

S–F and S–C Activation of SF₆ and SF₅ Derivatives at Rhodium: Conversion of SF₆ into H₂S**

Lada Zámotná, Thomas Braun,* and Beatrice Braun

Abstract: The degradation of SF₆ and SF₅ organyls by S–F and S–C bond-activation reactions at $[\{\text{Rh}(\mu\text{-H})(\text{dipp})\}_2]$ 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 SF₆ into H₂S was developed.

SF₆ is widely regarded as a chemically extremely stable gas.^[1] SF₆ 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, SF₆ is also known as one of the most powerful greenhouse gases.^[3] The activation of SF₆ 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 $[\text{Ni}(\text{PMe}_3)_4]$ and $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_3\text{tBu}_3)]$.^[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 SF₆ with $[\text{Cr}(\text{C}_5\text{Me}_5)_2]$ and $[\text{Ti}(1,3\text{-tBu}_2\text{C}_5\text{H}_3\text{-}(6,6\text{-dmch}))(\text{PMe}_3)]$ (6,6-dmch = 6,6-dimethylcyclohexadienyl), which yielded, among other compounds, $[\{\text{Cr}(\text{C}_5\text{Me}_5)(\mu_2\text{-F})\}_3(\mu_3\text{-S})]^+[\text{Cr}(\text{C}_5\text{Me}_5)(\text{F})_3]^-$ or SPMe_3 , respectively.

Some of the properties of SF₆ are maintained in its organic SF₅ derivatives.^[5] The SF₅ 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 SF₅ 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 SF₅ 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 SF₅ group is not known. A defluorination of the SF₅ 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 SF₅CH₂Br with *n*-butyllithium gave F₄S=CH₂ through an initial lithiation of the α -carbon atom.^[8g] So far, the cleavage of either S–F or S–C bonds in aromatic SF₅ compounds at transition-metal complexes has, to the best of our knowledge, not been observed. Note that a series of organometallic transformations of SF₅ compounds, such as palladium-catalyzed cross-coupling reactions, are known in which the C–SF₅ moiety remains stable.^[5a,6f,7c,9]

Herein, we show that carbon-bound SF₅ groups are not stable in the presence of rhodium hydrido species. We report the unprecedented defluorination of aryl SF₅ compounds and CF₃SF₅ by S–F and S–C bond-activation reactions under mild conditions. Furthermore, a remarkable reduction of SF₆ at $[\{\text{Rh}(\mu\text{-H})(\text{dipp})\}_2]$ (**1**; dipp = 1,3-bis(diisopropylphosphanyl)propane) in the presence of HSiEt₃ led exclusively to $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SSiEt}_3)(\text{dipp})_2]$ (**8**), FSiEt₃, and H₂. A unique cyclic process for the conversion of SF₆ into H₂S was developed.

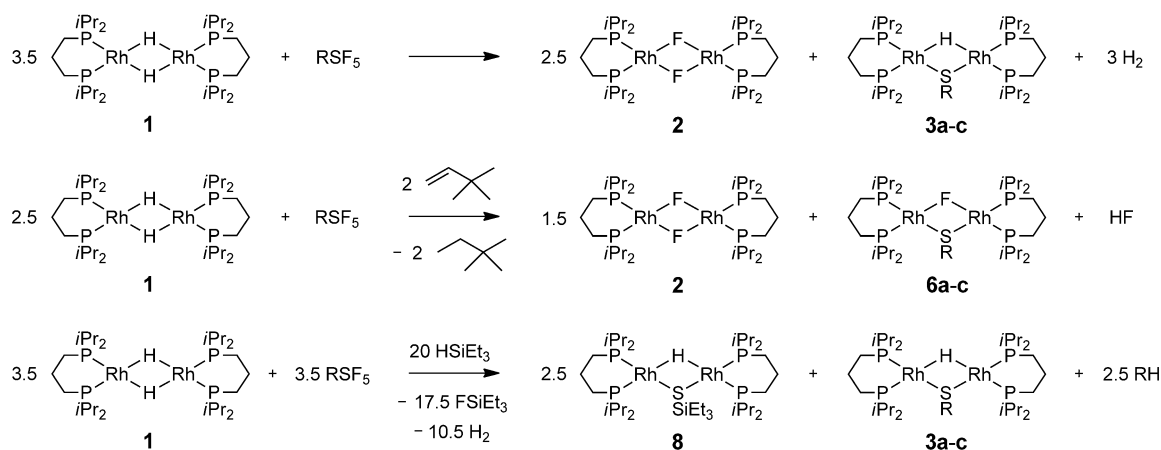
The treatment of $[\{\text{Rh}(\mu\text{-H})(\text{dipp})\}_2]$ (**1**) with PhSF₅ (0.3 equiv) for 120 h at 50 °C gave the fluorido complex $[\{\text{Rh}(\mu\text{-F})(\text{dipp})\}_2]$ (**2**) and the binuclear hydrido thiolato complex $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SPh})(\text{dipp})_2]$ (**3a**) in a 2.5:1 ratio, along with the formation of H₂ (Scheme 1). CH₃C₆H₄SF₅ and CF₃SF₅ 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 SF₅ compounds could be accelerated by the use of an excess (10 equivalents) of the SF₅ 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 ³¹P{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 Rh₂(μ-H)(μ-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 SF₅ substrates was monitored by ³¹P, ¹⁹F, and ¹H NMR spectroscopy. In each case, the hydrido

