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The ammine complex of tris(trifluoromethyl)borane, and some N-acyl derivatives. Crystal structure of $(CF_3)_3B \cdot NH_3$ and $(CF_3)_3B \cdot NH{=}CHN(CH_3)_2$ *

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Abstract

The complex $(CF_3)_3B \cdot NH_3$ (I) has been prepared both by catalytic hydrogenation of $(CF_3)_3B \cdot NH_2CH_2C_6H_5$ and by pyrolysis of $(CF_3)_3B \cdot NH_2CMe_2(CH_2)_2CH{=}CMe_2$. Compound I reacts with moisture and DMSO to form a trihydrate (II) and a 1:1 solvate (III), respectively. Deprotonation with KOH yields $K[(CF_3)_3BNH_2]$ (IV). The salt IV was alkylated with $n\text{-}C_4F_9SO_3CH_2CF_3$ to form $K[(CF_3)_3BNHCH_2CF_3]$ (V), whose protonation in DMSO yields $(CF_3)_3B \cdot NH_2CH_2CF_3 \cdot DMSO$ (VI). Acylation of IV with $(CH_3CO)_2O$, $(CF_3CO)_2O$ and C_6F_5COCl affords the salts $K[(CF_3)_3BNHCOR]$ (R = CH_3 (VII), CF_3 (VIII) and C_6F_5 (IX)), which give the corresponding acetamide adducts (X, XI, XII) upon treatment with HCl. The complex $(CF_3)_3B \cdot NCCH_3$ (XIII) was obtained by dehydration of X with P_4O_{10}. Reaction of IV with $(CF_3SO_2)_2O$ in the presence of DMF gives $(CF_3)_3B \cdot NH{=}CHNMe_2$ (XIV). Structural assignments are based on multinuclear NMR spectra. Mass spectral data for the molecular adducts are presented, and the vibrational spectra of II and XIII discussed. The crystal structures of I and XIV have been determined; while the average B–C bond distances in these two adducts are 1.612(9) and 1.616(5) Å, respectively, the B–N bond length in XIV (1.541(4) Å) is significantly shorter than that in I (1.595(8) Å).

1. Introduction

Continuing efforts have still not led to preparation of the free Lewis acid tris(trifluoromethyl)borane, $(CF_3)_3B$, but many of its complexes with secondary amines $(CF_3)_3B \cdot NHR^1R^2$ (**A**) have been synthesized [1,2]. These have been obtained by nucleophilic trifluoromethylation of the dichloro- (or dibromo-) (amino)borane $Cl_2BNR^1R^2$ with three equivalents of the reagents $P(NEt_2)_3/CF_3Br$ in CH_2Cl_2 [3] or $C_2(NMe_2)_4/CF_3I$ [4], according to eqn. (1).

$$Cl_2BNR^1R^2 \xrightarrow[-P(NEt_2)_3Cl^+ \text{ or } -C_2(NMe_2)_4^{2+}]{P(NEt_2)_3/CF_3Br \text{ or } C_2(NMe_2)_4/CF_3I} (CF_3)_3BNR^1R^{2\,-}$$

$$(CF_3)_3BNR^1R^{2\,-} + HCl \longrightarrow (CF_3)_3BNHR^1R^2\ (\mathbf{A}) + Cl^- \quad (1)$$

This reaction sequence has proved to be unsuitable for the synthesis of primary amine adducts $(CF_3)_3B \cdot NH_2R^1$ (**B**) starting from Cl_2BNHR^1. Furthermore, it has not proved possible to prepare tertiary amine adducts $(CF_3)_3B \cdot NR^1R^2R^3$ (**C**) or $(CF_3)_3B \cdot NH_3$ (I) by nucleophilic trifluoromethylation of $Cl_3B \cdot NR^1R^2R^3$ or $Cl_3B \cdot NH_3$. However, the complexes **A** can be deprotonated quantitatively in alkaline solution to yield anions (eqn. (2)), alkylation of which gives the tertiary amine complexes **C** [1].

$$(CF_3)_3B \cdot NHR^1R^2 \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} (CF_3)_3B \cdot NR^1R^{2-} \xrightarrow[-X^-]{+R^3X} (CF_3)_3B \cdot NR^1R^2R^3 \quad (2)$$

On the other hand, thermal degradation of the NHR^1R^2 group in complexes **A** proceeded *via* a Hofmann elimination to yield a primary amine derivative **B** when R^1 or R^2 was a tert-butyl group [1,2].

$$(CF_3)_3B \cdot NHR^1(C(CH_3)_3) \xrightarrow{\Delta} (CH_3)_2C{=}CH_2 + (CF_3)_3B \cdot NH_2R^1 \quad (3)$$

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* Dedicated to Professor M.G. Voronkov in recognition of his important and numerous contributions to organometallic chemistry.

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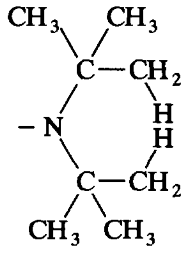
We were particularly interested in the ammine complex I, which is the parent of the amine complexes **A**, **B** and **C**, because it holds promise of interesting and flexible chemistry which might finally provide a route to the free Lewis acid $(CF_3)_3B$. An elegant route to I might involve use of double Hofmann elimination in the case of $(CF_3)_3B\cdot NH(^tBu)_2$. However, the latter compound, as well as the starting material, $Cl_2BN(^tBu)_2$, are, to our knowledge, still unknown. Thus we decided to seek a variant of reaction (3) for the synthesis of I.

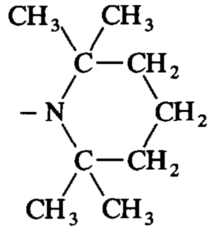
2. Results

2.1. *Synthesis of tris(trifluoromethyl)borane-ammine*

Although the thermal degradation of a $N(^tBu)$ group seemed to offer the most promising route to I, the non-availability of $Cl_2BN(^tBu)_2$, and hence of $(CF_3)_3B\cdot N(^tBu)_2^-$, had to be overcome by a slight chemical modification. The analogy between the $N(^tBu)_2$ and 2,2,6,6-tetramethylpiperidino (tmp) group is obvious, and attempts to synthesize $(CF_3)_3B\cdot H(tmp)$ had, indeed, yielded a product (**B1**) in which as shown in eqn. (4) one of the N–C bonds of the tmp ligand had opened, as in reaction (3), during work up with HCl [2].



