

Versatile Reaction Pathways of 1,1,3,3,3-Pentafluoropropene at Rh(I) Complexes $[\text{Rh}(\text{E})(\text{PEt}_3)_3]$ ($\text{E} = \text{H}, \text{GePh}_3, \text{Si}(\text{OEt})_3, \text{F}, \text{Cl}$): C-F versus C-H Bond Activation Steps

Maria Talavera^[a] and Thomas Braun^{*[a]}

Abstract: The reaction of the rhodium(I) complexes $[\text{Rh}(\text{E})(\text{PEt}_3)_3]$ ($\text{E} = \text{GePh}_3$ (**1**), H (**6**), F (**7**)) with 1,1,3,3,3-pentafluoropropene afforded the defluorinative germylation products *Z*/*E*-2-(triphenylgermyl)-1,3,3,3-tetrafluoropropene and the fluoro complex $[\text{Rh}(\text{F})(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_2]$ (**2**) together with the fluorophosphorane *E*-(CF_3) $\text{CH}=\text{CF}(\text{PFEt}_3)$. For $[\text{Rh}(\text{Si}(\text{OEt})_3)(\text{PEt}_3)_3]$ (**4**) the coordination of the fluoroolefin was found to give $[\text{Rh}\{\text{Si}(\text{OEt})_3\}(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_2]$ (**5**). Two equiv-

alents of complex **2** reacted further by C–F bond oxidative addition to yield $[\text{Rh}(\text{CF}=\text{CHCF}_3)(\text{PEt}_3)_2(\mu\text{-F})_3\text{Rh}(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)]$ (**9**). The role of the fluoro ligand on the reactivity of complex **2** was assessed by comparison with the analogous chlorido complex. The use of complexes **1**, **4** and **6** as catalysts for the derivatization of 1,1,3,3,3-pentafluoropropene provided products, which were generated by hydrodefluorination, hydrometallation and germylation reactions.

Introduction

The interest in hydrofluoroolefins (HFOs) is partly due to their lower ozone depletion and global warming potentials when compared to the ones for chlorofluorocarbons and hydrofluorocarbons, which resulted in the replacement of the latter as refrigerants by HFOs in automobile air conditioning systems.^[1] In addition, HFOs can be used as monomers in fluorinated polymers.^[2]

In order to safely use these compounds in industry, extended studies into their properties and reactivity is advisable.^[3] Furthermore, they might be considered as useful building blocks to generate molecules of higher value.^[4] One approach imparts the development of routes for main group or metal-mediated functionalization including both C–F and C–H bond activation reactions.^[5] In this regard, studies on the chemistry of HFOs such as 2,3,3,3-tetrafluoropropene, *E*-1,3,3,3-tetrafluoropropene, 3,3,3-trifluoropropene or hexafluoropropene have been in the focus of interest of several research groups.^[6] At rhodium, the high reactivity of rhodium(I) complexes $[\text{Rh}(\text{E})(\text{PEt}_3)_3]$ ($\text{E} = \text{H}, \text{F}, \text{GePh}_3, \text{B}(\text{O}_2\text{C}_2\text{Me}_4)$ or $\text{Si}(\text{OEt})_3$) towards fluoroaromatics and fluoroolefins has already been demonstrated.^[5a,7] The nature of the anionic ligand is crucial for the activation step for a number of reasons. Key factors include

the formation of the strong element-fluorine bonds, such as H–F, B–F, Ge–F or Si–F bonds, in C–F bond activation reactions, but also the control of regio- and chemoselectivities, which is related to the activation pathways.^[5a] However, the reactivity of pentafluoropropenes have been barely studied, neither at transition metal nor at main group element compounds. Notably, the Lentz group has previously described the catalytic hydrodefluorination of 1,1,3,3,3-pentafluoropropene using gallium hydrides^[8] as well as at titanium complexes in the presence of silanes.^[6a] No stoichiometric studies have been performed, yet.

Herein, the reactivity of 1,1,3,3,3-pentafluoropropene towards several rhodium (I) complexes is reported. The reaction routes impart coordination of the olefin as well as $\text{C}(\text{sp}^2)\text{-F}$ and $\text{C}(\text{sp}^2)\text{-H}$ bond activation pathways. In addition, the formation of a dirhodium(III) fluoro complex bearing bridging fluorides is described. Catalytic derivatization reactions of the olefin using both $\text{HSi}(\text{OEt})_3$ and HGePh_3 were achieved.

