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Structures of some organoarsenic fluorides

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Abstract

Arsenic pentafluoride (AsF_5) adds across the CC and CS double bonds of $H_2C{=}SF_4$, $F_3C{-}CH{=}SF_4$ and $F_2C{=}CH{-}SF_5$ with the formation of $AsF_4{-}CHR{-}SF_5$ ($R=H$, CF_3). In the case $R=CF_3$, a stable compound is obtained. Crystallography reveals a structure with a trigonal bipyramidally coordinated arsenic and the carbon substituent in an equatorial position. For $R=H$, the primary product dimerizes to $(F_5S{-}CH_2)_2AsF_2^+\ AsF_6^-$. Its first hydrolysis product $(F_5S{-}CH_2)_2AsFO \cdot AsF_5$ was identified via its crystal structure.

Introduction

Substituted phosphorus fluorides of the type R_xPF_{3-x}, R_xPF_{5-x}, R_xPOF_{3-x} and R_xPF_{6-x} have been well investigated [1]. Quite often not even preparation of the pure compound has been necessary since complete structural information can be obtained via ^1H, ^{13}C, ^{19}F and ^{31}P nuclear magnetic resonance spectroscopy. Moreover, in most cases, these compounds do not undergo intermolecular fluorine exchange. Hence the structural principles (pyramidal, trigonal bipyramidal, tetrahedral, octahedral) of these compounds are well established. Trigonal bipyramidal compounds, in particular, have been looked at in much detail. Among the few exceptions from the predicted molecular geometry are some members of the series $(CF_3)_xPF_{5-x}$ [2].

The state of the art concerning the corresponding arsenic compounds is different. ^{75}As nuclear magnetic resonance spectroscopy is not a valuable tool for structural elucidation because of the very high quadrupole moment, and ^{19}F NMR spectra very often suffer from intermolecular fluorine exchange. Nevertheless, a few compounds are known, e.g. $(C_6H_5)_3AsF_2$ is prepared by fluorination of $(C_6H_5)_3As$ with SF_4 [3] or H_2O_2/HF [4]. Systematic investigations with IF_5 as a fluorinating agent have afforded other Ar_3AsF_2 compounds ($Ar=C_6F_5$, $4\text{-}CF_3C_6H_4$, $4\text{-}FC_6H_4$) [5]. $(C_6F_5)_3AsF_2$ has also been obtained from $(C_6F_5)_3As$ by fluorination with elemental fluorine [6]. $(C_6H_5)_3AsF_2$ and $(C_6F_5)_3AsF_2$ have known crystal structures [7, 8]. In accordance with common bonding models, the fluorine atoms occupy the axial positions of a trigonal bipyramid. $(C_6F_5)_2AsF_3$ is prepared from $(C_6F_5)_2AsCl$ with IF_5 [5]. Pure $C_6F_5AsF_4$ has not yet been obtained [5], whereas $C_6H_5AsF_4$ was prepared from phenylarsenic acid and SF_4 [3]. In the case of $(C_6H_5)_2AsF_3$, a trigonal

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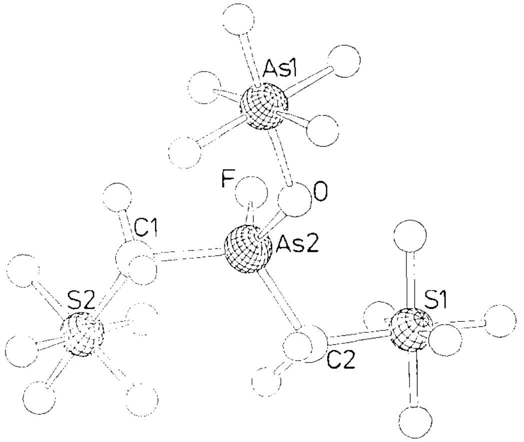
bipyramidal structure has been derived from ^{19}F NMR spectroscopy, for over a wide temperature range there is evidence that one equatorial and two axial fluorine atoms do not interchange [9].

Results and discussion

Our investigations of reactions on carbon–sulphur double bonds have yielded another method of obtaining substituted arsenic fluorides. In 1983, we showed that AsF_5 adds to $H_2C{=}SF_4$. The product was first described as $F_5S{-}CH_2{-}AsF_4$. We show here via the crystal structure that this assignment was incorrect. The reason for this wrong assignment certainly stems from the fact that usual analytical methods such as NMR spectroscopy and elemental analysis can hardly distinguish between the postulated and real structure. What was obtained instead of $F_5S{-}CH_2{-}AsF_4$ was $(F_5S{-}CH_2)_2AsFO{\cdot}AsF_5$. This requires reaction with water or glass which was impossible to avoid. Because of the low solubility only the final product is formed, even if the stoichiometry is changed.

