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Trifluoromethylborane adducts of glycine ☆

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Abstract

The *N*-borylated glycine derivatives $(CF_3)_2(^tBuCH_2CH_2)B\cdot NHMeCH_2COOH$ (**I**), $(CF_3)_3B\cdot NH_2CH_2COOH\cdot H_2O$ (**II**) and $(CF_3)_2HB\cdot NMe_2CH_2COOH$ (**III**) have been prepared by the following routes. Hydrolysis of $(CF_3)_2(^tBuCH_2CH_2)B\cdot N{=}CH_2CH_3$ yielded $(CF_3)_2(^tBuCH_2CH_2)B\cdot NH_2Me$ (**IV**), the nitrogen of which was alkylated by $BrCH_2COO^tBu$/MeLi to form the glycine ester $(CF_3)_2(^tBuCH_2CH_2)B\cdot NHMeCH_2COO^tBu$ (**V**). $(CF_3)_3B\cdot NHEt_2$ has been treated with KOH/Br_2 to yield $(CF_3)_3B\cdot NH_2$, which was alkylated by $BrCH_2COO^tBu$/MeLi to form the thermally unstable ester $(CF_3)_3B\cdot NH_2CH_2COO^tBu$ (**VI**). Similarly $K^+[(CF_3)_2HBNMe_2]^-$ has been alkylated by $BrCH_2COO^tBu$ to yield $(CF_3)_2HB\cdot NMe_2CH_2CO^tBu$ (**VII**). Treatment of **V–VII** with CF_3COOH furnished the free acids **I–III**. Compounds **I–VII** have been characterized by elemental analyses, mass, IR and multinuclear NMR spectroscopy.

Keywords: Trifluoromethylborane; Adducts; Glycine; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Replacement of alkyl groups by trifluoromethyl groups in a trialkylborane considerably enhances its Lewis acidity. Though free trifluoromethylboranes like $(CF_3)_3B$ or $(CF_3)_2BR$ are unstable and still unknown, many complexes of primary, secondary and tertiary amines have been prepared [1]. In contrast to typical trialkylborane amine complexes which usually dissociate at elevated temperature depending on the steric demand of the borane and amine component, trifluoromethylboranes with at least two CF_3 groups combine with amines to form stable adducts with a strong N–B bond. Therefore they are better regarded as 'ammonium salts' than as mere adducts. The protons bonded to the nitrogen in compounds like $(CF_3)_2R^1B\cdot NR^2R^3H$ ($R^1 = CF_3$, H, alkyl; R^2, R^3 = H, alkyl) are acidic, and one of them may be replaced by alkali (e.g. KOH) with the formation of stable salts $K^+[(CF_3)_2R^1BNR^2R^3]^-$. In these salts the nitrogen is a good nucleophile which may be alkylated by alkyl halides. If the alkyl halide is an α-bromocarboxylic acid ester (e.g. $BrCHR^4COO^tBu$), alkylation should give α-amino acid esters of the general formula $(CF_3)_2R^1B\cdot NR^2R^3CHR^4COO^tBu$. Hydrolysis of these esters should make the corresponding amino acids accessible. Here we report on our results.

2. Results

The general formula $(CF_3)_2R^1B\cdot NR^2R^3CHR^4COOH$ covers numerous possible *N*-borylated α-amino acids depending on R^1–R^4. Therefore we decided to synthesize three glycine derivatives (R^4 = H) with different degree of methyl substitution at the nitrogen (R^2, R^3 = H, Me) and different R^1 groups ($^tBuCH_2CH_2$, F_3C, H) attached to the boron: $(CF_3)_2(^tBuCH_2CH_2)B\cdot NHMeCH_2COOH$ (**I**), $(CF_3)_3B\cdot NH_2CH_2COOH$ (**II**) and $(CF_3)_2HB\cdot NMe_2CH_2COOH$ (**III**). The starting materials for these syntheses have already been described.

$(CF_3)_2(^tBuCH_2CH_2)B\cdot N{=}CH_2CH_3$ (**A**) has been obtained by a hydride-shift reaction [2] of $(CF_3)_2BNMe_2$ and $^tBuCH{=}CH_2$ according to Eq. (1).

$$(CF_3)_2BNMe_2 + {}^tBuCH{=}CH_2 \longrightarrow (CF_3)_2(^tBuCH_2CH_2)B\cdot N{=}CH_2CH_3 \quad (1)$$
(**A**)

The N=C double bond is hydrolyzed to form the methylamine borane $(CF_3)_2(^tBuCH_2CH_2)B\cdot NH_2CH_3$ (**IV**) [Eq. (2)]:

☆ Dedicated to Professor P. Paetzold on the occasion of his 60th birthday.

