(CH_3)_2]^+$/94 (12) $[F_2BNH(CH_3)_2]^+$/317 (9) $[M]^+$/198 (6) $[M-C_2F_5]^+$
VIII	94 (100) $[F_2BNH(CH_3)_2]^+$/43 (29) $[CH_3CO]^+$/132 (21) $[M-C_2F_5]^+$/58 (10) $[(CH_3)_2CO]^+$/251 (3) $[M]^+$
IX	83 (100) $[C_5H_7O]^+$/94 (24) $[F_2BNH(CH_3)_2]^+$/291 (10) $[M]^+$
X	94 (100) $[F_2BNH(CH_3)_2]^+$/106 (91) $[F_2BN(CH_3)_2CH]^+$/74 (48) $[CH_3CO_2CH_3]^+$/236 (17) $[M-OCH_3]^+$
XI	57 (100) $[C(CH_3)_3]^+$/94 (91) $[F_2BNH(CH_3)_2]^+$/236 (89) $[M-OC(CH_3)_3]^+$/254 (15) $[M-C_4H_7]^+$
XII	94 (100) $[F_2BNH(CH_3)_2]$/92 (89) $[FSi(CH_3)_3]^+$/233 (8) $[M-FSi(CH_3)_3]^+$
XIII	94 (100) $[F_2BNH(CH_3)_2]$/236 (77) $[M-O-C(CH_3)=CH_2]^+$/132 (10) $[(CH_3)_2NBFCH_2COO]^+$/293 (1) $[M^+]$
XIV	94 (100) $[F_2BNH(CH_3)_2]^+$/236 (37) $[M-O-CH_2-CH=CH_2]^+$/132 (33) $[(CH_3)_2NBFCH_2COO]^+$/293 (4) $[M^+]$
XV	45 (100) $[HN(CH_3)_2]^+$/94 (46) $[F_2BNH(CH_3)_2]^+$/87 (22) $[(CH_3)_2NCOCH_3]^+$/70 (21) $[(CH_3)_2NC_2H_2]^+$/280 (14) $[M]^+$/ 236 (7) $[M-N(CH_3)_2]^+$
XVI	94 (100) $[F_2BNH(CH_3)_2]^+$/101 (99) $[(CH_3)_2NCOC_2H_5]^+$/45 (95) $[HN(CH_3)_2]^+$/294 (15) $[M]^+$/250 (14) $[M-N(CH_3)_2]^+$
XVII	58 (100) $[C_2H_5NCH_3]^+$/94 (46) $[F_2BNH(CH_3)_2]^+$/73 (27) $[HN(C_2H_5)_2]^+$/308 (24) $[M]^+$/115 (19) $[CH_3CON(C_2H_5)_2]^+$/ 239 (11) $[M-CF_3]^+$/236 (10) $[M-N(C_2H_5)_2]^+$
XVIII	94 (100) $[F_2BNH(CH_3)_2]^+$/122 (29) $[CH_2ClCO_2C_2H_5]^+$/267 (9) $[M-C_2H_5F]^+$/270 (7) $[M-OC_2H_5]^+$/315 (3) $[M]^+$
XIX	88 (100) $[C_2H_5CO_2CH_3]^+$/94 (43) $[F_2BNH(CH_3)_2]^+$/57 (30) $[C_2H_5CO]^+$/106 (13) $[C_2HBF_2O]^+$/44 (11) $[C_2H_6N]^+$/ 250 (11) $[M-OCH_3]^+$/281 (1) $[M]^+$
XX	87 (100) $[C_3H_7CO_2]^+$/102 (98) $[C_3H_7CO_2CH_3]^+$/94 (68) $[F_2BNH(CH_3)_2]^+$/106 (19) $[C_2HBF_2O]^+$/264 (14) $[M-OCH_3]^+$/ 280 (4) $[M-CH_3]^+$
XXI	94 (100) $[F_2BNH(CH_3)_2]^+$/101 (96) $[C_3HO_4]^+$/106 (78) $[C_2HBF_2O]^+$/132 (46) $[H_2C(CO_2CH_3)_2]^+$/294 (34) $[M-OCH_3]^+$/ 44 (31) $[C_2H_6N]^+$/69 (28) $[CF_3]^+$/256 (25) $[M-CF_3]^+$/325 (2) $[M]^+$
XXII	57 (100) $[C(CH_3)_3]^+$/280 (25) $[M-OC(CH_3)_3-H_2C=C(CH_3)_2]^+$/298 (20) $[M-H_2C=C(CH_3)_2-C_4H_7]^+$/336 (9) $[M-OC(CH_3)_3]^+$/ 94 (8) $[F_2BNH(CH_3)_2]^+$
XXIII	86 (10) $[C_3H_6CO_2]^+$/94 (51) $[F_2BNH(CH_3)_2]^+$/160 (7) $[M-C_2F_5]^+$/279(5) $[M]^+$