Figure 1 and Table 1 show the results of the crystal structure analysis indicating that the compound is an arsenic oxide derivative. Similar materials are widely known in phosphorus chemistry but somewhat less frequently in arsenic chemistry, probably because the arsenic atom seeks a higher co-ordination number than four. Known triorganoarsenic oxides, $R_3As{=}O$, are formed by oxidation of triorganoarsanes and react with water with an increase



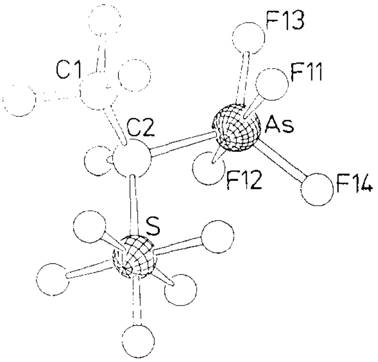


Fig. 1. Molecular structure of $(F_5S{-}CH_2)_2AsFO{\cdot}AsF_5$, XP plot. Important bond lengths [pm] and angles [°]: As1–O, 184.0(5); As2–O, 164.7(5); As2–C1, 190.5(8); As2–C2, 188.4(8); As1–F(11–15), 169.6–171.4(5); As2–F, 167.1(4); As1–O–As2, 127.3(3); C1–As2–C2, 117.8(3); O–As2–F, 108.1(2).

Fig. 2. Molecular structure of $F_5S{-}CH(CF_3){-}AsF_4$, XP plot. Important bond lengths [pm] and angles [°]: As–C2, 197.0(7); As–F11, 173.7(5); As–F12, 172.6(5); As–F13, 166.8(5); As–F14, 168.3(5); F11–As–F12, 175.2(2); F13–As–F14, 116.1(3).

TABLE 1

Fractional atomic coordinates of $(F_5S\text{–}CH_2)_2AsFO\cdot AsF_5$

Atom	x	y	z	B [10^4 pm^2]
As1	0.2535(1)	0.4020(1)	0.5888(1)	1.12
As2	0.1045(1)	0.2854(1)	0.4096(1)	0.98
S1	0.7586(3)	0.1222(2)	0.4036(1)	1.30
S2	0.2371(3)	0.3557(2)	0.2326(1)	1.39
F11	0.4112(6)	0.3274(4)	0.5417(3)	1.82
F12	0.0877(6)	0.4781(4)	0.6302(3)	1.83
F13	0.2778(7)	0.5223(4)	0.5240(3)	2.23
F14	0.2229(6)	0.2832(5)	0.6526(3)	2.07
F15	0.4101(6)	0.4579(5)	0.6679(3)	2.52
F	0.2254(6)	0.1603(4)	0.4268(3)	1.52
F31	0.6106(6)	0.1224(4)	0.3206(3)	2.28
F32	0.6501(7)	0.2195(5)	0.4471(3)	2.49
F33	0.9022(6)	0.1199(4)	0.4881(3)	1.83
F34	0.8643(7)	0.0224(4)	0.3623(3)	2.59
F35	0.6533(7)	0.0236(5)	0.4449(3)	2.67
F41	0.2701(6)	0.4910(4)	0.2132(3)	1.93
F42	0.0253(6)	0.3768(4)	0.2207(3)	2.03
F43	0.2040(7)	0.2174(4)	0.2487(3)	2.30
F44	0.4433(7)	0.3306(4)	0.2418(3)	2.36
F45	0.2216(7)	0.3284(4)	0.1338(3)	2.64
C1	0.2483(11)	0.3859(7)	0.3490(5)	1.20
C2	−0.1233(11)	0.2402(8)	0.3512(5)	1.46
O	0.0780(7)	0.3413(5)	0.5050(3)	1.25

in the coordination number [10]. $AsOCl_3$ prepared from $AsCl_3$ and ozone is also not stable [11]. Monomeric $AsOF_3$ does not seem to exist [12, 13].