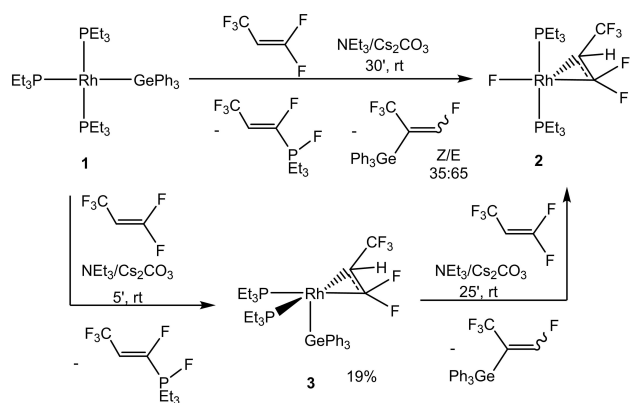
Results and Discussion

Treatment of the rhodium(I) germyl complex $[\text{Rh}(\text{GePh}_3)(\text{PEt}_3)_3]$ (**1**) with an excess of 1,1,3,3,3-pentafluoropropene in the presence of $\text{NEt}_3/\text{Cs}_2\text{CO}_3$ yielded, after 30 minutes, the rhodium fluoro complex $[\text{Rh}(\text{F})(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_2]$ (**2**). In addition, the formation of one equivalent of the fluorophosphorane *E*-(CF_3) $\text{CH}=\text{CF}(\text{PFEt}_3)$ as well as one equivalent of the defluorinative germylation products *Z*/*E*-2-(triphenylgermyl)-1,3,3,3-tetrafluoropropene (*Z*/*E* ratio 35:65) was observed (Scheme 1). NMR spectroscopic studies showed that the reaction does not occur at low temperature and, therefore, no intermediates were detected. However, after 5 minutes at room temperature (31% conversion of complex **1**), complex $[\text{Rh}(\text{GePh}_3)(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_2]$ (**3**) and complex **2** were identified with 19% and 12% conversion, respectively. Compound **3** then reacted further to

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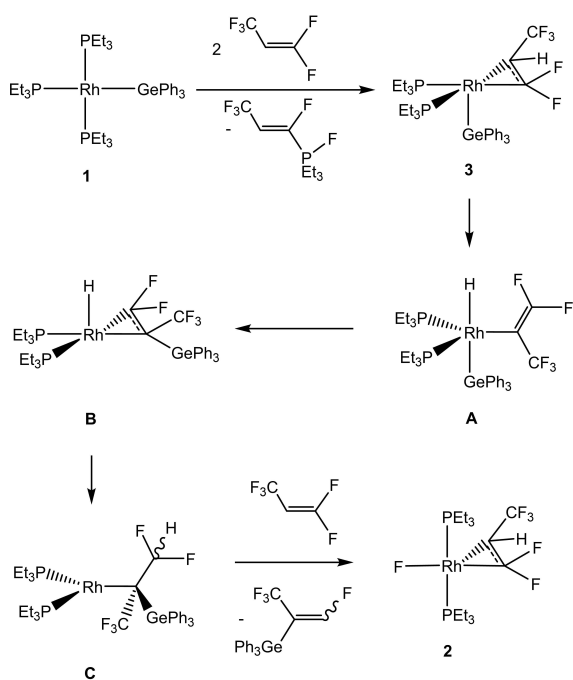
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Scheme 1. Reactivity of complex **1** towards 1,1,3,3,3-pentafluoropropene.

yield **2**. Note that in previous studies with other fluoroolefins the coordination at **1** was never observed, neither with nor without phosphine replacement.^[7c,e,f]

The formation of the gerylated olefins $Z/E-(CF_3)C(GePh_3)=CFH$ implies a $C(sp^2)-F$ bond activation, but also a $C(sp^2)-H$ bond activation resulting in a 1,2-hydrogen shift. This behaviour resembles the previously reported reactivity of complex **1** towards 2,3,3,3-tetrafluoropropene to give 1-(triphenylgermyl)-3,3,3-trifluoropropene.^[7f] Mechanistically, the formation of the fluorophosphorane supports an initial dissociation of a phosphine ligand upon coordination of the fluoroolefin to give complex **3** (Scheme 2). The dissociated phosphine will then react with the excess of olefin to yield $E-(CF_3)CH=CF(PFET_3)$. The

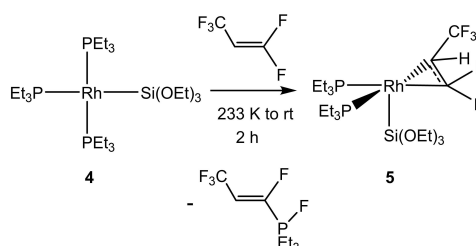


Scheme 2. Possible mechanism for the reaction of **1** with 1,1,3,3,3-pentafluoropropene to give complex **2**, $Z/E-(CF_3)C(GePh_3)=CFH$ and $E-(CF_3)CH=CF-(PFET_3)$.

oxidative addition reaction at the triethylphosphane has been demonstrated independently and was also previously described for other fluorinated olefins and phosphines.^[9] It is conceivable that complex **3** reacts further by $C-H$ bond oxidative addition yielding the rhodium(III) hydrido complex **A** (Scheme 2). This complex can rearrange to the rhodacyclopropane derivative **B**, which would react further to yield **C** by insertion into the $Rh-H$ bond. Finally, a β -fluoride elimination would follow. This last step would afford the gerylated olefin isomers as well as $[Rh(F)(PEt_3)_2]$, which is stabilized by the coordination of another molecule of 1,1,3,3,3-pentafluoropropene due to the absence of free phosphine.

