Competing C–H and C–F bond activation reactions of a fluorinated olefin at Rh: A fluorido vinylidene complex as an intermediate in an unprecedented dehydrofluorination step

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General Procedures, Methods and Materials

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures and, prior to use, distilled under argon. The rhodium complexes \([\text{Rh}(\text{H})(\text{PEt}_3)_3] \) (1), \([\text{Rh}(	ext{CH}_3)(\text{PEt}_3)_3] \) (2), \([\text{Rh}(\text{C}≡\text{CCF}_3)(\text{CO})(\text{PEt}_3)_3] \) (6) and \([\text{Rh}(\mu-\text{F})(\text{cyclooctene})_2] \) (4) were prepared as described in the literature. All reagents were obtained from commercial sources. Unless stated, NMR spectra were recorded at room temperature on a Bruker DPX 300 or a Bruker Avance 300 spectrometer using the solvent as the internal lock. \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) signals are referred to residual solvent signals, those of \(^{31}\text{P}\{^1\text{H}\}\) to 85\% H\(_3\)PO\(_4\) and the \(^{19}\text{F}\) NMR spectra to external CF\(_3\)Cl. \(^1\text{H}, ^{19}\text{F}, ^{31}\text{P}\{^1\text{H}\}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR signal assignments were supported or, when stated, determined by \(^1\text{H}, ^1\text{H}\) COSY, \(^{19}\text{F}, ^1\text{H}\) HETCOR, \(^{19}\text{F}, ^{19}\text{F}\) gCOSY, \(^{31}\text{P}, ^3\text{P}\) COSY, \(^1\text{H}, ^{13}\text{C}\) HMQC, \(^1\text{H}, ^{13}\text{C}\) HMBC, \(^{19}\text{F}, ^{13}\text{C}\) HMBC, \(^{19}\text{F}, ^{13}\text{C}\) HMQC and \(^1\text{H}, ^{31}\text{P}\) HMBC NMR experiments. The determined coupling constant values were confirmed by gNMR software simulations.\(^6\) Mass spectra of organometallic complexes were measured with a Micromass Q-Tof-2 instrument equipped with a Linden LIFDI source (Linden CMS GmbH). Infrared spectra were recorded with the Platinum ATR module of a Bruker FT-IR Alpha II spectrometer.

Caution! In some experiments traces of HF might be generated. Immediate access to proper treatment procedures in case of contact with HF-containing solutions must be ensured.

Reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt\(_3\))\(_3\)] (1)

In a Young NMR tube [Rh(H)(PEt\(_3\))\(_3\)] (1) (30 mg, 0.065 mmol) was dissolved in toluene-d\(_8\) (0.4 mL). The reaction mixture was frozen to 77 K, the NMR tube was degassed in vacuo, and pressurized with Z-1,3,3,3-tetrafluoropropene to 0.2 bar. The reaction was monitored at variable temperatures by NMR spectroscopy. At 233 K full conversion of complex 1 to complex \(\text{fac-}[\text{Rh}(\text{H})(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]\) (7) was observed. At 273 K a 90\% conversion, based on the \(^{19}\text{F}\) NMR spectrum, of 7 into [Rh\{\(\text{(E)-CH=CHCF}_3\}\}(\text{PEt}_3)_3] (2) was observed as well as the release of HF and traces of complexes [Rh\{\(\text{(E)-CF=CHCF}_3\}\}(\text{PEt}_3)_3] (3) and [Rh\{\(\text{(Z)-CH=CHCF}_3\}\}(\text{PEt}_3)_3] (4). Finally, after 10 minutes at room temperature, a mixture of [Rh\{\(\text{(E)-CH=CHCF}_3\}\}(\text{PEt}_3)_3] (2), [Rh\{\(\text{(E)-CF=CHCF}_3\}\}(\text{PEt}_3)_3] (3), [Rh\{\(\text{(Z)-
CH=CHCF₃)(PEt₃)₃ (4) and [Rh(F(HF)₂)(PEt₃)₃] (5) was detected in a 1:8:5 ratio. In addition, 3,3,3-trifluoropropene was observed.

When the reaction is directly warm up to room temperature, the same product mixture is observed. After 30 minutes, the ratio of complexes 2, 3, 4 and 5 is 3.8:2:1:4.4. After one day, [Rh(C≡CCF₃)(PEt₃)₃] (6) and complex 5 are the only products in a 1:1 ratio. Complexes 2, and 6 have been identified by comparison with literature. Complex 5 was identified by comparison with [Rh(FHF)(PEt₃)₃], however, P-F couplings are not observed which suggest the presence of more than one HF molecule leading to the proposed formula [Rh{F(HF)₂}(PEt₃)₃] (5). Addition of excess of NEt₃/C₆H₅CO₂H leads to the formation of [Rh(F)(PEt₃)₃].

The amount of HF in complex 5 was determined by adding ClSiEt₃ (0.059 mmol, 6.5 equiv) to a solution of complexes 6 and 5 (0.009 mmol of 5 based on the ³¹P{¹H} NMR ratio). After 10 min, full conversion of complex 5 into [Rh(Cl)(PEt₃)₃] and dihydrido chlorido rhodium(III) species was observed with a 45% conversion of ClSiEt₃ (determined directly from the ¹H NMR spectrum and supported by external standard of PhCF₃) into FSiEt₃ and F₂SiEt₂ (0.027 mmol in total). The 3 equivalents required would correspond to two HF moieties and the rhodium-bound fluorido ligand.

Analytical data for [Rh{(Z)-CH=CHCF₃}(PEt₃)₃] (4): ¹H NMR (300.1 MHz, C₆D₆): δ = 8.35 (dt, ³JHH = 14.1, ³JHPcis = 4.3 Hz, CH=); 6.61 (m, ddq in ¹H{¹F} NMR spectrum, dqd in ¹H{³¹P} NMR spectrum, ³JHH = 13.9, ⁴JH,trans = 11.8, ³JHF = 8.7, ⁴JH,Pcis ≈ ³JHH = 2.3 Hz, =CHCF₃) ppm; the resonances corresponding to the phosphine ligands are overlapped with the signals for the other compounds. ¹⁹F NMR (282.4 MHz, C₆D₆): δ = -59.7 (m, tt in ¹⁹F{¹H} NMR spectrum, ⁵JF,Pcis = 5.5, ⁵JF,Htrans ≈ ⁴JF,RH = 1.7 Hz, 3F, CF₃) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 12.5 (ddq, ³JF,RH = 154.6, ³JF,P = 38.9, ³JF,F = 4.9 Hz, 2P, Pcis) ppm; the resonance of Ptrans is overlapped with the signals for the other compounds.

Analytical data for [Rh{F(HF)₂}(PEt₃)₃] (5): ¹H NMR (300.1 MHz, C₆D₆): δ = 1.65-1.50 (m, q in ¹H{³¹P}), ³JHH = 7.7 Hz, 12H, Pcis(CH₂CH₃); 1.25-1.15 (m, q in ¹H{³¹P}), ³JHH = 7.2 Hz 6H, Ptrans(CH₂CH₃); 1.17-1.03 (m, t in ¹H{³¹P}), ³JHH = 7.7 Hz, 18H, Pcis(CH₂CH₃); 0.96 (dt, ³JHP = 14.9, ³JHH = 7.2 Hz, 9H, PtransCH₂CH₃); ¹⁹F NMR (282.4 MHz, C₆D₆): δ = -178 (br m, HF); -277.0 (m, 1F, Rh-F) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 45.83 (dt br,
$^1J_{P,Rh} = 187.7, \ 2J_{P,P} = 42.5 \ Hz, \ 1P, \ P_{trans}$; 23.26 (dd, $^1J_{P,Rh} = 139.6, \ 2J_{P,P} = 42.5 \ Hz, \ 2P, \ P_{cis}$) ppm

