S–F Activation Very Important Paper

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Catalytic Degradation of Sulfur Hexafluoride by Rhodium Complexes

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***Abstract:** The development of a safe and efficient method for the degradation of SF_6 is of current environmental interest, because SF_6 is one of the most potent greenhouse gases. SF_6 is thermally and chemically extremely inert, and therefore, it has been used in various industrial applications. However, this inertness results in a major challenge for its depletion. We report on a process for a catalytic degradation of SF_6 in the homogeneous phase by using rhodium complexes as precatalysts. The SF_6 activation reactions feature mild reaction conditions, low catalyst loadings, and a high selectivity. The employment of phosphines and hydrosilanes for scavenging the sulfur and fluorine atoms of the SF_6 molecule allows the selective transformation of SF_6 into nongaseous and nontoxic compounds.*

A controlled degradation of sulfur hexafluoride (SF_6) under mild conditions by a catalytic process can be considered as an environmental objective of considerable importance because an atmospheric emission of SF_6 can thus be prevented. SF_6 has been globally recognized as potent greenhouse gas with the highest global warming potential known, which is 23500 times higher than that of CO_2, with an atmospheric lifetime of about 3200 years.[1–3] Hence, it emerged among the six most prominent greenhouse gases included in the Kyoto Protocol.[1] SF_6 is widely used in a variety of industrial applications and processes owing to its unique properties, such as a low toxicity, extreme inertness, and a high dielectric constant.[4–8] It is mainly employed as a gaseous dielectric and electron-trapping agent for high-voltage power applications.[6,7] Prior to its usage in industry, SF_6 was not detected in the atmosphere, which indicates that its presence is entirely anthropogenic. Note that the global SF_6 concentration has grown from less than 1 ppt in 1975 to more than 8 ppt in 2008.[3] Taking into account that there are often no alternative chemicals to replace SF_6, increasing attention has been paid to control or even avoid its emission.[3,9–15]

In the past decade, SF_6 was mainly degraded or recycled by adsorption, separation, and decomposition methods.[11,13–16] Because of its chemical inertness approaches for a selective degradation of SF_6 are extremely challenging.[4,5,8] Methods for its decomposition include harsh conditions, such as high temperatures and pressure. Many studies involve the thermal and photoreductive decomposition of SF_6 in electric discharges associated with plasma etching, or a photolytic reaction at polyisoprene surfaces.[11,13–18] However, the products produced by these methods are mostly gaseous, toxic, and even corrosive, and include HF, F_2, SF_4, S_2F_{10}, SO_2F_2, S_2OF_{10}, SOF_2, SOF_4, H_2S, SO_2, and SO_3. To date, catalytic decompositions of SF_6 have only been achieved heterogeneously, mainly at metal phosphates.[16–18] However, these reactions require temperatures above 800 K and give SO_3, SO_2F_2, and HF as major products. Therefore, it is of current interest to develop alternative pathways for a selective degradation of SF_6. Reactions mediated by transition-metal complexes represent a promising approach to decompose SF_6 under mild conditions. Hitherto, the activation of SF_6 at transition metals was achieved at low-valent Ti, V, Cr, and Zr complexes as well as at Fe and at reduced Ni complexes.[19–21] In most of the cases the fate of the sulfur atom remained unclear. We previously reported on the degradation of SF_6 at the binuclear rhodium complex $[\{Rh(\mu\text{-}H)(dippp)\}_2]$.[22] In the presence of $HSiEt_3$ the reaction led selectively to fluorosilane, H_2, and the thiolato-bridged complex $[Rh_2(\mu\text{-}H)(\mu\text{-}SSiEt_3)(dippp)_2]$, which was obtained exclusively as the only sulfur-containing product. For an efficient decomposition of SF_6 a homogeneous catalytic process is still desirable.

Herein we report on the unprecedented catalytic degradation of SF_6 in a homogeneous phase by using rhodium complexes. Phosphines and silanes were employed as scavengers for the sulfur and fluorine atoms. Thus, the developed method allows the selective transformation of SF_6 into nongaseous phosphine sulfides and fluorosilanes and it proceeds under mild conditions.

