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C–F Activation and hydrodefluorination of fluorinated alkenes at rhodium †

Daniel Noveski, Thomas Braun,* Miriam Schulte, Beate Neumann and Hans-Georg Stammler
Fakultät für Chemie, Universität Bielefeld, Postfach 100131, 33501 Bielefeld, Germany.
E-mail: thomas.braun@uni-bielefeld.de

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Reaction of $[RhH(PEt_3)_4]$ (**9**) with hexafluoropropene (**1**) affords the C–F activation product $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**4**) as well as $Et_3P(F)\{(Z)\text{-}CF{=}CF(CF_3)\}$ (**11**). In contrast, addition of (*E*)-1,2,3,3,3-pentafluoropropene (**8**) to **9** yields $[Rh\{(E)\text{-}C(CF_3){=}CHF\}(PEt_3)_3]$ (**12**) together with $[RhF(PEt_3)_3]$ (**6**) and (*Z*)-1,3,3,3-tetrafluoropropene (**10**). Treatment of **12** with hydrogen effects the formation of 1,1,1-trifluoropropane (**2**) and the fluoro compounds $[RhF(PEt_3)_3]$ (**6**) and *cis-mer*-$[Rh(H)_2F(PEt_3)_3]$ (**7**). On treatment of **6** or of a mixture of **6** and **7** with $HSiPh_3$ the complexes $[RhH(PEt_3)_3]$ (**3**) and *cis-fac*-$[Rh(H)_2(SiPh_3)(PEt_3)_3]$ (**13**) are obtained. Both compounds are capable of the C–F activation of hexafluoropropene (**1**) to afford **4**. The molecular structure of complex **13** has been determined by X-ray crystallography.

Introduction

There has been considerable interest in the activation of carbon–fluorine bonds at transition metal centres in the last few years.[1–15] However, the formation of organofluorine compounds *via* C–F activation is still little developed. Recent examples include the stoichiometric[4,5] and catalytic[6–9] derivatisation of aromatic compounds by C–F activation. Thus, the catalytic conversion of hexafluorobenzene into pentafluorobenzene in the presence of hydrogen using a rhodium catalyst has been reported.[8] Comparable hydrodefluorination reactions at fluorinated alkenes are sparse and often not very selective.[1,10–14] The reactions include mainly the transformation of monofluorinated alkenes.[13]

The selective hydrodefluorination of perfluorinated alkenes remains a major challenge. However, a breakthrough has been reported very recently by W. D. Jones and coworkers. They described the conversion of highly fluorinated alkenes into less fluorinated derivatives using $[(\eta^5\text{-}C_5Me_5)_2ZrH_2]$ as the hydrogen source.[10,11] Note also that M. K. Whittlesey *et al.* showed that the reaction of hexafluoropropene with a ruthenium dihydride leads to a mixture of less fluorinated alkenes.[12] Recently, we achieved the conversion of hexafluoropropene (**1**) into 1,1,1-trifluoropropane (**2**) by rhodium induced hydrodefluorination (Scheme 1).[15] The reaction proceeds selectively and is very unique, because there is no indication of a defluorination of the trifluoromethyl group. The key step of the transformation is the activation of the fluorinated alkene at $[RhH(PEt_3)_3]$ (**3**) yielding $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**4**). Oxidative addition of hydrogen at **4** affords the rhodium(III) complex *cis-mer*-$[Rh(H)_2\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**5**). The dihydrido compound **5** converts in the presence of hydrogen into **2** and the fluoro complexes $[RhF(PEt_3)_3]$ (**6**) and *cis-mer*-$[Rh(H)_2F(PEt_3)_3]$ (**7**).

In this paper we describe studies on the activation and hydrodefluorination of hexafluoropropene (**1**) and (*E*)-1,2,3,3,3-pentafluoropropene (**8**) at $[RhH(PEt_3)_4]$ (**9**). In the latter case a metal derivative of the alkene as well as the hydrodefluorination product (*Z*)-1,3,3,3-tetrafluoropropene (**10**) has been obtained. Moreover, a cyclic process for the rhodium-mediated hydrodefluorination of **1** yielding **2** has been developed. Rhodium compounds, which are again suitable for C–F activation can be regained on treatment of $[RhF(PEt_3)_3]$ (**6**) and *cis-mer*-$[Rh(H)_2F(PEt_3)_3]$ (**7**) with a silane.

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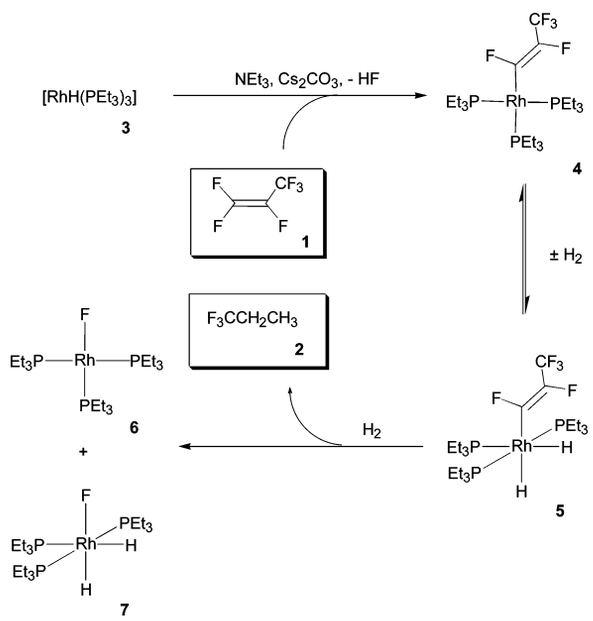

Scheme 1 C–F activation and hydrodefluorination of hexafluoropropene (**1**)

Results

1 Synthesis of fluoropropenyl complexes

Treatment of $[RhH(PEt_3)_4]$ (**9**) with hexafluoropropene (**1**) in the presence of triethylamine and Cs_2CO_3 affords the C–F activation product $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**4**) together with the phosphorane $Et_3P(F)\{(Z)\text{-}CF{=}CF(CF_3)\}$ (**11**)[16] (Scheme 2).

In contrast, a reaction of (*E*)-1,2,3,3,3-pentafluoropropene (**8**) with $[RhH(PEt_3)_4]$ (**9**) in the presence of the same combination of bases yields the fluoropropenyl complex $[Rh\{(E)\text{-}C(CF_3){=}CHF\}(PEt_3)_3]$ (**12**), the rhodium(I) fluoro compound $[RhF(PEt_3)_3]$ (**6**) as well as the alkene (*Z*)-1,3,3,3-tetrafluoropropene (**10**)[17] in a ratio ≈ 1 : 1 : 1 (Scheme 2). Furthermore there are traces (≈5%) of compound **4**, presumably generated by C–H activation. There is no indication for the formation of a phosphorane. Somewhat surprisingly, treatment of the phosphorane $Et_3P(F)\{(Z)\text{-}CF{=}CF(CF_3)\}$ (**11**) with the hydrido compound **9** also leads to the propenyl complex **12** and the rhodium fluoride **6** (ratio ≈ 1 : 1) as well as to considerable amounts of F_2PEt_3[18] (Scheme 2).