Analytical data for $fac$-[Rh(H)(CF$_3$CHHF)(PEt$_3$)$_3$] (7): $^1$H NMR (300.1 MHz, 233 K, toluene-d$_8$): $\delta = 5.85$ (d br, ddd in $^1$H [$^31$P] NMR spectrum, $^2J_{H,F} = 67.4, \ ^3J_{H,H} = 5.3, \ ^2J_{H,Rh} = 2.1 \ Hz, \ CHF$); 2.14 (m, overlapped with the signal for toluene-d$_8$, observed by a $^1$H-$^1$H COSY spectrum, CHCF$_3$); 1.55-1.78 (m, 6H, PCH$_2$CH$_3$); 1.32-1.54 (m, 6H, PCH$_2$CH$_3$); 0.93-1.18 (m, 24H, PCH$_2$CH$_3$ + PCH$_2$CH$_3$); 0.74 (dt, $^3J_{H,F} = 12.8, \ ^3J_{H,H} = 6.9 \ Hz, \ 9H, \ PCH$_2$CH$_3$); -13.22 (dq, $^2J_{H,F} = 160.0, \ ^2J_{H,Pa} \approx \ ^2J_{H,Pb} \approx \ ^3J_{H,F} = 19.8, \ ^1J_{H,Rh} = 12.2 \ Hz, \ 1H, \ RhH)$ ppm. $^{19}$F NMR (282.4 MHz, 253 K, toluene-d$_8$): $\delta = -49.6$ (q br, $^4J_{F,F} \approx \ ^4J_{F,F} \approx \ ^2J_{F,H} = 13 \ Hz, \ 3F, \ CF_3$); -182.7 (dm, $^2J_{F,H} = 68 \ Hz, \ 1F, \ CF$) ppm. $^{31}$P [$^1$H] NMR (121.4 MHz, 233K, toluene-d$_8$): $\delta = 19.29$ (dddq, $^1J_{P,Rh} = 135.4, \ ^3J_{P,Pb} = 29.5, \ ^2J_{P,Pc} = 26.0, \ ^4J_{P,P} = 16.2, \ ^3J_{P,F} = 13.0 \ Hz, \ 1P, \ P^a$); 10.85 (dq, $^1J_{P,Rh} = 111.9, \ ^3J_{P,F} \approx \ ^2J_{P,Pc} \approx \ ^2J_{P,Pa} = 29.7 \ Hz, \ P^b$); 0.87 (br dq, $^1J_{P,Rh} = 84.0, \ ^2J_{P,Pa} \approx \ ^2J_{P,Pb} \approx \ ^3J_{P,F} = 27.2 \ Hz, \ P^c$) ppm.

**Synthesis of [Rh{(E)-CH=CHCF$_3$}(PEt$_3$)$_3$] (2)**

In a Young NMR tube [Rh(CH$_3$)(PEt$_3$)$_3$] (8) (50 mg, 0.106 mmol) was dissolved in C$_6$D$_6$ (0.4 mL). The reaction mixture was frozen to 77 K, the NMR tube was degassed in vacuo, and pressurized with 3,3,3-trifluoropropene to 0.2 bar. After warming up to room temperature the reaction mixture was kept for 30 min before the volatiles were removed under vacuum. An orange/reddish oil, identified as [Rh{(E)-CH=CHCF$_3$}(PEt$_3$)$_3$] (2) by comparison with the literature,$^8$ was obtained. Yield: 57 mg (98%).

**Reaction of [Rh{(E)-CH=CHCF$_3$}(PEt$_3$)$_3$] (2) with Z-1,3,3,3-tetrafluoropropene**

In a Young NMR tube [Rh{(E)-CH=CHCF$_3$}(PEt$_3$)$_3$] (2) (31 mg, 0.056 mmol) was dissolved in C$_6$D$_6$ (0.4 mL). The reaction mixture was frozen to 77 K, the NMR tube was degassed in vacuo, and pressurized with Z-1,3,3,3-tetrafluoropropene to 0.2 bar. After warming up to
room temperature the NMR spectroscopic data of the reaction mixture revealed after 50 min the full conversion of 2 into [Rh{(E)-CF=CHCF\(_3\)}\((\text{PEt}_3)_3\)] (3) as well as the release of 3,3,3-trifluoropropene. For the analytical data of complex 3 see below.

**Reaction of [Rh\{(E)-CH=CHCF\(_3\)}\((\text{PEt}_3)_3\)] (2) with Et\(_3\)N·3HF**

In an NMR tube equipped with a PFA inliner [Rh\{(E)-CH=CHCF\(_3\)}\((\text{PEt}_3)_3\)] (2) (24 mg, 0.043 mmol) was dissolved in C\(_6\)D\(_6\) (0.3 mL). Then, excess of NEt\(_3\)·3HF (7 \(\mu\)L, 0.04 mmol) was added to the solution. After 5 minutes at room temperature, the NMR spectroscopic data of the reaction mixture revealed the full conversion of 2 into [Rh\{F(HF)\(_2\)}\((\text{PEt}_3)_3\)] (5) (see above) as well as the release of 3,3,3-trifluoropropene.

**Reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(CH\(_3\)](\text{PEt}_3)_3\)] (8)**

In a Young NMR tube [Rh(CH\(_3\)](\text{PEt}_3)_3\)] (8) (42 mg, 0.089 mmol) was dissolved in C\(_6\)D\(_6\) (0.4 mL). The reaction mixture was frozen to 77 K, the NMR tube was degassed in vacuo, and pressurized with Z-1,3,3,3-tetrafluoropropene to 0.2 bar. After warming up to room temperature the NMR spectroscopic data of the reaction mixture revealed after 50 min the full conversion of 8 into [Rh\{(E)-CF=CHCF\(_3\)}\((\text{PEt}_3)_3\)] (3) as well as the release of methane. Note that complex 3 is stable when the solvents were removed in vacuum to yield a reddish oil. When the formation of 3 was followed by low temperature NMR spectroscopy, complex fac-[Rh(CH\(_3\)](CF\(_3\)CHCHF)(\text{PEt}_3)_3\)] (9) was observed up to 253 K together with an unknown complex which might be an isomer of 9 in a 16:1 ratio, respectively. Complex 3 is stable up to 4h both in solution or as an oil and after 1d, [Rh(C≡CCF\(_3\))[\(\text{PEt}_3\)] (6) and [Rh\{F(HF)\(_2\)}\((\text{PEt}_3)_3\)] (5) in a 5.7:1 ratio are obtained. If NEt\(_3\)/Cs\(_2\)CO\(_3\) (2 equiv) are added, the dehydrofluorination requires 2 days but only complex 6 is obtained.

Analytical data for 3: \(^1\text{H NMR}\) (300.1 MHz, C\(_6\)D\(_6\)): \(\delta = 5.37\) (dq, \(^3J_{H,F} = 51.8, ^3J_{H,F} = 8.7\) Hz, 1H, =CH\(_2\)); 1.65 (q br, \(^3J_{H,H} = 7.6\) Hz, 12H, P\(_{\text{cis}}\)CH\(_2\)CH\(_3\)); 1.31 (quint d, \(^3J_{H,H} = 7.6, ^2J_{H,P} = 5.0\) Hz, 6H, P\(_{\text{trans}}\)CH\(_2\)CH\(_3\)); 1.02 (m, t in \(^1\text{H}[^{31}\text{P}]\) NMR spectrum, \(^3J_{H,H} = 7.6\) Hz, 18H, P\(_{\text{cis}}\)CH\(_2\)CH\(_3\)); 0.92 (dt, \(^3J_{H,P} = 14.1, ^3J_{H,H} = 7.8, 9H, P_{\text{trans}}\)CH\(_2\)CH\(_3\)) ppm. \(^{19}\text{F NMR}\) (282.4 MHz, C\(_6\)D\(_6\)): \(\delta = -26.6\) (ddqd, \(^3J_{F,H} = 52, ^3J_{F,P} = 41, ^4J_{F,F} = 41, ^2J_{F,Rh} = 9\) Hz, 1F, F); -54.1 (ddt, \(^4J_{F,F} = 13, ^3J_{F,H} = 9, ^5J_{F,P\text{cis}} = 5\) Hz, 3F, CF\(_3\)) ppm. \(^{31}\text{P}[^1\text{H}]\) NMR (121.4 MHz, C\(_6\)D\(_6\)): \(\delta = 18.29\) (dtd, \(^1J_{P,Rh} = 115.8, ^3J_{P,F} = 39.4, ^2J_{P,P} = 36.2\) Hz, P\(_{\text{trans}}\)); 14.9 (ddq, \(^1J_{P,Rh} = 148.9, ^2J_{P,P} = 39.4, ^3J_{P,F} = 41\) Hz).
$= 37.7$, $5J_{P,F} = 4.5$ Hz, $P_{cis}$ ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $C_6D_6$): $\delta = 221$ (dm in the $^{13}C$ domain, $^1J_{C,F} = 363$ Hz, observed in a $^1H,^{13}C$ HMBC NMR spectrum, $=CF$); 124 (qm in the $^{13}C$ domain, $^1J_{C,F} = 264$ Hz, observed in a $^1H,^{13}C$ HMBC NMR spectrum, $CF_3$); 106 (m, observed in a $^1H,^{13}C$ HMQC NMR spectrum, $P^{trans}CH_2CH_3$); 18 (m, observed in a $^1H,^{13}C$ HMQC NMR spectrum, $P^{cis}CH_2CH_3$); 9 (m, observed in a $^1H,^{13}C$ HMQC NMR spectrum, $PCH_2CH_3$) ppm.