Initial studies showed that a solution of $[Rh(H)(PEt_3)_3]$ (**1**) reacts with SF_6 at room temperature. The reaction resulted in the generation of F_2PEt_3 accompanied by the formation of a black solid, which indicates the decomposition of **1**. Consequently, the reaction was performed in the presence of a large excess of the phosphine PEt_3, which in principle allows for a regeneration of **1** after a fluorination of metal-bound PEt_3 to give F_2PEt_3. Note that, in the presence of free PEt_3 complex **1** is in equilibrium with the compound $[Rh(H)(PEt_3)_4]$ (**2**), and with an excess PEt_3 the equilibrium is shifted towards **2**.[23] The reaction of **1** with an excess SF_6 in the presence of 40 equivalents of free PEt_3 at room temperature gave several rhodium complexes,[24] of which we could identify $[Rh(PEt_3)_4][HF_2]$ (**3**), $[Rh(F)(PEt_3)_3]$ (**4**),[25] and $[\{Rh(\mu\text{-}F)(PEt_3)_2\}_2]$ (**5**) Compound **5** can be synthesized independently by treatment of **1** with $NEt_3{\cdot}3HF$ at low temperature. The NMR spectroscopic data of the reaction mixture also revealed the formation of F_2PEt_3 (2.1%) and the phosphine sulfide $SPEt_3$ (1.4%; Table 1, entry 2; yields are based on the amount of PEt_3 added to the reaction mixture). However, heating the reaction to 80°C yielded selectively the ionic complex $[Rh(PEt_3)_4][HF_2]$ (**3**) as the sole rhodium compound after 16 h reaction time. Monitoring the reaction

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Table 1: Rhodium catalyzed SF_6 degradation.

$$SF_6 + PR_3 \xrightarrow[\text{HSiR'}_3 \\ \text{- FSiR'}_3\text{, F}_2\text{PR}_3\text{, H}_2]{\text{Rh-catalyst precursor}} SPR_3$$

Entry	Catalyst precursor [mol %][a]	R	$HSiR'_3$[b]	Conditions	Yield SPR_3 [%][c]	TON[d]
1	–	Et	–	80 °C, 16 h	–[e]	0
2	**1**, 2.5	Et	–	RT, 16 h	1.4	0.6
3	**1**, 2.5	Et	–	80 °C, 16 h	7.1	2.8
4	**1**, 2.5	Et	–	80 °C, 2 days	12	4.8
5	–	Et	$HSiEt_3$	80 °C,16 h	–[e]	0
6	**1**, 2.5	Et	$HSiEt_3$	RT, 16 h	5.2	2.0
7	**1**, 2.5	Et	$HSiEt_3$	80 °C, 16 h	29	12[f]
8	**1**, 2.5	Et	$HSi\mathit{i}Pr_3$	80 °C, 16 h	27	11
9	**1**, 2.5	Et	$HSi(OEt)_3$	80 °C, 16 h	0.9	0.4
10	**1**, 0.2	Et	$HSiEt_3$	80 °C, 16 h	9.4	48
11	**1**, 0.2	Et	$HSiEt_3$	80 °C, 2 days	12	61
12	**1**, 0.2	Et	$HSiEt_3$	80 °C, 5 days	15	76
13	**1**, 0.2[g]	Et	$HSiEt_3$	80 °C, 16 h	9.3	47
14	**1**, 2.5	Me	$HSiEt_3$	80 °C, 16 h	36[h]	14[f]
15	**1**, 0.2	Me	$HSiEt_3$	80 °C, 2 days	17[h]	86
16	**1**, 2.5	$\mathit{i}Pr_3$	$HSiEt_3$	80 °C, 16 h	14	5.6
17	**1**, 0.2	$\mathit{i}Pr_3$	$HSiEt_3$	80 °C, 2 days	0.4	2.2
18	**1**, 2.5	*t*Bu	$HSiEt_3$	80 °C, 16 h	2.9[i]	1.1
19	**1**, 0.2	*t*Bu	$HSiEt_3$	80 °C, 2 days	0.4[i]	2.0
20	**1**, 2.5	Ph	$HSiEt_3$	80 °C, 16 h	6.4[i]	2.6
21	**1**, 0.2	Ph	$HSiEt_3$	80 °C, 2 days	1.6[i]	8.2
22	**6**, 2.5	Et	$HSiEt_3$	80 °C, 16 h	29	12[f]
23	**6**, 0.2	Et	$HSiEt_3$	80 °C, 2 days	8.4	42
24	**6**, 0.2	Et	$HSiEt_3$	80 °C, 5 days	17	86
25	KHF_2	Et	$HSiEt_3$	80 °C, 16 h	–[e]	0

