

**Competing C–H and C–F bond activation reactions of a
fluorinated olefin at Rh: A fluoro 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 procedures¹ and, prior to use, distilled under argon. The rhodium complexes [Rh(H)(PEt₃)₃] (**1**),² [Rh(CH₃)(PEt₃)₃] (**8**),³ [Rh(C≡CCF₃)(CO)(PEt₃)₃] (**6**)⁴ and [Rh(μ -F)(cyclooctene)₂]₂⁵ 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. ¹H and ¹³C{¹H} signals are referred to residual solvent signals, those of ³¹P{¹H} to 85% H₃PO₄ and the ¹⁹F NMR spectra to external CFCl₃. ¹H, ¹⁹F, ³¹P{¹H} and ¹³C{¹H} NMR signal assignments were supported or, when stated, determined by ¹H,¹H COSY, ¹⁹F,¹H HETCOR, ¹⁹F,¹⁹F gCOSY, ³¹P,³¹P COSY, ¹H,¹³C HMQC, ¹H,¹³C HMBC, ¹⁹F,¹³C HMBC, ¹⁹F,¹³C HMQC and ¹H,³¹P 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)(PEt₃)₃] (**1**)

In a Young NMR tube [Rh(H)(PEt₃)₃] (**1**) (30 mg, 0.065 mmol) was dissolved in toluene-d₈ (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 233K full conversion of complex **1** to complex *fac*-[Rh(H)(CF₃CHCHF)(PEt₃)₃] (**7**) was observed. At 273 K a 90% conversion, based on the ¹⁹F NMR spectrum, of **7** into [Rh{(E)-CH=CHCF₃}(PEt₃)₃] (**2**) was observed as well as the release of HF and traces of complexes [Rh{(E)-CF=CHCF₃}(PEt₃)₃] (**3**) and [Rh{(Z)-CH=CHCF₃}(PEt₃)₃] (**4**). Finally, after 10 minutes at room temperature, a mixture of [Rh{(E)-CH=CHCF₃}(PEt₃)₃] (**2**), [Rh{(E)-CF=CHCF₃}(PEt₃)₃] (**3**), [Rh{(Z)-

$\text{CH}=\text{CHCF}_3\}\text{(PEt}_3\text{)}_3]$ (**4**) and $[\text{Rh}\{\text{F}(\text{HF})_2\}\text{(PEt}_3\text{)}_3]$ (**5**) was detected in a 1:8:5 ratio. In addition, 3,3,3-trifluoropropene was observed.

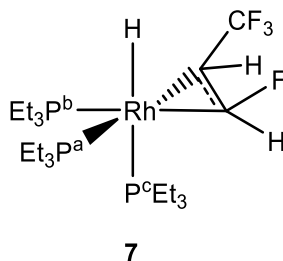
When the reaction is directly warm up to room temperature, the same product mixture is observed. After 30 minutes, the ratio of complexes **2**, **3**, **4** and **5** is 3.8:2:1:4.4. After one day, $[\text{Rh}(\text{C}\equiv\text{CCF}_3)\text{(PEt}_3\text{)}_3]$ (**6**) and complex **5** are the only products in a 1:1 ratio. Complexes **2**, and **6** have been identified by comparison with literature.^{4,7} Complex **5** was identified by comparison with $[\text{Rh}(\text{FHF})\text{(PEt}_3\text{)}_3]$,⁷ however, P-F couplings are not observed which suggest the presence of more than one HF molecule leading to the proposed formula $[\text{Rh}\{\text{F}(\text{HF})_2\}\text{(PEt}_3\text{)}_3]$ (**5**). Addition of excess of $\text{NEt}_3/\text{Cs}_2\text{CO}_3$ to remove the excess of HF, led to the formation of $[\text{Rh}(\text{F})\text{(PEt}_3\text{)}_3]$.⁷

The amount of HF in complex **5** was determined by adding ClSiEt_3 (0.059 mmol, 6.5 equiv) to a solution of complexes **6** and **5** (0.009 mmol of **5** based on the $^{31}\text{P}\{^1\text{H}\}$ NMR ratio). After 10 min, full conversion of complex **5** into $[\text{Rh}(\text{Cl})\text{(PEt}_3\text{)}_3]$ and dihydrido chlorido rhodium(III) species was observed with a 45% conversion of ClSiEt_3 (determined directly from the ^1H NMR spectrum and supported by external standard of PhCF_3) into FSiEt_3 and F_2SiEt_2 (0.027 mmol in total). The 3 equivalents required would correspond to two HF moieties and the rhodium-bounded fluorido ligand.

Analytical data for $[\text{Rh}\{\text{(Z)-CH}=\text{CHCF}_3\}\text{(PEt}_3\text{)}_3]$ (**4**): ^1H NMR (300.1 MHz, C_6D_6): $\delta = 8.35$ (dt, $^3J_{\text{H,H}} = 14.1$, $^3J_{\text{H,Pcis}} = 4.3$ Hz, $\text{CH}=\text{}$); 6.61 (m, ddq in $^1\text{H}\{^{19}\text{F}\}$ NMR spectrum, dqd in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 13.9$, $^4J_{\text{H,Ptrans}} = 11.8$, $^3J_{\text{H,F}} = 8.7$, $^4J_{\text{H,Pcis}} \approx ^3J_{\text{H,Rh}} = 2.3$ Hz, $=\text{CHCF}_3$) ppm; the resonances corresponding to the phosphine ligands are overlapped with the signals for the other products. ^{19}F NMR (282.4 MHz, C_6D_6): $\delta = -59.7$ (m, tt in $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum, $^5J_{\text{F,Pcis}} = 5.5$, $^5J_{\text{F,Ptrans}} \approx ^4J_{\text{F,Rh}} = 1.7$ Hz, 3F, CF_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): $\delta = 12.5$ (ddq, $^1J_{\text{P,Rh}} = 154.6$, $^2J_{\text{P,P}} = 38.9$, $^5J_{\text{P,F}} = 4.9$ Hz, 2P, P_{cis}) ppm; the resonance of P_{trans} is overlapped with the signals for the other compounds.

Analytical data for $[\text{Rh}\{\text{F}(\text{HF})_2\}\text{(PEt}_3\text{)}_3]$ (**5**): ^1H NMR (300.1 MHz, C_6D_6): $\delta = 1.65\text{-}1.50$ (m, q in $^1\text{H}\{^{31}\text{P}\}$, $^3J_{\text{H,H}} = 7.7$ Hz, 12H, $\text{P}_{\text{cis}}\text{CH}_2\text{CH}_3$); 1.25-1.15 (m, q in $^1\text{H}\{^{31}\text{P}\}$, $^3J_{\text{H,H}} = 7.2$ Hz 6H, $\text{P}_{\text{trans}}\text{CH}_2\text{CH}_3$); 1.17-1.03 (m, t in $^1\text{H}\{^{31}\text{P}\}$, $^3J_{\text{H,H}} = 7.7$ Hz, 18H, $\text{P}_{\text{cis}}\text{CH}_2\text{CH}_3$); 0.96 (dt, $^3J_{\text{H,P}} = 14.9$, $^3J_{\text{H,H}} = 7.2$ Hz, 9H, $\text{P}_{\text{trans}}\text{CH}_2\text{CH}_3$);. ^{19}F NMR (282.4 MHz, C_6D_6): $\delta = -178$ (br m, HF); -277.0 (m, 1F, Rh-F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): $\delta = 45.83$ (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)(CF₃CHCHF)(PEt₃)₃] (**7**): **¹H NMR** (300.1 MHz, 233 K, toluene-d⁸): δ = 5.85 (d br, ddd in ¹H{³¹P} 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-d⁸, observed by a ¹H-¹H COSY spectrum, CHCF₃); 1.55-1.78 (m, 6H, PCH₂CH₃); 1.32-1.54 (m, 6H, PCH₂CH₃); 0.93-1.18 (m, 24H, PCH₂CH₃ + PCH₂CH₃); 0.74 (dt, ³J_{H,P} = 12.8, ³J_{H,H} = 6.9 Hz, 9H, PCH₂CH₃); -13.22 (dq, ²J_{H,Pc} = 160.0, ²J_{H,Pa} ≈ ²J_{H,Pb} ≈ ³J_{H,F} = 19.8, ¹J_{H,Rh} = 12.2 Hz, 1H, RhH) ppm. **¹⁹F NMR** (282.4 MHz, 253 K, toluene-d⁸): δ = -49.6 (q br, ⁴J_{F,P} ≈ ⁴J_{F,F} ≈ ³J_{F,H} = 13 Hz, 3F, CF₃); -182.7 (dm, ²J_{F,H} = 68 Hz, 1F, CF) ppm. **³¹P{¹H} NMR** (121.4 MHz, 233K, toluene-d⁸): δ = 19.29 (dddqd, ¹J_{P,Rh} = 135.4, ³J_{P,Pb} = 29.5, ²J_{P,Pc} = 26.0, ⁴J_{P,F} = 16.2, ³J_{P,F} = 13.0 Hz, 1P, P^a); 10.85 (dq, ¹J_{P,Rh} = 111.9, ³J_{P,F} ≈ ²J_{P,Pc} ≈ ²J_{P,Pa} = 29.7 Hz, P^b); 0.87 (br dq, ¹J_{P,Rh} = 84.0, ²J_{P,Pa} ≈ ²J_{P,Pb} ≈ ³J_{P,F} = 27.2 Hz, P^c) ppm.

Synthesis of [Rh{(E)-CH=CHCF₃}(PEt₃)₃] (**2**)

In a Young NMR tube [Rh(CH₃)(PEt₃)₃] (**8**) (50 mg, 0.106 mmol) was dissolved in C₆D₆ (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=CHCF₃}(PEt₃)₃] (**2**) by comparison with the literature,⁸ was obtained. Yield: 57 mg (98%).

Reaction of [Rh{(E)-CH=CHCF₃}(PEt₃)₃] (**2**) with Z-1,3,3,3-tetrafluoropropene

In a Young NMR tube [Rh{(E)-CH=CHCF₃}(PEt₃)₃] (**2**) (31 mg, 0.056 mmol) was dissolved in C₆D₆ (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 $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) as well as the release of 3,3,3-trifluoropropene. For the analytical data of complex **3** see below.

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

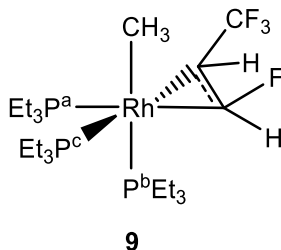
In an NMR tube equipped with a PFA inliner $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) (24 mg, 0.043 mmol) was dissolved in C_6D_6 (0.3 mL). Then, excess of $\text{NEt}_3\cdot 3\text{HF}$ (7 μL , 0.04 mmol) was added to the solution. After 5 minutes at room temperature, the NMR spectroscopic data of the reaction mixture revealed the full conversion of **2** into $[\text{Rh}\{\text{F}(\text{HF})_2\}(\text{PEt}_3)_3]$ (**5**) (see above) as well as the release of 3,3,3-trifluoropropene.

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

In a Young NMR tube $[\text{Rh}(\text{CH}_3)(\text{PEt}_3)_3]$ (**8**) (42 mg, 0.089 mmol) was dissolved in C_6D_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 $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**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*- $[\text{Rh}(\text{CH}_3)(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (**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, $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$ (**6**) and $[\text{Rh}\{\text{F}(\text{HF})_2\}(\text{PEt}_3)_3]$ (**5**) in a 5.7:1 ratio are obtained. If $\text{NEt}_3/\text{Cs}_2\text{CO}_3$ (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_6D_6): $\delta = 5.37$ (dq, $^3J_{\text{H,F}} = 51.8$, $^3J_{\text{H,H}} = 8.7$ Hz, 1H, =CH); 1.65 (q br, $^3J_{\text{H,H}} = 7.6$ Hz, 12H, $P_{\text{cis}}\text{CH}_2\text{CH}_3$); 1.31 (quint d, $^3J_{\text{H,H}} = 7.6$, $^2J_{\text{H,P}} = 5.0$ Hz, 6H, $P_{\text{trans}}\text{CH}_2\text{CH}_3$); 1.02 (m, t in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 7.6$ Hz, 18H, $P_{\text{cis}}\text{CH}_2\text{CH}_3$); 0.92 (dt, $^3J_{\text{H,P}} = 14.1$, $^3J_{\text{H,H}} = 7.8$, 9H, $P_{\text{trans}}\text{CH}_2\text{CH}_3$) ppm. $^{19}\text{F NMR}$ (282.4 MHz, C_6D_6): $\delta = -26.6$ (ddqd, $^3J_{\text{F,H}} = 52$, $^3J_{\text{F,P}} = 41$, $^4J_{\text{F,F}} = 13$, $^2J_{\text{F,Rh}} = 9$ Hz, 1F, F); -54.1 (ddt, $^4J_{\text{F,F}} = 13$, $^3J_{\text{F,H}} = 9$, $^5J_{\text{F,P}_{\text{cis}}} = 5$ Hz, 3F, CF_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6): $\delta = 18.29$ (dtd, $^1J_{\text{P,Rh}} = 115.8$, $^3J_{\text{P,F}} = 39.4$, $^2J_{\text{P,P}} = 36.2$ Hz, P_{trans}); 14.9 (ddq, $^1J_{\text{P,Rh}} = 148.9$, $^2J_{\text{P,P}}$

= 37.7, $^5J_{P,F} = 4.5$ Hz, P_{cis}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 221$ (dm in the ^{13}C domain, $^1J_{C,F} = 363$ Hz, observed in a $^1\text{H},^{13}\text{C}$ HMBC NMR spectrum, =CF); 124 (qm in the ^{13}C domain, $^1J_{C,F} = 264$ Hz, observed in a $^1\text{H},^{13}\text{C}$ HMBC NMR spectrum, CF_3); 106 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, =CH); 19 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, $\text{P}^{\text{trans}}\text{CH}_2\text{CH}_3$); 18 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, $\text{P}^{\text{cis}}\text{CH}_2\text{CH}_3$); 9 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, PCH_2CH_3) ppm.



Analytical data for **9**: ^1H NMR (300.1 MHz, 238 K, toluene- d^8): $\delta = 5.28$ (dd br, ddd in $^1\text{H}\{^{31}\text{P}\}$ 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, $^2J_{H,P_a} \approx ^2J_{H,P_c} = 7.9$, $^2J_{H,P_b} = 4.6$ Hz, 3H, RhCH_3) ppm. ^{19}F NMR (282.4 MHz, 238 K, toluene- d^8): $\delta = -49.1$ (dt br, $^4J_{F,P_c} = 19$, $^3J_{F,H} \approx ^3J_{F,Rh} = 9$ Hz, 3F, CF_3); -182.6 (m, t br in $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum, $J \approx 35$ Hz, 1F, F) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, 238K, toluene- d^8): $\delta = 8.269$ (dddqd, $^1J_{P,Rh} = 130.1$, $^3J_{P,P_a} = 30.62$, $^2J_{P,P_b} = 24.65$, $^4J_{P,F} = 20.10$, $^3J_{P,F} = 3.40$ Hz, 1P, P^c); 6.176 (ddddq, $^1J_{P,Rh} = 91.97$, $^3J_{P,F} = 28.88$, $^2J_{P,P_a} = 26.28$, $^2J_{P,P_c} = 24.65$, $^4J_{P,F} = 0.97$ Hz, 1P, P^b); -5.335 (ddddq, $^1J_{P,Rh} = 102.98$, $^3J_{P,F} = 42.27$, $^2J_{P,P_c} = 30.62$, $^2J_{P,P_b} = 26.28$, $^4J_{P,F} = -1.11$ Hz, 1P, P^a) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR shifts and coupling constants were determined by *gNMR* software.⁶

Reaction of $[\text{Rh}\{(\text{E})\text{-CF}=\text{CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with BF_3

In a PFA tube $[\text{Rh}\{(\text{E})\text{-CF}=\text{CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) (20 mg, 0.035 mmol) was dissolved in CD_2Cl_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 $[\text{Rh}(\text{PEt}_3)_4]\text{BF}_4$, a $[\text{Rh}(\text{PEt}_3)_2]\text{BF}_4$ derivative and $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$ (**6**) in a 1:2:2 ratio.