![Chemical Structure](image)

Analytical data for 9: $^1H$ NMR (300.1 MHz, 238 K, toluene-d$^8$): $\delta = 5.28$ (dd br, ddd in $^1H\{^{31}P\}$ NMR spectrum, $^2J_{H,F} = 67.9$, $^3J_{H,H} = 5.4$, $^2J_{H,Rh} = 2.3$ Hz, $CHF$); 1.95 (m br, 1H, $CHCF_3$); 1.49-1.76 (m, 18H, $PCH_2CH_3$); 0.86-1.24 (m, 27H, $PCH_2CH_3$); 0.74 (td, $^2J_{H,Pb} \approx ^2J_{H,Pe} = 7.9$, $^2J_{H,Pb} = 4.6$ Hz, 3H, Rh$CH_3$) ppm. $^{19}F$ NMR (282.4 MHz, 238 K, toluene-d$^8$): $\delta = -49.1$ (dt br, $^4J_{F,Pe} = 19$, $^3J_{F,H} \approx ^3J_{F,Rh} = 9$ Hz, 3F, $CF_3$); -182.6 (m, t br in $^{19}F\{^1H\}$ NMR spectrum, $J \approx 35$ Hz, 1F, F) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, 238K, toluene-d$^8$): $\delta = 8.269$ (dddq, $^1J_{P,Rh} = 130.1$, $^3J_{P,Pb} = 30.62$, $^2J_{P,Pc} = 24.65$, $^4J_{P,F} = 20.10$, $^3J_{P,F} = 3.40$ Hz, 1P, $P^a$); 6.176 (dddq, $^1J_{P,Rh} = 91.97$, $^3J_{P,F} = 28.88$, $^2J_{P,Pc} = 26.28$, $^2J_{P,Pc} = 24.65$, $^4J_{P,F} = 0.97$ Hz, 1P, $P^b$); -5.335 (dddq, $^1J_{P,Rh} = 102.98$, $^3J_{P,F} = 42.27$, $^2J_{P,Pc} = 30.62$, $^2J_{P,Pb} = 26.28$, $^4J_{P,F} = -1.11$ Hz, 1P, $P^{pa}$) ppm. $^{31}P\{^1H\}$ NMR shifts and coupling constants were determined by $g$NMR software.$^6$

**Reaction of [Rh(\((E)-CF=CHCF_3\))(PEt_3)_3] (3) with BF_3**

In a PFA tube [Rh((E)-CF=CHCF_3)(PEt_3)_3] (3) (20 mg, 0.035 mmol) was dissolved in CD$_2$Cl$_2$ (0.3 mL). The reaction mixture was frozen to 77 K, the PFA tube was degassed in vacuo, and a defined amount of BF$_3$ (0.04 mmol) was condensed into the reaction vessel using a stainless-steel vacuum line. After warming up to 263 K the NMR spectroscopic data of the reaction mixture revealed the full conversion of 3 into [Rh(PEt$_3$)$_4$]BF$_4$, a [Rh(PEt$_3$)$_2$]BF$_4$ derivative and [Rh(C=CCF$_3$)(PEt$_3$)$_3$] (6) in a 1:2:2 ratio.
Reaction of $[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (\text{PEt}_3)_3] (3)$ with LiBF$_4$

In an NMR tube equipped with a PFA inliner $[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (\text{PEt}_3)_3] (3)$ (20 mg, 0.035 mmol) was dissolved in THF-d$^8$ (0.3 mL). Then, LiBF$_4$ (4 mg, 0.043 mmol) was added to the solution. After 30 minutes at room temperature, the NMR spectroscopic data of the reaction mixture revealed the full conversion of 6 into $[\text{Rh}(\text{PEt}_3)_4]$BF$_4$, $[\text{Rh}(\text{THF-d}^8)(\text{PEt}_3)_2]$BF$_4$ and $[\text{Rh}(\text{C}≡\text{CCF}_3)(\text{PEt}_3)_3]$ (6) in a 5:2:3:1 ratio.

Reaction of $[\text{Rh}(E\text{-CF=CHCF}_3)(\text{PEt}_3)_3] (3)$ with CO or $^{13}$CO

Complex $[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (\text{PEt}_3)_3] (3)$ (60 mg, 0.10 mmol) was dissolved in toluene-d$^8$ (0.4 mL) and the solution was cooled to 77 K, degassed and treated with CO. After 5 min, the solution turned yellow and low temperature NMR measurements showed the formation of trans,cis-$[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (\text{CO})_2(\text{PEt}_3)_2]$ (10) and two unknown products (17:1:9 ratio, considering that all the products bear 2 phosphines) together with free phosphine. Then, volatiles were removed under vacuum for 1 day and an orange oil, identified as trans-$[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (\text{CO})(\text{PEt}_3)_2]$ (11), was obtained. Yield: 48 mg (95%).

The synthesis of the labeled derivatives trans,cis-$[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (^{13}\text{CO})_2(\text{PEt}_3)_2]$ (10') and trans-$[\text{Rh}\{(E)\text{-CF=CHCF}_3\} (^{13}\text{CO})(\text{PEt}_3)_2]$ (11') was performed following the same procedure using $^{13}$CO.

Analytical data for the main unknown product: $^1$H NMR (300.1 MHz, C$_6$D$_6$, 213 K): $\delta = 5.40$ (dq, $^3J_{H,F} = 47.9$, $^3J_{H,F} = 6.7$ Hz, 1H, =CH) ppm. $^{19}$F NMR (282.4 MHz, C$_6$D$_6$, 213 K): $\delta = -19.4$ (br, 1F, F); -55.2 (br, 3F, CF$_3$) ppm. $^{31}$P{$^1$H} NMR (121.4 MHz, C$_6$D$_6$, 201 K): $\delta = 24.9$ (d br, $^1J_{P,Rh} = 121$ Hz, PEt$_3$) ppm. $^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$, 213 K): $\delta = 111$ (m, observed in a $^1$H,$^{13}$C HMQC NMR spectrum, =CH) ppm.