most of the ester derivatives is $[M-OR]^+$, while the expulsion of $FSi(CH_3)_3$ is characteristic for **XII**.

As the vibrational spectra of **I–XXIII** are too complicated to be assigned, only few diagnostic IR-wave numbers are quoted in Table 3. The C–F stretching vibrations are usually associated with one or two strong and broad absorptions near 1100 cm^{-1}, while the NH absorption, revealing quite different bandshapes, is located between 3100 and 3200 cm^{-1}. For **XV–XVII** this absorption was not observed due to broadening. The (C≡N) stretching modes near 2250 cm^{-1} and the absorption of the carbonyl groups between 1590 and 1750 cm^{-1} provide important evidence for the constitution of the novel boranes.

TABLE 3. Selected IR-absorptions for I–XXIII (cm^{-1})

	ν(N–H)	ν(C≡N)	ν(C=O)	ν(C=C)	ν(C–F)
I	3105s b	2251s			1120vs, 1090vs
II	3170s b	2250m			1112vs, 1100vs
III	3100s b	2248s			1100sh, 1090vs
IV	3120s b	2238s			1092vs b
V	3150m b		1670s		1090vs b
VI	3180s		1646vs		1092vs
VII	3208m, 3180 m		1633vs	1513vs	1080vs vb
VIII	3180m b		1678s		1095vs b
IX	3155m		1662s	1609vs	1090vs b
X	3183m		1683vs		1090vs
XI	3160m vb		1680s		1090vs
XII	3220w, 3170 w		1680s		1093vs
XIII	3190s		1707s	1673w	1120s, 1092vs
XIV	3185m b		1690vs	1650w	1090vs b
XV			1598vs		1088vs
XVI			1602vs		1085vs
XVII			1586vs		1080vs
XVIII	3170m		1742vs		1094vs
XIX	3122m		1675vs		1060vs
XX	3180m		1680vs		1095vs, 1083vs
XXI	3180s		1752vs		1099vs
XXII	3115wb		1720vs		1125vs, 1110vs
XXIII	3165mb		1735vs		1100vs, 1070vs

5. X-ray structure determination

Crystals of **I** were grown from a solution in $CHCl_3/Et_2O$ and mounted in glass capillaries. X-ray counter measurements were made at 24°C with a Siemens AED-1 diffractometer employing Ni filtered Cu Kα radiation. The space group is *Pnma* with $a = 13.9364(7)$, $b = 11.1385(3)$, $c = 6.2765(3)$ Å, $Z = 4$ and

TABLE 4. Positional and isotropic or equivalent isotropic [a] temperature factors for $(NCCH_2)(CF_3)_2B\cdot NHMe_2$

