Reactivity of Xantphos-Type Rhodium Complexes Towards SF₄: SF₃ Versus SF₂ Complex Generation

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Abstract: S–F bond activation of sulfur tetrafluoride at [Rh(Cl)(XanPOP)](1) (XanPOP = 9,9-dimethyl-4,5-bis-(di-tert-butylphosphino)-xanthene) led to the formation of the cationic complex [Rh(F)(Cl)(SF₃)](XanPOP)·[BF₄] (2a) together with trans-[Rh(Cl)(F)(XanPOP)] (3) and cis-[Rh(Cl)(F)(XanPOP)] (4) which both could also be obtained by the reaction of SF₃Cl with 1. In contrast to that, the conversion of SF₃ at the methyl complex [Rh(Me)(XanPOP)] (5) gave the isolable and room-temperature stable cationic λ³-trifluorosulfanyl complex [Rh(Me)(SF₃)(XanPOP)]·[BF₄] (6). Treatment of 6 with the Lewis acids BF₃ or AsF₅ produced the dicaticon difluorosulfanyl complex [Rh(Me)(SF₃)(XanPOP)]·[AsF₅] (8a) or [Rh(Me)(SF₃)(XanPOP)]·[BF₄] (8b), respectively. Refluorination of 8a was possible with the use of dimethylglyme giving [Rh(Me)(SF₃)(XanPOP)]·[BF₄] (9). A reaction of 6 with trichloroisocyanuric acid (TClCA) gave the fluoro complex [Rh(Cl)(Cl)(F)(XanPOP)]·[Cl] (2b) together with chloromethane and SF₂Cl.

Introduction

Due to the high significance of fluorine containing organic building blocks in materials sciences, agricultural and pharmaceutical chemistry, their formation has gained in importance for the last half a century. However, the selective introduction of fluorine atoms into organic molecules remains a challenging task. Methods for fluorination include the deoxyfluorination of carbonyl compounds or alcohols on using sulfur tetrafluoride.[2] The latter gas is highly toxic, and its handling can be difficult. Hence, more convenient and commercially available SF₃ derivates such as diethylamino sulfur trifluoride (DAST), Deoxo-Fluor®, or Fluolead™ have been developed.[2c,3] Transition metal derivatives of SF₃ have also been reported, but studies on their reactivity are rather rare. SF₃ fluorosulfanyl complexes have been characterized spectroscopically for platinum, rhodium, and iridium, only.[4] The determination of structures in the solid state by X-ray diffraction was, so far, not described. Holloway and Ebsworth et al. reported on S–F bond oxidative addition reactions of SF₃ at Vaska-type complexes of rhodium and iridium to give [MX(F)(SF₃)(CO)(PET₂)] (M = Rh, Ir; X = Cl, Br, I, NCO, NCS). In the case of the rhodium compounds the reactions were unselective and the products were not stable.[4a,b] A selective oxidative addition was achieved by the Braun group to yield cis,trans-[Rh(F)(Cl)(SF₃)(CO)(PET₂)]₂, but again the complex is unstable and could not be isolated.[4b] Another interesting approach includes the synthesis of trans-[Pt(F)(Cl)(PCy₃)]₂ either by reaction of [Pt(PCy₃)]₂ with SF₃ or by activation of SF₃. In reactivity studies the deoxyfluorination of ethanol and benzophenone was achieved.[4a,5]

Herein we report on the reactivity of [Rh(Cl)(XanPOP)] towards SF₃. Reaction of SF₃ with 1 either as an equivalent or SF₃ complex. An unusually stable cationic Rh³⁺SF₃ compound [Rh(Me)(SF₃)(XanPOP)]·[BF₄] (6) was isolated and characterized crystallographically. Reactions of 6 with a Lewis acid or trichloroisocyanuric acid (TClCA) result in the generation of SF₃ complexes.

