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Ene-type and hydride-shift reactions of thiocarbonyl compounds with (dimethylamino)bis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ *

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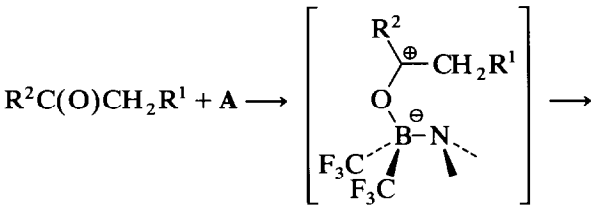
Abstract

(Dimethylamino)bis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (**A**), reacts with thiocarbonyl compounds of the general formula $R^2C(S)CH_2R^1$ to yield the triorganoboron adducts $(R^2C(S)CHR^1)(CF_3)_2B \cdot NHMe_2$: $R^2 = NMe_2$; R^1 = H (**I**), Me (**II**); R^2 = OEt; R^1 = H (**III**), Me (**IV**); R^2 = SEt; R^1 = H (**V**). When R^2 = SEt and R^1 = Me, the thioenol derivative $(MeHC{=}C(SEt)S)(CF_3)_2B \cdot NHMe_2$ (**VI**) is formed, while PhC(S)Me yields the analogous amine borane $(H_2C{=}C(Ph)S)(CF_3)_2B \cdot NHMe_2$ (**VII**). Compound **V** adds a second molecule of **A** to form $((NHMe_2 \cdot (CF_3)_2B)HC{=}C(SEt)S)(CF_3)_2B \cdot NHMe_2$ (**VIII**). Treatment of **A** with MeC(S)^{t}Bu at −40°C yields $(H_2C{=}C(^t Bu)S)(CF_3)_2B \cdot NHMe_2$ (**IX**) in an ene-type reaction. This rearranges at 20°C by a unimolecular process to the methyl-methyleneimine stabilized borane $(Me(^t Bu)C(H)S)(CF_3)_2B \cdot N(CH_3){=}CH_2$ (**X**). The identities of the novel compounds have been confirmed by multinuclear NMR IR and mass spectrometry.

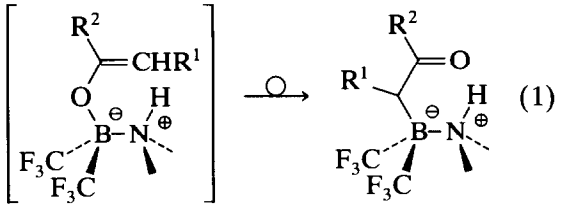
Key words: Ene-type reactions; Hydride-shift reactions; Thiocarbonyl compounds; Boron; Perfluoralkyl; Amine–borane

1. Introduction

In an earlier paper [1] reporting on reactions of $(CF_3)_2BNMe_2$ (**A**), we showed that carbonyl compounds (and similarly nitriles) having CH bonds α to the C=O (or C≡N) bond undergo an ene-type reaction leading to B–C bond formation (eqn. (1)).



(**B**)



(**C**) (**D**) (1)

Here the CH_2 group provides a proton for the conversion from **B** to **C**. In the absence of such a C–H bond (*e.g.* in the reaction of **A** with $(CF_3)_2CO$), a hydrogen atom of the $N(CH_3)_2$ group is instead transferred as a hydride to the carbenium centre in **B**, with the formation of a methyl-methyleneimine borane complex [2]. The surprising aspect of the process shown in eqn. (1) is the enol → carbonyl rearrangement **C** → **D** in which a B–C bond replaces a B–O linkage. This rearrangement **C** → **D** is fast, and it seems to be inhibited only in the reaction of **A** with Et_2CO [1]. One reason for the readiness of **C** to rearrange is certainly the strength of the C=O and B–C bonds formed.

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* Dedicated to Professor O.J. Scherer on the occasion of his 60th birthday.