Atom	x	y	z	U
C(1)	0.5773(2)	0.2500	−0.0029(5)	0.049(1)
C(2)	0.4749(2)	0.2500	−0.0468(4)	0.0384(9)
C(3)	0.4316(2)	0.1319(2)	0.3125(4)	0.0476(8)
C(4)	0.2627(2)	0.1424(4)	−0.0076(6)	0.082(1)
B	0.4094(2)	0.2500	0.1682(5)	0.0310(8)
F(1)	0.3685(1)	0.1134(2)	0.4710(3)	0.0687(7)
F(2)	0.5161(1)	0.1340(3)	0.4124(4)	0.103(1)
F(3)	0.4328(2)	0.0291(2)	0.2045(3)	0.109(1)
N(1)	0.6563(2)	0.2500	0.0334(6)	0.079(2)
N(2)	0.2974(2)	0.2500	0.1124(4)	0.0406(8)
H	0.266(4)	0.2500	0.26(1)	0.10(2)
H(2)	0.464(2)	0.181(3)	−0.124(5)	0.050(7)
H(4a)	0.2878(2)	0.1405(4)	−0.1482(6)	0.105(8)
H(4b)	0.1946(2)	0.1449(4)	−0.0135(6)	0.105(8)
H(4c)	0.2825(2)	0.0725(4)	0.0671(6)	0.105(8)

[a] $U=\frac{1}{3}\Sigma_i U_{ii}$ for the non-hydrogen atoms.

$d_{calc} = 1.60$ g/cm^3. A total of 4349 reflections ($\pm h$, $\pm k$, l; $3° \leqslant 2\theta \leqslant 140°$) were measured and corrected for the variation (< 2.5%) of the three periodically-measured standard reflections and absorption ($\mu = 16.0$ cm^{-1}, transmission 0.5649–0.3349). Equivalents were merged to yield 965 unique reflections, of which 951 were treated as observed ($F \geqslant 4\sigma(F)$).

The structure was solved by direct methods. During refinement special constraints were only applied to the hydrogen atoms of the CH_3 group (C–H 0.95 Å, H–C–H 109.5°, common temperature factor). Variation of the 88 parameters, which included an extinction correction of the form $F_c^* = F_c\ (1 - \chi F_c^2/\sin\Theta)$ where $\chi = 7.3(6) \times 10^{-6}$, converged with $R = 0.069$ and $R_w = 0.122$. The final coordinates are given in Table 4, the numbering scheme being defined in Fig. 1. The program SHELX-76 [8] was used to solve and refine the structure [9].

In order to estimate the effect of thermal foreshortening on the bond distances, a model in which rigid-body-motion parameters were supplemented by correlated oscillations [10] about the B–C(3) and B–N(2) bonds was fitted to the displacement parameters of all nonhydrogen atoms except C(1) and N(1). Excellent correspondence was obtained for observed and calculated U_{ij} values, $R = [\Sigma(\Delta U_{ij})^2/\Sigma U_{ij}^2]^{1/2} = 0.022$. Bond length corrections amount to 0.032(2) Å for the C–F bonds, the other corrections being about 0.01 Å. The average value for the corrected C–F bond length, 1.375(4) Å, agrees well with values reported for other aminebis(trifluoromethyl)borane structures [11].

6. Description and discussion of the crystal structure

As shown in Fig. 1, the groups bonded to the boron atom in I adopt a mutually staggered conformation. Since the N(1)–C(1)–C(2)–B–N(2)–H fragment lies on a crystallographic mirror plane, exact staggering is found for the CH_2CN and $NHMe_2$ groups. However, the CF_3 groups are rotated by 13(2)° about the B–C(3) bond away from the precisely staggered orientation. The latter rotation widens the short contact between the F(3) atom and the C(4) methyl group.

The B–CF_3 and B–N bond lengths in I are not exceptional. They show no significant deviations from those reported for acyclic amine adducts in which boron is bonded to two [11] or three [7] trifluoromethyl groups.