Results and Discussion

Reactivity of [Rh(Cl)(XanPOP)] (1) towards SF₃

A reaction of [Rh(Cl)(XanPOP)] (1) with two equivalents of SF₃ gave the cationic complex [Rh(Cl)(Cl)(SF₃)(XanPOP)]·[BF₄] (2a) as well as trans-[Rh(Cl)(F)(XanPOP)] (3) and cis-[Rh(Cl)(F)(XanPOP)] (4) and three unknown Rh complexes in a ratio of 1:0.5:1.5:0.2:0.2:0.1 (based on ³¹P{¹H} NMR data, Scheme 1). Mechanistically, the generation of 2a might proceed via an initial oxidative addition at 1, followed by a fluoride abstraction by an additional molecule of SF₃ to give the SF₃⁻ anion. A subsequent fluoride migration from the SF₃ ligand to the metal center results in the generation of 2a.

The complexes 3 and 4 were also obtained independently in ratio of 0.2:1 by treatment of 1 with an excess of SF₃Cl in toluene (Scheme 1). It can be assumed that the conversion involves a formation of SF₃, which in turn can result in the generation of 4 by fluorination, although the fate of the sulfur...
A formation of a sulfanyl complex was not observed.

The NMR data of the cation in 2a are described below. A signal at $\delta = 61.2$ ppm in the $^{19}$F NMR spectrum can be assigned to the SF₅⁻ anion. In the $^{19}$F NMR spectrum of 3 the fluorido ligands give a broad doublet at characteristic high field $\delta = -537.6$ ppm with couplings to rhodium ($^{1}J_{F,Rh} = 239$ Hz) and both phosphorus atoms ($^{3}J_{F,P} = 11$ Hz). The $^{31}$P($^{1}$H) NMR spectrum displays a doublet of triplets resulting from couplings to rhodium and both fluorido ligands ($^{4}J_{F,Rh} = 90$ Hz, $^{3}J_{F,P} = 11$ Hz) at $\delta = 42.0$ ppm with the coupling constant $^{2}J_{F,P}$ being typical for a trans-complex. Suitable crystals for structure determination of 3 in the solid state could be obtained from a solution of the reaction mixture in tetrahydrofuran (see Supporting Information, Figure S36 and Table S2). The $^{31}$P($^{1}$H) NMR spectrum of 4 shows a doublet of doublets $\delta = 41.5$ ppm with couplings to rhodium ($^{1}J_{Rh,P} = 87$ Hz) and to the fluorido ligand ($^{3}J_{F,P} = 11$ Hz). The resonance of the fluorido ligand at $\delta = -472.4$ ppm in the $^{19}$F NMR spectrum shows a broad doublet pattern resulting from the coupling to the metal center ($^{3}J_{F,Rh} = 220$ Hz). Suitable crystals for structure determination of 4 in the solid state were obtained from the reaction solution (see Supporting Information, Figure S37 and Table S2). The molecular structure in the solid state confirms the cis arrangement of the chlorido ligands.

Conversion of [Rh(Me)(⁵⁹⁵⁺xanPOP)] (5) into a cationic \(\lambda^1\)-trifluorosulfanyl Rh\(^{lll}\) complex