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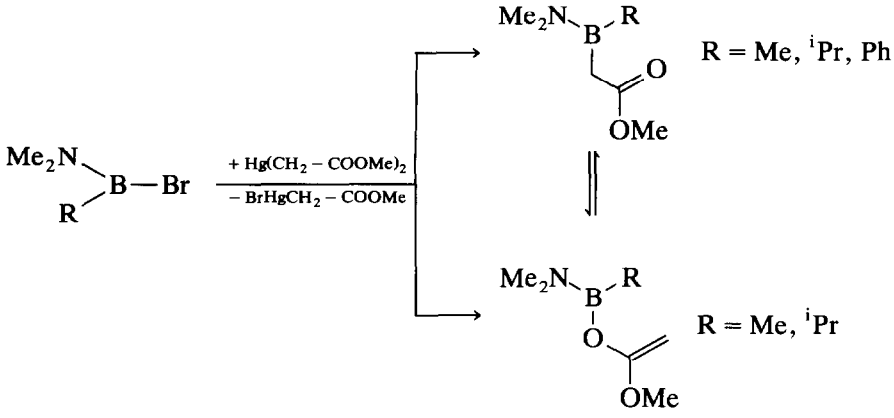
A somewhat related keto–enol equilibrium in boron chemistry has been previously observed. Whether $Me_2NB(R)OC(=CH_2)OMe$ or $Me_2NB(R)CH_2C(O)OMe$ was initially formed depended on the nature of the substituent R (Me, ^{i}Pr, Ph) [3] (Scheme 1). However, in that case boron has a coordination number of three, and the rearrangement presumably involves a four-membered cyclic transition state. No reactions following the route shown in eqn. (1) have been observed for aminoboranes in which the boron bears alkyl groups [4].

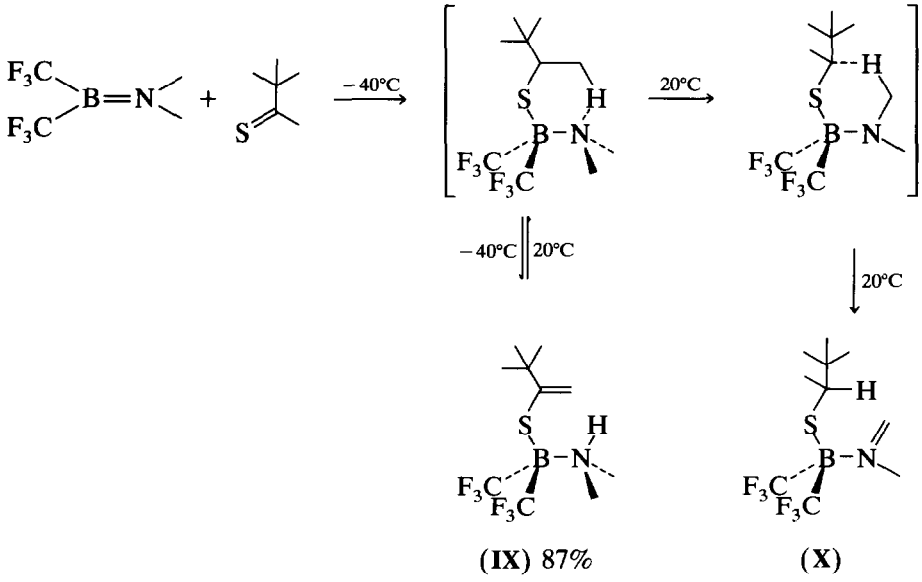
In order to further elucidate the course of the reaction depicted in eqn. (1), we have studied the behaviour of the thiocarbonyl compounds $R^2C(S)CH_2R^1$. These are expected to show a different reactivity towards **A**, the C=S bond being significantly weaker than the C=O bond. The results are described below.

2. Results

The reaction of **A** with a thiocarbonyl compound of the general formula $R^2C(S)CH_2R^1$, where $R^2 = NMe_2$ or OEt, and $R^1 = H$ or CH_3, proceeded in the same way (eqn. (2)) as was observed for the corresponding C=O derivatives (eqn. (1)). While a reaction time of hours rather than seconds was required, yields were still quantitative. When R^2 was SEt and R^1 was a CH_3 group, the reaction stopped at the enethiol intermedi-



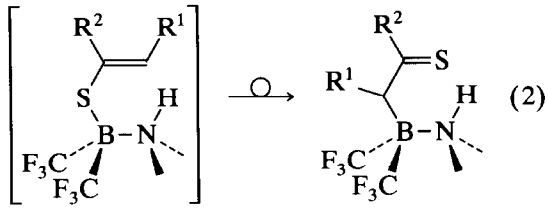
Scheme 1.



Scheme 2.

ate (**VI**), *i.e.* stage **C** in eqn. (1).