To our knowledge the investigation of **I** offers the first structural details of a BCH_2CN fragment. The B–CH_2CN bond appears to be a normal, covalent linkage, the length of which is essentially identical to that of the B–CF_3 bonds. In line with this observation the geometry of the cyanomethyl group lies much closer to that of acetonitrile [12] than to that calculated for the CH_2CN^- anion [13].

The 2.968(4) Å distance between the N(2) atom and the N(1″) atom of a screw-related molecule indicates that crystals of I contain infinite chains of hydrogen-bonded molecules. These hydrogen bonds are moderately bent at both the H and N(1″) atoms (N(2)–H ⋯ N(1″), 157(4)°; H ⋯ N(1″)–C(1″), 151(4)°).

From the amplitude of oscillation about the B–C(3) bond, a torsional barrier of 2.5(1) kcal/mol can be derived if a three-fold cosine potential function is assumed [10]. This value is smaller than those analogously determined for $(CF_3)_2B(Ph)CHN(^t\mathrm{Bu})Bz$ (**B**) (average 8(2) kcal/mol) and $(CF_3)_2B(OH)CH(Ph)NH(^t\mathrm{Bu})Bz$ (**C**) (3.2(2) and 10(2) kcal/mol [14]. The higher

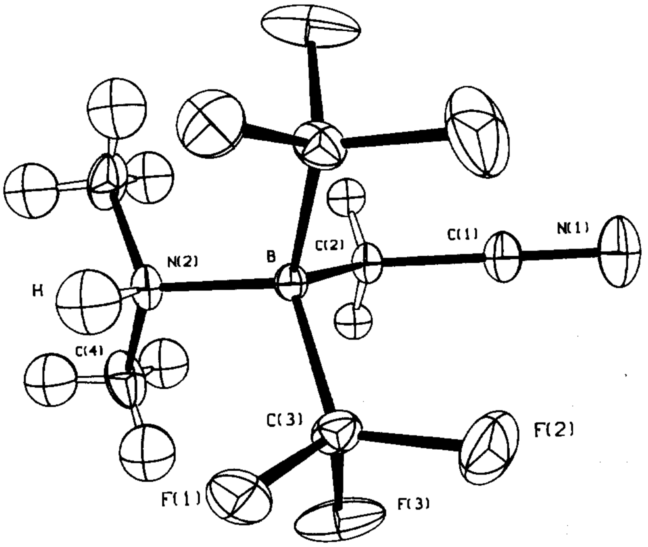


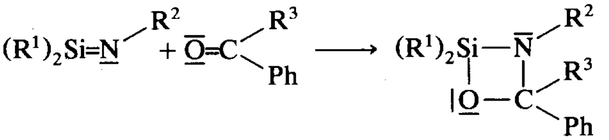
Fig. 1. A perspective drawing of I with 20% probability thermal ellipsoids.

barriers in **B** and **C** may be due in part to the greater steric obstruction of their CF_3 groups compared to that of the CF_3 groups in **I**.

The effect of packing forces on these barriers is difficult to assess. Obviously hydrogen bonding will significantly perturb the torsional potentials about the B–N(2) and B–C(2) bonds in **I** with respect to those of the isolated molecule. In fact the CH_2CN group is anchored in the crystal so well that non-rigid oscillations about the B–C(2) bond cannot be detected.