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$$(CF_3)_2(^tBuCH_2CH_2)B\cdot N{=}CH_2CH_3 \xrightarrow{+H_2O/-OCH_2} (CF_3)_2(^tBuCH_2CH_2)B\cdot NH_2CH_3 \quad (2)$$
(IV)

The synthesis of $(CF_3)_3B\cdot NH_3$ (**B**) has also been published already [3]. However it had only been obtained in a multistep synthesis in poor overall yield according to the reaction sequence outlined in Eq. (3).

$$Cl_2BN(^tBu)CH_2Ph \xrightarrow{CF_3Br/P(NEt_2)_3/CH_2Cl_2} [(CF_3)_3B\cdot N(^tBu)CH_2Ph]^- \xrightarrow{H^+/-H_2\ C{=}C(CH_3)_2} (CF_3)_3B\cdot NH_2CH_2Ph \xrightarrow{H_2/Ra\text{-}Ni/-H_3CPh} (CF_3)_3B\cdot NH_3 \quad (3)$$
(B)

Other adducts of $(CF_3)_3B$, e.g. $(CF_3)_3B\cdot NHEt_2$ can be synthesized on a molar scale in 77% yield [1], and such adducts would be converted into compound **B** if only a convenient method for removing the ethyl groups from the nitrogen were found. We achieved this by a simple oxidation using Br_2/KOH in water under conditions similar to the haloform reaction (Eq. (4)).

$$(CF_3)_3B\cdot NHEt_2 \xrightarrow{KOH/Br_2/H_2O} (CF_3)_3B\cdot NH_3 \quad (4)$$

Surprisingly the B–C and N–B bonds were unaffected. This is the result of the high steric demand of three CF_3 groups which create a fluorosphere around boron. The fate of the ethyl groups is unknown. Isolation of $(CF_3)_3B\cdot NH_3$ from the aqueous solution is achieved by extraction with ether. The whole procedure can be carried out on a molar scale.

The synthesis of the third starting material, $(CF_3)_2HB\cdot NHMe_2$ (**C**), according to Eq. (5) has been described in Ref. [3].

$$(CF_3)_2BNMe_2 + Bu_3SnH \longrightarrow (CF_3)_2HB\cdot NMe_2SnBu_3$$
$$(CF_3)_2HB\cdot NMe_2SnBu_3 + H_2O \longrightarrow (CF_3)_2HB\cdot NHMe_2 + HOSnBu_3 \quad (5)$$
(C)

Compounds **IV**, **B** and **C** contain at least one hydrogen atom bonded to nitrogen which can be replaced by alkali in ether. The potassium salts thus formed were reacted with bromoacetic acid t-butyl ester according to Eq. (6).

$$[(CF_3)_2HB\text{–}NMe_2]^- + BrCH_2COO^tBu \longrightarrow (CF_3)_2HB\cdot NMe_2CH_2COO^tBu + Br^- \quad (6)$$
(VII)

However the reaction of **IV** and **B** stopped when ~50% had reacted due to the equilibrium described by Eq. (7); therefore, addition of base was necessary to drive the reaction to completion. MeLi turned out to be suitable since deprotonation of the nitrogen was much faster than substitution reaction of MeLi with $BrCH_2COO^tBu$.

$$[(CF_3)_3B{-}NH_2]^- + (CF_3)_3B\cdot NH_2CH_2COO^tBu \rightleftarrows (CF_3)_3B\cdot NH_3 + [(CF_3)_3B{-}NHCH_2COO^tBu]^- \quad (7)$$

Careful adjustment of the pH to 5 furnished the free esters $(CF_3)_2(^tBuCH_2CH_2)B\cdot NHMeCH_2COO^tBu$ (**V**) and $(CF_3)_3B\cdot NH_2CH_2COO^tBu$ (**VI**) which like **VII** are sensitive to acids. Attempts to sublime **VI** led to extensive decomposition with the elimination of isobutylene. This is understandable because the nitrogen-bonded protons in **B** and also in **VI** are acidic, the acid strength being similar to acetic acid [4]. These esters **V–VII** were then cleaved by trifluoroacetic acid at ambient temperature to yield the free acids **I–III** in reasonable yields.