Analytical data for 10: $^1$H NMR (300.1 MHz, C$_6$D$_6$, 213 K): $\delta = 5.72$ (dq, $^3J_{H,F} = 47.2$, $^3J_{H,F} = 7.75$ Hz, 1H, =CH); 1.38 (m, q in a $^1$H{$^{31}$P} NMR spectrum, $^3J_{H,H} = 7.4$ Hz, 6H, P$_{cis}$CH$_2$CH$_3$); 1.0-1.1 (m, overlapped with other PEt$_3$ resonances, P$_{trans}$CH$_2$CH$_3$); 0.85 (m, t in $^1$H{$^{31}$P} NMR spectrum, $^3J_{H,H} = 7.4$ Hz, 9H, P$_{cis}$CH$_2$CH$_3$); 0.75 (m, t in $^1$H{$^{31}$P} NMR spectrum, $^3J_{H,H} = 6.4$ Hz, 9H, P$_{trans}$CH$_2$CH$_3$); ppm. $^{19}$F NMR (282.4 MHz, C$_6$D$_6$, 213 K): $\delta = -15.4$ (ddm, $^3J_{F,P} = 51$, $^3J_{F,H} = 50$ Hz, 1F, F); -54.7 (dt, $^4J_{F,F} = 11$, $^3J_{F,H} \approx 5J_{F,Pcis} = 7$ Hz, 3F,
$^{31}$P/$^1$H NMR (121.4 MHz, C$_6$D$_6$, 213 K): $\delta = 26.3$ (dddt, $^1$J$_{P,Rh} = 74.2, ^3$J$_{P,F} = 51.3, ^2$J$_{P,P} = 32.0$ Hz, 1P, P$_{trans}$); 5.34 (dqbr, $^1$J$_{P,Rh} = 121.4, ^2$J$_{P,P} = 32.0, ^3$J$_{F,P} \approx 5$J$_{F,F} = 5.7$ Hz, 1P, P$_{cis}$) ppm. $^{13}$C/$^1$H NMR (75.5 MHz, C$_6$D$_6$, 213 K): $\delta = 123$ (m in the $^{13}$C domain, $^1$J$_{C,F} = 256$ Hz, observed in a $^1$H/$^{13}$C HMBC NMR spectrum, CF$_3$); 110 (m, observed in a $^1$H/$^{13}$C HMOC NMR spectrum, $=CH$) ppm. Note that PEt$_3$ resonances are overlapped with the unknown products as well as the free phosphine.

Analytical data for 11: IR (cm$^{-1}$): $\tilde{\nu} = 1959$ (s, CO), 1597 (m, C=C). $^1$H NMR (300.1 MHz, C$_6$D$_6$): $\delta = 5.02$ (dqt, $^3$J$_{H,F} = 53.8, ^3$J$_{H,F} = 8.4, ^4$J$_{H,P} = 2.4, ^3$J$_{H,Rh} = 0.5$ Hz, 1H, $=CH$); 1.63 (m, q in $^1$H/$^{31}$P NMR spectrum, $^3$J$_{H,H} = 7.6, 12$H, PCH$_2$CH$_3$); 0.99 (dt, $^3$J$_{H,P} = 16.1, ^3$J$_{H,H} = 7.6, 18$H, PCH$_2$CH$_3$) ppm. $^{19}$F NMR (282.4 MHz, C$_6$D$_6$): $\delta = -43.5$ (dquint, $^3$J$_{F,H} = 54, ^4$J$_{F,F} \approx 2$J$_{F,Rh} = 13$ Hz, 1F, F); -55.1 (ddt, $^4$J$_{F,F} = 13, ^3$J$_{F,H} = 9, ^5$J$_{F,P} = 4$ Hz, 3F, CF$_3$) ppm. $^{31}$P/$^1$H NMR (121.4 MHz, C$_6$D$_6$): $\delta = 22.2$ (dq, $^1$J$_{P,Rh} = 131.5, ^5$J$_{P,F} = 4.3$ Hz, PEt$_3$) ppm. $^{13}$C/$^1$H NMR (75.5 MHz, C$_6$D$_6$): $\delta = 214$ (m in the $^{13}$C domain, $^1$J$_{C,F} = 340, ^1$J$_{C,Rh} = 57, ^3$J$_{C,F} = 17$ Hz observed in a $^{19}$F/$^{13}$C HMBC NMR spectrum, $=CH$); 197 (dm in the $^{13}$C domain, $^1$J$_{C,Rh} = 58$ Hz, observed in a $^1$H/$^{13}$C HMBC NMR spectrum, CO); 123.2 (qm in the $^{13}$C domain, $^1$J$_{C,F} = 272, ^3$J$_{C,F} = 18$ Hz, confirmed by a $^{19}$F/$^{13}$C HMBC NMR spectrum, CF$_3$); 108.0 (qqm, $^2$J$_{C,F} = 30, ^2$J$_{C,F} \approx ^3$J$_{C,P} = 5$ Hz, $=CH$); 8.2 (s, PCH$_2$CH$_3$); 17.6 (vt d, N = $^1$J$_{C,P} + ^3$J$_{C,P} = 13), ^2$J$_{C,Rh} = 1.3$ Hz, PCH$_2$CH$_3$) ppm.

Selected analytical data for 10*: $^{31}$P/$^1$H NMR (121.4 MHz, C$_6$D$_6$, 201 K): $\delta = 26.3$ (dddt, $^1$J$_{P,Rh} = 74.2, ^3$J$_{P,F} = 51.3, ^2$J$_{P,P} = 32.0, ^2$J$_{P,C} = 17.5$ Hz, 1P, P$_{trans}$); 5.34 (dq br, $^1$J$_{P,Rh} = 121.4, ^2$J$_{P,P} \approx ^2$J$_{P,C} = 30.0$ Hz, 1P, P$_{cis}$) ppm. $^{13}$C/$^1$H NMR (75.5 MHz, C$_6$D$_6$, 201 K): $\delta = 198.3$ (dddt, $^1$J$_{C,Rh} = 69.0, ^2$J$_{C,P,C} = 28.7, ^2$J$_{C,P} = ^2$J$_{C,F} = 17.7$ Hz, CO) ppm. Selected analytical data for 11*: IR (cm$^{-1}$): $\tilde{\nu} = 1917$ (s, $^{13}$CO), 1599 (m, C=C). $^{19}$F NMR (282.4 MHz, C$_6$D$_6$): $\delta = -43.5$ (dsext, $^3$J$_{F,H} = 54, ^4$J$_{F,F} \approx ^2$J$_{F,Rh} = 13$ Hz, 1F, F); -55.1 (ddt, $^4$J$_{F,F} = 13, ^3$J$_{F,H} = 9, ^5$J$_{F,P} = 4$ Hz, 3F, CF$_3$) ppm. $^{31}$P/$^1$H NMR (121.4 MHz, C$_6$D$_6$): $\delta = 22.2$ (ddq, $^1$J$_{P,Rh} = 131.5, ^2$J$_{P,C} = 14.2, ^5$J$_{P,F} = 4.3$ Hz, PEt$_3$) ppm. $^{13}$C/$^1$H NMR (75.5 MHz, C$_6$D$_6$, 201 K): $\delta = 196.6$ (ddt, $^1$J$_{C,Rh} = 55.6, ^2$J$_{C,P} = 13.9, ^3$J$_{C,F} = 12.5$ Hz, CO); 17.6 (vt t, N = $^1$J$_{C,P} + ^3$J$_{C,P} = 13), ^2$J$_{C,Rh} \approx ^3$J$_{C,C} = 1.3$ Hz, PCH$_2$CH$_3$) ppm.
**Reaction of [Rh(C≡CCF₃)(CO)(PEt₃)₃] (12) with NEt₃·3HF or HBF₄·Et₂O**

Complex [Rh(C≡CCF₃)(CO)(PEt₃)₃] (12) (0.06 mmol) was dissolved in CD₂Cl₂ (0.4 mL) and excess of NEt₃·3HF (7 μL, 0.04 mmol) or HBF₄·Et₂O (12 μL, 0.08 mmol) was added at around 243 K. The reaction mixture was slowly warmed up to room temperature. After 1 day 85% conversion of complex 12 to yield mainly [Rh{(Z)-C(PEt₃)≡CHCF₃}(CO)(PEt₃)₃]BF₄ (13·BF₄) with HBF₄·Et₂O was observed, while for HF, an 80% conversion to 13·FHF as the main product was obtained. When HBF₄ is used, another complex, which might be [Rh(CO)(PEt₃)₃]BF₄ was detected. Note that the reaction with NEt₃·3HF was performed in a PFA inliner.