Reaction of [Rh(*E*)-CF=CHCF₃](PEt₃)₃ (**3**) with LiBF₄

In an NMR tube equipped with a PFA inliner [Rh(*E*)-CF=CHCF₃](PEt₃)₃ (**3**) (20 mg, 0.035 mmol) was dissolved in THF-d⁸ (0.3 mL). Then, LiBF₄ (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 [Rh(PEt₃)₄]BF₄, [Rh(THF-d⁸)(PEt₃)₂]BF₄ and [Rh(C≡CCF₃)(PEt₃)₃] (**6**) in a 5:2.3:1 ratio.

Reaction of [Rh(*E*)-CF=CHCF₃](PEt₃)₃ (**3**) with CO or ¹³CO

Complex [Rh(*E*)-CF=CHCF₃](PEt₃)₃ (**3**) (60 mg, 0.10 mmol) was dissolved in toluene-d⁸ (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*-[Rh(*E*)-CF=CHCF₃](CO)₂(PEt₃)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*-[Rh(*E*)-CF=CHCF₃](CO)(PEt₃)₂ (**11**), was obtained. Yield: 48 mg (95%).

The synthesis of the labeled derivatives *trans,cis*-[Rh(*E*)-CF=CHCF₃](¹³CO)₂(PEt₃)₂ (**10'**) and *trans*-[Rh(*E*)-CF=CHCF₃](¹³CO)(PEt₃)₂ (**11'**) was performed following the same procedure using ¹³CO.

Analytical data for the main unknown product: ¹H NMR (300.1 MHz, C₆D₆, 213 K): δ = 5.40 (dq, ³J_{H,F} = 47.9, ³J_{H,H} = 6.7 Hz, 1H, =CH) ppm. ¹⁹F NMR (282.4 MHz, C₆D₆, 213 K): δ = -19.4 (br, 1F, F); -55.2 (br, 3F, CF₃) ppm. ³¹P{¹H} NMR (121.4 MHz, C₆D₆, 201 K): δ = 24.9 (d br, ¹J_{P,Rh} = 121 Hz, PEt₃) ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆, 213 K): δ = 111 (m, observed in a ¹H, ¹³C HMQC NMR spectrum, =CH) ppm.

Analytical data for **10**: ¹H NMR (300.1 MHz, C₆D₆, 213 K): δ = 5.72 (dq, ³J_{H,F} = 47.2, ³J_{H,H} = 7.75 Hz, 1H, =CH); 1.38 (m, q in a ¹H{³¹P} NMR spectrum, ³J_{H,H} = 7.4 Hz, 6H, P_{*cis*}CH₂CH₃); 1.0-1.1 (m, overlapped with other PEt₃ resonances, P_{*trans*}CH₂CH₃); 0.85 (m, t in ¹H{³¹P} NMR spectrum, ³J_{H,H} = 7.4 Hz, 9H, P_{*cis*}CH₂CH₃); 0.75 (m, t in ¹H{³¹P} NMR spectrum, ³J_{H,H} = 6.4, 9H, P_{*trans*}CH₂CH₃) ppm. ¹⁹F NMR (282.4 MHz, C₆D₆, 213 K): δ = -15.4 (ddm, ³J_{F,P} = 51, ³J_{F,H} = 50 Hz, 1F, F); -54.7 (dt, ⁴J_{F,F} = 11, ³J_{F,H} ≈ ⁵J_{F,P_{*cis*}} = 7 Hz, 3F,

CF_3) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6 , 213 K): $\delta = 26.3$ (ddd, $^1J_{P,Rh} = 74.2$, $^3J_{P,F} = 51.3$, $^2J_{P,P} = 32.0$ Hz, 1P, P_{trans}); 5.34 (ddquint, $^1J_{P,Rh} = 121.4$, $^2J_{P,P} = 32.0$, $^3J_{F,P} \approx ^5J_{P,F} = 5.7$ Hz, 1P, P_{cis}) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6 , 213 K): $\delta = 123$ (m in the ^{13}C domain, $^1J_{C,F} = 256$ Hz, observed in a 1H , ^{13}C HMBC NMR spectrum, CF_3); 110 (m, observed in a 1H , ^{13}C HMQC 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). 1H NMR (300.1 MHz, C_6D_6): $\delta = 5.02$ (dqtd, $^3J_{H,F} = 53.8$, $^3J_{H,H} = 8.4$, $^4J_{H,P} = 2.4$, $^3J_{H,Rh} = 0.5$ Hz, 1H, =CH); 1.63 (m, q in $^1H\{^{31}P\}$ NMR spectrum, $^3J_{H,H} = 7.6$, 12H, PCH_2CH_3); 0.99 (dt, $^3J_{H,P} = 16.1$, $^3J_{H,H} = 7.6$, 18H, PCH_2CH_3) ppm. ^{19}F NMR (282.4 MHz, C_6D_6): $\delta = -43.5$ (dq, $^3J_{F,H} = 54$, $^4J_{F,F} \approx ^2J_{F,Rh} = 13$ Hz, 1F, F); -55.1 (ddt, $^4J_{F,F} = 13$, $^3J_{F,H} = 9$, $^5J_{F,P} = 4$ Hz, 3F, CF_3) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): $\delta = 22.2$ (dq, $^1J_{P,Rh} = 131.5$, $^5J_{P,F} = 4.3$ Hz, PEt_3) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): $\delta = 214$ (m in the ^{13}C domain, $^1J_{C,F} = 340$, $^1J_{C,Rh} = 57$, $^3J_{C,F} = 17$ Hz observed in a ^{19}F , ^{13}C HMBC NMR spectrum, =CF); 197 (dm in the ^{13}C domain, $^1J_{C,Rh} = 58$ Hz, observed in a 1H , ^{13}C HMBC NMR spectrum, CO); 123.2 (qm in the ^{13}C domain, $^1J_{C,F} = 272$, $^3J_{C,F} = 18$ Hz, confirmed by a ^{19}F , ^{13}C HMBC NMR spectrum, CF_3); 108.0 (qqm, $^2J_{C,F} = 30$, $^2J_{C,F} \approx ^3J_{C,P} = 5$ Hz, =CH); 8.2 (s, PCH_2CH_3); 17.6 (vt d, $N = |^1J_{C,P} + ^3J_{C,P} = 13|$, $^2J_{C,Rh} = 1.3$ Hz, PCH_2CH_3) ppm.

Selected analytical data for **10'**: $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6 , 201 K): $\delta = 26.3$ (dddt, $^1J_{P,Rh} = 74.2$, $^3J_{P,F} = 51.3$, $^2J_{P,P} = 32.0$, $^2J_{P,C} = 17.5$ Hz, 1P, P_{trans}); 5.34 (dq br, $^1J_{P,Rh} = 121.4$, $^2J_{P,P} \approx ^2J_{P,C} = 30.0$, Hz, 1P, P_{cis}) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6 , 201 K): $\delta = 198.3$ (ddt, $^1J_{C,Rh} = 69.0$, $^2J_{C,Pc} = 28.7$, $^2J_{C,Pt} = ^3J_{C,F} = 17.7$ 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_6D_6): $\delta = -43.5$ (dsext, $^3J_{F,H} = 54$, $^4J_{F,F} \approx ^3J_{F,C} \approx ^2J_{F,Rh} = 13$ Hz, 1F, F); -55.1 (ddt, $^4J_{F,F} = 13$, $^3J_{F,H} = 9$, $^5J_{F,P} = 4$ Hz, 3F, CF_3) ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): $\delta = 22.2$ (ddq, $^1J_{P,Rh} = 131.5$, $^2J_{P,C} = 14.2$, $^5J_{P,F} = 4.3$ Hz, PEt_3) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6 , 201 K): $\delta = 196.6$ (dtd, $^1J_{C,Rh} = 55.6$, $^2J_{C,P} = 13.9$, $^3J_{C,F} = 12.5$ Hz, CO); 17.6 (vt t, $N = |^1J_{C,P} + ^3J_{C,P} = 13|$, $^2J_{C,Rh} \approx ^3J_{C,C} = 1.3$ Hz, PCH_2CH_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)₂]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): $\tilde{\nu}$ 1950 (s, CO). ¹H NMR (300.1 MHz, CD₂Cl₂): δ = 6.63 (dq, ³J_{H,P} = 36.4, ³J_{H,F} = 6.3, ⁴J_{H,P} ≈ ³J_{H,Rh} = 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, ³J_{F,H} ≈ ⁵J_{F,Pcis} = 4 Hz, 3F, CF₃) ppm. ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂): δ = 37.1 (dt, ²J_{P,Rh} = 4.8, ³J_{P,P} = 2.4 Hz, 1P, =CPEt₃); 14.5 (dq, ¹J_{P,Rh} = 125.0, ⁵J_{P,F} = 5.2, ³J_{P,P} = 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, ¹J_{C,F} = 260 Hz, observed in a ¹H, ¹³C HMBC NMR spectrum, CF₃); 136 (qm in the ¹³C domain, ²J_{C,F} = 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 $[\text{Rh}(\text{F})(\text{PR}_3)_2]_2$ (**14**) $\text{R} = i\text{Pr}$ (**a**), Et (**b**)

$[\text{Rh}(\text{F})(\text{cyclooctene})_2]_2$ (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 $[\text{Rh}(\text{F})(\text{P}i\text{Pr}_3)_2]_2$ (**14a**) with 3,3,3-trifluoropropyne

In a Young NMR tube $[\text{Rh}(\text{F})(\text{P}i\text{Pr}_3)_2]_2$ (**14a**) (50 mg, 0.056 mmol) was dissolved in C_6D_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-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 $[\text{Rh}(\text{F})(\text{CH}\equiv\text{CCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**15**) together with small unknown impurities.

Analytical data of **15**: IR (cm^{-1}): $\tilde{\nu}$ 1810 (m, $\text{C}\equiv\text{C}$). ^1H NMR (300.1 MHz, C_6D_6): $\delta = 4.52$ (qd, $^4J_{\text{H,F}} = 4.0$, $^2J_{\text{H,Rh}} = 1.5$ Hz, 1H, $\equiv\text{CH}$); 2.11 (m, sept in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 7.2$ Hz, 6H, $\text{PCH}(\text{CH}_3)_2$); 1.32 (m, d in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 7.0$ Hz, 18H, $\text{PCH}(\text{CH}_3)_2$); 1.17 (m, d in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 7.0$ Hz, 18H, $\text{PCH}(\text{CH}_3)_2$) ppm. ^{19}F NMR (282.4 MHz, Tol- d_8): $\delta = -47.7$ (dq, $^4J_{\text{F,H}} = 4$, $^4J_{\text{F,P}} \approx ^3J_{\text{F,Rh}} = 2$ Hz, 3F, CF_3); -242.9 (m br, d br at 233 K, $^1J_{\text{F,Rh}} = 87$ Hz, 1F, RhF) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, Tol- d_8): $\delta = 36.4$ (d, $^1J_{\text{P,Rh}} = 119.0$ Hz, $\text{P}i\text{Pr}_3$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, Tol- d_8 , 233 K): $\delta = 36.4$ (dd, $^1J_{\text{P,Rh}} = 119.0$, $^3J_{\text{P,F}} = 10.3$ Hz, $\text{P}i\text{Pr}_3$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta = 83$ (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, $\equiv\text{CH}$); 61 (dm in the ^{13}C domain, $^2J_{\text{C,F}} = 40$ Hz, observed in a $^1\text{H},^{13}\text{C}$ HMBC NMR spectrum, $\equiv\text{CCF}_3$); 21 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, $\text{PCH}(\text{CH}_3)_2$); 19.3 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, $\text{PCH}(\text{CH}_3)_2$); 18.9 (m, observed in a $^1\text{H},^{13}\text{C}$ HMQC NMR spectrum, $\text{PCH}(\text{CH}_3)_2$) ppm.

Rearrangement of $[\text{Rh}(\text{F})(\text{CH}\equiv\text{CCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**15**) in the presence of phosphine

In an NMR tube $[\text{Rh}(\text{F})(\text{CH}\equiv\text{CCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**15**) (30 mg, 0.055 mmol) was dissolved in C_6D_6 (0.4 mL). Then, excess of $\text{P}i\text{Pr}_3$ (23 μL , 0.12 mmol) was added to the solution. Complex **15**

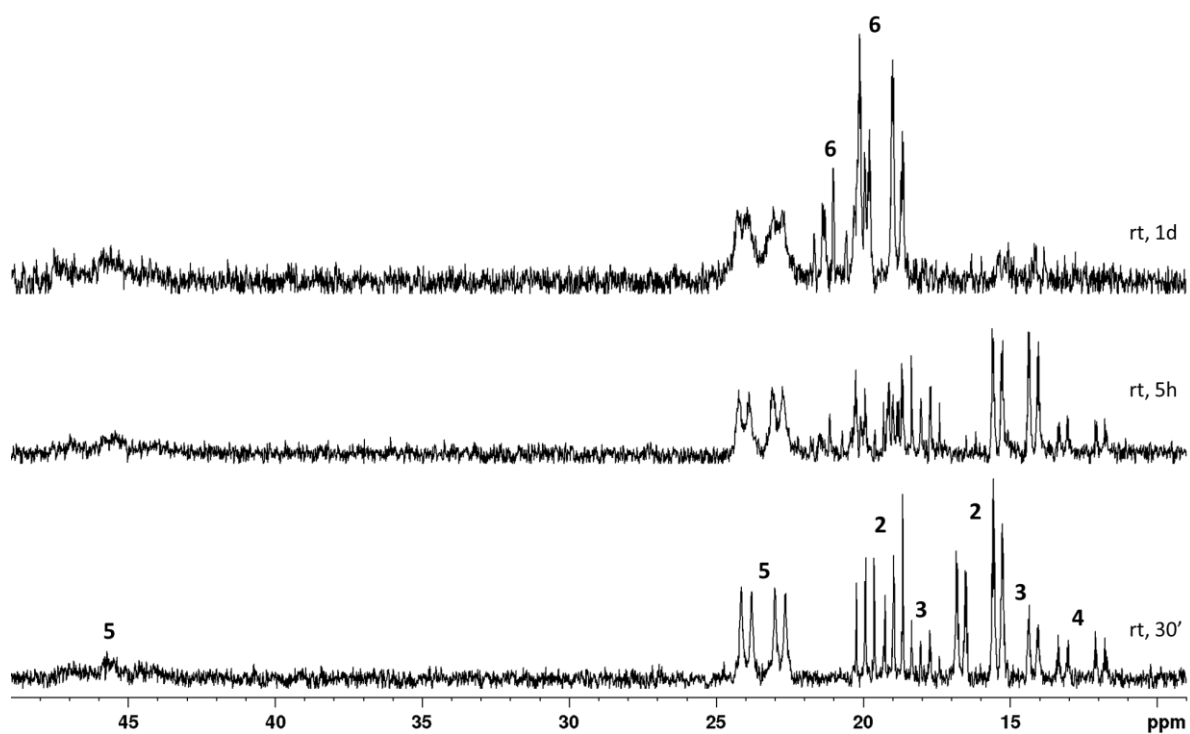
slowly converted into complex $[\text{Rh}(\text{F})(=\text{C}=\text{CHCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**16**). After 3 weeks at room temperature, the NMR spectroscopic data of the reaction mixture revealed full conversion of **15** into **16** together with some impurities. Using of NEt_3 instead of 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 $[\text{M}-\text{F}]^+$. ^1H NMR (300.1 MHz, C_6D_6): δ = 2.51 (m, sept in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 7.2$ Hz, 6H, $\text{PCH}(\text{CH}_3)_2$); 1.25 (dvt, d in $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum, $^3J_{\text{H,H}} = 7.1$ Hz, 36H, $\text{PCH}(\text{CH}_3)_2$); 0.67 (m, 1H, =CH) ppm. ^{19}F NMR (282.4 MHz, C_6D_6): δ = -52.2 (dt, $^3J_{\text{F,H}} = 7$, $^5J_{\text{F,P}} = 3$ Hz, 3F, CF_3); -208 (tdd, $^2J_{\text{F,P}} = 20$, $^1J_{\text{F,Rh}} = 11$, $^4J_{\text{F,H}} = 8$ Hz, 1F, RhF) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6): δ = 46.6 (ddq, $^1J_{\text{P,Rh}} = 139.9$, $^2J_{\text{P,F}} = 20.4$, $^5J_{\text{P,F}} = 2.7$ Hz, $\text{P}i\text{Pr}_3$) ppm. $^{19}\text{F},^{13}\text{C}$ HMBC NMR (282.4 / 75.5 MHz, C_6D_6): δ = -52/282 (m, Rh=C=C); -52/116 (m in ^{13}C domain, $^1J_{\text{C,H}} = 153$, $^1J_{\text{C,F}} = 268$ Hz, CF_3); -52/104 (d in ^{19}F domain, m in ^{13}C domain, $^1J_{\text{C,H}} = 153$, $^2J_{\text{C,F}} = 35$ Hz, =CH) ppm.

