

Reactions of $(CF_3)_2BNMe_2$ with Grignard and related reagents. Crystal and molecular structure of $(CF_3)(Mes)FB-FC=NMe_2$ and $Ph_3P-CH_2-(CF_3)_2B-NMe_2$ ¹

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Abstract

Dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (A), reacts with Grignard reagents $RMgBr$ to yield, after hydrolysis, the dimethylamine boranes $R(CF_3)_2B \cdot NHMe_2$ ($R = Me$ (I), Et (II), ⁱPr (III), $-CH_2CH=CH_2$ (IV), Ph (V), ^pTol (VI), ^oTol (VII), ^pC₆H₄ (VIII) and $-C \equiv CH$ (IX)). Alkynyltrimethylstannanes $Me_3Sn-C \equiv C-R$ ($R = Ph$, ⁿBu) add to A across the B=N double bond and yield $(R-C \equiv C)(CF_3)_2B \cdot NMe_2SnMe_3$, the hydrolysis of which gives $(Ph-C \equiv C)(CF_3)_2B \cdot NHMe_2$ (X) and $(^nBu-C \equiv C)(CF_3)_2B \cdot NHMe_2$ (XI) respectively. In contrast, mesitylmagnesiumbromide reacts with A to yield $(CF_3)(Mes)FB-FC=NMe_2$ (XII), hydrolysis of which furnishes $(CF_3)(Mes)FB-C(=O)NHMe_2$ (XIII). Of the phosphorus ylids, only $Ph_3P=CH_2$ and $Ph_3P=CHCH_3$ react with A to give the respective adducts $Ph_3P-CH_2-(CF_3)_2B-NMe_2$ (XIV) and $Ph_3P-CH(CH_3)-(CF_3)_2B-NMe_2$ (XV). $CF_3SO_3CH_3$ alkylates XIV at the nitrogen atom to form $[Ph_3P-CH_2-(CF_3)_2B-NMe_3]^+[CF_3SO_3]^-$ (XVI). The crystal and molecular structures of XII and XIV have been determined by X-ray methods.

Keywords: Boron; Dimethylaminobis(trifluoromethyl)borane; Grignard reagents

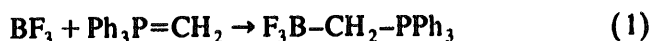
1. Introduction

Previous studies have shown that dimethylaminobis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ (A), enters into numerous, novel reactions in which the boron atom increases its coordination number from three to four [1]. This electrophilic character of A is the driving force for its ene-type reactions with nitriles R^1CH_2CN or carbonyl ($X = O$) and thiocarbonyl compounds ($X = S$) of the general formula $R^2C(X)CH_2R^1$ which readily take place to form dimethylamine boranes $(NCCR^1H)(CF_3)_2B \cdot NHMe_2$ ($R^1 = Me, Et, Cl, \dots$) or $(R^2C(X)CHR^1)(CF_3)_2B \cdot NHMe_2$ ($R^1 = H, Me, Et, \dots$; $R^2 = ^iBu, OEt, NMe_2, \dots$) [2,3]. Likewise, A combines with electron-rich alkenes $H_2C=CR^2CH_2R^1$ ($R^1 = H, Me, \dots$; $R^2 = Et, Ph, \dots$) to yield dimethylamine boranes $(R^1HC=CR^2CH_2)(CF_3)_2B \cdot NHMe_2$ [4]. These reactions have in common that the boron atom is C-alkylated.

However, such ene-type reactions of A require a reactant which has sufficiently activated hydrogen atoms.

In order to carry on chemistry of the unique trifluoromethylboron group, we have sought general methods for attaching substituents to boron which contain nucleophilic carbon atoms rather than activated CH bonds. Such nucleophilic carbon atoms occur, for example, in Grignard reagents $RMgX$, alkynylstannanes $R-C \equiv C-SnMe_3$ and ylids, and they are expected to add across the BN bond of A.

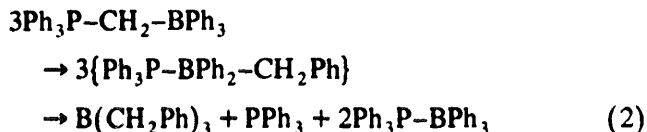
Methylenetriphenylphosphorane may be described by the two mesomeric structures $Ph_3P=CH_2 \leftrightarrow Ph_3P^{\oplus}-\overset{\ominus}{C}H_2$. The ylid structure evidently unveils more of the nucleophilic character of the methylene carbon atom. As a consequence many boranes readily form Lewis-acid-base complexes with $Ph_3P=CH_2$ according to Eq. (1).



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¹ Dedicated to Professor Dr. mult. Alois Haas on the occasion of his 65th birthday.

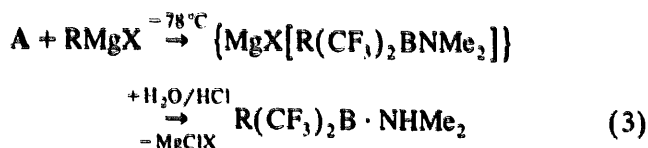
The thermal stability of these complexes depends crucially on the Lewis acidity of the corresponding borane [5]. While the Lewis-acid–base adducts of BH_3 or BF_3 with $\text{Ph}_3\text{P}=\text{CH}_2$ are stable at room temperature, BMe_3 does not form such a complex [5]. Other adducts were reported [6] to decompose at elevated temperature with the methylene group being inserted into B–C bonds according to Eq. (2).



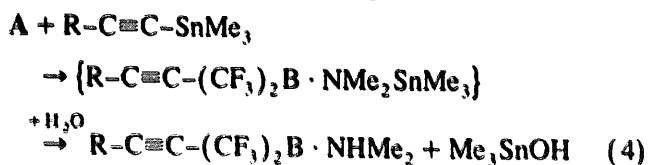
Presumably, the Lewis acidity of ordinary dialkylaminoboranes is too low to induce complexation by $\text{Ph}_3\text{P}=\text{CH}_2$, and to our knowledge no such adducts have been described; however, the enhanced Lewis acidity of boron in **A** might be sufficient to enable complex formation. Thus, we have tested alkylation reactions of **A** with alkylidene phosphoranes. Here we report on our results.

2. Results

$(\text{CF}_3)_2\text{BNMe}_2$ (**A**) reacts readily with various Grignard reagents RMgX in ether or THF at -78°C to yield the magnesium salts $\text{MgX}[\text{R}(\text{CF}_3)_2\text{BNMe}_2]$, which are unstable at room temperature. Hydrolysis with dilute aqueous HCl at -78°C followed by warming to ambient temperature furnished the dimethylamine boranes $\text{R}(\text{CF}_3)_2\text{B} \cdot \text{NHMe}_2$ ($\text{R} = \text{Me}$ (I), Et (II), ^iPr (III), $-\text{CH}_2\text{CH}=\text{CH}_2$ (IV), Ph (V), ^nTol (VI), ^oTol (VII), $^p\text{ClC}_6\text{H}_4$ (VIII), $-\text{C}\equiv\text{CH}$ (IX) in yields of 75 to 95% according to Eq. (3).



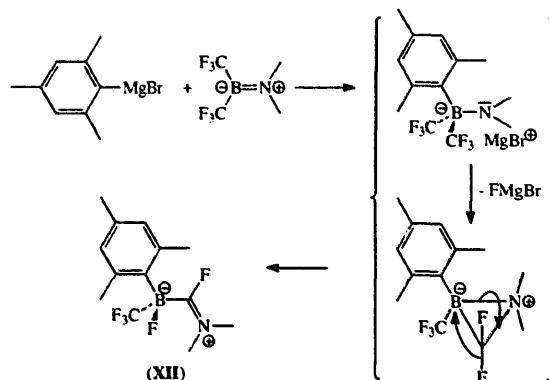
While SnMe_4 does not react at all with **A**, alkynyl stannanes $\text{R}-\text{C}\equiv\text{C}-\text{SnMe}_3$ ($\text{R} = \text{Ph}$, ^nBu) add readily at 0°C to the BN double bond, Eq. (4).



