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S–F Activation

S–F and S–C Activation of SF_6 and SF_5 Derivatives at Rhodium: Conversion of SF_6 into H_2S**

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Abstract: *The degradation of SF_6 and SF_5 organyls by S–F and S–C bond-activation reactions at $[\{Rh(\mu\text{-}H)(dippp)\}_2]$ under mild conditions is reported. Fluorido and thiolato species were identified as products or intermediates, and were characterized by X-ray diffraction analysis and multinuclear NMR spectroscopy. An unprecedented cyclic process for the conversion of the potent greenhouse gas SF_6 into H_2S was developed.*

SF_6 is widely regarded as a chemically extremely stable gas.[1] SF_6 has a high density, is nontoxic and nonflammable, and exhibits a high dielectric constant, which makes it ideally suited for some specific applications, for example, as a gaseous dielectric compound for high-voltage-power applications.[1,2] However, SF_6 is also known as one of the most powerful greenhouse gases.[3] The activation of SF_6 at transition-metal complexes has only been described by Ernst and co-workers, at low-valent Ti, V, Cr, and Zr complexes, as well as at $[Ni(PMe_3)_4]$ and $[Fe(C_5H_5)(C_6H_3t\text{Bu}_3)]$.[4] The formation of fluorido complexes or polyfluoride anions was observed in all cases. Sulfur-containing products could only be identified in the reactions of SF_6 with $[Cr(C_5Me_5)_2]$ and $[Ti(1,3\text{-}t\text{Bu}_2C_5H_3)(6,6\text{-dmch})(PMe_3)]$ (6,6-dmch = 6,6-dimethylcyclohexadienyl), which yielded, among other compounds, $[\{Cr(C_5Me_5)(\mu_2\text{-}F)\}_3(\mu_3\text{-}S)]^+[Cr(C_5Me_5)(F)_3]^-$ or $SPMe_3$, respectively.

Some of the properties of SF_6 are maintained in its organic SF_5 derivatives.[5] The SF_5 group is characterized by its high electronegativity, its high lipophilicity, and its significant steric demand. Its high stability and chemical inertness in organic compounds are generally accepted as characteristic features.[5–7] Compounds which contain a SF_5 building block are of increasing importance because of their various applications as bioactive compounds, liquid crystals, and advanced polymer materials.[5,6] Studies on the reactivity of the SF_5 moiety in organic derivatives are extremely rare.[7a,c,8] A nucleophilic attack by an azide anion at (pentafluorosulfanyl)propyl tosylate[8a] and a base-induced dehydropentafluorosulfanylation at olefinic double bonds to give alkynes[8d] have been reported. However, in these examples, the fate of the SF_5 group is not known. A defluorination of the SF_5 group upon the treatment of 1-bromo-4-(pentafluorosulfanyl)benzene with *n*-butyllithium led to a mixture of products, including bis(4-(pentafluorosulfanylphenyl))sulfane in very low yield (4%).[8e] The reaction of SF_5CH_2Br with *n*-butyllithium gave $F_4S{=}CH_2$ through an initial lithiation of the α-carbon atom.[8g] So far, the cleavage of either S–F or S–C bonds in aromatic SF_5 compounds at transition-metal complexes has, to the best of our knowledge, not been observed. Note that a series of organometallic transformations of SF_5 compounds, such as palladium-catalyzed cross-coupling reactions, are known in which the C–SF_5 moiety remains stable.[5a,6f,7c,9]

Herein, we show that carbon-bound SF_5 groups are not stable in the presence of rhodium hydrido species. We report the unprecedented defluorination of aryl SF_5 compounds and CF_3SF_5 by S–F and S–C bond-activation reactions under mild conditions. Furthermore, a remarkable reduction of SF_6 at $[\{Rh(\mu\text{-}H)(dippp)\}_2]$ (**1**; dippp = 1,3-bis(diisopropylphosphanyl)propane) in the presence of $HSiEt_3$ led exclusively to $[Rh_2(\mu\text{-}H)(\mu\text{-}SSiEt_3)(dippp)_2]$ (**8**), $FSiEt_3$, and H_2. A unique cyclic process for the conversion of SF_6 into H_2S was developed.