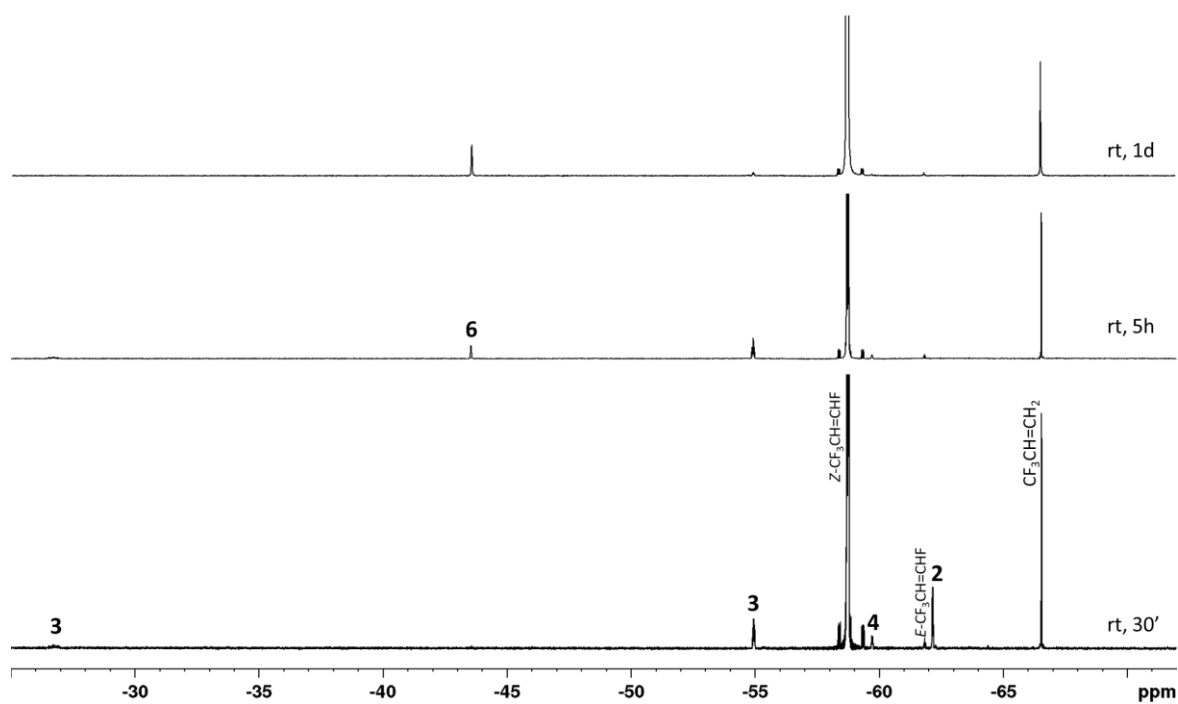
Reaction of $[\text{Rh}(\text{F})(=\text{C}=\text{CHCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**16**) with PEt_3

In a NMR tube $[\text{Rh}(\text{F})(=\text{C}=\text{CHCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**16**) (20 mg, 0.037 mmol) was dissolved in C_6D_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 $[\text{Rh}\{\text{F}(\text{HF})_2\}(\text{PEt}_3)_3]$ (**5**) and $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$ (**6**) (1:1 ratio) as well as the release of $\text{P}i\text{Pr}_3$ and small amounts of 3,3,3-trifluoropropene.

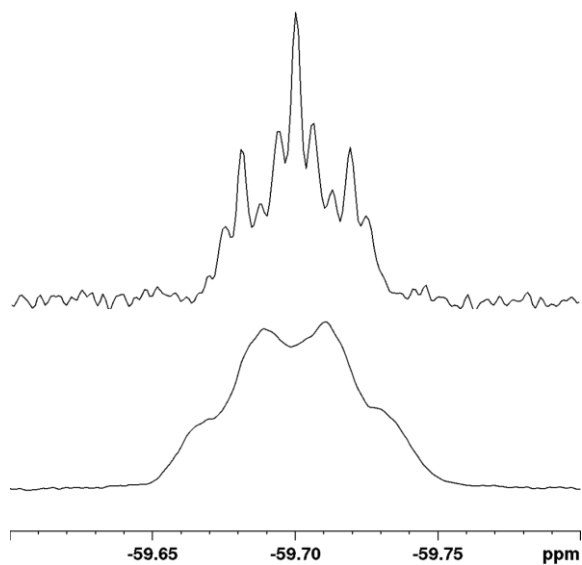
NMR Spectra



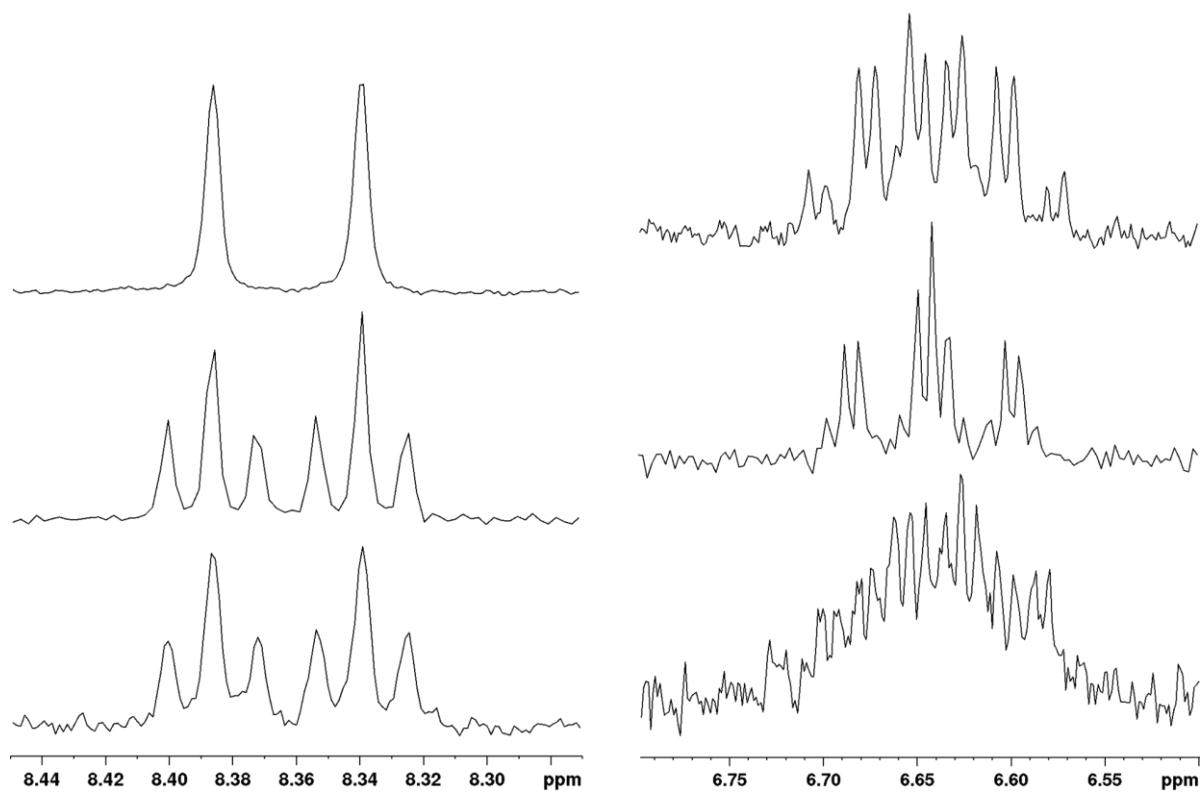
S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (1) in C_6D_6 at different times.



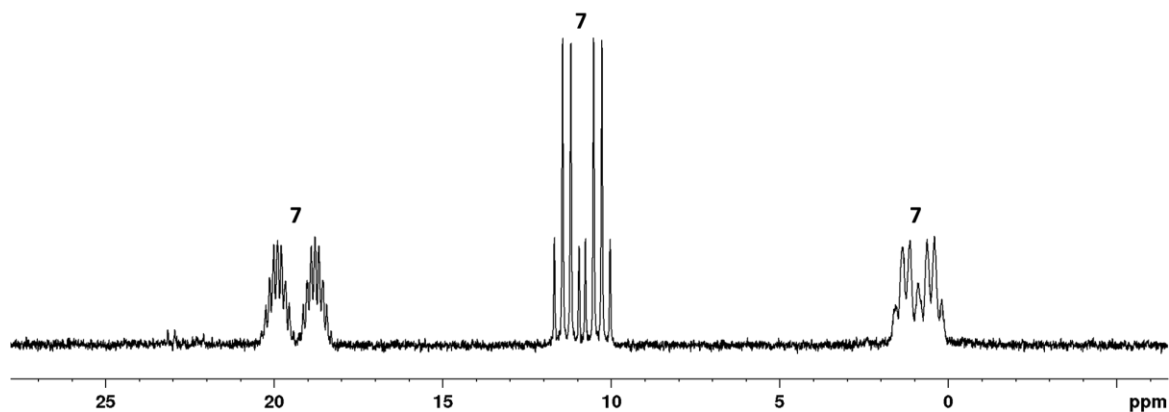
S2. ^{19}F NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (1) in C_6D_6 at different times.



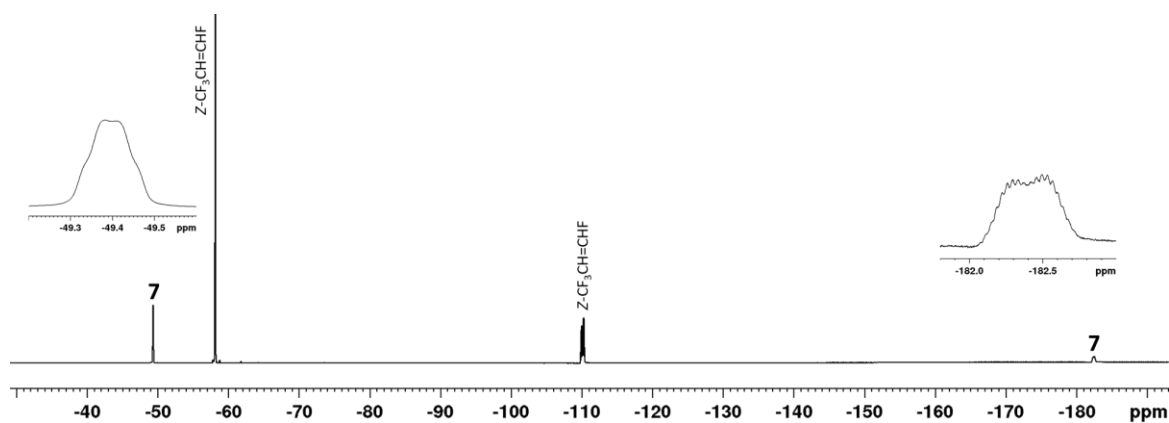
S3. Section of the ^{19}F NMR (bottom) and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra corresponding to complex $[\text{Rh}\{(\text{Z})\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**4**) in C_6D_6 .



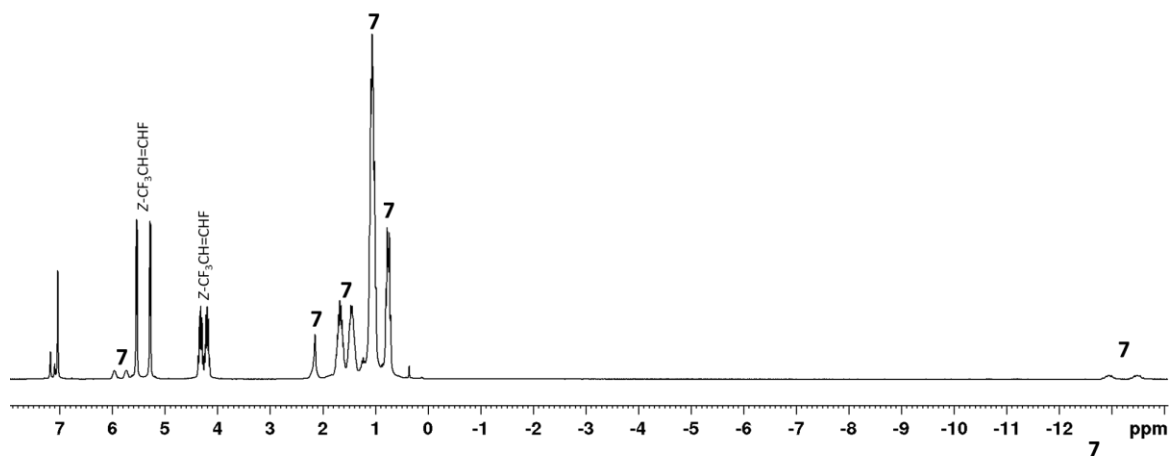
S4. Parts of the ^1H (bottom), $^1\text{H}\{^{19}\text{F}\}$ (middle) and $^1\text{H}\{^{31}\text{P}\}$ (top) NMR spectra corresponding to complex $[\text{Rh}\{(\text{Z})\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**4**) in C_6D_6 .



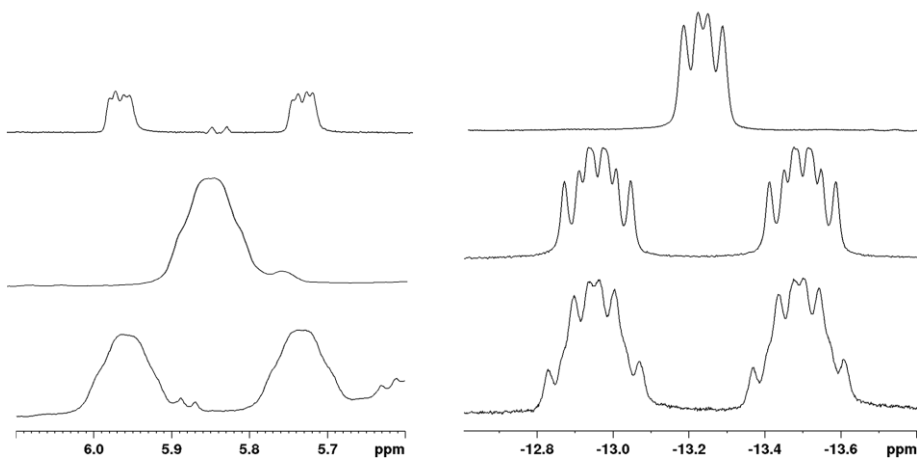
S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) in toluene- d^8 at 233 K.



