refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined as riding atoms with fixed isotropic displacement parameters. For 6017 independent reflections with $I > 2\sigma(I)$ and 433 parameters, $R1 = 0.058$ and $wR2 = 0.1181$.

[13] Crystal data for $[Cu(L^{Bn_3})(Cl_4cat)] \cdot CH_3CN$: $C_{35}H_{36}N_4O_2Cl_4Cu$, $M_r = 750.06$, crystal size $0.50 \times 0.35 \times 0.07$ mm, monoclinic, space group $P2_1/n$, $a = 9.802(2)$, $b = 27.759(5)$, $c = 13.049(2)$ Å, $\beta = 104.39(2)^\circ$, $V = 3439.2(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.447$ g cm^{-3}, $T = 173(2)$ K, radiation Mo$_{K\alpha}$ ($\lambda = 0.71073$ Å), 2θ max $= 50.10^\circ$. Data were collected on Siemens SMART system and the structure was solved by direct methods using SHELXTL-Plus V5.0 on an SGI INDY R4400-SC computer. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined as riding atoms with fixed isotropic displacement parameters. For 6038 independent reflections with $I > 2\sigma(I)$ and 444 parameters, $R1 = 0.0735$ and $wR2 = 0.1391$.

[14] Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408633 and -408634.

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Synthesis and Characterization of the Tetrahydroxyphosphonium Hexafluorometalates $P(OH)_4^+MF_6^-$ (M = As, Sb)

Rolf Minkwitz* and Stefan Schneider

The existence of the tetrahydroxyphosphonium ion, $P(OH)_4^+$ **1**, has been discussed for more than 60 years. The investigations were initiated by Hantzsch who erroneously postulated that nitratacidium perchlorate, $(HO)_2NO^+ClO_4^-$ **2**, was a product of the reaction of HNO_3 with $HClO_4$, but which actually yielded a nitryl salt.[1, 2] In 1937 Arlman studied the behavior of phosphorous acid, H_3PO_4 **3**, towards perchlorous acid on the assumption that **2** existed. He obtained a solid that he presumed had the formula $P(OH)_4^+ClO_4^-$, in analogy to Hantzsch, but gave no evidence for the constitution.[3] It was not until 1952 that the results were supported by Raman spectroscopic investigations.[4] In the following years **1** was proved to exist also in HNO_3, H_2SO_4, FSO_3H, and superacidic FSO_3H/SbF_5 solutions, but it was not possible to isolate it.[5–9] Finally, in 1995 **1** was assumed to be a structural element in a modification of KH_2PO_4, which was prepared at pH 10.[10] The formation of **1** can nevertheless hardly be imagined under these conditions.

Phosphorus acids with the general composition H_3PO_n in hydrogen fluoride yield fluorophosphorane for $n = 2$ and 3 [Eqs. (1) and (2)] and in the case of **3** ($n = 4$) they yield monofluorophosphoric acid **4** and water [Eq. (3)].[11, 12]

$$H_3PO_2 + 3\,HF \rightleftharpoons H_2PF_3 + 2\,H_2O \tag{1}$$

$$H_3PO_3 + 4\,HF \rightleftharpoons HPF_4 + 3\,H_2O \tag{2}$$

$$\underset{\mathbf{3}}{H_3PO_4} + HF \rightleftharpoons \underset{\mathbf{4}}{H_2PO_3F} + H_2O \tag{3}$$

In the superacidic systems HF/MF_5 (M = As, Sb), which are suitable for the isolation of thermolabile salts,[13–17] these acids show a differing reaction behavior. H_3PO_3 yields tetrafluorophosphorane [Eq. (2)] and hydronium salts.[18] A hydronium salt, as well as **4**, can also be expected for an analogous reaction of **3**. However, in contrast to this expectation we find only a singlet at $\delta = -2.4$ (δ^1H 7.1)[5–9] in the ^{31}P NMR spectrum (in SO_2 at −40 °C), and only the signals of the MF_6^- ions in the ^{19}F NMR spectrum. It follows that the reaction with **3** does not proceed according to Equation (3) but yields **1**-MF_6 [Eq. (4), M = As, Sb].

$$\underset{\mathbf{3}}{H_3PO_4} + HF/MF_5 \longrightarrow \underset{\mathbf{1}\text{-}MF_6}{P(OH)_4^+MF_6^-} \tag{4}$$