2.1. Properties and spectra

Compound **VII** is an oil; all other species are air-stable solids, soluble in polar organic solvents. The free acid **II** exhibits excellent solubility in water whereas **I** and **III** are less soluble than their sodium salts.

The ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **I–V** and **VII** were recorded, while **VI** was only characterized via a ^1H NMR spectrum. The chemical shifts which are set out in Table 1 are consistent with the proposed structures and only a few comments will be necessary. The ^{13}C resonances of the CF_3 groups were not detectable due to quadrupole broadening. Compounds **I** and **V** have an asymmetric nitrogen atom which splits the NMR signals of the B–CF_3 groups. The presence of a chiral centre in **I** and **V** is further documented by the appearance of ABX spin systems for the (B)$(CH_3)(H)NCH_2COOR$ protons (CH_2: δ ~4 (d) ppm, ^2J (H–H) ~18 Hz; δ ~3.4 (d,d) ppm, ^2J (H–H) ~18 Hz, ^3J (H–H) ~9 Hz). Deprotonation of **II** and **III** at the carboxylic group is indicated by the typical shift of the ^{13}C carbon signals of the carbonyl group, i.e. δ ^{13}C: $COOH$ = 167.46 ppm → COO^- = 171.54 ppm (**II**) and δ ^{13}C: $COOH$ = 165.32 ppm → COO^- = 169.70 ppm (**III**).

EI mass spectral data for **I–VII** are listed in Table 2. The $[M]^+$ peaks were weak if detectable at all, but the presence of the ions $[M-CF_3]^+$ and $[M-C_2F_5]^+$ is indicative of the molecular weight. Base peaks for compounds **I–III** are the fragments $[H_2C{=}NH_n(CH_3)_{2-n}]^+$ which reflect the degree of methyl substitution at nitrogen.

Table 1
NMR spectral data for compounds **I–VII** (δ in ppm) [a]

Chemical shift	I	II	III	IV	V	VI	VII
^1H							
$\delta(C(CH_3))_3$	0.88			0.88	0.86		
$\delta(OC(CH_3))_3$					1.53	1.55	1.46
$\delta(NCH_3)$	2.78		3.01	2.69	2.71		3.02
$\delta(NCH_2)$	3.54	3.48	3.79		3.31	3.82	3.69
	4.16				3.90	4.00	
$\delta(BH)$			~1.9				~1.9
$\delta(BCH_2)$	0.58			0.53	0.54		
$\delta(OH)$	~6.4	~5.5	9.38				
$\delta(NH)$	~4.9	~5.8		~3.9	~4.9	~5.1	
						~5.3	
$\delta(CCH_2)$	1.06			1.11	1.04		
^{19}F							
$\delta(CF_3)$	−63.1	−59.6	−58.4	−66.4	−63.2		−57.7
	−63.3				−63.3		
^{11}B							
$\delta(B)$	−7.0	−12.0	−7.6	−7.4	−7.0		−8.4
^{13}C							
$\delta(C(CH_3))_3$	28.89			28.86	28.86		27.50
					28.88		
$\delta(NCH_3)$	38.95		48.13	28.53	38.88		48.94
$\delta(NCH_2)$	52.61	41.85	59.10		53.49		61.30
$\delta(BCH_2)$	~8.0			~6.5	~8.1		
$\delta(C{=}O)$	171.11	167.46	165.32		167.39		164.39
$\delta(CCH_2)$	30.92			30.87	30.87		
$\delta(OC(CH_3))_3$					85.64		84.30
$\delta(CC(CH_3))_3$	37.51			37.85	37.52		

[a] **VI, VII** in $CDCl_3$ in CD_3CN. ^1H: 250.13 MHz. int. std. $CHCl_3$ = 7.27 ppm/CD_2HCN = 1.95 ppm. ^{13}C: 62.9 MHz. int. std. $CDCl_3$ = 77.0 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 compounds **I–VII** (*m/e* (%) [fragment]$^+$)

