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Activation of SF₆ at a Xantphos-Type Rhodium Complex

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S Supporting Information

ABSTRACT: As a rather inert gas, sulfur hexafluoride is still used as a dielectric in high-voltage power applications despite its high global warming potential. Its activation at transition metal complexes has been reported, but the fate of the sulfur-containing products is often unknown. The activation of SF₆ at $[Rh(H)\{^{tBu}xanPOP\}]$ ($^{tBu}xanPOP = 9,9$ -dimethyl-4,5-bis(ditertbutylphosphino)xanthene) at room temperature leads to the generation of the bifluorido complex [Rh(FHF){^{fBu}xanPOP}]. A subsequent regeneration of $[Rh(H){^{tBu}xanPOP}]$ completes a cyclic process for the degradation of SF₆. Furthermore, the SF₆ activation at $[Rh(H)\{^{tBu}xanPOP\}]$ in the presence of triethylsilane as a hydrogen source is described, which leads to the formation of the fluorido complex $[Rh(F)_2(H)\{^{tBu}xanPOP\}]$ as well as [Rh(SH)-{^{tBu}xanPOP}] and S(SiEt₃)₂ as sulfur-containing products.



 SF_6 is widely considered to be an extremely unreactive gas.¹ Due to its outstanding properties, such as chemical stability, low toxicity, and a high dielectric strength, SF₆ persists in being used as gaseous dielectric in high-voltage-power applications.^{1,7} SF₆ is a highly dense, nonflammable gas, but also has been recognized as the most potent greenhouse gas with an atmospheric lifetime of about 3200 years and a global warming potential which is 23 500 times higher than that of CO2. Before SF₆ was used for various applications, its concentration in the atmosphere was below the detection limit, suggesting that its presence today is entirely anthropogenic. The global SF_6 concentration rose from 1 ppt in 1975 to more than 8 ppt in 2008.^{3c} Considering that there are often no alternative compounds eligible for replacing SF₆, increasing attention has been paid to control or even avoid its emission. Within this context, an efficient and controlled depletion of SF_6 under mild conditions is of current interest.^{1f,3c,f,4} An interesting approach consists of SF₆ degradation reactions at transition metal complexes. While SF₆ was degraded or recycled in the past decade mainly by adsorption, separation, and decomposition methods usually under harsh conditions, reports on the activation of SF₆ at transition metal complexes are still scarce. $^{3f,4c-e,5}$ Degradation reactions of SF₆ are described at low-valent Ti, V, Cr, and Zr as well as at Fe and reduced Ni complexes. ^{5a,b,d,e} Sulfur-containing products were only identified in the reactions of SF_6 with $[Cr(C_5Me_5)_2]$ and [Ti- $(1,3^{t}Bu_{2}C_{5}H_{3})(6,6\text{-dmch})(PMe_{3})$ (6,6-dmch = 6,6-dimethylcyclohexadienyl) as well as with $K_2[(L^{tBu}Ni^I)_2(\mu-\eta^{1}:\eta^{1}-N_2^{2^{-}})]$ $(L^{tBu} = [(HC(CtBuNC_6H_3(Pr)_2)_2]^-), \text{ which yielded, among})$ other compounds, $[{Cr(C_5Me_5)(\mu_2-F)}_3(\mu_3-S)]^+[Cr(C_5Me_5) (F)_3$]⁻, SPMe₃ or $[(L^{tBu}Ni^{II})_2(\mu$ -S)]. We previously reported on the activation of SF_6 at a binuclear rhodium complex as well as on the catalytic degradation of SF_6 to give phosphinesulfides



and fluorosilanes with $[Rh(H)(PEt_3)_4]$ in the presence of PEt₃ and silane.^{5f-i} Furthermore, it was demonstrated that SF₆ can be activated at $[Pt(PR_3)_2]$ (R = Cy, *i*Pr) complexes generating the SF₃ complex *trans*- $[Pt(F)(SF_3)(PR_3)]$.^{5m,n} In addition, SF₆ was recently applied as a fluorinating agent, e.g., in a photoredox process for deoxyfluorination reactions using an iridium-based photocatalyst and diisopropylethyl amine as reductant to induce a fluorination of allylic alcohols.^{5j,k,m,n,6} Herein, we describe the reactivity of the pincer complex $[Rh(H)\{^{tBu}xanPOP\}] (1; {}^{tBu}xanPOP = 9,9-dimethyl-4,5-bis-$ (ditert-butylphosphino)-xanthene) toward SF₆. Hexaethyl disilathiane $S(SiEt_3)_2$ was obtained upon treatment of 1 with SF_6 in the presence of triethyl silane as hydrogen source.