$\text{R} = \text{Ph}$ (X), ^nBu (XI)

The Sn–N bond of the adducts was rapidly cleaved upon treatment with water, and the dimethylamine boranes **X** and **XI** were obtained in high yields.

The scope of the Grignard reaction is limited by the bulkiness of the ligand **R** in RMgX . Thus, no addition



Scheme 1. Reaction of MesMgBr with $(\text{CF}_3)_2\text{BNMe}_2$.

reaction was observed with the Grignard reagent with $\text{R} = ^i\text{Bu}$ — the same observation was made for the even more reactive $^i\text{BuLi}$ reagent. $\text{R} = \text{Mesityl}$ (**Mes**) seems to be a borderline case; that is, MesMgBr reacted with **A** in the temperature range from -78 to -30°C to yield an unexpected product which has the constitution $(\text{CF}_3)(\text{Mes})\text{FB}-\text{FC}=\text{NMe}_2$ (**XII**). A possible pathway for the reaction involving degradation of a CF_3 group is outlined in Scheme 1.

In the first reaction step the carbanion adds to the boron atom, but the bulkiness of the mesityl group probably weakens or prevents coordination of the nitrogen atom to the electrophilic MgBr fragment. Instead, the latter attracts and abstracts a fluorine atom from one of the CF_3 groups with possible formation of a transient BNC three-membered ring.

The likelihood of this pathway is supported by the reaction of **A** with the efficient difluorocarbene source CF_3SiF_3 (Eq. (5)) [1]. Conceivably, the product obtained here, $(\text{CF}_3)_2\text{FB}-\text{FC}=\text{NMe}_2$, is formed by rearrangement of an intermediate three-membered ring.

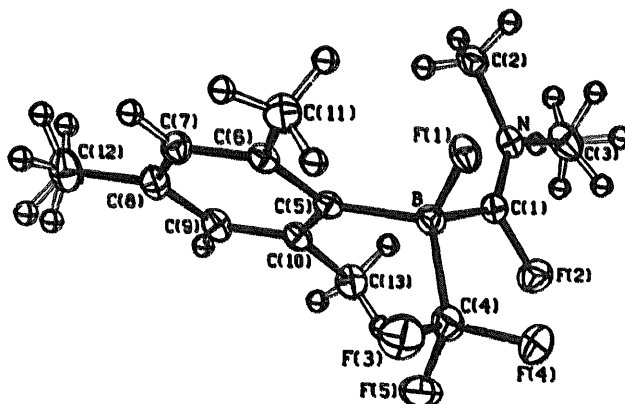
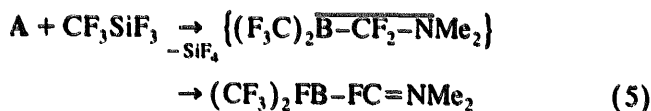


Fig. 1. A perspective drawing of **XII** with 20% probability thermal ellipsoids except for the hydrogen atoms.

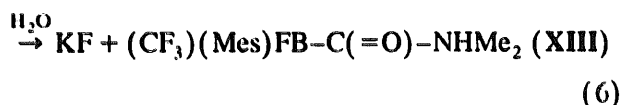
Table 1
Selected bond distances (Å) and angles (deg) in XII

| | | | |
|-------------|----------|-------------|----------|
| B–F(1) | 1.426(3) | N–C(2) | 1.464(3) |
| B–C(1) | 1.647(3) | N–C(3) | 1.470(3) |
| B–C(4) | 1.629(3) | C(1)–F(2) | 1.336(2) |
| B–C(5) | 1.628(3) | C(4)–F(3) | 1.361(3) |
| N–C(1) | 1.275(3) | C(4)–F(4) | 1.354(3) |
| | | C(4)–F(5) | 1.335(3) |
| F(1)–B–C(1) | 102.5(2) | B–C(1)–N | 128.4(2) |
| F(1)–B–C(4) | 105.6(2) | B–C(1)–F(2) | 118.5(2) |
| F(1)–B–C(5) | 114.1(2) | F(2)–C(1)–N | 113.0(2) |
| C(1)–B–C(4) | 108.8(2) | C(1)–N–C(2) | 120.1(2) |
| C(1)–B–C(5) | 114.0(2) | C(1)–N–C(3) | 123.8(2) |
| C(4)–B–C(5) | 111.1(2) | C(2)–N–C(3) | 116.1(2) |

The analogous migration of fluorine from carbon to boron (Scheme 1) with concomitant breaking of the BN bond would lead to XII.

The constitution of compound XII was deduced from analyses and spectra and confirmed by a single-crystal structure investigation (vide infra). After work-up in aqueous solution (Eq. (3)) XII contained up to 10% of an impurity which was identified as $(CF_3)(Mes)FB-C(=O)-NHMe_2$ (XIII). Compound XIII is formed by hydrolysis of XII and was obtained almost quantitatively when XII was treated with $KOH-H_2O$, Eq. (6).

XII + KOH



Not unexpectedly, methylenetriphenylphosphorane and A formed the Lewis-acid-base adduct $Ph_3P-CH_2-(CF_3)_2B-NMe_2$ (XIV) according to Eq. (7).



The constitution of XIV was deduced from NMR and mass spectral data and was confirmed by a single-crystal structure investigation (vide infra). The chemical shift

Table 2
Selected bond distances (Å) and angles (deg) in XIV

| | XIVa | XIVb | | XIVa | XIVb |
|-------------|----------|----------|---------------|----------|----------|
| B–N | 1.497(6) | 1.502(4) | P–C(5) | 1.784(4) | 1.786(3) |
| B–C(1) | 1.605(6) | 1.628(4) | P–C(6) | 1.793(4) | 1.793(3) |
| B–C(2) | 1.646(6) | 1.637(5) | P–C(12) | 1.804(8) | 1.803(3) |
| B–C(5) | 1.663(6) | 1.659(4) | P–C(18) | 1.808(4) | 1.811(3) |
| N–B–C(1) | 111.9(4) | 111.6(3) | C(5)–P–C(12) | 115.1(2) | 118.1(1) |
| N–B–C(2) | 112.7(4) | 113.3(3) | C(5)–P–C(18) | 107.2(2) | 105.7(1) |
| N–B–C(5) | 111.9(3) | 111.8(2) | C(6)–P–C(12) | 108.4(2) | 107.8(1) |
| C(1)–B–C(2) | 106.4(4) | 107.0(2) | C(6)–P–C(18) | 106.7(2) | 106.8(1) |
| C(1)–B–C(5) | 109.6(4) | 109.1(2) | C(12)–P–C(18) | 106.5(2) | 108.3(1) |
| C(2)–B–C(5) | 103.9(4) | 103.7(2) | B–N–C(13) | 120.5(4) | 119.4(3) |
| B–C(5)–P | 125.0(3) | 124.8(2) | B–N–C(4) | 122.2(4) | 122.3(3) |
| C(5)–P–C(6) | 112.4(2) | 113.0(1) | C(3)–N–C(4) | 109.0(4) | 110.0(3) |