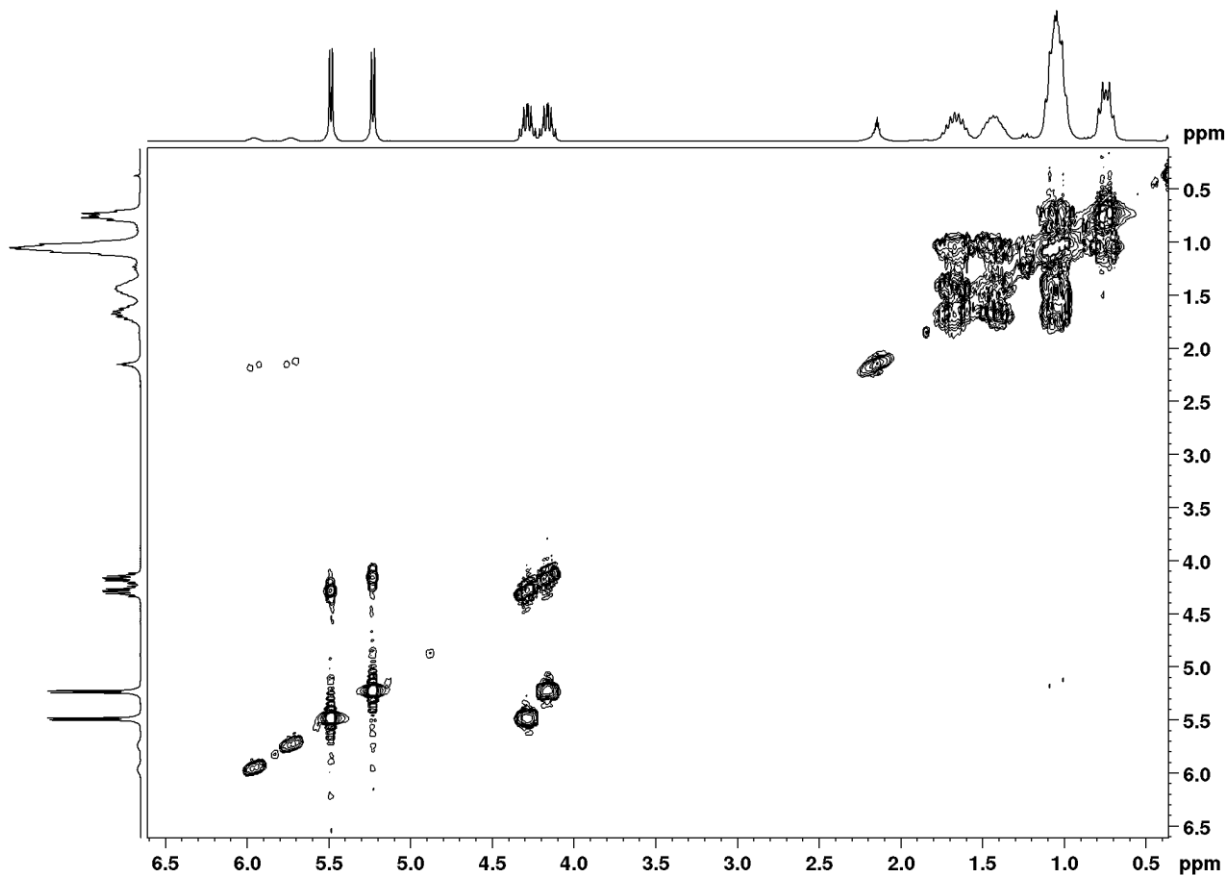
S6. ^{19}F NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) in toluene- d^8 at 233 K.



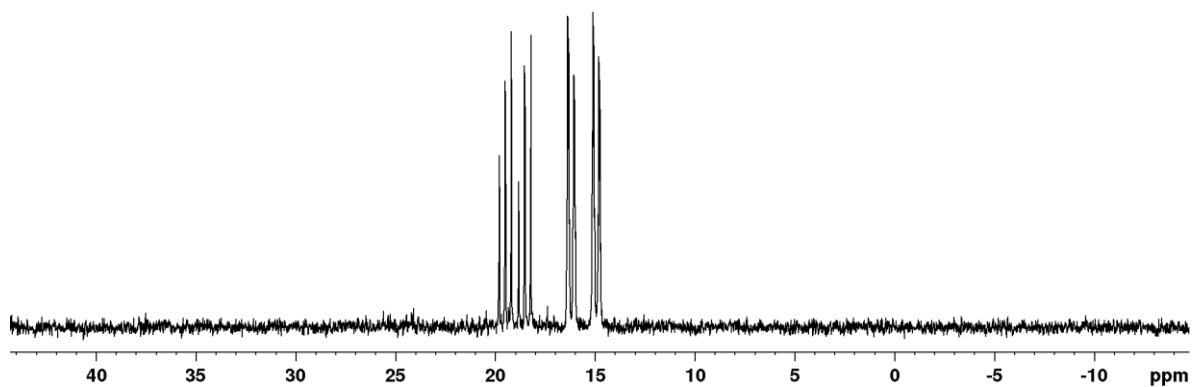
S7. ^1H NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) in toluene- d^8 at 233 K.



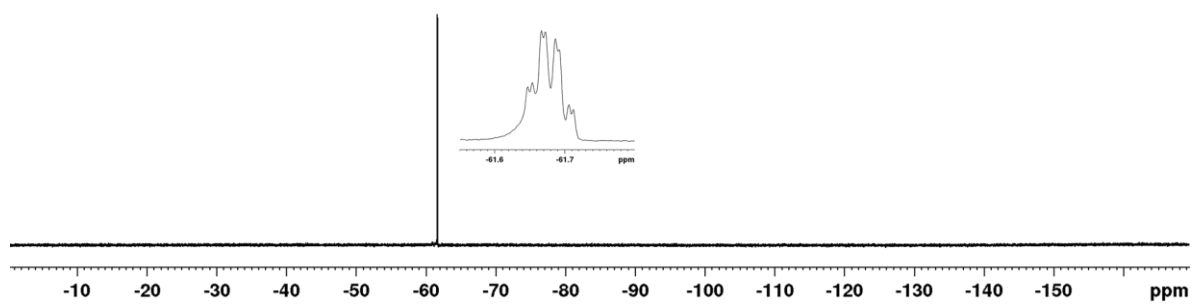
S8. Parts of the ^1H (bottom), $^1\text{H}\{^{19}\text{F}\}$ (middle) and $^1\text{H}\{^{31}\text{P}\}$ (top) NMR spectra corresponding to complex *fac*- $[\text{Rh}(\text{H})(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (**7**) in toluene- d_8 .



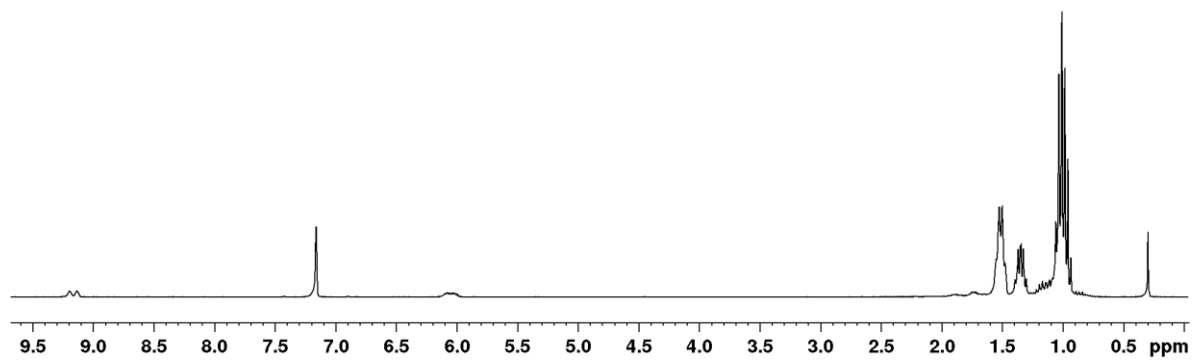
S9. ^1H ^1H COSY NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{H})(\text{PEt}_3)_3]$ (**1**) in toluene- d_8 at 223 K.



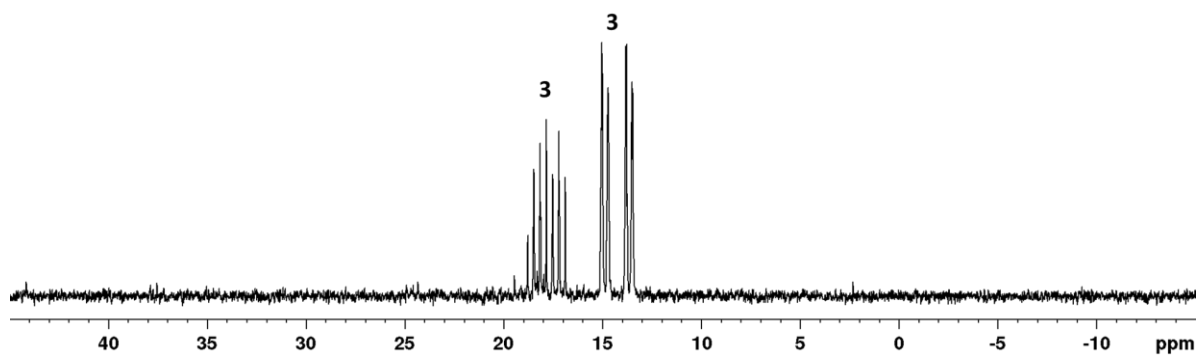
S10. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) in C_6D_6 .



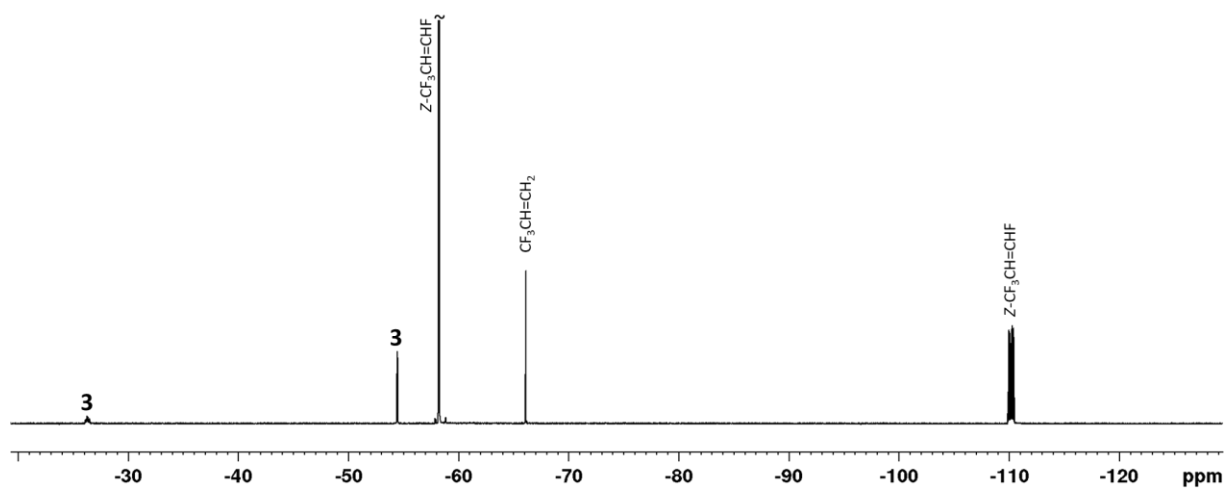
S11. ^{19}F NMR spectrum of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) in C_6D_6 .



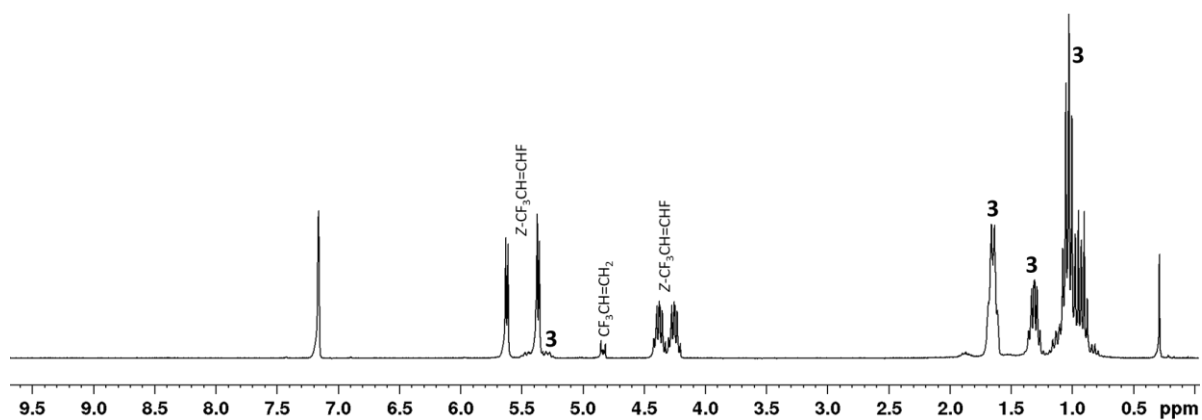
S12. ^1H NMR spectrum of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) in C_6D_6 .



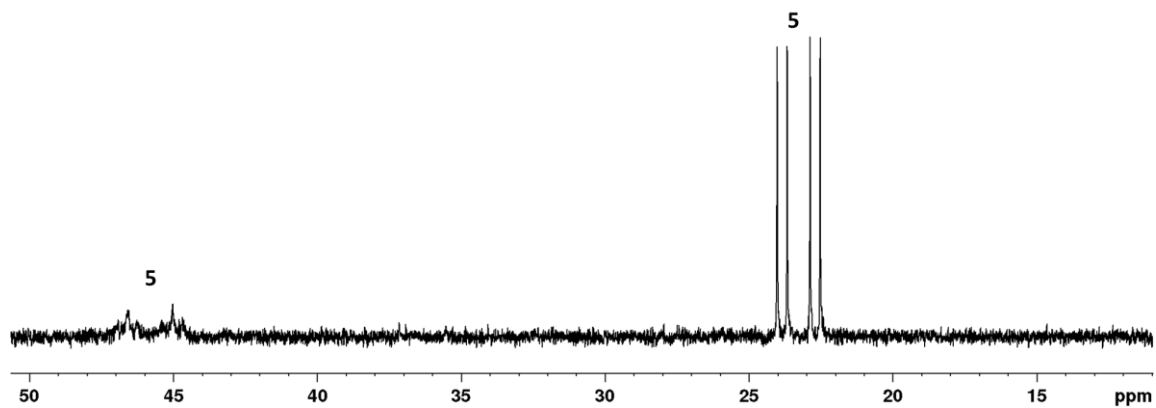
S13. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) with *Z*-1,3,3,3-tetrafluoropropene in C_6D_6 .



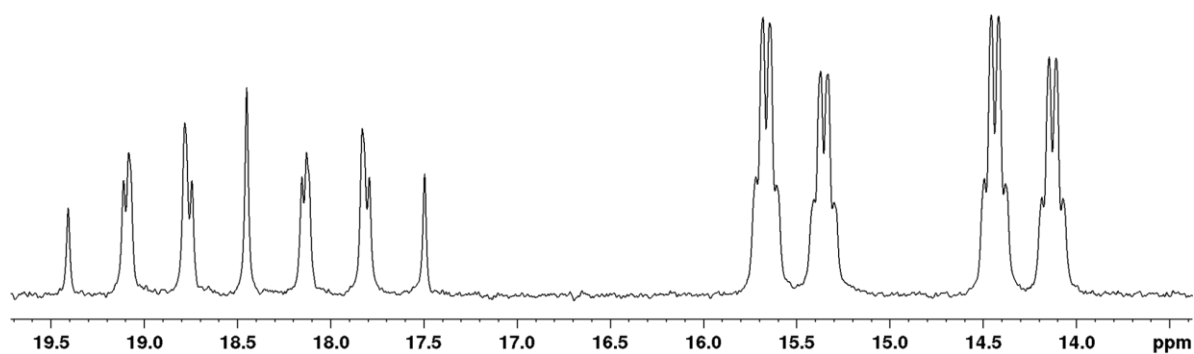
S14. ^{19}F NMR spectrum of the reaction of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) with *Z*-1,3,3,3-tetrafluoropropene in C_6D_6 .