$R^2C(S)CH_2R^1 + A \longrightarrow$

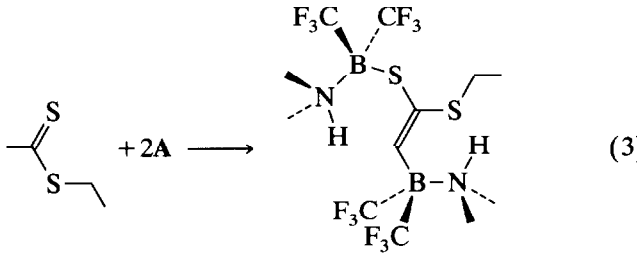


(2)

(**VI, VII**) (**I–V**)

Compound	R^1	R^2	Yield (%)
I	H	NMe_2	95
II	Me	NMe_2	93
III	H	OEt	93
IV	Me	OEt	89
V	H	SEt	96
VI	Me	SEt	80
VII	H	Ph	71

The compound PhC(S)Me reacted analogously and yielded **VII**. Dithioacetic acid ester was found to form a 1:2 adduct (**VIII**) with **A** (eqn. (3)). Compound **VIII**, which was also obtained by treatment of **V** with **A**, may be regarded as resulting from an ene-type reaction. No rearrangement of **VIII** with regeneration of the thiocarbonyl group was observed.



(3)

(**VIII**) 90%

However, t-butyl methyl thioketone reacts with **A** in a complicated fashion, as depicted in Scheme 2. Reaction at −40°C gave **IX** as crystals. When a solution of **IX** in CH_2Cl_2 was allowed to warm to ambient temperature, a rearrangement took place yielding **X**. This rearrangement was monitored by ^1H NMR spectroscopy by observing the disappearance of the $C{=}CH_2$ hydrogen atoms of **IX** and the growth of the $N{=}CH_2$ protons of **X**. Kinetic studies at 308, 313 and 318 K revealed that the rearrangement **IX** → **X** is of first order, with an activation energy E_a of 112 ± 19 kJ mol^{-1} K^{-1}.

3. Properties and spectra

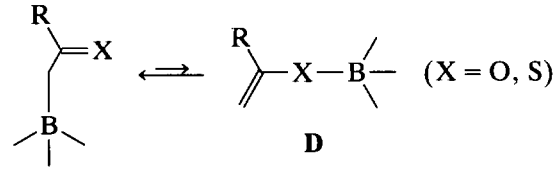
The novel amine-boranes **I–V** are colourless solids; their melting points are reported in the Experimental section. They are stable to air and moisture and soluble in polar organic solvents. Species with a B–S bond (**VI–X**) are generally sensitive to hydrolysis and should be handled in a dry atmosphere.

The ^1H, ^{19}F, ^{11}B and ^{13}C NMR spectra of **I–X** were recorded. The chemical shifts, which are set out in Table 1, are consistent with the proposed structures, and only a few comments are necessary. The ^{13}C resonances of the CF_3 groups were not detectable owing to quadrupole broadening. Compounds **II** and **IV** have an asymmetric carbon atom which should give rise to split NMR signals of both the $N{-}CH_3$ and $B{-}CF_3$ groups. However, only **II** showed this splitting in the ^1H, ^{19}F and ^{13}C spectra, while splitting only of two ^{13}C NCH_3 resonances was observed for **IV**. Nevertheless, the presence of a chiral centre in **IV** is indicated by the appearance of an ABX_3 spin system for the OCH_2CH_3 protons.

The EI mass spectral data for **I–IX** are listed in Table 2. In contrast to the usual behaviour of $CF_3{-}B$ compounds, they give relatively intense signals for the molecular ions $[M]^+$. A characteristic fragment of all compounds is the ion at *m/e* 94, assigned to $[F_2BNH(CH_3)_2]^+$.

4. Discussion

The investigation has established that for thiocarbonyl derivatives (X = S) of the $(CF_3)_2BN$ moiety the **C** ⇋ **D** tautomeric equilibrium lies further towards **D** than is the case with the corresponding carbonyl derivatives (X = O).



(X = O, S)

C **D**

On the other hand, the ene-type reactions observed with thioamides and thioesters, which are followed by a rearrangement, resemble those of the C=O derivatives to a surprising degree [1]. However, it should be noted that $CH_3C(O)CF_3$ and **A** also yield the stable enol derivative $(H_2C{=}C(CF_3)O)(CF_3)_2B \cdot NHMe_2$ [^1H NMR δ: 4.9, 4.80 (CH_2); 4.32 (NH); 2.79 (NCH_3) ppm. ^{11}B NMR δ: −3.2 ppm. ^{13}C NMR δ: 39.1 (NCH_3); 94.1 ($C{=}CH_2$); 145.6 ($C{=}CH_2$); 120.4 (CCF_3) ppm. ^{19}F NMR δ: −74.0 (CCF_3); −65.0 (BCF_3) ppm]. This showed no tendency to rearrange to a C-alkylated product even on prolonged heating at 60°C.