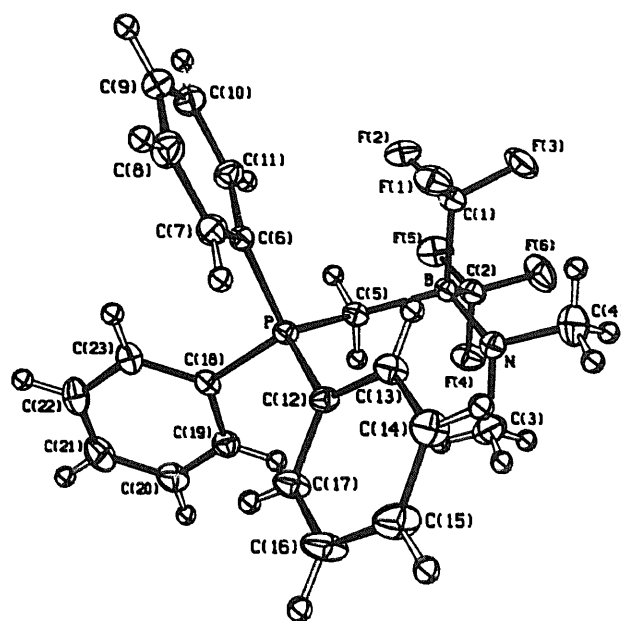


Fig. 2. A perspective drawing of XIVb with 20% probability thermal ellipsoids except for the hydrogen atoms.

of the $N(CH_3)_2$ protons ($\delta = 2.02$ ppm) resembles that of NMe_3 ($\delta = 2.12$ ppm), which indicates a three-coordinated nitrogen atom. The analogous reaction of $Ph_3P=CHCH_3$ with A at $-30^\circ C$ correspondingly formed the adduct $Ph_3P-CH(CH_3)-(CF_3)_2B-NMe_2$ (XV). Although XV could be isolated as a pure material, the yield was poor. Solutions of XV in CH_2Cl_2 showed decomposition at $20^\circ C$. XIV was methylated at nitrogen upon treatment with the strong methylating agent CF_3SO_3Me to yield $[Ph_3P-CH_2-(CF_3)_2B-NMe_3]^+[CF_3SO_3]^-$ (XVI). Analogous attempts with XV failed.

2.1. Description of the structure of XII

A drawing of XII is given in Fig. 1, and the most pertinent bond distances and angles are listed in Table

Table 3
NMR spectral data for I–XVI (δ ppm)^a

| | I | II | III | IV | V | VI | VII |
|---|--------|--------|--------|----------------|-------------------------|-------------------------|---|
| ¹ H | | | | | | | |
| δ (BN(CH ₃) ₂) | 2.72 | 2.71 | 2.79 | 2.72 | 2.69 | 2.73 | 2.72 |
| δ (BCH) | -0.04 | 0.60 | | 1.55 | | | |
| δ (NH) | ~ 4.0 | ~ 4.2 | ~ 4.0 | ~ 4.1 | ~ 4.3 | ~ 4.2 | ~ 4.6 |
| δ (=CH) | | | | 5.03 | | | |
| δ (=CH) | | | | 5.90 | | | |
| δ (C ₆ CH ₃) | | | | | | 2.37 | 2.47 |
| δ (CH _n -CH ₃) | | 0.86 | 0.97 | | | | |
| δ (C-CH ₂ -C) | | | | | | | |
| δ (C ₆ H _n) | | | | | ~ 7.35 ~ 7.56 | ~ 7.19 ~ 7.44 | ~ 7.20 ~ 7.56 |
| ¹⁹ F | | | | | | | |
| δ (BCF ₃) | -64.7 | -62.4 | -59.8 | -62.5 | -60.3 | -60.8 | -58.5 |
| δ (=CF) | | | | | | | |
| δ (O ₃ SCF ₃) | | | | | | | |
| δ (BF) | | | | | | | |
| ¹¹ B | | | | | | | |
| δ (B) | ~ -7.0 | ~ -6.5 | ~ -5.9 | ~ -7.9 | ~ -5.8 | ~ -7.0 | ~ -5.3 |
| ³¹ P | | | | | | | |
| δ (P(¹ H)) | | | | | | | |
| ¹³ C | | | | | | | |
| δ (BC) | ~ -3.4 | ~ 5.4 | ~ 13 | 21.3 | ~ 137 | ~ 133 | ~ 135 |
| δ (BN(CH ₃) _n) | 40.1 | 39.7 | 40.4 | 39.5 | 40.4 | 40.6 | 40.1 |
| δ (=C) | | | | 114.9 136.9 | | | |
| δ (=C) | | | | | | | |
| δ (O ₃ SCF ₃) | | | | | | | |
| δ (C ₆ CH ₃) | | | | | | 21.0 | 22.3 |
| δ (CH _n =CH ₃) | | 7.2 | 18.4 | | | | |
| δ (C-CH ₂ -C) | | | | | | | |
| δ (C ₆ H ₃) | | | | | 127.8 128.1 132.1 | 129.0 132.1 137.7 | 125.6 127.7 131.9 134.6 138.9 |

^a I–IX, XI, XIII–XVI in CDCl₃, X in CD₂Cl₂, XII CD₃CN. ¹H: 250.13 MHz, internal standard CHCl₃ = 7.27 ppm, CHDCl₂ = 5.31 ppm, CHD₂CN = 1.95 ppm. ¹³C: 62.9 MHz, internal standard CDCl₃ = 77.0 ppm, CD₂Cl₂ = 53.7 ppm, CD₃CN = 1.30 ppm. ¹⁹F: 235.3 MHz, internal standard CFCl₃. ¹¹B: 25.52 MHz, external standard BF₃·OEt₂.

1. While the B–C distances involving the trifluoromethyl and mesityl groups are nearly identical (1.629(3) Å and 1.628(3) Å respectively), that formed to the imino group is significantly longer, 1.647(3) Å. The latter distance agrees well with that involving the imino group in PhB(CF₃)₂-CH=N(Bz)^tBu (**B**), 1.643(7) Å [7]. In **XII** the B–C(1)–N angle is spread to 128.4(2)° in order to relieve repulsions between the methyl group

C(2) and the molecular core — the B, C(1), F(2), N, C(2), C(3) fragment being planar to within ± 0.03 Å. That a larger value, 133.0(4)°, was found for the corresponding angle in **B** is consistent with the bulkier imino group in that compound. The opening of the B–C(1)–N angle in **XII** appears to occur at the expense of the F(2)–C(1)–N angle (113.0(2)°) — the C(4)–B–C(1)–F(2) fragment exhibiting a synperiplanar conformation.

| VIII | IX | X | XI | XII | XIII | XIV | XV | XVI |
|-------------------------|---------------|----------------------------------|------------------------------|-------------------------|-------------------------|----------------------------------|----------------------------------|----------------------------------|
| 2.71 | 2.73 | 2.86 | 2.84 | 3.25 3.32 | 2.73 2.74 | 2.02 | 1.81 | 3.03 |
| ~ 4.4 | ~ 5.2 2.24 | ~ 4.5 | ~ 6.5 | | | 2.05 | 2.71 | 2.66 |
| | | | | 2.22 2.29 2.30 | 2.17 2.27 2.28 | | | |
| | | | 0.91 1.42 1.48 2.22 | | | | 1.58 | |
| ~ 7.35 ~ 7.49 | | ~ 7.34 ~ 7.47 | | 6.78 | 6.65 | ~ 7.5 ~ 7.7 | ~ 7.5 ~ 7.7 | ~ 7.6 ~ 7.9 |
| -60.4 | -63.9 | -63.5 | -63.9 | -64.8 -4.2 | -62.9 | -61.8 | -57.5 -60.2 | -57.5 |
| | | | | -202.2 | -197.9 | | | -78.7 |
| ~ -7.0 | ~ -11.7 | ~ -11.4 | ~ -11.5 | ~ 0.5 | ~ 1.0 | -8.8 | -9.2 | -7.4 |
| | | | | | | 30.1 | 27.0 | 27.4 |
| ~ 135 | ~ 85 | ~ 89 | ~ 82 | ~ 136 ~ 196 | ~ 143 ~ 197 | 10.0 | 16.5 | 7.6 |
| 40.5 | 40.2 | 41.1 | 40.7 | 39.2 41.5 | 32.7 37.4 | 40.1 | 39.7 | 52.5 |
| | 87.7 | 99.9 | 102.0 | | | | | |
| | | | | 20.9 23.1 23.2 | 20.9 23.6 23.7 | | | 120.7 |
| | | | 13.6 19.2 21.8 30.9 | | | | 6.7 | |
| 128.3 133.7 134.1 | | 123.5 128.7 128.8 132.1 | | 130.5 137.4 142.8 | 129.7 134.8 142.9 | 122.1 128.7 133.3 133.7 | 117.8 130.5 133.4 135.1 | 121.4 129.7 133.4 134.2 |