To assess the influence of the anionic ligand on the reactivity towards SF₅, the methyl complex [Rh(Me)(⁵⁹⁵⁺xanPOP)] (5) was synthesized. It can be speculated that a better $\sigma$-donor ligand would hamper fluoride migration from a putative SF₅ ligand to the metal. The starting compound, complex 5, was obtained by treatment of [Rh(Cl)(⁵⁹⁵⁺xanPOP)] (1) with MeLi (Scheme 1). The isotopeologe [Rh(¹³CH₃)(⁵⁹⁵⁺xanPOP)] (5') is accessible accordingly by a reaction of 1 with $^{13}$C labeled MeLi. The $^{31}$P($^{1}$H) NMR spectrum of 5 exhibits a doublet at $\delta = 50.5$ ppm for the phosphine atoms of the $^{13}$CH₃xanPOP pincer ligand with a coupling constant of $^{2}J_{Rh,P} = 177$ Hz. This value is in a typical range of other literature known xantphos-type rhodium complexes in the oxidation state $+1$. The signal for the methyl ligand in the $^{1}$H NMR spectrum of 5 appears at 0.53 ppm as a triplet of doublets due to couplings to phosphorus and rhodium ($^{1}J_{Rh,P} = 5.7$ Hz and $^{3}J_{F,Rh} = 2.9$ Hz). The isotopeologe 5' shows additional doublet couplings in the $^{31}$P($^{1}$H) NMR spectrum of $^{2}J_{P,F} = 11$ Hz and in the $^{1}$H NMR spectrum of $^{2}J_{F,C} = 122.8$ Hz. The $^{13}$C($^{1}$H) NMR spectrum displays a doublet of triplets at $\delta = -21.7$ ppm for the methyl ligand ($^{3}J_{Rh,C} = 34$ Hz and $^{3}J_{C,F} = 11$ Hz).

Red crystals suitable for single X-ray crystallography of 5 were obtained by recrystallization from methylcyclohexane (Figure 1). The structure of 5 reveals a distorted square-planar coordination geometry at the metal center in which both
phosphorus atoms of the \(^{4h}\)xanPOP ligand are located in a mutually trans-position. The Rh–P bond lengths (2.2678(3) Å and 2.2495(3) Å) are in accord to the data for literature known Rh–complexes bearing \(^{4h}\)xanPOP ligands, as for instance.\(^{24b}\) In contrast to this, the Rh–O bond length (2.2210(9) Å) in 5 is significantly shorter than the one in 1 and is comparable to the corresponding distance in alkenyl xanthos-type rhodium complexes.\(^{26}\) The angles P1–Rh1–P2 (161.618(12)°) and C32–Rh1–O1 (171.52(5)°) mirror clearly the distorted square-planar geometry.

Treatment of a dark red CDCl\(_3\) solution of complex 5 with two equivalents of SF\(_6\) at room temperature led to the formation of the ionic \(^{1,4}\)trifluorosulfanyl complex [Rh(Me)(F)(SF\(_6\))]\(^{2-}\) (7) together with the difluorido complex [Rh(Me)(F)\(_2\)]\(^{2-}\) (8) and four unknown rhodium complexes in minor amounts. [Rh\((^{1,4}\text{CH}_2)\text{SF}_3\)]\(^{2-}\) (6) was prepared in a similar manner starting from 5'. Unlike found for most of the literature-known SF\(_6\) salts, the anion in 6 does not decompose to SF\(_4\) and fluorine when 6 is stored at room temperature under an argon atmosphere.\(^{4,6,10}\)

Mechanistically, it can be assumed that an oxidative addition of SF\(_6\) at 1 yields initially [Rh(Me)(F)(SF\(_6\))]\(^{2-}\) (9). The latter reacts with a second equivalent of SF\(_6\) to give after fluoride abstraction 6 bearing the SF\(_4\) anion. A comparable reactivity pattern was described by Murdoch and coworkers with TeF\(_5\). Treatment of trans-[Rh(Cl)(CO)(PMe\(_3\))] with two equivalents of TeF\(_5\) resulted in the formation of trans-[Rh(Cl)(CO)(PMe\(_3\))(TeF\(_5\))]\(^{2+}\) (4).

