Chemical Science

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Cite this: *Chem. Sci.*, 2015, **6**, 4255

Consecutive C–F bond activation and C–F bond formation of heteroaromatics at rhodium: the peculiar role of $FSi(OEt)_3$†

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Received 10th March 2015
Accepted 9th May 2015

DOI: 10.1039/c5sc00877h

www.rsc.org/chemicalscience

C–F activation of 2,3,5,6-tetrafluoropyridine at $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ (**1**) yields $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) and $FSi(OEt)_3$, but in an unprecedented consecutive reaction $FSi(OEt)_3$ acts as a fluoride source to give $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**) by regeneration of the C–F bond and C–H activation. Analogous refluorination steps were observed for other 2-pyridyl rhodium complexes. NMR spectroscopic studies revealed a delicate balance between the feasibility for C–F bond formation accompanied by a C–H activation and the occurrence of competing reactions such as hydrodefluorinations induced by the intermediary presence of H_2.

Introduction

Fluorinated organic compounds are of considerable interest because of their wide range of applications in materials science and medicine.[1] Therefore, there is a strong demand to access new fluorinated building blocks, but there is also enormous interest regarding their reactivity. Transition-metal-mediated routes to fluoroorganics often involve fluorination of non-fluorinated precursors[2] or selective C–F bond cleavage reactions at highly fluorinated molecules.[3] The latter approach frequently comprises the formation of metalated fluorinated entities, which can then be functionalized in the coordination sphere of the transition metal *via* very sophisticated reaction pathways.[3] C–F bond activation steps are often challenged by the particularly high strength of the C–F bond.[4] One requirement to achieve the C–F bond cleavage is, therefore, the formation of very stable element–fluorine bonds, such as H–F, B–F, Al–F or Si–F bonds.[3m–r] Thus, suitable metal complexes for an initial activation step might possess hydrido, boryl or silyl ligands which react with highly fluorinated organics to yield HF, fluoroboranes or fluorosilanes and the metal complex bearing the fluorinated organyl ligand.[3l]

Another important issue in C–F bond activations can be their regio- and chemoselectivity. Often there is a preference of C–H activation over C–F activation, but there are also a considerable number of examples in which a C–F bond is cleaved in the presence of a C–H bond.[3,5] Previously, we reported that the rhodium(I) complexes $[RhH(PEt_3)_3]$ (**6**), $[Rh(Bpin)(PEt_3)_3]$ (HBpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane, pinacolborane) and $[Rh\{Si(OR)_3\}(PEt_3)_3]$ (R = Me, Et) are useful starting compounds for various C–F bond activation reactions.[6] For instance, $[RhH(PEt_3)_3]$ (**6**) reacted with pentafluoropyridine to give $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**4**) by C–F activation at the 4-position,[6e] whereas conversions with $[Rh(Bpin)(PEt_3)_3]$ and $[Rh\{Si(OR)_3\}(PEt_3)_3]$ (R = Me, **1**: R = Et) resulted in an activation at the 2-position to yield $[Rh(2\text{-}C_5NF_4)(PEt_3)_3]$.[6f,g] DFT calculations on the activation in the model compounds $[Rh(Bpin)(PMe_3)_3]$ and $[Rh\{Si(OMe)_3\}(PMe_3)_3]$ suggested a ligand-assisted reaction pathway, which involves a direct transfer of fluorine to the boron or silicon centers *via* four-membered transition states. For $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ (**1**) a phosphine dissociation seemed to occur prior to the C–F activation step. However, treatment of $[RhH(PEt_3)_3]$ (**6**) or $[Rh(Bpin)(PEt_3)_3]$ with 2,3,5,6-tetrafluoropyridine selectively led to $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**4**) by C–H activation. In contrast, $[Rh\{Si(OR)_3\}(PEt_3)_3]$ (R = Me, **1**: R = Et) reacted with 2,3,5,6-tetrafluoropyridine exclusively by a C–F activation at the 2-position to afford $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) and fluorosilane.[6e–g] Earlier, Marder and Perutz *et al.* observed, in a reaction of 2,3,5,6-tetrafluoropyridine with $[Rh(SiPh_3)(PMe_3)_3]$, C–F activation at the *ortho*-position as well as C–H activation accompanied with the formation of $FSiPh_3$ and $HSiPh_3$ in a nearly 1 : 1 ratio. The resulting products were stable towards $FSiPh_3$.[5f]