RESULTS AND DISCUSSION

The reduction of SF_6 (1 atm) with 1 at room temperature in toluene gave the bifluorido complex [Rh(FHF){^{tBu}xanPOP}] (2) as the only rhodium complex after 4 days according to the NMR spectroscopic and mass spectrometric (liquid injection field desorption ionization mass spectrometry LIFDI-MS) data (Scheme 1). At 50 °C the reaction was completed within 16 h.

Monitoring the reaction of 1 with SF_6 by NMR spectroscopy at room temperature revealed a full conversion of 1 already after 16 h as well as the formation of 2, $[Rh(F)_2(H)]$ -{ tBu xanPOP}] (3), [Rh(SH){ tBu xanPOP}] (4), and an unknown Rh(III) complex as intermediates (ratio: 10:3:2:1 according to the ${}^{31}P{}^{1}H{}$ NMR spectrum). Although the fate of the sulfur is not known in the conversion of 1 into 2, we tentatively presume mechanistically an initial precoordination

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Scheme 1. Activation of SF_6 at $[Rh(H){^{fBu}xanPOP}]$ (1)



of the SF₆ molecule via one or more fluorine atoms at the rhodium center, followed by electron transfer steps possibly via an inner-sphere mechanism to generate SF₅⁻ and a fluoride ion. ^{1a,5a,b,d-h,m,7} SF₅⁻ can then produce another fluoride ion and other sulfur fluorides which are further defluorinated.

The ³¹P{¹H} NMR spectrum of **2** at 298 K exhibits a signal at $\delta = 47.4$ ppm for the phosphine atoms of the ^{tBu}xanPOP ligand. The resonance features a characteristic coupling for a rhodium(I) compound, with a doublet coupling to rhodium of 148 Hz.⁸ The ¹⁹F NMR spectrum of complex **2** at 298 K shows two resonances at $\delta = -176.6$ ppm (see Figure 1a) and at $\delta =$



Figure 1. Part of the 19 F NMR spectrum of the bifluorido ligand of 2 at 298 K (a) and at 243 K (b).

-498.0 ppm (see Figure 2a). The signal at lower field is split into a doublet of doublets (${}^{1}J_{F,H}$ = 401 Hz, $J_{F,F}$ = 112 Hz) when the spectrum is recorded at 243 K (Figure 1b). It is simplified



Figure 2. Part of the ¹⁹F NMR spectrum of the bifluorido ligand of **2** at 243 K: (a) fully coupled; (b) ¹H decoupled.

to a doublet splitting pattern upon ¹H decoupling, and the signal can be assigned to the distal fluorine atom of the bifluorido ligand. The extraordinarily high-field shifted resonance at $\delta = -498.0$ ppm is attributed to the metal-bound fluorine atom.⁹ In the ¹⁹F{¹H} NMR spectrum recorded at 243 K, the splitting pattern of the resonance features doublet couplings to rhodium and to the distal fluorine atom of 184 and 111 Hz, respectively (Figure 2b).

The ¹H NMR spectrum of **2** at room temperature reveals a broad signal for the proton of the bifluorido ligand at $\delta = 12.46$ ppm, as depicted in Figure 3a. This resonance splits into a



Figure 3. Part of the 1 H NMR spectrum of 2 at 298 K (a) and at 243 K (b).

broad signal of higher order at 243 K, which is reminiscent of a doublet of doublets with apparent coupling constants of ${}^{1}J_{HE}$ = 402 Hz to the rhodium-bound distal fluorine atom and $J_{\rm HF}$ = 37 Hz to the proximal one (Figure 3b). The coupling constants are comparable to those found in other bifluorido complexes of rhodium such as $[Rh(FHF)(PEt_3)_3]$ (J = 382 Hz, 42 Hz), cis- $[Rh(FHF)(6-{}^{i}Pr)(PPh_{3})_{2}]$ (J = 370 Hz, 42 Hz; $6-{}^{i}Pr = 1,3$ bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidine), and [Rh- $(FHF)(COD)(P^{i}Pr_{3})]$ (J = 366 Hz, 32 Hz).^{9g,h,j} The ATR IR spectrum of 2 shows two broad absorption bands for the asymmetric stretching and bending modes of the bifluorido ligand at $\tilde{\nu} = 2549$ and $1871 \text{ cm}^{-1.91-n,10}$ Both bands appear at higher energy than those found for symmetric HF₂ salts such as Na⁺, Cs⁺, and K⁺ HF₂⁻ (1284–1372 cm⁻¹), indicating an asymmetric hydrogen bond within the Rh(FHF) fragment.¹¹ The energy values found for the two H-F stretching modes of 2 are also consistent to the corresponding data for literature known phosphine-based transition metal bifluorido complexes, e.g., $[Ru(F)(FHF)(dmpe)_2]$ (2452 and 1915 cm⁻¹; dmpe = 1,2-bis(dimethylphosphino)ethane) and trans-[Pd(FHF)(Me)- $(PPh_3)_2$ (2493 and 1904 cm⁻¹).¹

