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## Carbenoid reactions of trifluoromethylelement compounds. Part 6. Syntheses and characterization of difluoromethylphosphonium, arsonium and stibonium compounds from reactions of triorganopnicogens with Zn(CF<sub>3</sub>)Br·2D and Bi(CF<sub>3</sub>)<sub>3</sub><sup>1</sup>

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Dedicated to Professor Edgor Niecke on the occasion of his 60th birthday

## Abstract

(Difluoromethyl)triorganopnicogenium tetrachlorobismuthates are isolated in moderate to very good yields from the reactions of several  $R_3E$  derivatives(E=P, As) with the reagent Bi(CF<sub>3</sub>)<sub>3</sub>/AlCl<sub>3</sub>. (Difluoromethyl)triorganopnicogenium bromides are obtained from room temperature reactions of  $R_3E$ (E=P, As, Sb) with Zn(CF<sub>3</sub>)Br·2CH<sub>3</sub>CN. The compounds were characterized by their NMR and mass spectra and by comparison with literature data. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

 $Zn(CF_3)Br \cdot 2CH_3CN$  is a versatile tool for the introduction of difluoromethyl groups into organic and inorganic molecules [1]. Similar results were obtained using  $Cd(CF_3)_2$ complexes [2,3], which are excellent NMR sensors for the investigation of the basic reaction mechanisms.

On the basis of NMR spectroscopic measurements it was shown that formation of  $CF_2H$  groups proceeds via an ionic pathway by fluorine substitution at a  $CF_3$  group still bonded to the metal center rather than via "free" difluorocarbene, although this mechanism is proposed for some reactions at low temperatures [4,5].

Comparative studies of the reactions of  $Zn(CF_3)Br \cdot 2CH_3CN$ ,  $Cd(CF_3)_2 \cdot 2CH_3CN$  and  $Bi(CF_3)_3$  with  $N(CH_3)_3$  showed that the reactions involving  $Bi(CF_3)_3$  appear to proceed somewhat differently from the others [6].

In the foregoing papers [7,8] we showed that  $Zn(CF_3)Br \cdot 2D$ ,  $Cd(CF_3)_2 \cdot 2D$  and  $Bi(CF_3)_3$  are also excellent starting materials for the generation of diffuoromethyl-

containing compounds. On the basis of NMR spectroscopic studies [3,6], we proved that the reaction must be based on a two-step mechanism. The first step is the fluorine substitution at the CF<sub>3</sub> group still bonded to the metal center followed by the cleavage of the carbon–metal bond initiated by protons abstracted from the solvent, especially CH<sub>3</sub>CN, where the resulting CH<sub>2</sub>CN anion may also undergo addition reactions as shown in the reactions with *N*-morpholino-cycloalkenes [7].

Bi(CF<sub>3</sub>)<sub>3</sub> had been shown to react as a trifluoromethyl group transfer reagent [9,10] comparable to Bi(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> [11,12] and Bi(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [13–15] which are excellent phenylation reagents.

In continuation and extension of our prior work on difluoromethylations using trifluoromethylmetal compounds, we herein report on the syntheses of (difluoromethyl)triorganopnicogenium compounds.

## 2. Results and discussion

Three methods have been developed to give difluoromethylpnicogenium derivatives in sufficient to very good yields.

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## 2.1. Method A

The first method is the reaction of  $Bi(CF_3)_3$  with the corresponding triorganopnicogen in the presence of AlCl<sub>3</sub>.

$$\begin{split} Bi(CF_3)_3 + AlCl_3 + ER_3 + CH_3CN &\rightarrow [R_3ECF_2H]^+ \\ + [BiCl_4]^- + [AlF_4]^- + CF_3H + CF_2HCl + \cdots \end{split}$$

where E=P, As; R= $C_6H_5$ ,  $n-C_4H_9$ ,  $C_2H_5$ , N( $C_2H_5$ )<sub>2</sub>.

However, the mechanism is still not completely understood. The formation of the tetrachlorobismuthate anion and maximum yields of approximately 75% on the basis of the amount of Bi(CF<sub>3</sub>)<sub>3</sub> involved even in those cases when the base is added in excess clearly demonstrates that only one CF<sub>3</sub> group of Bi(CF<sub>3</sub>)<sub>3</sub> is converted into the CF<sub>2</sub>H group. The remaining CF<sub>3</sub> groups are converted into CF<sub>3</sub>H as the major product and smaller quantities of CF<sub>2</sub>HCl are formed.

The resonance of a further  $CF_2H$  compound is detected in the <sup>19</sup>F-NMR spectra of all reaction mixtures as a doublet at ca. -95 ppm, with a <sup>2</sup>J(<sup>19</sup>F-<sup>1</sup>H) coupling of 62±2 Hz. On the basis of literature data [18] this must be assigned to a  $CF_2H$ -substituted amine derived from the solvent acetonitrile. Involvement of  $CH_3CN$  in these types of reactions especially as a source of protons has been established in reactions in  $CD_3CN$  and in consecutive experiments [2,3,7].

The residue which precipitated was only roughly analyzed.  $[AlF_4]^-$  could be unambiguously identified on the basis of <sup>19</sup>F- and <sup>27</sup>Al-NMR spectra [16,17].

Reactions of AlX<sub>3</sub> with  $Cd(CF_3)_2$  complexes, Zn(CF<sub>3</sub>)Br·2CH<sub>3</sub>CN and Bi(CF<sub>3</sub>)<sub>3</sub> in the absence of strong bases proceed more-or-less indiscriminately yielding several unidentified fluorine-containing compounds [19].