Herein we report on the very peculiar role of $FSi(OEt)_3$ in C–F bond activation and C–F bond formation reactions of fluorinated pyridines at Rh. Although the promotion of C–F activation steps by the generation of fluorosilanes is well known, a consecutive refluorination with the fluorosilane as a fluoride source is unprecedented. Formally, this Si–F activation sets back the C–F activation process with consequences for the overall chemoselectivity of bond activation reactions at fluorinated heteroaromatics. Such a reversion of a C–F activation step

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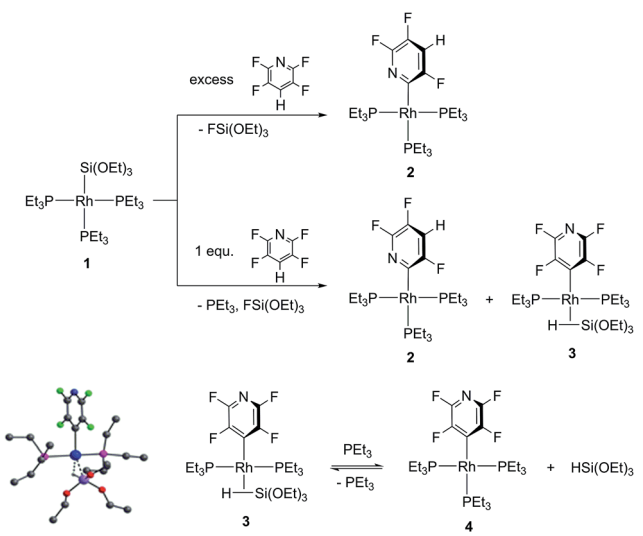
† Electronic supplementary information (ESI) available: Experimental procedures, additional spectra and computational details. See DOI: 10.1039/c5sc00877h

at a highly fluorinated aromatic ligand is unique and has never been considered before.[3,7]

Results and discussion

Treatment of $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ (**1**) with stoichiometric amounts of 2,3,5,6-tetrafluoropyridine at room temperature yielded the C–F activation product $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) as well as approximately 10% of the non-classical silane complex $[Rh(4\text{-}C_5F_4N)\{\eta^2\text{-}HSi(OEt)_3\}(PEt_3)_2]$ (**3**) by C–H activation (Scheme 1). Traces of $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**) were also present; this compound was previously synthesized and also characterized by X-ray crystallography.[6e] The activation of 2,3,5,6-tetrafluoropyridine at the *ortho* position might occur *via* a similar silyl ligand-assisted pathway as stated above. However, a slight excess of 2,3,5,6-tetrafluoropyridine led to the generation of **2** only.[6g] An independent reaction revealed that complex **4** reacts with $HSi(OEt_3)_3$ to give $[Rh(4\text{-}C_5F_4N)\{\eta^2\text{-}HSi(OEt)_3\}(PEt_3)_2]$ (**3**) and free phosphine. Addition of an excess of PEt_3 to the reaction solution of **3** led to the regeneration of **4** (Scheme 1).

Complex **3** could not be isolated in a pure form, because of the presence of **4**, and was characterized *via* NMR spectroscopy only. For the hydrogen atom of the metal-bound silane $HSi(OEt)_3$ a multiplet at $\delta = -12.9$ ppm was observed in the ^1H NMR spectrum. ^{19}F decoupling experiments revealed a doublet of triplets with a coupling constant of 20 Hz to the rhodium atom and a coupling constant of 14 Hz to the phosphorus atoms. The $^{29}Si,^1H$ HMBC NMR spectrum exhibited a resonance at $\delta = -39$ ppm in the ^{29}Si domain, which correlates to the signals of the Si–H hydrogen and the CH_2 groups of the ethoxy moieties. The spectrum revealed a hydrogen–silicon coupling constant of 65 Hz which is typical for non-classical silane complexes.[8] DFT calculations were performed to model the structure of **3** which is depicted in Scheme 1. The calculations confirmed the assignment as a η^2-silane complex and revealed a Si–H distance of 1.824 Å.