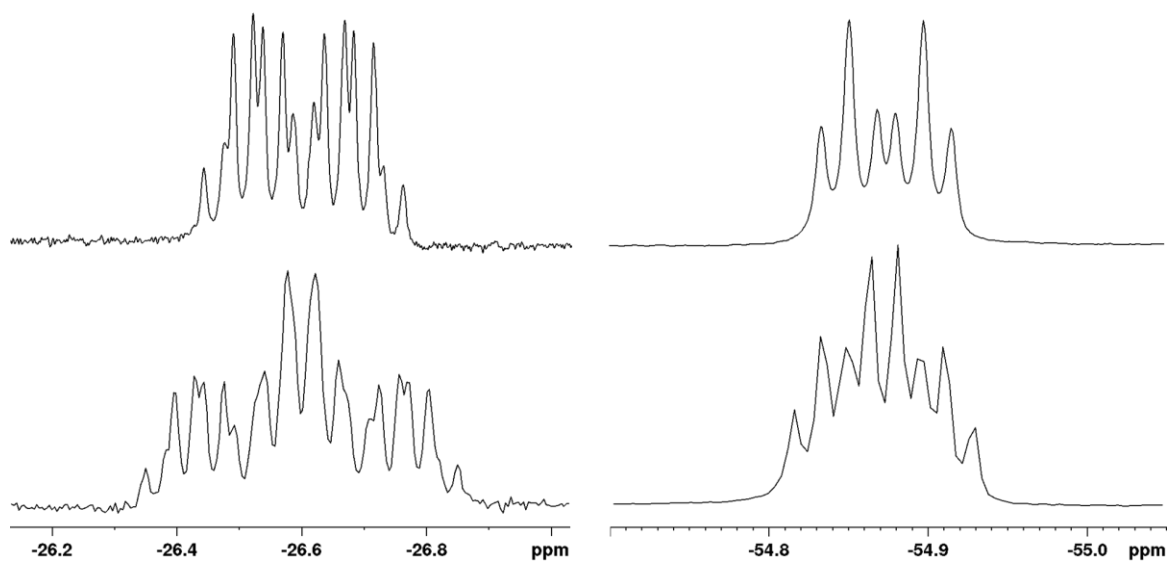
S15. ^1H NMR spectrum of the reaction of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) with *Z*-1,3,3,3-tetrafluoropropene in C_6D_6 .



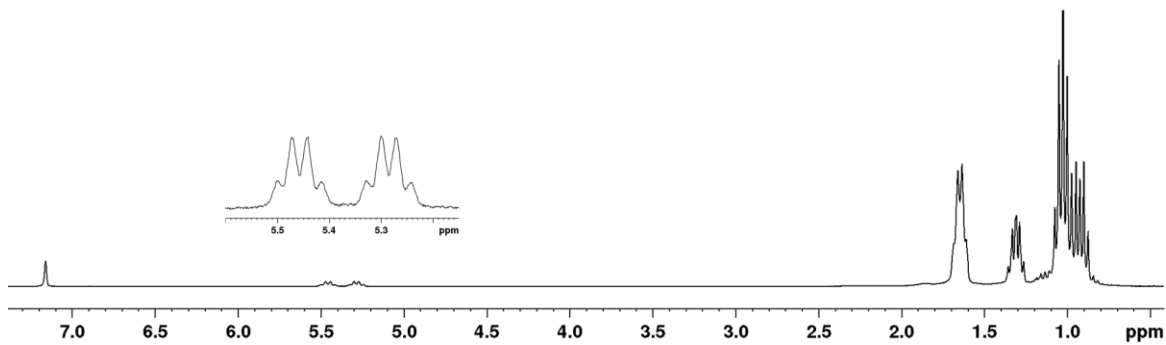
S16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of complex $[\text{Rh}\{(E)\text{-CH=CHCF}_3\}(\text{PEt}_3)_3]$ (**2**) with $\text{Et}_3\text{N}\cdot 3\text{HF}$ in C_6D_6 .



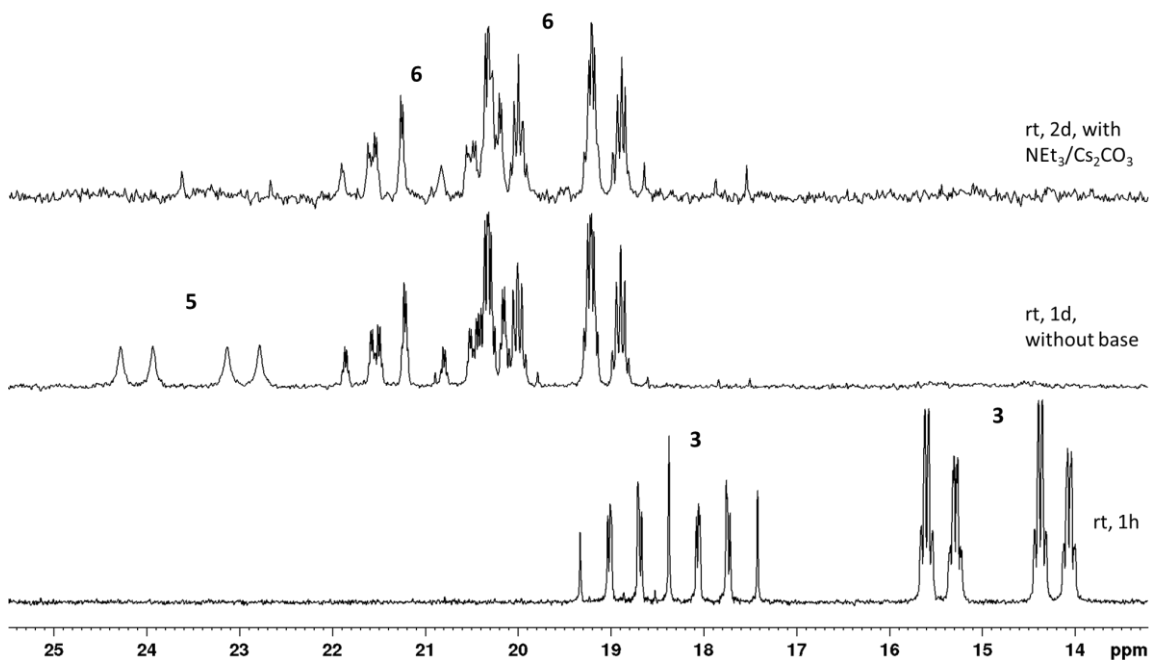
S17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) in C_6D_6 .



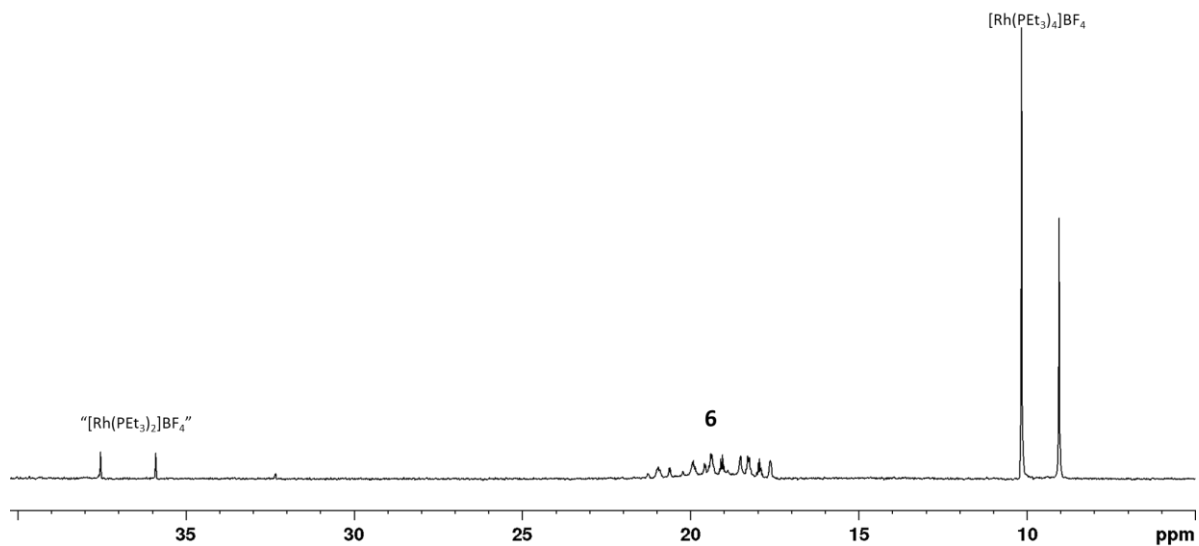
S18. ^{19}F (bottom) and $^{19}\text{F}\{^1\text{H}\}$ (top) NMR spectrum of complex $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) in C_6D_6 .



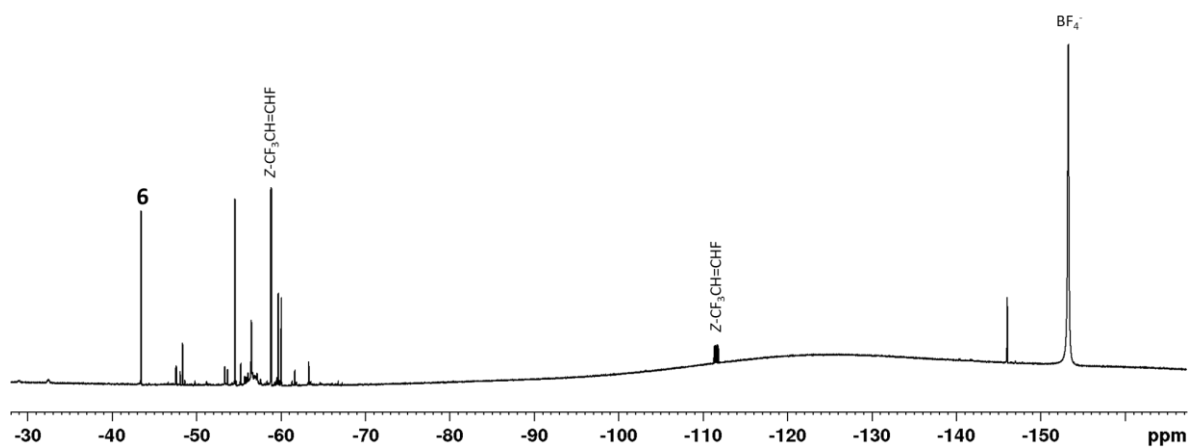
S19. ^1H NMR spectrum of complex $[\text{Rh}\{\textit{E}\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) in C_6D_6 .



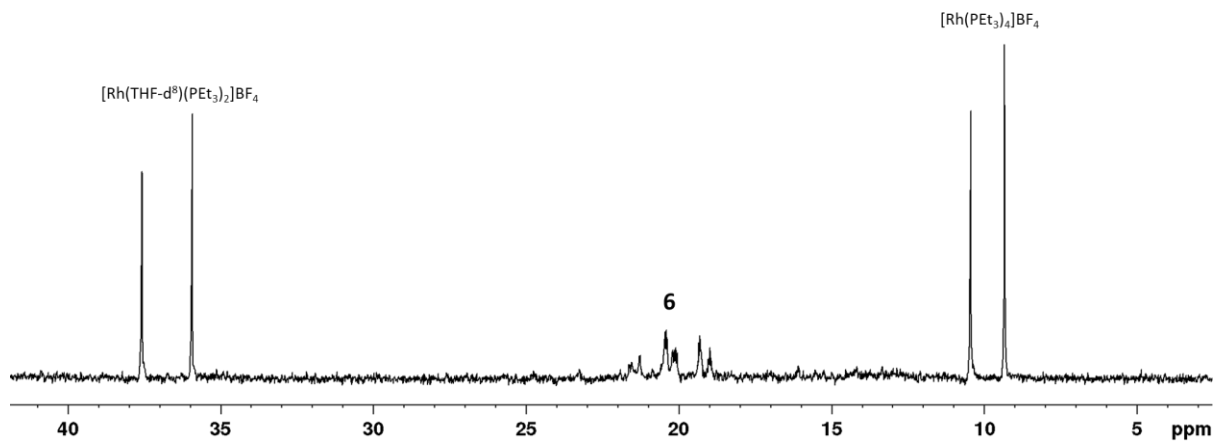
S20. Section of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of *Z*-1,3,3,3-tetrafluoropropene with $[\text{Rh}(\text{CH}_3)(\text{PEt}_3)_3]$ (**8**) in C_6D_6 at different times with and without presence of base.



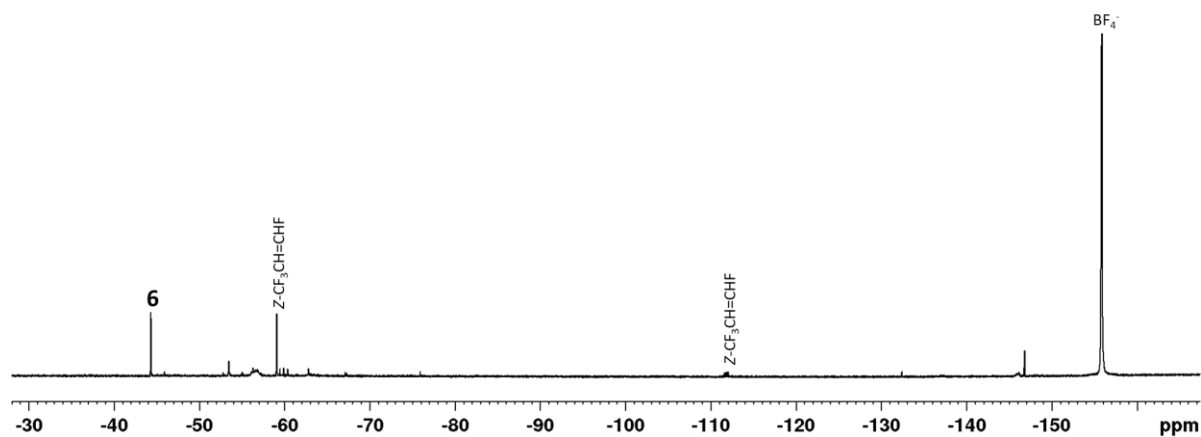
S21. ³¹P{¹H} NMR spectrum of the reaction of complex [Rh{(E)-CF=CHCF₃}(PEt₃)₃] (**3**) with BF₃ at 263 K in CD₂Cl₂.



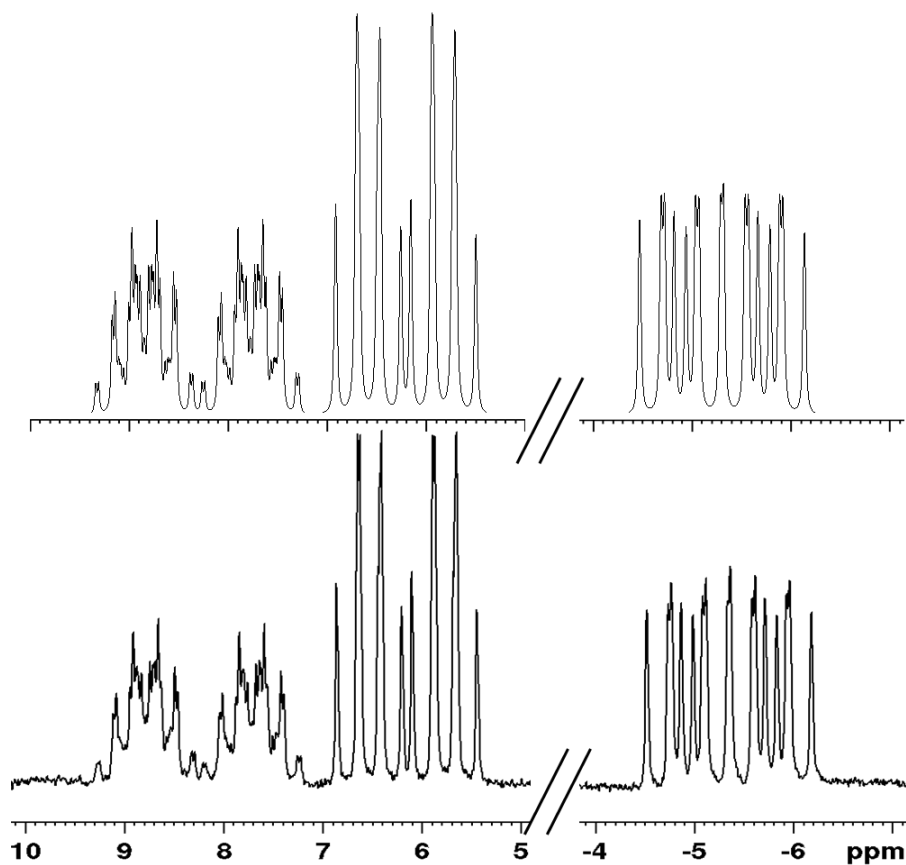
S22. ¹⁹F NMR spectrum of the reaction of complex [Rh{(E)-CF=CHCF₃}(PEt₃)₃] (**3**) with BF₃ at 263 K in CD₂Cl₂.