Analytical data for 13: IR (cm⁻¹): ̇ν 1950 (s, CO). ¹H NMR (300.1 MHz, CD₂Cl₂): δ = 6.63 (dqq, 3Jₗₚ = 36.4, 3Jₖₖ = 6.3, 4Jₗₚ ≈ 3Jₖₚ = 3.9 Hz, 1H, =CH) ppm; the resonances corresponding to the phosphine ligands are overlapped with the signals for the other products. ¹⁹F NMR (282.4 MHz, CD₂Cl₂): δ = -63.3 (q br, 3Jₖₖ ≈ 3Jₖₖ = 4 Hz, 3F, CF₃) ppm. ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂): δ = 37.1 (dt, 2Jₖₖ = 4.8, 3Jₖₖ = 2.4 Hz, 1P, =CPEt₃); 14.5 (dqd, 1Jₖₖ = 125.0, 2Jₖₖ = 5.2, 3Jₖₖ = 2.6 Hz, 2P, RhPEt₃) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂): δ = 192 (m, observed in a ¹H,¹³C HMBC NMR spectrum, CO); 166 (m, observed in a ¹H,¹³C HMBC NMR spectrum, =CPEt₃); 122 (qm in the ¹³C domain, 1Jₖₖ = 260 Hz, observed in a ¹H,¹³C HMBC NMR spectrum, CF₃); 136 (qm in the ¹³C domain, 2Jₖₖ = 37 Hz, observed in a ¹H,¹³C HMQC NMR spectrum, =CH) ppm.

**Reaction of [Rh(C≡CCF₃)(PEt₃)₃] (6) with Et₃N·3HF**

In an NMR tube equipped with a PFA inliner [Rh(C≡CCF₃)(PEt₃)₃] (6) (23 mg, 0.042 mmol) was dissolved in C₆D₆ (0.3 mL). Then, excess of NEt₃·3HF (15 μL, 0.092 mmol) was added to the solution. After 5 minutes at room temperature, the NMR spectroscopic data of the reaction mixture revealed 36% conversion of 6 into [Rh{F(HF)}₂(PEt₃)₃] (5) (see above). After one day, full conversion was achieved. In addition of complex 5 the release of Z-1,3,3,3-tetrafluoropropene and other fluorinated compounds was observed.
Synthesis of \([\text{Rh}(F)(\text{PR}_3)_2]_2\) (14) \(R = i\text{Pr (a), Et (b)}\)

\([\text{Rh}(F)(\text{cyclooctene})_2]_2\) (150 mg, 0.22 mmol) was dissolved in THF (10 mL) and the corresponding phosphine was added (4 eq., 0.88 mmol). The dark red solution was stirred for 1h and then the volatiles were removed under vacuum. The obtained product was washed with cold pentane (2 x 5 mL) and dried under vacuum. Complex 14a was obtained as a dark red solid while 14b is a brownish oil. Both complexes were identified by comparison with literature.\(^9,^{10}\) Yield: 171 mg (88% for 14a); 134 mg (85% for 14b).

Reactivity of \([\text{Rh}(F)(\text{PiPr}_3)_2]_2\) (14a) with 3,3,3-trifluoropropyne

In a Young NMR tube \([\text{Rh}(F)(\text{PiPr}_3)_2]_2\) (14a) (50 mg, 0.056 mmol) was dissolved in C\(_6\)D\(_6\) (0.4 mL). The reaction mixture was frozen to 77 K, the NMR tube was degassed \textit{in vacuo}, and pressurized with 3,3,3-tetrafluoropropyne (13 mg, 0.14 mmol). After warming up to room temperature the NMR spectroscopic data of the reaction mixture revealed after 5 min the full conversion of 14a into \([\text{Rh}(F)(\text{CH≡CCF}_3)(\text{PiPr}_3)_2]_2\) (15) together with small unknown impurities.

Analytical data of 15: IR (cm\(^{-1}\)): \(\tilde{\nu}\) 1810 (m, C≡C). \(^1\text{H}\) NMR (300.1 MHz, C\(_6\)D\(_6\)): \(\delta = 4.52\) (qd, \(\delta_{J_{HF}} = 4.0\), \(\delta_{J_{H,Rh}} = 1.5\) Hz, 1H, \(=\text{CH}\)); 2.11 (m, sept in \(^1\text{H}\{^{31}\text{P}\}\) NMR spectrum, \(\delta_{J_{HH}} = 7.0\) Hz, 6H, PCH(CH\(_3\))\(_2\)); 1.32 (m, d in \(^1\text{H}\{^{31}\text{P}\}\) NMR spectrum, \(\delta_{J_{HH}} = 7.0\) Hz, 18H, PCH(CH\(_3\))\(_2\)); 1.17 (m, d in \(^1\text{H}\{^{31}\text{P}\}\) NMR spectrum, \(\delta_{J_{HH}} = 7.0\) Hz, 18H, PCH(CH\(_3\))\(_2\)) ppm.

\(^{19}\text{F}\) NMR (282.4 MHz, Tol-d\(_8\)): \(\delta = -47.7\) (dq, \(\delta_{J_{FP}} = 4\), \(\delta_{J_{FP,Rh}} = 2\) Hz, 3F, CF\(_3\)); -242.9 (m br, d br at 233 K, \(\delta_{J_{FP,Rh}} = 87\) Hz, 1F, RhF) ppm. \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (121.4 MHz, Tol-d\(_8\)): \(\delta = 36.4\) (d, \(\delta_{J_{FP}} = 119.0\) Hz, PiPr\(_3\)) ppm. \(^{31}\text{P}\{^{1}\text{H}\}\) NMR (121.4 MHz, Tol-d\(_8\), 233 K): \(\delta = 36.4\) (dd, \(\delta_{J_{FP,Rh}} = 119.0\), \(\delta_{J_{FP,F}} = 10.3\) Hz, PiPr\(_3\)) ppm. \(^{13}\text{C}\{^{1}\text{H}\}\) NMR (75.5 MHz, C\(_6\)D\(_6\)): \(\delta = 83\) (m, observed in a \(^1\text{H},^{13}\text{C}\) HMOC NMR spectrum, \(=\text{CH}\)); 61 (m, observed in the \(^1\text{C}\) domain, \(\delta_{J_{CF}} = 40\) Hz, \(^1\text{H},^{13}\text{C}\) HMOC NMR spectrum, \(=\text{CCF}_3\)); 21 (m, observed in a \(^1\text{H},^{13}\text{C}\) HMOC NMR spectrum, \(=\text{CCF}_3\)); 19.3 (m, observed in a \(^1\text{H},^{13}\text{C}\) HMOC NMR spectrum, \(=\text{CCF}_3\)); 18.9 (m, observed in a \(^1\text{H},^{13}\text{C}\) HMOC NMR spectrum, \(=\text{CCF}_3\)) ppm.

Rearrangement of \([\text{Rh}(F)(\text{CH≡CCF}_3)(\text{PiPr}_3)_2]_2\) (15) in the presence of phosphine

In an NMR tube \([\text{Rh}(F)(\text{CH≡CCF}_3)(\text{PiPr}_3)_2]_2\) (15) (30 mg, 0.055 mmol) was dissolved in C\(_6\)D\(_6\) (0.4 mL). Then, excess of PiPr\(_3\) (23 \(\mu\)L, 0.12 mmol) was added to the solution. Complex 15
slowly converted into complex $[\text{Rh}(\text{F})=\text{C}=-\text{CHCF}_3)(\text{PiPr}_3)_2]$ (16). After 3 weeks at room temperature, the NMR spectroscopic data of the reaction mixture revealed full conversion of 15 into 16 together with some impurities. Using of NEt$_3$ instead of the phosphine did not reduce the reaction time.