I	44 (100) $[H_2C{=}NHCH_3]^+$; 56 (94) $[H_2C{=}C(CH_3)_2]^+$; 57 (72) $[C(CH_3)_3]^+$; 138 (11) $[F_2BNHCH_3CH_2COOH]^+$; 71 (9) $[C_5H_{11}]^+$; 118 (4) $[FBN(CH_3)CH_2COOH]^+$; 308 (4) $[M-CH_3]^+$; 188 (3) $[(F_3C)FBNHCH_3CH_2COOH]^+$; 238 (2) $[(F_3C)_2BNHCH_3CH_2COOH]^+$; 323 (1) $[M]^+$ 204 (1) $[M-C_2F_5]^+$; 254 (1) $[M-CF_3]^+$
II	30 (100) $[H_2C{=}NH_2]^+$; 78 (13) $[F_2BNHCH_2]^+$; 124 (11) $[F_2BNH_2CH_2COOH]^+$; 274 (4) $[M-F]^+$; 104 (7) $[FBNHCH_2COOH]^+$; 174 (7) $[M-C_2F_5]^+$; 154 (4) $[F_3CBNHCH_2COOH]^+$; 224 (1) $[M-CF_3]^+$
III	58 (100) $[H_2C{=}N(CH_3)_2]^+$; 59 (81) $[(H_3C)_3N]^+$; 44 (72) $[H_2C{=}NHCH_3]^+$; 74 (54) $[FHBN{=}CH_2(CH_3)]^+$; 92 (33) $[F_2BN{=}CH_2(CH_3)]^+$; 152 (12) $[M-C_2F_4H]^+$; 134 (9) $[M-C_2F_5]^+$; 103 (8) $[(H_3C)_2NCH_2COOH]^+$; 202 (5) $[M-CF_2H]^+$
IV	56 (100) $[H_2C{=}C(CH_3)_2]^+$; 57 (97) $[C(CH_3)_3]^+$; 80 (78) $[F_2BNH_2CH_3]^+$; 41 (26) $[C_3H_5]^+$; 79 (19) $[F_2BNHCH_3]^+$; 146 (3) $[M-C_2F_5]^+$; 250 (2) $[M-CH_3]^+$; 265 (2) $[M]^+$
V	57 (100) $[C(CH_3)_3]^+$; 56 (34) $[H_2C{=}C(CH_3)_2]^+$; 44 (37) $[H_2C{=}NHCH_3]^+$; 41 (13) $[C_3H_5]^+$; 238 (2) $[(F_3C)_2BNHCH_3CH_2COOH]^+$; 254 (2) $[M-C_9H_{17}]^+$; 308 (1) $[M-C_5H_{11}]^+$; 138 (1) $[F_2BNHCH_3CH_2COOH]^+$; 188 (1) $[(F_3C)FBNHCH_3CH_2COOH]^+$; 294 (1) $[M-C_6H_{13}]^+$
VI	57 (100) $[C(CH_3)_3]^+$; 30 (39) $[H_2C{=}NH_2]^+$; 59 (24) $[HOC(CH_3)_2]^+$; 334 (10) $[M-CH_3]^+$; 276 (11) $[M-OC(CH_3)_3]^+$
VII	57 (100) $[C(CH_3)_3]^+$; 58 (87) $[H_2C{=}N(CH_3)_2]^+$; 44 (57) $[H_2C{=}NHCH_3]^+$; 136 (10) $[M-C_2F_4-OC(CH_3)_3]^+$; 106 (7) $[F_2BNC_2H_3O]^+$; 184 (6) $[M-CF_3-H_2C{=}C(CH_3)_2]^+$; 134 (5) $[M-C_2F_5-H_2C{=}C(CH_3)_2]^+$; 159 (5) $[(H_3C)_2NCH_2COOC(CH_3)_3]^+$; 236 (5) $[M-OC(CH_3)_3]^+$; 186 (4) $[M-CF_2-OC(CH_3)_3]^+$

3. Discussion

While no information about an *N*-borylated glycine is available, to our knowledge only one trialkylborane glycine derivative, $(H_5C_2)_3B \cdot NH_2CH_2COOCH_3$, has been reported previously. This was obtained [5] according to Eq. (8).

$$(H_5C_2)_3B + NH_2CH_2COOCH_3 \longrightarrow (H_5C_2)_3B \cdot NH_2CH_2COOCH_3 \quad (8)$$