[a] Experiments were performed under 1 atm of SF_6 gas in [D_8]toluene as solvent. Typically, 0.9–3.1 mmol PR_3 were used; see the Supporting Information for experimental details. The mol % catalyst precursor based on the amount of PR_3 added. [b] Equivalent amounts of the hydrogen source and PR_3 were used. [c] Yields of SPR_3 are based on the amount of PR_3 used and were determined from ^{31}P NMR spectra by integration of product resonance signals versus the external standard, using an inverse gated ^1H decoupling pulse sequence. [d] TON = amount of SPR_3 (mol)/amount of Rh catalyst (mol); The amount of SPR_3 was calculated based on the amount of PR_3 used. [e] No reaction observed. [f] Complete conversion of $HSiEt_3$ to $FSiEt_3$ observed. [g] Neohexene added (1 equiv based on the amount of PEt_3). [h] $SPMe_3$ precipitated in part from the reaction mixture; the yield was determined from ^{31}P NMR spectra by integration of product resonances versus the external standard to determine the consumption of PMe_3, taking into account the generation of F_2PMe_3. [i] No formation of F_2PR_3 observed.

by NMR spectroscopy reveals that **3** is formed initially. This suggests that complex **3** actually serves as a catalyst precursor.

In addition, the formation of $SPEt_3$ (7.1 %), as the only sulfur containing species, and the generation of F_2PEt_3 (18 %) were observed (Scheme 1, Figure 1; Table 1, entry 3). The relatively large amount of $SPEt_3$ indicates that the S–F activation is catalytic with respect to the SF_6 molecules which are converted, with a TON of 2.8 (TON = mol of $SPEt_3$/mol of **1**). The yield of $SPEt_3$ can be increased by longer reaction times. Thus, after 2 days, 12 % $SPEt_3$ were formed, which is equivalent to a TON of 4.8 for the degradation of SF_6 molecules (Table 1, entry 4).

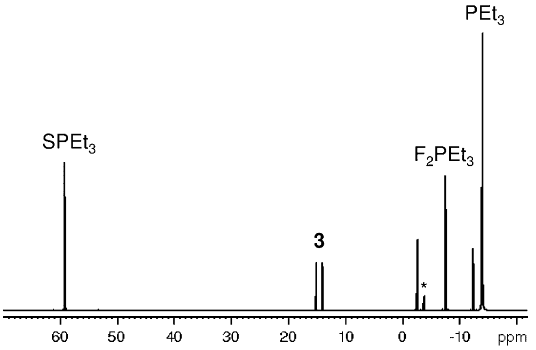
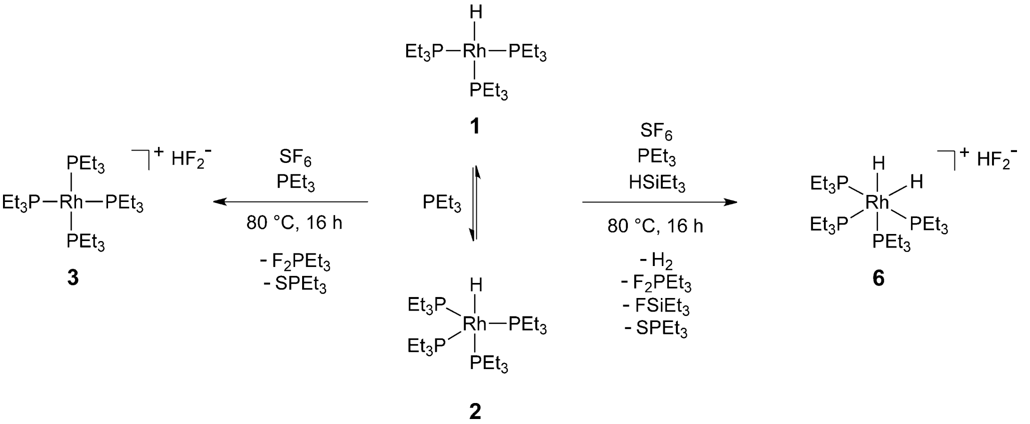