The crystals of 6 were studied by single X-ray crystallography (Figure 2). Note that structural data of a \(^{1,4}\)trifluorosulfanyl complex in the solid state were not reported before. There is a disorder of the metal bound sulfur atom S1 and the equatorial fluorine atom F3 with an occupancy of 0.44:0.56 (see Supporting Information, Figure S3B). The SF\(_4\) anion of 6 shows an average S–F\(_{\text{equatorial}}\) bond length of 1.72 Å and S–F\(_{\text{axial}}\) bond length of 1.580(3) Å, which is similar to data found for other solid-state structures reported for this anion.\(^{6,10,13–16}\) The structure of the cationic part in 6 exhibits a slightly distorted square-planar coordination geometry at the rhodium atom with the \(^{1,4}\)trifluorosulfanyl ligand located in a trans position to the ether function of the phosphine with O1–Rh1–S1a and O1–Rh1–S1b angles of 169.78(17)° and 170.6(2)°, respectively. The Rh–S bond lengths (Rh1–S1a 2.195(9) Å, Rh1–S1b 2.164(11) Å) are significantly longer when compared to the one in [Rh-(SH)xanPOP)]\(^{2+}\) (Rh–S 2.2865(4) Å) or in various cationic xanthos-type Rh\(^{1,4}\)-S complexes as for instance [Rh-xanPOP\((^\text{4h}\text{CH}_2\text{COMe})(^\text{4h}\text{Me})\text{SBF}_4]\) (Rh–S 2.3373(14) Å, xanPOP = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, \(\text{Ar}^2 = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_4\)).\(^{11,13} \) The SF\(_4\) ligand displays an Rh–F interaction of 2.418(3) Å, which results in a small F1–S1a–Rh angle of 72.3(3)° as well as the significantly elongated bond between the sulfur atom and the fluoro ligand F1 of 1.880(7) Å.

Figure 1. Molecular structure of 5 (ORTEP, ellipsoids are set at 50% probability. All hydrogen atoms are omitted for clarity. Selected distances [Å] and bond angles [°]: Rh1–P1 2.2678(3), Rh1–P2 2.2495(3), Rh1–O1 2.2210(9), Rh1–C32 2.0651(13); P1–Rh1–P2 161.618(12), C32–Rh1–O1 171.52(5), C32–Rh1–P1 98.21(4), C32–Rh1–P2 98.02(4), P1–Rh1–O1 82.95(2), P2–Rh1–O1 82.28(2).

Figure 2. Molecular structure of 6 (ORTEP, ellipsoids are set at 50% probability. All hydrogen atoms are omitted for clarity. Selected distances [Å] and bond angles [°]: Rh1–P1 2.3999(12), Rh1–P2 2.3939(11), Rh1–O1 2.220(3), Rh1–C1 2.070(5), Rh1–S1a 2.195(9), Rh1–F1 2.418(3), S1a–F1 1.880(7), S1a–F2 1.680(7), S1a–F3a 1.585(8), S2–F8 1.580(3), S2–F7 1.705(3), S2–F6 1.712(3), S2–F5 1.727(3), S2–F4 1.728(3), P1–Rh1–P2 163.79(4), S1a–Rh1–O1 169.78(17), C1–Rh1–O1 134.10(14), C1–Rh1–P1 88.83(14), C1–Rh1–P2 88.83(14), C1–Rh1–S1a 102.42(2), P1–Rh1–O1 82.13(8), P2–Rh1–O1 81.67(8), S1a–Rh1–P1 103.63(8), S1a–Rh1–F2 92.48(14), F1–S1a–Rh1 72.3(3), F2–S1a–Rh1 102.0(4), F3a–S1a–Rh1 113.3(4), F3a–S1a–F1 82.3(4), F3a–S1a–F2 88.1(4).

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\(^{4,6,10}\) The struc-
At 193 K the $^{31}$P($^1$H) NMR spectrum of 6 displays an AB pattern, which was simulated (Figure 3). The inequivalent phosphorus atoms $P_a$ and $P_b$ couple to rhodium ($^3J_{P_a,Rh} = 103.3$ Hz, $^3J_{P_b,Rh} = 95.5$ Hz) to each other ($^3J_{P_a,P_b} = 292.0$ Hz) and to one of the three sulfur bound fluorine atoms, with coupling constants $^3J_{P_a,F_a} = 28.4$ Hz and $^3J_{P_b,F_b} = 37.1$ Hz. The signal in the $^{13}$C($^1$H) NMR spectrum of 6 at $\delta = 7.8$ ppm is significantly low-field shifted by about 28 ppm when compared to the corresponding resonance for 5. It appears as a doublet of multiplets with $^3J_{C,Rh} = 30$ Hz.

