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Selective and Reversible Fluoride Complexation from Water by a Cyclic Tri(phosphonio)methanide Dication

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Dedicated to Professor Dieter Fenske on the occasion of his 75th birthday.

Abstract: Tri(phosphonio)methanide dication 3^{2+} , prepared from a trifluoromethylsulfanylphosphonium dication (1^{2+}) via an intramolecular electrophilic aromatic substitution reaction, is an unexpected P-based, water resistant Lewis acid, which is capable to selectively and reversibly bind fluoride ions from organic / aqueous solution. The formed complex is an unusual fluorophosphorane ([3-F]OTf). The multiple donor-acceptor interactions of 3^{2+} that are crucial for the fluoride fixation have been elucidated by quantum chemical calculation. Compound [3-F]OTf can also be used as a convenient anhydrous fluoride ion source and was probed as a suitable catalyst of the silylotrifluoromethylation of various aldehydes.

The complexation and recognition of anions, particularly fluoride ions (F⁻), by molecular receptors is an intensively investigated field of research.^[1,2] Fluoride ion sensing and complexation in aqueous solution still gains increasing attention, since these ions are known to be highly toxic at high doses, but beneficial for the human body if the concentration is low.^[3] However, F⁻-complexation in the presence of water is challenging due to the high polarizing effects of the F⁻ anion especially associated with the high hydration energy (515 kJ mol⁻¹).^[4] To overcome this problem, a series of main group Lewis acids were introduced for the binding of F⁻ ions. Especially boranes are effective Lewis acids. Gabbaï and co-workers impressively demonstrated the application of several boron-based receptors which detect F⁻ ions at the ppm level in aqueous media.^[5] Some of the boranes are, however, only stable in acidic media due to competitive reaction with OH- ions. In recent years, the same group also established water-resistant antimony(V) compounds with remarkable sensitivity towards F ions.^[6,7] The Lewis acidity of these antimony(V) compounds originates mainly from the capability of the Sb-atom to form hypercoordinate complexes, thus, offering additional coordination sites.^[7-9] Certain phosphonium cations also possess a high F⁻ affinity^[10,11], when hypercoordination is possible.^[12,13] As they are more environmentally benign species, they are interesting targets for F⁻ capture. So far, they have not been recognized as water resistant Lewis acid, which are capable of selectively bind fluoride anions.

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Chart 1. Enhancement of fluoride affinity by electronic modifications (left). Intermolecular substitution reactions at 1²⁺ to yield [2-Nu]²⁺ (right).

In addition, ³¹P as NMR active nucleus would also allow to follow F⁻ complexation by NMR spectroscopy. In order to prepare waterstable phosphonium based salts that are capable of F⁻ complexation, a significantly enhanced Lewis acidity is required (Chart 1). The implementation of electron withdrawing substituents (I)^[14,15] and/or the increase of the overall charge of the cations by the introduction of onio-substituents (II)^[16] are suitable concepts to achieve this goal (Chart 1, left). In addition, the Lewis acidity can furthermore be enhanced by the incorporation of strained rings (III)^[17] and/or by using bidentate Lewis acids (IV).^[18]

We recently reported on the high yielding synthesis of the very Lewis acidic triflyloxyphosphonium salt $1[OTf]_2$ which contains the trifluoromethylsulfonyl-group as excellent leaving group (Chart 1, right). Dication 1^{2+} reacts with a series of nucleophiles to undergo intermolecular substitution reactions to give functionalized phosphonium cations of type $[2-Nu]^{2+}$.^[19]



 $\label{eq:scheme1.Synthesis of 3[OTf]_2 \textit{via} an intramolecular electrophilic aromatic substitution (S_EAr) reaction; a) -HOTf, 1.5 h, 210 °C, 10^{-1} mbar, 82\%.$

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Figure 1. Molecular structure of 3^{2+} (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50 % probability); selected bond lengths in Å and angles in °; 3^{2+} : P1–C1 1.752(2), P2–C1 1.762(2), P3–C1 1.759(2), P1-C1-P3 125.1(1), P2-C1-P1 110.18(1), P3-C1-P2 124.4(1), C1-P1-C2 100.04(8), C1-P2-C3 99.97(8).