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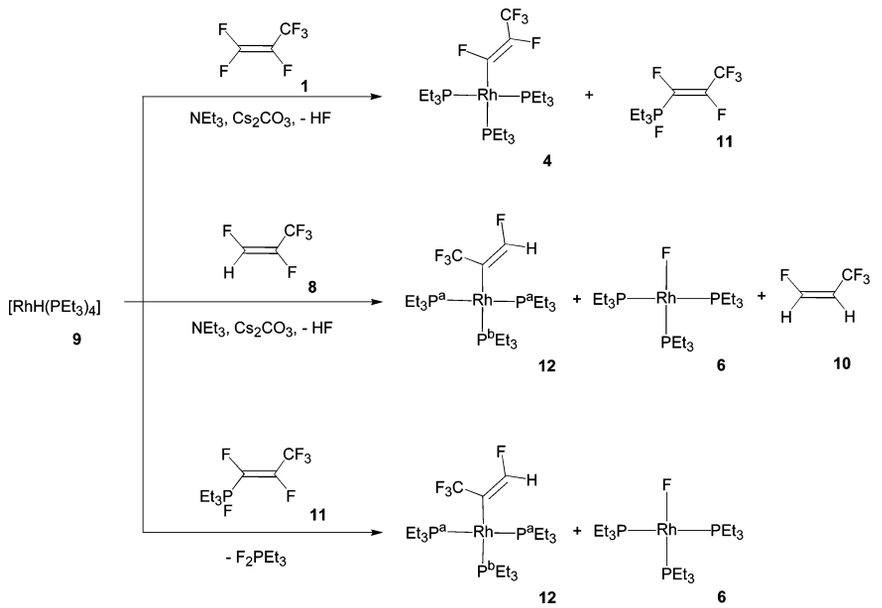


Scheme 2 Formation of fluoropropenyl complexes

Compounds **4** and **6** have been described before and have been characterised by their NMR data.[15] In addition we also acquired a ^{19}F–^{13}C HMQC NMR spectrum of **4** to get some information on the chemical shifts of the signals for the propenyl ligand in the ^{13}C NMR spectrum. The 2D spectrum shows a cross-peak which connects the signal for the fluorines of the CF_3 group to a resonance at $\delta(^{13}C)$ 122. It also exhibits a strong correlation of the fluorine at $\delta(^{19}F)$ −174.4 to a carbon centre at $\delta(^{13}C)$ 146 and of the fluorine at $\delta(^{19}F)$ −95.4 to a carbon nucleus at $\delta(^{13}C)$ 200. We assign the latter signal to the CF moiety in the α-position of the vinyl ligand.[19] The appearance of the correlation peak to the β-carbon atom at the intersection to $\delta(^{13}C)$ 146 is consistent with previous assignments of the resonance at higher field in the ^{19}F NMR spectrum to the fluorine in the β-position in perfluoropropenyl ligands.[20,21]

The ^{31}P NMR spectrum of **12** is of higher order and has been simulated (Fig. 1).[22] The coupling constants determined resemble these found for [Rh{(*Z*)-CF=CF(CF_3)}(PEt_3)$_3$] (**4**), except for the coupling $J_{P^b,F}$ = 19.8 Hz.[15] This value might reflect the *trans* position of the olefinic fluorine to the rhodium at the double bond. The ^{19}F NMR spectrum of **12** displays a resonance at δ −68.6 for the fluorine atoms of the CF_3 group and a signal at δ −118.0 with a coupling to the olefinic proton of 77 Hz. In the ^1H NMR spectrum the resonance for the olefinic proton can be found at δ 7.27 with the same coupling constant. This value indicates a *geminal* configuration of the proton and the fluorine atom at the double bond.[17,23–26] Furthermore, the signals in the ^{19}F NMR spectrum exhibit a coupling between the fluorines at the trifluoromethyl group and the olefinic fluorine with a coupling constant of 16 Hz. This suggests a *cis* configuration of a trifluoromethyl moiety in α-position and the olefinic fluorine.[21,26] More evidence for the configuration at the double bond in **12** is given by ^1H–^{13}C HMQC and ^{19}F–^{13}C HMQC NMR spectra (Fig. 2). In the ^1H–^{13}C NMR spectrum there is a strong correlation of the proton at $\delta(^1H)$ 7.27 with a carbon atom at $\delta(^{13}C)$ 143. The ^{19}F–^{13}C NMR spectrum shows a cross-peak connecting the resonance for the fluorine at $\delta(^{19}F)$ −118.0 also with the intersection to $\delta(^{13}C)$ 143 (Fig. 2). This observation clearly proves the geminal position of the olefinic fluorine and proton at the β-carbon atom. Finally, a ^{19}F–^{13}C HMQC/HMBC NMR spectrum reveals the chemical shift for the signal of the α-carbon atom of the propenyl ligand at $\delta(^{13}C)$ 236 (Fig. 3). Overall, we assign the configuration at the double bond in **12** as (*E*)-RhC(CF_3)=CHF (Scheme 2).

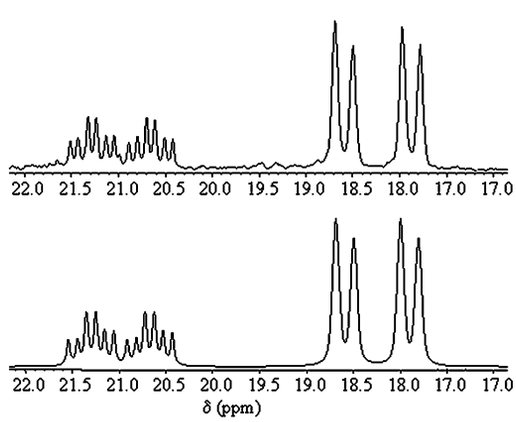


Fig. 1 $^{31}P\{^1H\}$ NMR spectrum of complex **12**; simulated (below) and observed (above) using the following coupling constants (Hz): $^1J_{RhP^a}$ = 139.5, $^3J_{P^aF}$ = 5.1, $^2J_{P^aP^b}$ = 39.1, $^1J_{RhP^b}$ = 126.5, $^3J_{P^bF}$ = 19.8; labeling of atoms as shown in Scheme 2.