The rearrangement of **IX** to **X** is unexpected. So far only carbonyl compounds such as $(CF_3)_2C{=}O$, carrying

no α-C–H bonds [2], have been found to undergo hydride-shift reactions with **A**, while several terminal alkenes showed an ambivalent behaviour [5]. For example, $H_2C{=}C(^tBu)Me$ combined with **A** to give a 1:4 mixture of $(H_2C{=}C(^tBu)CH_2)(CF_3)_2B \cdot NHMe_2$ and $(Me(^tBu)HCCH_2)(CF_3)_2B \cdot N(CH_3){=}CH_2$. In this case, steric crowding was assumed to account for the preference for the product formed by a hydride shift. In the case of $MeC(S)^tBu$, this explanation does not hold because $MeC(O)^tBu$ reacts smoothly with **A** to give $(^tBuC(O)CH_2)(CF_3)_2B \cdot NHMe_2$ [1]. Here the greater strength of the C=O than of the C=S bond means that

TABLE 1. NMR spectral data for compounds **I–X** (δ in ppm) [a]

	I	II	III	IV	V	VI	VII	VIII	IX	X
^1H										
$\delta(BCH_n)$	2.33	2.99	2.43	2.74	2.69			1.36		
$\delta(BN(CH_3)_n)$	2.78	2.68	2.85	2.71	2.83	2.89	2.68	2.70	2.94	3.79
		2.79						2.84		
$\delta(CSN(CH_3)_2)$	3.38	3.37								
	3.50	3.48								
$\delta(NH)$	8.51	9.17	6.54	6.79	6.88	6.88	3.60	5.87	4.9	
								6.69		
$\delta(CH{-}CH_3)$		1.41		1.27		1.85				1.18
$\delta(C(CH_3)_3)$									1.18	0.96
$\delta(=CH_n)$						6.56	5.71	6.34	5.09	7.91
							5.82		5.39	8.46
$\delta(CH_n{-}CH_3)$			4.52	4.53	3.21	2.85		3.03		2.72
				4.57						
$\delta(CH_2{-}CH_3)$			1.40	1.41	1.32	1.21		1.30		
$\delta(C_6H_5)$							~ 7.5			
^{19}F										
$\delta(CF_3)$	−63.7	−59.7	−63.0	−60.6	−62.5	−62.0	−61.9	−56.6	−61.2	−60.4
		−60.9						−57.4		−62.2
^{11}B										
$\delta(B)$	−8.7	−8.6	−8.5	−7.8	−8.2	−3.4	−4.0	−4.2	−3.0	−3.1
								−9.5		
^{13}C										
$\delta(BCH_n)$	29.0	32.0	39.7	43.5	41.2					
$\delta(BN(CH_3)_n)$	39.2	40.5	39.8	39.5	39.7	39.3	40.1	40.5	40.4	48.4
		40.8		40.2				40.8		
$\delta(CSN(CH_3)_2)$	42.4	41.9								
	44.6	44.7								
$\delta(C(CH_3)_3)$									29.4	27.4
$\delta(C(CH_3)_3)$									39.6	35.5
$\delta(CH_n{-}CH_3)$			69.0		31.3	27.9		30.0		48.3
$\delta(CH_n{-}CH_3)$			13.3	13.1	11.7	14.4		14.6		20.3
						23.8				
$\delta(C{=}CH_n)$						145.2	124.8	148.0	112.8	
$\delta(N{=}CH_2)$										170.4
$\delta(C{=}CH_n)$						123.3	143.3	134.8	153.5	
$\delta(C_6H_5)$							126.9			
							127.5			
							128.6			
							132.9			
$\delta(C{=}S)$	204.4	211.2	228.0	231.8	228.0					
$\delta(BCH{-}CH_3)$		19.3		12.3						

[a] **I–VII** and **IX–X** in $CDCl_3$, **VIII** 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 in order of decreasing intensity (*m/e* (relative intensity (%)) [fragment]$^+$) for I–IX