Scheme 1 Reactivity of **1** towards 2,3,5,6-tetrafluoropyridine to yield **2** and **3**. Computed structure of **3**; hydrogen atoms of the Et groups are omitted for clarity.

Remarkably, the NMR spectra of the mixture of the complexes $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**), phosphine, triethoxyfluorosilane and $[Rh(4\text{-}C_5F_4N)\{\eta^2\text{-}HSi(OEt)_3(PEt_3)_2]$ (**3**), which is in equilibrium with complex $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**), after 18 h showed only distinct signals for the complex **4**. No resonances for the fluorosilane were detected. Monitoring this conversion by ^{31}P and ^{19}F NMR spectroscopy confirmed the assumption that **4** can be generated from **2** and fluorosilane. Consequently, $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ (**1**) was treated with 2,3,5,6,-tetrafluoropyridine and the volatiles (solvent and fluorosilane) were subsequently removed from the reaction mixture and a solution of phosphine in $[D_8]$-toluene was added. This led to a mixture of $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**), $[Rh(4\text{-}C_5F_4N)\{\eta^2\text{-}HSi(OEt)_3(PEt_3)_2]$ (**3**) and $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**) (80 : 8 : 12). Without the presence of fluorosilane, no conversion of **2** into **4** was observed within 3 h. However, addition of $FSi(OEt)_3$ triggered the generation of **4** from **2**, which again confirmed the involvement of fluorosilane in the fluorination reaction. Using $FSi(OMe)_3$ for the fluorination reaction also led to a conversion of **2** into **4**, whereas using $FSiEt_3$ did not. Furthermore, small amounts of hydrogen were detected by ^1H NMR spectroscopy. However, the fate of the silicon containing units was ambiguous. $^{29}Si,^1H$ HMBC NMR spectra after a reaction of **2** with $FSi(OEt)_3$ confirmed the formation of $Si(OEt)_4$, $(EtO)_3Si\text{-}OSi(OEt)_3$ and other siloxanes, which could not be further characterized. We ascribe this to a fluorination pathway proceeding *via* intermediate fluorosilicate anions, which might be formed in the presence of the glass surface of the reaction vessel. Silicate anions are known to undergo spontaneous and manifold condensation reactions.[9] Note that a conversion of **2** into **4** was considerably slower and competing reaction pathways became dominant (see below) when the reaction was performed in a PFA tube instead of a glass NMR tube.

In order to test this hypothesis and the involvement of fluorosilicate anions in the conversion of **2** into **4**, the reaction was performed in the presence of NaOEt to induce the formation of silicate anions from fluorosilane. This led to a faster conversion of **2** into **4**. After 9 h, **2** was fully consumed (Fig. 1). Additionally, the generation of $Si(OEt)_4$ was observed by NMR spectroscopy. A reaction in $[D_8]$-THF instead of $[D_8]$-toluene led to a slight increase of the reaction rate. Addition of EtOH instead of ethanolate also led to an increase of the reaction rate, but the concomitant evolution of H_2 resulted in the generation of additional hydrodefluorination products (29%, see also below).[10] The use of ethanol-D_6 led to the formation of $Si(OEt)_3(OCD_2CD_3)$, as was evident from a ^2H NMR spectrum.

The formation of hydrogen was only observed at the beginning of the fluorination reaction, because it undergoes a number of subsequent reactions (Scheme 2). (i) The complex $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**) and H_2 are in equilibrium with the oxidative addition product $[Rh(H)_2(4\text{-}C_5F_4N)(PEt_3)_3]$ (**5**), which was identified in the reaction solution.[6d] (ii) Complex **5** can release 2,3,5,6-tetrafluoropyridine and form $[RhH(PEt_3)_3]$ (**6**), which explains the detection of small amounts of 2,3,5,6-tetrafluoropyridine. (iii) In a reaction competing with the generation