Thus, the synthetic potential of Bi(CF<sub>3</sub>)<sub>3</sub> in the systems investigated must be considered to be of great interest.  $[(C_6H_5)_3P(CF_2H)][BiCl_4]$ ,  $[(n-C_4H_9)_3P(CF_2H)][BiCl_4]$  and  $[(C_2H_5)_3As(CF_2H)][BiCl_4]$  were obtained by this method on a preparative scale in good yields with comparative ease.

The first symmetric diphosphonium derivative was obtained from the reaction with 1,2-bis(diphenylphosphino)ethane in 74% yield. However, elemental analysis as well as <sup>19</sup>F-NMR data indicate that the product obtained also contained a low amount of the monodifluoromethylated compound and possibly a difluoromethylphosphane.

The reaction of Bi(CF<sub>3</sub>)<sub>3</sub> and P[N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>, the strongest base in this series, was performed in the absence of AlCl<sub>3</sub>. After stirring equimolar amounts of both derivatives in CH<sub>3</sub>CN at ambient temperature for 24 h, an unidentified residue precipitated. After filtration, the mother liquor was diluted with diethyl ether and distilled off together with CH<sub>3</sub>CN. The remaining solid was dried in vacuo giving {[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N]<sub>3</sub>P(CF<sub>2</sub>H)}[HF<sub>2</sub>] in 61% yield. The NMR values agree with literature data [20].

$$\begin{split} & [(C_2H_5)_2N]_3P + Bi(CF_3)_3 \\ & \rightarrow \{[(C_2H_5)_2N]_3PCF_2H\}[HF_2] + \cdots \end{split}$$

This reaction again gives evidence for CH<sub>3</sub>CN being the source of the proton and implies that fluorine substitution occurs in some cases even in the absence of an auxiliary acid.

## 2.2. Method B

Method B is an extension of our previous work on the use of  $Zn(CF_3)Br \cdot 2CH_3CN$  as a source for the formation of derivatives containing  $CF_2H$  groups.

The reactions of  $Zn(CF_3)Br \cdot 2CH_3CN$  with  $P(C_6H_5)_3$ ,  $P[N(C_2H_5)_2]_3$ ,  $As(C_6H_5)_3$  and  $Sb(C_6H_5)_3$  proceed in  $CH_2Cl_2$  solution at room temperature or below giving the corresponding(difluoromethyl)triorganopnicogenium bromides.

$$\begin{split} &Zn(CF_3)Br \cdot 2CH_3CN + ER_3 \rightarrow [R_3ECF_2H]Br \\ &+ \langle ZnF(CH_2CN) \rangle + CH_3CN \end{split}$$

where E=P (81% yield), As (84% yield), Sb (3% yield);  $R=C_6H_5$ .

However, the reaction of  $P[N(C_2H_5)_2]_3$  yielded a surprising result. The products obtained were a nearly 1:1 mixture of  $\{[(C_2H_5)_2N)]_3P(CF_2H)\}Br$  (40%) and  $[(C_2H_5)_2N]_2-P(CF_2H)F_2$  (42%).

$$\begin{split} &Zn(CF_3)Br \cdot 2CH_3CN + [(C_2H_5)_2N]_3P \\ & \rightarrow \{[(C_2H_5)_2N]_3P(CF_2H)\}Br + [(C_2H_5)_2N]_2P(CF_2H)F_2 \end{split}$$

The formation of the difluorophosphorane must be considered as a double exchange of bromide and diethylamide by intermediately formed zinc fluorides [21]. The reactions of Zn(CF<sub>3</sub>)Br·2CH<sub>3</sub>CN and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>As and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb, respectively, were studied as examples at room temperature without an additional acid or base giving  $[(C_6H_5)_3As(CF_2H)]Br$  in very good yield (84%), whereas only traces of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sb(CF<sub>2</sub>H)]Br were isolated. Reactions with  $Bi(C_6H_5)_3$  did not give any evidence for the formation of  $[(C_6H_5)_3Bi(CF_2H)]$  compounds.

The addition of  $BF_3$  to the reactants as used in the synthesis of group 16 derivatives [2] effects an acceleration of the reaction together with formation of a couple of by-products.

## 2.3. Method C

Although the reaction of  $E(C_6H_5)_3$  (E=P, As, Sb) and  $Zn(CF_3)Br \cdot 2CH_3CN$  proceeded without an additional auxiliary acid, reactions of  $Zn(CF_3)Br \cdot 2ER_3$  in the presence of AlCl<sub>3</sub>·ER<sub>3</sub> were tested.

The 1:1 adducts of ER<sub>3</sub> (E=As, Sb; R=C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>) and the Lewis-acid (AlCl<sub>3</sub> or BF<sub>3</sub>) were prepared in advance in CH<sub>2</sub>Cl<sub>2</sub> solution by combining both reactants. The adducts were formed in exothermal reactions and the adducts with E(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> were characterized on the basis of their <sup>1</sup>H-NMR spectra (Table 1).

Table 1  $^1\text{H-NMR}$  data of the 1:1 adducts of  $E(C_2H_5)_3$  (E=As, Sb) and BF\_3 or AlCl\_3 (CH\_2Cl\_2, 20^\circ\text{C})

E	As		Sb	
	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(\mathrm{CH}_3)$
E(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1.07	0.79	1.27	1.24
$E(C_2H_5)_3 \cdot BF_3^a$	1.70	1.16		
$E(C_2H_5)_3 \cdot AlCl_3$	1.65	1.15	1.50	1.15

<sup>a 19</sup>F-NMR:  $\delta(BF_3) = -125$  ppm, broad.