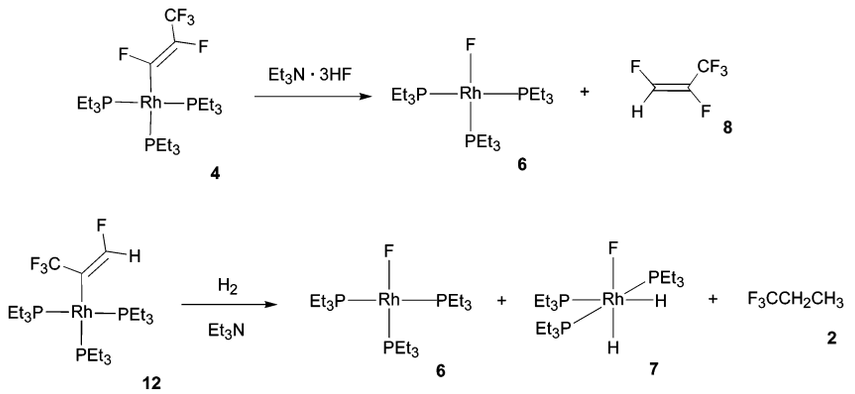
2 Reactivity of fluoropropenyl complexes

Investigations by NMR spectroscopy reveal that addition of hydrogen to a solution of [Rh{(*E*)-C(CF_3)=CHF}(PEt_3)$_3$] (**12**) leads to the generation of 1,1,1-trifluoropropane (**2**) as well as to the fluoro complexes [RhF(PEt_3)$_3$] (**6**) and *cis-mer*-[Rh(H)$_2$F(PEt_3)$_3$] (**7**) (Scheme 3). This conversion resembles the reaction of [Rh{(*Z*)-CF=CF(CF_3)}(PEt_3)$_3$] (**4**) with hydrogen, which has been described in the introduction. We proved in an independent experiment that **7** is formed by oxidative addition of H_2 to **6**. Complex **7** is only stable in solution and readily loses hydrogen under vacuum.

The rhodium–carbon bond in **4** can not only be cleaved with hydrogen (Scheme 1), but also on treatment of a solution of **4** with $Et_3N{\cdot}3HF$ yielding an alkene. An NMR experiment showed that on using substoichiometric amounts of "HF" the fluoro compound [RhF(PEt_3)$_3$] (**6**) and the (*E*)-1,2,3,3,3-pentafluoropropene (**8**) are generated (Scheme 3).

3 Synthesis, molecular structure and reactivity of *cis-fac*-[Rh(H)$_2$($SiPh_3$)(PEt_3)$_3$] (13)

A reaction of complex [RhF(PEt_3)$_3$] (**6**) with a slight excess of $HSiPh_3$ gives $FSiPh_3$ and compound [RhH(PEt_3)$_3$] (**3**) as well as minor amounts (5–10%) of the silyl complex *cis-fac*-[Rh(H)$_2$($SiPh_3$)(PEt_3)$_3$] (**13**) (Scheme 4). If a larger excess of $HSiPh_3$ is used, the amount of **13** increases. In an independent reaction



Scheme 3 Reactivity of fluoropropenyl complexes.

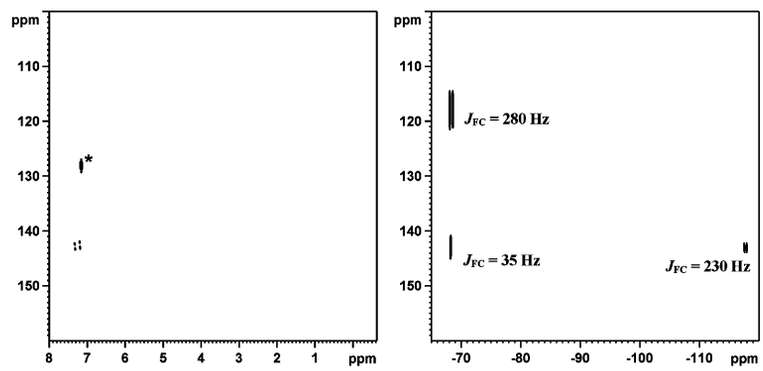


Fig. 2 Left: $^{1}H\{^{13}C\}$–^{13}C HMQC NMR spectrum of **12**, * indicates C_6D_5H, the signal at $\delta(^{1}H)$ exhibits the $^{1}H,^{19}F$-coupling of 77 Hz; right: $^{19}F\{^{1}H\}$–^{13}C HMQC NMR spectrum of **12**, one-bond correlations show a large $^{19}F,^{13}C$-coupling.

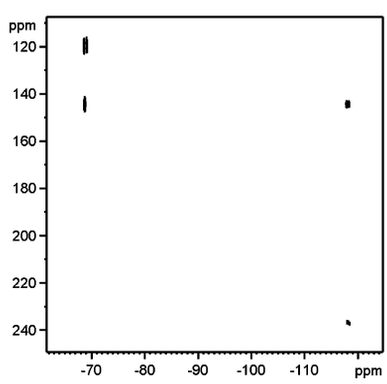


Fig. 3 $^{19}F\{^{1}H\}$–^{13}C HMQC/HMBC NMR spectrum of **12**, optimised on long-range couplings, no supression of one-bond correlations.

$[RhH(PEt_3)_4]$ (**9**) was also treated with $HSiPh_3$ yielding **13**, which indicates that the silyl complex is formed by oxidative addition of $HSiPh_3$ at $[RhH(PEt_3)_3]$ (**3**). Moreover, we could show that a mixture of **6** and the dihydrido compound *cis-mer*-$[Rh(H)_2F(PEt_3)_3]$ (**7**) gives also **3** together with **13**.[27]

The ^{31}P NMR spectrum of **13** displays a doublet of doublets at δ 11.6 and a doublet of triplets at δ 4.2. The $J_{P,P}$ coupling of 17 Hz and the $J_{Rh,P}$ couplings of 103.3 Hz and 87.2 Hz are compatible with the assignment as a rhodium(III) compound.[8,15] The multiplet at δ −10.74 in the ^{1}H NMR spectrum has a pattern which implies a large coupling to a phosphorus nucleus in the *trans* position and is assigned to the two hydrido ligands *cis* to each other.

The molecular structure of **13** determined by X-ray crystal structure analysis is shown in Fig. 4. Colourless crystals were obtained from hexane at −30 °C. Selected bond length and angles are summerised in Table 1. Note that the asymmetric unit contains three independent molecules, only one of which is shown as an ORTEP diagram. The phosphine ligands occupy the three facial coordination sites of a highly distorted octahedron at rhodium. The P–Rh–P angles to the *cis* phosphines as well as the

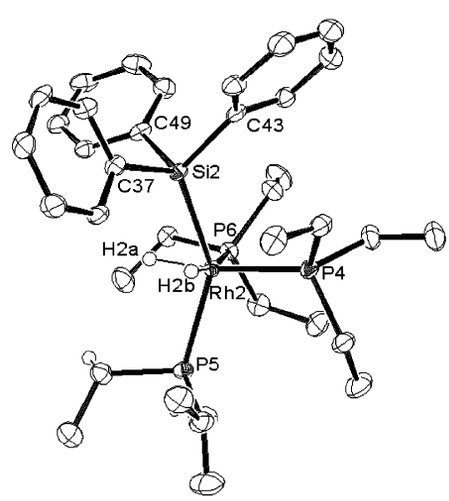


Fig. 4 An ORTEP diagram of **13**. Ellipsoids are drawn at the 50% probability level. Only one of the three independent molecules in the asymmetric unit is shown.