The $^{19}$F NMR spectrum of 6 at 193 K (Figure 4) shows one broad signal at $\delta = 62.2$ ppm for the SF$_3^-$ anion$^{4a,b,i,12b,13}$ and three signals with an integral ratio of 1:1:1 for each fluorine atom of the λ$_4$-trifluorosulfanyl ligand at $\delta = 25.6$ (F$_e$), $-46.7$ (F$_a$) and $-51.1$ ppm (F$_b$). Compared to the NMR data of literature known SF$_3^-$ compounds the signals for F$_e$ and F$_a$ are significantly shifted to higher field. However, an additional interaction of a S–F moiety with the rhodium center has only been identified for 6, and the dissimilar NMR data suggest that this interaction also persists in solution at 193 K. No apparent coupling is observed between F$_e$ and F$_b$ neither in the $^{19}$F NMR spectrum nor in the corresponding $^{13}$F, $^{19}$F-COSY NMR spectrum (Supporting Information, Figure S16).

A multiplication of the FID with a Gaussian function reveals several coupling constants. Simulation of the signal at $\delta = -51.1$ ppm (F$_b$) gives coupling constants for the couplings to one sulfur bound fluorine atom $^3J_{F_b,F_a} = 104.9$ Hz, to the metal center of $^3J_{F_b,Rh} = 21.1$ Hz, as well as to both phosphorus atoms with $^3J_{F_b,P_a} = 30.2$ Hz and $^3J_{F_b,P_b} = 35.9$ Hz. The latter values are in good agreement with data from the simulation of the $^{31}$P($^1$H) NMR spectrum (see Figure 3).

Variable-temperature $^{31}$P and $^{19}$F NMR studies of 6 were performed (Figure 5). At 193 K the $^{31}$P NMR spectrum reveals two signals for the inequivalent phosphorus atoms which coalesce to one signal with a doublet of multiplet pattern at 298 K. In the $^{19}$F NMR spectra the signals at $\delta = 25.6$ and $-51.1$ ppm for the axial fluorine atoms F$_e$ and F$_a$ broaden above 193 K. Simultaneously all three signals converge into the resonance assigned to F$_b$, resulting in a triplet like pattern above 253 K. An integration against an external standard confirms that three fluorine atoms can be assigned to the latter signal. These observations are consistent with the conversion of the low-temperature conformation of 3 into a structure, which does not exhibit a Rh–F interaction and the three fluorine atoms bound...
to sulfur exchange on the NMR time-scale. However, it is intriguing that the resulting signal at \( \delta = -42 \text{ ppm} \) at 298 K seems to develop from the resonance for \( F_n \). We suggest that a fluxional structure at room temperature must resemble considerably the environment of \( F_n \). Tentatively, the fluxional structure might adopt a trigonal bipyramidal configuration at sulfur with the free electron pair in the axial position, or a (distorted) trigonal pyramidal structure with Rh at the apical position.

To get a further insight into the structure of 6, DFT calculations were performed (Figure 6). The calculated minimum structure of the cation in vacuum is largely in agreement with the data obtained from single X-ray crystallography. The Rh–S–F angle of 70.06° as well as the Rh–F distance (2.3825 Å) mirror the Rh–F interaction. The absence of a bond critical point in an AIM analysis and an only moderate Wiberg bond index suggests that the interaction between the sulfur bound fluoride and the metal center has no significant covalent contribution. Moreover, a relaxed scan of the potential energy surface was performed with gradual changes of the F–S–Rh angle in 5-degree steps (see Supporting Information). The gradual change of the angle resembles a pathway for a putative migration of a fluoride from the SF\(_3\) ligand to the metal center to give a SF\(_3\) fluorido complex. The figure confirms that the structure determined in vacuum indeed represents the energetic minimum.