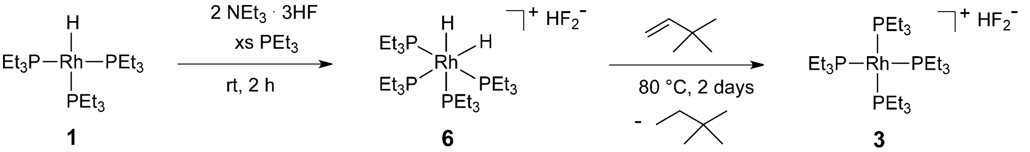
Figure 1. $^{31}P\{^1H\}$ NMR spectrum of the catalytic reaction of SF_6 with PEt_3; after 16 h reaction time at 80 °C (Table 1, entry 3); * = $P(C_6H_5F)_3$ (external standard).

Complex **3** was synthesized in an independent manner. The reaction of **1** with 2 equivalents $NEt_3{\cdot}3\,HF$ in the presence of an excess PEt_3 gave $[Rh(H)_2(PEt_3)_4][HF_2]$ (**6**) in 79 % yield after 2 h at room temperature (Scheme 2).[26–28] Subsequent treatment of **6** with neohexene resulted in the formation of **3**. The complexes **3** and **6** were characterized by NMR and IR spectroscopy as well as by liquid-injection field desorption ionization mass spectrometry (LIFDI-MS). LIFDI-MS data for complex **6** revealed a peak at *m*/*z* 577.28 which can be assigned to the molecular ion $[M]^+$ and a peak at *m*/*z* 459.25 which corresponds to the molecular ion $[M^+\text{-}PEt_3]$. The $^{31}P\{^1H\}$ NMR spectrum of **6** displays two signals at $\delta =$ 25.0 ppm and 9.3 ppm with the expected doublet of triplets splitting pattern in a 1:1 ratio, consistent with a *cis*-configuration of the hydrido ligands at the metal center. The phosphorus–rhodium coupling constants are 98.6 Hz and 86.6 Hz, typical for a rhodium center in the +III oxidation state.[25,29] In the ^1H NMR spectrum of **6**, the resonance for the hydrido ligands appears as a multiplet at $\delta = -12.04$ ppm. It simplifies to a doublet in the phosphorus decoupled spectrum ($^1J_{H,Rh} = 11.2$ Hz), which confirms the mononuclear structure of **6**. For the $[HF_2]^-$ counter anion in **6** a characteristic broad resonance is found in the ^1H NMR spectrum at $\delta = 12.14$ ppm and in the ^{19}F NMR spectrum at $\delta = -173.2$ ppm.[30–32] The IR spectrum of **6** showed characteristic broad bands at 2720 and 1777 cm^{-1}. Both frequencies are close to those found in simple bifluoride salts and can be assigned to the $[HF_2]^-$ ion.[31–34] Compound **3** is only stable in solution and in the presence of free PEt_3. The cation $[Rh(PEt_3)_4]^+$ was described before.[35]

To increase the efficiency of the catalytic process, silanes were added to the reaction mixture as a hydrogen source and fluoride scavenger. Silanes reconvert fluorido complexes into hydrido species.[25,36–38] Initial reactivity studies at **1** revealed that the complex reacts with $HSiEt_3$ to form the dihydrido silyl complex *cis*-*fac*-$[Rh(H)_2(SiEt_3)(PEt_3)_3]$ (**7**).[39] However, in the presence of an excess PEt_3 a reductive elimination of the silane occurred immediately to yield the hydrido compound **2**. Clearly **7** is not an active species in the catalytic cycle, but can serve as a resting state. Complex **7** was characterized in solution by NMR spectroscopy, as it loses $HSiEt_3$ already in vacuo. The complex is fluxional on the NMR time-scale as it was found for the structurally related



Scheme 1. Catalytic Degradation of SF_6 at $[Rh(H)(PEt_3)_3]$ (**1**). Left: Reaction in the presence of PEt_3; Table 1, entry 3; Reaction conditions: 78 μmol **1**, 3.1 mmol PEt_3, 1 atm SF_6, solvent: [D$_8$]toluene. Right: Reaction in the presence of PEt_3 and $HSiEt_3$; Table 1, entry 7; Reaction conditions: 32 μmol **1**, 1.3 mmol PEt_3, 1.3 mmol $HSiEt_3$, 1 atm SF_6, solvent: [D$_8$]toluene.