Likewise, the rhodium(I) silyl complex $[Rh\{Si(OEt)_3\}(PEt_3)_3]$ (**4**) reacted with an excess of 1,1,3,3,3-pentafluoropropene to give $[Rh\{Si(OEt)_3\}(CF_3CHCF_2)(PEt_3)_2]$ (**5**) after slowly warming up from 233 K to room temperature (Scheme 3). Complex **5** does not react to complex **2** but decompose in solution, however, its formation supports the structure proposed for complex **3** further. Note that the formation of the coordination product is the common reaction pathway of complex **4** towards fluoroolefins.^[5a]

The complexes **3** and **5** were characterized by NMR spectroscopy, only. The $^{31}P\{^1H\}$ NMR spectra show two inequivalent signals at 3.0 and 12.3 ppm for **3** and 13.4 and 21.6 ppm for **5**. While the resonances at lower field appear as doublet of multiplets with similar coupling constants to rhodium, the upper field resonances slightly differ. Thus, complex **5** shows a doublet of doublet of doublet of doublets due to coupling to Rh, both fluorine atoms of the coordinated olefin with comparable coupling constants and the coupling to the other phosphorus with 11.9 Hz. However, at complex **3** the phosphorus-phosphorus coupling constant is only 1.9 Hz and coupling to the CF_3 moiety is also observable as an extra quartet (3.9 Hz). In the ^{19}F NMR spectra, three resonances are observable, one for the CF_3 group as multiplet and two for the inequivalent fluorine atoms of the CF_2 moiety with a geminal F,F coupling of 150 and 163 Hz for complexes **3** and **5**, respectively. These values suggest a high $C(sp^3)$ character of the CF_2 group. The 1H NMR spectra show for complexes **3** and **5** the CH resonance at 2.77 and 2.75 ppm, respectively, which is indicative of a $C(sp^3)-H$ moiety. In order to further support the metallacyclopropane configuration, the structures of the rotational isomers bearing the CF_3 group either orientated towards the silyl/germyl ligand or towards the vacant coordination site were optimized by DFT calculations (BP86/def2-SVP). The lowest



Scheme 3. Reactivity of complex **4** towards 1,1,3,3,3-pentafluoropropene.

energy isomers exhibit an *anti*-conformation for the CF₃ moiety and the silyl/germyl ligand (Figure 1) and a C–C bond distance of 1.463 Å for both complexes was found, which is in good agreement with the rhodacyclopropane model. Note that comparable silyl complexes with other coordinated olefins such as hexafluoropropene have been described in a similar manner.^[7e,10]

The reaction of the hydrido complex [Rh(H)(PEt₃)₃] (**6**) with 1,1,3,3,3-pentafluoropropene gave after 5 minutes the rhodium(I) fluoro complex [Rh(F)(PEt₃)₃] (**7**) as the only rhodium complex together with *Z/E*-(CF₃)CH=CHF (*Z/E* ratio 90:10). However, after 10 h, complex **2** and the *E*-pentafluorophosphorane derivative are obtained in a 1:1 ratio (Scheme 4). The obtaining of complex **7** as reaction intermediate suggests that in this case dissociation of the phosphine does not take place in order to activate the fluoroolefin, or the rebinding process is faster than the reactivity of the free phosphine towards the olefin. The former hypothesis was confirmed by following the reaction at variable temperature. Thus, at 233 K the coordination of the olefin to form *fac*-[RhH(CF₃CHCF₂)(PEt₃)₃] (**8**) was observed. The latter evolves to the rhodium(I) fluoro complex **7** at 273 K without observation of free triethylphosphane at any temperature.

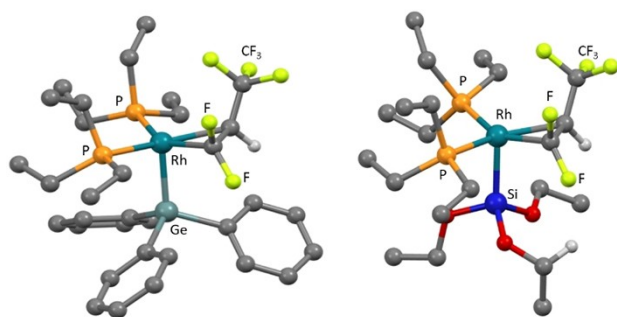
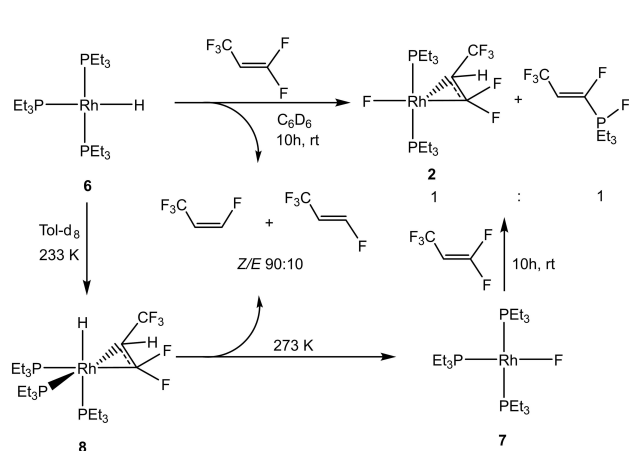


Figure 1. DFT optimized structure (BP86/def2-SVP) of the most stable isomer of complexes **3** (left) and **5** (right). All hydrogen atoms except for the one at the fluorinated moiety are omitted for clarity.