In extension of these previous studies, we have now discovered that 1[OTf]₂ undergoes an unusual intramolecular CH-activation followed by a phosphonionation reaction to give cyclic tri(phosphonio)methanide salt 3[OTf]2 when heated to 210 °C for 1.5 h under dynamic vacuum (≈10¹ mbar). The compound is obtained as air and moisture stable solid in good yields (82%, Scheme 1). The ³¹P{¹H} NMR spectrum of 3[OTf]₂ displays an AX₂ spin system where the A-part resonates as a triplet at $\delta(P_A) = 19.6$ ppm, and is assigned to the exocyclic P atom. The X-part, a doublet at $\delta(P_M)$ = 37.9 ppm (²J_{PP} = 23 Hz), is assigned to the endocyclic P atoms. The molecular structure of cation 3²⁺ is displayed in Figure 1 and shows a planar annulated bicycle as base unit with a trigonal planar arrangement for the central C1 atom (angle sum: 359.6(5)°). All P-C bond lengths (C1-P1 1.752(2) Å, C1-P2 1.762(2) Å, C1-P3 1.759(2) Å) are essentially equal and are slightly shorter than typical PV-C bond lengths (e.g. [Ph₄P]+: $P-C_{(average)}$ 1.80(1) Å) as a result of the negative hyperconjugation from the p-type lone pair at C1 into the $\sigma^*(P-C_{Ph})$ orbitals.^[20] A strongly distorted tetrahedral geometry is observed for the P1and P2 atoms caused by the ring strain in the five membered cycle, resulting in more acute C-P-C angles in the five-membered ring (C1-P1-C2 100.04(8)°, C1-P2-C3 99.97(8)°). As a consequence, a flattening of the trigonal pyramids (angle sum: P1(C1, C14, C8): 340.6(3)°; P2(C1, C20, C26): 339.7(3)°) is observed which might facilitate hypercoordination at the P1/P2 atoms.

The mechanism of formation of 3[OTf]₂ was investigated by DFT calculations. The proposed reaction pathway can be best described as an intramolecular electrophilic aromatic substitution (S_EAr) (for energy profile, see SI, Figure S4.2.4).^[21] A concerted mechanism has been identified, in which the elimination of the OTf- group of 3^{2+} occurs simultaneously with the backside attack by one of the aromatic rings of the triphenylphosphonio moiety to give Intermediate I (WHELAND intermediate) via the transition state TS (Scheme 1).^[21] A subsequent deprotonation step of the Intermediate I occurs barrier-less.^[22] The reaction barrier to the transition state **TS** was calculated to be $\Delta E^{\#}$ = +38.6 kcal/mol at the MP2 level, and the reaction energy of $\Delta E_r = -7.1$ kcal/mol has been computed for the complete system. The HOMO was computed for dication 32+ and shows a large participation of the C1 atom and the shape of the orbital indicates π -conjugation over the whole CP₃ fragment as a consequence of the aforementioned negative hyperconjugation (see SI, Figure S4.2.2.).^[21] In contrast, the LUMO is partially localized at the two endocyclic P atoms and, therefore, represent the active centers for the interaction with nucleophiles. Thus, 3[OTf]₂ was reacted with BH₃·THF and [AuCl(tht)] (tht = tetrahydrothiophene) in order to elucidate the nucleophilicity of this compound. However, in both cases, no reaction was observed, consistent with the above-mentioned π -conjugation, which substantially reduces the nucleophilicity at the C1 atom. In contrast, the reaction of 3[OTf]₂ with a source of F⁻ anions (e.g. KF, AgF, [Bu₄N]F) gives quantitatively [3-F]OTf as a result of the addition of a F⁻ anion to one of the electrophilic endocyclic P atoms. It is important to note that the related covalent Ph₄PF derivative is not observed in solutions such as CD₃CN, CHCl₃ or DMSO and only the ionic form [Ph₄P]F was observed in various solvents and the solid state so far.[7,23] [3-F]OTf shows a good stability towards moisture and is conveniently prepared by reacting 3[OTf]₂ under standard reaction conditions using either a solution of [Bu₄N]F in THF (1 M; 4-7 wt% H₂O), AgF or KF as fluoride source. No special care needs to be taken and the starting materials can be used without prior drying. [3-F]OTf is obtained as colorless and air stable solid in very good to excellent yield (Scheme 2; [Bu₄N]F: 80%, KF: 94%, AgF: 89%). The ³¹P{¹H} NMR spectrum of [3-F]OTf displays an AMUX spin system. The A part resonates at $\delta(P_A) = -55.0$ ppm and is assigned to the penta-coordinated P-atom (Figure 3). The observed ${}^{1}J_{PF}$ coupling constant of 546 Hz results from the coupling to the covalently bonded F atom and is slightly smaller in magnitude than those typically observed for difluorophosphoranes (e.g. Ph_3PF_2 : ${}^1J(P_AF_X) =$ 665 Hz)^[24]. The M part resonates at $\delta(P_M) = 20.3$ ppm and the U part at $\delta(P_U) = 25.3$ ppm. They are assigned to remaining exocyclic and endocyclic P-atoms, respectively. Correspondingly, the ¹⁹F{¹H} NMR spectrum shows a ddd resonance $\delta(F_X) = 56.3 \text{ ppm} (X-\text{part of the spin system}).$