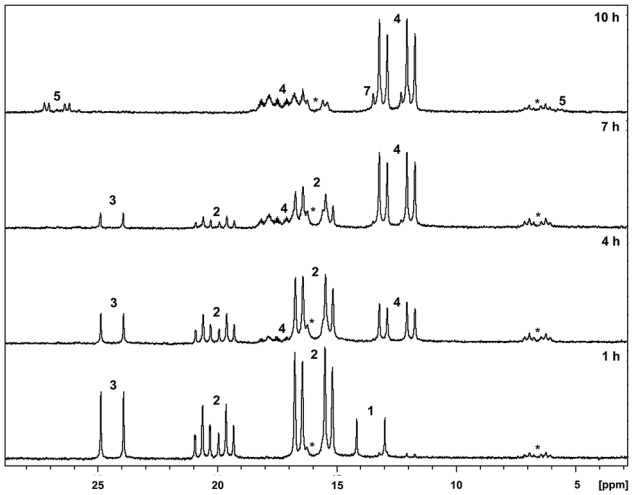
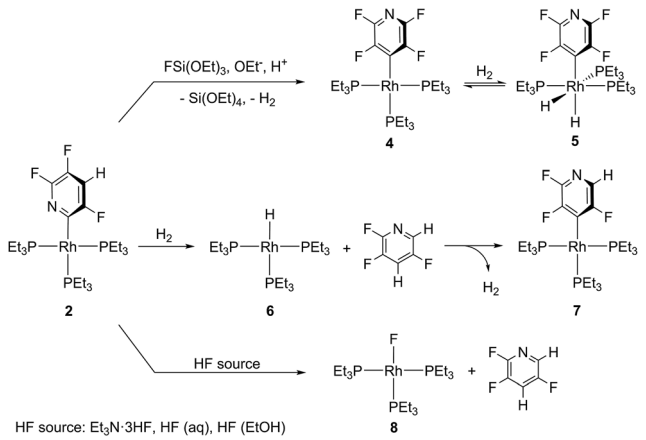
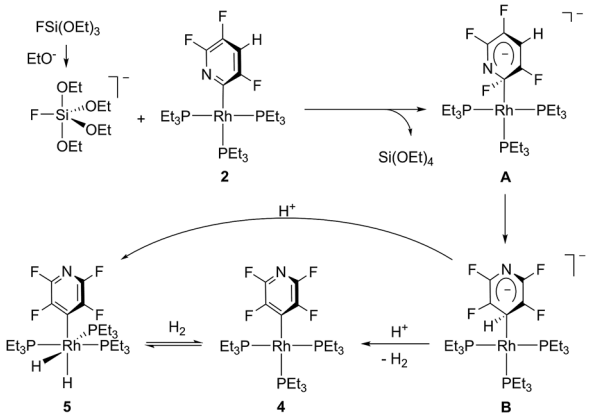


Fig. 1 Parts of the $^{31}P\{^{1}H\}$ NMR spectra (121.5 MHz in $[D_8]$toluene) which reveal the fluorination of **2** in the presence of $FSi(OEt)_3$ and NaOEt to yield **4**. In side reactions **5**, **7** and *cis,fac*-$[Rh(H)_2\{Si(OEt)_3\}(PEt_3)_3]$ (*) were formed.



Scheme 2 Reactivity of **2** towards $FSi(OEt)_3$, H_2 and HF.

of **4** from $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**), the formation of $[Rh\{4\text{-}(2,3,5\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**7**) was observed, which can be explained by a reaction **2** with H_2 to give 2,3,5-trifluoropyridine and $[RhH(PEt_3)_3]$ (**6**), and a subsequent C–H activation at the 4-position of the 2,3,5-trifluoropyridine at **6** (Scheme 2). The reaction steps that led to the generation of **7** or 2,3,5-trifluoropyridine were confirmed by independent experiments. Note that hydrogenolysis was reported before for pentafluoropyridine to yield 2,3,5,6-tetrafluoropyridine in the presence of H_2.[6d] (iv) Finally, complex **6** might react further with $HSi(OEt)_3$, which stems from $[Rh(4\text{-}C_5F_4N)\{\eta^2\text{-}HSi(OEt)_3(PEt_3)_2]$ (**3**) to give *cis,fac*-$[Rh(H)_2\{Si(OEt)_3\}(PEt_3)_3]$.[6g] Note that the ratio of products formed in the competing reactions strongly depended on the reaction conditions. In the presence of ethanol more hydrodefluorination products were detected, whereas ethanolate favored the fluorination reaction (for product ratios and reaction conditions see ESI†).