Si–Rh–P angles are considerably larger than 90°. The rhodium-silicon bond lengths in all three molecules are longer than the distances found in *cis-fac*-$[Rh(H)_2(SiClPh_2)(PMe_3)_3]$ [2.314(2) Å] and *cis-fac*-$[Rh(H)_2\{Si(C_6H_4CF_3)_3\}(PMe_3)_3]$ [2.338(4) Å].[28]

On treatment of a solution of **13** with hexafluoropropene complex $[Rh\{(Z)\text{-}CF{=}CF(CF_3)\}(PEt_3)_3]$ (**4**) is formed together with considerable amounts of $FSiPh_3$ (Scheme 4). A similar reaction is observed when a mixture of $[RhH(PEt_3)_3]$ (**3**) and **13** is used as starting material.

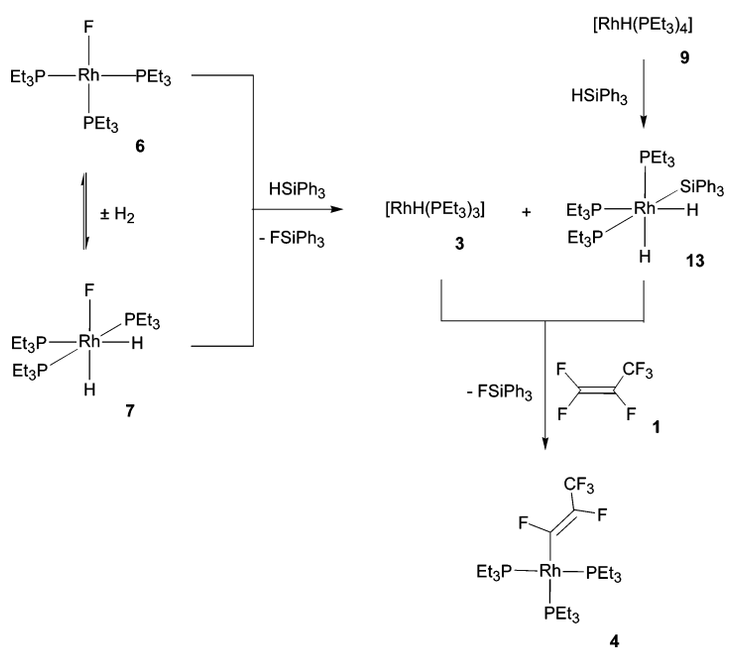
Discussion

1 C–F activation of fluorinated alkenes

The C–F activation of fluorinated propene derivatives using rhodium hydrido complexes is shown in Schemes 1 and 2. The

Table 1 Selected bond lengths (Å) and angles (°) of *cis-fac*-[Rh(H)$_2$(SiPh$_3$)(PEt$_3$)$_3$] (**13**) with the estimated standard deviations in parentheses

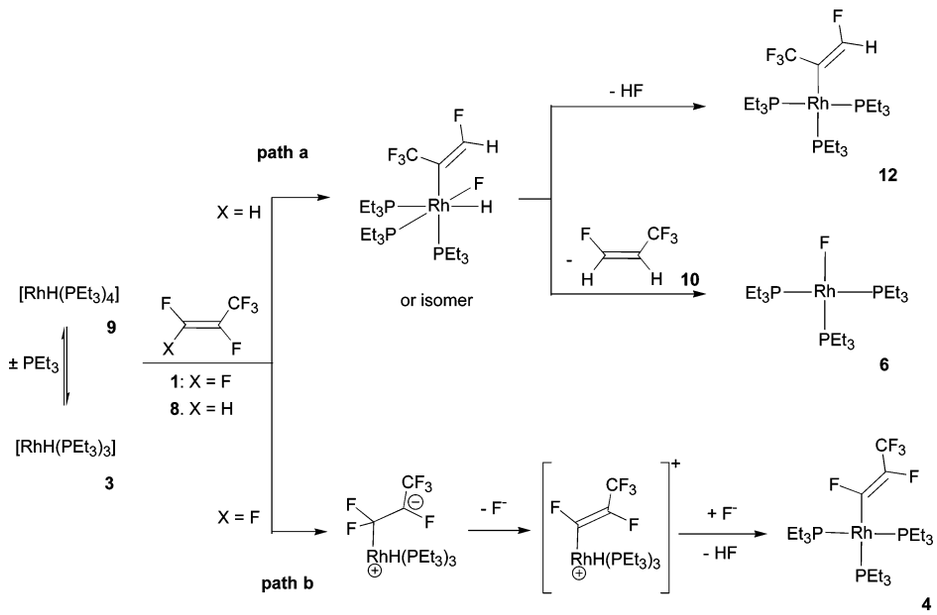
Rh(1)–Si(1)	2.3571(10)	Rh(2)–P(5)	2.3796(9)
Rh(1)–P(1)	2.3594(10)	Rh(2)–H(2A)	1.48(3)
Rh(1)–P(3)	2.3609(10)	Rh(2)–H(2B)	1.47(4)
Rh(1)–P(2)	2.3627(11)	Rh(3)–P(7)	2.3573(9)
Rh(1)–H(1A)	1.52(4)	Rh(3)–P(8)	2.3649(9)
Rh(1)–H(1B)	1.51(5)	Rh(3)–P(9)	2.3700(9)
Rh(2)–Si(2)	2.3548(9)	Rh(3)–Si(3)	2.3718(9)
Rh(2)–P(4)	2.3613(9)	Rh(3)–H(3A)	1.54(3)
Rh(2)–P(6)	2.3705(9)	Rh(3)–H(3B)	1.48(4)
Si(1)–Rh(1)–P(1)	101.57(4)	P(6)–Rh(2)–H(2A)	85.4(13)
Si(1)–Rh(1)–P(3)	99.21(3)	P(5)–Rh(2)–H(2A)	83.4(13)
P(1)–Rh(1)–P(3)	103.47(3)	Si(2)–Rh(2)–H(2B)	72.7(16)
Si(1)–Rh(1)–P(2)	139.89(4)	P(4)–Rh(2)–H(2B)	82.9(16)
P(1)–Rh(1)–P(2)	104.76(4)	P(6)–Rh(2)–H(2B)	168.9(16)
P(3)–Rh(1)–P(2)	103.39(4)	P(5)–Rh(2)–H(2B)	82.1(16)
Si(1)–Rh(1)–H(1A)	67.1(14)	H(2A)–Rh(2)–H(2B)	86(2)
P(1)–Rh(1)–H(1A)	166.5(14)	P(7)–Rh(3)–P(8)	103.86(3)
P(3)–Rh(1)–H(1A)	86.2(14)	P(7)–Rh(3)–P(9)	103.51(3)
P(2)–Rh(1)–H(1A)	81.7(14)	P(8)–Rh(3)–P(9)	103.84(3)
Si(1)–Rh(1)–H(1B)	73.1(17)	P(7)–Rh(3)–Si(3)	98.40(3)
P(1)–Rh(1)–H(1B)	82.0(17)	P(8)–Rh(3)–Si(3)	143.44(3)
P(3)–Rh(1)–H(1B)	171.5(17)	P(9)–Rh(3)–Si(3)	98.59(3)
P(2)–Rh(1)–H(1B)	81.1(18)	P(7)–Rh(3)–H(3A)	165.6(12)
H(1A)–Rh(1)–H(1B)	87(2)	P(8)–Rh(3)–H(3A)	82.5(12)
Si(2)–Rh(2)–P(4)	100.82(3)	P(9)–Rh(3)–H(3A)	87.1(12)
Si(2)–Rh(2)–P(6)	97.89(3)	Si(3)–Rh(3)–H(3A)	70.1(12)
P(4)–Rh(2)–P(6)	104.97(3)	P(7)–Rh(3)–H(3B)	85.0(15)
Si(2)–Rh(2)–P(5)	142.06(3)	P(8)–Rh(3)–H(3B)	78.2(16)
P(4)–Rh(2)–P(5)	103.66(3)	P(9)–Rh(3)–H(3B)	170.3(16)
P(6)–Rh(2)–P(5)	103.17(3)	Si(3)–Rh(3)–H(3B)	75.2(16)
Si(2)–Rh(2)–H(2A)	67.1(13)	H(3A)–Rh(3)–H(3B)	83.7(19)
P(4)–Rh(2)–H(2A)	165.5(13)		