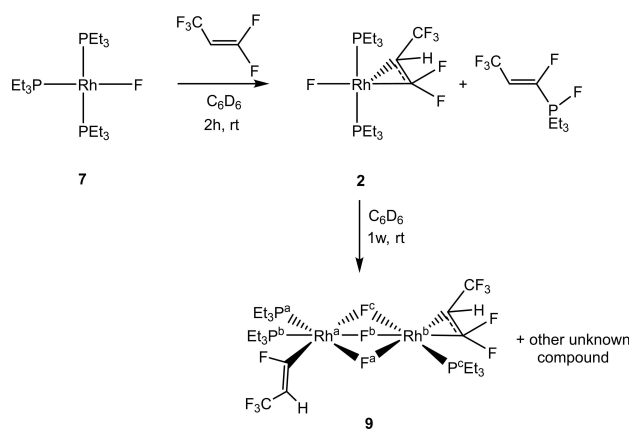


Scheme 4. Reactivity of rhodium(I) hydrido complex **6** towards 1,1,3,3,3-pentafluoropropene.

The ³¹P{¹H} NMR spectrum of complex **8** shows at 253 K three resonances at 22.3, 7.1 and 2.7 ppm which integrate in a 1:1:1 ratio. The Rh,P coupling constants for the two signals at higher field are lower than 100 Hz, which is in accordance with the oxidation state +III at rhodium.^[11] In the ¹⁹F NMR spectrum, the resonance of the CF₃ appears at –50.5 ppm as a broad signal, while for the CF₂ moiety two resonances were found with a F,F coupling of 134 Hz, which supports the C(sp³) character of the CF₂ group.^[12] Apart from that, coupling to phosphorus atoms and the CF₃ moiety are observable at 263 K. However, the most characteristic feature is the hydrido resonance at –12.67 ppm in the ¹H NMR spectrum, which appears as a broad doublet with 160.6 Hz due to the coupling to the phosphine in the *trans*-position. The formation of **8** is supported by previous studies where the coordination of a fluoroolefin to the rhodium hydrido complex **6** took place at low temperatures, and no phosphine dissociation was observed.^[7e–g]

In order to confirm the nature of complex **2**, an independent reaction of [Rh(F)(PEt₃)₃] (**7**) with 1,1,3,3,3-pentafluoropropene was performed. Indeed, after 2 h full conversion into [Rh(F)(CF₃CHCF₂)(PEt₃)₂] (**2**) and *E*-(CF₃)CH=CF(PFet₃) in a 1:1 ratio was observed (Scheme 5).

The ³¹P{¹H} NMR spectrum of complex **2** displayed two resonances for the phosphorus atoms as part of an AB system at 27.6 and 24.9 ppm. Both signals show a large *trans* P,P coupling of 387.5 Hz and P–Rh coupling constants typical for Rh(I) complexes (126.6 and 128.9 Hz).^[7b,c,f,11c] The non-equivalence of the phosphines is due to the arrangement of the coordinated olefin which is demonstrated by the multiplicity of its resonances. Therefore, the phosphine at 27.6 ppm exhibits a doublet of doublet of triplets due to the already mentioned couplings to phosphorus and rhodium as well as coupling to the fluoro ligand and one of the fluorine atoms at the CF₂ moiety. In contrast, the second phosphine shows an extra quartet due to the coupling to the CF₃ moiety. In the ¹⁹F NMR spectrum, four resonances for the CF₃ moiety, the two fluorine atoms of the CF₂ group and the rhodium bound fluoro ligand



Scheme 5. Independent synthesis of complex **2** from the rhodium(I) fluoro complex **7** and 1,1,3,3,3-pentafluoropropene and its evolution to the dirhodium(III) complex **9**.

are displayed. The fluoro signal appears at -225.6 ppm as a doublet of pseudo triplets due to the coupling to rhodium (61 Hz) and the two phosphorus atoms (29 Hz).^[13] Compared to complexes **3** and **5**, the fluorine atoms of the CF_2 group reveal a lower F,F coupling constant (83 Hz) which indicates a lower $\text{C}(\text{sp}^3)$ character, although, as before, both the hydrogen shift for the CH moiety (2.04 ppm) in the ^1H NMR spectrum and the C–C bond distance of the olefin obtained by DFT calculations (1.441 Å) support a metallacyclopropyl configuration (Figure 2). Note that other complexes with a coordinated olefin with C–C bond distances close to a single bond have been assigned as Rh(I) complexes.^[14]