Also the 1:2 adducts of  $Zn(CF_3)Br \cdot 2ER_3$  (E=As, Sb; R=C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>) were prepared in advance by adding the corresponding arsenic or antimony compound to a solution of  $Zn(CF_3)Br \cdot 2CH_3CN$  in  $CH_2Cl_2$ . The formation of the adducts is indicated by a significant lowfield shift of the fluorine resonances of  $Zn(CF_3)Br/Zn(CF_3)_2$  of ca. 3–4 ppm.

Combining the two solutions gave an exothermal reaction. Stirring overnight led to the formation of the corresponding CF<sub>2</sub>H derivatives. The reaction was terminated after approximately 16 h of stirring by adding a saturated solution of NH<sub>4</sub>Br in ethanol or an aqueous HCl solution. Excess Zn(CF<sub>3</sub>)Br was converted into CF<sub>3</sub>H and ZnBrX (X=Cl, Br) by this step; intermediates with structural units [XZnCF<sub>2</sub>E(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]Br or [XZnCF<sub>2</sub>E(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]Br were converted into the corresponding difluoromethyl arsonium and stibonium compounds, respectively.

 $Zn(CF_3)Br \cdot 2ER_3 + MX_3 \cdot ER_3$ 

$$\begin{array}{l} \rightarrow [Br - Zn - CF_2 - ER_3][MX_3F] \\ \xrightarrow{NH_4Br/C_2H_5OH} Br - Zn - Br + M(OC_2H_5)_3 \end{array}$$

 $+ [R_3E(CF_2H)]Br$ 

where  $MX_3$ =AlCl<sub>3</sub>, BF<sub>3</sub>; E=As, Sb; R=C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>.

The intermediates in these reactions,  $[XZnCF_2ER_3]Br$ were detected in the <sup>19</sup>F-NMR spectra ( $\delta$ (ZnCF<sub>2</sub>As) -92±1 ppm,  $\delta$ (ZnCF<sub>2</sub>Sb) -88±1 ppm, cf. [6] for the corresponding ammonium intermediates).

The yields of the products were between 30% and 33% for the arsenic compounds and only traces for the antimony derivatives due to complicated work up of the reaction mixtures.

Thus, the formation, especially of the arsenic derivative, reveals that a self-dissociation of  $Zn(CF_3)Br$  complexes occurs even at room temperature according to

$$Zn(CF_3)Br \cdot 2D \rightarrow \begin{bmatrix} D \\ | \\ Br \\ ZnCF_2 \\ | \\ D \end{bmatrix}^+ +F^-$$

As already suggested previously, the electron deficiency at the  $M-CF_2^+$  group is compensated by a base, i.e.  $ER_3$ . Proton abstraction from  $CH_3CN$  or the addition of a proton source, i.e.  $NH_4^+$ ,  $C_2H_5OH$ ,  $H_2O$  finally gives the corresponding difluoromethylpnicogen derivative. On the basis of NMR spectroscopic measurements the triphenyl derivatives appear to be salt-like compounds in solution, dissociating into  $[(C_6H_5)_3E(CF_2H)]^+$  and  $Br^-$  ions. Therefore, the(difluoromethyl)triphenyl derivatives must be suggested as tetrahedral tetraorganopnicogenium bromides without significant cation anion interaction in solution.

In contrast, the ethyl derivatives appear to be covalent compounds. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of the triethyl derivatives suggest that covalent trigonal bipyramidal species with two magnetically inequivalent ethyl groups have been formed. However, the NMR data are in contrast to the VSEPR model [22], which predicts that the most electronegative ligands, i.e.  $CF_2H$  and Br, should occupy axial positions. On the basis of the NMR measurements and the detection of the M<sup>+</sup> peak in the mass spectrum, a covalent compound consisting of two isomers like



might be assumed, whereas the corresponding (difluoromethyl)triethylarsonium tetrachlorobismuthate appears to be an ionic species in solution and in the solid state.

## 3. Experimental

All reactions were carried out in a dry nitrogen atmosphere using Schlenk techniques. Commercially available phosphines and arsines were used after purification by common methods. AlCl<sub>3</sub> was carefully dried in vacuo before use.

 $Zn(CF_3)Br \cdot 2CH_3CN$  was prepared according to Ref. [23]; Bi(CF<sub>3</sub>)<sub>3</sub> according to Ref. [24,25].

 $As(C_2H_5)_3$  was prepared according to Ref. [26];  $Sb(C_2H_5)_3$  by analogy with Ref. [27].

The adducts of  $BF_3 \cdot As(C_2H_5)_3$ ,  $AlCl_3 \cdot E(C_2H_5)_3$  (E=As, Sb) were prepared in  $CH_2Cl_2$  solution and used as obtained after <sup>1</sup>H-NMR spectroscopic control (Table 1).

The adducts  $Zn(CF_3)Br \cdot 2ER_3$  were prepared in advance adding the corresponding triorganopnicogen compound to a well-stirred solution of  $Zn(CF_3)Br \cdot 2CH_3CN$  in  $CH_2Cl_2$  at room temperature. The exchange was monitored by <sup>19</sup>F-NMR spectroscopy, a significant lowfield shift indicated the formation of the adducts. Isolation of the new adducts and use as starting materials in separate reactions did not give better yields or a more convenient working up.