The NBO analysis of the frontier orbitals of 6 suggests the presence of a stereoelectron lone pair at the sulfur atom, which is in accordance with the literature on DFT calculations of other \( \lambda^3\)-trifluorosulfanyl complexes (HOMO-4, Supporting Information: Figure S42).\(^{(4a,g,i)}\)

**Reactivity of \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{SF}_4] (3) towards Lewis acids and trichloroisocyanuric acid (TCICA)**

Remarkably, treatment of 6 with BF\(_3\) in a 2:1 molar ratio led to the generation of the unique dicatonic SF\(_3\) complex \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{BF}_4]_2\), as well as of SF\(_4\) (8a, Scheme 2). \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{BF}_4]_2\) (8a’) was generated in a similar manner starting from 6’. Likewise, a reaction of 6 with arsenic pentfluoride gave \(\text{[Rh(Me)(SF\(_3\))]^{(\text{phx} \times \text{xanPOP})}}[\text{AsF}_4]_2\) (8b), which slowly crystallized in dichloromethane (Scheme 2). Lewis-acid induced fluoride abstraction reactions from SF\(_3\) ligands were reported before at trans-\([\text{Ir}(X)(\text{F})(\text{SF}_3)](\text{CO})(\text{PET})_3\] (X = Cl, F) and trans-\([\text{Pt}(\text{F})(\text{SF}_3])(\text{PET})_3\] (R = Ir, Cy), but in these cases monocatonic complexes were formed.\(^{(4a,k,l)}\)

Adding an excess of dimethylamine to the reaction mixture containing \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{BF}_4]_2\) (8a) resulted in the regeneration of compound \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{BF}_4]\) (9, Scheme 2). Apparently the BF\(_4\) anion acts as the fluoride source. In contrast to the reported refluorination reactions at trans-\([\text{Ir}(\text{Cl})(\text{F})(\text{SF}_3)](\text{CO})(\text{PET})_3\] by treatment with NHMe\(_2\), the adduct BF\(_3\)-NHMe\(_2\) was not detected, presumably because of the presence of SF\(_4\). Note, that the complex 8b is fairly stable in vacuum but decomposes after treatment with dimethylamine (to unknown products).

**Scheme 2. Formation of the dicatonic SF\(_3\) complexes \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{BF}_4]_2\) (8a) and \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{AsF}_4]_2\) (8b) and dimethylamine-induced refluorination of 8a to get \([\text{Rh}(\text{Me})(\text{SF}_3)]^{(\text{phx} \times \text{xanPOP})}][\text{BF}_4]\) (9).**

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**Figure 6. DFT-optimized structure of the cationic part of 6; all hydrogen atoms as well as the tert-butyl groups at the phosphorus atoms have been omitted for clarity. B3LYP/cc-pvdz with Grimme D3 dispersion correction including Becke-Jones damping (RECP with corresponding cc-pvdz basis set for Rh).**
Treatment of the reaction mixture containing [Rh-F(Cl)(SF\(_2\))\(n\)(xanPOP)]\(x\)(AsF\(_6\)) (2a) with an excess of BF\(_3\) did not lead to an abstraction of the fluorido ligand and the generation of a dication, but merely to an anion exchange at 2a of SF\(_2\) to BF\(_3\) to give [Rh-F(Cl)(SF\(_2\))\(n\)(xanPOP)]\(BF_4\) (2c) with a simultaneous formation of SF\(_6\) which was detected in the \(^{19}\)F NMR spectrum of the reaction mixture.