Gas-phase diffusion of *n*-hexane into the reaction solution at 273 K produced dark red crystals suitable for X-ray diffraction (Figure 4). The crystal structure displayed a substitutional disorder of the bifluorido ligand and a chloride ligand, which occupies 21% of the sites. The complexes cocrystallized in the monoclinic space group $P2_1/c$. Because 1 was synthesized from $[Rh(Cl){^{fBu}xanPOP}]$, chlorine containing impurities could be the source of the chlorido complex.¹³ The Rh1–F1–F2 angle in 2 of 133.2(2)° is in the range found for bifluorido complexes of rhodium in the oxidation state + I (121.4–147.2°).⁹ⁿ The F1–F2 distance (2.339(5) Å) is comparable to those in literature-known structures such as in $[Rh(FHF)(COD)-(PPh_3)]$ (Rh–F 2.083(2) Å; F–F 2.3310(34) Å), trans-



Figure 4. Molecular structure of **2**. (ORTEP, ellipsoids are set at 50% probability. The chlorido ligand and all hydrogen atoms are omitted for clarity except for H2, which was located in the difference Fourier map and freely refined.) Selected distances [Å] and bond angles [°]: Rh1–P1 2.2700(6), Rh1–P2 2.2662(6), Rh1–O1 2.1344(14), Rh1–F1 2.021(3), F2–H2 0.84(8), F1–F2 2.339(5); Rh1–F1–F2 133.2(2), P1–Rh1–P2 166.31(2), F1–Rh1–O1 176.67(11), F1–Rh1–P1 99.04(8), F1–Rh1–P2 93.28(8), P1–Rh1–O1 83.42(4), P2–Rh1–O1 84.05(4).

 $[Rh(FHF)(Ph_2PF)(Ph_3P)_2] (Rh-F 2.082(1) Å; F-F 2.329(2) Å), and in Rh(FHF)(6-Me)(PPh_3)_2 (6-Me = 1,3-bis(methyl)-3,4,5,6-tetrahydropyrimidin-2-ylidine; Rh-F 2.1460(12) Å; F-F 2.343(2) Å). The Rh1-F1 bond (2.021(3) Å) in$ **2**is rather short and is in the range found in Rh(I) fluorido complexes (2.018–2.060 Å).

Treatment of the bifluorido complex **2** with cesium fluoride led to the abstraction of the coordinated HF to give [Rh(F){^{fBu}xanPOP}] (**5**) according to the NMR spectroscopic and LIFDI-MS data (Scheme 1). The ³¹P{¹H} NMR spectrum of **5** at 263 K reveals a doublet for the ^{fBu}xanPOP ligand at δ = 45.9 ppm with a coupling constant of ¹J_{P,Rh} = 157 Hz. The ¹⁹F NMR spectrum (263 K) shows a resonance signal for the fluorido ligand at δ = -530.6 ppm with a doublet coupling to rhodium of 208 Hz. A reaction of **5** with HSiEt₃ at 50 °C led to its full conversion into the hydrido complex **1** along with the formation of FSiEt₃ after 2 h, which completes a cyclic process for the degradation of SF₆ (Scheme 1).

Late transition metal fluorido complexes can be highly reactive. Treatment with hydrogen sources, such as silanes, often lead to the formation of the hydrido compounds, ^{5h,i,14} yet the reduction of SF_6 (1 atm) with 1 (30.0 mg, 0.05 mmol) in the presence of HSiEt₃ (15 equiv) at ambient temperature led to the formation of $[Rh(F)_2(H){}^{fBu}xanPOP{}]$ (3) as the main product as well as $[Rh(SH)\{^{tBu}xanPOP\}]$ (4) and two additional rhodium complexes, which could not be identified (10:4:3:1 ratio after 2 days according to ³¹P{¹H} NMR spectrum). Additionally, the compounds $S(SiEt_3)_2$ (6), $FSiEt_3$ and H_2 were formed (Scheme 2).¹⁵ Surprisingly, complex 1 shows no reactivity toward HSiEt₃ as it has been observed for the ^{iPr}xanPOP complex to give [Rh(SiEt₃){^{iPr}xanPOP}].^{5h,i,16} However, the formation of 1 and 6 together with unknown minor products was observed on treatment of 4 with HSiEt₃ at 50 °C, whereas 4 is not reactive toward H₂. The ${}^{31}P{}^{1}H$ NMR spectrum of rhodium(III) complex 3 reveals a resonance for the chelating ^{tBu}xanPOP ligand at δ = 63.2 ppm (¹J_{P,Rh} = 111 Hz) with a doublet of triplets splitting pattern. The ¹⁹F NMR spectrum displays one broad doublet for the metal bound

