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Carbon–Fluorine Bond Activation

Catalytic C–F Bond Activation of Hexafluoropropene by Rhodium: Formation of (3,3,3-Trifluoropropyl)silanes**

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Dedicated to Professor Helge Willner on the occasion of his 60th birthday

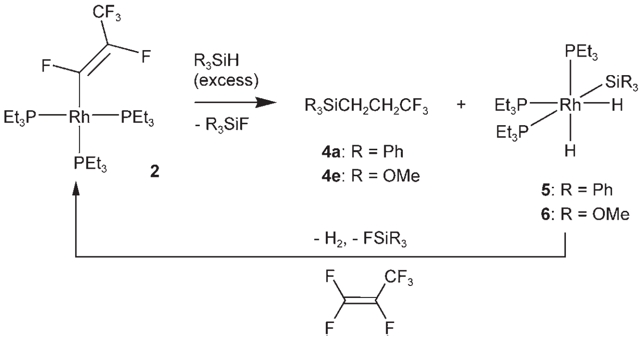
The activation of carbon–fluorine bonds by transition-metal centers is an established process in organometallic chemistry.[1] Current interests include the development of new routes to higher-value fluorinated compounds from easily accessible precursors. The strategy involves the selective cleavage of a C–F bond in a highly fluorinated substrate to obtain fluorinated building blocks that then can be functionalized further in the coordination sphere of the metal.[1,2] There have been striking advances in the synthesis of fluorinated molecules using C–F activation reactions, but catalytic reactions are still rare. The transformations include a very limited number of cross-coupling reactions.[3,4] In another exceptional example, carbon–silicon bonds are formed by catalytic conversions of functionalized fluorobenzenes, such as fluoroacetophenones or (fluorophenyl)oxazolines, with hexamethyldisilane using $[Rh(cod)_2]BF_4$ as catalyst (cod = cyclooctadiene).[5] Most of the other examples that have been reported involve simple hydrodefluorination steps.[1,2]

Very little has been reported on stoichiometric or even catalytic transformations that involve the cleavage of a C–F bond in a fluorinated olefin.[1,4,6–8] Again, almost all of the reactions involve hydrodefluorinations. The only exception involves a palladium-catalyzed cross-coupling reaction of 1,1-difluoro-2-naphtylpropene with [(tolyl)ZnCl] to give mono- and ditolyl derivatives.[4] Holland and co-workers showed that hexafluoropropene can be converted catalytically into a mixture of pentafluoropropenes with a turnover number (TON) of 9.8.[7] Here, a diketiminate iron(II) fluoro complex served as the catalyst. In a very recent example, Peterson and McNeill reported on the rhodium-catalyzed hydrodehalogenation of vinylfluoride or chlorofluoroethylenes in the presence of $HSiEt_3$ to give ethane with comparable TONs.[8]

We have already shown that hexafluoropropene can be converted into 1,1,1-trifluoropropene by using dihydrogen as hydrogen source, but the transformation was not catalytic.[9,10] The hydrodefluorination reaction is based on the activation of hexafluoropropene by $[RhH(PEt_3)_3]$ (**1a**) to yield the rhodium derivative $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**2**). The latter complex reacts with dihydrogen to give 1,1,1-trifluoropropene and the fluoro complex $[RhF(PEt_3)_3]$ (**3**).

Herein we present our results on the reactivity of **2** with tertiary silanes. The studies led to the development of a catalytic process for the conversion of hexafluoropropene into (3,3,3-trifluoropropyl)silanes by C–F bond activation. The reactions proceed at room temperature with good TONs and are very selective. They are unique in that 1) they involve a rare catalytic C–F bond activation of a fluorinated alkene, and 2) the catalytic cycle, along with the hydrodefluorination steps, involves the formation of a C–Si bond.

Treatment of a solution of **2** with an excess Ph_3SiH led to the selective formation of the (3,3,3-trifluoropropyl)silane **4a** and the dihydridosilyl complex *cis-fac*-$[Rh(H)_2(SiPh_3)(PEt_3)_3]$ (**5**)[10] (Scheme 1). An experiment with substoichiometric amounts of Ph_3SiH also gave selectively the silane **4a** and complex **5**, but the starting compound **2** was still present.