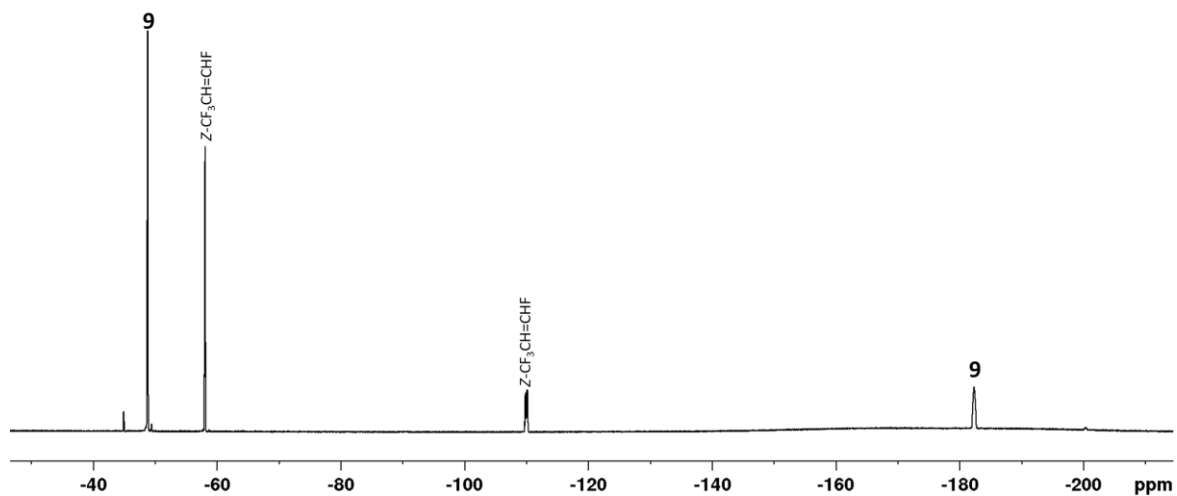
S23. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of complex $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with LiBF_4 in THF-d^8 .



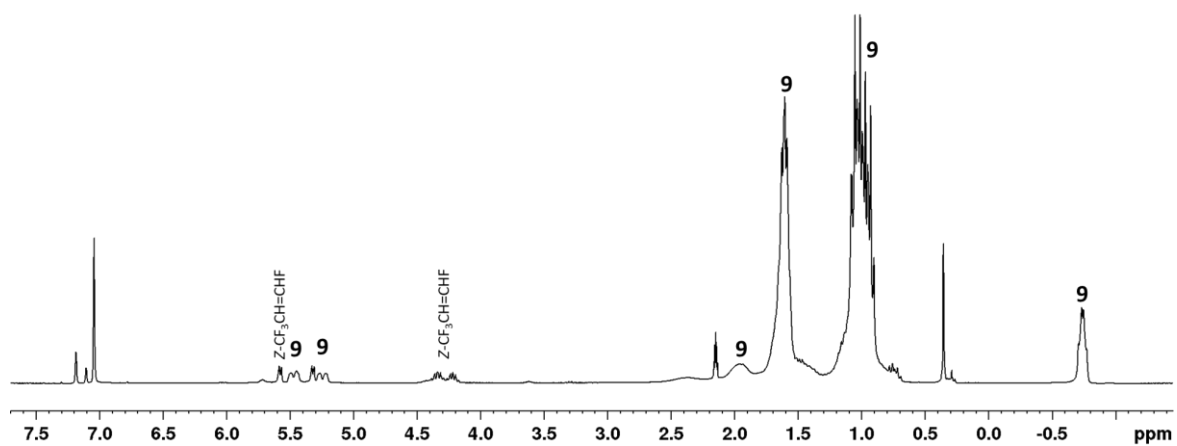
S24. ^{19}F NMR spectrum of the reaction of complex $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with LiBF_4 in THF-d^8 .



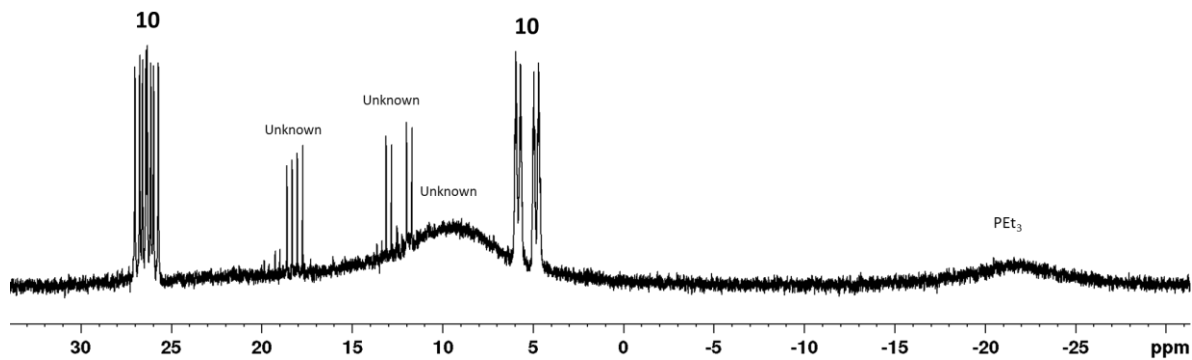
S25. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $\text{fac-}[\text{Rh}(\text{CH}_3)(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (**9**) in toluene-d^8 at 213 K: experimental (bottom), simulated (top).⁶



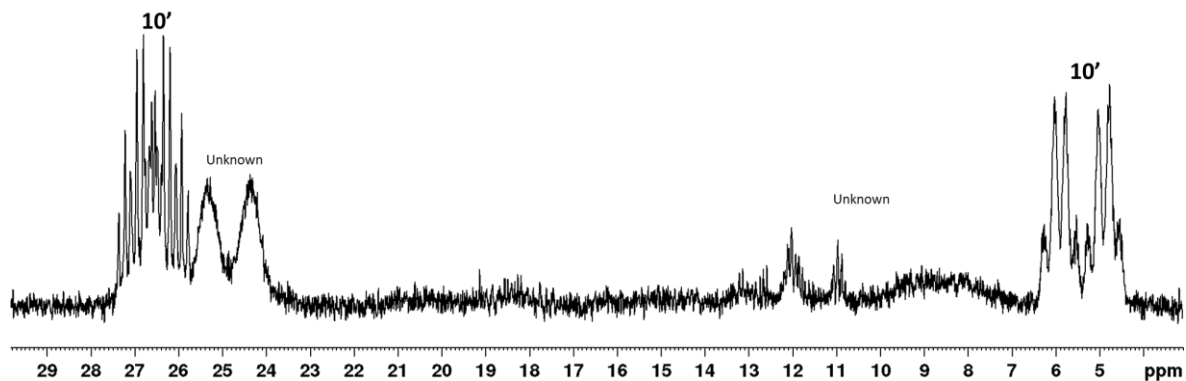
S26. ^{19}F NMR spectrum of complex *fac*- $[\text{Rh}(\text{CH}_3)(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (**9**) in toluene- d^8 at 238 K.



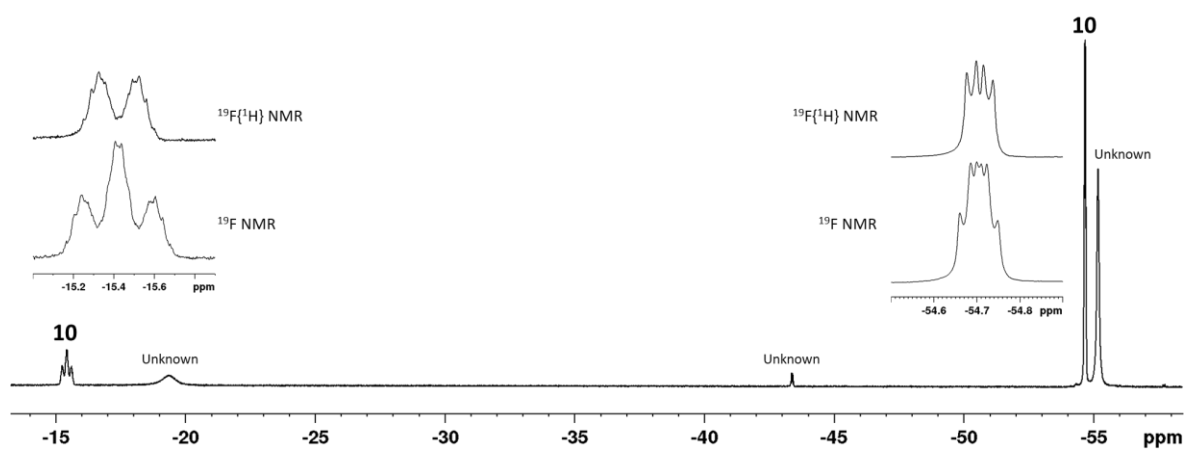
S27. ^1H NMR spectrum of complex *fac*- $[\text{Rh}(\text{CH}_3)(\text{CF}_3\text{CHCHF})(\text{PEt}_3)_3]$ (**9**) in toluene- d^8 at 238 K.



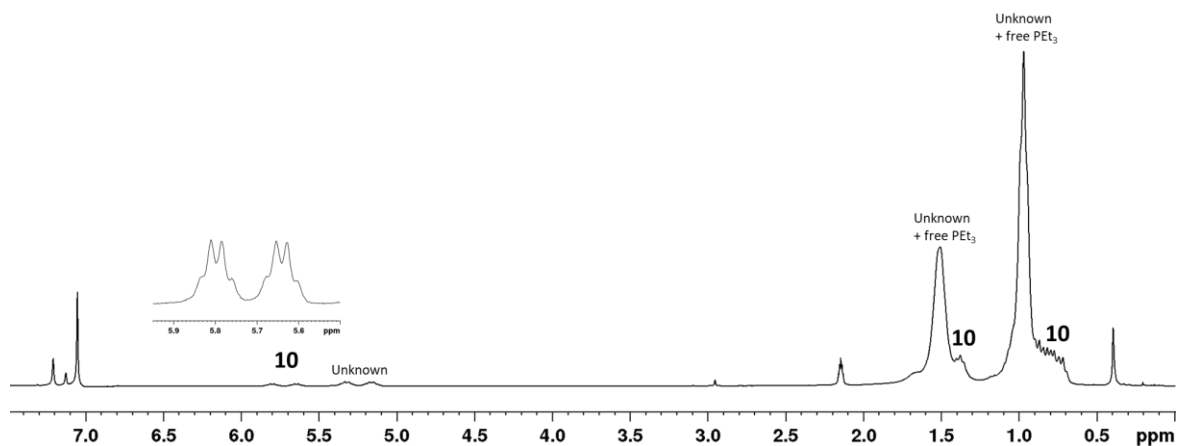
S28. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with CO in toluene- d^8 at 213 K.



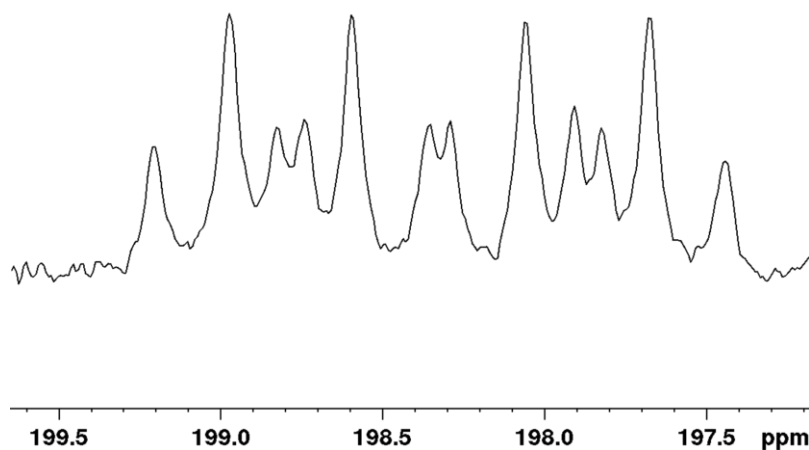
S29. Section of $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with ^{13}CO in toluene- d^8 at 201 K.



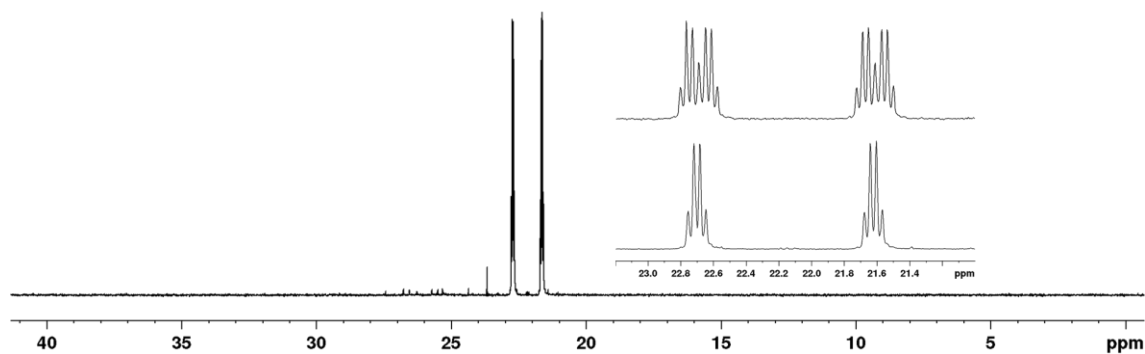
S30. ^{19}F NMR spectrum of the reaction of $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with CO in toluene- d^8 at 213 K.



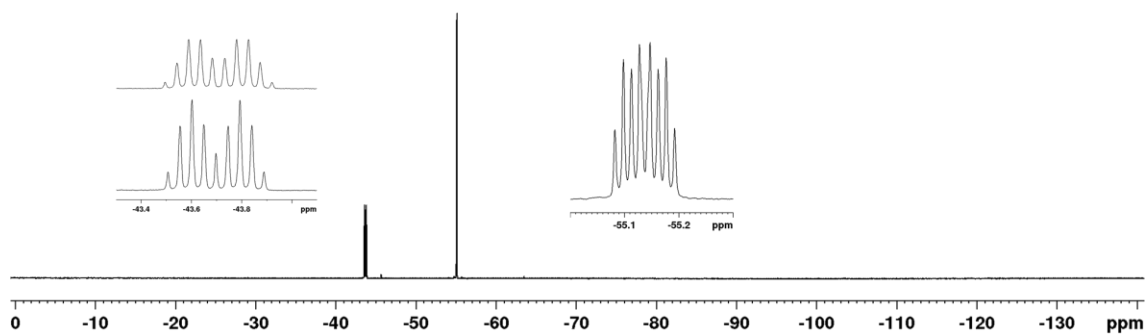
S31. ^1H NMR spectrum of the reaction of $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with CO in toluene- d^8 at 213 K.



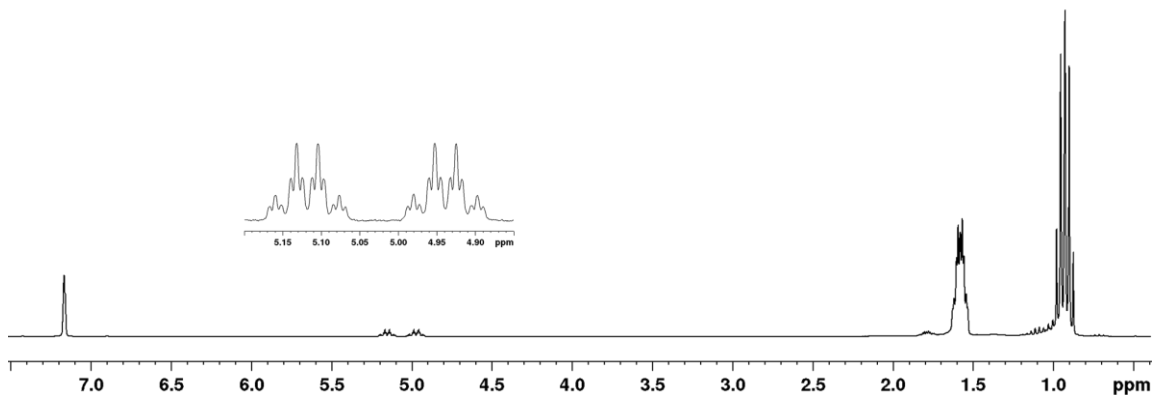
S32. Section of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{PEt}_3)_3]$ (**3**) with ^{13}CO in toluene- d^8 at 201 K.



