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The Tris(trifluoromethyl)methyl Phosphonium Ion, $P(CF_3)_3CH_3^+$, Preparation and Structure

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The $P(CF_3)_3CH_3^+$ ion is synthesized as $P(CF_3)_3CH_3^+AsF_6^-$ by methylation in a $MeF/SO_2/AsF_5$ system or as $P(CF_3)_3CH_3^+Sb_2F_{11}^-$ in a $MeF/HF/SbF_5$ system at low temperatures. In contrast to $(CF_3)_3(CH_3)P^+AsF_6^-$, $P(CF_3)_3CH_3^+Sb_2F_{11}^-$ is a stable, colorless crystalline solid. A crystal structure determination shows the presence of a slightly distorted tetrahedral phosphonium cation with P−C(F) distances of 188.1−188.7(4) and a P−C(H) bond length of 176.7(4) pm. The phosphonium salt $(CF_3)_3(CH_3)P^+AsF_6^-$ was also obtained by abstraction of a fluoride ion from the anion $[(CF_3)_3(CH_3)PF_2]^-$ salt using AsF_5.

Introduction

Phosphorus(III) compounds are the most versatile ligands in transition metal complex chemistry. Even the weak electron donor PF_3 can act as a complex ligand.[1] PF_3 can be protonated only by one of the strongest Brönstedt acids, HF/SbF_5, to PF_3H^+. The crystalline compound decomposes already below 0 °C loosing of PF_3.[2] Calculated proton affinities of PF_3 are the lowest of all considered phosphanes (676 kJ mol^{-1};[3] exptl, 695.3 kJ mol^{-1})[4] and $P(CF_3)_3$ (689 kJ mol^{-1}). The scarcity of the known $P(CF_3)_3$ metal complexes[5] may also be interpreted in terms of very weak donor ability. In contrast to fluorine, the CF_3 group has no π-donor properties which could to some extent compensate its strong electron-withdrawing effect. Thus, stepwise introduction of a trifluoromethyl group into a phosphane molecule should result in a nucleophilicity and basicity decrease. As expected, trifluoromethyldimethylphosphine[6] is easily methylated in methylen chloride using methyl iodide/$AgBF_4$ (3 days) or methyl triflate at room temperature (30 min),[7] whereas bis(trifluoromethyl) methyl phosphine[8] is only methylated by methyl triflate at 100 °C for 24 h as a neat substance.[9] Later, it was shown that PF_3 and $P(CF_3)_3$ act rather as Lewis acids than as Lewis bases, forming relatively stable phosphoranides[10,11] which, contrary to PF_3H^+, could be handled at room temperature.

The molecular structure of $P(CF_3)_3$ is known in detail,[12] but a systematic investigation of its chemical properties is not yet available, except that it reacts spontaneously with oxygen to form $O{=}P(OCF_3)_3$. $O{=}P(CF_3)_3$, although a known compound, is not formed in this way.[13] Chlorination affords $Cl_2P(CF_3)_3$;[14] fluorination with SF_4 affords $F_2P(CF_3)_3$.[15]

Experimental Section

Caution! *Handling anhydrous HF or compounds that produce HF upon hydrolysis like AsF_5 or SbF_5 requires eye and skin protection.*

All reactions not dealing with HF were carried out under an atmosphere of dry nitrogen. The glassware to be used was

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usually kept overnight in a drying oven at 160 °C and then cooled in the flow of dry nitrogen. Reactions with gases were carried out using standard vacuum techniques in a system made of Pyrex glass and stopcocks lubricated with "Waker" medium-duty silicon grease; thick-walled round-bottom Pyrex tubes with Teflon stopcocks served as reaction vessels. Nonvolatile air and moisture-sensitive materials were handled in an inert atmosphere (glovebox "M. Braun Unilab 1200/780" with an integrated refrigerator and gas purifying unit).

All of the reactions with AsF_5 participation were carried out in SO_2, serving the role of a moderately coordinating solvent able to stabilize highly electrophilic phosphorus centers. A typical reaction vessel was a Pyrex NMR tube with a Teflon stopcock. Due to the instability of the compounds synthesized (when not stabilized by a solvent), the products were not isolated but were only characterized by multinuclear NMR spectrometry.