Scheme 1. Reactivity of **2** towards silanes.

As **5** is in equilibrium with **1a**, it can be used as the starting compound for the C–F bond activation of hexafluoropropene (Scheme 1).[10] Based on these results, we could develop catalytic cycles for the formation of trifluoropropylsilanes from hexafluoropropene. In an initial experiment we investigated the reaction of hexafluoropropene with an excess of Ph_3SiH in the presence of **2** as catalytic precursor (0.7% based on the amount of silane). We observed a selective transformation of hexafluoropropene into **4a** at room temperature

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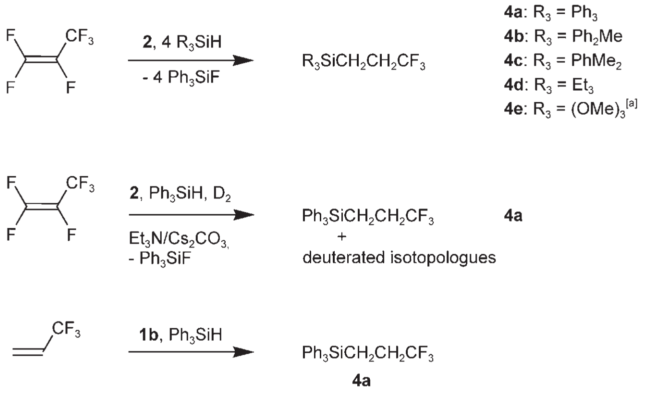
with a TON of 90 based on the amounts of (3,3,3-trifluoropropyl)silane **4a** produced (Scheme 2, Table 1). The silane **4a** was characterized by NMR spectroscopy, mass spectrometry and elemental analysis.[11] The ^1H NMR spectrum shows two signals of higher order for the methylene groups at $\delta = 1.57$ and 2.13 ppm. The signals can be properly simulated as AA′ and BB′ parts of an AA′BB′X_3 spin system (see the Supporting Information).[12] Ph_2MeSiH and $PhMe_2SiH$ can also be used in comparable transformations to give the (3,3,3-trifluoropropyl)silanes **4b** and **4c** with a TON of 35 for both catalytic cycles. Et_3SiH converts into **4d**, whereas no reaction was observed for *i*Pr_3SiH (Table 1).



Scheme 2. Catalytic derivatization of fluorinated alkenes; [a] Et_3N/Cs_2CO_3 was added.

Table 1: Catalytic formation of (3,3,3-trifluorpropyl)silanes from hexafluoropropene.

Entry	Substrate	Product	TON
1	$HSiPh_3$	**4a**	90
2[a]	$HSiPh_3/H_2$	**4a**	54
3	$HSiPh_2Me$	**4b**	35
4	$HSiPhMe_2$	**4c**	35
5	$HSiEt_3$	**4d**	12
6	$HSi(OMe)_3$	**4e**	2.5
7[a]	$HSi(OMe)_3$	**4e**	15