The crystal structure presented consists of $(F_5S\text{–}CH_2)_2AsFO\cdot AsF_5$ units that show only weak intermolecular interaction. Its description as an adduct may not fully be justified because of the nature of the material. It is capable of being sublimed without decomposition, and the distances within the $As{=}O\ldots AsF_5$ bridge of 164.7(5) and 184.0(5) pm would also allow the zwitterionic formulation $As^+\text{–}O\text{–}AsF_5{}^-$. In spite of the usual difficulties of distinguishing F from O by X-ray methods, the bridging atom is clearly oxygen. This is obvious not only from the short As–O bond length, but also from the fact that setting a fluorine atom into the oxygen position increases the vibrational amplitudes quite considerably and the R-value slightly.

The structure obtained explains the NMR data, if exchange of all (As–)F atoms is assumed. Probably the postulated $F_5S\text{–}CH_2\text{–}AsF_4$ is formed first. This might dismutate to $(F_5S\text{–}CH_2)_2AsF_3\cdot AsF_5$, which in turn might hydrolyse to $(F_5S\text{–}CH_2)_2AsFO\cdot AsF_5$. The first step of this postulated reaction chain can be demonstrated since $F_3C\text{–}CH{=}SF_4$ or $F_2C{=}CH\text{–}SF_5$ both react with AsF_5 giving $F_5S\text{–}CH(CF_3)\text{–}AsF_4$ which no longer dismutates. In contrast to the compound described above, $F_5S\text{–}CH(CF_3)\text{–}AsF_4$ is a volatile liquid. The arsenic-bonded fluorine atoms are not resolved, but their coupling with the

TABLE 2

Fractional atomic coordinates of F_5S–$CH(CF_3)$–AsF_4

Atom	x	y	z	B [10^4 pm^2]
As	0.4877(0)	0.1695(1)	0.2007(0)	1.42
S	0.8651(3)	0.0889(2)	0.1257(3)	1.38
C1	0.7974(11)	0.3054(7)	0.1904(9)	1.55
C2	0.7567(10)	0.1908(6)	0.2230(9)	1.19
F11	1.4333(6)	0.2427(4)	0.0411(5)	1.77
F12	0.5220(7)	0.0962(4)	0.3590(6)	2.84
F13	0.3600(7)	0.2568(4)	0.2714(6)	2.31
F14	0.3741(7)	0.0633(4)	0.1157(7)	2.64
F21	1.0272(6)	0.0774(4)	0.2604(6)	2.07
F22	0.7041(6)	0.0978(4)	−0.0116(5)	1.90
F23	0.7534(6)	0.0015(4)	0.1915(5)	2.08
F24	0.9790(7)	0.1730(4)	0.0595(5)	1.88
F25	0.9533(6)	−0.0015(4)	0.0507(6)	2.15
F31	0.9752(7)	0.3298(4)	0.2423(5)	2.15
F32	0.7546(7)	0.3366(4)	0.0533(5)	2.00
F33	0.6992(7)	0.3717(4)	0.2628(6)	2.08
H	0.8038	0.1876	0.3078	

other NMR sensitive groups shows the existence of four magnetically equivalent (As–)F atoms. Here the arsenic atom has a coordination number of five. To support this structure further, an X-ray determination has been undertaken despite the low melting point of −60 °C (see Fig. 2 and Table 2. The trigonal bipyramidal geometry around the arsenic atom is obvious, as is the equatorial position of the carbon ligand. The bond lengths and angles within the trigonal bipyramid are as expected (see Fig. 2).

Experimental

Hydrolytically sensitive materials were handled in a glove box with automatic gas (argon) purification (M. Braun Co., Oberschleissheim). NMR: JEOL FX 90 Q instrument with $CFCl_3$ or TMS as external standards, 84.25 and 89.55 MHz, positive chemical shifts according to IUPAC convention. Mass spectra: Variant MAT 711 instrument; EI, 80 eV. Infrared spectra: Perkin-Elmer 85 spectrophotometer. Single-crystal structures: Enraf Nonius CAD 4 diffractometer, MoKα radiation graphite monochromator.

AsF_5 was obtained from Ozark Mahoning Co. and used without further purification. $H_2C{=}SF_4$ [14], F_3C–$CH{=}SF_4$ [15] and $F_2C{=}CH$–SF_5 [16] were prepared according to literature methods.