$(N(^tBu)_2)$



(*tmp*)

$$(CF_3)_3B\cdot N[C(CH_3)_2CH_2]_2CH_2^- \xrightarrow[-Cl^-]{HCl} (CF_3)_3B\cdot NH_2C(CH_3)_2CH_2CH_2CH{=}C(CH_3)_2 \quad \textbf{(B1)} \qquad (4)$$

Compound **B1**, which was obtained in a moderate yield of 22%, appeared to be a promising precursor for I. Cleavage of the remaining N–C bond according to eqn. (5) did take place at 160°C, to give I in almost quantitative yield.

$$(CF_3)_3B\cdot NH_2C(CH_3)_2CH_2CH_2CH{=}C(CH_3)_2 \xrightarrow[3\ \text{days}]{160°} \underset{\text{(I)}}{(CF_3)_3B\cdot NH_3} + CH_2[CH{=}C(CH_3)_2]_2 \qquad (5)$$

It is well established that O- and N-benzyl compounds can be catalytically hydrogenated to yield toluene and the corresponding OH and NH derivatives, *e.g.* eqn. (6) [5].

$$R_2N\text{–}CH_2C_6H_5 \xrightarrow{H_2/\text{Raney–Ni}} R_2NH + CH_3C_6H_5 \qquad (6)$$

We found that $(CF_3)_3B\cdot NH_2CH_2C_6H_5$ (**B2**), obtained according to eqn. (3) with $R^1 = CH_2C_6H_5$ [2], also undergoes N–C cleavage, eqn. (7), to yield I almost quantitatively. The use of Pd on charcoal instead of Raney-Ni as a catalyst gives essentially the same result; however, the reaction takes five times longer.

$$(CF_3)_3B\cdot NH_2CH_2C_6H_5 \xrightarrow{H_2,\ \text{Raney–Ni, 80°C}} I + CH_3C_6H_5 \qquad (7)$$

2.2. *Properties of $(CF_3)_3B\cdot NH_3$ (I)*

Compound I is a colourless solid which can be sublimed at 60°C and 0.1 torr. It reacts reversibly with moist air to give, according to elemental analyses, a trihydrate $(CF_3)_3B\cdot NH_3\cdot 3H_2O$ (II) in a yield of 94%. Prolonged exposure to moist air eventually gives a tetrahydrate, which was characterized by a single crystal X-ray structural study [6]. The H_2O solvate molecule can be removed by sublimation to a cold finger in a dynamic vacuum, to give anhydrous I. A slightly more stable 1:1 adduct is formed with dimethylsulfoxide, $(CF_3)_3B\cdot NH_3\cdot DMSO$ (III). The ammine complex was unambiguously characterized by mass spectroscopy and an X-ray structural study, as described below. The trihydrate II and the DMSO adduct III were characterized by elemental analyses, NMR and vibrational spectroscopy, and, in some cases, also mass spectroscopy. Aqueous solutions of I are acidic. The pK_a value estimated by potentiometric titration of a 0.1 M solution with 10^{-3} M NaOH is about 5, which is comparable to that of acetic acid.

Thermally I is very stable, no difluorocarbene, the decomposition product typical of CF_3 derivatives of electropositive elements, being formed at temperatures of up to 250°C. No oxidation occurred even when elemental fluorine was passed through an aqueous solution of I.

2.3. *$K[(CF_3)_3B \cdot NH_2]$ (IV) and its derivatives*

Deprotonation of I was readily brought about by use of an excess of powdered KOH in ether, and the potassium salt $K[(CF_3)_3BNH_2]$ (IV) was obtained quantitatively by evaporation of the solvent from the filtered etheral solution. The salt IV is a colourless solid decomposing above 250°C. It is soluble in polar organic solvents.

Some N-alkylation and acylation reactions of IV were studied. Alkylation was achieved with n-$C_4F_9SO_3CH_2CF_3$ in DMSO according to eqn. (8).

$$2\,K[(CF_3)_3BNH_2] + \text{n-}C_4F_9SO_3CH_2CF_3 \xrightarrow{\text{DMSO}} K[\text{n-}C_4F_9SO_3] + \text{III} + K[(CF_3)_3BNHCH_2CF_3]\ (\text{V}) \qquad (8)$$

Protonation of the potassium salt V with CF_3COOH afforded the 2,2,2-trifluoro-ethylamine-borane complex VI, eqn. (9), the yield with respect to 1/2 IV being *ca.* 90%. Clearly, VI is a stronger acid

$$\text{V} + CF_3COOH \xrightarrow{\text{DMSO}} K[CF_3COO] + (CF_3)_3BNH_2CH_2CF_3 \cdot \text{DMSO}\ (\text{VI}) \qquad (9)$$

than I, otherwise VI rather than V would be formed by the reaction shown in eqn. (8).

Attempts were made to acylate IV with various anhydrides and acyl halides in order to obtain amide complexes of $(CF_3)_3B$. These may be more readily amenable to BN cleavage than amine complexes, and should also allow systematic chemical modifications of the NHCOR ligand in order to weaken the BN bond more effectively.

The reactivities of $(CH_3CO)_2O$, $(CF_3CO)_2O$, C_6F_5COCl and $(CF_3SO_2)_2O$ towards IV showed marked differences. While the first anhydride reacted

TABLE 1. Physical properties and NMR spectra of II–XIV (δ in ppm, J in Hz) [a]

	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
M.p. (°C)	40	164	286 (dec.)	152	65	178 (dec.)	85	231	70	–	93	234	198
^1H													
$\delta(CCH_3)$						1.87			2.40			2.80	
$\delta(NCH_3)$													3.00 3.20
$\delta(NCH_2)$				3.25	3.63								
$\delta(N{=}CHN)$													7.52
$\delta(NH/OH)$	~5	5.54	0.06	0.19	6.9	2.39 5.08	2.64 5.59	2.26 5.64	~7 7.6	6.3 12.7	8.4 11.8		5.75
$^3J(HF)$				10.0	8.6								
$^3J(HCNH)$													15.9
$^1J(H^{14}N)$	~45	48.4											
^{19}F													
$\delta(BCF_3)$	−66.5	−66.7	−66.7	−64.5	−65.2	−64.0	−64.9	−64.2	−64.8	−64.7	−64.7	−65.8	−65.8
$\delta(CCF_3)$				−74.0	−70.7	−75.7			−75.4				
$^2J(BF)$	27.3	28.3	25.6	25.2		27.1	27.6	27.4	29.5	27.8			27.7
^{11}B													
$\delta(B)$	−15.3	−15.6	−13.7	−13.5	−13.7	−14.9	−14.3	−14.3	−14.4	−14.2	−13.9	−15.1	−14.4
^{13}C													
$\delta(NCH_3)$													36.1 44.4
$\delta(CCH_3)$												122.0	
$\delta(CCH_3)$						25.4			21.9			5.3	
$\delta(CCF_3)$				128.1	122.7		117.4			117.5			
$\delta(BCF_3)$			135.8	135.4		134.5	133.2	133.6					
$\delta(NCH_2)$				46.7	44.4								
$\delta(BN{=}C)$													158.1
$\delta(C{=}O)$						174.7	160.3	160.9	181.9	160.4	167.4		
$^1J(CF)(B)$			310.6	312.0		306.7	308	307.5					
$^1J(CF)(C)$				277.2	278.3		286.0			288.0			
$^2J(CF)(C)$				31.5	35.4		34.6			34.5			
$^1J(CB)$			72.5	72.9		74.6	76.4	77.0					

[a] VI in $CDCl_3$, II–V and VII–XIV in CD_3CN. ^1H: 250.13 MHz, int. std. $CHCl_3 = 7.27$ ppm/$CHD_2CN = 1.95$ ppm. ^{13}C: 62.9 MHz, int. std. $CDCl_3 = 77.0$ ppm/$CD_3CN = 1.3$ ppm. ^{19}F: 84.67 MHz, int. std. $CFCl_3$. ^{11}B: 25.52 MHz, ext. std. $BF_3 \cdot OEt_2$.