Scheme 2. Reaction of [3-F]OTf with different sources of F⁻ anions; a) [Bu₄N]F, -[Bu₄N]OTf, THF, rt, 1 h, 80%; b) +1.1 eq. AgF, -AgOTf, CH₃CN, 3 h, 89%; c) +1.5 eq. KF, +18-crown-6 (20 mol%), -KOTf, THF, 12 h, 94%).



Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum (CD₃CN, 300 K, top) and $^{19}F-^{31}P\{^{19}F\}$ -HOESY NMR spectrum of [3-F]OTf (mixing time: 3.3 s, CD₂Cl₂, 300 K, bottom).

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Figure 3. Molecular structure obtained from X-ray diffraction (left) and DFT optimized structure of $[3-F]^+$ (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50 % probability); selected bond lengths in Å and angles in °; X-ray structure [computed values]: P1-C1 1.791(3) [1.797], P2-C1 1.735(2) [1.731], P3-C1 1.749(2) [1.745], P1-C2 1.878(2) [1.897], P2-C3 1.784(2) [1.798], P1-F1 1.766(1) [1.789], P3...F1 2.518(2) [2.579], F1...C1 2.419(3) [2.449], F1-P1-C1 85.72(9) [86.15], F1-P3-C43 177.25(9) [174.86].

The ¹⁹F-³¹P{¹⁹F}-HOESY NMR spectrum displays a correlation peak for the P_{M} atom and the F_{X} atom as a consequence of through space coupling which indicates a dipolar interaction between the P_M and F_X atoms in solution (Figure 2). The molecular structure of cation [3-F]+ is depicted in Figure 3 (left) and represents a rare example of a structurally characterized tetraorganylsubstituted fluorophosphorane of the general formula R4PF (R = alkyl, aryl).^[25] The F1 atom in cation [3-F]⁺ occupies one of the axial positions of the trigonal bipyramidal bonding environment around the P1 atom. This bonding situation leads to a significant elongation of the P1-C1 bond (1.791(3) Å) compared to the P2-C1 (1.735(2) Å) and P3-C1 (1.749(2) Å) and can be explained as a result of the increased electron density at the P1 atom due to the additional F⁻ donor. The P1-C2 bond involving the backbone-aryl group with a value of 1.878(2) Å is almost 0.1 Å longer compared to the P2-C3 bond (1.784(2) Å). The P-F bond follows the same trend (1.766(1) Å) and is significant longer than a typical P-F bond as observed in difluorophosphoranes (cf. Ph₃PF₂: 1.663(2) Å)^[26], evincing already a certain degree of weakness of this bond. The more acute C2-P1-C1 angle of 92.9(1)° in [3-F]⁺ compared to dication 3²⁺ facilitated by the trigonal bipyramidal geometry of the P atom enables a further release of ring strain visible by the more relaxed angles around the sp² hybridized C atoms within the 5-membered ring (32+ vs. [3-F]+: P1-C1-P2: 110.18(9)° vs. 115.6(1)°; P1-C2-C3 113.9(1)° vs. 118.2(2)°). Noticeable is the short F1...P3 contact (2.518(2) Å, SvdW(F-P) 3.27 Å^[27]) and the linear arrangement of the F1-P3-C43 fragment (177.25(9)°) being similar to the bonding environment of the P atom in the related bidentate B/P-based fluoride complex (1- $Mes_2BF-2-MePh_2P-(C_6H_4)$ (P....F: 2.666(2) Å, F-P-C_{Ph}: 176.36(9)°)^[28] and therefore indicate a donor-acceptor interaction. A further donor acceptor interaction is indicated by the short F1…C1 contact (2.419 Å, $\Sigma_{vdW(F-C)}$ 3.02 Å^[27]) and the small F1-P1-C1 angle (85.72(9)°). These donor-acceptor interactions were characterized computationally by using the Natural Bond Orbital (NBO) analysis (Figure 3, right).^[21] A very remarkable finding derived from the NBO analysis is that the lone pairs LP(1), LP(3) and LP(4) of the F1 atom act as electron donors which are interacting with the $\sigma^*(P3-C43)$ and $\sigma^*(P2-C1)$ acceptor orbitals (Table S4.2.1, SI). For the LP(3), the orbital contribution is significant, and the concomitant stabilization energy due to the electron donation from this lone pair of F1 to the $\sigma^*(P3-C43)$ orbital $(n \rightarrow \sigma^*)$ is $E^{(2)} = -4.18$ kcal mol⁻¹ and to the $\sigma^{*}(P2-C1)$ orbital is