Handling of samples containing HF was performed using Teflon PFA ((poly)perfluorether-tetrafluoroethylene) tubes that are sealed at one end and equipped at the other end with a metal valve and thus are connectable to a stainless steel vacuum line. HF was dried through several trap-to-trap condensations and stored in a stainless steel tank over BiF_5. SbF_5 was purchased from Fluor Chem, United Kingdom, and distilled twice in a vacuum from room temperature to −40 °C. The resulting SbF_5 is highly viscous at room temperature and always kept in closed vessels. AsF_5 was purchased from ABCR. $P(CF_3)_3$ is a highly flammable liquid with a low boiling point of 17 °C. It can explode in liquid state exposed to air, and the explosion may have quite a long induction time. $P(CF_3)_3$ is prepared according to ref 16. During its preparation from CF_3Br, the latter can initially mask ignition of the phosphane, so a very intensive flame may occur after disappearance of the main amount of CF_3Br. A very simple preparation from $(CH_3)_3SiCF_3$ and PCl_3 and CsF catalysis has also been tested.[17] The resulting $P(CF_3)_3$ prepared by this method is always contaminated with 20−50% $(CH_3)_3SiF$. Separation of $P(CF_3)_3$ and $(CH_3)_3SiF$ is almost impossible due to their similar physical data. CH_3F is from laboratory stock.

NMR spectra were recorded on a JEOL multinuclear instrument at 400 MHz for ^1H and a Bruker DPX-200 spectrometer operating at 200.13 MHz for ^1H, 50.32 MHz for ^{13}C, 188.31 MHz for ^{19}F, and 81.01 MHz for ^{31}P. Spectra are recorded relative to $CFCl_3$ (^{19}F) and H_3PO_4 (^{31}P) as external standards. Raman spectra were recorded on a Bruker RFS 1005 instrument with ND-YAG laser excitation, λ = 1064 nm; IR spectra were recorded on a Bruker Vector 22 instrument.

Attempts to generate $(CF_3)_3PH^+$. $P(CF_3)_3$ is condensed in a 2:1 molar solution of HF/SbF_5 in a PFA tube at −196 °C. The mixture is warmed to −78 °C. The two components do not mix at this temperature, even after many days of storage. Slow warming results in dissolution of the $P(CF_3)_3$ under simultaneous formation of a voluminous colorless crystalline solid. At room temperature, all volatiles are in vacuo. The analysis by NMR shows that all $P(CF_3)_3$ has been converted to $P(CF_3)_3F_2$; for numerical data, see ref 14. The crystalline colorless solid is mostly SbF_3, as identified by its lattice constants.

$P(CF_3)_3(CH_3)^+$ AsF_6^-. Method A. Attempts to methylate with methyltriflate failed. In 2.95 g (12.1 mmol) of AsF_5 in 30 g of dry SO_2 was condensed 0.44 g (13 mmol) of MeF. The mixture was warmed up to −30 °C and stirred at this temperature for 2 h. Afterward, 2.87 g (12.1 mmol) of $(CF_3)_3P$ was condensed in the reaction mixture, which was stirred for 22 h at a temperature range of −30 to −10 °C. All volatiles were in vacuo in a high vacuum at −40 °C, leading to the formation of a white flaky precipitate which decomposed quickly above −30 °C. The yield is quantitative (NMR). $(CF_3)_3(CH_3)PF$[19] has been isolated as one decomposition product in 89% yield.

^{19}F NMR (SO_2): δ −50.36 (br.d., 9F, CF_3, $^2J_{PF} = 125.48$ Hz), −53.79 (br.s., $[AsF_6]^- + AsF_5$). $^{31}P\{^1H\}$ NMR (SO_2): δ 42.38 (dec.). ^{31}P NMR (SO_2): δ 42.38 (dec.q., $^2J_{PH} = 16.33$ Hz). ^1H NMR (SO_2): δ 3.73 (br.s., 12H, $^+N(CH_3)_4$), 3.92 (d. dec, 3H, P-CH_3, $^4J_{HF} = 0.7$ Hz). $^{13}C\{^1H\}$ NMR (SO_2): δ 120.29 (d.q., CF_3, $^1J_{CF} = 321.72$ Hz, $^1J_{PH} = 145.23$ Hz), 14.47 (d., CH_3, $^1J_{PC} = 119.5$ Hz). NMR yield: quantitative.

Method B. In 0.15 g (0.4 mmol) of $[(CF_3)_3(CH_3)PF_2]^-N(CH_3)_4^+$[20] was condensed 0.96 g (20 mmol) of SO_2 and 0.12 g (0.7 mmol) AsF_5. The reaction mixture was warmed up to room temperature within 45 min. ^{19}F NMR (SO_2): δ −50.36 (br.d., 9F, CF_3, $^2J_{PF} = 125.48$ Hz), −53.79 (br.s., $[AsF_6]^- + AsF_5$). $^{31}P\{^1H\}$ NMR (SO_2): δ 42.38 (dec.). ^{31}P NMR (SO_2): δ 42.38 (dec.q., $^2J_{PH} = 16.33$ Hz). ^1H NMR (SO_2): δ 3.73 (br.s., 12H), 3.92 (br.d., 3H). ^{13}C NMR (SO_2): δ 120.29 (d.q., CF_3, $^1J_{CF} = 321.72$ Hz, $^1J_{PH} = 145.23$ Hz), 14.47 (d., CH_3, $^1J_{PC} = 119.5$ Hz). NMR yield: quantitatively.