I	103(100)[C_4H_9NS]$^+$; 296(49)[M]$^+$; 70(47)[C_4H_8N]$^+$; 94(19)[$F_2BNH(CH_3)_2$]$^+$; 227(12)[M − CF_3]$^+$; 263(10)[M − SH]$^+$; 88(6)[$(CH_3)_2NCS$]$^+$; 277(3)[M − F]$^+$
II	117(100)[$C_5H_{11}NS$]$^+$; 84(82)[$C_5H_{10}N$]$^+$; 310(66)[M]$^+$; 94(38)[$F_2BNH(CH_3)_2$]$^+$; 277(32)[M − SH]$^+$; 88(16)[$(CH_3)_2NCS$]$^+$; 291(6)[M − F]$^+$; 241(5)[M − CF_3]$^+$
III	94(100)[$F_2BNH(CH_3)_2$]$^+$; 236(64)[M − SC_2H_5]$^+$; 297(61)[M]$^+$; 104(16)[C_4H_8SO]$^+$; 252(11)[M − OC_2H_5]$^+$; 228(4)[M − CF_3]$^+$; 278(3)[M − F]$^+$
IV	94(100)[$F_2BNH(CH_3)_2$]$^+$; 311(35)[M]$^+$; 118(31)[$C_5H_{10}SO$]$^+$; 250(8)[M − SC_2H_5]$^+$; 292(2)[M − F]$^+$; 266(1)[M − OC_2H_5]$^+$
V	94(100)[$F_2BNH(CH_3)_2$]$^+$; 252(75)[M − SC_2H_5]$^+$; 313(60)[M]$^+$; 285(12)[M − C_2H_4]$^+$; 59(10)[CH_3CS]$^+$; 294(3)[M − F]$^+$
VI	94(100)[$F_2BNH(CH_3)_2$]$^+$; 327(48)[M]$^+$; 72(33)[CH_3CHCS]$^+$; 101(30)[C_5H_9S]$^+$; 185(18)[$C_4H_{10}BF_2NS_2$]$^+$; 134(8)[$C_5H_{10}S_2$]$^+$; 308(2)[M − F]$^+$; 266(2)[M − SC_2H_5]$^+$
VII	94(100)[$F_2BNH(CH_3)_2$]$^+$; 136(59)[$C_6H_5CSCH_3$]$^+$; 329(48)[M]$^+$; 103(47)[$C_6H_5CCH_2$]$^+$; 77(19)[C_6H_5]$^+$; 121(18)[C_6H_5CS]$^+$; 91(12)[C_7H_7]$^+$
VIII	94(100)[$F_2BNH(CH_3)_2$]$^+$; 280(51)[M − $S(CF_3)_2BNH(CH_3)_2$]$^+$; 506(30)[M]$^+$; 252(5)[M − $S(CF_3)_2BNH(CH_3)_2$ − C_2H_4]$^+$; 92(15)[$F_2BN{=}CH_2CH_3$]$^+$
IX	94(100)[$F_2BNH(CH_3)_2$]$^+$; 116(31)[$(CH_3)_3CCSCH_3$]$^+$; 309(21)[M]$^+$; 92(12)[$F_2BN{=}CH_2CH_3$]$^+$; 59(11)[CH_3CS]$^+$; 57(11)[$(CH_3)_3C$]$^+$

X, the thermodynamically more stable product, is formed rather than the hypothetical isomer (^{t}BuC(S)-CH_2)$(CF_3)_2B \cdot NHMe_2$.

5. Experimental details

5.1. Dimethylamine-[(dimethylamino)thiocarbonylmethyl]bis(trifluoromethyl)borane (I), dimethylamine-[(1-dimethylamino)thiocarbonylethyl]bis(trifluoromethyl)borane (II), dimethylamine(ethoxythiocarbonylmethyl)bis(trifluoromethyl)borane (III), dimethylamine-(1-ethoxythiocarbonylethyl)bis(trifluoromethyl)borane (IV), dimethylamine-(ethylthio-thiocarbonylmethyl)bis(trifluoromethyl)borane (V), dimethylamine-(2-ethylthio-1-thiabut-2-ene-1-yl)bis(trifluoromethyl)borane (VI)