NMR spectra were recorded on Bruker spectrometers operating at 200 or 300 MHz.  $CCl_3F$  [<sup>19</sup>F],  $(CH_3)_4Si$  [<sup>1</sup>H, <sup>13</sup>C] and H<sub>3</sub>PO<sub>4</sub> (85%) [<sup>31</sup>P] were used as external standards. Electron impact (EI) mass spectra were run on a modified Varian MAT CH5 spectrometer.

Fluorine was analyzed according to Ref. [28], chlorine according to Ref. [29] and bismuth according to Ref. [30].

## 3.1. Method A

# 3.1.1. (Difluoromethyl)triphenylphosphonium tetrachlorobismuthate

To a solution of 0.6 g (1.44 mmol) Bi(CF<sub>3</sub>)<sub>3</sub> and 0.38 g (1.45 mmol) triphenylphosphine in 5 ml acetonitrile, 0.32 g (2.40 mmol) AlCl<sub>3</sub> was added at  $-40^{\circ}$ C. The reaction mixture was stirred for 1 h at  $-20^{\circ}$ C and then for 2 h at ambient temperature. The precipitate was filtered off and the solvent was distilled off under reduced pressure. After distillation, the precipitate was recrystallized from acetone to give 0.74 g (77% relative to Bi(CF<sub>3</sub>)<sub>3</sub>) (difluoromethyl)-triphenylphosphonium tetrachlorobismuthate decomposing at ca. 200°C.

Elemental analysis for C<sub>19</sub>H<sub>16</sub>BiCl<sub>4</sub>F<sub>2</sub>P: [found (calculated)] Bi 31.08% (31.48%), Cl 20.97% (21.35%), F 5.29% (5.72%). <sup>19</sup>F-NMR ((CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  –126.06 ppm, dd, <sup>2</sup>*J*(<sup>19</sup>F-<sup>1</sup>H)=46.7 Hz, <sup>2</sup>*J*(<sup>31</sup>P-<sup>19</sup>F)=78.1 Hz; (CH<sub>3</sub>CN)  $\delta$  –125.15 ppm, dd, <sup>2</sup>*J*(<sup>19</sup>F-<sup>1</sup>H)=47.2 Hz, <sup>2</sup>*J*(<sup>31</sup>P-<sup>19</sup>F)=78.3 Hz.

The <sup>19</sup>F-NMR data are in good agreement with those given in [20].

<sup>1</sup>H-NMR (CD<sub>3</sub>CN):  $\delta$ (C<sub>6</sub>H<sub>5</sub>, CF<sub>2</sub>H) 7.79–7.85 ppm, overlapping signals.

<sup>31</sup>P{<sup>1</sup>H}-NMR (CH<sub>3</sub>CN):  $\delta$  +22.3 ppm, t, <sup>2</sup>*J*(<sup>31</sup>P-<sup>19</sup>F)= 77.3 Hz.

<sup>13</sup>C{<sup>1</sup>H}-NMR (CH<sub>3</sub>CN):  $\delta$ (C-1) 113.99 ppm, <sup>1</sup>J(<sup>31</sup>P-<sup>13</sup>C)=85.2 Hz,  $\delta$ (CF<sub>2</sub>H) 116.40 ppm, <sup>1</sup>J(<sup>19</sup>F-<sup>13</sup>C)= 269.6 Hz, <sup>1</sup>J(<sup>31</sup>P-<sup>13</sup>C)=56.5 Hz,  $\delta$ (C-3,5) 132.97 ppm, <sup>3</sup>J(<sup>31</sup>P-<sup>13</sup>C)=12.7 Hz,  $\delta$ (C-2,6) 136.84 ppm, <sup>2</sup>J(<sup>31</sup>P-<sup>13</sup>C)= 10.2 Hz,  $\delta$ (C-4) 138.90 ppm, <sup>4</sup>J(<sup>31</sup>P-<sup>13</sup>C)=2.5 Hz.

The ring-carbon resonances were assigned by analogy with Ref. [31].

## 3.1.2. (Difluoromethyl)-n-tributylphosphonium tetrachlorobismuthate

Obtained by the same method from 0.57 g (1.37 mmol) Bi(CF<sub>3</sub>)<sub>3</sub>, 0.26 g (1.29 mmol)  $(n-C_4H_9)_3P$  and 0.26 g (1.95 mmol) AlCl<sub>3</sub>. After distilling off CH<sub>3</sub>CN, the precipitate was recrystallized from acetone to give 0.60 g (77% relative to  $(n-C_4H_9)_3P$ ) (difluoromethyl)-*n*-tributylphosphonium tetrachlorobismuthate which decomposed above 200°C.

Elemental analysis for  $C_{13}H_{28}BiCl_4F_2P$ : [found (calculated)] Bi 34.15% (34.59%), Cl 23.02% (23.47%).

<sup>19</sup>F-NMR (CD<sub>3</sub>CN):  $\delta$  –127.7 ppm, dd, <sup>2</sup>*J*(<sup>19</sup>F–<sup>1</sup>H)= 47.4 Hz, <sup>2</sup>*J*(<sup>31</sup>P–<sup>19</sup>F)=67.0 Hz.

<sup>1</sup>H-NMR (CD<sub>3</sub>CN):  $\delta$ (CH<sub>3</sub>) 0.93 ppm, 9H,  $\delta$ (β, γ-CH<sub>2</sub>) 1.53 ppm, 12H,  $\delta$ (α-CH<sub>2</sub>) 2.52 ppm, 6H,  $\delta$ (CF<sub>2</sub>H) 7.27 ppm, dt, <sup>2</sup>J(<sup>19</sup>F–<sup>1</sup>H)=47.4 Hz, <sup>2</sup>J(<sup>31</sup>P–<sup>1</sup>H)=27.2 Hz <sup>1</sup>H.