Such a simple synthesis, however, cannot be transferred into trifluoromethylboron chemistry due to the instability of free trifluoromethylboranes, e.g. $(CF_3)_3B$. Two or three CF_3 groups attached to boron change the chemistry and character of boranes drastically. Thus the N–B bond is stronger than in related amine boranes where the boron carries alkyl groups. The steric demand of the CF_3 substituents protects the B–C bond, especially in $(CF_3)_3B \cdot NHR_2$ derivatives, to such an extent that cleavage reactions with carboxylic acids or oxidative cleavage with bromine does not occur. In the glycine derivatives **I–III**, the borane fragments [$(CF_3)_2(^tBuCH_2CH_2)B$–, $(CF_3)_3B$– and $(CF_3)_2HB$–] behave more like alkyl groups linked to nitrogen than weakly bonded Lewis acids.

4. Experimental details

4.1. Methylamine bis(trifluoromethyl)(3,3-dimethylbutyl)borane (IV)

A solution of 18 g (65 mmol) of $(CF_3)_2(^tBuCH_2CH_2)B \cdot N{=}CH_2CH_3$ [2] in 80 ml of CH_2Cl_2 was stirred with 50 ml of 1 M KOH for 6 h. The aqueous phase was acidified with HCl, separated and the organic layer again stirred with 50 ml of 1 M KOH. The aqueous phase was again acidified, the organic layer separated and dried over Na_2SO_4, the solvent evaporated and the residue sublimed at 40 °C/10^{-1} mbar. Pure **IV** was obtained as colourless needles by crystallization from CH_2Cl_2/pentane/toluene mixtures at −28 °C. Yield 12.6 g (73%). M.p. 51 °C. IR (cm^{-1}): 3320 m $\nu_{as}(NH_2)$; 3288 m $\nu_s(NH_2)$; 1598 s $\delta(NH_2)$; 1114 vs, 1090 vsb $\nu(CF_3)$.

The ^1H and ^{13}C NMR spectra of the mother liquor showed that it contained ca. 24% of $(CF_3)_2(^tBuCH_2CH_2)B \cdot NHMe_2$ (^1H NMR: δ $N(CH_3)_2 = 2.77$ ppm ^{13}C NMR: δ $N(CH_3)_2 = 40.0$ ppm; δ $C(CH_3)_3 = 37.6$ ppm; δ $(CCH_2) = 30.9$ ppm).

4.2. Bis(trifluoromethyl)(3,3-dimethylbutyl)borane N-methylglycine t-butyl ester (V)

To a stirred solution of 11 g (41 mmol) of **IV** in 40 ml of dry ether, 44 ml of 1 M MeLi/ether and 8.6 g (44 mmol) of $BrCH_2COO^tBu$ were added. After 20 min, 44 ml of 1 M MeLi/ether were further added and stirring was continued for 2 h. Then the reaction mixture was hydrolyzed with 40 ml of water and the pH adjusted to 5 using HCl. The organic layer was separated, dried over Na_2SO_4 and the solvent evaporated. Pure **V** was obtained after sublimation at 50 °C/10^{-1} mbar. Yield: 11.7 g (75%). M.p. 50 °C. IR (cm^{-1}): 3215 m ν(N–H); 1725 vs ν(C=O); 1095 vs, 1088 vs, 1074 vs $\nu(CF_3)$.

4.3. Bis(trifluoromethyl)(3,3-dimethylbutyl)borane N-methylglycine (I)

To 8.0 g (21 mmol) of **V** dissolved in 15 ml of $CHCl_3$, 1 ml of CF_3COOH was added at ambient temperature. After 6 h all volatile material was removed in vacuo and **I** recrystallized from $CHCl_3$. Yield: 4.9 g (72%). M.p. 140 °C. IR (cm^{-1}): 3234 m ν(N–H); 1731 vs ν(C=O); 1110 vs, 1090 vs, 1074 vs $\nu(CF_3)$.

4.4. Ammine tris(trifluoromethyl)borane (B)

To a stirred suspension of 8.7 g (0.03 mol) of $(CF_3)_3B \cdot NHEt_2$ [1] in 200 ml of water, 48 g (0.3 mol) of Br_2 and 42 g (0.75 mol) of KOH were added in four portions over 5 d at ambient temperature. The end of the reaction was indicated by the formation of an almost clear solution. The reaction mixture was brought to pH 2–3 by adding H_2SO_4, and excess bromine was destroyed with Na_2SO_3. Compound **B** was extracted from the aqueous acidified solution with three 200 ml portions of ether. The ether was evaporated and the residue was sublimed twice at 40 °C/10^{-1} mbar to yield 5.2 g (0.022 mol) (73%) of pure **B**.