(eqn. (10)) to give the expected acetamido salt VII quantitatively, reaction of the second (eqn. (11))

$$\mathrm{IV} + (CH_3CO)_2O \longrightarrow CH_3COOH + K[(CF_3)_3B \cdot NHCOCH_3](\mathrm{VII}) \quad (10)$$

proceeded sluggishly, and gave the trifluoroacetamido derivative VIII in 82% yield.

$$2\,\mathrm{IV} + (CF_3CO)_2O \longrightarrow K[(CF_3)_3B \cdot NHCOCF_3](\mathrm{VIII}) + K[CF_3COO] + \mathrm{I} \quad (11)$$

The formation of I and $K[CF_3COO]$ shows that (in contrast to acetic acid in eqn. (10)) trifluoroacetic acid is a stronger acid than I. Reaction (11) is considerably accelerated when DMF is used as solvent. On the other hand, in acylation of IV with C_6F_5COCl a base is required to take the reaction to completion, eqn. (12).

$$\mathrm{IV} + C_6F_5COCl + KOH \longrightarrow K[(CF_3)_3B \cdot NHCOC_6F_5](\mathrm{IX}) + KCl + H_2O \quad (12)$$

The potassium salts VII–IX were isolated as solids and fully characterized. They are readily converted into the corresponding amide complexes with HCl, the acetamide and trifluoroacetamide adducts being obtained as solvates (eqn. (13)).

$$K[(CF_3)_3B \cdot NHCOR] \xrightarrow{HCl} KCl + (CF_3)_3B \cdot NH_2COR \quad (13)$$

$R = CH_3$: $X \cdot H_2O$

$R = CF_3$: $XI \cdot Et_2O$, $XI \cdot 2\,DMF$

$R = C_6F_5$: XII

The H_2O, Et_2O and DMF donor molecules could not be removed *in vacuo* without decomposition. The acyl compounds are acidic, and their pK_a values, ~ 2.7 (X) and ~ 2 (XI, XII), were determined as described for I.

With the aim of synthesizing nitrile adducts, the amide complexes were treated with P_4O_{10}. Thus X was converted (eqn. (14)) into the novel acetonitrile complex of $(CF_3)_3B$, complex XIII being isolated in 80% yield by sublimation.

$$(CF_3)_3B \cdot NH_2COCH_3 \xrightarrow[-H_2O]{P_4O_{10}} (CF_3)_3B \cdot NCCH_3\ (\mathrm{XIII}) \quad (14)$$

Whereas traces of moisture are sufficient to reconvert XIII into X, no replacement of the CH_3CN in XIII by pyridine or trimethylphosphane was observed even at 180°C, where XIII started to decompose rapidly. Under the same conditions, XI and XII did not react with P_4O_{10}.

Attempts to synthesize a trifluoromethylsulphonamide by treatment of IX with $(CF_3SO_2)_2O$ in DMF gave an unexpected product, the identity of which was determined by an X-ray diffraction study. The solvent

TABLE 2. Selected ions (^{11}B only) and their relative intensities in the mass spectra of I (II), III, VI and X–XIV

m/e	I	III	VI	X [a]	XI [a]	XII	XIII	XIV
$[M-F]^+$	8	0.1	1	2	2	1	6	
$[M-F-DMSO]^+$		6	7					
$[M-C_2F_5]^+$				2		1	2	14
290 $[CF_3BNHCOC_6F_5]^+$						3		
260 $[F_2BNH_2COC_6F_5]^+$						44		
195 $[C_6F_5CO]^+$						23		
194 $[C_6F_5CNH]^+$						100		
162 $[F_2BNH_2COCF_3]^+$					23			
148 $[F_2BNH_2CH_2CF_3]^+$			20					
121 $[F_2BNHCHN(CH_3)_2]^+$								100
108 $[F_2BNH_2COCH_3]^+$				100				
97 $[CF_3CO]^+$					6			
96 $[CF_3BNH_2]^+$	10	8						
96 $[CF_3CNH]^+$					100			
94 $[F_2BNH(CH_3)_2]^+$								14
90 $[F_2BNCCH_3]^+$				5			100	
80 $[F_2BNH_2CH_3]^+$			100					
78 $[(CH_3)_2SO]^+$		44	69					
69 $[CF_3]^+$			4	8	35	4	5	
66 $[F_2BNH_3]^+$	100	100						
63 $[CH_3SO]^+$		38	48					

[a] Refers to unsolvated species.

DMF took part in the reaction, eqn. (15), and a dimethylformamidine complex was obtained.

$$\mathrm{IV} + \mathrm{Me_2NCHO} \xrightarrow{(\mathrm{CF_3SO_2})_2\mathrm{O}} \mathrm{K[CF_3SO_3]} + \mathrm{CF_3SO_3H} + \mathrm{(CF_3)_3BNH{=}CHNMe_2}\ (\mathrm{XIV}) \quad (15)$$

2.4. Physical properties and spectra

The physical properties and the ^{1}H, ^{19}F, ^{11}B and ^{13}C NMR spectral data for II–XIV are set out in Table 1. The spectra are in agreement with the proposed structures and require only a few comments. The ^3J(HNCH) coupling constant, 15.9 Hz, suggests that XIV is the *trans* isomer. Two signals are observed in the NH and OH regions for VII–XII. The ^{15}N spectrum of XI (in acetone/DMF, $\delta(^{15}N)$ −283.0 ppm, ^1J(NH) 81.6 Hz, ^1J(NB) 19.5 Hz, ext. std. CH_3NO_2) shows that only one hydrogen is bonded to nitrogen. From these observations we conclude that XI has the enol structure $(CF_3)_3B \cdot NH{=}C(OH)CF_3$, and we assume that the same is also true for X and XII. The appearance of the quartet in the ^{15}N NMR spectrum of II (in acetone, δ ^{15}N −368.0 ppm, ^1J(NH) 71.0 Hz) shows that three hydrogens are bonded to nitrogen. Detection by routine ^{13}C NMR spectroscopy of the CF_3 carbon atoms bonded to boron was only possible for the anionic species IV, V, VII, VIII and IX. The ^{19}F and ^{13}C parameters of the C_6F_5 groups of IX and XII, and the data related to the donor solvents, are not included in Table 1, but are given in the Experimental section.