Scheme 2. Independent synthesis of the precatalysts **3** and **6**.

complex *cis-fac*-$[Rh(H)_2(SiPh_3)(PEt_3)_3]$,[25,29] which exhibits NMR spectroscopic data that are comparable to those of **7** (see the Supporting Information).

The reaction of SF_6 with PEt_3 and $HSiEt_3$ in the presence of 2.5 mol% **1** gave selectively $SPEt_3$ as the only sulfur-containing product in 29% yield after 16 h at 80°C, equivalent to a TON of 12 based on the decomposition of SF_6 molecules (Scheme 1, Figure 2; Table 1, entry 7). $FSiEt_3$ (>99%) and F_2PEt_3 (30%) were generated concomitantly along with the formation of H_2. The ionic rhodium(III) dihydrido complex $[Rh(H)_2(PEt_3)_4][HF_2]$ (**6**) was detected as the sole organometallic species. Note that the reaction proceeded with a lower selectively by using a ratio of $HSiEt_3$ and PEt_3 which is not 1:1. The TON is then limited by the amount of hydrosilane used, because it is entirely converted into $FSiEt_3$. However, on employment of a lower catalyst loading of 0.2 mol% **1** a TON of 48 was achieved after 16 h at 80°C (Table 1, entry 10). Furthermore, a remarkable increase in the conversion was observed after 2 days and 5 days reaction time to give TON of 61 and 76, respectively (Table 1, entries 11,12). Adding neohexene as trapping agent for the formed H_2 has a negligible effect on the conversion to give $SPEt_3$ in 9.3% yield with a TON of 47 after 16 h at 80°C (Table 1, entry 13). No decomposition of SF_6 was observed without rhodium catalyst (Table 1, entries 1,5,25), which indicates that the S–F activation and conversion of SF_6 proceeds at the rhodium center. In addition, SF_6 does not react with KHF_2, the $[HF_2]^-$ ion being the anion in **3** and **6** (Table 1, entry 25).

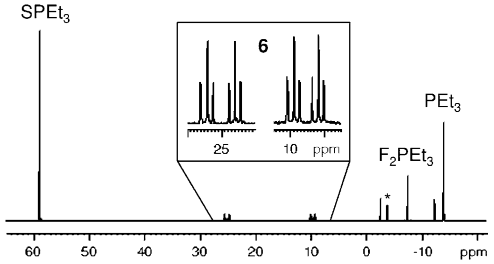


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of the rhodium-catalyzed reaction of SF_6 with PEt_3 and $HSiEt_3$; after 16 h reaction time at 80°C (Table 1, entry 7); * = $P(C_6H_5F)_3$ (external standard).

Note that in our previous study on employing binuclear rhodium compounds for SF_6 activation[22] the cleavage of the sulfur–rhodium bonds turned out to be a major restriction to accomplish a catalytic pathway. We attributed this to the bridging sulfur atom between two rhodium centers at $[Rh_2(\mu\text{-}H)(\mu\text{-}SSiEt_3)(dippp)_2]$, which makes the rhodium–sulfur interaction very stable. We therefore assume that reactions at cationic rhodium centers, such as in **3** or **6**, do not lead to binuclear sulfide species, which might hamper a catalytic turnover. Indeed, further studies revealed that the ionic complex **6** is also able to catalyze the degradation of SF_6 with $HSiEt_3$ and PEt_3. The reaction proceeded also selectively to yield H_2 as well as F_2PEt_3, $FSiEt_3$, and $SPEt_3$ as the only SF_6 decomposition products. By using 2.5 mol% of **6**, the TON for the $SPEt_3$ formation after 16 h at 80°C was 12 (Table 1, entry 22), which is identical to the reaction with **1** as catalyst precursor (Table 1, entry 7). By employing 0.2 mol% of **6** a higher TON of 86 was achieved (Table 1, entry 24). Note that no intermediates were observed by NMR spectroscopy during the reaction. As above for the reactions without silane, we assume that **3** is formed initially.