The B–F(1) bond length in XII (1.426(3) Å), like those reported for $[\text{B}(\text{C}_6\text{F}_5)_2\text{F}]^-$ (1.428(6) Å) [8] and $[\text{B}(\text{CH}_3)_2\text{F}_3]^-$ (1.424(5) Å) [9] anions, appears to be weakened inductively with respect to those in borates in which only trifluoromethyl groups are allowed to replace some of the fluoro substituents — examples being $\text{K}[\text{BF}_4]$ (1.386(3) Å) [10], $\text{K}[\text{B}(\text{CF}_3)_2\text{F}_3]$ (1.391(5) Å) [11] and $\text{Cs}[\text{B}(\text{CF}_3)_2\text{F}_2]$ (1.391(4) Å) [12].

2.2. Description of the structure of XIV

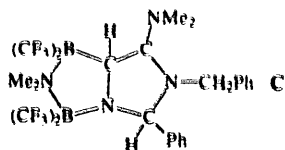
Although two crystallographic modifications of XIV have been investigated, the molecular structures found in these crystals are so closely related that one drawing (Fig. 2) is sufficient to define the labelling and describe the stereochemical details. Of the two crystals studied, the triclinic modification (XIVb) proved to be the better

scatterer. As a result, the standard deviations of the bond distances and angles obtained with this specimen are lower than those derived for **XIVa** (Table 2).

The methylene carbon (C(5)) of the ylid is strongly coordinated to the boron. While the average B–C(5) bond length (1.661(4) Å) is probably longer than the mean B–CF₃ distance (1.63(2) Å), the former is as short or shorter than the bonds of boron to the bulky alkylammonium groups of (CF₃)₂(OH)B–CH(Ph)–NH(Bz)¹Bu (1.673(4) Å [7]) or (CF₃)₂(OH)B–CH(SiMe₃)–HNMe₂ (1.690(4) Å [13]). Steric crowding is also evident in **XIV** — repulsive interactions between the bulky B(CF₃)₂NMe₂ and PPh₃ substituents opening the average B–C(5)–P angle to 124.9(2)°.

With the formal π-bonding electrons of the P=CH₂ fragment of the ylid now localized in the B–C(5) bond, the average P–C(5) bond length becomes 0.126(9) Å longer than that reported for the free ylid (1.661(8) Å [14]) and almost equals the length of the mean P–C(Ph) bonds (1.802(8) Å) of **XIV**. Thus, the P–C(5) linkage may be viewed as a nearly normal σ bond.

Coordination of the ylid to **A** transforms the B=N π-bonding electrons of **A** into the nitrogen lone pair of **XIV**. As a result, the average B–N bond is lengthened by 0.072(7) Å with respect to the value found in the gas phase for **A** [15]. The former may be compared with the 1.476(5) Å bond between the tricoordinate amide nitrogen and quaternary boron in the heterocyclic compound **C** — the only other such linkage to be characterized structurally [16].



The possibility of N(pπ) → B hyperconjugative strengthening of these bonds has been discussed, since B–N distances in amine borane adducts are 0.1 Å longer. In connection with this, the sum of the bond angles at the tertiary nitrogen atom is of interest. The sum in **XIV** (average 351.7(4)°) like that in **C** (348.9(5)°) indicates that, despite a marked flattening of the nitrogen valencies, trigonal hybridization is not realized.

3. Properties and spectra

The compounds **I–XVI** are colourless solids or oily liquids. Their melting points are given in Section 5. With the exception of **XV**, they are not sensitive towards air and moisture and are soluble in polar organic solvents like CH₂Cl₂ and CH₃CN.

The ¹H, ¹⁹F, ¹¹B and ¹³C NMR spectra of **I–XVI** were recorded. The shift data, which are set out in Table 3, are consistent with the proposed structures, and only a few comments will be necessary.

3.1. ¹H spectra

Compound **III** gives rise to a pseudo singlet due to an accidental degeneracy of the HC and C(CH₃)₂ hydrogen atoms. The NH resonance of **XIII** is supposedly broadened due to rapid exchange and was not observed.

3.2. ¹⁹F spectra

Compound **XII** exhibits a resonance δ(BF) at –202.7 ppm shifted to high field. This shift is larger than that for [(C₆F₅)₃BF][–] (δ(BF) = –190 ppm [17]) which was previously considered to be the upper limit for a fluorine bonded directly to boron.

3.3. ¹³C spectra

As usual, the resonances of the CF₃ groups were not found in the ¹³C NMR spectra due to quadrupole broadening by the boron nucleus. The NCH₃ carbon atoms in compound **XII** show a significant coupling. While the signal at 39.2 ppm is split into a doublet with ³J(CF) = 12.0 Hz, the resonance at 41.5 ppm appears as a doublet of doublets, with ³J(CF) = 5.0 Hz and ⁴J(CF) = 1.6 Hz. Even the methyl C-atoms in the ortho position of the phenyl ring absorbing at 23.1 and 23.2 ppm show a 'quintet' fine structure owing to ⁴J(CF) and ⁵J(CF) coupling, both coupling constants being ca. 1.6 Hz.

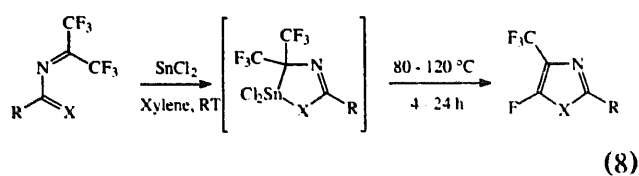
The ¹³C NMR spectra of **V**, **VI** and **VIII** allow an assessment of the substituent effect of the –(CF₃)₂B·NHMe₂ group. The average Δδ values of the phenyl carbon atoms determined for compounds **V**, **VI** and **VIII** are comparable with those of phenyl rings substituted by CH₂X groups [18]. The small negative Δδ_{3/5} and Δδ₄ values show that neither strong inductive nor mesomeric effects can be ascribed to the (CF₃)₂B·NHMe₂ group. The rather large Δδ C_{2/6} value might be due to the relative bulkiness of the two CF₃ groups.

| Group | Δδ C ₁ (ipso) | Δδ C _{2/6} (ortho) | Δδ _{3/5} (meta) | Δδ ₄ (para) |
|---|-----------------------------|--------------------------------|-----------------------------|---------------------------|
| (CF ₃) ₂ B·NHMe ₂ | ~ +8.5 | ~ +3.5 | –0.4 | –0.8 |
| CH ₂ NH ₂ | +14.9 | +1.4 | –0.1 | –1.9 |
| CH ₂ SCH ₃ | +9.8 | +0.4 | –0.1 | –1.6 |

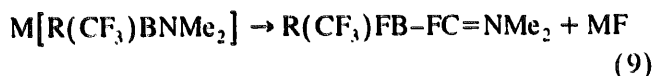
4. Discussion

The low thermal stability of the magnesium salts MgX[R(CF₃)₂BNMe₂] is in contrast to the stability of

the analogous potassium salts $K[R(CF_3)_2BNMe_2]$ which can be obtained by treatment of the dimethylamine boranes with KOH–ether. Obviously the MgX cation which is a stronger Lewis acid than a potassium cation is not sufficiently complexed either by the ether solvent or the nitrogen atom of **A**. This solvation or complexation also seems to depend on the bulkiness of the residue **R** that has become attached to boron. Thus the reaction of **A** with $MesMgBr$ is one of the few reactions reported so far in which a CF_3 group is selectively defluorinated by a cation with preservation of the carbon–element bond. A similar defluorination reaction has been observed by Burger and Helmreich [19] in the synthesis of five-membered heterocyclic rings using $SnCl_2$ (Eq. (8)).