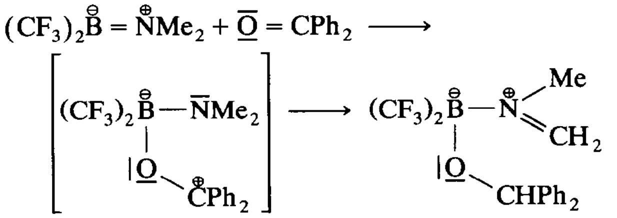
7. Discussion

To our knowledge, no ene reaction involving aminoboranes has been reported previously. These reactions are favoured by the polarity $\overset{\delta+\,\delta-}{B{=}N}$ of the boron–nitrogen bond, the reactivity of which can be compared with that of a silicon–nitrogen double bond. Thus both **A** and $({}^tBu)_2Si{=}N{}^tBu$ [15] undergo ene reactions with alkenes, and we shall describe further examples of those involving **A** in a forthcoming contribution. However, the reactions of iminosilanes and **A** with carbonyl compounds lacking an active hydrogen atom in γ position to the acidic centre proceed in a different fashion. Whereas iminosilanes yield four-membered heterocycles by a [2 + 2] cycloaddition reaction (eqn. (4)) [16], **A** and benzophenone selectively stabilize an intermediately-formed adduct by hydride transfer (eqn. (5)), by analogy with eqn. (2) [5].



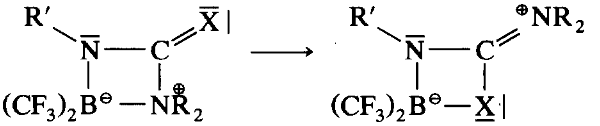
(4)

$R^1 = R^2 = {}^tBu,\ R^3 = H;\ R^1 = {}^iPr,\ R^2 = 2,6-({}^iPr)_2C_6H_3,\ R^3 = Ph$



(5)

We interpret the failure of **A** and the ease of iminosilanes to form cycloadducts with carbonyl compounds to four effects. First, since the Si–N and Si–O bonds in the ring are considerably longer than the respective B–N and B–O bonds would be, the cyclosilanes would be sterically less congested than the cycloboranes. Second, a tricoordinate nitrogen atom in the cyclosilanes causes less crowding between exocyclic groups than would a tetracoordinate nitrogen atom of the cycloborane. Indeed the reported rearrangements of [2 + 2] cycloadducts of **A** with cyanates and isothiocyanates (eqn. (6)) [4] support this suggestion.



(6)

TABLE 5. Elemental analyses

Compound	Formula	Analyses (Found (calc.) (%)			
		C	H	F	N
I	$C_6H_9BF_6N_2$	30.98 (30.78)	3.99 (3.88)	48.70 (48.74)	
II	$C_6H_8BClF_6N_2$	26.60 (26.83)	2.94 (3.01)	41.87 (42.48)	
III	$C_7H_{11}BF_6N_2$	33.78 (33.88)	4.42 (4.47)	45.74 (45.98)	
IV	$C_8H_{13}BF_6N_2$	36.39 (36.67)	4.88 (5.00)	42.91 (43.52)	
V	$C_{10}H_{18}BF_6NO$	40.34 (40.96)	6.05 (6.19)	38.00 (38.91)	
VI	$C_{12}H_{14}BF_6NO$	46.23 (46.02)	4.30 (4.51)	36.99 (36.43)	
VII	$C_{11}H_{14}BF_6NO_2$	42.36 (41.65)	4.44 (4.45)	36.60 (35.97)	
VIII	$C_7H_{12}BF_6NO$	33.19 (33.48)	4.74 (4.82)	44.82 (45.43)	
IX	$C_{10}H_{16}BF_6NO$	40.35 (41.25)	5.38 (5.54)	40.00 (39.18)	
X	$C_7H_{12}BF_6NO_2$	31.28 (31.47)	4.48 (4.53)		5.01 (5.25)
XI	$C_{10}H_{18}BF_6NO_2$	38.06 (38.84)	5.62 (5.87)		4.09 (4.53)
XII	$C_9H_{18}BF_6NO_2Si$	33.08 (33.23)	5.47 (5.58)		3.92 (4.31)
XIII	$C_9H_{14}BF_6NO_2$	36.78 (36.87)	4.76 (4.82)		4.64 (4.78)
XIV	$C_9H_{14}BF_6NO_2$	36.50 (36.87)	4.63 (4.82)		4.45 (4.78)
XV	$C_8H_{15}BF_6N_2O$	34.48 (34.29)	5.35 (5.40)		9.92 (10.01)
XVI	$C_9H_{17}BF_6N_2O$	36.82 (36.76)	5.80 (5.83)		9.40 (9.53)
XVII	$C_{10}H_{19}BF_6N_2O$	38.69 (38.99)	6.10 (6.22)		8.78 (9.09)
XVIII	$C_8H_{13}BClF_6NO_2$	30.27 (30.46)	3.99 (4.15)		4.32 (4.44)
XIX	$C_8H_{14}BF_6NO_2$	34.11 (34.19)	4.90 (5.02)		4.82 (4.98)
XX	$C_9H_{16}BF_6NO_2$	36.50 (36.64)	5.36 (5.47)		4.62 (4.75)
XXI	$C_9H_{14}BF_6NO_4$	33.38 (33.26)	4.29 (4.34)		4.14 (4.31)
XXII	$C_{15}H_{26}BF_6NO_4$	43.84 (44.03)	6.19 (6.40)		3.23 (3.42)
XXIII	$C_8H_{12}BF_6NO_2$	34.30 (34.44)	4.25 (4.34)		4.89 (5.02)