The presence of **1** in HF/MF_5 at −60 °C can be directly proved as an intermediate in the reaction of **3** to **4**. Before **4** can be formed water has to be removed from **1**, which proceeds after a 1,3 proton transfer, for which a considerable energy barrier of 200 kJ mol^{-1} was calculated.[19]

With the HF/MF_5 system not only was proof for **1**-MF_6 obtained but also its isolation and crystallization were achieved (Figure 1, Table 1). The crystal structural investigation shows that all P–O bond lengths (152.9(2) to 153.6(2) pm) are equivalent within the accuracy of the measurement. In comparison to **3** (154.7(4) to 155.1(4) pm) the bond lengths are shortened.[20, 21] Compound **1** shows almost S_4 symmetry, with O-P-O angles between 101.2(1)° and

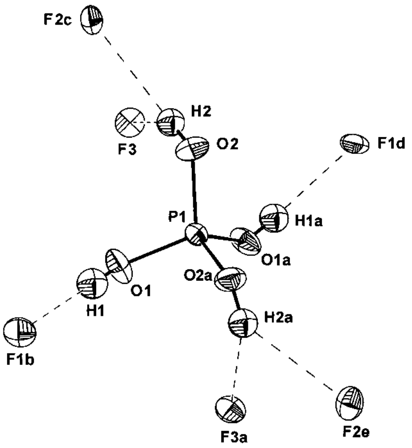

Figure 1. View of the structure of **1** showing the H···F contacts and atom labels. Selected bond lengths [pm]: F2c···H2 218(4), F3···H2 220(4), F1d···H1a 199(4), F2e···H2a 218(4), F3a···H2a 220(4), F1b···H1 199(4).

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Table 1. Selected bond lengths [pm] and angles [°] of **1**-SbF_6. The atoms of the anions in Figure 1 are not completely shown.[a]

Sb1 – F1	189.4(1)	O1-P1-O2	114.2(1)
Sb1 – F2	188.1(1)	O1a-P1-O2	112.3(1)
Sb1 – F3	187.0(1)	O2-P1-O2a	101.2(1)
P1 – O1	152.9(2)	F3-Sb1-F2	89.95(6)
P1 – O2	153.6(2)	F3-Sb1-F1	89.80(6)
		F2-Sb1-F1	90.09(6)

[a] The standard deviations are valid for the last digit of the values. Symmetry operation: (a) = $-x$, y, $0.5 - z$.

114.2(1)°. In the crystal the cations are situated on the twofold rotation axis and the anions located in an inversion center. Cations and anions are linked three-dimensionally by hydrogen bonds so that each cation is linked to six anions (Figure 2) through both simple and bifurcated hydrogen bonds. The H ··· F distances of the bifurcated hydrogen bonds (218(4) and 220(4) pm) are significantly longer than those of the simple hydrogen bonds (only 199(5) pm; Figure 1). This seems to be also reflected in the vibrational spectra (Figure 3, Table 2). The position and contour of the bands and lines depends on the influence of the crystal field. Relatively broad bands were measured in the IR spectra. In the Raman spectra two lines with a separation of approximately 100 cm^{-1} that lie in the range of the stretching vibration of OH and OD, respectively, can be clearly distinguished. The different hydrogen bonds are responsible for these two lines, which was confirmed for **1**-SbF_6 by X-ray crystallography. The stretching vibrations of the hydroxyl groups with bifurcated hydrogen bonds can be found at the higher frequencies 3379/3372 cm^{-1} in $P(OH)_4^+$ and at 2559/2551 cm^{-1} in $P(OD)_4^+$. The vibrations of the OH and OD groups that contribute to simple hydrogen bonds are registered at 3262/3287 cm^{-1} and 2433/2428 cm^{-1}.

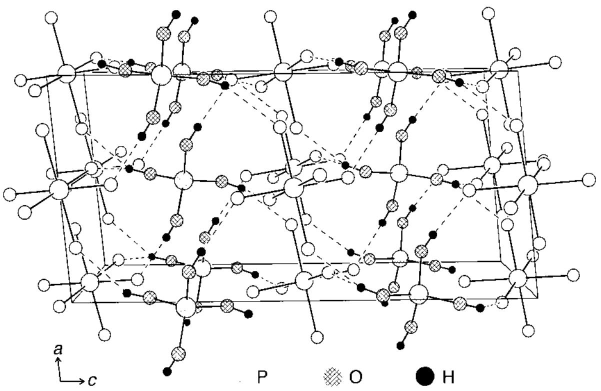

Figure 2. Section of the structure of **1**-SbF_6, showing the arrangement of the ions in the unit cell.