For a possible enhancement of the catalytic SF_6 activation, we investigated other silanes as hydrogen sources. With 2.5 mol% of **1**, SF_6 was treated with PEt_3 and either with HSi*i*Pr$_3$ or $HSi(OEt)_3$. The reaction with HSi*i*Pr$_3$ (Table 1, entry 8) proceeded slightly worse than with $HSiEt_3$ (Table 1, entry 7) to give $SPEt_3$ in 27% yield with a TON of 11. By using $HSi(OEt)_3$ the yield of $SPEt_3$ decreased dramatically to 0.9% (TON 0.4; Table 1, entry 9). In addition, treatment with gaseous H_2 resulted in a low conversion (TON 1.3) as well, consistent with the fact that H_2 is also formed during the reaction. Moreover, we also tested a variety of different phosphines PR_3 ($R = Me$, *i*Pr, *t*Bu, Ph) as alternative sulfur-trapping agents. The reactions were accomplished in the presence of $HSiEt_3$, which turned out to be the best suitable hydrogen source, and catalyst loadings of 2.5 mol% **1** as well as 0.2 mol% **1** (Table 1, entries 14–21). Before adding SF_6 to the reaction mixtures, the exchange of the rhodium-bound PEt_3 ligands and the added phosphines PR_3 ($R = Me$, *i*Pr, *t*Bu, Ph) at the metal center was detected by NMR spectroscopy, resulting in the formation of a number of organometallic species as well as of PEt_3. All reactions gave the corresponding phosphine sulfides SPR_3 as the major sulfur-containing products.[40] Minor amounts of $SPEt_3$ were also obtained, which originate from the catalyst precursor **1**. $FSiEt_3$ and H_2 were formed in all cases, whereas the generation of the fluorophosphoranes F_2PR_3 was only found in the reactions with PEt_3, PMe_3, and $PiPr_3$. Interestingly, the steric demand of the alkyl phosphines plays a certain role (Table 1, entries 7,10–19). Thus, the TON increased in the order $PtBu_3 < PiPr_3 < PEt_3 < PMe_3$. The maximum TON of 86 was achieved in the reaction of SF_6 with PMe_3 and $HSiEt_3$ in the presence of 0.2 mol% **1** (entry 15). The reactions with PPh_3 (Table 1, entries 20,21) do not follow this trend, presumably due to the different electronic properties of the aromatic phosphine compared to the alkyl phosphines.

In conclusion, we have shown that rhodium(I) complexes effectively catalyze the degradation and transformation of SF_6. A chemical activation of a SF_6 molecule generally requires strong reductive conditions and often involves single-electron transfer steps to give SF_5^- and a fluoride ion.[5,8,19–22,41,42] Mechanistically, we therefore suggest a pre-coordination of SF_6 through one or more fluorine atoms at a cationic rhodium species which originates from **3**, because such an interaction is facilitated at a cationic fragment. The complexes **1**, **2**, **6**, and **7** can serve as catalyst precursors and/or resting states. In a subsequent step it is conceivable that the first S–F bond is cleaved by an inner-sphere electron transfer. After the first S–F bond cleavage step a rapid degradation of the SF_x ($x = 1$–5) moieties might occur in the coordination sphere of the metal to give initially rhodium fluorido and sulfido species. The sulfido species are then converted into an active compound to react with the next SF_6 molecule by the formation of phosphine sulfides, fluorophosphoranes, and fluorosilanes. Compared to the reactions which proceed heterogeneously, the developed catalytic conversions are distinguished by the mild reaction conditions, low catalyst loadings, and high selectivity. Furthermore, the SF_6 decomposition products are non-gaseous and much less toxic.

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Keywords: cationic complexes · rhodium · S–F activation · sulfur hexafluoride · transition-metal catalysis

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