<sup>31</sup>P-NMR (CD<sub>3</sub>CN):  $\delta$  +39.32 ppm, t, <sup>2</sup>*J*(<sup>31</sup>P-<sup>19</sup>F)= 67.1 Hz.

## 3.1.3. 1,2-Bis((difluoromethyl)diphenylphosphonio)ethane bis(tetrachlorobismuthate)

The compound was obtained by the same method from 1.00 g (2.40 mmol)  $Bi(CF_3)_3$ , 0.48 g (1.20 mmol) 1,2-bis-(diphenylphosphano)ethane and 0.48 g (3.60 mmol)  $AlCl_3$ . After evaporation of CH<sub>3</sub>CN, the precipitate was recrystallized from acetone to give 0.89 g (74%) 1,2-bis((difluoromethyl)diphenylphosphonio)ethane bis(tetrachlorobismuthate) containing a low percentage of the mono(difluoromethyl) compound and a further difluoromethylphosphorus compound.

Elemental analysis for  $C_{28}H_{26}Bi_2Cl_8F_4P_2$ : [found (calculated)] Bi 34.41% (34.77%), Cl 23.17% (23.60%), F 5.94% (6.32%).

<sup>19</sup>F-NMR (CD<sub>3</sub>CN):  $\delta$  –127.4 ppm, m, <sup>2</sup>*J*(<sup>19</sup>F–<sup>1</sup>H)= 46.4 Hz, <sup>2</sup>*J*(<sup>31</sup>P–<sup>19</sup>F)=79.2 Hz.

<sup>1</sup>H-NMR (CH<sub>3</sub>CN):  $\delta$ (C<sub>6</sub>H<sub>5</sub>, CF<sub>2</sub>H) 7.00–7.35 ppm, overlapping signals,  $\delta$ (CH<sub>2</sub>) 2.05 ppm, t, <sup>3</sup>*J*(<sup>31</sup>P–<sup>1</sup>H)= 4.4 Hz.

## 3.1.4. (Difluoromethyl)triethylarsonium

## tetrachlorobismuthate

The compound was obtained from 0.60 g (1.44 mmol)  $Bi(CF_3)_3$ , 0.70 g (4.32 mmol) ( $C_2H_5$ )<sub>3</sub>As and 0.57 g (4.27 mmol) AlCl<sub>3</sub> in 78% yield (0.63 g relative to  $Bi(CF_3)_3$ ) as solid decomposing above 200°C.

Elemental analysis for  $C_7H_{16}AsBiCl_4F_2$ : [found (calculated)] Bi 36.78% (37.06%), Cl 25.41% (25.15%), F 6.39% (6.74%).

<sup>19</sup>F-NMR (CH<sub>3</sub>CN):  $\delta$  –119.2 ppm, d, <sup>2</sup>*J*(<sup>19</sup>F–<sup>1</sup>H)= 48.7 Hz.

## 3.1.5. (Difluoromethyl)tris(diethylamino)phosphonium bifluoride

A solution of 0.52 g (1.25 mmol) Bi(CF<sub>3</sub>)<sub>3</sub> and 0.30 g (1.21 mmol) [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N]<sub>3</sub>P in 5 ml CH<sub>3</sub>CN was stirred for 24 h at ambient temperature. The precipitate was filtered off and the solvent was diluted with diethylether. The residue obtained after solvent evaporation was dried in vacuo. The yield was 0.25 g (61% relative to [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N]<sub>3</sub>P). The spectral data correspond with those given in Ref. [20]. The resonance of the [HF<sub>2</sub>]<sup>-</sup> anion was detected in the <sup>19</sup>F-NMR spectrum at  $\delta$  –148 to –149 ppm as a broad unresolved signal.

### 3.2. Method B

### 3.2.1. (Difluoromethyl)triphenylphosphonium bromide

A solution of 0.89 g (3.00 mmol)  $Zn(CF_3)Br \cdot 2CH_3CN$ and 0.89 g (3.39 mmol) ( $C_6H_5$ )<sub>3</sub>P in 10 ml dichloromethane was stirred for 48 h at ambient temperature. The precipitate was filtered and the solvent was distilled off at reduced pressure. After evaporation of  $CH_2Cl_2$  the precipitate was washed with a  $CH_2Cl_2/(C_2H_5)_2O$  mixture and dried in high vacuo. The yield was 0.95 g (81% relative to  $Zn(CF_3)Br \cdot 2CH_3CN$ ). M.p. 200–202°C. The spectroscopic data were identical with those given above.

## 3.2.2. (Difluoromethyl)tris(diethylamino)phosphonium bromide and (difluoromethyl)bis-(diethylamino)difluorophosphorane

A solution of 1.20 g (4.85 mmol)  $[(C_2H_5)_2N]_3P$  and 3.17 g (10.69 mmol) Zn(CF<sub>3</sub>)Br·2CH<sub>3</sub>CN in 20 ml dichloromethane was stirred for 24 h at ambient temperature. The precipitate was filtered off, and the solvent was distilled off under reduced pressure. After distilling off CH<sub>2</sub>Cl<sub>2</sub>, the precipitate was washed with diethylether and dried in high vacuo. The yield of (difluoromethyl)tris(diethylamino)phosphonium bromide was 0.74 g (40%). The analytical and spectral data correspond fairly well with those given in [20]. After diethylether evaporation (difluoromethyl)bis(diethylamino)difluorophosphorane was obtained as a colourless oil. The yield was 0.54 g (42%).