$P(CF_3)_3CH_3^+Sb_2F_{11}^-$. In a drybox, 1 g (4.6 mmol) of SbF_5 was put into an 8-mm-outer-diameter PFA tube. Using a metal vacuum line, subsequently, 10 mL of HF, 300 mg (0.49 mol) of $P(CF_3)_3$, and 700 mg (20.5 mol) of CF_3F were added. The tube was sealed and warmed to 40 °C. A colorless precipitate was formed.

Then, the tube was opened at 40°, and all excess CH_3F was pumped away at −78 °C along with some HF. The tube was sealed again and warmed to +40 °C, until all of the solid was dissolved. Recrystallization by slow cooling to 25 °C afforded 407 mg (66%) of colorless or sometimes slightly beige $[P(CF_3)_3CH_3]^+Sb_2F_{11}^-$, mp (decomp.) = 110 °C.

NMR (all in HF). ^1H: δ 2.77, $^2J_{P-H} = 16$ Hz. ^{19}F: δ −52.78, $^2J_{P-F} = 127$ Hz, −125.26 (broad, Sb−F), −195.79 (HF). ^{31}P: δ −42.70, $^2J_{P-H} = 15-16$ Hz, q, $^2J_{P-F} = 127$ Hz, decett. $^{13}C\{^1H\}$: δ 119.4 , $^1J_{C-F} = 315$ Hz, q, $^1J_{P-C} = 142$ Hz; −2.70 ppm, $^1J_{P-C} = 20$ Hz.

Raman spectrum (solid): 745(20), 660(80), 650(60), 606(15), 553(10), 482(10), 393(25), 279(40), 256(100), 229(15), 179(15), 120(20) cm^{-1}. IR spectrum (AgCl) solid): 2927(2), 2851(w), 1639 (w), 1203(w), 11253(w), 666(s), 445(m) cm^{-1}.

A suitable crystal was selected and mounted on a Bruker Smart CCD 1000 TU diffractometer with the help of a special device.[21] Mo Kα radiation, graphite, monochromator, a scan width of 0.3° in ω, and a measuring time of 10 s per frame were used. A total of 1800 frames were taken, thus covering a full sphere until $2\theta = 61°$. Semiempirical absorption correction (SADABS) was used by equalizing symmetry-equivalent reflections. The structure is solved and refined by the ShelX programs.[22] All atoms except hydrogen are refined anisotropically; hydrogen atoms are refined isotropically with a single displacement parameter for all three hydrogen atoms. Experimental details are collected in Table 1 and results in Table 2.

Results and Discussion

$P(CF_3)_3$, in contrast to PF_3, cannot be protonated by HF/SbF_5. At −78 °C, the two components do not even mix, and upon warming the mixture, even under very careful

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(20) Phosphoranide $[(CF_3)_3PF]^-$ was methylated quantitatively at RT using methyl iodide to give the corresponding $[(CF_3)_3P(CH_3)F_2]^-$, see ref 10.

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Table 1. Crystal Data and Structure Refinement for $[P(CF_3)_3CH_3]^+[Sb_2F_{11}]^-$

empirical formula	$C_4H_3F_{20}PSb_2$
fw	708.03
temp, K	173
space group	*Pbca*
a, pm	1352.2(2)
b, pm	1366.4(2)
c, pm	1759.7(3)
vol, 10^6 pj m^3	3251.2
Z	8
d (calcd) Mg/m^3	2.883
abs coeff, mm^{-1}	3.62
cryst size	0.03 × 0.1 × 0.2 mm
reflns	
measured	54777
independent	4979
params	255
final R indices $I \geq 4\sigma(I)$	R1 = 0.031
all data	R1 = 0.058
	wR2 = 0.073

Table 2. Selected Bond Lengths (pm) and Bond Angles (deg) for $[P(CF_3)_3CH_3]^+[Sb_2F_{11}]$

P−C(F)	188.1−188.7(4)
P−C(H)	176.7(4)
C−F	129.2−131.9(5)
C−H	89−103 (5)
C(F)−P−C(F)	105.7−106.6(2)
C(H)−P−C(F)	111.9−113.4 (2)
Sb−F (terminal)	183.3−185.1(3)
Sb−F (bridge)	201.8, 202.7(3)
Sb−F−Sb	160.4(2)

control of the temperature, a redox reaction inevitably sets in $P(CF_3)_3F_2$ is formed quantitatively and is easily detected by its known ^{19}F and ^{31}P NMR spectra.[14] It may be the loss of solvation or lattice energy of the larger $P(CF_3)_3H^+$ cation, as compared to the PF_3H^+ cation, that prevents protonation in condensed phases.