Figure 4. Spectral change of the UV/Vis spectrum monitored at 303 nm by gradual increase of [Bu₄N]F concentration of a solution of 3^{2+} (4·10⁻⁵ M) in THF / MeOH (3:1, v/v); dashed curve displays fit by iteration (K = 9.6 (±0.8)·10⁴ M⁻¹, R² = 0.977).

 $E^{(2)} = -1.61$ kcal mol⁻¹, thus representing a major factor in the stabilization of this compound. Furthermore, two additional LPs of the F1 atom also interact with the $\sigma^*(P3-C43)$ and $\sigma^*(P2-C1)$ orbitals with similar stabilization energies (-1.3 kcal mol⁻¹). This donor-acceptor interaction renders 3^{2+} as an interesting chelate for F⁻ complexation.

UV/Vis spectroscopic investigations were performed to derive information about the sensitivity of F⁻ complexation of **3**²⁺. A gradual increase of the [Bu₄N]F concentration of a solution of **3**[OTf]₂ (4·10⁻⁵ M) in THF / MeOH (3:1, v/v) results in a decrease of the absorption band at 303 nm in the UV/Vis spectrum due to F⁻ complexation by **3**²⁺ to form **[3-F]**⁺.^[21] F⁻ concentrations below 0.1 ppm are detectable under these conditions. By monitoring the absorption at 303 nm and using a 1:1 binding isotherm, an F⁻ binding constant of 9.6 ± 0.8·10⁴ M⁻¹ can be determined (Figure 4).^[21] It has to be noted that under these conditions the borane Mes₃B does not show any F⁻ complexation.^[29]

The selectivity of dication 3^{2+} towards F⁻ complexation, was probed by adding 10 eq. of other anions (CN⁻, Cl⁻, l⁻, CO₃²⁻, SCN⁻, N₃⁻) to solutions of 3[OTf]₂ in acetonitrile, respectively. The ³¹P NMR spectra of the reaction mixtures display in all cases 3^{2+} as the only species, thus anion complexation can be excluded. Although, dication 3^{2+} shows no detectable F⁻ complexation in water (H₂O / THF 9:1 (v/v), THF; addition of THF is necessary to dissolve 3[OTf]₂, determined by NMR spectroscopy), it features remarkable F⁻ extraction properties in a biphasic system containing water and CDCl₃ (1:1, v/v). This is demonstrated by adding aqueous solutions of [Bu₄N]F·3 H₂O with different F⁻ concentrations (0.025 M, 1 eq. / 0.05 M, 2 eq. / 0.075 M, 3 eq.; 1 mL) to solutions of 3[OTf]₂ in CDCl₃ (0.025 M, 1 mL). After stirring of the biphasic systems for 15 minutes, the organic phase was analyzed by ³¹P NMR spectroscopy to determine the rate of F⁻ extraction.