The EI mass spectral data for I, III, VI and X–XIV are listed in Table 2. Although the M^+ peak was not observed, the $[M-F]^+$ fragment is indicative of the molecular weight. The mass spectra of compound I and its trihydrate II are identical. On the other hand, the presence of the *m/e* 294 fragment $[M-F]^+$ of the DMSO solvate III indicates that this solvate is stable even in the gas phase. The base peak is generally a $[F_2BNR_3]^+$ fragment, where R_3 represents the substituents on nitrogen.

2.5. Vibrational spectra

The IR Raman data are given in the Experimental section. Since the ammine complex II and the acetonitrile adduct XIII are the most symmetrical and simplest derivatives of $(CF_3)_3B$, we investigated their vibrational spectra, and the data are given in Table 3 in some detail. The $(CF_3)_3B$–N fragment is isoelectronic with $(CF_3)_3CF$, and the comparison in Fig. 1 of the Raman spectra of $(CF_3)_3CF$ [7] and II immediately reveals their close similarity: not only the vibrational wavenumbers but also the relative intensities are very similar. Thus the interpretation of the vibrational spectrum of I (or II) can be made by analogy with that of $(CF_3)_3CF$ (Table 3), which is based on a normal coordinate analysis [7]. In general the vibrational wavenumbers for II and XIII are smaller than those of $(CF_3)_3CF$ and so the bonds in II and XIII are weaker. One exception concerns the e fundamental $\nu_{as}(BC_3)$ (IR ~ 1008, Ra 1030 cm^{-1}), which is higher than the corresponding vibration $\nu_{as}(CC_3)$ in $(CF_3)_3CF$ (996 cm^{-1}). This behaviour is attributed to the repulsive interaction of the former with the e vibration $\rho(NH_3)$ observed at 822 cm^{-1}. Except for this mode, all the vibrations of the NH_3 group correspond nicely to those of $F_3B \cdot NH_3$: $\nu_{as}(NH_3)$ 3343, $\nu_s(NH_3)$ 3279, $\delta_{as}(NH_3)$ 1599, $\delta_s(NH_3)$ 1438, $\rho(NH_3)$ 863 cm^{-1} [8].

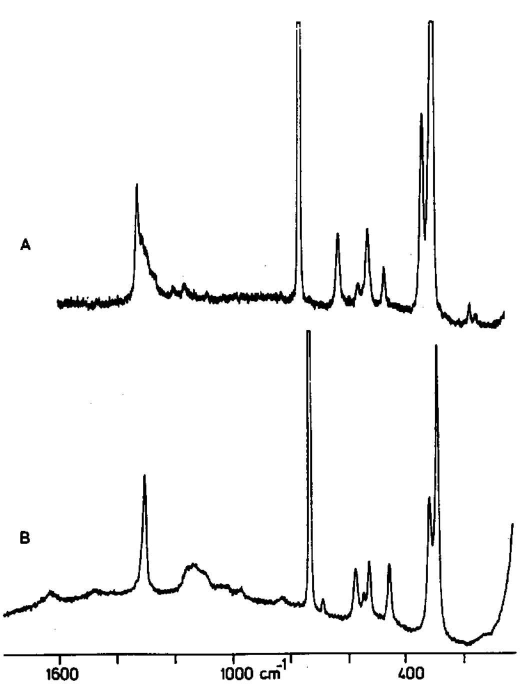


Fig. 1. Comparison of the Raman spectrum of $(CF_3)_3CF$ (A) with that of $(CF_3)_3B \cdot NH_3 \cdot 3H_2O$ (B).

The vibrations of the $NCCH_3$ fragment of XIII are in agreement with those reported for $Br_3B \cdot NCCH_3$ [9]: $\nu_{as}(CH_3)$ 2990.5, $\nu_s(CH_3)$ 2918.2, ν(NC) 2362.0, $\delta_{as}(CH_3)$ 1392.2, $\delta_s(CH_3)$ 1351.2, ρ (CH_3) 1031.6, ν(CC) 1019.7, ν(BN) 706.6 and δ(NCC) 428.3 cm^{-1}. An exception is δ (NCC) of XIII at 498 cm^{-1}, which appears to be shifted to higher wavenumbers by coupling with the rocking fundamental of the $B(CF_3)_3$ fragment. Experimental evidence has also been found for the BNC bending mode (105 cm^{-1}), which has been calculated to occur at 81 cm^{-1} in Cl_3BNCCH_3 and 54 cm^{-1} in Br_3BNCCH_3 [9]. The $^{10}B/^{11}B$ shifts of ν(CC) (13 cm^{-1}), ν(BN) (12 cm^{-1}) and $\nu_{as}(BC_3)$ (27 cm^{-1}) correspond to those in Br_3BNCCH_3 [9] and thus confirm the suggested assignment. The corresponding isotope shifts in II are not so obvious because of the broader bands and the superposition of $\nu_{as}(BC_3)$ and $\nu(BN)$ in the IR spectrum.

2.6. X-ray structural determinations

Crystals of I and XIV were mounted in glass capillaries, the former being sealed under argon in order to prevent hydrolysis. Lattice constants and intensity data were determined with a Siemens AED-1 diffractometer. The intensities were corrected for the small fluctuations of the standard reflections and absorption. Crystal data are listed in Table 4.

The structures were solved by direct methods and refined by full-matrix least-squares techniques. Dispersion-corrected, relativistic Hartree–Fock scattering factors were used for all atoms except hydrogen (SDS) [10]. Only nonhydrogen atoms were assigned anisotropic temperature factors. Hydrogen atoms were detected in difference Fourier syntheses. Those in the CH_3 groups in XIV were placed in calculated positions (C–H: 0.95 Å) and refined as rigid groups, but no extra constraints were applied to the other hydrogen atoms. The final atom coordinates are listed in Tables 5 and 6, the numbering schemes being defined in Figs. 2 and 3. An extinction correction of the form $F_c^* = F_c(1 - xF_c^2/\sin\theta)$, $x = 5(1) \times 10^{-6}$, was applied for XIV. The structure factors were assigned unit weights for I and

TABLE 3. Vibrational spectra of $(CF_3)_3CF$, $(CF_3)_3B \cdot NH_3 \cdot 3H_2O$ and $(CF_3)_3B \cdot NCCH_3$ in cm^{-1}