Scheme 2. Activation of SF_6 at $[Rh(H){^{tBu}xanPOP}]$ in the Presence of $HSiEt_3$



fluorine atoms at high field of $\delta = -526.9 \text{ ppm} ({}^{1}J_{\text{F,Rh}} = 189 \text{ Hz})$ indicating the chemical equivalency of the fluorido ligands. ${}^{5f}g_{9,9a-k,m,14a,17}$ The ${}^{1}\text{H}$ NMR spectrum shows for the hydrido ligand a doublet of triplets of triplets at $\delta = -19.31$ ppm due to the coupling to the rhodium atom and two equivalent fluorine and phosphorus atoms (${}^{1}J_{\text{H,Rh}} = 26.9 \text{ Hz}$, ${}^{2}J_{\text{H,P}} = 8.2 \text{ Hz}$, ${}^{2}J_{\text{H,F}} = 4.8 \text{ Hz}$). The coupling constants were assigned based on the corresponding ${}^{1}\text{H}\{{}^{31}\text{P}\}$ NMR spectrum.

The molecular structure of 3 in the solid state was determined by X-ray crystallography (Figure 5). Red crystals



Figure 5. Molecular structure of 3. (ORTEP, ellipsoids are set at 50% probability. All hydrogen atoms are omitted for clarity, except for H1, which was located in the difference Fourier map and freely refined.) Selected distances [Å] and bond angles [°]: Rh1–P1 2.3075(8), Rh1–P2 2.3054(8), Rh1–O1 2.291(2), Rh1–F1 2.006(2), Rh1–F2 2.0120(19), Rh1–H1 1.54(3), F1–H1 2.00(3), F2–H1 2.90(3); P1–Rh1–P2 163.87(3), F1–Rh1–P1 92.29(6), F1–Rh1–P2 94.23(6), F1–Rh1–H1 67.2(12), F2–Rh1–H1 109.1(12), F1–Rh1–O1 104.60(8), F2–Rh1–O1 79.11(8).

of **3** were obtained by *n*-hexane gas-phase diffusion into the reaction solution at 293 K. The structure of **3** reveals a distorted octahedral coordination geometry at the metal center in which both phosphorus atoms of the ^{tBu}xanPOP ligand occupy the axial positions. The fluorido ligands are located in a mutually *trans*-position. The metal bound hydrogen atom was located in the difference Fourier map and refined freely. To the best of our knowledge, there is so far only one Rh(III) complex bearing fluorido ligands structurally described.^{9m}

The Rh1–O1 bond length (2.291(2) Å) is larger than the corresponding bond lengths in $[Rh(Cl)(H)_2\{^{HBu}xanPOP\}]$ (2.254(3) Å)^{8a} or $[Rh(Cl)(\eta^2-O_2)\{^{HBu}xanPOP\}]$ (2.193(2) Å)^{8d} and represents, to the best of our knowledge, the longest Rh–O distance found in $^{HBu}xanPOP$ complexes of Rh(III). The F1-Rh1-O1 angle $(104.60(8)^{\circ})$ differs significantly from the F2-Rh1-O1 angle $(79.11(8)^{\circ})$ and the F1-H1 distance is 2.001 Å, which would be shorter than the sum of the van der Waals radii.¹⁸ Therefore, DFT calculations were performed to get a closer insight into the minimum structure of 3 (Figure 6).



Figure 6. DFT-optimized structure of **3**; all hydrogen atoms have been omitted for clarity, except of the metal-bound one.

In the calculated structure the F–H distances are 2.631 and 2.426 Å. This small difference might be due to the strain induced by the metal-bound pincer ligand. The calculated structure is, therefore, consistent with the NMR data which show no large F,H coupling and suggests an equivalence of the fluorido ligands on the NMR time-scale. Hence, the distortion in the structure of **3** in the solid state might be attributed to packing effects. In order to clarify this further, a relaxed scan calculation has been performed using a stepwise decrease of the shorter F–H distance starting from the calculated gas-phase structure toward the determined structure in the solid state. This analysis delivers an energy difference of only 19.9 kJ/mol, thus supporting the assumption that the short F–H distance in the solid state is most probably due to packing effects.