Elemental analysis for  $C_9H_{21}F_4N_2P$ : [found (calculated)] F 28.65% (28.76%).

<sup>19</sup>F-NMR [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O]:  $\delta$ (PF<sub>2</sub>) –66.86 ppm, d, <sup>1</sup>J(<sup>31</sup>P–<sup>19</sup>F)= 771 Hz,  $\delta$ (CF<sub>2</sub>H) –127.70 ppm, ddt, <sup>2</sup>J(<sup>19</sup>F–<sup>1</sup>H)= 52 Hz, <sup>2</sup>J(<sup>31</sup>P–<sup>19</sup>F)=110 Hz, <sup>3</sup>J(<sup>19</sup>F–<sup>19</sup>F)=10.5 Hz.

<sup>31</sup>P-NMR [CH<sub>2</sub>Cl<sub>2</sub>]:  $\delta$  -66.67 ppm, ttd, <sup>1</sup>*J*(<sup>31</sup>P-<sup>19</sup>F)= 771 Hz, <sup>2</sup>*J*(<sup>31</sup>P-<sup>19</sup>F)=110 Hz, <sup>2</sup>*J*(<sup>31</sup>P-<sup>1</sup>H)=35 Hz.

<sup>1</sup>H-NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$ (CF<sub>2</sub>H) 5.9 ppm, tdt, <sup>2</sup>J(<sup>19</sup>F–<sup>1</sup>H)= 52 Hz, <sup>2</sup>J(<sup>31</sup>P–<sup>1</sup>H)=35 Hz, <sup>3</sup>J(<sup>19</sup>F–<sup>1</sup>H)=6.5 Hz.

## 3.2.3. (Difluoromethyl)triphenylarsonium bromide

(Difluoromethyl)triphenylarsonium bromide was obtained from 1.00 g (3.27 mmol) ( $C_6H_5$ )<sub>3</sub>As and 3.00 g (10.12 mmol) Zn(CF<sub>3</sub>)Br·2CH<sub>3</sub>CN in 84% yield (1.20 g). M.p. 200°C (dec.).

Elemental analysis for  $C_{19}H_{16}AsBrF_2$ : [found (calculated)] F 8.26% (8.69%).

<sup>19</sup>F-NMR [CH<sub>2</sub>Cl<sub>2</sub>]:  $\delta$  –115.4 ppm, d, <sup>2</sup>*J*(<sup>19</sup>F–<sup>1</sup>H)= 48.7 Hz.

### 3.2.4. (Difluoromethyl)triphenylstibonium bromide

Prepared from 1.20 g (3.40 mmol)  $(C_6H_5)_3Sb$  and 3.00 g (10.12 mmol) Zn(CF<sub>3</sub>)Br·2CH<sub>3</sub>CN. After working up (see above) only ca. 0.05 g (ca. 3%) of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SbCF<sub>2</sub>H]Br were obtained as a grayish solid. The NMR-data correspond with those given below.

## 3.3. Method C

A typical procedure is given for the reaction of  $Zn(CF_3)Br \cdot 2As(C_2H_5)_3$  and  $AlCl_3 \cdot As(C_2H_5)_3$ .

In a Schlenk-tube 3.25 g (20.05 mmol)  $As(C_2H_5)_3$  were dissolved in 20 ml  $CH_2Cl_2$  at ambient temperature. 2.67 g (20.02 mmol) of  $AlCl_3$  were added. An exothermal reaction

resulted. The mixture was stirred for 1 h until the reaction mixture had cooled to ambient temperature. A solution (suspension) of  $Zn(CF)_3Br \cdot 2As(C_2H_5)_3$ (10.54 g (19.57 mmol) in 20 ml CH<sub>2</sub>Cl<sub>2</sub>) was slowly dropped into the solution of  $AlCl_3 \cdot As(C_2H_5)_3$  when a strong exothermal reaction with evolution of gaseous products started. Stirring overnight gave a brown solution from which some white solid precipitated. <sup>19</sup>F-NMR spectroscopic control showed the resonances of  $[(C_2H_5)_3A_8(CF_2H)]^+$ ,  $[(C_2H_5)_3A_8CF_2 ZnX]^+$ ,  $Zn(CF_3)X$  as well as low intensity resonances of Zn(C<sub>2</sub>F<sub>5</sub>)-derivatives. The reaction was terminated by addition of 20 ml of a saturated ethanolic NH<sub>4</sub>Br solution or an aqueous HCl solution (10 ml) to decompose unreacted  $Zn(CF_3)Br$  complexes and convert  $[(C_2H_5)_3AsCF_2ZnX]^+$ into the difluoromethyl derivative. The mixture was heated for 24 h at 80°C. After precipitation of the solid products the solution was decanted. The residue was suspended in CH<sub>2</sub>Cl<sub>2</sub>; insoluble components were filtered off. The organic fractions were combined, and all volatile components were distilled off in vacuo until a brown solid remained. The solid was eluated by column chromatography (Al<sub>2</sub>O<sub>3</sub>, length of the column 10 cm, diameter 4 cm). Eluation was started with a 10:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and ethylacetate. The ratio was varied to 1:1. (Difluoromethyl)triethylarsonium bromide finally was eluated using a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixture (5:1 v/v). The dark brown fraction was dried in vacuo until a brown solid was obtained which was washed with hot water to give a yellow aqueous solution.