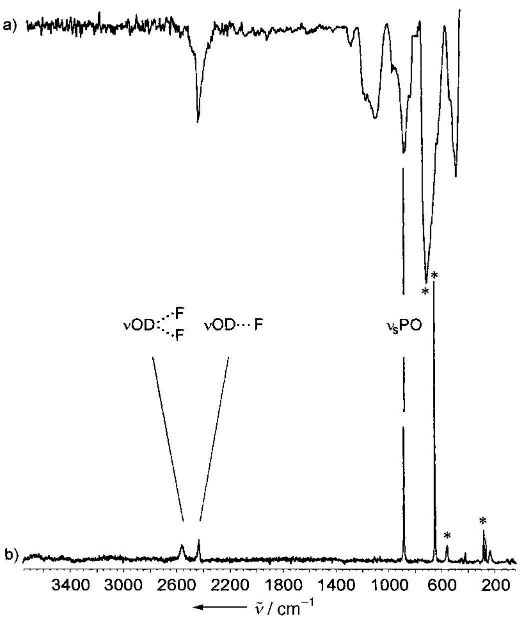

Figure 3. Solid state IR (a) and Raman spectrum (b) of $P(OD)_4^+$-SbF_6^-. Anion vibrations are marked by an *. IR spectrum was recorded at −40 °C (CsI plate) and the Raman spectrum at −78 °C.

Experimental Section

H_3PO_4 **3** (Fluka >99%) was used without further purification. $(Me_3SiO)_3PO$ (Fluka) was used for the preparation of the deuterated salts and the trimethylsilyl groups were removed as Me_3SiF. AsF_5 was prepared

Table 2. Vibrational frequencies [cm^{-1}][a] of $P(OX)_4^+MF_6^-$ (M = AS, Sb; X = H, D) and assigments.[a]

$P(OH)_4^+$				$P(OD)_4^+$				Tentative assignment	
SbF_6^-		AsF_6^-		SbF_6^-		AsF_6^-			
Raman	IR	Raman	IR	Raman	IR	Raman	IR		
3379 (20)		3372 (34.3)		2559 (34.2)	2555 vw	2551 (22.9)	2549 vw	ν	OX
3262 (32.8)	3270 b	3287 (21.4)	3281 b	2433 (33.0)	2430 s	2428 (35.6)	2430 b,s	ν	OX
1112 (0.2)	1106 m	1109 (0.1)	1105 m	1114 (0.3)	1107 m	1111 (0.1)	1112 m	δ_{as}	POX
	1017 s		1011 s		1017 m		1012 m	δ_s	POX
896 (57.7)	893 m	894 (55.7)	893 m	891 (67.3)	887 s	895 (79.4)	887 s	ν_s	PO
		591 (0.2)				588 (14.9)		δ	PO_2
462 (4.7)		460 (1.5)				466 (0.9)		δ	PO_2
		449 (3.8)		431 (7.5)	433 m	424 (10.2)	422 m,sh	τ_{as}	PO
		371 (10.4)				368 (7)		τ_{as}	PO_2
		361 (4.7)				361 (9.1)		τ	PO
		330 (6.8)				307 (24.8)		δ_s	PO_2
275 (25.7)				276 (22.4)				τ_s	PO_2
	669 vs		703 vs		664 vs		703 vs	ν	MF_6^-
658 (100)		694 (100)		659 (100)		695 (100)			
574 (17.2)		571 (2.9)		567 (21.6)		562 (11.5)			
			396 s				98 s		
293 (9.8)		378 (6.2)		293 (14.5)		377 (14.1)			

[a] Relative intensity is shown in brackets; abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong, b = broad, sh = shoulder.

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by reaction of the elements and condensed fractionally, SbF_5 was fractionally distilled, and HF and DF were dried with fluorine.[13]

MF_5 (M = As, Sb; 3 mmol) was dissolved in HF/DF (ca. 5 g) in a KEL-F reactor. After freezing the solution $H_3PO_4/(Me_3SiO)_3PO$ (3 mmol) was added under inert gas (N_2) at −196 °C. The reaction mixture was slowly warmed to −60 °C and kept at this temperature until a clear solution formed. The excess of HF, DF, and Me_3SiF was subsequently removed at −60 °C in a dynamic vacuum. $P(OX)_4^+MF_6^-$ (X = H, D; M = As, Sb) remained as a colorless solid that was stable up to −10 °C for M = As and −3 °C for M = Sb.

