# Competing $\mathbf{C}-\mathbf{H}$ and $\mathbf{C}-\mathbf{F}$ 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 ${ }^{1}$ and, prior to use, distilled under argon. The rhodium complexes $\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1}),{ }^{2}\left[\mathrm{Rh}\left(\mathrm{CH}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{8}),{ }^{3}\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{3}\right]$ $(6)^{4}$ and $\left[\mathrm{Rh}(\mu-\mathrm{F})(\text { cyclooctene })_{2}\right]_{2}{ }^{5}$ 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. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ signals are referred to residual solvent signals, those of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ to $85 \% \mathrm{H}_{3} \mathrm{PO}_{4}$ and the ${ }^{19} \mathrm{~F}$ NMR spectra to external $\mathrm{CFCl}_{3} .{ }^{1} \mathrm{H},{ }^{19} \mathrm{~F},{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR signal assignments were supported or, when stated, determined by ${ }^{1} \mathrm{H},{ }^{1} \mathrm{H}$ COSY, ${ }^{19} \mathrm{~F},{ }^{1} \mathrm{H}$ HETCOR, ${ }^{19} \mathrm{~F},{ }^{19} \mathrm{~F}$ gCOSY, ${ }^{31} \mathrm{P},{ }^{31} \mathrm{P}$ COSY, ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC, ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC, ${ }^{19} \mathrm{~F},{ }^{13} \mathrm{C}$ HMBC, ${ }^{19} \mathrm{~F},{ }^{13} \mathrm{C}$ HMQC and ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}$ HMBC NMR experiments. The determined coupling constant values were confirmed by $g N M R$ 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 $\mathbf{Z}$-1,3,3,3-tetrafluoropropene with $\left[\mathbf{R h}(\mathbf{H})\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (1)

In a Young NMR tube $\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1})(30 \mathrm{mg}, 0.065 \mathrm{mmol})$ was dissolved in toluene- $\mathrm{d}_{8}$ $(0.4 \mathrm{~mL})$. 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 $\mathbf{1}$ to complex fac- $\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (7) was observed. At 273 K a $90 \%$ conversion, based on the ${ }^{19} \mathrm{~F}$ NMR spectrum, of $\mathbf{7}$ into $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ was observed as well as the release of HF and traces of complexes $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ and $\left[\mathrm{Rh}\left\{(Z)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (4). Finally, after 10 minutes at room temperature, a mixture of $\quad\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right] \quad(\mathbf{2}), \quad\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right] \quad(\mathbf{3}), \quad[\mathrm{Rh}\{(Z)-$
$\left.\left.\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (4) and $\left[\mathrm{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (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, $\mathbf{4}$ and $\mathbf{5}$ is 3.8:2:1:4.4. After one day, $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{6})$ and complex 5 are the only products in a $1: 1$ ratio. . Complexes $\mathbf{2}$, and $\mathbf{6}$ have been identified by comparison with literature. ${ }^{4,7}$ Complex 5 was identified by comparison with $\left[\mathrm{Rh}(\mathrm{FHF})\left(\mathrm{PEt}_{3}\right)_{3}\right]$, ${ }^{7}$ however, P-F couplings are not observed which suggest the presence of more than one HF molecule leading to the proposed formula $\left[\mathrm{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](5)$. Addition of excess of $\mathrm{NEt}_{3} / \mathrm{Cs}_{2} \mathrm{CO}_{3}$ to remove the excess of HF , led to the formation of $\left[\operatorname{Rh}(\mathrm{F})\left(\mathrm{PEt}_{3}\right)_{3}\right]{ }^{7}$

The amount of HF in complex 5 was determined by adding $\mathrm{ClSiEt}_{3}$ ( $0.059 \mathrm{mmol}, 6.5$ equiv) to a solution of complexes $\mathbf{6}$ and $\mathbf{5}\left(0.009 \mathrm{mmol}\right.$ of 5 based on the ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR ratio). After 10 min, full conversion of complex 5 into $\left[\mathrm{Rh}(\mathrm{Cl})\left(\mathrm{PEt}_{3}\right)_{3}\right]$ and dihydrido chlorido rhodium(III) species was observed with a $45 \%$ conversion of $\mathrm{ClSiEt}_{3}$ (determined directly from the ${ }^{1} \mathrm{H}$ NMR spectrum and supported by external standard of $\mathrm{PhCF}_{3}$ ) into $\mathrm{FSiEt}_{3}$ and $\mathrm{F}_{2} \mathrm{SiEt}_{2}$ ( 0.027 mmol in total). The 3 equivalents required would correspond to two HF moieties and the rhodium-bounded fluorido ligand.