After drying in vacuo, the product was washed with ethylacetate and recrystallized from aqueous methanol (1:1 v/v).  $[(C_2H_5)_3A_8(CF_2H)]Br$  crystallized as colourless or light brownish crystals of up to 10 mm length. The yield was 1.89 g (33% relative to Zn(CF<sub>3</sub>)Br·2As(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>).

A similar procedure was used for all other arsenic and antimony compounds.

The analytical data are summarized in the following section.

 $(C_2H_5)_3As(CF_2H)Br.$  Yield 33%; light brownish crystals. <sup>19</sup>F-NMR [CD<sub>3</sub>CN]:  $\delta(CF_2H) - 118.0$  ppm, <sup>2</sup> $J(^{19}F^{-1}H) =$ 

48 Hz,  ${}^{1}J({}^{19}\text{F}-{}^{13}\text{C})=282$  Hz,  ${}^{1}\Delta({}^{12/13}\text{C}-{}^{19}\text{F}) -0.143$  ppm. {}^{1}\text{H-NMR} [CD\_{3}\text{CN}]: \delta(\text{CF}\_{2}\text{H}) 7.7 ppm, t,  ${}^{2}J({}^{19}\text{F}-{}^{1}\text{H})=$ 

48 Hz;  $\delta(CH_2(ax))$  2.7 ppm, q;  $\delta(CH_2(eq))$  1.9 ppm, q;  $\delta(CH_3(ax))$  1.3 ppm, t;  $\delta(CH_3(eq))$  1.1 ppm, t.

<sup>13</sup>C{<sup>1</sup>H}-NMR [CD<sub>3</sub>CN]:  $\delta$ (CF<sub>2</sub>H) 120.0 ppm, t, <sup>1</sup>*J*(<sup>19</sup>F– <sup>13</sup>C)=282 Hz;  $\delta$ (CH<sub>2</sub>) 21.8 and 15.5 ppm;  $\delta$ (CH<sub>3</sub>) 8.0 and 7.0 ppm. An assignment to axial or equatorial positions could not be made on the basis of decoupled spectra due to NOE-effects influencing intensity and integration.

 $[(C_6H_5)_3As(CF_2H)]Br.$  Yield 30%, white microcrystalline solid.

<sup>19</sup>F-NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$ (CF<sub>2</sub>H) -115.0 ppm, d, <sup>2</sup>J(<sup>19</sup>F-<sup>1</sup>H)=48 Hz, <sup>1</sup>J(<sup>19</sup>F-<sup>13</sup>C)=288 Hz, <sup>1</sup> $\Delta$ (<sup>12/13</sup>C-<sup>19</sup>F) -0.135 ppm.

<sup>1</sup>H-NMR [(CD<sub>3</sub>)<sub>2</sub>CO]:  $\delta$ (CF<sub>2</sub>H) 7.9 ppm, t, <sup>2</sup>*J*(<sup>19</sup>F–<sup>1</sup>H)= 48 Hz, 1H,  $\delta$ (C<sub>6</sub>H<sub>5</sub>) 7.6 ppm, overlapping multiplets, 15H.

<sup>13</sup>C{<sup>1</sup>H}-NMR [(CD<sub>3</sub>)<sub>2</sub>CO]: δ(C-4) 137.0 ppm; δ(C-2,6) 133.0 ppm; δ(C-3,5) 131.0 ppm; δ(CF<sub>2</sub>H) 117.0 ppm, t, <sup>1</sup>*J*(<sup>19</sup>F<sup>-13</sup>C)=288 Hz. C-1 was not observed due to line broadening caused by the quadrupole resonance of the arsenic nucleus.

MS (20 eV, 160°C): 306 (45%,  $[As(C_6H_5)_3]^+$ ), 229 (10%,  $[As(C_6H_5)_2]^+$ ), 154 (10%,  $[AsBr]^+$ ), 152 (100%,  $[AsC_6H_5]^+$ ), 51 (20%,  $[CF_2H]^+$ ).

The mass spectrometric breakdown pattern with the exception of the ions 154 and 51 corresponds with that for  $As(C_6H_5)_3$  [32].

(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Sb(CF<sub>2</sub>H)Br. Yield: traces; colourless solid.

<sup>19</sup>F-NMR [CH<sub>2</sub>Cl<sub>2</sub>]:  $\delta$ (CF<sub>2</sub>H) – 115.1 ppm, d, <sup>2</sup>*J*(<sup>19</sup>F–<sup>1</sup>H)= 48 Hz, <sup>1</sup>*J*(<sup>19</sup>F–<sup>13</sup>C)=282.5 Hz.

<sup>1</sup>H-NMR [CH<sub>2</sub>Cl<sub>2</sub>]:  $\delta$ (CF<sub>2</sub>H) 6.72 ppm, t, <sup>2</sup>*J*(<sup>19</sup>F<sup>-1</sup>H)= 48 Hz,  $\delta$ (CH<sub>2</sub>) 2.40 and 2.24 ppm, q,  $\delta$ (CH<sub>3</sub>) 1.40 and 1.37 ppm, t. A final assignment could not be made due to overlapping signals.

<sup>13</sup>C-NMR [CH<sub>2</sub>Cl<sub>2</sub>]:  $\delta$ (CF<sub>2</sub>H) 115.0 ppm, t, <sup>1</sup>*J*(<sup>19</sup>F–<sup>13</sup>C)= 283 Hz. The signals of the CH<sub>3</sub>CH<sub>2</sub> groups are located between 20 and 0 ppm but broadened and partially split due to unsuccessful decoupling.