Analytical data of 16: IR (cm$^{-1}$): $\tilde{\nu}$ 1638 (m, C=C). LIFDI (Toluene): $m/z$ 517 [M-F]$^+$. $^1$H NMR (300.1 MHz, C$_6$D$_6$): $\delta = 2.51$ (m, sept in $^1$H{$^{31}$P} NMR spectrum, $^3J_{H,H} = 7.2$ Hz, 6H, PCH(CH$_3$)$_2$); 1.25 (dvt, d in $^1$H{$^{31}$P} NMR spectrum, $^3J_{H,H} = 7.1$ Hz, 36H, PCH(CH$_3$)$_2$); 0.67 (m, 1H, =CCH) ppm. $^{19}$F NMR (282.4 MHz, C$_6$D$_6$): $\delta = -52.2$ (dt, $^3J_{F,H} = 7$, $^5J_{F,P} = 3$ Hz, 3F, CF$_3$); -208 (tdd, $^2J_{F,P} = 20$, $^1J_{F,Rh} = 11$, $^4J_{F,H} = 8$ Hz, 1F, RhF) ppm. $^{31}$P{$^{1}$H} NMR (121.4 MHz, C$_6$D$_6$): $\delta = 46.6$ (dq, $^1J_{P,Rh} = 139.9$, $^2J_{P,F} = 20.4$, $^5J_{P,F} = 2.7$ Hz, PiPr$_3$) ppm. $^{19}$F,$^{13}$C HMBC NMR (282.4 / 75.5 MHz, C$_6$D$_6$): $\delta = -52/282$ (m, Rh=C=C); -52/116 (m in $^{13}$C domain, $^1J_{C,H} = 153$, $^1J_{C,F} = 268$ Hz, CF$_3$); -52/104 (d in $^{19}$F domain, m in $^{13}$C domain, $^1J_{C,H} = 153$, $^2J_{C,F} = 35$ Hz, =CH) ppm.

**Reaction of [Rh(F)(=C=CHCF$_3$)(PiPr$_3$)$_2$] (16) with PEt$_3$**

In a NMR tube [Rh(F)(=C=CHCF$_3$)(PiPr$_3$)$_2$] (16) (20 mg, 0.037 mmol) was dissolved in C$_6$D$_6$ (0.4 mL). Then, excess of PEt$_3$ (37 µL, 0.25 mmol) was added to the solution. After 1 hour at room temperature the NMR spectroscopic data of the reaction mixture revealed the full conversion of 16 into [Rh{F(HF)$_2$}(PEt$_3$)$_3$] (5) and [Rh(C≡CCF$_3$)(PEt$_3$)$_3$] (6) (1:1 ratio) as well as the release of PiPr$_3$ and small amounts of 3,3,3-trifluoropropene.
NMR Spectra

S1. $^{31}$P{${ }^{1}$H} NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt$_3$)$_3$] (1) in C$_6$D$_6$ at different times.

S2. $^{19}$F NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt$_3$)$_3$] (1) in C$_6$D$_6$ at different times.
S3. Section of the $^{19}$F NMR (bottom) and $^{19}$F–$^{1}$H NMR spectra corresponding to complex [Rh{(Z)-CH=CHCF$_3$}(PEt$_3$)$_3$] (4) in C$_6$D$_6$.

S4. Parts of the $^1$H (bottom), $^1$H–$^{19}$F (middle) and $^1$H–$^{31}$P (top) NMR spectra corresponding to complex [Rh{(Z)-CH=CHCF$_3$}(PEt$_3$)$_3$] (4) in C$_6$D$_6$. 
S5. $^{31}$P{¹H} NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt₃)₃] (1) in toluene-d₈ at 233 K.

S6. $^{19}$F NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt₃)₃] (1) in toluene-d₈ at 233 K.

S7. ¹H NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt₃)₃] (1) in toluene-d₈ at 233 K.
S8. Parts of the $^1$H (bottom), $^1$H{$^{19}$F} (middle) and $^1$H{$^{31}$P} (top) NMR spectra corresponding to complex \textit{fac-}(Rh(H)(CF$_3$CHCHF)(PEt$_3$)$_3$) \( (7) \) in toluene-d$_8$.

S9. $^1$H $^1$H COSY NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with [Rh(H)(PEt$_3$)$_3$] \( (1) \) in toluene-d$_8$ at 223 K.
S10. $^{31}$P-$^{1}$H NMR spectrum of complex $[\text{Rh}\{(E)-\text{CH}=\text{CHCF}_{3}\}(\text{PEt}_{3})_{3}]$ (2) in C$_6$D$_6$.

S11. $^{19}$F NMR spectrum of complex $[\text{Rh}\{(E)-\text{CH}=\text{CHCF}_{3}\}(\text{PEt}_{3})_{3}]$ (2) in C$_6$D$_6$.

S12. $^{1}$H NMR spectrum of complex $[\text{Rh}\{(E)-\text{CH}=\text{CHCF}_{3}\}(\text{PEt}_{3})_{3}]$ (2) in C$_6$D$_6$. 
S13. \textsuperscript{31}P\{^1\text{H}\} NMR spectrum of the reaction of complex [Rh\{\(E\)-CH=CHCF\_3\}(PEt\_3)\_3] (2) with Z-1,3,3,3-tetrafluoropropene in C\(_6\)D\(_6\).

S14. \textsuperscript{19}F NMR spectrum of the reaction of complex [Rh\{\(E\)-CH=CHCF\_3\}(PEt\_3)\_3] (2) with Z-1,3,3,3-tetrafluoropropene in C\(_6\)D\(_6\).

S15. \textsuperscript{1}\text{H} NMR spectrum of the reaction of complex [Rh\{\(E\)-CH=CHCF\_3\}(PEt\_3)\_3] (2) with Z-1,3,3,3-tetrafluoropropene in C\(_6\)D\(_6\).
S16. $^{31}$P{$^1$H} NMR spectrum of the reaction of complex [Rh{$^1$E-CH=CHCF}$_3$]{PEt$_3$}$_3$ (2) with Et$_3$N·3HF in C$_6$D$_6$.

S17. $^{31}$P{$^1$H} NMR spectrum of complex [Rh{$^1$E-CF=CHCF}$_3$]{PEt$_3$}$_3$ (3) in C$_6$D$_6$.

S18. $^{19}$F (bottom) and $^{19}$F{$^1$H} (top) NMR spectrum of complex [Rh{$^1$E-CF=CHCF}$_3$]{PEt$_3$}$_3$ (3) in C$_6$D$_6$. 
S19. $^1$H NMR spectrum of complex $[\text{Rh}\{(E)-\text{CF}=\text{CHCF}_3\}(\text{PEt}_3)_3]$ (3) in C$_6$D$_6$.

S20. Section of $^{31}$P{$^1$H} NMR spectra of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{CH}_3)(\text{PEt}_3)_3]$ (8) in C$_6$D$_6$ at different times with and without presence of base.
S21. $^{31}$P$^1$H NMR spectrum of the reaction of complex [Rh{(E)-CF=CHCF$_3$}(PEt$_3$)$_3$] (3) with BF$_3$ at 263 K in CD$_2$Cl$_2$.

S22. $^{19}$F NMR spectrum of the reaction of complex [Rh{(E)-CF=CHCF$_3$}(PEt$_3$)$_3$] (3) with BF$_3$ at 263 K in CD$_2$Cl$_2$. 
S23. $^{31}$P{\textsuperscript{1}H} NMR spectrum of the reaction of complex $[\text{Rh}\{(E)-\text{CF=CHCF}_3\}(\text{PEt}_3)_3]$ (3) with LiBF$_4$ in THF-d$^8$.

S24. $^{19}$F NMR spectrum of the reaction of complex $[\text{Rh}\{(E)-\text{CF=CHCF}_3\}(\text{PEt}_3)_3]$ (3) with LiBF$_4$ in THF-d$^8$.

S25. $^{31}$P{\textsuperscript{1}H} NMR spectrum of complex $\text{fac-}[\text{Rh}\{(\text{CH}_3)\text{CF}_3\text{CHCHF}\}(\text{PEt}_3)_3]$ (9) in toluene-d$^8$ at 213 K: experimental (bottom), simulated (top).$^6$
S26. $^{19}$F NMR spectrum of complex $\text{fac-}[\text{Rh(}_{\text{CH}_3}(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (9) in toluene-$d_8$ at 238 K.

S27. $^1$H NMR spectrum of complex $\text{fac-}[\text{Rh(}_{\text{CH}_3}(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (9) in toluene-$d_8$ at 238 K.