Further evidence for the identity of the hydrosulfido complex 4 is provided by its independent synthesis by treatment of 1 with H_2S (Scheme 3). Complex 4 was characterized by NMR

Scheme 3. Synthesis of $[Rh(SH){^{fBu}xanPOP}]$ (4) by Reaction of 1 with H₂S



spectroscopy, LIFDI-MS, elemental analysis, and IR spectroscopy as well as by X-ray crystallography. The ³¹P{¹H} NMR spectrum of 4 shows a resonance signal for the ^{fBu}xanPOP ligand at δ = 54.8 pm (¹J_{P,Rh} = 149 Hz) with the expected doublet splitting pattern. The ¹H NMR spectrum shows a signal with a splitting pattern of a triplet of doublets at δ = -1.70 ppm (³J_{H,P} = 13.8 Hz, ²J_{H,Rh} = 2.5 Hz) for the thiolate proton. The chemical shift is in the range for transition metal SH ligands.¹⁹ In a ³¹P decoupling experiment, the signal simplifies to a doublet which confirms the ²J_{H,Rh} coupling constant that is comparable to the corresponding coupling in [Rh(SH)(CO)(PPh₃)₂] of ²J_{H,Rh} = 1.6 Hz.^{19a} The ATR IR spectrum of 4 shows one weak absorption band for the S–H stretching mode at $\tilde{\nu}$ = 2547 cm⁻¹ which is in the same range as

the bands of the complex $[Rh(H)(SH)(pp_3)]CF_3SO_3$ ($\tilde{\nu} = 2560 \text{ cm}^{-1}$, pp = tris(2-(diphenylphosphino)ethyl)phosphine).^{19c} Suitable crystals for V are 100

Suitable crystals for X-ray diffraction analysis of compound 4 were obtained from a toluene solution at 193 K. The molecular structure in the solid state is shown in Figure 7.



Figure 7. Molecular structure of 4. (ORTEP, ellipsoids are set at 50% probability. C–H hydrogen atoms were omitted for clarity. The sulfurbound hydrogen atom H1 was located in the difference Fourier map and freely refined.) Selected distances [Å] and bond angles [°]: Rh1–P1 2.2836(4), Rh1–P2 2.2594(4), Rh1–O1 2.1828(11), Rh1–S1 2.2865(4); P1–Rh1–P2 162.655(16), S1–Rh1–O1 171.74(12), Rh1–S1–H1 106.9(11), S1–Rh1–P1 95.209(16), S1–Rh1–P2 100.103(17), O1–Rh1–P1 83.24(3), O1–Rh1–P2 82.73(3).

Furthermore, the formation of the sulfur-containing disilathiane $S(SiEt_3)_2$ (6) during the conversion of SF_6 with 1 in the presence of $HSiEt_3$ was ascertained by GC-MS measurement and NMR experiments. The ¹H,²⁹Si HMBC NMR spectrum of a sample taken from the crude reaction mixture shows the cross peaks for $HSiEt_3$, $FSiEt_3$, and 6 as the only silicon containing compounds (Figure 8).²⁰ The ¹H,²⁹Si HMBC spectrum of 6 reveals two cross-peaks at $\delta = 1.1/22.0$



Figure 8. ¹H,²⁹Si HMBC NMR spectrum of HSiEt₃, FSiEt₃ and $S(SiEt_3)_2$ (6). The measured sample was taken after 5 days from the reaction mixture of the reaction of SF₆ (1 atm) with 1 in the presence of triethylsilane.

ppm and $\delta = 0.7/22.0$ ppm. 6 was also synthesized independently by a reaction of ClSiEt_3 with Li_2S at room temperature. Disilathianes have a range of application as reactants in organic chemistry for instance in the synthesis of thiols, in conversion of acetals and aldehydes into thioxo derivatives and in reduction processes of aromatic azides to form amines. Disilathianes are also used for the production of metal sulfides and discussed as precursors for the synthesis of transition metal sulfide monolayers by atomic layer deposition.²¹

SUMMARY AND CONCLUSIONS

Despite its chemical inertness, SF₆ was successfully converted by treatment of $[Rh(H){^{tBu}xanPOP}]$ (1) at room temperature into the bifluorido complex $[Rh(FHF)\{^{tBu}xanPOP\}]$ (2). Complex 1 was regenerated by conversion of 2 into the fluorido complex $[Rh(F)]^{tBu}$ xanPOP}] (3) and subsequent treatment of the latter with HSiEt₃. Furthermore, SF₆ reacted with 1 in the presence of an excess of HSiEt₃ to afford the difluorido complex $[Rh(F)_2(H)]^{tBu}$ xanPOP}] (3), which is stable toward HSiEt₃. Moreover, the sulfur-containing products were identified to be the hydrosulfido complex [Rh(SH)- ${^{tBu}xanPOP}$] (4) and S(SiEt₃)₂ (6). No generation of phosphanesulfides was observed as in the reaction of SF_6 with $[Rh(H)(PEt_3)]$.^{Sh,i} However, in the SF_6 activation reactions at $[{Rh(\mu-H)(dippp)}_2]$ (dippp = 1,3-bis-(diisopropylphosphanyl)propane) in the presence of HSiEt₃ the thiolato-bridged complex $[Rh_2(\mu-H)(\mu-SSiEt_3)(dippp)_2]$ was obtained.^{5f,g} In contrast, hydrosulfido complex 4 is mononuclear and features a SH ligand. This might be due to the sterical demand of the ^{tBu}xanPOP ligand.