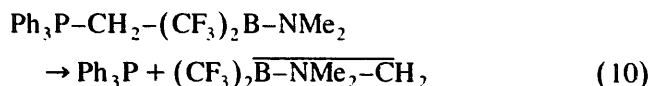
Whether the defluorination reaction according to Eq. (9) observed for $R = Mes$ may, under appropriate reaction conditions, be of general applicability for other groups has still to be investigated.



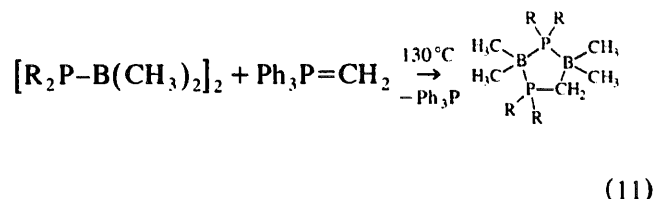
($M = MgX, Li, Me, Sn, \dots$)

The considerable thermal stability and lack of reactivity of adduct **XIV** was surprising. Although we did not expect any insertion of CH_2 into a $B=CF_3$ bond in

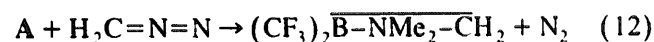
analogy to Eq. (2) even under forcing conditions, we expected that **XIV** would react under liberation of Ph_3P to form the azonia–borata–cyclopropane system according to Eq. (10).



This expectation seemed to find support in an analogous reaction of dialkylphosphino–dimethylborane dimers. Reportedly these dimers combine with $Ph_3P=CH_2$ to form five-membered heterocycles according to Eq. (11) [20].



The azonia–borata–cyclopropane ring strived for, which is a reactive building block in trifluoromethylboron chemistry [1], has been previously obtained from diazomethane and **A** according to Eq. (12) [21].



Since upscaling of this reaction may be hazardous, a procedure according to Eq. (10) would be attractive and was indeed the reason for our efforts. However, **XIV** did not show any tendency to form the desired product even when heated in vacuo to ca. $140\text{ }^\circ\text{C}$, at which point it began to decompose under liberation of **A**.

The low thermal stability of **XV** compared with **XIV** is surprising. This must be ascribed to the steric demand

Table 4
Selected electron impact mass spectral data in the order of decreasing intensity (m/e (relative intensity (%)) [fragment]⁺) for **I–XV**

| | |
|-------------|---|
| I | 94(100)[F ₂ BNH(CH ₃) ₂] ⁺ ; 90(89)[M - C ₂ F ₅] ⁺ ; 44(62)[NC ₂ H ₆] ⁺ ; 74(7)[FBN(CH ₃) ₂] ⁺ |
| II | 94(100)[F ₂ BNH(CH ₃) ₂] ⁺ ; 104(28)[M - C ₂ F ₅] ⁺ ; 44(20)[NC ₂ H ₆] ⁺ ; 154(1)[M - CF ₃] ⁺ |
| III | 94(100)[F ₂ BNH(CH ₃) ₂] ⁺ ; 44(34)[NC ₂ H ₆] ⁺ ; 118(9)[M - C ₂ F ₅] ⁺ ; 168(2)[M - CF ₃] ⁺ |
| IV | 94(100)[F ₂ BNH(CH ₃) ₂] ⁺ ; 44(21)[NC ₂ H ₆] ⁺ ; 74(16)[FBN(CH ₃) ₂] ⁺ ; 116(4)[M - C ₂ F ₅] ⁺ ; 235(1)[M] ⁺ |
| V | 44(100)[NC ₂ H ₆] ⁺ ; 152(76)[M - C ₂ F ₅] ⁺ ; 74(63)[FBN(CH ₃) ₂] ⁺ ; 94(17)[F ₂ BNH(CH ₃) ₂] ⁺ ; 157(16)[C ₆ H ₅ BF ₂ NH ₂ CH ₃] ⁺ ; 271(15)[M] ⁺ ; 202(9)[M - CF ₃] ⁺ |
| VI | 166(100)[M - C ₂ F ₅] ⁺ ; 44(67)[NC ₂ H ₆] ⁺ ; 171(41)[H ₃ CC ₆ H ₄ BF ₂ NH ₂ CH ₃] ⁺ ; 285(28)[M] ⁺ ; 74(21)[FBN(CH ₃) ₂] ⁺ |
| VII | 44(100)[NC ₂ H ₆] ⁺ ; 74(61)[FBN(CH ₃) ₂] ⁺ ; 166(42)[M - C ₂ F ₅] ⁺ ; 171(19)[H ₃ CC ₆ H ₄ BF ₂ NH ₂ CH ₃] ⁺ ; 285(13)[M] ⁺ |
| VIII | 44(100)[NC ₂ H ₆] ⁺ ; 186(59)[M - C ₂ F ₅] ⁺ ; 74(54)[FBN(CH ₃) ₂] ⁺ ; 191(20)[C ₁₀ H ₄ BF ₂ NH ₂ CH ₃] ⁺ ; 305(14)[M] ⁺ |
| IX | 100(100)[M - C ₂ F ₅] ⁺ ; 44(81)[NC ₂ H ₆] ⁺ ; 74(26)[FBN(CH ₃) ₂] ⁺ ; 94(14)[F ₂ BNH(CH ₃) ₂] ⁺ ; 128(7)[C ₅ H ₅ BNF ₂] ⁺ ; 150(3)[M - CF ₃] ⁺ |
| X | 44(100)[NC ₂ H ₆] ⁺ ; 176(49)[M - C ₂ F ₅] ⁺ ; 115(22)[C ₉ H ₇] ⁺ ; 295(16)[M] ⁺ ; 94(8)[F ₂ BNH(CH ₃) ₂] ⁺ ; 226(3)[M - CF ₃] ⁺ |
| XI | 94(100)[F ₂ BNH(CH ₃) ₂] ⁺ ; 156(79)[M - C ₂ F ₅] ⁺ ; 44(73)[NC ₂ H ₆] ⁺ ; 206(7)[M - CF ₃] ⁺ ; 275(2)[M] ⁺ |
| XII | 56(100)[NC ₂ H ₆] ⁺ ; 224(64)[M - CF ₃] ⁺ ; 91(19)[C ₇ H ₇] ⁺ ; 77(18)[C ₆ H ₅] ⁺ ; 105(12)[C ₈ H ₉] ⁺ ; 124(12)[F ₂ BCFN(CH ₃) ₂] ⁺ ; 115(9)[C ₉ H ₇] ⁺ ; 293(7)[M] ⁺ |
| XIII | 44(100)[NC ₂ H ₆] ⁺ ; 72(89)[OCN(CH ₃) ₂] ⁺ ; 91(29)[C ₇ H ₇] ⁺ ; 105(12)[C ₈ H ₉] ⁺ ; 203(10)[M - CF ₃] ⁺ ; 223(6)[M - CO - 2HF] ⁺ ; 243(4)[M - CO - HF] ⁺ ; 291(2)[M] ⁺ |
| XIV | 275(100)[C ₁₀ H ₁₆ P] ⁺ ; 183(95)[C ₁₂ H ₈ P] ⁺ ; 92(68)[F ₂ BN(=CH ₂)CH ₃] ⁺ ; 262(52)[C ₁₈ H ₁₅ P] ⁺ ; 108(28)[C ₆ H ₅ P] ⁺ ; 350(19)[M - C ₂ F ₅] ⁺ ; 400(15)[M - CF ₃] ⁺ ; 469(∼1)[M] ⁺ |
| XV | 92(100)[F ₂ BN(=CH ₂)CH ₃] ⁺ ; 262(22)[C ₁₈ H ₁₅ P] ⁺ ; 108(21)[C ₆ H ₅ P] ⁺ |

of the dimethylamino and the two CF₃ groups, which allows only a slim fourth ligand, like –CH₂PPh₃, to tightly coordinate to boron.