$(CF_3)_3CF$ [a]		$(CF_3)_3B \cdot NH_3 \cdot 3H_2O$		$(CF_3)_3B \cdot N{\equiv}CCH_3$		Assignment
IR_g	$Raman_l$	IR_s	$Raman_l$	IR_s	$Raman_s$	
				105 wb		$\delta\ (-/-/B-N{\equiv}C)$
	166 w	133 w	130 vw	145 w	145 w	$\delta_{as}\ (CC_3/BC_3/BC_3)$
	189 w p	155 w	155 vw p			$\delta_s\ (CC_3/BC_3/BC_3)$
265 w	265 w	212 w		237 vw	236 w	$\delta\ (CCF/CBN/CBN)$
316 w	316 vs p	291 w	288 s p	286 w	288 s	$\rho\ CF_3/CF_3/CF_3$
321 w	321 m		300 sh	349 w	350 vw	$\rho\ CF_3/CF_3/CF_3$
351 w	351 m	313 vw	316 m	311 vw	311 s	$\rho\ CF_3/CF_3/CF_3$
484 m	484 w p	452 m	456 m p		442 w	$\nu\ CC_3/BC_3/BC_3$
				498 wb		$\delta\ (-/-/N{\equiv}C-C)$
542 s	542 m	518 w	524 m	522 m	520 m	$\delta_{as}\ (CF_3/CF_3/CF_3)$
574 w	574 w		543 w		544 w	$\delta_{as}\ (CF_3/CF_3/CF_3)$
641 vw	641 m p	568 w	573 m p		530 m	$\delta_{as}\ (CF_3/CF_3/CF_3)$
734 vs		680 s	684 w	693 s	693 w	$\delta_s\ (CF_3/CF_3/CF_3)$
774 w	774 vs p	724 w	728 vs p	723 m	723 m	$\delta_s\ (CF_3/CF_3/CF_3)$
		822 mb	830 vwb			$\rho\ (-/NH_3/-)$
				844 s	842 m	
1172 vs	1165 w p		975 w p	856 w [b]		$\nu\ (CF/BN/BN)$
		1008 vsb		904 vs	900 vwb	
996 vvs	995 vs		1030 w	931 m [b]		$\nu_{as}\ (CC_3/BC_3/BC_3)$
				1081 s		$\rho\ (-/-/CH_3)$
				1035 m	1037 m	$\nu\ (-/-/C-C)$
				1048 w [b]	1050 vw [a]	
1204 s	1200 w	1100 vsb	1100 w	1120 vsb	1125 w	
1245 w	1240 vw		↕			$\nu\ (CF_3/CF_3/CF_3)$
1278 vvs	1270 w p	1150 vsb	1148 w	1160 vsb	1160 m	
1300 vvs	1296 w					
1332 sh	1327 m p		1294 m p	1289 vs	1289 s	$\nu\ (CF_3/CF_3/CF_3)$
1322 vs	1315 w	1302 vs	1303 w	1302 m	1302 w	
		1433 m				
		1455 m	~ 1465 vw p	1367 m	1368 s	$\delta_s\ (-/NH_3/CH_3)$
		1472 m				
		1590 m	~ 1620 w	1410 vw	1412 vw	$\delta_{as}\ (-/NH_3/CH_3)$
		1620 m		2371 s	2376 s	$\nu\ (-/-/N{\equiv}C)$
		~ 3000 wb				$\nu\ (-/OH)$
		3300 sh	3305 vw	2952 m	2958 s	$\nu_s\ (-/NH_3/CH_3)$
		3330 m	3335 vw	3025 w		$\nu_{as}\ (-/NH_3/CH_3)$
			3620 w			
		3660 w				$\nu\ (-/OH)$
			3680 w			

[a] According to ref. 7, fundamentals only. [b] ^{10}B species.

TABLE 4. Crystallographic data for I and XIV

	I	XIV
Formula	$(CF_3)_3B \cdot NH_3$	$(CF_3)_3B \cdot NHCHNMe_2$
MW	234.9	289.9
Space group	*Pnma*	$P\bar{1}$
a (Å)	10.1750(9)	6.8805(7)
b (Å)	10.817(2)	8.7495(9)
c (Å)	7.1178(8)	9.794(1)
α (°)	90	89.394(7)
β (°)	90	77.794(7)
γ (°)	90	76.079(9)
Z	4	2
D_c (g/cm^3)	1.99	1.72
t (°C)	24	26
λ (Å)	0.71073	1.54184
2θ limits (°)	4–55	3–130
Measured reflections	4766	3802
Unique reflections	944	1901
Observed ($F \geq 4\sigma(F)$)	761	1715
μ (λ) cm^{-1}	2.6	19.4
Transmission	0.910–0.967	0.415–0.763
R	0.099	0.073
R_w	0.070	0.110
$\Delta\rho$ (e/Å^3)	0.39/−0.36	0.44/−0.26
Parameters	77	180

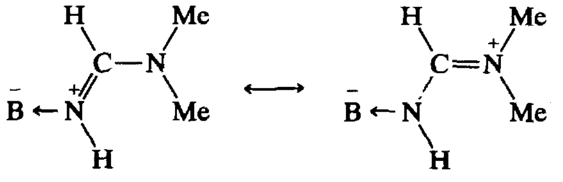
empirical weights, $w^{-1} = \sigma^2(F) + (0.01\,F)^2$, for XIV [11*]. The programs SHELX-76 [12a] and SHELXS-86 [12b] were used for the solution and refinement of the structures.

2.7. Description and discussion of the crystal structures

Selected bond distances and angles of I and XIV are set out in Tables 7 and 8, respectively. As can be seen from Figs. 2 and 3, the CF_3 groups in I and XIV adopt roughly staggered conformations with respect to the bonds formed by the boron atoms. Since the F(1), C(1), B, N and H(1) atoms of I lie on a crystallographic mirror plane, deviations from the staggered conformation of the $(CF_3)_3B$ group are smaller in I than in XIV, which is an asymmetric molecule. Interestingly, each CF_3 group in XIV is by rotated 13(1)° about the corresponding B–C bond away from the staggered conformations, the direction of the rotations preserving the local C_3 axis of the $(CF_3)_3B$ fragment.

The NH_3 group coordinates to the boron in I so as to complete the all-staggered conformation. The B–N distance in this compound falls within the 1.589(5)–1.606(8) Å range previously found for B–N bonds in amine adducts of $(CF_3)_3B$ (Table 9).

The B–N bond length in XIV, 1.541(4) Å, is markedly shorter than those determined for the above-mentioned amine adducts. This shortening may be due in part to the lower nitrogen coordination number and different nitrogen hybridization in XIV. Furthermore, the formamidine group may be a relatively good electron donor, since resonance can distribute over both nitrogen atoms the formal positive charge acquired by complex formation.



Such resonance is possible in XIV because the atoms of the B, N(1), C(4), N(2), C(5), C(6) fragment are planar to within ±0.02 Å, and the insignificant difference (0.005(6) Å) between the C(4)–N(1) and C(4)–N(2) bond lengths points to the delocalization of the double bond in this moiety.

Because the plane of the formamidine group is almost exactly perpendicular to the N(1), B, C(2) plane, a hyperconjugative interaction between electrons in the 2pπ orbital of the N(1) atom and a parallel 2p orbital of the boron atom should weaken the B–C(2) bond. Since this bond is only 0.013(7) Å longer than the

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* Reference number with an asterisk indicates a note in the list of references.