EXPERIMENTAL SECTION

All experiments were performed on a Schlenk line under an atmosphere of argon or in an argon-filled drybox with dioxygen levels below 10 ppm. All solvents were purified, dried and degassed by conventional methods and distilled under an atmosphere of argon prior to use. $[Rh(H){^{tBu}xanPOP}]$ (1; $^{tBu}xanPOP = 9,9$ -dimethyl-4,5bis(ditert-butylphosphino)xanthene) and $S(SiEt_3)_2$ were prepared according to literature procedures.^{8a,21d} HSiEt₃ was purchased from Sigma-Aldrich. SF₆ was a gift of Solvay Fluor GmbH. Microanalyses were performed with a HEKAtech Euro EA Elemental Analyzer. The NMR spectra were recorded at 298 K (if not stated otherwise) on a Bruker DPX 300 or a Bruker Avance III 300 spectrometer. The ¹H NMR chemical shifts were referenced to residual toluene- d_7 at δ = 7.09 ppm and δ = 2.09 ppm or to residual benzene- d_5 at δ = 7.16 ppm. The ¹⁹F NMR and ³¹P{¹H} spectra were referenced to external CFCl₃ at δ = 0.0 ppm and 85% H_3PO_4 at δ = 0.0 ppm. Abbreviation for virtual coupling constants: $N = {}^{3}J_{H,P} + {}^{5}J_{H,P}$. Mass spectra were recorded on a Micromass Q-Tof-2 instrument equipped with a Linden LIFDI source (Linden CMS GmbH). GC-MS spectra were measured on an Agilent 6890N gas-phase chromatograph (Agilent 19091S-433 Hewlett-Packard) equipped with an Agilent 5973 Network mass selective detector at 70 eV. IR spectra were recorded with a Bruker Vertex 70 spectrometer equipped with an ATR unit (diamond). The crystallographic data were collected at a BRUKER D8 VENTURE area detector, Mo K α radiation ($\lambda = 0.71073$ Å). All measurements were performed at 100.00(2) K. Multiscan absorption corrections implemented in SADABS²² were applied to the data. The structures were solved by intrinsic phasing method (SHELXT-2013)²³ and refined by full-matrix least-squares procedures based on F^2 with all measured reflections $(SHELXL-2013)^{24}$ with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model except for H2 in complex 1, H1 in complex 3, and H1 in complex 4 which were found in the difference Fourier map and freely refined.

DFT-calculations were performed using the Gaussian 09 (revision D.01) program package²⁵ and the BP86 functional. Def2-svp basis sets were employed for all atoms except rhodium, which was described on using a RECP with the associated def2-svp basis set.²⁶ Dispersion effects were taken into account using the Grimme D3 dispersion correction with Becke–Jones damping.²⁷ Frequency calculations were run for all stationary points to identify them as minima (no negative eigenvalues). Energies were corrected for zero-point energy. The xyz-coordinates for the calculated structure of 3 are given in the Supporting Information.