5. Experimental

5.1. Dimethylamine-methylbis(trifluoromethyl)borane (I), dimethylamine-ethyl-bis(trifluoromethyl)borane (II), dimethylamine-isopropylbis(trifluoromethyl)-borane (III), dimethylamine-allylbis(trifluoromethyl)borane (IV), dimethylamine-phenylbis(trifluoromethyl)borane (V), dimethylamine-p-tolylbis(trifluoromethyl)-borane (VI), dimethylamine-o-tolylbis(trifluoromethyl)-borane (VII), dimethylamine-p-chlorophenylbis(trifluoromethyl)borane (VIII), dimethylamine-ethynylbis(trifluoro-methyl)borane (IX), 3,4,5,5-pentafluoro-4-mesityl-2-methyl-2-azonia-4-borata-pent-2-ene (XII): general procedure

A Grignard solution prepared from 87 mmol RBr and 109 mmol Mg turnings in 400 ml ether was cooled to –78 °C and 72.5 mmol (14.0 g) A added dropwise under efficient stirring. The reaction mixture was stirred for 20–30 min at –78 °C and 150 ml water and 50 ml 2 M HCl were added. After warming to room temperature, the ether phase was separated, dried over MgSO₄ and the ether and other volatile material removed in vacuo at 20 °C. The products were recrystallized from

Table 5
Elemental analyses

| Compound formula | Analyses found;(calc.) (%) | | |
|--|----------------------------|-------------|------------|
| | C | H | N |
| I C ₅ H ₁₀ BF ₆ N | 29.0;(28.74) | 6.7;(4.82) | 6.8;(6.70) |
| II C ₆ H ₁₂ BF ₆ N | 33.0;(32.32) | 5.4;(5.42) | 6.2;(6.28) |
| III C ₇ H ₁₄ BF ₆ N | 37.5;(35.48) | 6.4;(5.95) | 6.1;(5.91) |
| IV C ₇ H ₁₂ BF ₆ N | 36.1;(35.78) | 5.4;(5.15) | 6.0;(5.96) |
| V C ₁₀ H ₁₂ BF ₆ N | 44.6;(44.32) | 4.4;(4.46) | 4.9;(5.17) |
| VI C ₁₁ H ₁₄ BF ₆ N | 46.1;(46.35) | 4.9;(4.95) | 5.5;(4.91) |
| VII C ₁₁ H ₁₄ BF ₆ N | 45.4;(46.35) | 4.9;(4.95) | 5.2;(4.91) |
| VIII C ₁₀ H ₁₁ BClF ₆ N | 39.5;(39.32) | 3.7;(3.63) | 4.7;(4.59) |
| IX C ₆ H ₈ BF ₆ N | 32.8;(32.92) | 3.9;(3.68) | 6.6;(6.40) |
| X C ₁₂ H ₁₂ BF ₆ N | 48.8;(48.85) | 4.2;(4.10) | 4.8;(4.75) |
| XI C ₁₀ H ₁₆ BF ₆ N | 43.6;(43.67) | 5.9;(5.86) | 5.0;(5.09) |
| XII C ₁₃ H ₁₇ BF ₅ N | 53.3;(53.28) | 5.9;(5.85) | 4.5;(4.78) |
| XIII C ₁₃ H ₁₈ BF ₄ NO | 53.8;(53.64) | 6.6;(6.23) | 5.1;(4.81) |
| XIV C ₂₃ H ₂₃ BF ₆ NP | 57.7;(58.88) | 4.81;(4.94) | 2.9(2.99) |
| XV C ₂₄ H ₂₅ BF ₆ NP | 58.4;(59.65) | 5.2;(5.21) | 2.8(2.90) |
| XVI C ₂₅ H ₂₆ BF ₆ NO ₃ PS | 46.8;(47.41) | 4.1;(4.14) | 2.1(2.21) |

ether (–78 °C) or purified by sublimation (50–90 °C/10^{–2} mbar). Compound XII, which contained ca. 10% XIII formed by hydrolysis (vide infra), was crystallized from CHCl₃.

Compound I: (yield ca. 75%) m.p. 40 °C; IR cm^{–1}: 3162 s ν(NH); 1094, 1019 vs ν(CF).

Compound II: (yield ca. 80%) IR cm^{–1}: 3275 m ν(NH); 1094 vs b ν(CF).

Table 6
Crystal data and refinement details for XII and XV

| | XII | XIVa | XIVb |
|--|---|--------------------|--|
| Formula | C ₁₃ H ₁₇ BF ₅ N | | C ₂₃ H ₂₃ BF ₆ NP |
| MW | 293.09 | | 469.22 |
| Space group | P2 ₁ /c | C2/c | P $\bar{1}$ |
| a (Å) | 8.7301(8) | 21.645(3) | 9.088(1) |
| b (Å) | 11.2889(9) | 11.383(1) | 11.365(1) |
| c (Å) | 14.640(1) | 18.855(2) | 12.131(1) |
| α (deg) | 90 | 90 | 67.474(7) |
| β (deg) | 93.625(9) | 90.84(2) | 82.559(7) |
| γ (deg) | 90 | 90 | 84.047(8) |
| Z | 4 | 8 | 2 |
| D _c (g cm ^{–3}) | 1.352 | 1.342 | 1.360 |
| t (°C) | 23 | 25 | 25 |
| 2θ-limits (deg) | 4.5–50 | 5–50 | 5–55 |
| Measured reflections | 5623 | 6476 | 5524 |
| Unique reflections | 2522 | 4082 | 5242 |
| Observed (F _o ≥ σ(F _o)) | 1886 | 2060 | 2988 |
| Crystal size (mm ³) | 0.25 × 0.26 × 0.55 | 0.17 × 0.22 × 0.44 | 0.12 × 0.44 × 0.46 |
| μ (mm ^{–1}) | 0.084 | 0.134 | 0.136 |
| Transmission | 0.9256–0.9820 | 0.9622–0.9844 | 0.9441–0.9844 |
| Extinction parameter ^a (× 10 ³) | 4.6(7) | 0.21(5) | 4.1(6) |
| R | 0.046 | 0.063 | 0.053 |
| Rw | 0.048 | 0.046 | 0.049 |
| Δρ (e Å ^{–3}) | 0.22– – 0.18 | 0.25– – 0.25 | 0.35– – 0.26 |
| Parameters | 205 | 296 | 302 |

^a The extinction correction has the form F_c' = F_c(1 – xF_c²/sinθ).

Compound III: (yield ca. 80%) m.p. 36 °C; IR cm^{-1} : 3274 m $\nu(\text{NH})$; 1094 vs b $\nu(\text{CF})$.

Compound IV: (yield ca. 80%) IR cm^{-1} : 3229 m $\nu(\text{NH})$; 1652 m $\nu(\text{C}=\text{C})$; 1105, 1020 vs $\nu(\text{CF})$.

Compound V: (yield ca. 95%) m.p. 64 °C; IR cm^{-1} : 3287 m $\nu(\text{NH})$; 1096 vs b $\nu(\text{CF})$.