At room temperature the \(^{31}\)P(H) NMR spectrum of the green reaction mixture containing 8a shows a doublet of triplets at \(\delta = 65.5\) with couplings to rhodium of \(J_{\text{P,Rh}} = 87\) Hz and to both fluorine atoms of the SF\(_2\) ligand with a coupling constant of \(J_{\text{F,F}} = 27\) Hz. The latter coupling constant is in accordance with couplings to an SF\(_2\) ligand bound to a transition metal center.\(^{[4a,d]}\) At 203 K the \(^{19}\)F NMR spectrum shows four resonances at \(\delta = 86.5, 34.0, -31.6\) and \(-149.0\) ppm with an integral ratio of 2:2:2:8. The signal at high field can be assigned to the BF\(_3\) anions.\(^{[14]}\) The two broad low-field shifted signals correspond to resonances of SF\(_6\) which is presumably generated by fluoride abstraction from the SF\(_3\) anion in 6.\(^{[9]}\)

The SF\(_2\) ligand can be assigned to the broad triplet at \(\delta = -31.6\) ppm, which is in a typical range for SF\(_2\) ligands.\(^{[4a,e,f,i]}\) Upon heating up to room temperature the signal sharpens to a triplet of doublets with coupling constants \(J_{\text{F,F}} = 27\) Hz and \(J_{\text{P,Rh}} = 8\) Hz. The \(^{19}\)C(H) NMR spectrum of 8a shows a doublet at \(\delta = 32.4\) ppm for the methyl ligand, which is significantly low-field shifted when compared to the signal of the monocationic \(\lambda^1\)trifluorosulfanyl complex 6’ (\(\Delta\delta = 24.6\) ppm). The coupling constant to rhodium is \(J_{\text{P,Rh}} = 24\) Hz.

Crystals of 8b were examined by single X-ray diffraction analysis to determine the structure in the solid state (Figure 7). There is a disorder of the AsF\(_6\)\(n\) anions as well as the SF\(_2\) ligand, which does not allow for any discussion of the S–F bond lengths. The cation exhibits a slightly distorted square-pyramidal coordination geometry at the rhodium atom with the SF\(_2\) ligand located in a trans position to the ether function of the xanPOP ligand.\(^{[15]}\) The Rh1–S1 bond of 2.126(4) Å is slightly shorter when compared to the corresponding bond length in the SF\(_2\) complex 6. No short contacts between the sulfur atom S1 and any fluorine atom of AsF\(_6\) are apparent. The minimum structure of the cation [Rh(Me)(SF\(_2\))\(n\)(xanPOP)]\(+\) was also determined by DFT methods (Figure 8). The sulfur-fluorine bonds are calculated to be 1.604 Å and 1.609 Å.

SF\(_2\) group containing compounds can be oxidized by various methods to access SF\(_3\) or SF\(_6\) moieties.\(^{[18]}\) For instance, it has been shown that trichloroisocyanuric acid (TCICA) can be used for an oxidation of disulfides to access after subsequent fluorination SF\(_2\) groups.\(^{[19,20]}\) In contrast, treatment of 6 with 10 equiv. of TCICA in acetonitrile-d\(_3\) led within 16 h to the formation of [Rh(F)(Cl)(SF\(_2\))\(n\)(xanPOP)]\(+\) (2b), in which the cation is probably stabilized by chloride as counter anion (Scheme 3). In addition, the \(^{31}\)P(H) and \(^{19}\)F NMR data reveal the presence of a cationic Rh\(_{III}\) complex (30%) and a Rh\(_{II}\)-fluorido complex (11%) together with five other minor products (less than 3%) (Supporting Information, Figures S30 and S31).

