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C–H and C–F Bond Activation Reactions of Fluorinated Propenes at Rhodium: Distinctive Reactivity of the Refrigerant HFO-1234yf

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Dedicated to Prof. Helmut Werner on the occasion of his 85th birthday

Abstract: The reaction of $[Rh(H)(PEt_3)_3]$ (**1**) with the refrigerant HFO-1234yf (2,3,3,3-tetrafluoropropene) affords an efficient route to obtain $[Rh(F)(PEt_3)_3]$ (**3**) by C–F bond activation. Catalytic hydrodefluorinations were achieved in the presence of the silane $HSiPh_3$. In the presence of fluorosilane the fluorido complex **3** provides a C–H bond activation followed by a 1,2-fluorine shift to produce $[Rh\{(E)\text{-}C(CF_3)=CHF\}(PEt_3)_3]$ (**4**). Similar rearrangements of HFO-1234yf were observed at $[Rh(E)(PEt_3)_3]$ (E = Bpin (**6**), C_7D_7 (**8**), Me (**9**)). The ability to favor C–H bond activation using $[Rh(F)(PEt_3)_3]$ (**3**) and fluorosilane is also demonstrated with 3,3,3-trifluoropropene. Studies are supported by DFT calculations.

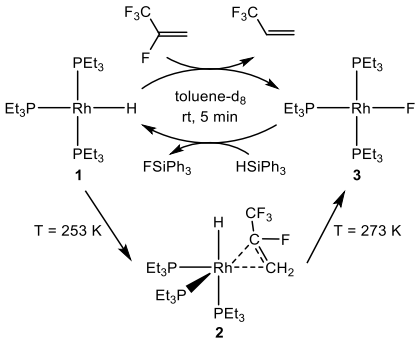
Fluorinated building blocks are not only an important inclusion in hydrofluorocarbons used in pharmaceuticals, agrochemicals and materials, but are also employed in refrigeration and air conditioning.[1] The chemical, physical and environmental properties of hydrofluoroolefins have led to their ubiquity in cooling agents.[2]

Extensive research has been performed on the reactivity of late transition metal complexes towards perfluorinated or highly fluorinated olefins.[3] Carbon-fluorine bond activation[3a-d, 4] can occur through the formation of a thermodynamically favored F–B, F–Si or F–H bond, among others, implying that metal complexes bearing boryl, silyl or hydrido ligands are useful for C–F bond activation reactions.[5] In recent years, we have shown the capabilities of various rhodium(I) complexes $[Rh(E)(PEt_3)_3]$ (E = H (**1**), Bpin (**6**, pin = pinacolate, $O_2C_2Me_4$), $Si(OEt)_3$, $GePh_3$) in C–F bond activation reactions of olefins such as hexafluoropropene[6], 3,3,3-trifluoropropene[7] and *cis*-1,2,3,3,3-pentafluoropropene.[6a] In contrast, C–H activation steps at fluoroolefins are very rare and usually restricted to olefins not fluorinated at the double bond. One example by Cowie *et al.* demonstrates simultaneous C–F and C–H bond activations of various polyfluorinated ethylene derivatives using a diiridium hydrido carbonyl complex.[3h] Though C–H bond activations at rhodium are well-known with fluoroaromatics and also occur at $[Rh(E)(PEt_3)_3]$,[6e, 8] they are often competing with C–F bond activation reactions.[3b, 9]

The fluoroolefin 2,3,3,3-tetrafluoropropene, HFO-1234yf, has been identified as a replacement for the refrigerant 1,1,1,2-tetrafluoroethane, HFC-134a, which was used in automobile air conditioning systems.[10] Even with the interesting properties of this olefin, reactivity studies with HFO-1234yf have been little described.[11] Ogoshi *et al.* reported on catalytic monodefluoroborylations using a copper catalyst and B_2pin_2[11e] as well as on catalytic monodefluorosilylations with a copper fluorido complex and $PhMe_2Si(Bpin)$.[11g] Recently, Crimmin *et al.* presented oxidative addition reactions of HFO-1234yf via the activation of the $C(sp^2)$–F bond at an aluminium(I) complex.[11h]

In this paper, we present the development of a new strategy for C–H bond activation reactions: Conversions of HFO-1234yf and 3,3,3-trifluoropropene are initiated by a rhodium fluorido complex in the presence of fluorosilane. Activation of HFO-1234yf is distinctive and involves the subsequent rearrangement of the fluorinated moiety by a 1,2-fluorine shift.