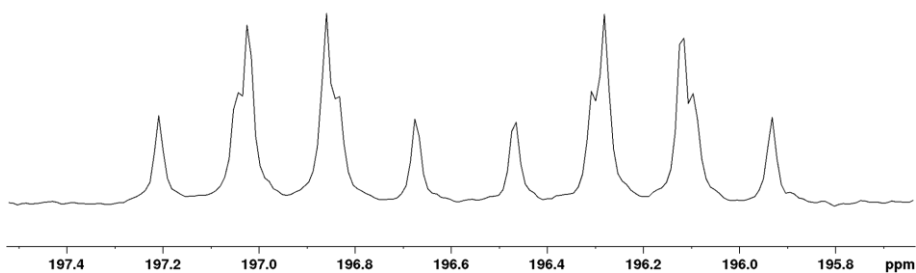
S33. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex *trans*- $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{CO})(\text{PEt}_3)_2]$ (**11**) in C_6D_6 . The signals for **11** (bottom) and **11'** (top) are shown for comparison.



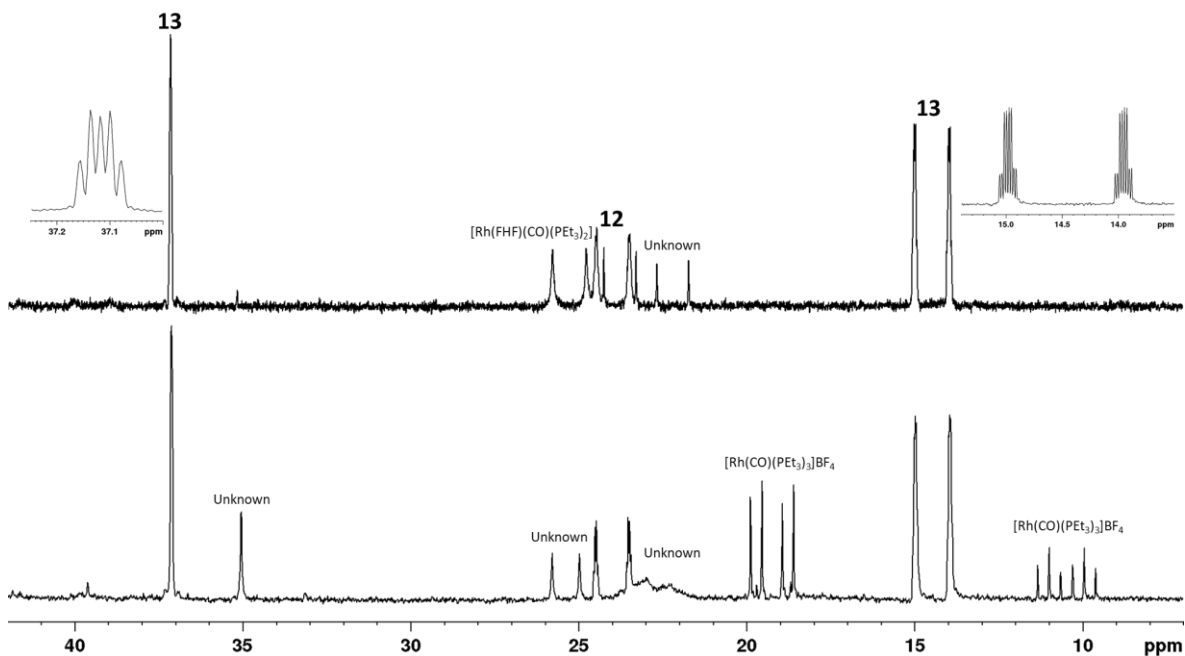
S34. ^{19}F NMR spectrum of complex *trans*- $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{CO})(\text{PEt}_3)_2]$ (**11**) in C_6D_6 . The signals for **11** (bottom) and **11'** (top) are shown for comparison.



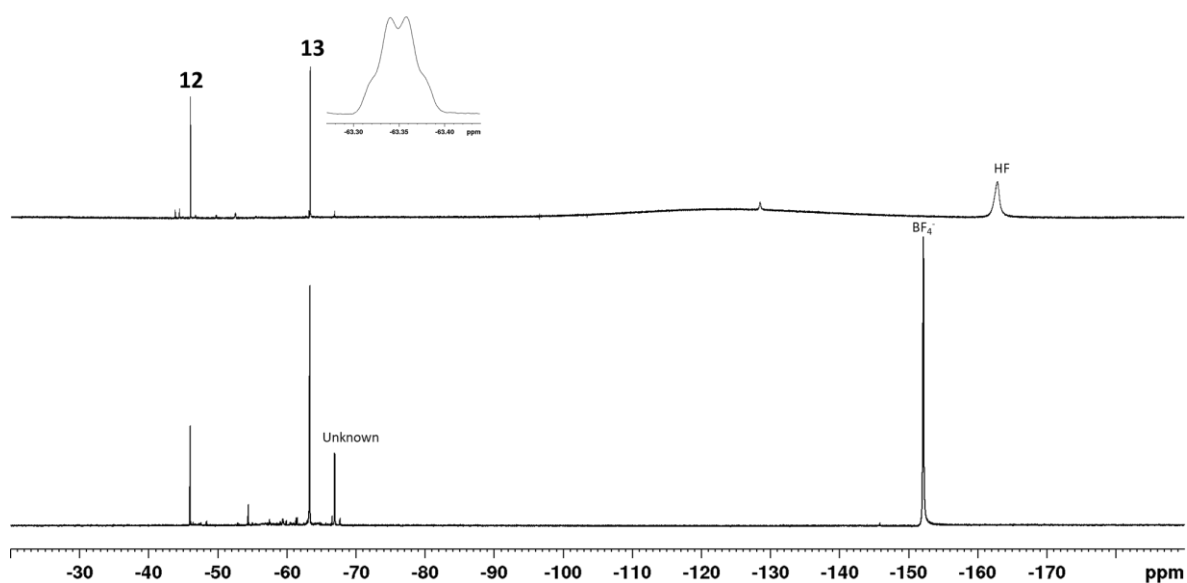
S35. ^1H NMR spectrum of complex *trans*- $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{CO})(\text{PEt}_3)_2]$ (**11**) in C_6D_6 (no changes in complex **11'**).



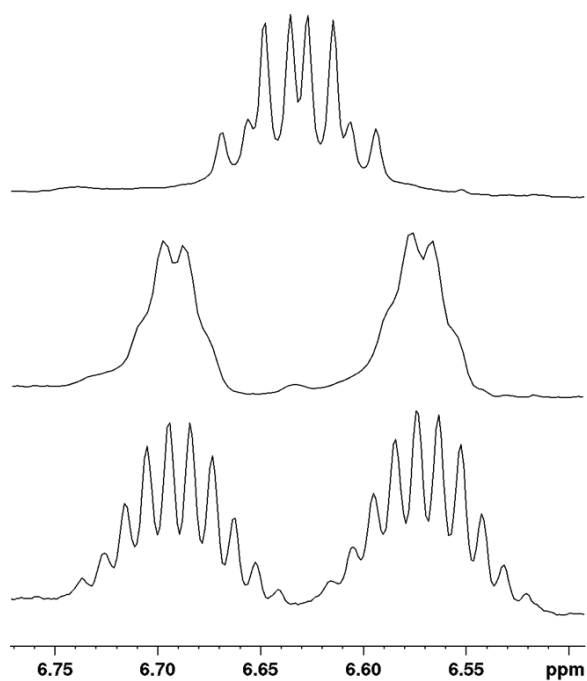
S36. Section of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex *trans*- $[\text{Rh}\{(E)\text{-CF=CHCF}_3\}(\text{}^{13}\text{CO})(\text{PEt}_3)_2]$ (**11'**) in C_6D_6 .



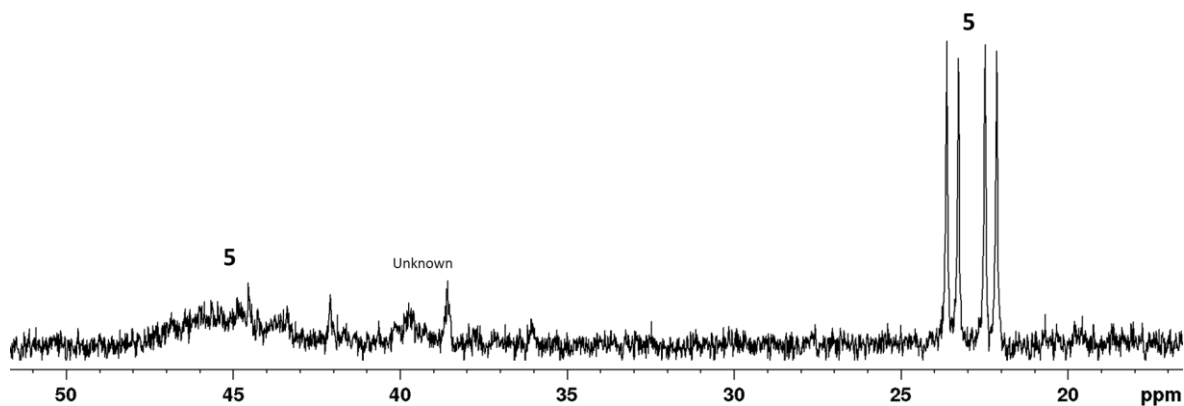
S37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{CO})(\text{PEt}_3)_3]$ (**12**) with HF (top) or HBF_4 (bottom) in CD_2Cl_2 .



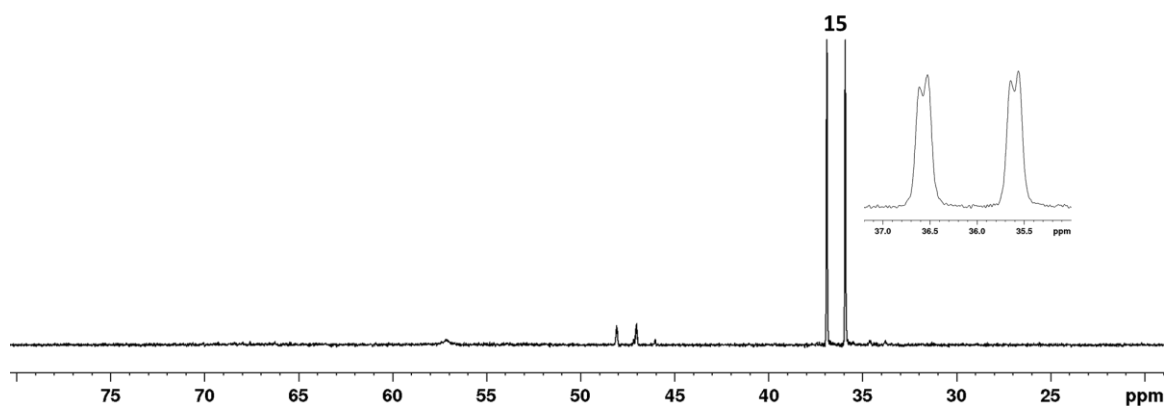
S38. ^{19}F NMR spectrum of the reaction of $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{CO})(\text{PEt}_3)_3]$ (**12**) with HF (top) or HBF₄ (bottom) in CD_2Cl_2 .



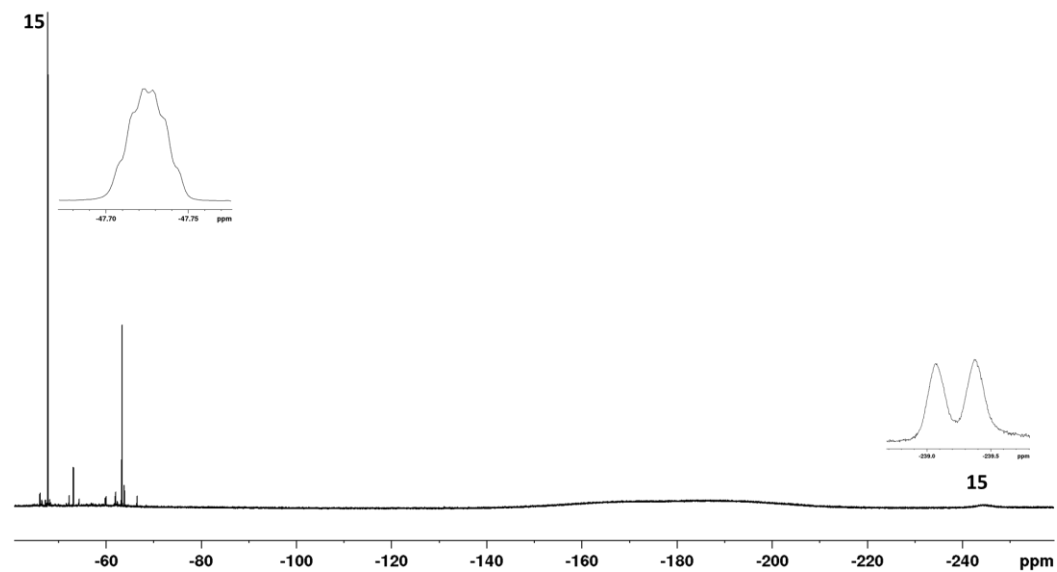
S39. Section of the ^1H NMR (bottom), $^1\text{H}\{^{19}\text{F}\}$ NMR (middle) and $^1\text{H}\{^{31}\text{P}\}$ NMR (top) of complex $[\text{Rh}\{(\text{Z})\text{-C}(\text{PEt}_3)=\text{CHCF}_3\}(\text{CO})(\text{PEt}_3)_2]^+$ (**13**) corresponding to the vinyl proton of the phosphonioalkenyl ligand in CD_2Cl_2 .



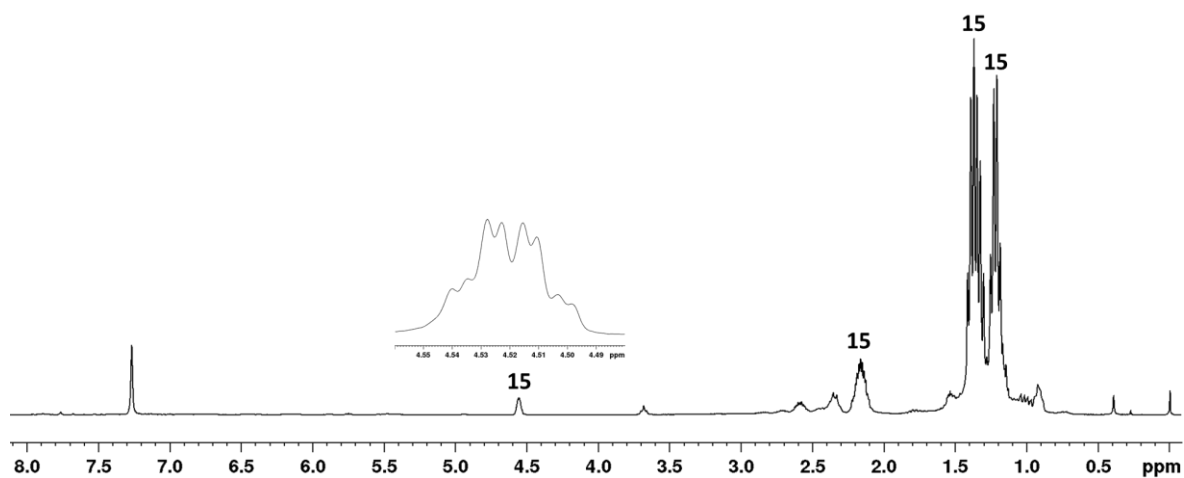
S40. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of $[\text{Rh}(\text{C}\equiv\text{CCF}_3)(\text{PEt}_3)_3]$ (**6**) with $\text{Et}_3\text{N}\cdot 3\text{HF}$ in C_6D_6 .