Analytical data for $\left[\operatorname{Rh}\left\{(Z)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{4}):{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}\left(300.1 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=8.35$ (dt, ${ }^{3} J_{\mathrm{H}, \mathrm{H}}=14.1,{ }^{3} J_{\mathrm{H}, \mathrm{Pcis}}=4.3 \mathrm{~Hz}, \mathrm{CH}=$ ); $6.61\left(\mathrm{~m}\right.$, ddq in ${ }^{1} \mathrm{H}\left\{{ }^{19} \mathrm{~F}\right\}$ NMR spectrum, dqd in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, ${ }^{3} J_{\mathrm{H}, \mathrm{H}}=13.9,{ }^{4} J_{\mathrm{H}, \mathrm{Ptrans}}=11.8,{ }^{3} J_{\mathrm{H}, \mathrm{F}}=8.7,{ }^{4} J_{\mathrm{H}, \text { Pcis }} \approx{ }^{3} J_{\mathrm{H}, \mathrm{Rh}}=2.3 \mathrm{~Hz}$, $\left.=\mathrm{CHCF}_{3}\right) \mathrm{ppm}$; the resonances corresponding to the phosphine ligands are overlapped with the signals for the other products. ${ }^{19} \mathbf{F}$ NMR $\left(282.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=-59.7\left(\mathrm{~m}, \mathrm{tt}\right.$ in ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum, $\left.{ }^{5} J_{\mathrm{F}, \text { Pcis }}=5.5,{ }^{5} J_{\mathrm{F}, \text { Ptrans }} \approx{ }^{4} J_{\mathrm{F}, \mathrm{Rh}}=1.7 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right) \mathrm{ppm} .{ }^{\mathbf{3 1} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}(121.5}$ $\mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=12.5$ (ddq, $\left.{ }^{1} \mathrm{~J}_{\mathrm{P}, \mathrm{Rh}}=154.6,{ }^{2} J_{\mathrm{P}, \mathrm{P}}=38.9,{ }^{5} \mathrm{~J}_{\mathrm{P}, \mathrm{F}}=4.9 \mathrm{~Hz}, 2 \mathrm{P}, \mathrm{P}_{c i s}\right) \mathrm{ppm}$; the resonance of $\mathrm{P}_{\text {trans }}$ is overlapped with the signals for the other compounds.

Analytical data for $\left[\operatorname{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{5}):{ }^{1} \mathbf{H} \mathbf{N M R}\left(300.1 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=1.65-1.50(\mathrm{~m}$, q in $\left.{ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.7 \mathrm{~Hz}, 12 \mathrm{H}, \mathrm{P}_{\mathrm{cis}} \mathrm{CH}_{2} \mathrm{CH}_{3}\right) ; 1.25-1.15\left(\mathrm{~m}, \mathrm{q}\right.$ in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.2 \mathrm{~Hz}$ $6 \mathrm{H}, \mathrm{P}_{\text {trans }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); 1.17-1.03 (m, t in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.7 \mathrm{~Hz}, 18 \mathrm{H}, \mathrm{P}_{\mathrm{cis}} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); $0.96(\mathrm{dt}$, ${ }^{3} J_{\mathrm{H}, \mathrm{P}}=14.9,{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{H}}=7.2 \mathrm{~Hz}, 9 \mathrm{H}, \mathrm{P}_{\text {trans }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); ${ }^{19} \mathbf{F}$ NMR ( $282.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=-178$ (br $\mathrm{m}, \mathrm{H} F) ;-277.0(\mathrm{~m}, 1 \mathrm{~F}, \mathrm{Rh}-F) \mathrm{ppm} .{ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}\left(121.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=45.83(\mathrm{dt} \mathrm{br}$,
$\left.{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=187.7,{ }^{2} J_{\mathrm{P}, \mathrm{P}}=42.5 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{\text {trans }}\right) ; 23.26\left(\mathrm{dd},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=139.6,{ }^{2} J_{\mathrm{P}, \mathrm{P}}=42.5 \mathrm{~Hz}, 2 \mathrm{P}, \mathrm{P}_{c i s}\right)$ ppm