Scheme 4 Reactivity of **6** and **13**.

reaction of (*E*)-1,2,3,3,3-pentafluoropropene (**8**) at [RhH(PEt$_3$)$_4$] (**9**) is distinctively different to the reactivity of hexafluoropropene (**1**) towards **9**. While the latter leads to a metal derivative of the alkene [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (**4**) and the phosphorane Et$_3$P(F){(*Z*)-CF=CF(CF$_3$)} (**11**), the alkene **8** gives the propenyl complex [Rh{(*E*)-C(CF$_3$)=CHF}(PEt$_3$)$_3$] (**12**), but also the fluoro compound [RhF(PEt$_3$)$_3$] (**6**) and the hydrodefluorination product (*Z*)-1,3,3,3-tetrafluoropropene (**10**). The generation of the phosphorane **11** on treatment of [RhH(PEt$_3$)$_4$] (**9**) with hexafluoropropene (**1**) can easily be explained by the liberation of phosphine, because **9** is in equilibrium with [RhH(PEt$_3$)$_3$] (**3**) and PEt$_3$, and it has also been shown that PEt$_3$ reacts with **1** to give **11**.[16,29] The reactive species for the C–F activation at rhodium is therefore presumambly complex **3**, which can on treatment with **1** readily be converted into **4**.[15]

The C–F activation reactions proceed in the presence of Et$_3$N as a base to trap the HF generated, but the yields are better on using Et$_3$N and Cs$_2$CO$_3$. Note that adducts of HF and Et$_3$N are known as fluorinating agents, which can initiate further reactivity.[15,30] This can be avoided by adding Cs$_2$CO$_3$ to the reaction solution. In this case Et$_3$N serves probably as a phase-transfer agent.[8] It should be mentioned that there are only a few examples on the activation of a C–F bond in fluorinated alkenes reported in the literature.[1,9–14,31–33] The activation of hexafluorobenzene yielding [Rh(C$_6$F$_5$)(PMe$_3$)$_3$] has been described by Aizenberg and Milstein.[8]



Scheme 5 Possible mechanisms of the C–F activation of fluorinated propene derivatives.

Moreover, complex *cis-fac*-$[Rh(H)_2(SiPh_3)(PEt_3)_3]$ (**13**) also reacts with hexafluoropropene (**1**) yielding the C–F activation product **4** (Scheme 4). The concomitant generation of $FSiPh_3$ indicates that a silyl complex is the active species for the C–F activation of the fluorinated molecule. This is presumably the rhodium(I) complex $[Rh(SiPh_3)(PEt_3)_3]$, which might be generated from **13**, but could not be identified yet.[9,34] However, an alternative reaction pathway consists of an initial release of $HSiPh_3$ from **13** and subsequent C–F activation. The formation of $FSiPh_3$ could then be explained by a reaction of $HSiPh_3$ with HF. An independent experiment shows that treatment of $HSiPh_3$ with $Et_3N{\cdot}3HF$ gives indeed $FSiPh_3$.

Concerning the mechanism of the C–F activation of the fluorinated propenes at rhodium hydride centres several possibilties are conceivable. We believe that an initial electron transfer process from the metal to the fluorinated substrate is not very likely, because of the unfavourable redox potential of hexafluoropropene (**1**).[8,9,35,36] Such a process would only be conceivable, if one assumes a precoordination of the fluorocarbon at the metal or rapid irreversible dissociation of F^- from a propenyl anion followed by a deprotonation of the metal.[37] We also exclude a reaction pathway *via* alkene insertion into the rhodium-hydrogen bond followed by elimination of HF from the alkyl complex formed, because it would probably lead to diastereomers.[32,38,39]

In contrast, there are indications for an oxidative addition of (*E*)-1,2,3,3,3-pentafluoropropene (**8**) at rhodium followed by reductive elimination of HF giving $[Rh\{(E)\text{-}C(CF_3)=CHF\}(PEt_3)_3]$ (**12**) (Scheme 5, path a).[40] Such a mechanism also explains the formation of the fluoro complex $[RhF(PEt_3)_3]$ (**6**) as well as of (*Z*)-1,3,3,3-tetrafluoropropene (**10**). Thus, both compounds can be be generated after reductive elimination of the alkene **10** from the initial oxidative addition product. Note that a reaction pathway *via* alkene (*syn*-)insertion into the rhodium–hydrogen bond and subsequent (*syn*-)β-fluorine elimination would also lead to **6**, but not to **10**.[41] A stereoselective reaction would rather give the alkenes (*E*)-1,3,3,3-tetrafluoropropene or 2,3,3,3-tetrafluoropropene.

For the activation of hexafluoropropene (**1**), which has been reported before,[15] there is no formation of **6** or of a lower fluorinated alkene. This does not exclude an analogous reaction pathway *via* a rhodium(III) intermediate yielding $[Rh\{(Z)\text{-}CF=CF(CF_3)\}(PEt_3)_3]$ (**4**), but it seems to be not very likely (Scheme 5). Moreover, the formation of **6** and (*E*)-1,2,3,3,3-pentafluoropropene (**8**) on treatment of **4** with $Et_3N{\cdot}3HF$ indicates a preference for reductive elimination of an alkene and not of HF from a possible oxidative addition product.