In a 1:1 stoichiometry (3^{2+} :F⁻) conversion of ~76% to [3-F]⁺ is observed, a 1:2 stoichiometry gives ~98% of [3-F]⁺ and a 1:3 stoichiometry result in quantitative conversion to [3-F]⁺. With respect to the extraction ability of F⁻ from water and the high selectivity towards F⁻ anions, 3[OTf]₂ might be a versatile extracting agent to remove F⁻ from industrial waste water.^[30] Cation 3^{2+} is capable of reversible F⁻ complexation as evidenced by the addition of Me₃SiOTf or AlCl₃ to solutions of [3-F][OTf], which result in the complete consumption of [3-F]⁺ and quantitative regeneration of 3^{2+} . Quantitative pH-value controlled recovery of 3[OTf]₂ is possible by treatment of [3-F][OTf] with acidic water (0.1 M HCl_{aq}; pH 2) in a biphasic system (H₂O / CHCl₃) (determined by NMR

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 $\label{eq:Scheme 3. Silylotrifluoromethylation of selected aldehydes using \callet 3 h reaction time; isolated yields.$

spectroscopy). In contrast, using neutral water (pH = -7) under same conditions, almost no consumption of [3-F1+ is observed (~92% of [3-F]+, determined by NMR spectroscopy). Since cation [3-F]⁺ can be prepared starting from "wet" fluoride sources and shows reversible F⁻ complexation, it might be applicable as a convenient, anhydrous fluoride source. In general, metal fluorides or tetraalkylammonium fluorides (e.g. [Me₄N]F, [Bu₄N]F) are used as F⁻ source for fluorination reactions and catalytic applications.^[31,32] However, low solubility in organic solvents and high hygroscopicity limit their application.^[31,33,34] Anhydrous [Bu₄N]F indeed shows high solubility in organic solvents, but is unstable at room temperature, highly hygroscopic and requires hexafluorobenzene as F source for its synthesis.[35,36] In this context, [3-F]OTf can serve as an anhydrous and highly stable F⁻ source (air stable, thermally stable up to 250 °C). This is demonstrated by using [3-F]OTf as catalyst (1 mol%) for silylotrifluoromethylation reactions of several aldehydes with Me₃SiCF₃ to selectively yield the corresponding silyl ethers 4a-g in less than 1 h (Scheme 3; 4g: 3 h for quantitative formation; conversions monitored and quantified by ¹H NMR spectroscopy; isolated yields: 76-93%). The structure of 4F was confirmed by X-ray analysis (see SI, Figure S2.10.6.4).^[21] In these reactions, [3-F]⁺ behaves as an initiator to activate Me₃SiCF₃, similar to the [Bu₄N]F catalyzed reactions.^[32,37] After completeness of the reactions the ³¹P NMR spectra of the reaction mixtures show complete consumption of [3-F]+ and quantitative regeneration of 32+.

In conclusion, the highly fluorophilic tri(phosphonio)methanide dication $\mathbf{3}^{2+}$ was synthesized starting from the triflyloxyphosphonium dication $\mathbf{1}^{2+}$ that eliminates HOTf at elevated temperatures. The reaction mechanism to form $\mathbf{3}^{2+}$ was investigated by DFT and *ab initio* calculations and was identified as an electrophilic aromatic substitution (S_EAr) reaction. Dication $\mathbf{3}^{2+}$ is capable for selective and reversible F⁻ ion complexation from water in a biphasic system (H₂O/CHCl₃) to give **[3-F]**⁺. Due to reversible fluoride complexation, cation **[3-F]**⁺ represents a soluble and anhydrous source of F⁻ ions, which catalyzes silylotrifluoromethylation reactions of aldehydes.

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COMMUNICATION

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A highly fluorophilic tri(phosphonio)methanide salt is presented capable of selectively and reversibly complex fluoride ions from organic / aqueous solution. The obtained unique fluorophosphorane salt serves as excellent catalyst for silylotrifluoromethylation of aldehydes.



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Selective and Reversible Fluoride Complexation from Water by a Cyclic Tri(phosphonio)methanide Dication