The treatment of $[\{Rh(\mu\text{-}H)(dippp)\}_2]$ (**1**) with $PhSF_5$ (0.3 equiv) for 120 h at 50 °C gave the fluorido complex $[\{Rh(\mu\text{-}F)(dippp)\}_2]$ (**2**) and the binuclear hydrido thiolato complex $[Rh_2(\mu\text{-}H)(\mu\text{-}SPh)(dippp)_2]$ (**3a**) in a 2.5:1 ratio, along with the formation of H_2 (Scheme 1). $CH_3C_6H_4SF_5$ and CF_3SF_5 were activated in a similar manner at **1** to yield the fluorido complex **2** and the hydrido thiolato complexes **3b** and **3c**, respectively, in a 2.5:1 ratio (Scheme 1). The reaction of **1** with the aromatic SF_5 compounds could be accelerated by the use of an excess (10 equivalents) of the SF_5 substrates to enable full conversion within 48 h at room temperature. Compound **2** was described previously.[10] Complexes **3a** and **3b** were synthesized independently by the treatment of **1** with the corresponding thiophenols RSH (1 equiv; Scheme 2).[11] The $^{31}P\{^1H\}$ NMR spectrum of **3a** displays two doublets of multiplets at $\delta = 45.9$ and 38.9 ppm as part of an AA′BB′XX′ spin system (X,X′ = Rh). In the ^1H NMR spectrum, the resonance for the hydrido ligand appears as a multiplet at $\delta = -10.14$ ppm; it simplifies to a triplet in the phosphorus-decoupled spectrum ($^1J_{Rh,H} = 21.8$ Hz). The NMR spectroscopic data of **3b** and **3c** are very similar to those of **3a**. The molecular structures of **3a** and **3b** in the solid state were determined by X-ray crystallography (Figure 1; the structure of **3b** resembles that of **3a**: see the Supporting Information).[12] Complex **3a** exhibits a nearly planar $Rh_2(\mu\text{-}H)(\mu\text{-}SPh)$ moiety with a trigonal-pyramidal geometry of the sulfido ligand. Each rhodium center shows a slightly distorted square-planar coordination sphere. The distance between the rhodium atoms is 2.8850(2) Å.

The reaction of **1** with the SF_5 substrates was monitored by ^{31}P, ^{19}F, and ^1H NMR spectroscopy. In each case, the hydrido

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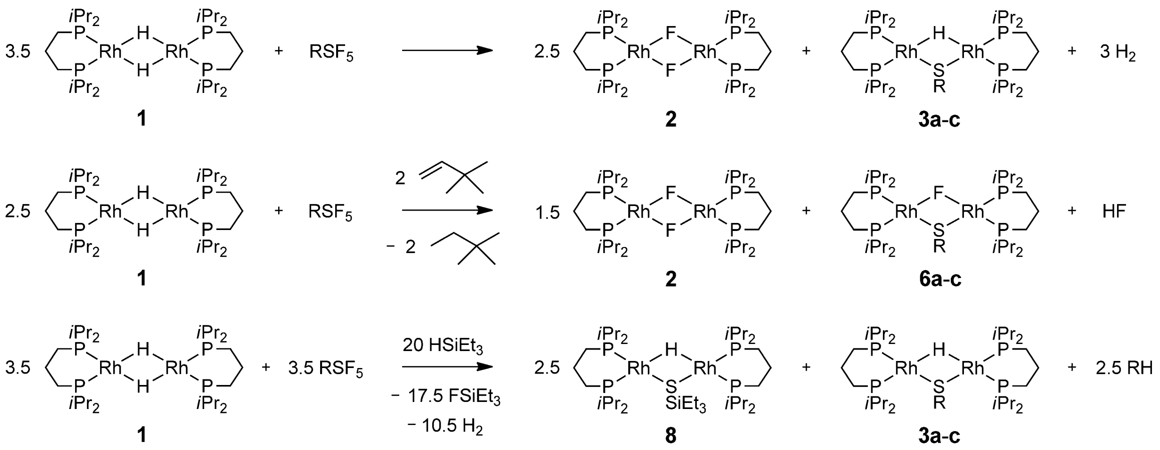
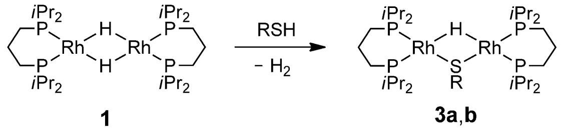


Scheme 1. S–F and S–C activation of pentafluorosulfanyl compounds at $[\{Rh(\mu\text{-}H)(dippp)\}_2]$ (**1**); **a**: R = Ph, **b**: R = $C_6H_4CH_3$, **c**: R = CF_3.



Scheme 2. Synthesis of the hydrido thiolato complexes **3a**,**b**; **a**: R = Ph, **b**: R = $C_6H_4CH_3$.