Treatment of $[Rh(H)(PEt_3)_3]$ (**1**) with HFO-1234yf at room temperature provided selectively the rhodium fluorido complex $[Rh(F)(PEt_3)_3]$ (**3**) and 3,3,3-trifluoropropene conveniently and efficiently, in contrast to previous methods to access **3**, which require sources of HF and longer reaction times.[6b, 7, 12] The intermediate *fac*-$[Rh(H)(CH_2=CFCF_3)(PEt_3)_3]$ (**2**) of this reaction, identified by NMR spectroscopy at 253 K (see SI), exhibits the coordination of the olefin at the rhodium center of **1** (Scheme 1). When warmed up by 20 K, the carbon-fluorine bond activation occurred, resulting in the formation of complex **3** as well as the release of 3,3,3-trifluoropropene. Presumably, the mechanism from intermediate **2** to complex **3** follows an insertion into the Rh–H bond and a *β*-fluoride elimination. A nucleophilic attack of **1** at HFO-1234yf to yield **3** and the trifluoropropene without **2** as intermediate can be an alternative mechanism, although this requires a dissociation of the olefin from **2**. Previously, olefin coordination was observable with hexafluoropropene[6f] or 3,3,3-trifluoropropene[7, 13] coordinating rhodium or nickel complexes, and *β*-fluoride elimination reactions have been also proposed in other systems using transition metals.[3e, 14]



Scheme 1. Reaction of rhodium hydrido complex **1** with HFO-1234yf.

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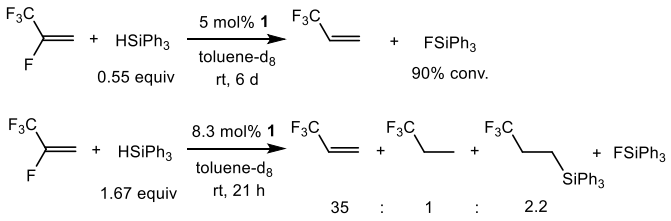
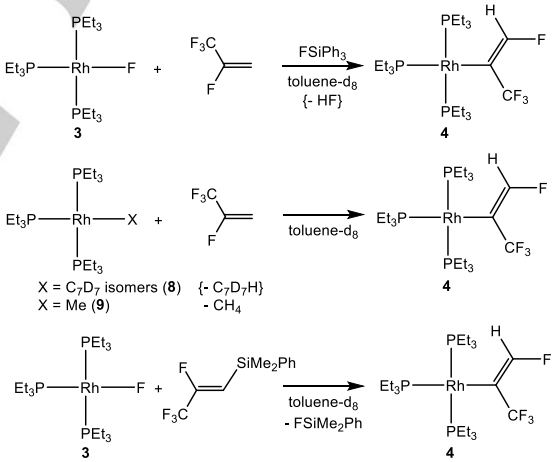
In order to study the catalytic hydrodefluorination of HFO-1234yf to obtain 3,3,3-trifluoropropene, $HSiPh_3$ and the olefin were reacted in a ≈0.55:1 ratio with 5 mol% of complex **1** as a catalyst, achieving 90% of conversion based on the consumption of silane (Scheme 2). This catalytic reaction represents one of the few examples of catalytic C(sp^2)–F bond hydrodefluorination of an olefin by late transition metals.[4b, 15] In contrast, using an excess of $HSiPh_3$ in regard to HFO-1234yf (≈1.67:1 ratio) and 8.3 mol% of complex **1** as a catalyst, 1,1,1-trifluoro-3-triphenylsilylpropane and 1,1,1-trifluoropropane can be observed in addition to 3,3,3-trifluoropropene in a 2.2:1:35 ratio, respectively, together with $FSiPh_3$ (Scheme 2). The hydrosilylation and hydrogenation products stem from 3,3,3-trifluoropropene.[16] Note that the rhodium(I) fluorido complex **3** reacts immediately with $HSiPh_3$ to form rhodium(I) hydrido complex **1** and $FSiPh_3$.[6a]



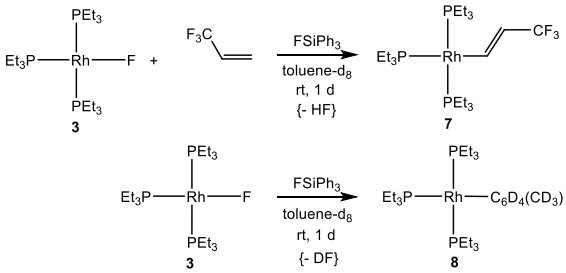
Scheme 2. Catalytic hydrodefluorination of HFO-1234yf.