We failed to methylate $P(CF_3)_3$ using methyltriflate. We used the system $MeF/SO_2/AsF_5$ (methoxysulfinyl hexafluoroarsenate), which was successfully introduced for methylation of the extremely weak nucleophile NSF_3.[22] Tris(trifluoromethyl)methylphosphonium hexafluoroarsenate, $P(CF_3)_3(CH_3)^+AsF_6^-$ was obtained in quantitative yield after the reaction of $P(CF_3)_3$ and $[MeOSO]^+AsF_6^-$ in SO_2 at −30 °C (Scheme 1).

The colorless salt proved to be very unstable and decomposed immediately at room temperature to give as one major product the phosphorane $(CF_3)_3(CH_3)PF$.[19] However, it could be stored at −30 °C for some weeks without any decomposition. Due to the thermal instability, it was characterized only by multinuclear NMR spectroscopy methods.

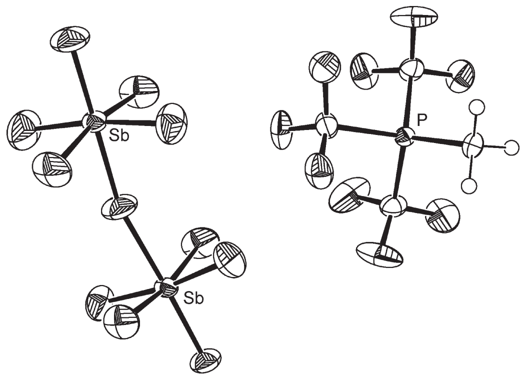
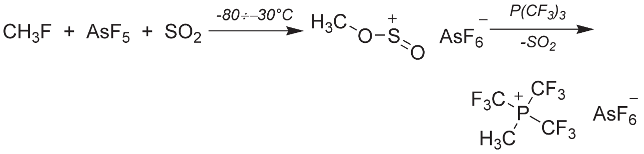
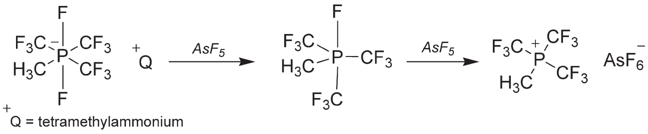


Figure 1. The structure of $P(CF_3)_3CH_3{}^+Sb_2F_{11}{}^-$ in the crystal. ORTEP representation, 50% probability plot. Shown is one molecular unit.

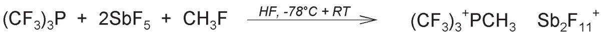
Scheme 1



Scheme 2



Scheme 3



The phosphonium salt $P(CF_3)_3(CH_3)^+AsF_6^-$ was also generated by abstraction of the fluoride ion from the $[(CF_3)_3(CH_3)PF_2]N(CH_3)_4$ salt (see Scheme 2). Both experiments established the high thermal stability of the phosphonium salt in SO_2. It was found that the NMR spectra did not change even after heating of the solution up to 50 °C. The stabilization effect may be caused by the solvating SO_2.

In contrast to the hexafluoroarsenate, $[(CF_3)_3CH_3P]^+$-$Sb_2F_{11}^-$ is a stable, colorless crystalline solid which was synthesized starting from $(CF_3)_3P$, SbF_5, and CH_3F (Scheme 3).

$[(CF_3)_3CH_3P]^+Sb_2F_{11}^-$ has been characterized by spectroscopic means, see the Experimental Section. Multiplicity and chemical shifts of the NMR spectra unequivocally prove again the qualitative structure of the $P(CF_3)_3CH_3^+$ cation. The crystal structure (see Figure 1 and Table 2) offers more detail. The $P-CF_3$ bond lengths are longer than the $P-CH_3$ bond length, as is often observed in cases where CF_3 groups are not bonded to electron-rich centers. Typical examples are $Ge(CH_3)_4$, $\nu_{Ge-C} = 194.5(3)$;[23] pm, $Ge(CF_3)_4$, 198.9(5) pm;[24] $Sn(CH_3)_4$, $\nu_{Sn-C} = 214.4$ pm;[25] $Sn(CF_3)_4$, 220.1(5) pm.[26] The CF_3-P-CF_3 angles are about 105° and are thus larger than in $P(CF_3)_3$ (97.2(7)°) but still smaller than the tetrahedral angle. This may be explained by the higher group electronegativity of CF_3 versus CH_3 and consequently a higher p character in the $P-CF_3$ bonds.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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