S28. $^{31}$P{\^{1}H} NMR spectrum of the reaction of $[\text{Rh}(\{E\}-\text{CF}=\text{CHCF}_3)(\text{PEt}_3)_3]$ (3) with CO in toluene-$d_8$ at 213 K.
**S29.** Section of $^{31}\text{P}^{1}\text{H}$ NMR spectrum of the reaction of $[\text{Rh}\{\text{(E)}-\text{CF} = \text{CHCF}_3\}\text{(PEt}_3\text{)}_3\} \text{ (3)}$ with $^{13}\text{CO}$ in toluene-$d^8$ at 201 K.

**S30.** $^{19}\text{F}$ NMR spectrum of the reaction of $[\text{Rh}\{\text{(E)}-\text{CF} = \text{CHCF}_3\}\text{(PEt}_3\text{)}_3\} \text{ (3)}$ with CO in toluene-$d^8$ at 213 K.

**S31.** $^1\text{H}$ NMR spectrum of the reaction of $[\text{Rh}\{\text{(E)}-\text{CF} = \text{CHCF}_3\}\text{(PEt}_3\text{)}_3\} \text{ (3)}$ with CO in toluene-$d^8$ at 213 K.
S32. Section of the $^{13}$C{$^{1}$H} NMR spectrum of the reaction of [Rh{$^{(E)}$-CF=CHCF$_3$}(PEt$_3$)$_3$] (3) with $^{13}$CO in toluene-d$_8$ at 201 K.

S33. $^{31}$P{$^{1}$H} NMR spectrum of complex trans-[Rh{$^{(E)}$-CF=CHCF$_3$}(CO)(PEt$_3$)$_2$] (11) in C$_6$D$_6$. The signals for 11 (bottom) and 11' (top) are shown for comparison.

S34. $^{19}$F NMR spectrum of complex trans-[Rh{$^{(E)}$-CF=CHCF$_3$}(CO)(PEt$_3$)$_2$] (11) in C$_6$D$_6$. The signals for 11 (bottom) and 11' (top) are shown for comparison.
S35. $^1$H NMR spectrum of complex trans-\([\text{Rh}\{(E)-\text{CF}=\text{CHCF}_3\}\text{(CO)(PEt}_3\text{)}_2]\) (11) in \(\text{C}_6\text{D}_6\) (no changes in complex 11').

S36. Section of the $^{13}$C($^1$H) NMR spectrum of complex trans-\([\text{Rh}\{(E)-\text{CF}=\text{CHCF}_3\}\{^{13}\text{CO}\text{(PEt}_3\text{)}_2]\) (11') in \(\text{C}_6\text{D}_6\).

S37. $^{31}$P($^1$H) NMR spectrum of the reaction of $[\text{Rh}(\text{C≡CCF}_3)(\text{CO})(\text{PEt}_3)_3]$ (12) with HF (top) or HBF$_4$ (bottom) in CD$_2$Cl$_2$. 
**S38.** $^{19}$F NMR spectrum of the reaction of [Rh(C≡CCF$_3$)(CO)(PEt$_3$)$_3$] (12) with HF (top) or HBF$_4$ (bottom) in CD$_2$Cl$_2$.

**S39.** Section of the $^1$H NMR (bottom), $^1$H{$^{19}$F} NMR (middle) and $^1$H{$^{31}$P} NMR (top) of complex [Rh{(Z)-C(PEt$_3$)=CHCF$_3$}(CO)(PEt$_3$)$_2$]$^+$ (13) corresponding to the vinyl proton of the phosphonioalkenyl ligand in CD$_2$Cl$_2$. 
S40. $^{31}$P{$^1$H} NMR spectrum of the reaction of [Rh(C≡CCF$_3$)(PEt$_3$)$_3$] (6) with Et$_3$N·3HF in C$_6$D$_6$.

S41. $^{31}$P{$^1$H} NMR spectrum of complex [Rh(F)(CH≡CCF$_3$)(Pr$_3$)$_2$] (15) in Tol-d$_8$ at 233 K.

S42. $^{19}$F NMR spectrum of complex [Rh(F)(CH≡CCF$_3$)(Pr$_3$)$_2$] (15) in Tol-d$_8$ showing the Rh-F ligand resonance at 233 K.
S43. $^1$H NMR spectrum of complex $[\text{Rh(F)}(\text{CH}≡\text{CCF}_3)(\text{PiPr}_3)_2]$ (15) in C$_6$D$_6$.

S44. $^{31}$P{$^1$H} NMR spectrum of complex $[\text{Rh(F)}(=\text{C}≡\text{C}H\text{CF}_3)(\text{PiPr}_3)_2]$ (16) in C$_6$D$_6$.

S45. Sections of the $^{19}$F NMR (bottom) and the $^{19}$F{$^1$H} NMR (top) spectra of complex $[\text{Rh(F)}(=\text{C}≡\text{C}H\text{CF}_3)(\text{PiPr}_3)_2]$ (16) in C$_6$D$_6$. 
S46. $^{19}$F, $^{13}$C HMBC NMR spectrum of complex $[\text{Rh}(\text{F})(=\text{C}═\text{CHCF}_3)(\text{PiPr}_3)_2]$ (16) in C$_6$D$_6$.

S47. $^{31}$P$^1$H NMR spectrum of the reaction of complex $[\text{Rh}(\text{F})(=\text{C}═\text{CHCF}_3)(\text{PiPr}_3)_2]$ (16) with PEt$_3$ in C$_6$D$_6$. 
S48. $^{19}$F NMR spectrum of the reaction of complex $[\text{Rh}(\text{F})(=\text{C}CHCF_3)(\text{PiPr}_3)_2]$ (16) with PEt$_3$ in C$_6$D$_6$.

**DFT calculations**

**Computational details for geometry optimization of all the calculated complexes**

Calculations were run using the Gaussian 09 (Revision D.01) program package.$^{11}$ All rhodium complexes were calculated using the BP86 functional. Rhodium was described with RECPs and the associated def2-SVP basis sets.$^{12,13}$ All the other atoms were described with def2-SVP basis sets. A Grimme D3 dispersion correction with Becke-Johnson damping was included.$^{14,15}$ All calculated structures were identified as minima (no negative eigenvalues).

**Geometry optimization of both possible rotamers of complexes 7 and 9**

Complex 7

Complex 7a

Energies in Hartree (corrected for zero-point energy): -2361.736294 for complex 7 and -2361.734125 for complex 7a. Accordingly, structure 7 is slightly favored by 5.7 kJ/mol.
Complex 9

Complex 9a

Energy in Hartree (corrected for zero-point energy): -2400.978525 for complex 12 and -2400.978446 for complex 9a. Accordingly, both structures are possible as complex 9 is only favored by 0.2 kJ/mol.

**Geometry optimization of complex 10**

In order to optimize the structure of complex 10, calculations with different initial structures were run, which did not non-converge except for the structure shown in Figure S49.

Energy in Hartree (corrected for zero-point energy): -2008.420899.