Treatment of [Rh(H){^{tBu}xanPOP}] with SF₆ at Room Temperature. In a PFA tube $[Rh(H){^{tBu}xanPOP}]$ (1) (38 mg, 0.06 mmol) was dissolved in toluene- d_8 (0.3 mL). The PFA tube was inserted into a Young NMR tube. The sample was degassed in vacuo at -196 °C, pressurized with gaseous SF₆ to 1 atm and allowed to warm up to room temperature. By monitoring the reaction by NMR spectroscopy, the ${}^{31}P{}^{1}H$, ${}^{1}H$ and ${}^{19}F$ spectroscopic data revealed a complete conversion of 1 after 16 h into [Rh(FHF){^{tBu}xanPOP}] (2), $[Rh(F)_2(H){^{fBu}xanPOP}]$ (3), $[Rh(SH){^{fBu}xanPOP}]$ (4) and an unknown Rh(III) complex (¹H NMR (300 MHz, C₆D₆, 298 K) δ = -16.22 (d, ${}^{1}J_{H,Rh} = 42$ Hz, RhH) ppm. ${}^{31}P{}^{1}H$ NMR (121.5 MHz, C_6D_6 , 298 K) δ = 78.8 (d, ${}^1J_{P,Rh}$ = 118 Hz) ppm (ratio: 10:3:2:1 according to the ${}^{31}P{}^{1}H$ NMR spectrum). After 4 days the spectroscopic data as well as mass spectrometric analysis (LIFDI-TOF) showed only the presence of complex 2. The reaction mixture was filtered. All volatile compounds of the filtrate were removed under reduced pressure to obtain $\overline{2}$ (35 mg, 0.05 mmol, 83%) as a dark red powder. Analytical data for 2: ¹H NMR (300 MHz, toluene-d₈, 298 K) δ = 12.39 (s, br, 1H FHF); 7.62 (s, br, 2H, ArH); 6.95 (d, J = 7.5 Hz, 2H, ArH); 6.77(t, J = 7.5 Hz, 2H, ArH); 1.56 (vt, N = 13.6 Hz, 36H, $C(CH_3)_3$; 1.06 (s, 6H, $C(CH_3)_2$). ¹H NMR (300 MHz, toluene- d_8 , 243 K) $\delta = 12.20$ (dd, s in ¹H{¹⁹F} NMR, ¹J_{H,F} = 402 Hz, J_{H,F} = 37 Hz, 1H, FHF); 1.61 (vt, N = 12.5 Hz, s in ¹H{³¹P} NMR, 36H, C(CH₃)₃); 1.01 (s, 6H, $C(CH_3)_2$) ppm. ¹⁹F NMR (282.4 MHz, toluene- d_8 , 243 K) $\delta = -178.2$ (dd, d in ¹⁹F{¹H} NMR, ¹*J*_{F,H} = 401 Hz, *J*_{F,F} = 112 Hz, 1F, HF); -498.0 (m, dd in ¹⁹F{¹H} NMR, ¹*J*_{F,Rh} = 184 Hz, *J*_{F,F} = 111 Hz, 1F, RhF) ppm. ³¹P{¹H} NMR (121.5 MHz, toluene-*d*₈, 243 K) δ = 47.4 (d, ${}^{1}J_{P,Rh}$ = 148 Hz) ppm. IR (ATR, diamond): $\tilde{\nu}$ = 2549 (br. m, FHF), 1871 (br. m, FHF) cm⁻¹.

Formation of [Rh(F){ lBu **xanPOP**}] **(5).** A toluene- d_8 solution of 2 (35 mg, 0.05 mmol) was treated with CsF (10 equiv). By monitoring the reaction by NMR spectroscopy, the $^{31}P{}^{1}H$ and ^{19}F spectroscopic data revealed the formation of [Rh(F){ lBu xanPOP}] **(5).** The reaction mixture was filtered. All volatile compounds of the filtrate were removed under reduced pressure to obtain 5 (25 mg, 0.04 mmol, 80%) as a dark red powder. ¹H NMR (300 MHz, toluene- d_8) δ = 7.77 (m, 2H, ArH); 6.97 (m, 2H, ArH); 6.82 (t, *J* = 7.6 Hz, 2H, ArH); 1.62 (vt, *N* = 13.5 Hz, 36H, C(CH₃)₃); 1.13 (s, 6H, C(CH₃)₂) ppm. ¹⁹F NMR (282.4 MHz, toluene- d_8) δ = -530.6 (d, d in $^{19}F{}^{1}H{}$ NMR, $^{1}J_{F,Rh}$ = 207 Hz, RhF) ppm. ³¹P{ $^{1}H{}$ NMR (121.5 MHz, toluene- d_8) δ = 45.9 (d, $^{1}J_{P,Rh}$ = 157 Hz, $^{2}J_{P,F}$ = 2 Hz) ppm. **Treatment of [Rh(F){^{lBu}xanPOP}] (5) with HSiEt₃. A toluene-d_8**

Treatment of [Rh(F){^{fBu}xanPOP}] (5) with HSiEt₃. A toluene- d_8 solution of 5 was treated with HSiEt₃ (10 equiv) at 50 °C. By monitoring the reaction by NMR spectroscopy, the ³¹P{¹H} and ¹H spectroscopic data revealed a full conversion of 5 into [Rh(H)-{^{fBu}xanPOP}] (1) after 2 h as well as the formation of FSiEt₃.