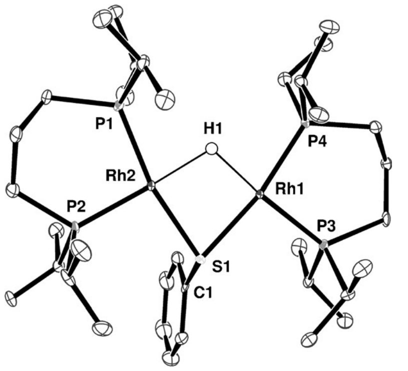


Figure 1. Molecular structure of **3a** (ORTEP, ellipsoids are set at 50% probability). All hydrogen atoms except for the bridging hydride are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–S1 2.3129(10), Rh2–S1 2.3131(11), S1–C1 1.785(2), C1-S1-Rh1 112.32(13), Rh1-S1-Rh2 77.167(15).

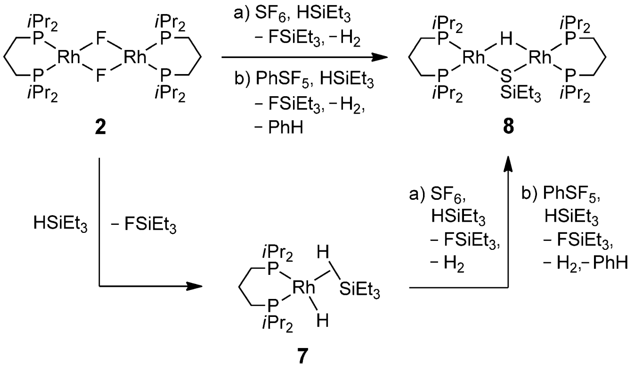
fluorido complex $[Rh_2(\mu\text{-}H)(\mu\text{-}F)(dippp)_2]$ (**4**) was detected as an intermediate, as well as considerable amounts of HF. The binuclear tetrahydrido compound $[Rh_2(H)(\mu\text{-}H)_3(dippp)_2]$ (**5**) was also present and presumably serves as the resting state after the reaction of **1** with H_2.[13] Complex **4** was characterized by NMR spectroscopy and liquid injection field desorption ionization mass spectrometry (LIFDI MS). The signal for the bridging hydrogen atom appears at $\delta = -10.43$ ppm in the ^{1}H NMR spectrum. The $^{19}F\{^1H\}$ NMR spectrum shows a multiplet for the fluorido ligand at $\delta = -355.6$ ppm, which is a characteristic chemical shift for rhodium fluorido complexes.[10a,14]

Mechanistically, we tentatively suggest that the reaction of the dihydrido complex **1** with a SF_5 organyl compound leads initially to the cleavage of a S–F bond with the concomitant generation of HF and a rhodium tetrafluorosulfanyl intermediate $[Rh_2(\mu\text{-}H)(\mu\text{-}SF_4R)(dippp)_2]$. HF can in turn react with hydrido compounds, such as **1**, to give H_2, as well as fluorido complexes, such as **4** and subsequently **2**, although the reverse reaction is also conceivable (see below).[10a,15] The formation of fluorido complexes by the protonation of hydrido compounds with HF is in accordance with the observation that the reaction of **1** with $PhSF_5$ in the presence of Cs_2CO_3/NEt_3 led to smaller amounts of **2**. Note that **3a–c** did not react with $Et_3N{\cdot}3HF$. Rhodium fluorido complexes can alternatively be formed by the migration of fluorine atoms from sulfur to a rhodium center; the resulting complexes can subsequently also yield HF in the presence of a hydrido ligand or H_2 as a hydrogen source.[16] H_2 may induce additional S–F bond-cleavage steps at Rh, including HF formation once again, as well as the generation of rhodium complexes with low-valent fluorinated sulfur-containing ligands. Overall, the reduction of the sulfur-containing ligands occurs formally by conversion of the hydrido ligands into HF or H_2. No rhodium intermediates containing a S–F moiety could be detected by NMR spectroscopy. This result indicates that the first S–F bond-cleavage step is the rate-determining step.