*S49. Optimized structure of complex 10. Hydrogen atoms of the phosphine ligands have been omitted for clarity.*
Table S1. Cartesian coordinates of all optimized structures

| Complex 7 | Complex 7a | Complex 9 | Complex 9a |
|-----------|------------|-----------|------------|
| Rh 0.01200 -0.35730 -0.29248 | Rh -0.00970 0.14701 1.00867 | Rh 0.13909 1.18916 1.33096 | Rh -0.00164 -0.05461 -0.26856 |
| P 0.02092 0.62015 0.92927 | P -0.20063 0.62015 0.92927 | P -0.19803 0.28096 0.24832 | P 0.00606 -1.28036 1.48322 |
| C 1.46053 1.45444 0.16973 | C -3.52002 -0.00729 -0.15986 | C -3.52002 -0.00729 -0.15986 | C 1.32386 1.76879 0.05215 |
| H -0.37240 -0.26430 -1.72003 | H -2.26430 0.13089 2.74197 | H -2.26430 0.13089 2.74197 | H -3.54008 -0.26839 0.99321 |
| H 4.08618 2.42138 1.97390 | H 1.89863 2.13166 2.76009 | H 1.89863 2.13166 2.76009 | H -2.31285 0.57719 0.55883 |
| H 1.11417 -2.14138 -0.69881 | H -0.29007 -2.23490 1.13434 | H -0.29007 -2.23490 1.13434 | H -0.31685 -0.65491 -0.30365 |
| H 3.07583 3.09049 3.23070 | H -3.2081 0.10319 -0.06384 | H -3.2081 0.10319 -0.06384 | H -0.93956 -2.68672 1.49974 |
| H 1.30343 2.76546 -1.71572 | H 1.33916 2.99205 1.78662 | H 1.33916 2.99205 1.78662 | H -0.94966 -0.30234 1.23581 |
| H 0.49231 -0.02718 3.35922 | H -1.86242 -2.42138 1.97390 | H -1.86242 -2.42138 1.97390 | H -0.94966 -0.30234 1.23581 |
| C 3.37205 1.00134 0.01828 | C 3.37205 1.00134 0.01828 | C 3.37205 1.00134 0.01828 | C 3.06252 1.52545 -0.73232 |
| H 1.86734 2.33449 2.73444 | H -2.23094 -3.02682 -0.13360 | H -2.23094 -3.02682 -0.13360 | H 0.79690 3.46662 -0.61793 |
| H 1.17993 3.38529 -0.70250 | H 1.34528 2.41668 1.85868 | H 1.34528 2.41668 1.85868 | H 1.69463 2.17224 1.85080 |
| H 1.20005 1.26818 0.07781 | H -0.01766 2.43340 0.58233 | H -0.01766 2.43340 0.58233 | H 1.11199 -1.41619 0.81216 |
| H 1.20005 1.26818 0.07781 | H -0.01766 2.43340 0.58233 | H -0.01766 2.43340 0.58233 | H 1.11199 -1.41619 0.81216 |
| H 1.86734 2.33449 2.73444 | H -2.23094 -3.02682 -0.13360 | H -2.23094 -3.02682 -0.13360 | H 0.79690 3.46662 -0.61793 |

32
|     | C       | O          | H          |
|-----|---------|------------|------------|
|     | 2.2441  | -2.2254    | -1.6688    |
|     | 2.22209 | -1.33257   | -2.69318   |
| F   | 2.32841 | -3.61909   | -2.24399   |
| F   | 3.45040 | -2.94285   | -1.02296   |
| H   | 1.37736 | -2.72352   | 0.19086    |
| H   | 0.42840 | 0.10213    | -1.75376   |

**Complex 10**

|     | Rh      | P          | C          |
|-----|---------|------------|------------|
|     | -0.22596 | -0.61361   | 0.17227    |
| P   | -2.57543 | -0.50446   | -0.13877   |
| C   | 1.65386 | 1.87587    | -1.87440   |
| C   | 1.85437 | 2.24784    | 0.95853    |
| C   | -0.71133 | 3.01010   | -0.19722   |
| P   | 0.48356 | 1.66179    | -0.48835   |
| C   | -3.35549 | -2.00963   | 0.64444    |
| C   | -4.67993 | -2.58485   | -0.12412   |
| C   | -3.8424 | 3.57283    | -2.57898   |
| C   | -2.8204 | 0.88425    | -2.66631   |
| C   | -3.4716 | 0.84423    | 0.56482    |
| C   | -5.09725 | 0.44085   | 0.74360    |
| C   | 1.83978 | 2.03154    | 2.43446    |
| C   | 2.06135 | 3.11130    | -2.17404   |
| H   | -3.36822 | -1.99439   | 1.95030    |
| H   | -2.56525 | -2.86158   | 0.27955    |
| H   | -4.27441 | -0.39954   | -1.90347   |
| H   | -2.82429 | -1.36527   | -2.36551   |
| H   | -2.95949 | 1.79035    | -2.29021   |
| H   | -2.9427 | 0.82022    | -3.79011   |
| H   | -1.51749 | 0.85004    | -2.61895   |
| H   | -3.07935 | 1.78911    | 0.34494    |
| H   | -3.00179 | 0.79481    | 1.80489    |
| H   | -5.44419 | 0.84549    | -0.29495   |
| H   | -5.39725 | 1.75447    | 1.24809    |
| H   | -5.43071 | -0.03006   | 2.12751    |
| C   | -1.20812 | 3.55282    | 1.17904    |
| H   | -4.59974 | 2.73502    | -1.21163   |
| H   | -5.46852 | 1.81510    | 0.06451    |
| H   | -4.99284 | -3.90330   | 0.35726    |
| H   | 2.78329 | 1.67918    | -0.63316   |
| H   | 2.04984 | 3.31408    | 0.70831    |
| H   | 0.43542 | 1.69491    | -2.59996   |
| H   | 1.91275 | 0.94240    | -1.91718   |
| H   | 1.45001 | -0.03338   | -2.04340   |
| H   | 2.42177 | 3.10369    | -3.22935   |
| H   | 2.95333 | 3.19868    | -1.52289   |
| H   | -2.07113 | 4.24416    | 1.08314    |
| H   | -0.41623 | 4.09165    | 1.73663    |
| H   | -1.32788 | 2.68020    | 1.80757    |
| H   | -0.22865 | 3.95084    | -0.72646   |
| H   | -1.55626 | 2.77535    | -0.83952   |
| H   | 1.70928 | -0.94026   | 0.40706    |
| C   | 2.75609 | -1.09010   | -0.54256   |
| H   | 2.43359 | -1.13033   | -1.03020   |
| H   | 0.75906 | 2.61098    | 2.81964    |
| H   | 2.51782 | 2.54270    | 3.00716    |
| H   | 1.43951 | 0.96342    | 2.05230    |
| F   | 2.24090 | -0.95148   | 1.66773    |
| F   | 4.21416 | -1.17566   | -0.25465   |
| F   | 4.70540 | -0.02719   | 0.21807    |
| F   | 4.91865 | -1.35701   | -1.40959   |
| F   | 4.56048 | -2.18768   | 0.58234    |
| C   | -0.55358 | -0.90747   | 2.01029    |
| O   | -0.80252 | -1.18982   | 3.14706    |
| C   | -0.15985 | -1.09007   | -1.37700   |
| O   | -0.13609 | -2.37842   | -2.32904   |
References

1. D. D. Perrin and W. L. F. Armaegro, *Purification of Laboratory Chemicals*, Butterworth/Heinemann, London/Oxford, 3rd edn., 1988.
2. T. Braun, D. Noveski, M. Ahijado and F. Wehmeier, *Dalton Trans.*, 2007, 3820-3825.
3. P. Zhao and J. F. Hartwig, *Organometallics*, 2008, 27, 4749-4757.
4. C. N. von Hahmann, M. Talavera, C. Xu and T. Braun, *Chem. Eur. J.*, 2018, 24, 11131-11138.
5. J. Vicente, J. Gil-Rubio, D. Bautista, A. Sironi and N. Masciocchi, *Inorg. Chem.*, 2004, 43, 5665-5675.
6. P. H. M. Budzelaar *gNMR*, Version 4.1; Adept Scientific plc: Letchworth, 2001.
7. D. Noveski, T. Braun and S. Krückemeier, *J. Fluorine Chem.*, 2004, 125, 959-966.
8. M. Talavera, C. N. von Hahmann, R. Müller, M. Ahrens, M. Kaupp and T. Braun, *Angew. Chem. Int. Ed.*, 2019, 58, 10688-10692, *Angew. Chem.*, 2019, 131, 10798-10802.
9. J. Gil-Rubio, B. Weberndörfer and H. Werner, *J. Chem. Soc., Dalton Trans.*, 1999, 1437-1444.
10. L. Zámostná and T. Braun, *Angew. Chem. Int. Ed.*, 2015, 54, 10652-10656.
11. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox *Gaussian 09*, Revision D.01; Gaussian, Inc.: Wallingford CT, 2016.
12. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, 77, 123-141.
13. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305.
14. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, 32, 1456-1465.
15. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, 132, 154104.