Third, the nitrogen lone pair may contribute to the bonding in the cyclosilane and hence stabilize the ring structure, and finally the iminosilanes do not possess a hydrogen atom in a position which corresponds to that used for hydride transfer in eqn. (5).

8. Experimental

Compounds prepared were as follows: cyanomethyl-bis(trifluoromethyl)borane-dimethylamine (**I**), chloro-cyanomethyl-bis(trifluoromethyl)borane-dimethylamine (**II**), 1-cyanoethyl-bis(trifluoromethyl)borane-dimethylamine (**III**), 1-cyanopropyl-bis(trifluoromethyl)borane-dimethylamine (**IV**), tert-butylcarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**V**), phenylcarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**VI**), 5-methyl-2-furylcarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**VII**), methylcarbonylmethyl-bis-(trifluoromethyl)borane-dimethylamine (**VIII**), 2-methyl-1-propenylcarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**IX**), methoxycarbonylmethyl-bis (trifluoromethyl)borane-dimethylamine (**X**), tert-butoxycarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**XI**), bis(trifluoromethyl)-trimethylsiloxycarbonylmethylborane-dimethylamine (**XII**), 1-methylethenyloxycarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**XIII**), allyloxycarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**XIV**), dimethylaminocarbonoylmethyl-bis(trifluoromethyl)borane-dimethylamine (**XV**), 1-dimethylaminocarbonylethyl-bis (trifluoromethyl)borane-dimethylamine (**XVI**), diethylaminocarbonylmethyl-bis(trifluoromethyl)borane-dimethylamine (**XVII**), ethoxycarbonylchloromethyl-bis (trifluoromethyl)borane-dimethylamine (**XVIII**), 1-methoxycarbonylethyl-bis(trifluoromethyl)borane-dimethylamine (**XIX**), 1-methoxycarbonyl-n-propyl-bis (trifluoromethyl)borane-dimethylamine (**XX**), bis (methoxycarbonyl)methyl-bis(trifluoromethyl)borane-dimethylamine (**XXI**), bis-(tert-butoxycarbonyl)-methyl-bis(trifluoromethyl)borane-dimethylamine (**XXII**), bis(trifluoromethyl)(1-oxa-cyclopenta-2-one-3-yl)borane-dimethylamine (**XXIII**).