Scheme 3 Simplified mechanistic proposal for the fluorination of **2** to yield **4**.

A proposed mechanism for the fluorination of **2** is shown in Scheme 3. Although we assume a rather complicated reaction pattern, we exemplify the fluorination process by the intermediary formation of pentacoordinated fluorosilicate anions such as $[FSi(OEt)_4]^-$. The latter might be formed by the reaction of $FSi(OEt)_3$ and OEt^- or ethanol.[11] The use of ethanol requires an additional base like PEt_3.[9c,12] For such a model a transfer of F^- to the *ortho*-carbon atom of the pyridyl ligand of $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) would yield a Meisenheimer-type intermediate **A** (Scheme 3).[13] Alternatively, the fluoride anion can be bound to the rhodium atom and then migrate to the carbon atom to give the same intermediate species **A**. In **A** the rhodium atom can migrate from the 2-position of the anionic tetrafluoropyridyl ligand to the 4-position to give **B**. Similar rearrangements, though proceeding *via* an intermediary η^2-coordination of the aromatic compounds, were observed for reversible C–H activation reactions at the nickel fluorophenyl complex $[NiH(2,3,5,6\text{-}C_6F_4H)(PEt_3)_2]$.[14] During the formation of **4** from **2** no such intermediates were observed and we suggest a sigmatropic 1,3-rearrangement as is known for allyl complexes.[15] Dihydrogen elimination by protonation with adventitious water, which might for instance be generated in condensation reactions of silicate anions,[9] gives $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**). Alternatively the hydride can migrate to the metal center and protonation yields $[Rh(H)_2(4\text{-}C_5F_4N)(PEt_3)_3]$ (**5**).

To support a possible involvement of fluorosilicate anions in the conversion of $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) into $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**), complex **2** was treated with tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF), which is a source of F^-.[16] However, the formation of compound **4** was observed only in very small amounts. In addition, 10% of $[RhF(PEt_3)_3]$ (**8**) and considerable amounts (42%) of rhodium complexes were generated, which could not be identified further.[6b] Note also, that the addition of CsF and LiF suppressed the conversion of $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) and $FSi(OEt)_3$ into $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**).

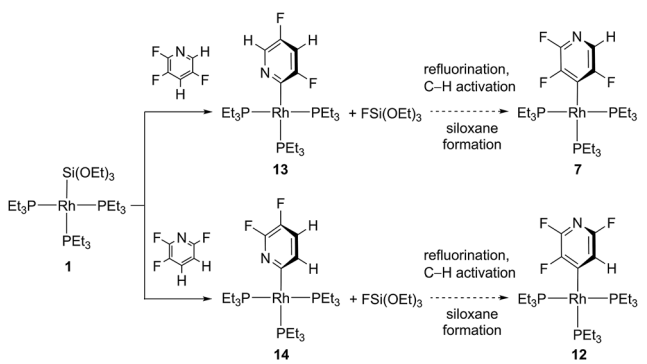
Furthermore, the possible involvement of HF in the fluorination reaction of **2** to yield **4** was elucidated. Notably, **2** did not convert to **4**, either with $NEt_3 \cdot 3HF$ or with HF in aqueous or

ethanolic solution as fluorinating agents. Instead, the generation of $[RhF(PEt_3)_3]$ (**8**) and 2,3,5-trifluoropyridine was observed (Scheme 2). In contrast, $[Rh(4\text{-}C_5F_4N)(PEt_3)_3]$ (**4**) or $[Rh\{4\text{-}(2,3,5\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**7**) showed no reactivity towards HF sources at room temperature.[17]