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Analytical data for $f a c-\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](7):{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}(300.1 \mathrm{MHz}, 233 \mathrm{~K}$, toluene- $\left.\mathrm{d}^{8}\right): \delta=5.85\left(\mathrm{~d} \mathrm{br}\right.$, ddd in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, ${ }^{2} J_{\mathrm{H}, \mathrm{F}}=67.4,{ }^{3} J_{\mathrm{H}, \mathrm{H}}=5.3,{ }^{2} J_{\mathrm{H}, \mathrm{Rh}}=$ $2.1 \mathrm{~Hz}, \mathrm{CHF}$ ); 2.14 ( m , overlapped with the signal for toluene- $\mathrm{d}^{8}$, observed by a ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum, $\mathrm{CHCF}_{3}$ ); 1.55-1.78 (m, $6 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{CH}_{3}$ ); 1.32-1.54 (m, $6 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{CH}_{3}$ ); 0.93-1.18 ( $\mathrm{m}, 24 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{CH}_{3}+\mathrm{PCH}_{2} \mathrm{CH}_{3}$ ); $0.74\left(\mathrm{dt},{ }^{3} J_{\mathrm{H}, \mathrm{P}}=12.8,{ }^{3} J_{\mathrm{H}, \mathrm{H}}=6.9 \mathrm{~Hz}, 9 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{CH}_{3}\right)$; $13.22\left(\mathrm{dqd},{ }^{2} J_{\mathrm{H}, \mathrm{Pc}}=160.0,{ }^{2} J_{\mathrm{H}, \mathrm{Pa}} \approx{ }^{2} J_{\mathrm{H}, \mathrm{Pb}} \approx{ }^{3} J_{\mathrm{H}, \mathrm{F}}=19.8,{ }^{1} J_{\mathrm{H}, \mathrm{Rh}}=12.2 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Rh} H\right) \mathrm{ppm} .{ }^{19} \mathbf{F}$ NMR ( $282.4 \mathrm{MHz}, 253 \mathrm{~K}$, toluene- $\mathrm{d}^{8}$ ): $\delta=-49.6\left(\mathrm{q} \mathrm{br},{ }^{4} J_{\mathrm{F}, \mathrm{P}} \approx^{4} J_{\mathrm{F}, \mathrm{F}} \approx^{3} J_{\mathrm{F}, \mathrm{H}}=13 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right.$ ); $-182.7\left(\mathrm{dm},{ }^{2} J_{\mathrm{F}, \mathrm{H}}=68 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{CF}\right) \mathrm{ppm} .{ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}\left(121.4 \mathrm{MHz}, 233 \mathrm{~K}\right.$, toluene-d $\left.{ }^{8}\right): \delta=$ 19.29 (dddqd, ${ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=135.4,{ }^{3} J_{\mathrm{P}, \mathrm{Pb}}=29.5,{ }^{2} J_{\mathrm{P}, \mathrm{Pc}}=26.0,{ }^{4} J_{\mathrm{P}, \mathrm{F}}=16.2,{ }^{3} J_{\mathrm{P}, \mathrm{F}}=13.0 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}^{\mathrm{a}}$ ); $10.85\left(\mathrm{dq},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=111.9,{ }^{3} J_{\mathrm{P}, \mathrm{F}} \approx{ }^{2} J_{\mathrm{P}, \mathrm{Pc}} \approx{ }^{2} J_{\mathrm{P}, \mathrm{Pa}}=29.7 \mathrm{~Hz}, \mathrm{P}^{\mathrm{b}}\right) ; 0.87\left(\mathrm{br} \mathrm{dq},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=84.0,{ }^{2} J_{\mathrm{P}, \mathrm{Pa}}\right.$ $\left.\approx^{2} J_{\mathrm{P}, \mathrm{Pb}} \approx{ }^{3} J_{\mathrm{P}, \mathrm{F}}=27.2 \mathrm{~Hz}, \mathrm{P}^{\mathrm{c}}\right) \mathrm{ppm}$.

## Synthesis of $\left[\mathrm{Rh}\left\{(E)-\mathbf{C H}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (2)

In a Young NMR tube $\left[\mathrm{Rh}_{\left.\left(\mathrm{CH}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{8})(50 \mathrm{mg}, 0.106 \mathrm{mmol}) \text { was dissolved in } \mathrm{C}_{6} \mathrm{D}_{6} .40}\right.$ $(0.4 \mathrm{~mL})$. 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 $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (2) by comparison with the literature, ${ }^{8}$ was obtained. Yield: 57 mg ( $98 \%$ ).

## Reaction of $\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right) 3\right]$ (2) with $Z-1,3,3,3$-tetrafluoropropene

In a Young NMR tube $\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](2)(31 \mathrm{mg}, 0.056 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}(0.4 \mathrm{~mL})$. 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 $\mathbf{2}$ into $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ as well as the release of 3,3,3trifluoropropene. For the analytical data of complex 3 see below.