4.5. Tris(trifluoromethyl)borane glycine t-butyl ester (VI) and tris(trifluoromethyl)borane glycine monohydrate (II)

To a stirred solution of 8.0 g (34 mmol) of $(CF_3)_3B \cdot NH_3$ (**B**) in 80 ml of ether, 10 g of powdered KOH were added and stirring was continued for 15 min. The solution was filtered, the ether distilled off and the potassium salt $K[(CF_3)_3BNH_2]$ carefully dried in vacuo. The salt was dissolved in 50 ml of dry ether and 6.9 g (35 mmol) of $BrCH_2COO^tBu$ added with stirring. After 20 min, 34 ml of 1 M MeLi/ether were added and stirring continued for 2 h. To the reaction mixture, 40 ml water were added, the pH adjusted to 5 using HCl, the organic layer separated, dried over Na_2SO_4 and the solvent evaporated. Attempts to sublime the dark oily residue led to extensive elimination of isobutylene; hence only small amounts of pure **VI** could be obtained. The residue was treated with 2 ml of CF_3COOH at room temperature, all volatile material removed in vacuo and **II** separated by repeated crystallization from $CHCl_3$ with admission of moisture, the material crystallizing in thin colourless plates as a monohydrate. Yield: 4.2 g (40%). TG and DTA experiments revealed a melting point of ~92 °C accompanied by elimination of the water of crystallization and decomposition at 141 °C. A pK value of 2.7 was determined by titration of a 0.03 M aqueous solution of **II** with 0.1 N NaOH. IR (cm^{-1}): 3200 w ν(N–H); 1729 vs ν(C=O); 1615 s $\delta_s(NH_2)$; 1284 vs $\delta(CH_2)$; 1134 vs, 1113 vs $\nu(CF_3)$.

Table 3
Elemental analyses

Compound	Formula	Analyses [Found (calc.)] (%)		
		C	H	N
I	$C_{11}H_{20}BF_6NO_2$	40.8 (40.89)	6.6 (6.24)	4.5 (4.34)
II	$C_5H_7BF_9NO_3$	19.4 (19.32)	2.2 (2.27)	4.4 (4.51)
III	$C_6H_{10}BF_6NO_2$	28.5 (28.49)	3.9 (3.98)	5.4 (5.54)
IV	$C_9H_{18}BF_6N$	40.8 (40.78)	6.8 (6.85)	5.2 (5.28)
V	$C_{15}H_{28}BF_6NO_2$	47.5 (47.51)	7.4 (7.44)	3.7 (3.69)
VII	$C_{10}H_{18}BF_6NO_2$	38.1 (38.86)	5.6 (5.87)	5.0 (4.53)

4.6. Bis(trifluoromethyl)borane N,N-dimethylglycine t-butyl ester (VII)

To a stirred solution of 4.0 g (20.6 mmol) of $(CF_3)_2HB \cdot NHMe_2$ [3] in 60 ml of ether was added 8 g of powdered KOH and stirring continued for 15 min. The solution was filtered and 4.1 g (21 mmol) of $BrCH_2COO^tBu$ were added at ambient temperature. The reaction mixture was stirred for 2 h, filtered, the ether removed in vacuo and the residue sublimed at 45 °C/10^{-1} mbar. Yield: 4.7 g (74%). IR (cm^{-1}): 1744 s ν(C=O); 2466 m ν(B–H); 1277 s $\delta(CH_3)$; 1103 vs, 1058 vs $\nu(CF_3)$.

4.7. Bis(trifluoromethyl)borane N,N-dimethylglycine (III)

To a solution of 3 g (9.7 mmol) of **VII** in 10 ml of $CHCl_3$ was added 1 ml of CF_3COOH at ambient temperature. After a few minutes **III** crystallized (colourless needles) and was recrystallized from $CHCl_3$. Yield: 1.99 g (81%). M.p. 132 °C IR (cm^{-1}): 2474 m ν(B–H); 1742 vs ν(C=O); 1120 vs, 1099 vs, 1078 vs $\nu(CF_3)$. A pK value of 2.8 was determined by titration of a 0.005 M aqueous solution of **III** with 0.1 N NaOH.

For elemental analyses, see Table 3.

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