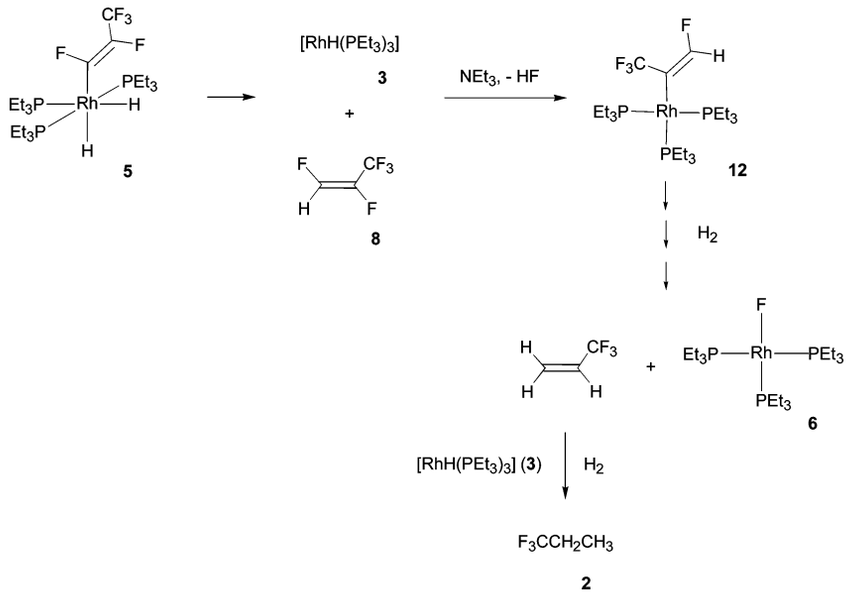
We therefore propose an alternative mechanism for the formation of **4**. It consists of the generation of a Meisenheimer intermediate by nucleophilic attack of the rhodium centre at the fluorinated molecule (Scheme 5, path b).[2,31] Loss of fluoride followed by deprotonation at the metal centre would then give complex **3** together with HF. The regioselectivity observed is in accordance with this assumption as the attack of "organic nucleophiles" at hexafluoropropene (**1**) occurs at the expected position.[36,42] In contrast, for a nucleophilic attack of $[RhH(PEt_3)_3]$ (**9**) at (*E*)-1,2,3,3,3-pentafluoropropene (**8**) one would expect a different isomer of **12** than observed.[36,42]

Overall, we have indications for two distinctive different mechanisms for the C–F activation of **1** and **8**. Comparable reaction pathways to the mechanisms discussed above are in principle all conceivable for the activation of hexafluoropropene (**1**) at $[Rh(SiPh_3)(PEt_3)_3]$. At the moment, the mechanism for the reaction of $Et_3P(F)\{(Z)\text{-}CF=CF(CF_3)\}$ (**11**) with $[RhH(PEt_3)_4]$ (**9**) yielding $[Rh\{(E)\text{-}C(CF_3)=CHF\}(PEt_3)_3]$ (**12**), $[RhF(PEt_3)_3]$ (**6**) and F_2PEt_3 is not clear.

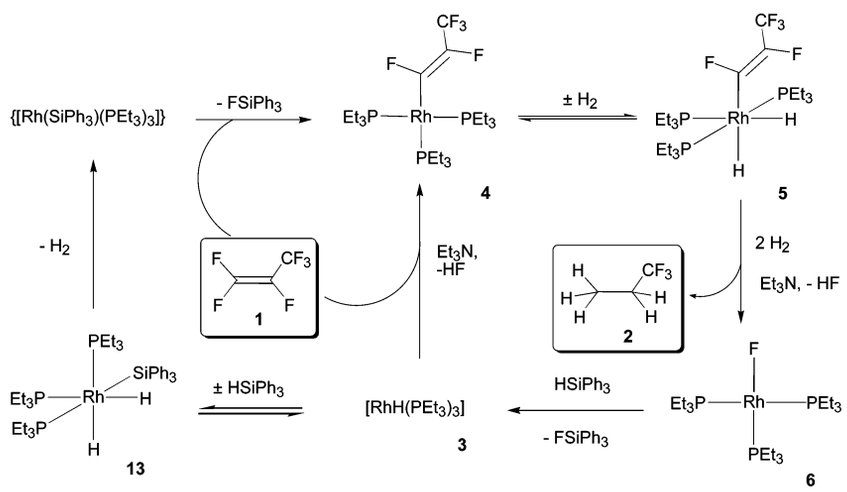
2 Hydrodefluorination of fluorinated propenes

Two different hydrodefluorination reactions have been elaborated involving the C–F activation of (*E*)-1,2,3,3,3-pentafluoropropene (**8**). Thus, cleavage of the carbon–fluorine bond in **8** leads directly to the formation of the less fluorinated alkene (*Z*)-1,3,3,3-tetrafluoropropene (**10**), but also to the rhodium derivative $[Rh\{(E)\text{-}C(CF_3)=CHF\}(PEt_3)_3]$ (**12**) (Scheme 2). Beyond, compound **12** converts in the presence of hydrogen into 1,1,1-trifluoropropane (**2**) (Scheme 3).

In addition, the activation of **8** *and* its transformation into **2** is important, because the reactions provide some evidence concerning the mechanism of the transformation of hexafluoropropene (**1**) into 1,1,1-trifluoropropane (**2**). Thus, the formation of **2** from **4** might proceed *via* reductive elimination of **8** from *cis-mer*-$[Rh(H)_2\{(Z)\text{-}CF=CF(CF_3)\}(PEt_3)_3]$ (**5**) followed by repetition of C–F activation and analogous cleavage reactions (Scheme 6).[8] Such a reaction pathway would involve both steps described above. Hydrogenation of the 3,3,3-trifluoropopene obtained as initial product affords the 1,1,1-trifluoropropane (**2**).[43] However, we can not exclude entirely other mechanisms, which involve α- or β-fluorine elimination reactions with concomitant formation of HF and subsequent hydrogenation of the generated propynyl ligand.[3,5,41]



Scheme 6 Possible mechanisms for the formation of **2**.



Scheme 7 Cyclic process for the synthesis of **2** from **1**.