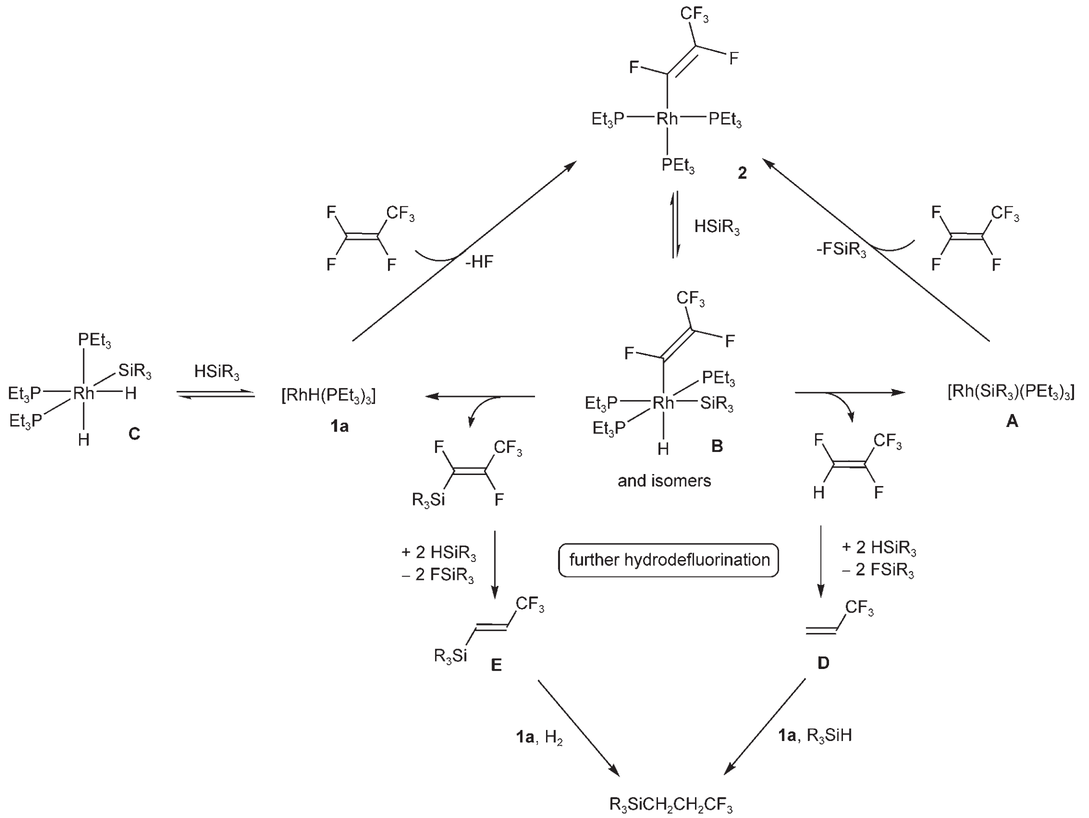
[a] Base added: NEt_3/Cs_2CO_3.

To further test the limits of this catalytic route, we checked the reactivity of **2** towards the electronically very different silane $(MeO)_3SiH$.[13] In a stoichiometric experiment we found that on treatment of **2** with $(MeO)_3SiH$, the trifluoropropylsilane **4e** and the hydrido complex *cis-fac*-$[Rh(H)_2\{Si(OMe)_3\}(PEt_3)_3]$ (**6**) were generated (Scheme 1). Complex **6** can be synthesized through an independent reaction pathway by treatment of the hydride **1a** with $(MeO)_3SiH$. The rhodium–phosphorus coupling constants in the ^{31}P NMR spectra of **6**, as well as a T_1 relaxation time of 1.2 s at 300 K (600 MHz) for the hydride nuclei (^1H NMR: $\delta = -11.34$ ppm), suggest the presence of classical hydrido ligands at a Rh^{III} center.[14] A catalytic experiment showed that **2** can also be used as a catalytic precursor to convert hexafluoropropene into **4e** in the presence of $(MeO)_3SiH$, but the TONs were very low (2.5). However, addition of the bases Et_3N/Cs_2CO_3 led to a TON of 15 for the conversion of hexafluoropropene into **4e** (Scheme 2, Table 1).

Mechanistically, the C–F bond activation steps might be induced by the Rh^I hydrido species $[RhH(PEt_3)_3]$ (**1a**) or by a Rh^I silyl species $[Rh(SiR_3)(PEt_3)_3]$ (**A**; Scheme 3). Both complexes should be capable to form products from C–F bond activation such as **2** along with HF or fluorosilane, respectively.[9,15] The mechanism of the C–F bond activation steps is, as yet, not clear. It might involve an oxidative addition of a C–F bond or an olefin-insertion/β-fluorine-elimination pathway.[1,6f,10,15,16] However, oxidative addition of tertiary silanes to the Rh^I propenyl intermediates leads to Rh^{III} hydrido complexes. In the case of **2** this complex would be an isomer of **B** (Scheme 3). After reductive elimination of the less-fluorinated alkene, both reaction cycles are completed by generation of either **1a** or **A**. The former can be in equilibrium with dihydridosilyl species **C** (for example, **5** or **6**) which can be considered as resting states of the catalytic system. In a final step, after three defluorination reactions, a hydrogenation of 3,3,3-trifluoropropene **D** or hydrosilylation of the silylalkene **E** occurs (Scheme 3). The fact that the catalytic reactions are very selective and that only the trifluoropropane with one silyl group was formed might indicate that at least two C–F bond activation steps are followed by a reductive elimination of a C–H bond to give the silyl species $[Rh(SiR_3)(PEt_3)_3]$ (**A**). Finally we note that complexes such as *cis-mer*-$[Rh(H)_2\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$[9] can be produced from **2** and H_2, and these complexes may play a minor role in the catalytic conversions.