Surprisingly, the reaction solution of the stoichiometric conversion of **1** to **3** in the presence of HFO-1234yf and one equivalent of $HSiPh_3$, showed on a slower time scale after 19 h the formation of [Rh{(*E*)-C(CF_3)=CHF}(PEt_3)$_3$] (**4**).[6a] Additionally, minor amounts of $[Rh(PEt_3)_4]^+$ (**5**)[17] and a complex which is presumably $[Rh(\eta^6\text{-}C_7D_8)(PEt_3)_2]^+$ (see SI), as well as 3,3,3-trifluoropropene and $FSiPh_3$ were observed.[18] We assume that the initially formed counteranion of the cationic species is $F_2SiPh_3^-$ (see also below), which then transforms into SiF_5^-. The same reaction pathway can also be seen using $HSiEt_3$ instead of $HSiPh_3$. It was then intriguing to discover that in an independent reaction the rhodium fluorido complex **3**, $FSiPh_3$ and HFO-1234yf within 1 h yielded the rhodium complex **4** by C–H activation (Scheme 3), as well as $[Rh(PEt_3)_4]^+$ (**5**) in a 92:8 ratio and again minor amounts of $[Rh(\eta^6\text{-}C_7D_8)(PEt_3)_2]^+$.[19] These results together with the absence of a reaction between free phosphine or pure complex **3** and HFO-1234yf when there is no silicon species present in the reaction mixture, allow us to assume that the fluorosilane plays an important role in the reaction. Importantly, in a PFA inliner the reaction proceeded more slowly, completing in 3 h, suggesting that the formally generated HF is consumed by the glass of the NMR tube. However, in PFA, the HF is not evident in the reaction mixtures but instead reacts further with $FSiPh_3$ to provide F_2SiPh_2 and benzene, which were both observed by GC/MS. Furthermore, using the proton sponge, 1,8-bis(dimethylamino)naphthalene in a PFA inliner the reaction duration decreased to 1.5 h. Consistent with that observation, DFT calculations reveal that a reaction from **3** to give **4** and HF would be uphill by ΔG = +49 kJ/mol (all reported reaction and activation free energies are calculated at 298.15 K and 0.1 MPa). If the trapping of HF is modeled by the generation of benzene and F_2SiPh_2, the conversion is exergonic by ΔG = -87 kJ/mol.

At this stage two distinct reaction steps may be identified: (i) a C–H activation of HFO-1234yf and (ii) a rearrangement of the fluorinated moiety involving a 1,2-fluorine shift. These two steps have been probed in independent reactions. Thus, the system **3**/$FSiPh_3$ was tested as a tool for C–H bond activation. Indeed, in a reaction with 3,3,3-trifluoropropene after 3 h the formation of [Rh{(*E*)-CH=CH(CF_3)}(PEt_3)$_3$] (**7**) (see SI) as well as complex **5** in a 70:30 ratio was observed (Scheme 4). Note that this reaction also took place when using $FSi(OEt)_3$. Furthermore, the reactivity of complex **3** with $FSiPh_3$ was tested in the absence of the olefin. C–D activation of the solvent toluene-d_8 occurred, forming within 1 day isomers of [Rh(C_7D_7)(PEt_3)$_3$] (**8**) (SI) and **5** in a 95:5 ratio, respectively, as well as fluorosilicates (Scheme 4). To study the fluoride migration, the rhodium methyl complex [Rh(Me)(PEt_3)$_3$] (**9**), which is known to perform C–H activation reactions,[20] was treated with HFO-1234yf. The isolated mixture of isomers of [Rh(C_7D_7)(PEt_3)$_3$] (**8**) were also tested independently with HFO-1234yf, and both reactions gave **4** (Scheme 3). Note that the conversion of [Rh(Me)(PEt_3)$_3$] (**9**) and HFO-1234yf into **4** and methane is also computed to be exergonic by ΔG = -103 kJ/mol. Importantly, the production of pure complex **4** demonstrates that the fluorine shift proceeds without the need of fluorosilane. This observation is further supported by a reaction of **3** with the silane *Z*-(CF_3)CF=CH($SiMe_2Ph$) (SI) which also yields **4** and $FSiMe_2Ph$ by Si–C bond cleavage instead of C–H activation (Scheme 3).