The conversions of hexafluoropropene (**1**) and (*E*)-1,2,3,3,3-pentafluoropropene (**8**) into **2** involve the first examples of a selective and complete hydrodefluorination of a perfluorinated alkene, in which only the fluorines at the double bond have been replaced by hydrogen.[10,11,44] Moreover, dihydrogen has been used for the reduction of the fluorovinyl ligands after the activation of the alkene at rhodium. Note that in the zirconium mediated conversion of hexafluoropropene into propane a zirconium hydride is the main hydrogen source.[10]

3 A cyclic process for the hydrodeflorination of hexafluoropropene

A cylic process for the transformation of hexafluoropropene (**1**) into 1,1,1-trifluoropropane (**2**) has been developed (Scheme 7). The crucial step after the activation and hydrodefluorination of the fluorinated substrate is the conversion of the complexes $[RhF(PEt_3)_3]$ (**6**) and $[Rh(H)_2F(PEt_3)_3]$ (**7**) into the compounds $[RhH(PEt_3)_3]$ (**3**) and *cis-fac*-$[Rh(H)_2(SiPh_3)(PEt_3)_3]$ (**13**) on treatment with $HSiPh_3$. Note that other replacements of a fluoro ligands at late transition metals using silanes reagents have been described.[2,9,45] Compound **13** can also be prepared independently on treatment of $[RhH(PEt_3)_4]$ (**9**) with $HSiPh_3$. Complex **13** or a mixture of **3** and **13** reacts with hexafluoropropene (**1**) and the C–F activation product [Rh{(*Z*)-CF=CF(CF_3)}(PEt_3)$_3$] (**4**) is reformed. Overall 1,1,1-trifluoropropane (**2**) can be prepared from hexafluoropropene (**1**), $HSiPh_3$ and hydrogen in the coordination sphere of rhodium. Further studies on the basis of these results and on a possible reactivity of **4** towards silanes will reveal, if a catalytic process can be developed.

Conclusions

In conclusion, the hydrodefluorination of (*E*)-1,2,3,3,3-pentafluoropropene (**8**) yielding (*Z*)-1,3,3,3-tetrafluoropropene (**10**) has been achieved. Furthermore, we demonstrated the selective transfer of the fluorinated alkenyl unit in **8** into a non-fluorinated alkyl group at rhodium. The reaction proceeds *via* C–F activation and hydrodefluorination steps in the presence of H_2. The conversion gives some evidence for the mechanism of a comparable transformation of hexafluoropropene (**1**) into 1,1,1-trifluoropropane (**2**).

In addition, a cyclic process for the hydrodefluorination of **1** has been developed allowing the recovery of rhodium complexes, which are again suitable for C–F activation. Current studies deal with the development of a catalytic cycle.

We believe that the reactions described respresent a new and general method to prepare hydrofluorocarbons, some of which are of current interest as compounds with less or no ozone depletion potential.[46]

Experimental

Most of the synthetic work was carried out on a Schlenk line or a nitrogen-filled glove box with oxygen levels below 10 ppm. All solvents were purified and dried by convential methods and distilled under argon before use. Benzene-d_6 and toluene-d_8 were dried by stirring over potassium and then distilled under vacuum. The silane $HSiPh_3$ and $Et_3N{\cdot}3HF$ were obtained from Aldrich. $[RhH(PEt_3)_4]$ (**9**), $[RhF(PEt_3)_3]$ (**6**) and (*E*)-1,2,3,3,3-pentafluoropropene (**8**) were prepared according to the literature.[15,16,24,29]

The NMR spectra were recorded on a Bruker DRX 500 (^1H, ^{31}P and ^{19}F NMR) or a Bruker Avance 600 (^1H NMR and 2D spectra) spectrometer equipped with a triple resonance probehead (^{13}C, ^1H, ^{19}F). The ^1H NMR chemical shifts were referenced to residual C_6D_5H at δ 7.15 or toluene-d_7 at δ 2.1. The $^{13}C\{^1H\}$ spectra were referenced to C_6D_6 at δ 128.0. The $^{31}P\{^1H\}$ NMR spectra are reported downfield of an external solution of H_3PO_4 (85%). The ^{19}F NMR spectra were referenced to external C_6F_6 at δ −162.9. The infrared spectrum was recorded on a Bruker IFS-66 spectrometer.

Formation of [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (4) and Et$_3$P(F){(*Z*)-CF=CF(CF$_3$)} (11)

Cs_2CO_3 (60 mg, 0.18 mmol) was added to a solution of $[RhH(PEt_3)_4]$ (**9**) (101 mg, 0.18 mmol) and Et_3N (26 μL, 0.18 mmol) in benzene (5 mL). A slow stream of hexafluoropropene (**1**) was then passed for 2 min through the reaction mixture. The yellow suspension was filtered and the solvent was removed from the filtrate in vacuo yielding a yellow oil. The ^{31}P and ^{19}F NMR data of the residue reveal the formation of **4** and **11** (ratio ≈ 1 : 1). Compounds **4** and **11** were identified by comparison of the NMR data with the values found in the literature.[15,16]

Synthesis of [RhF(PEt$_3$)$_3$] (6), (*Z*)-1,3,3,3-tetrafluoropropene (10) and [Rh{(*E*)-C(CF$_3$)=CHF}(PEt$_3$)$_3$] (12)

(a) A slow stream of hexafluoropropene (**1**) was passed for 5 min through a solution of PEt_3 (60 μL, 0.40 mmol) in benzene (3 mL), giving a solution of $Et_3P(F)\{(Z)$-CF=CF$(CF_3)\}$ (**11**). A solution of $[RhH(PEt_3)_4]$ (**9**) (202 mg, 0.35 mmol) in benzene (2 mL) was then added, the reaction mixture was stirred for 1 h at room temperature, and the volatiles were removed under vacuum. The remaining brown oil consisted of the complexes **6** and **12** (ratio ≈ 1 : 1), which were characterised by NMR spectroscopy, as well as of considerable amounts of F_2PEt_3.[18]

(b) A slow stream of **1** was passed for 5 min through a solution of PEt_3 (150 μL, 1.02 mmol) in benzene (5 mL). The solvent was removed under vacuum giving a yellow oil of $Et_3P(F)\{(Z)$-CF=CF$(CF_3)\}$ (**11**). The oil was dissolved in benzene (2 mL) and water was added (20 μL, 1.11 mmol). After distillation under vacuum a solution was obtained containing (*E*)-1,2,3,3,3-pentafluoropropene (**8**). This solution was then added to a suspension of $[RhH(PEt_3)_4]$ (**9**) (24 mg, 0.04 mmol), Cs_2CO_3 (50 mg, 0.15 mmol), and Et_3N (20 μL, 0.15 mmol) in benzene (2.5 mL). The reaction mixture was stirred for 1 h at room temperature and the volatiles were distilled under vacuum. The distillate consisted of a solution of **10**, which was characterised by NMR spectroscopy.[17] The remaining brown oil consisted of the complexes **6** and **12** (ratio ≈ 1 : 1) as well as small amounts (≈5%) of **4**. Complexes **4** and **6** werde identified by comparison of the NMR spectroscopic data.[15] Selected spectroscopic data for **12**: ^1H NMR (600 MHz, C_6D_6): δ 7.27 (dm, J_{FH} = 77 Hz, =CH), (the resonances for the CH_2CH_3 group are obscured by similar groups of **6**, which is present in the reaction solution). ^{31}P NMR (202.5 MHz, C_6D_6): δ 20.4 (P^b *trans* to Rh*C*), 17.6 (P^a); for simulation of coupling constants see Fig. 1; labeling of atoms as in Scheme 2. ^{19}F NMR (470.4 MHz, C_6D_6): δ −69.3 (dm, J_{FF} = 16 Hz, 3 F, CF_3), −118.2 (dddd, J_{FH} = 77, J_{PF} = 20, J_{FF} = 16, J = 5 Hz, 1 F, =CF).