Evidence for the fluorido thiolato complexes $[Rh_2(\mu\text{-}F)(\mu\text{-}SR)(dippp)_2]$ as intermediates was provided by the reactions of **1** with RSF_5 in the presence of neohexene, which acts as a trapping agent for H_2.[17] The transformation yielded the complex **2** as well as $[Rh_2(\mu\text{-}F)(\mu\text{-}SR)(dippp)_2]$ (**6a–c**), in each case in a 1.5:1 ratio, along with HF and neohexane (Scheme 1). Apparently, H_2 was removed in part and does not convert **6a–c** into **3a–c**. Furthermore, no formation of the tetrahydrido complex **5** was observed. Indeed, in an independent reaction, complex **6a** was converted into **3a** and HF by treatment with H_2. Compounds **6a–c** were characterized in solution by NMR spectroscopy and LIFDI MS. The resonances for the bridging fluorido ligands appear in the $^{19}F\{^1H\}$ NMR spectra at high field ($\delta = -390.8$ ppm for **6a**).

It is known that fluorido complexes can be highly reactive. Reactions with silanes, such as $HSiEt_3$, as a hydrogen source often lead to the formation of hydrido compounds.[10a,15] Thus, it was demonstrated that $[\{Rh(\mu\text{-}F)(dippp)\}_2]$ (**2**) can be converted into the η^2-silane complex $[Rh(H)(\eta^2\text{-}HSiEt_3)(dippp)]$ (**7**). The latter undergoes transformation into the binuclear hydrido complex **1** on a slower timescale.[10a] Remarkably, the reaction of **1** with RSF_5 in the presence of $HSiEt_3$ resulted in both S–F and C–S cleavage reactions of the SF_5 compounds to yield **3a–c** as well as the silylthiolato complex **8** in a 1:2.5 ratio (Scheme 1). RH and H_2 were generated concomitantly, and $FSiEt_3$ was obtained as the only fluorinated product. The use of H_2 as a reductant, instead of $HSiEt_3$,[18] resulted predominantly in the formation of the tetrahydrido complex **5**, which is not suitable for S–F activation.

Complexes **3a**,**b** showed no reactivity towards $HSiEt_3$. Monitoring of the reaction of **1** with RSF_5 and $HSiEt_3$ by NMR spectroscopy revealed the presence of complexes **7** and $[Rh_2(H)(\mu\text{-}H)_3(dippp)_2]$ (**5**). The dihydrido complex **1** did not react with the silane $HSiEt_3$ to give **7**.[10a] It is therefore likely that $[Rh(H)(\eta^2\text{-}HSiEt_3)(dippp)]$ (**7**) serves as an intermediate in the generation of **8**. Indeed, in an independent reaction, **7** was generated by the treatment of **2** with $HSiEt_3$ and then treated with $PhSF_5$ in the presence of $HSiEt_3$ to yield exclusively **8**, with concomitant elimination of $FSiEt_3$, H_2, and benzene (Scheme 3b). The fluorido complex **2** showed no reactivity towards $PhSF_5$, but in the presence of $HSiEt_3$, **8** was formed only.



Scheme 3. S–F bond-activation reactions at **2** and **7**.

The high-field region of the ^1H NMR spectrum of **8** displays a multiplet centered at $\delta = -11.46$ ppm for the bridging hydride. In the $^{29}Si\{^1H\}$ NMR spectrum of **8**, a broad multiplet for the silicon atom is observed at $\delta = 22.1$ ppm. The molecular structure of **8**, which was determined by X-ray diffraction, differs from the structure of **3a**, as it is characterized by a bent geometry of the $Rh_2(\mu\text{-}H)(\mu\text{-}SSiEt_3)$ moiety, with a hinge angle θ of 142.9(6)° (Figure 2).[12] The geometry around the rhodium centers is close to square-planar. The S–Si distance is 2.1586(7) Å and is comparable to those found in other silylthiolato-bridged complexes, for example, in $[\{Zn(SSi\mathit{t}Bu_3)_2\}_2]$ or $[\{(\mathit{t}Bu_3SiS)Fe\}_2(\mu\text{-}SSi\mathit{t}Bu_3)_2]$.[19]

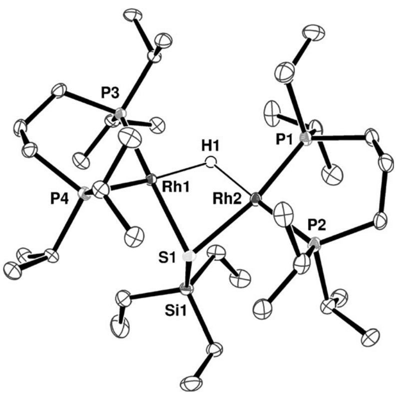
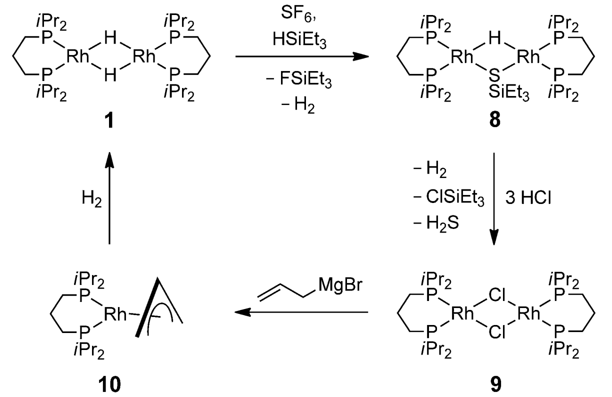