Treatment of [Rh(H){^{fBu}xanPOP}] with SF₆ in the Presence of HSiEt₃ at Room Temperature. In a PFA tube [Rh(H){^{fBu}xanPOP}] (1) (30.0 mg, 0.05 mmol) and HSiEt₃ (120 μL, 0.77 mmol) were dissolved in toluene- d_8 (0.2 mL). The PFA tube was inserted into a Young NMR tube. The sample was degassed in vacuo at -196 °C, pressurized with gaseous SF₆ to 1 atm, and allowed to warm up to room temperature. After 4 days the ³¹P{¹H}, ¹H, and ¹⁹F spectroscopic data revealed a complete conversion of 1 into [Rh(F)₂(H)-{^{fBu}xanPOP}] (3) as the main product, [Rh(SH){^{fBu}xanPOP}] (4), and two unknown rhodium complexes (¹H NMR (300 MHz, C₆D₆, 298 K) δ = -14.94 (m, dd in ¹H{³¹P} NMR, ¹J_{H,Rh} = 20.2 Hz, ²J_{H,H} = 8.2 Hz, RhH); -21.20 (m, dd in ¹H{³¹P} NMR, ¹J_{H,Rh} = 20.1 Hz, ²J_{H,H} = 8.3 Hz, RhH) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆, 298 K) δ = 78.0 (d, ¹J_{P,Rh} = 117 Hz); 37.4 (d, ¹J_{P,Rh} = 110 Hz) ppm.) together

with the formation of H₂ and FSiEt₃. Mass spectrometric analysis as well as a ¹H, ²⁹Si HMBC NMR spectrum revealed the formation of S(SiEt₃)₂ (6). Analytical data for 3: ¹H NMR (300 MHz, toluene-*d*₈) δ = 7.55 (m, 2H, ArH); 7.14 (m, 2H, ArH); 6.97 (t, *J* = 7.5 Hz, 2H, ArH); 1.47 (vt, *N* = 14.0 Hz, 36H, C(CH₃)₃); 1.27 (s, 6H, C(CH₃)₂); -19.60 (dtt, ¹J_{H,Rh} = 26.9 Hz, ²J_{H,P} = 8.2 Hz, ²J_{H,F} = 4.8 Hz, 1H, RhH) ppm. The signals for other hydrogen atoms of the ^{tBu}xanPOP ligand could not be assigned due to the overlap with the signals of other products present in the reaction mixture. ¹⁹F NMR (282.4 MHz, toluene-*d*₈) δ = -526.9 (d, br, ¹J_{F,Rh} = 189 Hz, Rh(F)₂) ppm. ³¹P{¹H} NMR (121.5 MHz, toluene-*d*₈) δ = 63.2 (dt, ¹J_{P,Rh} = 111 Hz, ²J_{P,F} = 10 Hz) ppm.

Synthesis of [Rh(SH){^{tBu}xanPOP}] (4). In a 50 mL Schlenk tube [Rh(H){^{tBu}xanPOP}] (1) (197.5 mg, 0.33 mmol) was dissolved in toluene (5 mL). The sample was degassed in vacuo at -196 °C, allowed to warm up to room temperature and pressurized with gaseous H₂S to 1 atm. After stirring for 2 h, all volatile compounds were removed in vacuo. The residue was washed with hexane (4×3) mL) to give a dark red solid of 4 (203.0 mg, 97%). Elemental analysis (%) calcd for C₃₁H₄₉OP₂RhS (634.65): C 58.67, H 7.78, S 5.05; found: C 58.42, H 7.77, S 5.12. LIFDI-TOF-MS (toluene): calcd for $C_{31}H_{49}OP_{2}RhS^{+}$ [M]⁺: m/z 634.20; found: 634.19. ¹H NMR (300 MHz, C_6D_6) $\delta = 7.78$ (m, dd in ¹H{³¹P} NMR, J = 7.6, 1.7 Hz, 2H, ArH); 6.98 (dd, J = 7.6, 1.7 Hz, 2H, ArH); 6.76 (t, J = 7.6 Hz, 2H, ArH); 1.57 (vt, N = 13.4 Hz, s in ¹H{³¹P} NMR, 36H, C(CH₃)₃); 1.18 (s, 6H, C(CH₃)₂), -1.78 (td, ${}^{3}J_{H,P} = 13.8$ Hz, ${}^{2}J_{H,Rh} = 2.5$ Hz, 1H, SH) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆) δ = 54.8 (d, ¹J_{P,Rh} = 149 Hz) ppm. IR (ATR, diamond): $\tilde{\nu} = 2547$ (w, SH)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00858.

Crystallographic data of the compounds 2-4 and [Rh(I){^{tBu}xanPOP}], computational details of the DFT calculations, crystallographic data as well as additional experimental data and spectra (PDF)

Optimized structure of $[Rh(F)_2(H){^{tBu}xanPOP}]$ (3) (XYZ)

Accession Codes

CCDC 1584179–1584182 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(15) Note that the complex $[Rh(F)\{^{tBu}xanPOP\}]$ (5) reacts with H_2 to yield $[Rh(H)\{^{tBu}xanPOP\}]$ (1) and not $[Rh(F)(H)_2\{^{tBu}xanPOP\}]$. Thus, the presence of the latter can be excluded.

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