TABLE 6. Selected bond distances (Å) and angles (°) in I

B–C(2)	1.629(4)	C(3)–F(1)	1.344(3)
B–C(3)	1.627(3)	C(3)–F(2)	1.334(3)
B–N(2)	1.600(3)	C(3)–F(3)	1.331(3)
C(1)–N(1)	1.124(5)	C(2)–H(2)	0.92(3)
C(1)–C(2)	1.454(4)	N(2)–H	1.01(6)
N(2)–C(4)	1.496(3)	H–N(1″)	2.01(6)
C(2)–B–C(3)	110.8(1)	N(1)–C(1)–C(2)	179.2(4)
C(2)–B–N(2)	111.4(2)	C(1)–C(2)–B	113.1(2)
C(3)–B–N(2)	107.9(2)	B–C(3)–F(1)	114.3(2)
C(3)–B–C(3′) [a]	108.0(2)	B–C(3)–F(2)	114.5(2)
B–N(2)–C(4)	115.2(2)	B–C(3)–F(3)	114.5(2)
B–N(2)–H	103(4)	F(1)–C(3)–F(2)	103.4(2)
H–N(2)–C(4)	108(2)	F(1)–C(3)–F(3)	104.7(2)
C(4)–N(2)–C(4′)	106.5(4)	F(2)–C(3)–F(3)	104.1(2)

[a] $x', y', z' = x, 0.5 - y, z$; $x'', y'', z'' = x - 0.5, 0.5 - y, 0.5 - z$.

8.1. General procedure

To a stirred solution of 11 mmol of the nitrile or carbonyl starting material in 20 ml dry pentane, 2.00 g (10.4 mmol) $(CF_3)_2BNMe_2$ was added dropwise at 4°C. (For **VIII** a 5-fold excess of Me_2CO was used to suppress the formation of $O{=}C[CH_2B(CF_3)_2NHMe_2]_2$). The mixture was allowed to warm to room temperature with stirring during 1 h. The solvent and other volatile by-products were removed *in vacuo* at ambient temperature, and the residue was purified by sublimation *in vacuo* if necessary. For yields see text, and for elemental analyses see Table 5.

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References and notes

1 R. Hausser-Wallis, H. Oberhammer, H. Bürger and G. Pawelke, *J. Chem. Soc., Dalton Trans.*, (1987) 1839.

2 D. J. Brauer, H. Bürger, F. Dörrenbach, G. Pawelke and W. Weuter, *J. Organomet. Chem.*, *378* (1989) 125.

3 A. Ansorge, D. J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke and W. Weuter, *J. Organomet. Chem.*, *396* (1990) 253.

4 A. Ansorge, D. J. Brauer, H. Bürger, F. Dörrenbach, T. Hagen, G. Pawelke and W. Weuter, *J. Organomet. Chem.*, *407* (1991) 283.

5 H. Bürger, T. Hagen and G. Pawelke, *J. Fluorine Chem.*, *55* (1992) 323.

6 D. F. Shriver and B. Swanson, *Inorg. Chem.*, *10* (1971) 1354.

7 A. Ansorge, D. J. Brauer, H. Bürger, B. Krumm and G. Pawelke, *J. Organomet. Chem.*, (JOM 22761) in press.

8 G. M. Sheldrick, SHELX-76, *Program for Crystal Structure Determination*, University of Cambridge, UK, 1976.

9 Additional crystallographic data may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, by quoting the deposit number CSD-56531, the authors and the literature reference.

10 J. D. Dunitz, V. Schomaker and K. N. Trueblood, *J. Phys. Chem.*, *92* (1988) 856.

11 D. J. Brauer, H. Bürger, G. Pawelke, W. Weuter and J. Wilke, *J. Organomet. Chem.*, *329* (1987) 293.

12 J. Demaison, A. Dubrulle, D. Boucher and J. Burie, *J. Mol. Spectrosc., 76* (1979) 1.
13 K. E. Edgecombe and R. J. Boyd, *Can. J. Chem., 61* (1983) 45.
14 A. Ansorge, D. J. Brauer, H. Bürger, F. Dörrenbach, B. Krumm and G. Pawelke, *Z. Naturforsch. Teil B*, *47* (1992) 772.
15 N. Wiberg, K. Schurz and G. Fischer, *Angew. Chem.*, *97* (1985) 1058.
16 S. Vollbrecht, U. Klingebiel and D. Schmidt-Bäse, *Z. Naturforsch., Teil B, 46* (1991) 709.