Complex $[\text{Rh}(\text{F})(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_2]$ (**2**) is not stable in solution, and after a week at room temperature, the dinuclear rhodium (III) complex $[\text{Rh}(\text{CF}=\text{CHCF}_3)(\text{PEt}_3)_2(\mu\text{-F})_3\text{Rh}(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)]$ (**9**) was identified (Scheme 5). To the best of our knowledge, complex **9** represents the first example of a dirhodium(III)

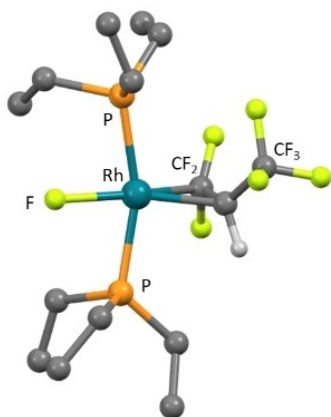


Figure 2. DFT optimized structure (BP86/def2-SVP) of complex **2**. Hydrogens of the phosphine ligands are omitted for clarity.

complex bearing bridging fluoro ligands. The formation of complex **9** would imply the dimerization of two molecules of complex **2** with a concomitant C–F bond oxidative addition of the coordinated olefin and a loss of a phosphine ligand. Note that oxidative additions of C–F bonds of fluoroolefins to obtain the corresponding fluoro vinyl complex are very rare.^[69,15]

LIFDI (liquid injection field desorption/ionization) mass spectrometry of complex **9** showed the molecular ion peak at m/z 862 as well as a peak at m/z 730 corresponding to olefin loss. However, the characterization of complex **9** was mainly performed using NMR spectroscopy supported by simulations with the *gNMR* software.^[16] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed three resonances at low field (56.4, 46.1 and 43.5 ppm) as doublet of doublet of multiplets with large coupling constants to rhodium (170–185 Hz) and fluorine (135–160 Hz). These values for coupling constants are typical for binuclear rhodium complexes with halogenido bridges as well as phosphines in a *trans* position to a fluoro ligand, while the chemical shifts are similar to other binuclear rhodium-halogenido bridged complexes bearing triethylphosphane.^[7c,11b,17] The ^{19}F NMR spectrum of **9** exhibits eight resonances which correlate in the $^{19}\text{F},^{19}\text{F}$ gCOSY NMR spectrum demonstrating that all belong to the same complex (Figure 3).

The three signals for the fluoro ligands appear at -336.9 , -297.9 and -271.3 ppm as broad quartet-like features with coupling values up to 160 Hz due to couplings presumably to the other two fluoro ligands in a *cis* position and a respective phosphorus atom in the *trans* position. The values of the couplings are in accordance with literature.^[11b,17c,18] The two resonances corresponding to the CF_2 moiety appear at -84.8 and -94.3 ppm as doublet of multiplets and doublet of doublet of quartet of doublet of doublets with a *geminal* F,F coupling of 98 Hz, which is a bit larger than the corresponding value for complex **2** and indicates some $\text{C}(\text{sp}^3)$ character. The latter signal

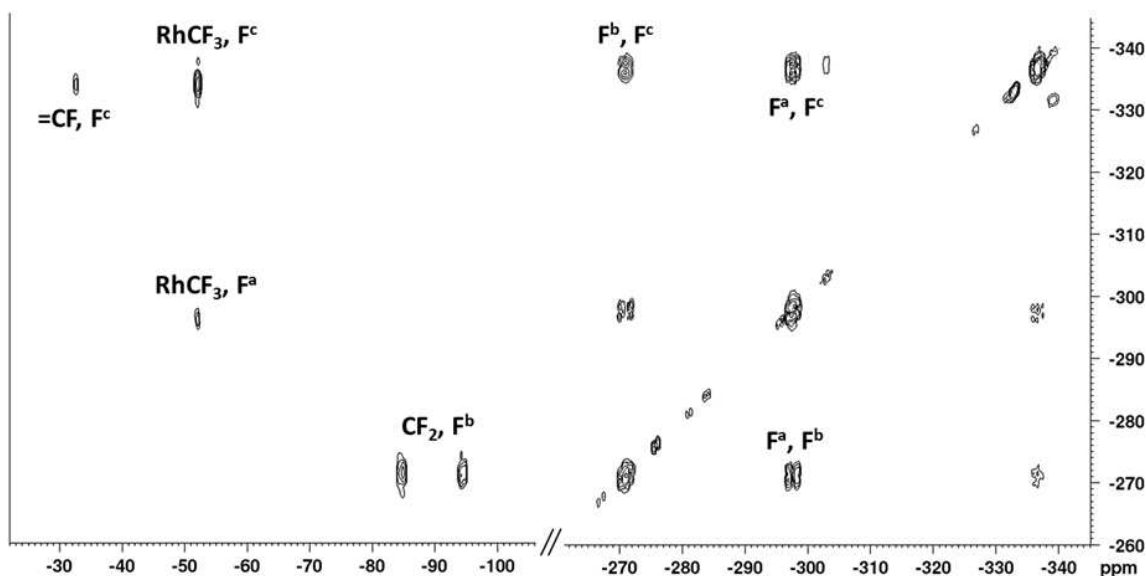


Figure 3. Fluorido ligands sections of the $^{19}\text{F},^{19}\text{F}$ gCOSY NMR of complex **9** showing the correlation to the other fluorine resonances (left) and between each other (right).