Analytical instruments: Raman: Jobin-Yvon T64000, Ar^+ laser (λ = 514,5 nm) Spectra Physics; IR: Bruker IFS 113v; NMR: Bruker DPX300; X-ray diffractometer: Nonius Mach 3.

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[20] Crystal structure analysis of **1**-SbF_6: crystals obtained from HF solution, monoclinic, space group *C*2/*c* (No. 15), $a = 684.3(1)$, $b = 783.5(1)$, $c = 1426.6(2)$ pm, $\beta = 95.47(1)^\circ$, $Z = 4$, $V = 761.4(2) \times 10^6$ pm^3; $\rho_{calcd} = 2.920$ g cm^{-3}, crystal dimensions: 0.22 × 0.14 × 0.14 mm^3, $Mo_{K\alpha}$ radiation ($\lambda = 71.069$ pm), $2\theta/\omega$ scans, $2\theta_{max} = 65.0^\circ$, $T = 193$ K. Of the 2375 measured reflections, 1421 were independent, and 1134 were used in the refinement (σ to 2σ). Lp and absorption correction (ψ scans), $\mu(Mo_{K\alpha}) = 5.035$ mm^{-1}, min/max transmission 0.78/0.91, structure solution method: Patterson, difference-Fourier-synthesis; SHELXS-86, SHELXL-93, PARST, PLATON, MISSYM, 64 free parameters, hydrogen atoms determined and refined experimentally from ΔF, $R = 0.0206$, $wR = 0.0501$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, refinement method: full matrix least-squares on F^2; min./max. residual electron density = −1.073/0.501 e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (fax: (+49) 7247-808-666; e-mail crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408840.
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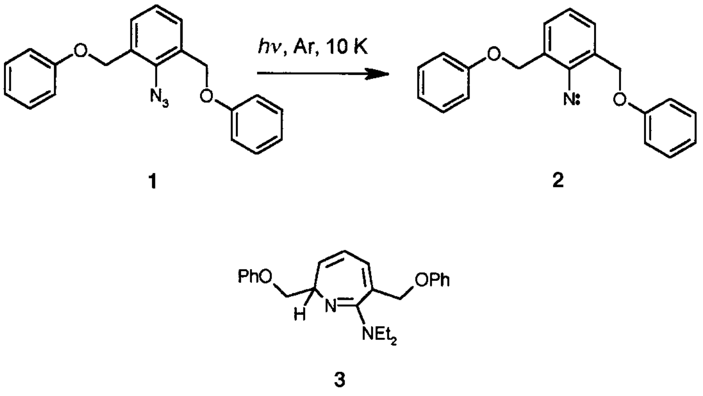
Photochemistry of *ortho*-Phenoxymethyl-Substituted Aryl Azides: A Novel Nitrene Rearrangement En Route to Isolable Iminoquinone Methides?[**]

Götz Bucher[*] and Hans-Gert Korth

Aryl azides show a fascinating and complex photochemistry, which only recently could be elucidated in detail.[1–5] A singlet nitrene is formed as the primary reaction intermediate, which subsequently either adds intramoleculary to a neighboring C=C bond of the aromatic system,[1, 2] or relaxes to the ground-state triplet nitrene via intersystem crossing (ISC). The efficiency of spin inversion depends, among others, on the temperature and on the substitution pattern. Low temperatures favor ISC, and 2,6-bisubstitution retards addition to the C=C bond for steric reasons.[6] If only one *ortho* position is substituted, nitrene cycloaddition usually favors the unsubstituted side.[6] In the course of our own studies on ortho-substituted aryl azides we have synthesized 2,6-bis(phenoxy methyl)-1-azidobenzene **1**, and we have investigated its photochemistry by means of product analysis and matrix isolation spectroscopy.

Photolysis of **1**, which was matrix isolated in Ar at 10 K, yielded a new product **2** (Scheme 1). The UV/Vis spectrum of **2** is typical of a triplet aryl nitrene with a weak band in the visible part of the spectrum that extends to 530 nm, and sharp bands at 398, 296, and 288 nm (Figure 1). The infrared spectrum of **2** does not show bands that would be typical of products of nitrene rearrangement;[7] for instance, there are no bands at about 1890 cm^{-1} (typical for a didehydroazepine[2]). Photolysis of **1** is initially very efficient, but comes to a



Scheme 1.

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