Dihydrogen can be formed within the catalytic cycle either by reaction of HF with free tertiary silane to give fluorosilane or by reaction of HF with the hydride **1a** to give the fluoro complex $[RhF(PEt_3)_3]$ (**3**). In principle **1a** can be regenerated from **3** by reaction of **3** with a tertiary silane.[10,17] We have no indication that *cis-fac*-$[Rh(H)_2(SiPh_3)(PEt_3)_3]$ (**5**) serves as dihydrogen source because we did not observe any loss of H_2 from **5** in stoichiometric experiments. Instead **5** was found to liberate only Ph_3SiH.

To determine the possible influence of H_2 on the catalytic transformations, we studied the catalytic activity of **2** towards hexafluoropropene in the presence of H_2 *and* Ph_3SiH. The conversions were performed in benzene at room temperature in the presence of the bases Et_3N/Cs_2CO_3 to trap the HF that may have been generated. We obtained selectively the silane **4a** together with Ph_3SiF as the only fluorinated products (Scheme 2) with a TON of 54 based on the formation of **4a**. We did not observe the generation of propane or 1,1,1-trifluoropropane, which suggests that no hydrogenation of 3,3,3-trifluoropropene occurred. The use of D_2 instead of H_2 resulted in the formation of considerable amounts of **4a**, but also of several deuterated isotopologues of **4a**, which were not characterized. The ^2H spectrum also reveals deuterium exchange between the free silane and D_2, as indicated by the presence of Ph_3SiD. Nevertheless, D_2 might play a particular role in the catalytic cycle either in the hydrodefluorination steps or in a hydrogenation reaction of a silyl derivative of 3,3,3-trifluoropropene. The generation of the nondeuterated compound **4a** is remarkable and indicates that the hydrosilylation of 3,3,3-trifluoropropene is an important step.



Scheme 3. Possible reaction pathways for the formation of (3,3,3-trifluoroproyl)silanes from hexafluoropropene.

Indeed, in an independent experiment we showed that $[RhH(PEt_3)_4]$ (**1b**) can serve as a catalyst for the hydrosilylation of 3,3,3-trifluoropropene, and silane **4a** was obtained with a TON of 138 (unoptimized, Scheme 2).

In conclusion, we have reported the catalytic conversion of hexafluoropropene and tertiary silanes to give (3,3,3-trifluoropropyl)silanes. The reactions proceed at room temperature with reasonable TONs and are highly selective. According to the NMR spectroscopic data, hexafluoropropene is converted quantitatively into the (3,3,3-trifluoropropyl)silanes. The conversions also represent the first catalytic C–F bond activation of a highly fluorinated alkene that does not result in simple hydrodefluorination products. Instead higher-value fluorinated compounds are formed. We propose that the defluorination of hexafluoropropene initially results in either 3,3,3-trifluoropropene or a silyl derivative of 3,3,3-trifluoropropene by replacement of the fluorine with a hydrogen or silicon atom. These defluorination reactions are coupled consecutively with a catalytic hydrosilylation or hydrogenation reaction. Notably the transformation can be applied for electronically very different silanes such as Ph_3SiH, Et_3SiH, and $(MeO)_3SiH$. The product **4e** is used as starting compound for the formation of aerogels and polysilsesquioxanes.[18]

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