Synthesis of *cis-mer*-[Rh(H)$_2$F(PEt$_3$)$_3$] (7)

A slow stream of hydrogen was passed for 1 min through a solution of $[RhF(PEt_3)_3]$ (**6**) (43 mg, 0.09 mmol) in toluene-d_8 (1.5 mL). The ^{19}F and ^{31}P NMR data of the solution reveal the formation of **7**. The reaction is quantitative according to the NMR spectra. Complex **7** has been identified by comparison of the NMR data.[15]

Reaction of [Rh{(*Z*)-CF=CF(CF$_3$)}(PEt$_3$)$_3$] (4) with Et$_3$N·3HF

A solution of **4** (37 mg, 0.06 mmol) in C_6D_6 (0.5 mL) was treated with a solution of $Et_3N{\cdot}3HF$ in THF (10 μL, 0.01 mmol). The ^1H, ^{19}F and ^{31}P NMR spectroscopic data reveal the formation of **6** and (*E*)-1,2,3,3,3-pentafluoropropene (**8**).[24]

Synthesis of *cis-fac*-[Rh(H)$_2$(SiPh$_3$)(PEt$_3$)$_3$] (13)

$[RhH(PEt_3)_4]$ (**9**) (90 mg, 0.16 mmol) was suspended in hexane (10 mL), and $HSiPh_3$ (42 mg, 0.16 mmol) was added, giving a pink solution. The reaction mixture was then stirred for 2 h at room temperature and the volatiles were removed under vacuum. The remaining pink solid was dissolved in hexane (10 mL) and the solution was filtered through a cannula. Colourless crystals precipitated at −35 °C. Yield 75.1 mg (71%) (Found: C, 59.53; H, 8.39%. $C_{36}H_{62}SiRhP_3$ requires: C, 59.99; H, 8.66%). IR [KBr, ν/cm^{-1}]: 1972, 2061 (RhH). ^1H NMR (toluene-d_8, 600 MHz, 198 K): δ 8.16 (m, 6 H, Ph), 7.34 (t, J_{HH} = 7.7 Hz, 6 H, Ph), 7.23 (t, J_{HH} = 7.6 Hz, 3 H, Ph), 1.70–0.78 (m, 45 H, CH_2CH_3), −10.74 (m, 2 H, RhH). ^{31}P NMR (202.5 MHz, toluene-d_8, 198 K): δ 11.6 (dd, J_{RhP} = 103.3, J_{PP} = 17 Hz, P *trans* to H), 4.2 (dt, J_{RhP} = 87.2, J_{PP} = 17 Hz, P *trans* to Si).

Formation of [RhH(PEt$_3$)$_3$] (3) and *cis-fac*-[Rh(H)$_2$(SiPh$_3$)(PEt$_3$)$_3$] (13) from [RhF(PEt$_3$)$_3$] (6)

A solution of **6** (68 mg, 0.14 mmol) in C_6D_6 (1.5 mL) was treated with $HSiPh_3$ (48 mg, 0.19 mmol). The ^1H and ^{31}P NMR data of the solution reveal the formation of $[RhH(PEt_3)_3]$ (**3**) and minor amounts (5–10%) of **13**. Selected NMR spectroscopic data for **3** (see also ref. 29): ^1H NMR (600 MHz, toluene-d_8, 198 K): δ −7.61 (dm, br, J_{PH} = 107.2, Hz, RhH). ^{31}P NMR (202.4 MHz, toluene-d_8, 198 K): δ 25.4 (dd, J_{RhP} = 153.7, J_{PP} = 29.8 Hz), 21.9 (dt, J_{RhP} = 137.7, J_{PP} = 29.8 Hz, P *trans* to Rh*H*).

Synthesis of [Rh{CF=CF(CF$_3$)}(PEt$_3$)$_3$] (4) from *cis-fac*-[Rh(H)$_2$(SiPh$_3$)(PEt$_3$)$_3$] (13)

A slow stream of hexafluoropropene (**1**) was passed for 3 min through a solution of **13** (56.9 mg, 0.08 mmol) and NEt_3 (40 μL, 0.28 mmol) in benzene (5 mL). The reaction mixture was then stirred for 1 h at room temperature and the volatiles were removed under vacuum. The remaining brown oil was dissolved in benzene (5 mL), and the solution was filtered through a cannula. Removing the solvent *in vacuo* gave a yellow oil. The ^{19}F and ^{31}P NMR data of the solution reveal the formation of **4** and $FSiPh_3$.[15,47] Yield 67 mg (60%).

Structure determination for complex 13

Colourless crystals of **13** were obtained from a solution in ether at −30 °C. Diffraction data were collected for a block with dimensions 0.30 × 0.25 × 0.16 mm on a Nonius Kappa CCD diffractometer.

Crystal data for **13**: $C_{36}H_{62}P_3RhSi$, M = 718.77, monoclinic, space group $P2_1/c$, a = 28.465(3), b = 17.3500(14), c = 22.700(3) Å, β = 96.928(11)°, U = 11129(2) Å^3, Z = 12, T = 104(2) K, μ(Mo-Kα) = 0.645 mm^{-1}, 223527 reflections measured, 32417 unique (R_{int} = 0.0842). The structure was solved by direct methods (SHELXTL PLUS) and refined with full-matrix least square methods on F^2 (SHELX-97).[48,49] The structure can also be solved assuming a smaller, but also monoclinic, unit cell which is one third of the cell used, but the reciprocal lattice

shows undoubtedly reflections for the big cell. Using the small cell yields heavy disordering. Final R_1, wR_2 values on all data: 0.1171, 0.1139. R_1, wR_2 values for 18916 reflexions with $I_o > 2\sigma(I_o)$: 0.0481, 0.0813.

Hydrogen atoms were fixed at the calculated positions using a riding model except hydrogens bound at rhodium, which were refined isotropically. The disordered atoms were also refined isotropically; ratio in brackets: C20 (72 : 28), C23 and C24 (76 : 24), C26 (77 : 23) and C30 (78 : 22). All other atoms were refined anisotropically.

CCDC reference number 207704.

See http://www.rsc.org/suppdata/dt/b3/b306635e/ for crystallographic data in CIF or other electronic format.

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