In order to investigate the scope of this unique fluorination reaction at $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**) further, we synthesized several fluoroaryl complexes by C–H activation at $[Rh(CH_3)(PEt_3)_3]$ (**9**).[18] On treatment with 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, 2,3,5-trifluoropyridine or 2,3,6-trifluoropyridine the complexes $[Rh(2,3,4,6\text{-}C_6F_4H)(PEt_3)_3]$ (**10**), $[Rh(2,3,5,6\text{-}C_6F_4H)(PEt_3)_3]$ (**11**), $[Rh\{4\text{-}(2,3,5\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**7**) and $[Rh\{4\text{-}(2,3,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**12**) were accessible. These were then treated with $FSi(OEt)_3$ or $FSiEt_3$ in the presence of OEt^-, but in neither case was a fluorination of the aromatic ligand observed. Apparently, a pyridyl ligand is more susceptible to fluorination than a phenyl ligand. In addition, complexes with the rhodium atom at the 2-position of the pyridyl ligand were less stable than the isomer with the aromatic ligand bound at the 4-position. Note that previous DFT calculations indicated that $[Rh(4\text{-}C_5F_4N)(PMe_3)_3]$ was 13 kcal mol^{-1} more stable than $[Rh(2\text{-}C_5F_4N)(PMe_3)_3]$.[6g]

Consequently, we synthesized pyridyl complexes that bear the metal at the 2-position of the heterocycle and are less fluorinated than $[Rh\{2\text{-}(3,5,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**2**). This can be achieved by C–F bond activation of 2,3,6- or 2,3,5-trifluoropyridine at $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ (**1**) (Scheme 4). Remarkably, the reactions led solely to the cleavage of the C–F bond at the *ortho* position to the nitrogen atom in both cases, even when C–F activation was competing with C–H activation at the 2-position.[3,5,6h,19]

$[Rh\{2\text{-}(3,5\text{-}C_5F_2H_2N)\}(PEt_3)_3]$ (**13**) and $[Rh\{2\text{-}(5,6\text{-}C_5F_2H_2N)\}(PEt_3)_3]$ (**14**) were only characterized by NMR spectroscopy, because small amounts of **7** or **12** were always present. Note that the signal for the fluorine atom at the *ortho* position to the nitrogen atom in **13** characteristically appears at low field in the ^{19}F NMR spectrum.[5a,h,6,20] However, conversions of **13** and **14** in the presence of $FSi(OEt)_3$ led to the formation of the products of fluorination $[Rh\{4\text{-}(2,3,5\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**7**) and $[Rh\{4\text{-}(2,3,6\text{-}C_5F_3HN)\}(PEt_3)_3]$ (**12**) (Scheme 4). These conversions took place at a slower rate when compared to the reaction of **2** with $FSi(OEt)_3$. This is consistent with the observation that competing hydrogenolysis reactions yielded the hydrodefluorination products $[RhH(PEt_3)_3]$ (**6**) and 3,5-difluoropyridine or 2,3-difluoropyridine before **13** and **14** were fully consumed to give **7** and **12**. However, after 21 h the generation proceeded, with up to 58% for **7** and after 15 h 68% for **12** at room temperature. Conversions of **13** or **14** in a PFA tube, or in the presence of EtOH or OEt^- proceeded with very low selectivity to give a range of products (in part unidentified), but very small amounts of **7** or **12**.



Scheme 4 C–F activation of trifluoropyridines at **1** and consecutive fluorination reactions.

Conclusion

In conclusion, we have reported the unique regeneration of C–F bonds at rhodium bound pyridyl ligands as a subsequent step after a C–F bond activation reaction. The crucial role of the fluorosilane $FSi(OEt)_3$ is peculiar and it can stimulate both C–F bond cleavage and C–F bond generation. Such involvement of fluorosilanes in consecutive C–F bond activation and C–F bond formation reactions to regenerate the same C–F bond is unprecedented and has never been considered before. The observations are of fundamental importance in understanding the selectivity of C–F bond cleavage steps at transition metal centers. Selective C–H activation preceded by reversible C–F activation might also have consequences for the overall C–F *versus* C–H activation selectivity. For comparison, however, $[RhH(PEt_3)_3]$ (**6**) or $[Rh(Bpin)(PEt_3)_3]$ react selectively with 2,3,5,6-tetrafluoropyridine to yield $[Rh(4\text{-}C_5NF_4)(PEt_3)_3]$ (**4**) and H_2 or HBpin by C–H activation and there are no indications for an intermediate C–F activation step.[6d-f]

Acknowledgements

Support from the research training group "Fluorine as a Key Element" funded by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We would also like to thank Dr Mike Ahrens for the DFT calculations and Dr Sabrina Kalläne for an additional NMR experiment.

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