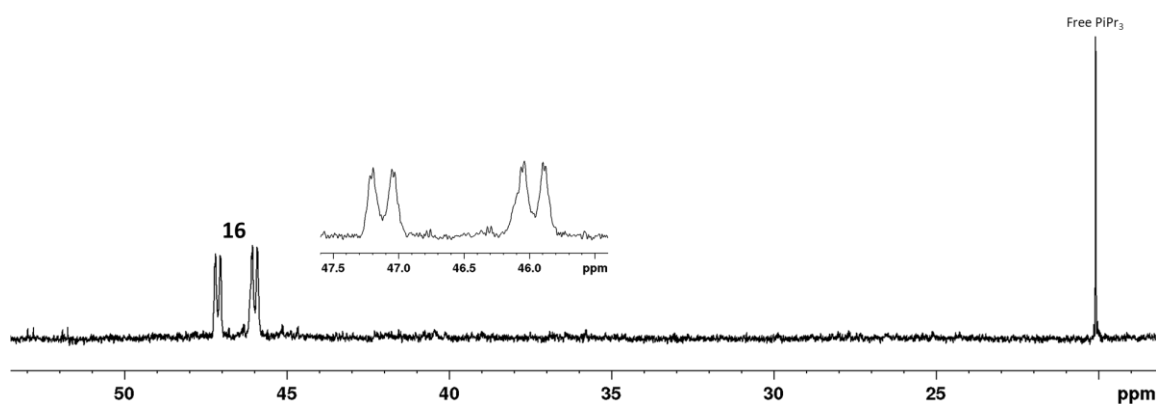
S41. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $[\text{Rh}(\text{F})(\text{CH}\equiv\text{CCF}_3)(\text{PiPr}_3)_2]$ (**15**) in Tol-d_8 at 233 K.



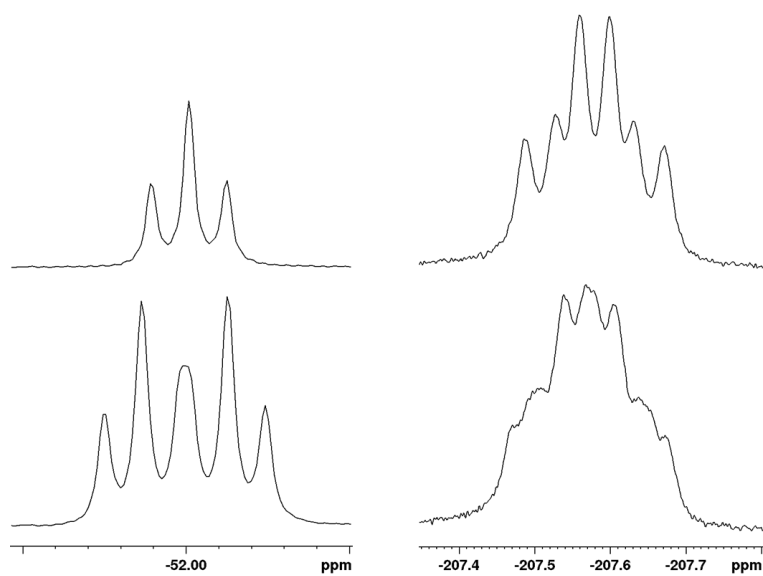
S42. ^{19}F NMR spectrum of complex $[\text{Rh}(\text{F})(\text{CH}\equiv\text{CCF}_3)(\text{PiPr}_3)_2]$ (**15**) in Tol-d_8 showing the Rh-F ligand resonance at 233 K.



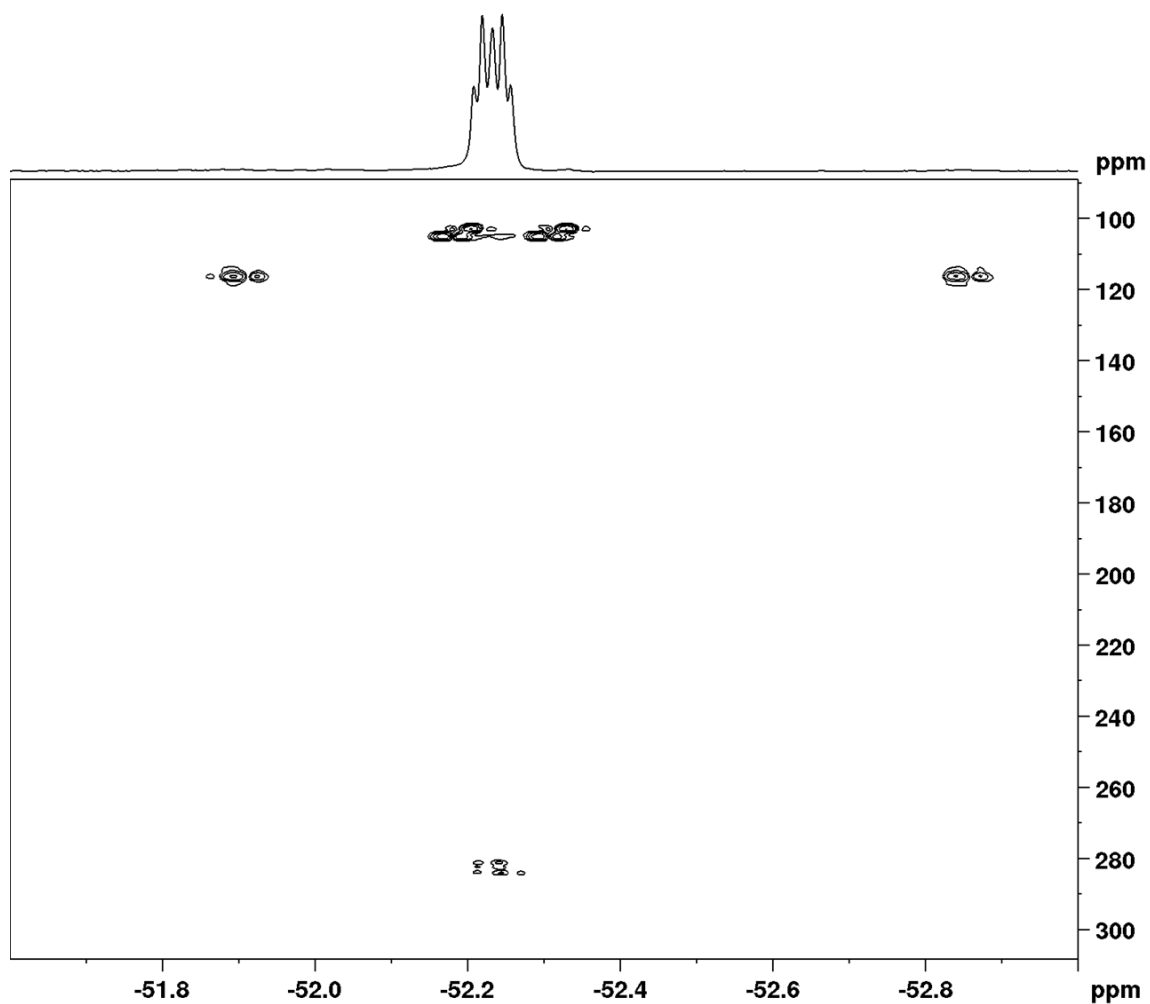
S43. ^1H NMR spectrum of complex $[\text{Rh}(\text{F})(\text{CH}\equiv\text{CCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**15**) in C_6D_6 .



S44. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex $[\text{Rh}(\text{F})(=\text{C}=\text{CHCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**16**) in C_6D_6 .



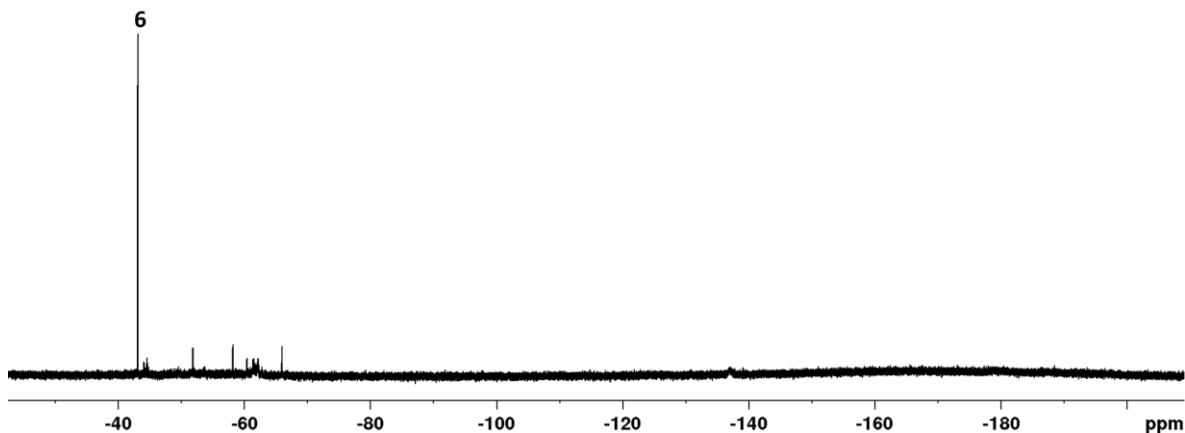
S45. Sections of the ^{19}F NMR (bottom) and the $^{19}\text{F}\{^1\text{H}\}$ NMR (top) spectra of complex $[\text{Rh}(\text{F})(=\text{C}=\text{CHCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**16**) in C_6D_6 .



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_6D_6 .



S47. $^{31}\text{P}\{^1\text{H}\}$ 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_6D_6 .



S48. ^{19}F NMR spectrum of the reaction of complex $[\text{Rh}(\text{F})(=\text{C}=\text{CHCF}_3)(\text{P}i\text{Pr}_3)_2]$ (**16**) with PEt_3 in C_6D_6 .

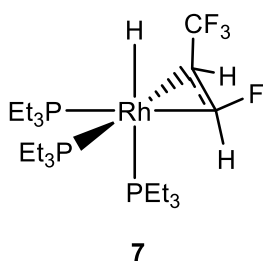
DFT calculations

Computational details for geometry optimization of all the calculated complexes

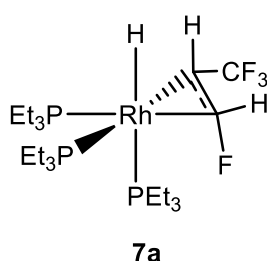
Calculations were run using the Gaussian 09 (Revision D.01) program package.¹¹ All rhodium complexes were calculated using the BP86 functional. Rhodium was described with RECPs and the associated def2-SVP basis sets.^{12,13} All the other atoms were described with def2-SVP basis sets. A Grimme D3 dispersion 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**

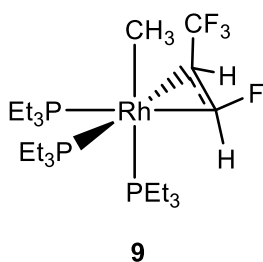


Complex **7a**

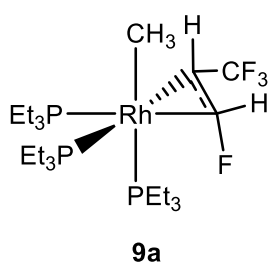


Energies in Hartree (corrected for zero-point energy): -2361.736294 for complex **7** and -2361.734125 for complex **7a**. Accordingly, structure **7** is slightly favored by 5.7 kJ/mol.

Complex **9**



Complex **9a**

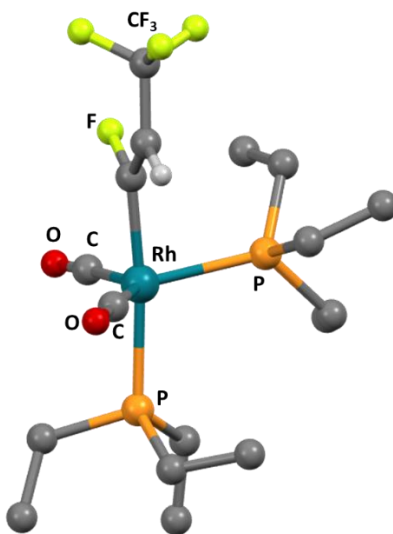


Energy in Hartree (corrected for zero-point energy): -2400.978525 for complex **12** and -2400.978446 for complex **9a**. Accordingly, both structures are possible as complex **9** is only favored by 0.2 kJ/mol.

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.

C	2.24411	-2.22154	-1.66888	H	1.58267	-0.45724	-2.75137	C	2.38685	2.60746	0.97254	H	1.53071	-0.83856	-2.66508
F	2.22209	-1.33205	-2.69196	C	2.27692	-2.11441	-1.65117	F	2.34843	2.36779	2.30198	C	2.10636	-2.47025	-1.47554
F	2.32841	-3.46190	-2.24399	H	-0.13281	0.94839	-1.87668	F	2.59890	3.95970	0.83693	C	-0.00172	1.06957	-2.45988
F	3.45040	-2.04285	-1.02296	F	2.78633	-2.68648	-2.78760	F	3.54085	2.01956	0.50011	H	-0.57622	2.01749	-2.43785
H	1.37736	-2.72352	0.19086	F	1.88892	-3.15826	-0.85898	H	1.42180	2.44669	-0.86438	H	-0.40070	0.46037	-3.29816
H	0.42640	0.10213	-1.75376	F	3.35304	-1.53490	-1.02639	C	0.52368	0.16599	2.35997	H	1.04684	1.32433	-2.72569
								H	0.01891	-0.69362	2.84657	F	2.59290	-3.08418	-2.59967
								H	0.23446	1.09070	2.88694	F	1.62943	-3.48008	-0.68675
								H	1.61582	0.03327	2.49321	F	3.21189	-1.96874	-0.83445
Complex 10															
Rh	-0.22596	-0.61361	0.17527												
P	-2.57543	-0.50446	-0.13877												
C	1.26586	1.83767	-1.87440												
C	1.85437	2.24784	0.93543												
C	-0.71133	3.10110	-0.19722												
P	0.48356	1.66179	-0.18853												
C	-3.33549	-2.09963	0.46444												
C	-4.67593	-2.55485	-0.12412												
C	-3.16424	-0.37958	-1.89580												
C	-2.62604	0.83942	-2.64631												
C	-3.47816	0.84423	0.76482												
C	-5.00925	0.84605	0.74360												
C	1.61978	2.03154	2.43446												
C	2.06155	3.11130	-2.17404												
H	-3.38622	-1.99439	1.57030												
H	-2.55025	-2.86158	0.27955												
H	-4.27441	-0.39954	-1.90347												
H	-2.82429	-1.31627	-2.38651												
H	-2.99549	1.79035	-2.20921												
H	-2.94217	0.82022	-3.70911												
H	-1.51789	0.85804	-2.61895												
H	-3.07835	1.78911	0.34494												
H	-3.09117	0.79481	1.80489												
H	-5.41419	0.84549	-0.28945												
H	-5.39925	1.75447	1.24809												
H	-5.43071	-0.03006	1.27512												
C	-1.20812	3.55282	1.17994												
H	-4.59784	-2.75502	-1.21163												
H	-5.48652	-1.81510	0.02461												
H	-4.99824	-3.50130	0.35756												
H	2.75239	1.67918	0.61332												
H	2.04984	3.31808	0.70631												
H	0.43542	1.69891	-2.59996												
H	1.91275	0.94240	-1.97178												
H	1.45691	4.03338	-2.04380												
H	2.42177	3.10369	-3.22395												
H	2.95433	3.19686	-1.52289												
H	-2.07113	4.24416	1.08314												
H	-0.41623	4.09165	1.73663												
H	-1.52788	2.69520	1.80575												
H	-0.22865	3.95084	-0.72646												
H	-1.55626	2.77535	-0.83952												
C	1.78928	-0.94026	0.40706												
C	2.75059	-1.09010	-0.54256												
H	2.47339	-1.13033	-1.60320												
H	0.75906	2.61098	2.81964												
H	2.51782	2.34278	3.00716												
H	1.43951	0.96342	2.65230												
F	2.24890	-0.95148	1.69773												
C	4.21416	-1.17586	-0.25465												
F	4.70540	-0.02719	0.32107												
F	4.91365	-1.35301	-1.40939												
F	4.56048	-2.18768	0.58234												
C	-0.55358	-0.96747	2.03239												
O	-0.80025	-1.19882	3.14876												
C	-0.15985	-1.69607	-1.37750												
O	-0.13689	-2.37842	-2.32704												

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