be a key factor in transition metal mediated fluorination reactions as well as C–F bond activation.^[7g,15,20]

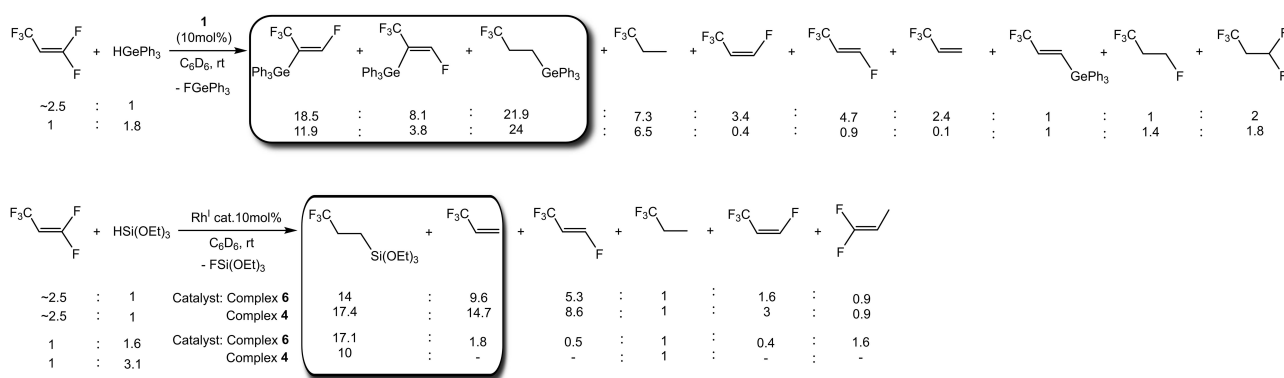
In order to promote the C–F bond activation of the coordinated olefin at **11**, one equivalent of HGePh₃ or HSi(OEt)₃ was added. After one day, the formation of the rhodium(III) hydrido complexes [RhCl(H)(GePh₃)(PEt₃)₂] (**12**) and [RhCl(H){Si(OEt)₃}(PEt₃)₂] (**13**), respectively, was observed (Scheme 6). Thus, instead of promoting the C–F bond activation to give an alkenyl complex or by generating ClGePh₃ or ClSi(OEt)₃, the olefin dissociation was found with a concomitant oxidative addition reaction of the germane or silane.

The ³¹P{¹H} NMR spectra of complexes **12** and **13** exhibit a unique doublet with a phosphorus-rhodium coupling constant of around 110 Hz, which is between the typical values for Rh(I) and Rh(III) complexes. In addition, the resonances for the hydrido ligands appear at high field at –17.27 and –16.56 ppm for **12** and **13**, respectively, in the ¹H NMR spectra as doublet of triplets with coupling constants of around 20–28 Hz to rhodium and 14 Hz to the two equivalent phosphines. In the case of complex **13**, a ¹H,²⁹Si HMBC NMR spectrum was recorded and a cross peak identified the silicon resonance at –31 ppm as a doublet of 54 Hz in the silicon domain, which would correspond to a Rh₂Si coupling constant. In addition, in the proton domain, a doublet of doublets of triplets is visible due to the coupling with rhodium, silicon and phosphorus nuclei. A H₂Si coupling constant of 22 Hz was found, suggesting that complex **13** bears a weak interaction at the silane.^[21] Additionally, T₁ measurements were performed in order to clarify the bonding situation. In the case of complex **12**, a minimum T₁ of 398 ms was obtained at 235 K, while for complex **13**, 528 ms at 219 K were determined at 300 MHz in both cases. The T₁ times of complexes **12** and **13** resemble those of the non-classical silane complexes [Rh(X){HSi(OEt)₃}(PEt₃)₂] (X = C₆F₅, C₆F₄H or C₅F₄N) previously described.^[22] However, in all cases proton-silicon coupling constants between 49 and 80 Hz were observed and DFT calculations supported the non-classical arrangement with a Si–H bond of 1.824 Å for the pyridyl derivative.^[22a] In an attempt to get a better insight, DFT calculations (B3LYP/cc-pVTZ) were performed for complexes **12** and **13**. Contrary to the T₁ measurement results, the optimized structures of **12** and

13 exhibit a structure supporting the presence of classical hydrido complexes with a distorted square pyramidal geometry bearing the germyl or silyl ligands in the apical position and H–Ge/Si distances of 2.644 and 2.314 Å, respectively. However, the H–Si distance is close to the limit for secondary interactions between the silicon atom and the hydrogen atom described.^[23] In addition, the IR band for the Rh–H bond appears at 1951 cm^{–1} in **12**, which supports a hydrido silyl complex as the η² stretching bands are usually more red-shifted.^[21] Overall, the data are not fully conclusive, but suggest the presence of a classical complex, possibly with a very weak H–Si interaction.