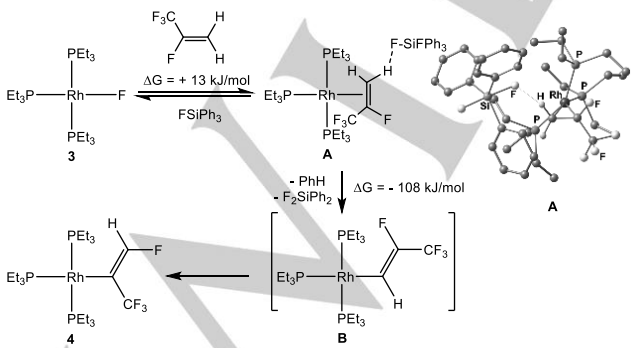
Scheme 3. Activation of HFO-1234yf and (CF_3)CF=CH($SiMe_2Ph$); $[Rh(PEt_3)_4]^+$ (**5**) was observed in the formation of **4** from **3** and $FSiPh_3$ (ratio **4**:**5** = 92:8).[18]



Scheme 4. C–H activations at **3** and fluorosilane; as second product $[Rh(PEt_3)_4]^+$ (**5**) was observed for the generation of **7** (ratio **7**:**5** = 70:30).[18]

Based on these results, the following mechanism is suggested (Scheme 5). It is conceivable that a fluorosilicate could be formed *in situ* by the reaction of $FSiPh_3$ with the fluorido complex **3**,[21] by abstracting the fluorido ligand. Prior or concomitant olefin coordination to rhodium leads to intermediate **A**, which in our DFT computations features an interaction of the fluorosilicate with the C–H bond at the metal-bound olefin.[22] A C–H bond activation transpires next from **A**, giving intermediate **B** and the regeneration of fluorosilane together with HF with a computed free-energy barrier of $\Delta G^{\ddagger}$ = +38 kJ/mol relative to **A** for the C–H bond in the *trans* position to the CF_3 group. This step is exergonic by ΔG = -108 kJ/mol, if the generation of F_2SiPh_2 and benzene is considered (Scheme 5 and Scheme S47 in SI). The conversion is zero-order in the decrease of **3** and the formation of **4**. When using the deuterated HFO-1234yf[23] a small kinetic isotope effect of 1.2 was observed, which is consistent with the proposed intermediate **A** and a transition state for the C–H activation step still featuring a C–H interaction.[24] Note that it has been suggested recently that C_6F_6 can act as a fluoride shuttle to abstract a proton from the backbone of an imidazolinium cation.[25]

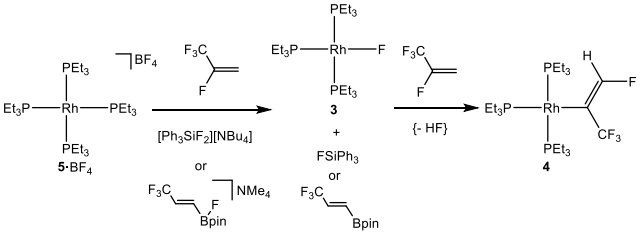
The subsequent rearrangement from **B** into **4** might proceed via metallacyclopropene complexes generated from the vinyl ligand[26] or the generation of a fluorido complex bearing trifluoropropyne as a ligand. Both mechanistic possibilities were evaluated by DFT methods (see Scheme S48-S50 in the SI), and fluoride migration is seen to be the rate-determining step in both cases. However, the barrier for insertion/deinsertion of Rh into the C–F bond of the olefin (cf. S48) is lower than the one for migration of fluoride across the C–C bond (cf. S49) in the metallacyclopropene intermediate ($\Delta G^{\ddagger}$ = +153 kJ/mol vs +174 kJ/mol), rendering the former mechanism the favored reaction pathway. Overall the computed barriers appear somewhat high for a room-temperature reaction. Note that the fluorine shift and subsequent steps are fast, and no intermediates could be observed by NMR spectroscopy, even at low temperature. Using THF-d_8 as solvent did not increase the reaction rate or provide intermediates. Note that Hu and coworkers have proposed that a 1,2-fluorine shift at cyclopropyl-substituted fluoroepoxides might proceed via a concerted mechanism or a tight ion-pair.[27] Lewis-acid-induced transformations at halogenated alkanes were also reported.[1d, 28]



Scheme 5. Proposed mechanism to form complex **4**.