Furthermore, the formation of SF\(_2\)Cl was detected by \(^{19}\)F NMR spectroscopy. The \(^1\)H NMR spectrum reveals the generation of CH\(_2\)Cl (\(\delta = 3.01\) ppm, satellites: doublet, \(J_{\text{F,F}} = 150.4\) Hz). Its resonance correlates in a \(^1\)H,\(^13\)C-HMQC NMR spectrum with a \(^1\)C signal at \(\delta = 26.4\) ppm.\(^{[19]}\)

The \(^{31}\)P(H) NMR spectrum of 2b at room temperature shows a doublet of triplets of triplets at \(\delta = 69.6\) ppm with couplings to the metal center (\(J_{\text{P,Rh}} = 77\) Hz), the two fluorine atoms of the SF\(_2\) ligand (\(J_{\text{F,F}} = 28\) Hz) and to the fluorido ligand (\(J_{\text{F,F}} = 6\) Hz). The coupling constant between phosphorus and the fluorido ligand suggests that the fluorido ligand is located in a cis position to the ether function of the xanPOP ligand.\(^{[10]}\) The

**Figure 7. Structure of the cation in [Rh(Me)(SF\(_2\))\(n\)(xanPOP)](AsF\(_6\)) (8b). ORTEP, ellipsoids are set at 50% probability. All hydrogen atoms, the 8Bu groups as well as the AsF\(_6\)\(n\) anions have been omitted for clarity. Selected distances (Å) and bond angles (°): Rh1–P1 2.414(15), Rh1–P2 2.435(15), Rh1–O1 1.599(14), Rh1–S1 2.044(7), Rh1–O2 2.037(14), Rh1–O3 1.866(14), Rh1–O4 1.835(14), Rh1–F1 1.355(12), Rh1–F2 1.338(12), Rh1–F3 1.343(12), Rh1–F4 1.329(12), Rh1–F5 1.323(12), Rh1–F6 1.325(12).**

**Scheme 3. Formation of [Rh(F)(Cl)(SF\(_2\))\(n\)(xanPOP)]\(+\) (2b) together with the generation of SF\(_2\)Cl and CH\(_2\)Cl upon treatment of [Rh(Me)(SF\(_2\))\(n\)(xanPOP)]\(+\) (6) with trichloroisocyanuric acid (TCICA).**

Chem. Eur. J. 2022, 28, e202000626 (6 of 8)
The oxidation with TCICA can formally be described by oxidative chlorination steps of the SF$_2$ anion as well as the (anionic) CH$_3$ ligand. At the same time chlorination of the Rh complex occurred to give the cation [Rh(F)(Cl)(SF$_5$)(anXPOP)] and chloride as counter anion. A concomitant fluoride migration from the SF$_2$ ligand to the metal results in the generation of the SF$_2$ fluorido complex 2b.

**Conclusion**

In conclusion, rhodium $^{19}$F-anXPOP complexes allow for the synthesis of SF$_2$ and SF$_5$ complexes. A unique cationic SF$_3$ complex [Rh(Me)(SF$_5$)($^{19}$F-anXPOP)][SF$_5$] (6) was synthesized which displays an additional Rh–F interaction in the solid state and is in solution at low temperature. A SF$_1$ complex has not been characterized crystallographically before. A corresponding chloride complex is not accessible as fluoride migrates to the metal to give [Rh(F)(Cl)(SF$_5$)(anXPOP)][SF$_5$] (2a). Absorption of fluoride from 6 with BF$_3$ leads to a dicationic SF$_2$ species. TCICA does not lead to the oxidation of the $\lambda^5$-trifluorosulfanyl ligand, but to chlorination of the SF$_2$ anion and methyl ligand.

**Experimental Section**

Full details of experimental procedures, complex synthesis and characterization, NMR data, IR data and crystallographic data as well as computational details can be found in the Supporting Information.

Deposition Numbers 2113737 (for 4), 2113738 (for 6), 2113739 (for 5), 2113740 (for 8b), 2113741 (for 7-C4H8O), 2120896 (for 3) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** fluorido complexes · rhodium · S–F activation · sulfur fluorides · sulfur tetrafluoride

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