Bis(pentafluorosulphanyl)methyl arsenic fluoride oxide, arsenic pentafluoride adduct, $(F_5S\text{–}CH_2)_2AsFO\cdot AsF_5$

$H_2C{=}SF_4$ (3.0 g, 24 mmol) and 50 ml $C_2F_4Cl_2$ were condensed into a glass trap. The solution was kept at −100 °C and 4 g (24 mmol) arsenic pentafluoride were also condensed into the trap. A colourless precipitate was formed immediately. All volatile components were pumped off at −72 °C and the remaining solid filled into a sublimator under anhydrous conditions. Sublimation under rotary pump vacuum (*c.* 10^{-2} mbar) between room temperature and −20 °C afforded a colourless, hydrolytically very sensitive powder. ^{1}H NMR (in CD_2Cl_2) δ: 4.8 (quint) ppm, J(H–F) = 8 Hz. ^{19}F NMR: AB_4 system, δ(A) = 75.0, δ(B) = 81.6, δ(As–F) = −44.6 ppm, J(AB) = 138.4 Hz. Elemental analysis: Calculated: C, 4.27; H, 0.71; As, 26.65; F, 54.06; S, 11.41%. Found: C, 4.23; H, 0.79; As, 25.86; F, 58.10; S, 11.09%.

Single crystals were obtained by recrystallisation from $C_4F_9SO_2F$. A suitable crystal was mounted at −154 °C on the Enraf Nonius CAD 4 diffractometer with the help of a special device [17]. For further experimental details concerning the crystal structure see Table 3. The structure was solved using the SHELXS 76 and SHELXS 86 programs [18]. Absorption corrections were made according to Walker and Stuart [19] since embedding the colourless crystal in paraffin oil prevented the application of an experimental absorption correction, and the psi-scan method was only partly applicable because of the geometry of the diffractometer. For results of the crystal structure analyses, see Tables 1 and 3.

1-Pentafluorosulphanyl-2,2,2-trifluoroethyl arsenic tetrafluoride, $F_5S–CH(CF_3)–AsF_4$

$F_2C{=}CH–SF_5$ (9.5 g, 50 mmol) or likewise $F_3C–CH{=}SF_4$ or a mixture of both were condensed into a glass trap, followed by 5 ml $CFCl_3$. The

TABLE 3

Experimental details arising from crystal structure analyses

formula	$C_2H_4As_2F_{16}OS_2$	$C_2HAsF_{13}S$
a [pm]	752.8(1)	737.6(2)
b [pm]	1120.8(2)	1250.9(4)
c [pm]	1551.8(4)	943.7(5)
α [°]	90.0	90.0
β [°]	98.63(2)	101.90(3)
γ [°]	90.0	90.0
V [10^6 pm^3]	1294.5	852.0
space group	$P2_1/n$ (N.14)	Cc (N.9)
Z	4	4
T (°C)	−158	−158
octands	$\pm h, +k, +l$	$\pm h, +k, +l$
θ [°]	2–25	2–25
scan	ω–θ	ω–2θ
reflexions:		
measured	2325	1575
symmetry independent	2113	1311
with $I \geq 3\sigma(I)$	1965	1232
parameters	216	146
R	0.040	0.039
Rw	0.034	0.032

mixture was warmed until a homogeneous solution was formed, then cooled again with liquid N_2 and 8.5 g (50 mmol) AsF_5 condensed in. The sealed ampoule was warmed for 2 h to room temperature. Fractional condensation from room temperature into −55 °C and −196 °C cold traps afford a colourless liquid product (m. p., −60 °C; decomp., *c.* 80 °C), in the −55 °C trap; yield, 16.5 g (92%). ^{1}H NMR (liquid) δ: 5.6 ppm. ^{19}F NMR: $AB_4C_4D_3X$ spectrum, $\delta = 79.0$ (A), 67.9 (B), −43.3 (C), −61.1 (D) ppm; J(AB) = 140.4, J(BC) = 6.3, J(BD) = 12.5, J(BX) = 3.2, J(CD) = 6.3, J(DX) = 6.3 Hz. Mass spectra m/z: 341 ($M^+ - 1$, 1%); 190 ($C_2HF_7S^+$, 35%); 171 ($C_2HF_6S^+$, 11%); 151 ($AsF_4{}^+$, 4%); 132 ($AsF_3{}^+$, 7%); 127 ($SF_5{}^+$, 78%); 113 ($ASF_2{}^+$, 10%); 89 ($SF_3{}^+$, 100%). Crystals were grown in $CFCl_3$ at −78 °C. X-Ray measurement and structural analysis were as described above; for results, see Tables 2 and 3.

Further details regarding the crystal structure determinations can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Informations mbH, D-7514 Eggenstein-Leopoldshafen 2, under quotation of the deposit number CSD 55674, name of authors and journal.

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