Figure 2. Molecular structure of **8** (ORTEP, ellipsoids are set at 50% probability). All hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–S1 2.3600(5), Rh2–S1 2.3816(5), S1–Si1 2.1586(7), Rh1-S1-Rh2 75.908(15).

In an extraordinary reaction, complex **1** proved to be highly reactive towards SF_6. In the presence of $HSiEt_3$, the treatment of **1** with SF_6 gave **8**, $FSiEt_3$, and H_2 as the only products after 72 h at 50 °C (Scheme 4). In analogy to the reactions with the SF_5 compounds, the η^2-silane hydrido complex **7** was detected as an intermediate during the course of the reaction, as well as the tetrahydride **5**. Independent reactions revealed that the treatment of **7** or **2** in the presence of $HSiEt_3$ gives **8** selectively (Scheme 3a). We did not observe any formation of $[Rh_2(\mu\text{-}H)(\mu\text{-}SF)(dippp)_2]$, in analogy to the generation of **3a–c** from **1**. It is likely that a μ-SF species would be highly unstable, but might be converted into **8** by loss of HF and the addition of $HSiEt_3$. This reactivity would explain the formation of complex **8** as the only product in the reaction starting from **1**. In the absence of $HSiEt_3$, full conversion of **1** was also observed upon treatment with SF_6 gas (1 atm) at room temperature for 1 day: The fluorido complex **2** was formed in approximately 70% yield according to the ^{31}P NMR spectra. However, we were not able to



Scheme 4. Activation at SF_6 and a cyclic process for its conversion into H_2S.

characterize any sulfur-containing species. LIFDI MS studies indicated the formation of several rhodium–sulfur clusters, most of which appeared to be trinuclear.

A reaction of complex **8** with HCl (3 equiv) yielded the chlorido compound [{Rh(μ-Cl)(dippp)}$_2$] (**9**)[20] along with H_2, $ClSiEt_3$, and H_2S. A reaction of **8** with DCl gave D_2S. Treatment of the chlorido complex **9** with an allyl Grignard reagent afforded [Rh(η^3-C_3H_5)(dippp)] (**10**), which was converted into the hydrido compound **1** by the addition of H_2[13] (Scheme 4). These reactions complete a cyclic process for the transformation of SF_6 into H_2S.

In conclusion, we have shown that the binuclear rhodium hydrido complex **1** effects the defluorination of SF_5 organyl compounds and of SF_6 under mild conditions to give sulfido species. Notably, the oxidation state of the rhodium centers remains +I, whereas the sulfur atom is formally reduced by oxidation of the hydrido ligands. Studies on chemical transformations of SF_6 are generally scarce and often involve reductive reaction conditions.[1,4,21] An initial electron-transfer step is also conceivable for the reaction of **1** and **7** with SF_6 and the SF_5 compounds. However, it is alternatively feasible that the first activation step occurs at the highly reactive 14-electron complex [Rh(H)(dippp)], which could be generated from **1** or **7**.[10,13] The transformation of thiolato complex **8** into H_2S paves the way for an unprecedented cyclic process for the conversion of SF_6 into H_2S. We believe that these results open up new opportunities for the degradation of SF_6 and even its transformation into valuable reagents. SF_6 and CF_3SF_5 have been identified as greenhouse gases with enormous global-warming potential.[3]

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[11] The treatment of **1** with PhSH gave **3a** and [{Rh(μ-SPh)(dippp)}$_2$] as a by-product (ca. 10%). [{Rh(μ-SPh)(dippp)}$_2$] could be synthesized independently by the use of an excess of PhSH; the molecular structure was determined by X-ray crystallography (see the Supporting Information).

[12] See the Supporting Information for supplementary crystallographic data of **3a**,**b** and **8**. CCDC 957478 (**3a**), 957479 (**3b**), and 957480 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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