Compound VI: (yield ca. 95%) m.p. 66 °C; IR cm^{-1} : 3275 m $\nu(\text{NH})$; 1091 vs b $\nu(\text{CF})$.

Compound VII: (yield ca. 90%) m.p. 74 °C; IR cm^{-1} : 3294 m $\nu(\text{NH})$; 1085 vs b $\nu(\text{CF})$.

Compound VIII: (yield ca. 90%) m.p. 83 °C; IR cm^{-1} : 3224 m $\nu(\text{NH})$; 1095 vs b $\nu(\text{CF})$.

Compound IX: (yield ca. 80%) m.p. 35 °C; IR cm^{-1} : 3282 s $\nu(\text{NH})$; 2073 w $\nu(\text{C}\equiv\text{C})$; 1104 vs $\nu(\text{CF})$.

Compound XII: (yield ca. 75%) dec. 122 °C; IR cm^{-1} : 1667 s $\nu(\text{C}=\text{N})$; 1067, 1061, 1054 vs $\nu(\text{CF})$.

5.2. Dimethylamine-phenylethynylbis(trifluoromethyl)borane (X), dimethylamine-*n*-butylethynylbis(trifluoromethyl)borane (XI): general procedure

To a stirred solution of 18 mmol $\text{R}-\text{C}\equiv\text{C}-\text{SnMe}_3$ ($\text{R} = \text{Ph}$, ^nBu) [22] in 10 ml CH_2Cl_2 , 19 mmol (3.7 g) **A** were added dropwise at 4 °C. Stirring was continued for 45 min at 20 °C and all volatile material was pumped off. Ethanol (3 ml) and water (9 ml) were added while stirring. The organic layer was separated and the products were purified by sublimation at 80 °C/ 10^{-2} mbar.

Compound X: (yield ca. 84%) m.p. 34 °C; IR cm^{-1} : 3280 m $\nu(\text{NH})$; 3060, 3030, 2978 w $\nu(\text{CH})$; 2187 m $\nu(\text{C}\equiv\text{C})$; 1100 vs $\nu(\text{CF})$.

Table 8

Coordinates and equivalent isotropic temperature factors^a for the nonhydrogen atoms of XIVa

| Atom | x | y | z | U |
|-------|------------|------------|------------|-----------|
| P | 0.43287(5) | 0.2165(1) | 0.41034(5) | 0.0472(4) |
| F(1) | 0.2722(1) | 0.2473(2) | 0.4076(1) | 0.083(1) |
| F(2) | 0.2848(1) | 0.2651(2) | 0.2955(2) | 0.101(1) |
| F(3) | 0.2269(1) | 0.3866(2) | 0.3494(2) | 0.102(1) |
| F(4) | 0.3919(1) | 0.5798(3) | 0.3075(1) | 0.103(1) |
| F(5) | 0.3358(2) | 0.4739(2) | 0.2401(2) | 0.110(1) |
| F(6) | 0.2948(1) | 0.5908(2) | 0.3132(2) | 0.103(1) |
| N | 0.3414(2) | 0.4640(3) | 0.4432(2) | 0.063(2) |
| C(1) | 0.2820(2) | 0.3295(4) | 0.3564(3) | 0.066(2) |
| C(2) | 0.3409(2) | 0.5106(4) | 0.3072(3) | 0.068(2) |
| C(3) | 0.3923(3) | 0.5347(4) | 0.4673(3) | 0.098(3) |
| C(4) | 0.2853(3) | 0.5057(5) | 0.4760(3) | 0.109(3) |
| C(5) | 0.4053(2) | 0.3342(3) | 0.3561(2) | 0.054(2) |
| C(6) | 0.3898(2) | 0.0837(3) | 0.3965(2) | 0.048(2) |
| C(7) | 0.3766(2) | 0.0093(4) | 0.4520(2) | 0.059(2) |
| C(8) | 0.3471(2) | -0.0956(4) | 0.4399(3) | 0.073(2) |
| C(9) | 0.3297(2) | -0.1260(5) | 0.3727(4) | 0.088(3) |
| C(10) | 0.3429(3) | -0.0547(5) | 0.3180(3) | 0.110(3) |
| C(11) | 0.3730(3) | 0.0494(5) | 0.3298(3) | 0.089(2) |
| C(12) | 0.4356(2) | 0.2472(3) | 0.5042(2) | 0.049(2) |
| C(13) | 0.3815(2) | 0.2703(4) | 0.5411(2) | 0.056(2) |
| C(14) | 0.3845(2) | 0.2958(4) | 0.6124(2) | 0.069(2) |
| C(15) | 0.4403(3) | 0.2935(5) | 0.6478(2) | 0.083(2) |
| C(16) | 0.4933(2) | 0.2653(5) | 0.6128(2) | 0.082(2) |
| C(17) | 0.4911(2) | 0.2421(4) | 0.5415(2) | 0.062(2) |
| C(18) | 0.5113(2) | 0.1859(4) | 0.3844(2) | 0.049(2) |
| C(19) | 0.5529(2) | 0.2767(4) | 0.3749(2) | 0.064(2) |
| C(20) | 0.6140(2) | 0.2534(5) | 0.3595(2) | 0.073(2) |
| C(21) | 0.6335(2) | 0.1402(6) | 0.3536(2) | 0.075(2) |
| C(22) | 0.5933(3) | 0.0502(5) | 0.3623(2) | 0.076(2) |
| C(23) | 0.5319(2) | 0.0715(4) | 0.3775(2) | 0.062(2) |
| B | 0.3414(2) | 0.4110(4) | 0.3705(3) | 0.051(2) |

$$^a U = \frac{1}{3} \sum_i \sum_j \bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$$

Compound XI: (yield ca. 79%) IR cm^{-1} : 3277 m $\nu(\text{NH})$; 2964, 2936 w $\nu(\text{CH})$; 2203 w $\nu(\text{C}\equiv\text{C})$; 1100 vs $\nu(\text{CF})$.

5.3. 4,5,5,5-Tetrafluoro-4-mesityl-2-methyl-2-azonia-4-borata-pentan-3-one (XIII)

An excess KOH in 5 ml ether was stirred with 15 mmol **XII** for 4 h at ambient temperature. After 30 ml water was added, the ether was evaporated and the product was filtered, washed with water and dried.

Compound XIII: (yield ca. 55%) m.p. 94 °C; IR cm^{-1} : 3335 s $\nu(\text{NH})$; 1605 m $\nu(\text{C}=\text{O})$; 1095, 1044, 1010 vs $\nu(\text{CF})$.

5.4. 3,3-Bis(trifluoromethyl)-2-methyl-5,5,5-triphenyl-2-aza-5-phosphonia-3-borata-pentane (XIV), 3,3-bis(trifluoromethyl)-2,4-dimethyl-5,5,5-triphenyl-2-aza-5-phosphonia-3-borata-pentane (XV): general procedure

To a suspension of 10 mmol $[\text{Ph}_3\text{PCH}_2\text{R}]\text{Br}$ ($\text{R} = \text{H}$, Me) in 30 ml ether, 4 g of a 15% $^n\text{BuLi}$ solution in