 $\begin{array}{l} MS\ (20\ eV,\ 85^{\circ}C):\ 338\ (1\%,\ M^+),\ 295\ (10\%,\ [Sb(C_2H_5)-(CH_3)(CF_2H)Br]^+),\ 280\ (5\%,\ [Sb(C_2H_5)(CF_2H)Br]^+),\ 259\ (20\%,\ [Sb(C_2H_5)_3(CF_2H)]^+),\ 251\ (60\%,\ [Sb(CF_2H)Br]^+),\ 244\ (100\%,\ \ [Sb(C_2H_5)(CH_3)Br]^+),\ 230\ (40\%,\ [Sb(C_2H_5)_2(CF_2H)]^+),\ 215\ (12\%,\ \ [Sb(CH_3)Br]^+),\ 208\ (11\%,\ [Sb(C_2H_5)_3]^+),\ 201\ (4\%,\ \ [Sb(C_2H_5)(CF_2H)]^+),\ 179\ (61\%,\ \ [Sb(C_2H_5)_2]^+),\ 150\ (49\%,\ \ [Sb(C_2H_5)]^+),\ 121\ (3\%,\ \ [Sb]^+). \end{array}$ 

 $[(C_6H_5)_3Sb(CF_2H)]Br$ . The yield was extremely low; only the <sup>19</sup>F-NMR spectrum could be recorded.

<sup>19</sup>F-NMR [CH<sub>2</sub>Cl<sub>2</sub>]:  $\delta$ (CF<sub>2</sub>H) – 106.1 ppm, d, <sup>2</sup>*J*(<sup>19</sup>F–<sup>13</sup>C) = 47 Hz, <sup>1</sup>*J*(<sup>19</sup>F–<sup>13</sup>C) = 300 Hz.

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### References

- [1] W. Tyrra, D. Naumann, J. Prakt. Chem. 338 (1996) 283.
- [2] D. Naumann, R. Möckel, W. Tyrra, Angew. Chem., Int. Ed. Engl. 33 (1994) 323.
- [3] R. Möckel, W. Tyrra, D. Naumann, J. Fluorine Chem. 73 (1995) 229.
- [4] R. Eujen, B. Hoge, J. Organomet. Chem. 503 (1995) C51.
- [5] L.J. Krause, J.A. Morrison, J. Am. Chem. Soc. 103 (1981) 2995.
- [6] S.V. Pasenok, N.V. Kirij, Yu.L. Yagupolskii, D. Naumann, W. Tyrra, A. Fitzner, Z. Anorg. Allg. Chem., in press.
- [7] W. Tyrra, D. Naumann, S.V. Pasenok, Yu.L. Yagupolskii, J. Fluorine Chem. 70 (1995) 181.
- [8] R. Miethchen, M. Hein, D. Naumann, W. Tyrra, Liebigs Ann. (1995) 1717.
- [9] W. Tyrra, D. Naumann, Can. J. Chem. 69 (1991) 327.
- [10] W. Tyrra, D. Naumann, Can. J. Chem. 67 (1989) 1949.
- [11] R.A. Abramovitch, D.H.R. Barton, J.-P. Finet, Tetrahedron 44 (1988) 3039.
- [12] J.-P. Finet, Chem. Rev. 89 (1989) 1487.
- [13] A.O. Miller, G.G. Furin, Izv. Akad. Nauk, Ser. Khim. (1994) 171.
- [14] A.O. Miller, G.G. Furin, Russ. Chem. Bull. 43 (1994) 168.
- [15] H.J. Frohn, S. Görg, G. Henkel, M. Läge, Z. Anorg. Allg. Chem. 621 (1995) 1251.
- [16] N. Herron, D.L. Thorn, R.L. Harlow, F. Davidson, J. Am. Chem. Soc. 115 (1993) 3028.
- [17] W. Tyrra, Dissertation, Universität Dortmund, 1989.
- [18] D.J. Brauer, H. Bürger, M. Grunwald, G. Pawelke, J. Wilke, Z. Anorg. Allg. Chem. 537 (1986) 63.
- [19] R.Yu. Garlyauskajte, W. Tyrra, unpublished results.
- [20] M.J. van Hamme, D.J. Burton, P.E. Greenlimb III, Org. Magn. Res. 11 (1978) 275.
- [21] R. Bartsch, O. Stelzer, R. Schmutzler, Z. Naturforsch. 36b (1981) 1349.
- [22] J.E. Huheey, Anorganische Chemie, Walter de Gruyter, Berlin, Aufl., 1988, p. 222.
- [23] D. Naumann, W. Tyrra, B. Kock, W. Rudolph, B. Wilkes, J. Fluorine Chem. 67 (1994) 91.
- [24] W. Tyrra, D. Naumann, J. Organomet. Chem. 334 (1987) 323.
  - [25] D. Naumann, R. Schlengermann, W. Tyrra, J. Fluorine Chem. 66 (1994) 79.
  - [26] W. Steinkopf, J. Müller, Chem. Ber. 54 (1921) 841.
  - [27] W.J.C. Dyke, W.C. Davies, W.J. Jones, J. Chem. Soc. (1930) 463.
  - [28] A.D. Campbell, P.A. Dawson, Mikrochim. Acta (1983) 489.
  - [29] G. Jander, K.F. Jahr, H. Knoll, Maßanalyse, Walter deGruyter, Berlin, 1973, p. 300.
  - [30] R. Pribil, Komplexone in der Chemischen Analyse, Verlag der Wissenschaften, Berlin, 1961.
  - [31] G.A. Gray, J. Am. Chem. Soc. 95 (1973) 7736.
  - [32] C. Glidewell, J. Organomet. Chem. 116 (1976) 199.