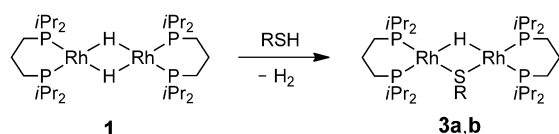
[*] L. Zámotná, Prof. Dr. T. Braun, Dr. B. Braun
Department of Chemistry, Humboldt-Universität zu Berlin
Brook-Taylor-Strasse 2, 12489 Berlin (Germany)
E-mail: thomas.braun@chemie.hu-berlin.de

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Scheme 1. S–F and S–C activation of pentafluorosulfanyl compounds at $[\{\text{Rh}(\mu\text{-H})(\text{dipp})\}_2]$ (**1**); **a**: R = Ph, **b**: R = $\text{C}_6\text{H}_4\text{CH}_3$, **c**: R = CF_3 .



Scheme 2. Synthesis of the hydrido thiolato complexes **3a,b**; **a**: R = Ph, **b**: R = $\text{C}_6\text{H}_4\text{CH}_3$.

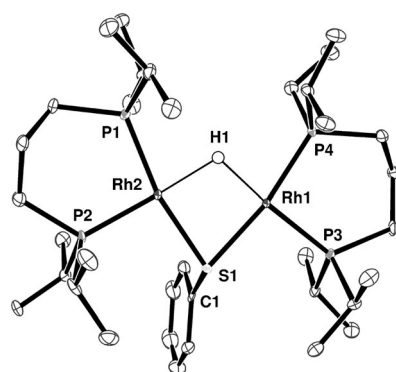


Figure 1. Molecular structure of **3a** (ORTEP, ellipsoids are set at 50% probability). All hydrogen atoms except for the bridging hydride are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-S1 2.3129(10), Rh2-S1 2.3131(11), S1-C1 1.785(2), C1-S1-Rh1 112.32(13), Rh1-S1-Rh2 77.167(15).

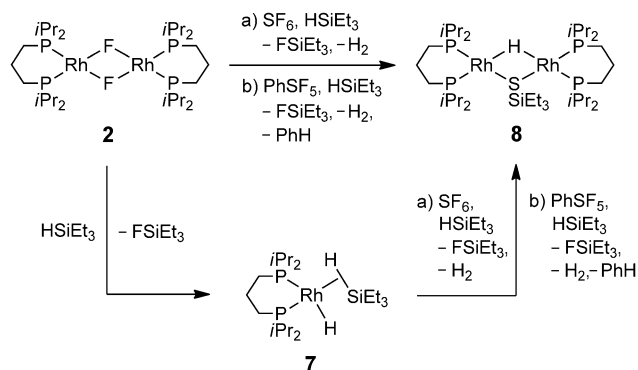
fluorido complex $[\text{Rh}_2(\mu\text{-H})(\mu\text{-F})(\text{dipp})_2]$ (**4**) was detected as an intermediate, as well as considerable amounts of HF . The binuclear tetrahydrido compound $[\text{Rh}_2(\text{H})(\mu\text{-H})_3(\text{dipp})_2]$ (**5**) was also present and presumably serves as the 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 ^1H NMR spectrum. The $^{19}\text{F}\{^1\text{H}\}$ 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 $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SF}_4\text{R})(\text{dipp})_2]$. 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 $\text{Cs}_2\text{CO}_3/\text{NEt}_3$ led to smaller amounts of **2**. Note that **3a-c** did not react with $\text{Et}_3\text{N}\cdot 3\text{HF}$. 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 $[\text{Rh}_2(\mu\text{-F})(\mu\text{-SR})(\text{dipp})_2]$ 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 $[\text{Rh}_2(\mu\text{-F})(\mu\text{-SR})(\text{dipp})_2]$ (**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 $^{19}\text{F}\{^1\text{H}\}$ NMR spectra at high field ($\delta = -390.8$ ppm for **6a**).