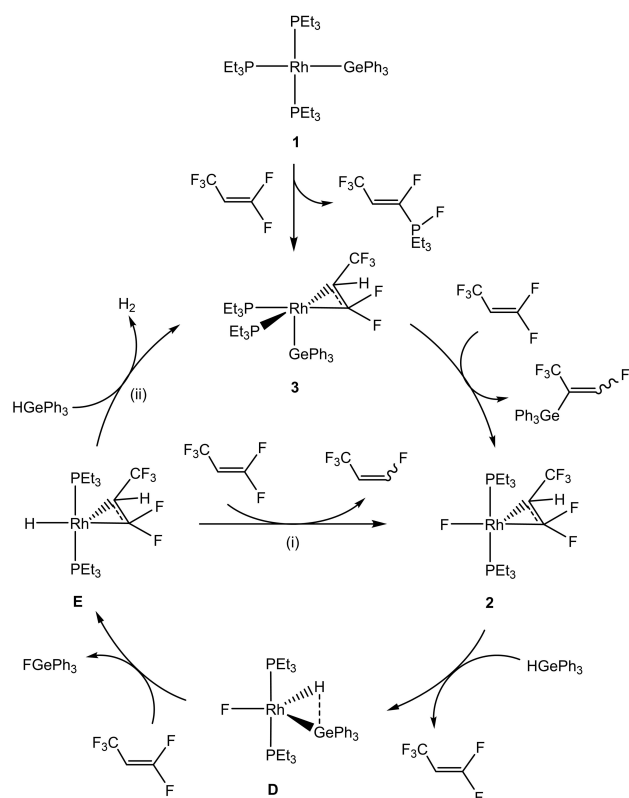
Based on the stoichiometric reactions where *Z/E*-2-(triphenylgermyl)-1,3,3,3-tetrafluoropropene were obtained as organic products, the catalytic activation of 1,1,3,3,3-pentafluoropropene with triphenylgermane using approximately 2.5 equivalents of olefin was attempted. Thus, 10 mol% of [Rh(GePh₃)(PEt₃)₃] (**1**) was used as catalyst and after 1 day, full conversion of the tertiary germane was achieved, resulting in the generation of the germane derivatives CF₃CH₂CH₂GePh₃ and *Z/E*-CF₃C(GePh₃)=CFH as major products in a mixture of at least 10 compounds, which are formed by hydrodefluorination, hydrogermylation or dehydrogenative germylation steps (Scheme 7). Note that fluorophosphorane is also observed in the reaction mixture. The low selectivity of the reaction stems from initial hydrodefluorination reactions to produce both isomers of 1,3,3,3-tetrafluoropropene as well as the double hydrodefluorination product 3,3,3-trifluoropropene. This is demonstrated by the reaction performed with an olefin: triphenylgermane ratio of 1:1.8. In this case, the reaction is slightly more selective due to the competitive reactivity of the less fluorinated olefins with the excess of the hydrogen source. Competing processes could then take place where the four olefins in solution can react either with HGePh₃ or with dihydrogen formed in the process. As a result, there was no full conversion of 1,1,3,3,3-pentafluoropropene even in 2 days.

As mentioned, the main products are CF₃CH₂CH₂GePh₃ and *Z/E*-CF₃C(GePh₃)=CFH. The former stems from the hydrogermylation of 3,3,3-trifluoropropene, which indicates a more pronounced reactivity of this olefin with respect to any reactivity of 1,3,3,3-tetrafluoropropene isomers. On the other hand, the



mixture of Z/E - $\text{CF}_3\text{C}(\text{GePh}_3)=\text{CFH}$ arises from the initial reaction of complex **1** with 1,1,3,3,3-pentafluoropropene to form complex $[\text{Rh}(\text{F})(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_3]$ (**2**) via complex $[\text{Rh}(\text{GePh}_3)(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_3]$ (**3**) (see above). To complete a cyclic process, complex **2** would react with free HGePh_3 to form the fluorido complex **D**, an analogous complex to **12**, which, by elimination of FGePh_3 , could yield with 1,1,3,3,3-pentafluoropropene complex $[\text{Rh}(\text{H})(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_3]$ (**E**) (Scheme 8). Then, two pathways might take place: i) a C–F bond activation would occur to release 1,3,3,3-tetrafluoropropene and regenerate complex **2** or ii) the oxidative addition of HGePh_3 would happen followed by the reductive elimination of dihydrogen regenerating complex **3** in presence of 1,1,3,3,3-pentafluoropropene. The released dihydrogen would then be consumed in subsequent hydrogenation reactions to give products such as tri-, tetra- or pentafluoropropene.