TABLE 5. Positional and isotropic or equivalent isotropic temperature factors [a] for $(CF_3)_3B \cdot NH_3$

Atom	x	y	z	U
B	0.1172(6)	0.2500	−0.0119(9)	0.038(2)
C(1)	0.1311(7)	0.2500	0.211(1)	0.069(3)
C(2)	0.1814(5)	0.1273(4)	−0.1051(7)	0.061(2)
F(1)	0.2510(5)	0.2500	0.2746(7)	0.146(3)
F(2)	0.0726(4)	0.1544(4)	0.2928(5)	0.137(2)
F(3)	0.3095(3)	0.1205(3)	−0.0909(6)	0.109(2)
F(4)	0.1361(3)	0.0224(3)	−0.0365(7)	0.116(2)
F(5)	0.1590(5)	0.1209(4)	−0.2866(5)	0.161(2)
N	−0.0360(5)	0.2500	−0.0597(9)	0.051(2)
H(1)	−0.056(9)	0.2500	−0.18(1)	0.11(4)
H(2)	−0.087(6)	0.182(5)	−0.013(9)	0.13(3)

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

TABLE 6. Positional and isotropic or equivalent isotropic temperature factors [a] for $(CF_3)_3B \cdot NHCHNMe_2$

Atom	x	y	z	U
B	0.0344(5)	0.6705(4)	0.7395(3)	0.052(1)
C(1)	0.0563(6)	0.7572(4)	0.8783(4)	0.069(1)
C(2)	0.1256(8)	0.7604(5)	0.6038(4)	0.083(2)
C(3)	−0.2034(6)	0.6769(4)	0.7476(6)	0.085(2)
C(4)	0.3141(5)	0.4290(3)	0.7683(3)	0.054(1)
C(5)	0.5875(7)	0.2196(5)	0.8147(5)	0.085(2)
C(6)	0.3270(7)	0.1639(4)	0.6939(5)	0.084(2)
F(1)	−0.0758(5)	0.8978(3)	0.9100(3)	0.116(1)
F(2)	0.2440(4)	0.7856(3)	0.8699(3)	0.098(1)
F(3)	0.0268(5)	0.6735(3)	0.9944(2)	0.106(1)
F(4)	0.0654(6)	0.9169(3)	0.6170(3)	0.131(2)
F(5)	0.0693(6)	0.7203(4)	0.4859(3)	0.119(2)
F(6)	0.3287(5)	0.7272(5)	0.5728(4)	0.130(2)
F(7)	−0.2330(4)	0.5841(3)	0.6486(4)	0.122(2)
F(8)	−0.3174(4)	0.8204(3)	0.7295(5)	0.131(2)
F(9)	−0.2970(4)	0.6261(4)	0.8712(4)	0.132(2)
N(1)	0.1481(4)	0.4949(3)	0.7249(3)	0.0528(9)
N(2)	0.4046(4)	0.2785(3)	0.7575(3)	0.060(1)
H(1)	0.118(6)	0.427(5)	0.684(4)	0.06(1)
H(4)	0.389(4)	0.491(4)	0.811(3)	0.047(8)
H(5A)	0.6972(7)	0.1598(5)	0.7457(5)	0.095(8)
H(5B)	0.5450(7)	0.1526(5)	0.8858(5)	0.095(8)
H(5C)	0.6319(7)	0.3002(5)	0.8545(5)	0.095(8)
H(6A)	0.4206(7)	0.0632(4)	0.6840(5)	0.13(1)
H(6B)	0.3112(7)	0.1999(4)	0.6041(5)	0.13(1)
H(6C)	0.1980(7)	0.1561(4)	0.7479(5)	0.13(1)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j \mathbf{a}_i \cdot \mathbf{a}_j a_i^* a_j^* U_{ij}$ for non-hydrogen atoms.

TABLE 7. Selected bond distances (Å) and angles (°) in I

B–N	1.595(8)	C(2)–F(3)	1.309(5)
B–C(1)	1.594(9)	C(2)–F(4)	1.319(5)
B–C(2)	1.621(6)	C(2)–F(5)	1.314(6)
C(1)–F(1)	1.301(8)	N–H(1)	0.85(9)
C(1)–F(2)	1.328(5)	N–H(2)	0.96(6)
N–B–C(1)	107.4(6)	B–N–H(2)	117(4)
N–B–C(2)	107.9(3)	H(1)–N–H(2)	102(5)
C(1)–B–C(2)	111.8(4)	H(2)–N–H(2′)	100(7)
C(2)–B–C(2′) [a]	109.9(5)	B–C–F [b]	114(1)
B–N–H(1)	116(6)	F–C–F [b]	105(1)

[a] x', y', $z' = x$, $0.5 - y$, z. [b] Mean with standard deviation.

average of the other two B–C distances, there is no significant lengthening.

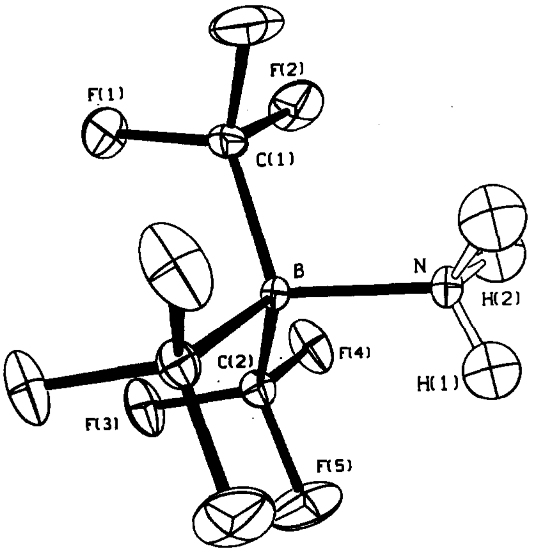

Fig. 2. Perspective drawing of $(CF_3)_3B \cdot NH_3$.

3. Experimental details

3.1. *Ammonia tris(trifluoromethyl)borane-water(1,1,3) (II), ammonia-dimethylsulfoxide tris(trifluoromethyl)borane(1,1,1) (III), potassium aminotris(trifluoromethyl) borate (IV)*

A mixture of 16.3 g (0.05 mol) of $(CF_3)_3B \cdot NH_2CH_2C_6H_5$ [2] in 100 ml of EtOH and 1 g of Raney–Ni was heated under reflux under hydrogen for 8 h. After filtration, EtOH and toluene were pumped off *in vacuo* and I was purified by sublimation at 60°C and 10^{-1} torr. $(CF_3)_3B \cdot NH_3$ reacts readily with moist air to give a stable trihydrate (II) (yield 13.6 g (94%)) and with dimethylsulfoxide to give a 1 : 1 solvate (III).