The aminoborane $(CF_3)_2BNMe_2$ (2.10 g, 10.8 mmol) was added dropwise to a stirred solution consisting of 10.3 mmol of the thiocarbonyl component in 15 ml of dry CH_2Cl_2 at 4°C. The stirred mixture was allowed to warm to room temperature during 1 h (**I, III, IV, V, VI**) or 4 h (**II**). The solvent and other volatile by-products were removed *in vacuo* at ambient temperature, and the residue was purified by sublimation *in vacuo* at 10^{-1} mbar: **I** and **II** at 60°C; **III, IV** and **V** at 40°C. Compound **VI** was obtained as a thermally unstable, moisture-sensitive oil, which could not be further purified. **I** m.p. 99°C. IR (cm^{-1}): 1100 (vs); 1078 (vs); 1048 (s, CF_3). **II** m.p. 96°C. IR (cm^{-1}): 1089 (vs); 1063 (s); 1054 (s, CF_3). **III** m.p. 41°C. IR (cm^{-1}): 1093 (vs b, CF_3). **IV** m.p. 38°C. IR (cm^{-1}): 1090 (vs b, CF_3). **V** m.p. 57°C. IR (cm^{-1}): 1092 (vs); 1063 (s); 1042 (s, CF_3). **VI** IR (cm^{-1}): 1098 (vs); 1053 (s); 1041 (s, CF_3).

5.2. 2,8-Dimethyl-3,3,7,7-tetrakis(trifluoromethyl)-5-thioethyl-2,8-diazonia-3,7-diborata-6-thia-non-4-ene (VIII)

Compound **VIII** was obtained by a procedure similar to that used for **V** when 2 equiv. of **A** were used. The residue was filtered off and washed with dry CH_2Cl_2. M.p. ~ 98°C (dec.). IR (cm^{-1}): 3135 (s, NH); 1560 (m, C=C); 1094 (vs); 1054 (vs); 1045 (s, CF_3).

5.3. Dimethylamine-(2-phenyl-1-thia-prop-2-ene-1-yl)bis(trifluoromethyl)borane (VII), dimethylamine-(2-t-butyl-1-thia-prop-2-ene-1-yl)bis(trifluoromethyl)borane (IX)

A solution consisting of 7.3 mmol of the thioketone in 20 ml of dry CH_2Cl_2 was placed in an ampoule. The ampoule was connected to a vacuum line and cooled to liquid nitrogen temperature when 1.5 g (7.8 mmol) of $(CF_3)_2BNMe_2$ were condensed in. The ampoule was closed and the mixture stirred at −40°C until the colour of the thioketone had disappeared. All volatile

TABLE 3. Elemental analyses

Compound	Formula	Analyses (found/(calc.)%)		
		C	H	N
I	$C_8H_{15}BF_6N_2S$	32.39/(32.45)	5.06/(5.11)	9.42/(9.46)
II	$C_9H_{17}BF_6N_2S$	34.71/(34.86)	5.56/(5.53)	8.88/(9.03)
III	$C_8H_{14}BF_6NOS$	31.91/(32.35)	4.72/(4.75)	4.62/(4.72)
IV	$C_9H_{16}BF_6NOS$	34.45/(34.75)	5.16/(5.18)	4.69/(4.50)
V	$C_8H_{14}BF_6NS_2$	30.51/(30.69)	4.50/(4.51)	4.38/(4.47)
VII	$C_{12}H_{14}BF_6NS$	34.71/(43.79)	5.56/(4.29)	8.88/(4.26)

products were removed *in vacuo* at 0°C and the residue recrystallized from dry CH_2Cl_2/pentane at low temperature. Compounds **VII** and **IX** are sensitive to moisture and decomposed when sublimation was attempted. **VII**: m.p. ~ 50°C (dec.). IR (cm^{-1}): 1095 (vs); 1085 (vs); 1065 (s, CF_3). **IX**: m.p. ~ 53°C (dec.). IR (cm^{-1}): 1090 (vs); 1060 (s); 1035 (s, CF_3).

5.4. Methylmethyleneimine-(2-t-butyl-1-thia-prop-1-yl)-bis(trifluoromethyl)borane (X)

Compound **IX** (1.0 g) was dissolved in carefully dried CH_2Cl_2 contained in a well dried flask and the solution kept at room temperature for 24 h. Removal of the solvent gave **X**, which according to its NMR spectrum was 90% pure. Attempts to purify **X** further by sublimation at 35°C and 10^{-1} mbar pressure resulted in partial decomposition. For yields see text, and for elemental analyses see Table 3.

Acknowledgement

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