As it has been observed with E -1,3,3,3-tetrafluoropropene at rhodium PEt_3 complexes, reactions with silanes might be more selective than the reactions using tertiary germanes as hydrogen source.^[7f] Therefore, a catalytic reaction was performed with an olefin: $\text{HSi}(\text{OEt})_3$ ratio of around 2.5:1 and 10 mol% of the rhodium complexes **4** or **6** as catalysts, which led to full conversion of the hydrido source in 1 h. A better selectivity was achieved and 6 products were obtained. Again, mono and dihydrodefluorination reactions were observed, but now, 3,3,3-trifluoropropene reacted faster than in presence of tertiary germane and the generation of 1,1,1-trifluoro-3-trieth-



Scheme 8. Proposed catalytic cycle for the formation of the defluorinative germylation products Z/E - $\text{CF}_3\text{C}(\text{GePh}_3)=\text{CFH}$ and 1,3,3,3-tetrafluoropropenes.

oxysilylpropane, 1,1,1-trifluoropropene and 1,1-difluoropropene was observed due to hydrosilylation, hydrogenation and C–F bond activation reactions (Scheme 7). While the former resembles the previously described, hydrodefluorination followed by hydrosilylation of hexafluoropropene,^[24] the latter stems from the stoichiometric reaction of complex **4** with 3,3,3-trifluoropropene.^[7e] Notably, when 1.6 equivalents of silane were used, full conversion of $\text{HSi}(\text{OEt})_3$ was observed prior to the full consumption of 1,1,3,3,3-pentafluoropropene due to the faster reactivity of the less fluorinated olefins towards silanes, to give, with better selectivity, 1,1,1-trifluoro-3-triethoxysilylpropane as main product. Consequently, when at least 3 equivalents of silane were used, only 1,1,1-trifluoro-3-triethoxysilylpropane and 1,1,1-trifluoropropene were obtained in a 10:1 ratio with **4** as catalyst (Scheme 7). When comparing the catalytic activity of complex **4** with its stoichiometric reactivity shown above, it can be concluded that complex **4** is not capable of performing C–F bond activation while its mixture with silane activate such bonds, due to the probable formation of a rhodium hydrido complex.^[24–25]

Conclusions

The paper demonstrates that C–F bond activation reactions at rhodium centres allow for a derivatization of 1,1,3,3,3-pentafluoropropene, but control of the C–F bond activation step can be critical to achieve selectivity. The use of HGePh_3 to promote C–F bond cleavage seems to open up unusual reaction pathways, which include the generation of Z/E - $(\text{CF}_3)\text{C}(\text{GePh}_3)=\text{CHF}$. Decisive steps for an activation at $[\text{Rh}(\text{GePh}_3)(\text{PEt}_3)_3]$ (**1**) impart a C–H bond germylation of the olefin at the metal center followed by olefin insertion into a Rh–H bond and a final β -fluoro elimination. In contrary, $[\text{Rh}\{\text{Si}(\text{OEt})_3\}(\text{PEt}_3)_3]$ (**4**) does not trigger bond activation. These reaction patterns are in contrast to C–F bond activation reactions of heteroaromatics at $[\text{Rh}(\text{E})(\text{PEt}_3)_3]$ ($\text{E} = \text{GePh}_3, \text{B}(\text{O}_2\text{C}_2\text{Me}_4)$ or $\text{Si}(\text{OEt})_3$), for which ligand-supported C–F bond cleavage steps were proposed.^[7a,c,26] Nevertheless, the described reaction pathways for 1,1,3,3,3-pentafluoropropene can also be set into a broader context and compared with characteristic C–H bond and C–F bond reaction pathways of the rhodium(I) complexes $[\text{Rh}(\text{E})(\text{PEt}_3)_3]$ towards olefins.^[5o,7c,e,f,10] Some similarities are found for tetrafluoropropenes, but the distinctive behavior of the germane versus the silane is pronounced.

Furthermore, an oxidative addition of the fluoroolefin at PEt_3 to give the pentafluorophosphorane E - $(\text{CF}_3)\text{CH}=\text{CF}(\text{PFEt}_3)$ plays a crucial role for some reaction pathways, because it allows for phosphine trapping after dissociation of phosphines in the *trans*-position to the anionic ligand at $\text{Rh}(\text{I})$.

Although C–F bond oxidative addition of fluoroolefins has been previously described as mechanistic step in catalytic reactions, rhodium fluorido vinyl complexes were not characterized. $[\text{Rh}(\text{CF}=\text{CHCF}_3)(\text{PEt}_3)_2(\mu\text{-F})_3\text{Rh}(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)]$ (**9**) is formed by such an oxidative addition step from $[\text{Rh}(\text{F})(\text{CF}_3\text{CHCF}_2)(\text{PEt}_3)_2]$ (**2**) and the key-role of the fluorido ligand

in C–F bond activation was probed by studies on the reactivity of $[\text{Rh}(\text{Cl})(\text{CF}_3\text{CHCF}_2)(\text{PETe}_3)_2]$ (**11**), which does not react further.

Finally, most of the catalytic reactions developed are of low selectivity, but yield functionalized building blocks by conversions of olefins, which are initially formed by hydrodefluorination of 1,1,3,3,3-pentafluoropropene. Possible pathways then include hydrodefluorination, hydrogenation, hydrogermylation/hydrosilylation and defluorinative germylation. However, a catalytic process for the conversion of 1,1,3,3,3-pentafluoropropene into 1,1,1-trifluoro-3-triethoxysilylpropane was developed with a good selectivity.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–F bond activation · fluorine · fluoro complexes · germylation · rhodium

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