TABLE 8. Selected bond distances (Å) and angles (°) in XIV

B–N(1)	1.541(4)	C(1)–F(1)	1.337(4)
B–C(1)	1.615(5)	C(1)–F(2)	1.358(4)
B–C(2)	1.625(5)	C(1)–F(3)	1.351(4)
B–C(3)	1.609(5)	C(2)–F(4)	1.331(5)
N(1)–C(4)	1.304(4)	C(2)–F(5)	1.367(5)
N(1)–H(1)	0.81(4)	C(2)–F(6)	1.326(6)
N(2)–C(4)	1.309(4)	C(3)–F(7)	1.350(5)
N(2)–C(5)	1.464(5)	C(3)–F(8)	1.343(5)
N(2)–C(6)	1.446(5)	C(3)–F(9)	1.369(6)
C(4)–H(4)	0.99(3)		
N(1)–B–C(1)	112.6(3)	C(4)–N(2)–C(5)	120.2(3)
N(1)–B–C(2)	109.4(3)	C(4)–N(2)–C(6)	122.4(3)
N(1)–B–C(3)	106.4(3)	C(5)–N(2)–C(6)	117.4(3)
C(1)–B–C(2)	108.5(3)	N(1)–C(4)–N(2)	125.9(3)
C(1)–B–C(3)	109.3(3)	N(1)–C(4)–H(4)	122 (2)
C(2)–B–C(3)	110.6(3)	N(2)–C(4)–H(4)	112 (2)
B–N(1)–C(4)	127.3(3)	B–C–F [a]	113.4(6)
B–N(1)–H(1)	125(3)	F–C–F [a]	105.2(9)
C(4)–N(1)–H(1)	107(3)		

[a] Mean with standard deviation.

TABLE 9. Structural comparison of $(CF_3)_3B$ adducts

Compound	B–N (Å)	B–C (Å) [a]	C–B–C (°) [a]	Ref.
$(CF_3)_3B \cdot NH_3$	1.595(8)	1.612(9)	111.2(6)	
$(CF_3)_3B \cdot NH_2Et$	1.589(5)	1.615(3)	110.8(6)	1
$(CF_3)_3B \cdot NHEt_2$	1.596(8)	1.613(4)	108.9(7)	1
$(CF_3)_3B \cdot NH(CH_2)_6$	1.606(8)	1.631(4)	109.9(5)	2
$(CF_3)_3B \cdot NHCHNMe_2$	1.541(4)	1.616(5)	109.5(6)	

[a] Mean with standard deviation defined as the larger of $[\Sigma(1-\bar{1})/N(N-1)]^{1/2}$ and $[\Sigma\sigma^2(1)]^{1/2}N$.

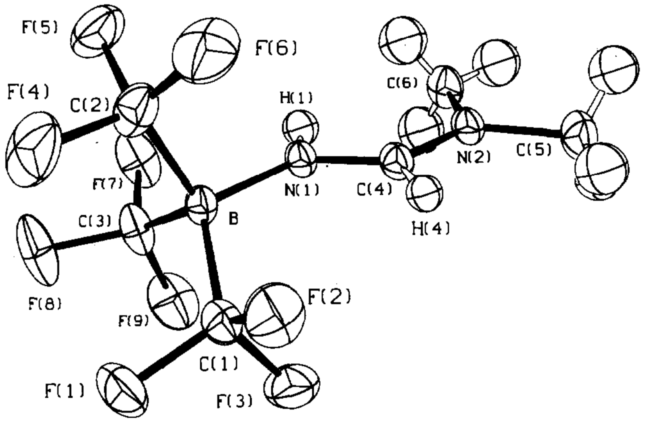

Fig. 3. Perspective drawing of $(CF_3)_3B \cdot NH{=}CHNMe_2$.

The potassium salt (IV) was obtained by the reaction of II with a three-fold excess of powdered KOH suspended in ether. The ethereal solution of IV was filtered and the solvent evaporated *in vacuo* to give IV in quantitative yield. Alternatively I was obtained in quantitative yield by heating $(CF_3)_3B \cdot NH_2C(CH_3)_2(CH_2)_2CH{=}C(CH_3)_2$ [2] in a sealed ampoule for 3 days at 160°C.

III, IR (cm^{-1}): 3320m, ν(NH); 1631 m, 1604 m, $\delta_{as}(NH_3)$; 1483 s, $\delta_s(NH_3)$; 1294 vs, 1137 vs, 1112 vs, $\nu(CF_3)$; 1023 vs, ν(S=O). Raman (cm^{-1}): 3330 w, ν(NH); 1024 m, ν(S=O); 726 vs, $\delta_s(CF_3)$; 718 m, $\nu_{as}(SC_2)$, 681 vs, $\nu_s(SC_2)$.

IV, IR (cm^{-1}): 3410 m, ν(NH); 1621 wb, $\delta(NH_2)$; 1290 s, 1128 vs, 1080 vs, 1039 vs, $\nu(CF_3)$; 892 vs, ν(BN); 680 s, $\delta_s(CF_3)$. Raman (cm^{-1}): 724 vs, $\delta_s(CF_3)$. For IR and Raman spectra of II see Table 2. Elemental analyses are set out in Table 10.

3.2. Potassium 2,2,2-trifluoroethylaminotris(trifluoromethyl)borate (V), tris(trifluoromethyl)borane-2,2,2-trifluoroethylamine-dimethylsulfoxide (VI)

A solution of 2.7 g (10 mmol) of IV in 20 ml DMSO was treated with 8.7 g (22 mmol) of $C_4F_9SO_3CH_2CF_3$ at room temperature for 1 h. The potassium salt V was protonated by addition of CF_3COOH and the solution filtered. The solvent was removed *in vacuo* at 30°C, and VI was separated by sublimation from III, which is formed in an equimolar amount.

III, Sublimation 100°C/10^{-1} torr, yield 1.4 g (89%). V, IR (cm^{-1}): 3343 m, ν(NH); 1115 vs, $\nu(CF_3)$. VI, Sublimation 40°C/10^{-1} torr, yield 1.8 g (91%). IR (cm^{-1}): 1612 m, $\delta_s(NH_2)$; 1130 vsb, ν (CF_3). Raman (cm^{-1}): 1020 m, ν(S=O); 728 vs, $\delta_s(CF_3)$; 720 s, $\nu_{as}(SC_2)$; 681 vs, $\nu_s(SC_2)$.