It is known that fluoro 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 $[\{\text{Rh}(\mu\text{-F})(\text{dipp})\}_2]$ (**2**) can be converted into the η^2 -silane complex $[\text{Rh}(\text{H})(\eta^2\text{-HSiEt}_3)(\text{dipp})]$ (**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 $[\text{Rh}_2(\text{H})(\mu\text{-H})_3(\text{dipp})_2]$ (**5**). The dihydrido complex **1** did not react with the silane HSiEt_3 to give **7**.^[10a] It is therefore likely that $[\text{Rh}(\text{H})(\eta^2\text{-HSiEt}_3)(\text{dipp})]$ (**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 fluoro 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 $^{29}\text{Si}\{^1\text{H}\}$ 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 $\text{Rh}_2(\mu\text{-H})(\mu\text{-SSiEt}_3)$ moiety, with a hinge angle θ of $142.9(6)^\circ$ (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

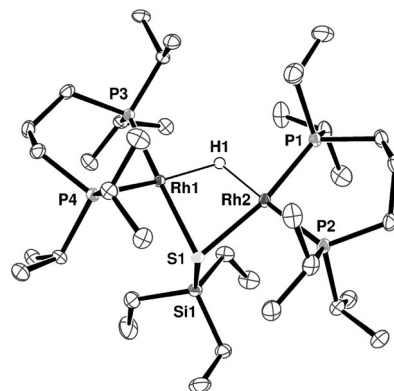
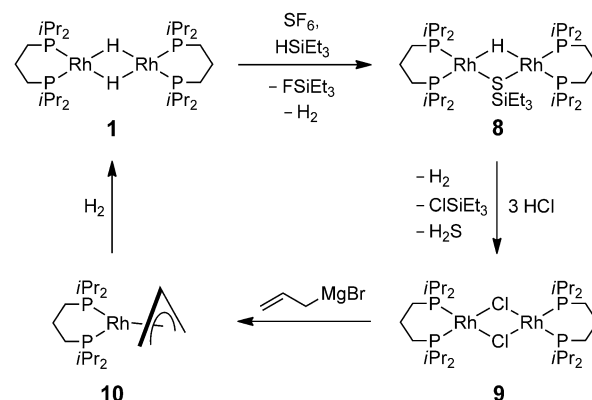


Figure 2. Molecular structure of **8** (ORTEP, ellipsoids are set at 50% probability). All hydrogen atoms except for H1 are omitted for clarity. Selected bond lengths [Å] and angles $^\circ$: Rh1–S1 $2.3600(5)$, Rh2–S1 $2.3816(5)$, S1–Si1 $2.1586(7)$, Rh1–S1–Rh2 $75.908(15)$.

example, in $[\{\text{Zn}(\text{SSi}t\text{Bu}_3)_2\}_2]$ or $[\{(t\text{Bu}_3\text{SiS})\text{Fe}\}_2(\mu\text{-SSi}t\text{Bu}_3)_2]$.^[19]

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



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

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 $[\text{Rh}_2(\mu\text{-H})(\mu\text{-SF})(\text{dipp})_2]$, in analogy to the generation of **3a–c** from **1**. It is likely that a $\mu\text{-SF}$ 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 fluoro complex **2** was formed in approximately 70% yield according to the ^{31}P NMR spectra. However, we were not able to

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 $[\{\text{Rh}(\mu\text{-Cl})(\text{dipp})\}_2]$ (**9**)^[20] along with H₂, ClSiEt₃, and H₂S. A reaction of **8** with DCl gave D₂S. Treatment of the chlorido complex **9** with an allyl Grignard reagent afforded $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)(\text{dipp})]$ (**10**), which was converted into the hydrido compound **1** by the addition of H₂^[13] (Scheme 4). These reactions complete a cyclic process for the transformation of SF₆ into H₂S.

In conclusion, we have shown that the binuclear rhodium hydrido complex **1** effects the defluorination of SF₅ organyl compounds and of SF₆ 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 SF₆ 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 SF₆ and the SF₅ compounds. However, it is alternatively feasible that the first activation step occurs at the highly reactive 14-electron complex $[\text{Rh}(\text{H})(\text{dipp})]$, which could be generated from **1** or **7**.^[10,13] The transformation of thiolato complex **8** into H₂S paves the way for an unprecedented cyclic process for the conversion of SF₆ into H₂S. We believe that these results open up new opportunities for the degradation of SF₆ and even its transformation into valuable reagents. SF₆ and CF₃SF₅ have been identified as greenhouse gases with enormous global-warming potential.^[3]

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- [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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