Table 7

Coordinates and equivalent isotropic thermal parameters^a for the nonhydrogen atoms of XII

| Atom | x | y | z | U |
|-------|------------|------------|------------|-----------|
| F(1) | 0.0592(1) | 0.0674(1) | 0.10020(8) | 0.0578(5) |
| F(2) | 0.1445(2) | 0.2544(1) | -0.0741(1) | 0.0775(6) |
| F(3) | -0.0050(2) | 0.2800(1) | 0.1921(1) | 0.0873(7) |
| F(4) | -0.0860(2) | 0.2885(1) | 0.0517(1) | 0.0855(6) |
| F(5) | 0.1103(2) | 0.3892(1) | 0.0995(1) | 0.0845(7) |
| N | 0.2411(2) | 0.0766(2) | -0.0651(1) | 0.0505(6) |
| C(1) | 0.1861(2) | 0.1623(2) | -0.0208(1) | 0.0498(8) |
| C(2) | 0.2890(3) | -0.0326(2) | -0.0174(2) | 0.0625(9) |
| C(3) | 0.2554(4) | 0.0776(3) | -0.1646(2) | 0.082(1) |
| C(4) | 0.0452(3) | 0.2828(2) | 0.1060(2) | 0.0588(9) |
| C(5) | 0.3089(2) | 0.1712(2) | 0.1565(1) | 0.0410(7) |
| C(6) | 0.3171(2) | 0.1087(2) | 0.2401(1) | 0.0445(7) |
| C(7) | 0.4497(3) | 0.1132(2) | 0.2982(1) | 0.0508(8) |
| C(8) | 0.5769(2) | 0.1790(2) | 0.2786(1) | 0.0528(8) |
| C(9) | 0.5687(2) | 0.2407(2) | 0.1972(2) | 0.0530(8) |
| C(10) | 0.4397(2) | 0.2384(2) | 0.1368(1) | 0.0442(7) |
| C(11) | 0.1858(3) | 0.0358(2) | 0.2741(2) | 0.0614(9) |
| C(12) | 0.7189(3) | 0.1822(3) | 0.3437(2) | 0.077(1) |
| C(13) | 0.4481(3) | 0.3111(2) | 0.0509(2) | 0.0620(9) |
| B | 0.1537(3) | 0.1686(2) | 0.0887(2) | 0.0464(9) |

$$^a U = \frac{1}{3} \sum_i \sum_j \bar{a}_i \cdot \bar{a}_j a_i^* a_j^* U_{ij}$$

hexane were added at -50°C . The stirred mixture was warmed to 20°C , cooled to -30°C again as ca. 2.0 g A were added dropwise until the colour of the methylenephosphoranes had disappeared. Solvent and unreacted volatile material were removed at $20^{\circ}\text{C}/10^{-2}$ mbar and XIV (XV respectively) were recrystallized from CHCl_3 .

Compound XIV: (yield ca. 58%) dec. 140°C ; IR cm^{-1} : 1107, 1075 vs $\nu(\text{C-F})$.

Compound XV: (yield ca. 34%) dec. 110°C ; IR cm^{-1} : 1104, 1065, 1035 vs $\nu(\text{C-F})$.

5.5. 3,3-Bis(trifluoromethyl)-2,2-dimethyl-5,5,5-triphenyl-2-azonia-5-phosphonia-3-borata-pentane-trifluoromethanesulphonate (XVI)

Onto a solution of 10 mmol (4.7 g) XIV in 50 ml CH_2Cl_2 40 mol $\text{CF}_3\text{SO}_3\text{CH}_3$ were condensed in vacuo and stirred for 12 h. Removal of all volatile material at $20^{\circ}\text{C}/10^{-2}$ mbar gave pure XVI in quantitative yield.

Compound XVI: (yield ca. 99%) dec. 178°C ; IR cm^{-1} : 1193 vs $\nu(\text{C-F})$. For mass spectral data see Table 4; for elemental analyses see Table 5.

Table 9

Coordinates and equivalent isotropic temperature factors^a for the nonhydrogen atoms of XIVb

| Atom | x | y | z | U |
|-------|------------|------------|------------|-----------|
| P | 0.33229(8) | 0.66115(8) | 0.65691(7) | 0.0373(3) |
| F(1) | 0.3506(2) | 0.5494(2) | 0.9672(2) | 0.0672(9) |
| F(2) | 0.1150(2) | 0.5898(2) | 0.9759(2) | 0.0730(9) |
| F(3) | 0.2445(3) | 0.6525(2) | 1.0750(1) | 0.081(1) |
| F(4) | 0.1359(2) | 0.9945(2) | 0.7752(2) | 0.0765(9) |
| F(5) | 0.0077(2) | 0.8465(2) | 0.8821(2) | 0.082(1) |
| F(6) | 0.1453(3) | 0.9110(2) | 0.9645(2) | 0.095(1) |
| N | 0.4192(3) | 0.8216(2) | 0.8304(2) | 0.055(1) |
| C(1) | 0.2459(4) | 0.6440(3) | 0.9662(3) | 0.053(1) |
| C(2) | 0.1353(4) | 0.8794(3) | 0.8691(3) | 0.057(2) |
| C(3) | 0.4604(4) | 0.9326(4) | 0.7251(3) | 0.074(2) |
| C(4) | 0.4992(5) | 0.8136(5) | 0.9286(4) | 0.098(3) |
| C(5) | 0.2213(3) | 0.7543(3) | 0.7304(2) | 0.042(1) |
| C(6) | 0.3124(3) | 0.4930(3) | 0.7333(2) | 0.039(1) |
| C(7) | 0.4306(4) | 0.4065(3) | 0.7298(3) | 0.052(1) |
| C(8) | 0.4123(4) | 0.2771(3) | 0.7822(3) | 0.064(2) |
| C(9) | 0.2775(5) | 0.2335(4) | 0.8381(3) | 0.068(2) |
| C(10) | 0.1597(4) | 0.3178(4) | 0.8417(3) | 0.066(2) |
| C(11) | 0.1752(4) | 0.4468(3) | 0.7902(3) | 0.055(1) |
| C(12) | 0.5281(3) | 0.6877(3) | 0.6322(2) | 0.041(1) |
| C(13) | 0.6117(3) | 0.6491(3) | 0.7298(3) | 0.051(1) |
| C(14) | 0.7612(3) | 0.6707(3) | 0.7111(3) | 0.065(2) |
| C(15) | 0.8282(4) | 0.7287(4) | 0.5972(3) | 0.079(2) |
| C(16) | 0.7475(4) | 0.7636(4) | 0.4998(3) | 0.075(2) |
| C(17) | 0.5972(3) | 0.7442(3) | 0.5171(3) | 0.057(1) |
| C(18) | 0.2617(3) | 0.7061(3) | 0.5125(2) | 0.042(1) |
| C(19) | 0.2441(3) | 0.8347(3) | 0.4398(3) | 0.054(1) |
| C(20) | 0.1876(4) | 0.8713(4) | 0.3307(3) | 0.065(2) |
| C(21) | 0.1494(4) | 0.7802(5) | 0.2934(3) | 0.075(2) |
| C(22) | 0.1671(4) | 0.6539(4) | 0.3627(3) | 0.071(2) |
| C(23) | 0.2236(3) | 0.6155(3) | 0.4725(3) | 0.054(1) |
| B | 0.2652(4) | 0.7760(3) | 0.8495(3) | 0.041(1) |

^a $U = \frac{1}{3} \sum_i \sum_j \bar{a}_i \cdot \bar{a}_j \cdot a_i^* a_j^* U_{ij}$

5.6. X-ray structure determinations

Crystals of XII, XIVa and XIVb were sealed in glass capillaries. Diffraction data were measured with a Siemens AED-1 diffractometer employing Zr-filtered Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for the variations of the three hourly-monitored standard reflections and absorption. All structures were solved with SHELXS-86 [23] and refined with SHELX-76 [24]. All hydrogen atoms were placed in idealized positions ($\text{C-H} = 0.95 \text{ \AA}$). While the methyl groups of XIVa, all methylene groups and phenyl hydrogens were refined with riding models, the methyl groups of XII and XIVb were varied as rigid groups. Crystal data and refinement details are given in Table 6, and the final coordinates of nonhydrogen atoms are listed in Table 7, Tables 8 and 9. (Additional crystallographic details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, by quoting the deposit numbers CSD-405417 for XII and CSD-405416 for XIVa or CSD-405415 for XIVb, the names of the authors and the literature reference.)

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