TABLE 10. Elemental analyses

Compound	Formula	Analyses (Found (calc.) (%))			
		C	H	F	N
II	$C_3H_9BF_9NO_3$	12.51	3.26	58.9	
		(12.47)	(3.15)	(59.18)	
III	$C_5H_9BF_9NOS$	19.38	2.88	54.2	4.59
		(19.18)	(2.90)	(54.63)	(4.48)
IV	$C_3H_2BF_9KN$	13.75	0.73	60.7	
		(13.20)	(0.74)	(62.64)	
V	$C_5H_3BF_{12}KN$	17.25	0.90	63.9	3.74
		(16.92)	(0.85)	(64.23)	(3.95)
VI	$C_7H_{10}BF_{12}NOS$	21.32	2.61	57.3	3.40
		(21.28)	(2.56)	(57.71)	(3.55)
VII	$C_5H_4BF_9KNO$	19.16	1.31	54.0	4.75
		(19.06)	(1.28)	(54.28)	(4.45)
VIII	$C_5HBF_{12}KNO$	16.22	0.3	60.5	3.68
		(16.27)	(0.27)	(61.79)	(3.80)
IX	$C_{10}HBF_{14}KNO$	25.63	0.3	55.9	3.46
		(25.72)	(0.22)	(56.96)	(3.00)
X	$C_5H_7BF_9NO_2$	19.95	2.49	57.6	4.26
		(20.36)	(2.40)	(57.98)	(4.57)
XI	$C_9H_{12}BF_{12}NO_2$	25.66	3.28		3.90
		(26.69)	(2.99)		(3.46)
XII	$C_{10}H_2BF_{14}NO$	27.78	0.83	60.2	3.22
		(28.00)	(0.47)	(62.01)	(3.27)
XIII	$C_5H_3BF_9N$	23.32	1.20	65.5	5.49
		(23.19)	(1.17)	(66.05)	(5.41)
XIV	$C_6H_8BF_9N_2$	25.20	2.86	58.1	9.7
		(24.85)	(2.79)	(58.97)	(9.66)

3.3. Potassium acetamidotris(trifluoromethyl)borate (VII), tris(trifluoromethyl)borane-acetamide-monohydrate (X), potassium trifluoroacetamidotris(trifluoromethyl)borate (VIII), tris(trifluoromethyl)borane-trifluoroacetamide-diethylether (XI), potassium pentafluorobenzamidotris(trifluoromethyl)borate (IX), tris(trifluoromethyl)borane-pentafluorobenzamide (XII)

A mixture of 2.7 g (10 mmol) of IV and 20 ml of $(CH_3CO)_2O$ was stirred for 2 h at room temperature. Removal of volatile material *in vacuo* left pure VII as a solid residue in almost quantitative yield. This was stirred with moist Et_2O/HCl for 10 min, and KCl and filtered off. Volatile material was removed *in vacuo*, and X was sublimed at 50°C/10^{-1} torr, yield 95%. Similarly, IV was stirred with 25 ml $(CF_3CO)_2O$ for 2 days at reflux temperature, compound I was removed by sublimation, and VIII was obtained in a yield of 82%. Treatment of VIII with E_2O/HCl yielded 65% of $IX \cdot Et_2O$, b.p. ~ 85°C/10^{-1} torr. Alternatively acylation with $(CF_3CO)_2O$ was performed in DMF. After addition of Et_2O/HCl, $(CF_3)_3BNH_2COCF_3 \cdot 2DMF$ ($XI \cdot 2DMF$) was obtained in an overall yield of 92%. A solution of 27 g (10 mmol) of IV in 20 ml of Et_2O was stirred with 4.6 g (20 mmol) of C_6F_5COCl at room temperature for 1 h, then 1.0 g (17 mmol) of KOH pellets was added, and stirring was continued for another hour; after filtration the solution was evaporated to dryness to yield 90% of X. Compound XII, sublimation 60°C/10^{-1} torr, was made similarly, yield 91%.

VII, IR (cm^{-1}): 3439 m, $\nu(NH)$; 1647 vs, $\nu(C{=}O)$; 1511 vs, $\delta(NH)$; 1120, 1099 vs, $\nu(CF_3)$. X, IR (cm^{-1}): 3680 m, 3660 m, 3600 m, $\nu(OH)$; 3422 m, 3405 m, $\nu(NH)$; 1681 s, $\nu(C{=}O)$; 1130 vs, $\nu(CF_3)$. Raman (cm^{-1}): 1684 m, $\nu(C{=}O)$; 736 vs, $\delta_s(CF_3)$. VIII, IR (cm^{-1}): 3690 m, $\nu(OH)$; 3420 m, $\nu(NH)$; 1706 vs, $\nu(C{=}O)$; 1190, 1110 vs, $\nu(CF_3)$. XI, IR (cm^{-1}): 3660 m, $\nu(OH)$; 3416 m, $\nu(NH)$; 1708 vs, $\nu(C{=}O)$; 1190, 1115 vs, $\nu(CF_3)$. Raman (cm^{-1}): 1684 m, $\nu(C{=}O)$; 736 vs, $\delta_s(CF_3)$. IX, IR (cm^{-1}): 3410 m, $\nu(NH)$; 1660 vs, $\nu(C{=}O)$; 1508 vs, $\nu(C{=}C)$; 1112, 1090 vs, $\nu(CF_3)$.

NMR data for the C_6F_5 group: δ (^{19}F) (ppm): -142.5, -155.2, -161.8. δ (^{13}C) (ppm)/$^1J(CF)$ (Hz): 142.2/251.8; 138.5/250.9; 144.5/248.0; 116.1

XII, IR (cm^{-1}): 3412 m, $\nu(NH)$; 1665 vs, $\nu(C{=}O)$; 1510 vs, $\nu(C{=}C)$; 1130, 1108 vs, $\nu(CF_3)$.

NMR data for the C_6F_5 group: δ (^{19}F) (ppm): -138.7, -146.0, -159.2. δ (^{13}C) (ppm)/$^1J(CF)$ (Hz): 145.3/259.1, 138.9/249.7, 145.0/251.0, 107.2.

3.4. Tris(trifluoromethyl)borane-acetonitrile (XIII)

A solution of 2.95 g (10 mmol) of XI in 20 ml of anhydrous CH_3CN was refluxed with 5 g of P_4O_{10} for 12 h. After decantation of the solution, CH_3CN was distilled off *in vacuo*, and XIII was purified by sublimation at 100°C/10^{-1} torr, yield 2.0 g (80%). For vibrational spectral data see Table 2.

3.5. Tris(trifluoromethyl)borane-dimethylformamidine (XIV)

A solution of 1.35 g (5 mmol) of IV in 5 ml of DMF was treated with 2.8 g (10 mmol) of $(CF_3SO_2)_2O$ and the mixture was stirred for 8 h at ambient temperature. Then 10 ml of H_2O were slowly added, and VII was extracted with three portions of CH_2Cl_2. After removal of the solvent *in vacuo*, XIV was purified by sublimation at 130°C/10^{-1} torr, yield 1.2 g (83%).

XIV, IR (cm^{-1}): 3403 m, $\nu(NH)$; 1703 vs, $\nu(C{=}N)$; 1120 vsb, $\nu(CF_3)$. Raman (cm^{-1}): 1433 vs, $\delta_s(CH_3)$; 1139 vs, $\nu(C{-}N)$; 735 s, $\delta_s(CF_3)$.

Acknowledgments

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