A comparable reactivity of HFO-1234yf was further observed in a reaction of the boryl complex $[Rh(Bpin)(PEt_3)_3]$ (**6**) with HFO-1234yf affording, in 10 min, again complex **4** and the cationic rhodium(I) complex **5** in a 93:7 ratio.[29] The reaction was monitored by low temperature NMR spectroscopy revealing at 253 K the generation of the hydrido complex **2** as an intermediate, which can be explained by an initial C–H activation of HFO-1234yf to afford the rhodium hydrido complex **1** and presumably concomitant generation of a fluorinated vinylborane. At 273 K complex **2** evolves to yield **3** by C–F bond activation of HFO-1234yf as observed before (Scheme 1). Finally, the rhodium fluorido complex **3** reacted further in the presence of HFO-1234yf to give the final products **4** and cationic complex **5** at 283 K. The latter step is presumably mediated by Lewis-acidic borane species instead of a fluorosilane.

Independently, efforts to generate the cation $[Rh(\eta^2\text{-}CH_2CFCF_3)(PEt_3)_3]^+$ from **3** on using various Lewis acids such as BF_3 or borate salts like $NaBAr^F{}_4$ (sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) were not successful but always led to complex **5** with the corresponding counteranion. The reactions of **5**·BF_4 with HFO-1234yf and TBAT (tetrabutylammonium difluorotriphenylsilicate) or the anionic fluoroboronate, $[(E)\text{-}CF_3CH{=}CH(BpinF)]NMe_4$ (see SI) as a model for a vinylfluoroborate, were then investigated. Indeed, complex **5**·BF_4 evolves to complex **4** within days through complex **3** as an intermediate (Scheme 6). For the reaction of **5**·BF_4 with TBAT the initial generation of complex **3** and fluorosilane was observed after 5 min. Full conversion into complex **4** was achieved after 3 days. Apparently, refluorination of the cation **5** is favored, but on a much slower time scale the activation of HFO-1234yf is competing and occurs. The latter is slower presumably because of low concentration of a borane or silane as a fluoride acceptor. Therefore, a reaction of **5**·BF_4, HFO-1234yf, TBAT and $FSiPh_3$ was performed and indeed the reaction was finished after 2 d. This is consistent with the fact that a reaction of **3**, $FSiPh_3$, TBAT and HFO-1234yf (1.5 d) was faster than the conversion of **3** with TBAT and HFO-1234yf into **4** (2 w), but slower than the reaction of **3** with $FSiPh_3$ and HFO-1234yf (1 h).



Scheme 6. Formation of complex **4** from the cation complex **5**·BF_4.[18]

In conclusion, a unique system to activate C–H bonds has been reported, which involves a fluorido complex and a mildly acidic fluorosilane.[30] The C–H activation step is induced by a F···H interaction involving the C–H bond and a fluorosilicate. Remarkably, at HFO-1234yf, a C–H activation followed by a 1,2-fluorine shift occur. While C–F bond activation and C–H bond activation are two well-known reactions, the combination of both

is scarce.[3h, 31] The reported strategy might open new routes for the synthesis of fluorinated building blocks.

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Keywords: C–F activation • C–H activation • fluorido complexes • fluorinated refrigerants • silanes

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[18] Note that full conversion of the rhodium precursor was achieved after the given reaction time according to the NMR data.

[19] Formation of phosphine and **5** can be explained by a dissociation of PEt_3 from a cationic intermediate which resembles **A** (Scheme 5) leading in toluene as solvent to the cationic diphosphine rhodium complex $[Rh(\eta^6\text{-}C_7D_8)(PEt_3)_2]^+$. In addition, presence of a small amount of an unidentified precipitate suggests the formation of rhodium compounds without phosphine ligands.

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[29] The counteranion of **5** could not be identified until $[BF_4]^-$ was observed after a few hours. Note that HF can react with Bpin derivatives to form BF_3 and then, $[BF_4]^-$. In fact, when $Et_3N/CsCO_3$ is added to trap HF, full conversion to complex **4** is observed.

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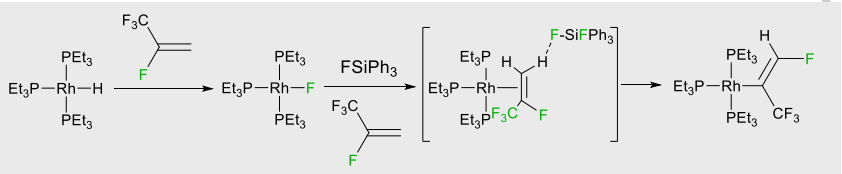

Using the refrigerant HFO-1234yf together with $[RhH(PEt_3)_3]$, a C–F bond activation occurs to produce a rhodium fluorido complex. This reaction is followed by a C–H bond activation mediated by the fluorosilane and a subsequent 1,2-fluorine shift.

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