## Reaction of $\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (2) with $\mathrm{Et}_{3} \mathrm{~N} \cdot 3 \mathrm{HF}$

In an NMR tube equipped with a PFA inliner $\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})(24 \mathrm{mg}$, $0.043 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}(0.3 \mathrm{~mL})$. Then, excess of $\mathrm{NEt}_{3} \cdot 3 \mathrm{HF}(7 \mu \mathrm{~L}, 0.04 \mathrm{mmol})$ 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 $\left[\mathrm{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (5) (see above) as well as the release of 3,3,3-trifluoropropene.

## Reaction of Z-1,3,3,3-tetrafluoropropene with $\left[\mathrm{Rh}\left(\mathrm{CH}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (8)

In a Young NMR tube $\left[\mathrm{Rh}\left(\mathrm{CH}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{8})(42 \mathrm{mg}, 0.089 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ $(0.4 \mathrm{~mL})$. 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 $\mathbf{8}$ into $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ as well as the release of methane. Note that complex $\mathbf{3}$ is stable when the solvents were removed in vacuum to yield a reddish oil. When the formation of $\mathbf{3}$ was followed by low temperature NMR spectroscopy, complex fac- $\left[\mathrm{Rh}\left(\mathrm{CH}_{3}\right)\left(\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](9)$ was observed up to 253 K together with an unknown complex which might be an isomer of $\mathbf{9}$ in a 16:1 ratio, respectively. Complex $\mathbf{3}$ is stable up to 4 h both in solution or as an oil and after 1 d , $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (6) and $\left[\mathrm{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](5)$ in a 5.7:1 ratio are obtained. If $\mathrm{NEt}_{3} / \mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2 equiv) are added, the dehydrofluorination requires 2 days but only complex 6 is obtained.

Analytical data for 3: ${ }^{1} \mathbf{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=5.37\left(\mathrm{dq},{ }^{3} J_{\mathrm{H}, \mathrm{F}}=51.8,{ }^{3} J_{\mathrm{H}, \mathrm{F}}=8.7 \mathrm{~Hz}\right.$, $1 \mathrm{H},=\mathrm{CH}) ; 1.65\left(\mathrm{q} \mathrm{br},{ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.6 \mathrm{~Hz}, 12 \mathrm{H}, \mathrm{P}_{c i s} \mathrm{CH}_{2} \mathrm{CH}_{3}\right.$ ); 1.31 (quint d, ${ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.6,{ }^{2} J_{\mathrm{H}, \mathrm{P}}=$ $5.0 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{P}_{\text {trans }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); $1.02\left(\mathrm{~m}, \mathrm{t}\right.$ in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, ${ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.6 \mathrm{~Hz}, 18 \mathrm{H}$, $\mathrm{P}_{\text {cis }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); 0.92 (dt, ${ }^{3} J_{\mathrm{H}, \mathrm{P}}=14.1,{ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.8,9 \mathrm{H}, \mathrm{P}_{\text {trans }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ) ppm. ${ }^{19} \mathbf{F}$ NMR (282.4 $\mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=-26.6$ (ddqd, $\left.{ }^{3} J_{\mathrm{F}, \mathrm{H}}=52,{ }^{3} J_{\mathrm{F}, \mathrm{P}}=41,{ }^{4} \mathrm{~J}_{\mathrm{F}, \mathrm{F}}=13,{ }^{2} J_{\mathrm{F}, \mathrm{Rh}}=9 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{~F}\right) ;-54.1$ $\left(\mathrm{ddt},{ }^{4} J_{\mathrm{F}, \mathrm{F}}=13,{ }^{3} J_{\mathrm{F}, \mathrm{H}}=9,{ }^{5} J_{\mathrm{F}, \text { Pcis }}=5 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right) \mathrm{ppm} .{ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}\left(121.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta$ $=18.29\left(\mathrm{dtd},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=115.8,{ }^{3} J_{\mathrm{P}, \mathrm{F}}=39.4,{ }^{2} J_{\mathrm{P}, \mathrm{P}}=36.2 \mathrm{~Hz}, \mathrm{P}_{\text {trans }}\right) ; 14.9\left(\mathrm{ddq},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=148.9,{ }^{2} J_{\mathrm{P}, \mathrm{P}}\right.$
$\left.=37.7,{ }^{5} J_{\mathrm{P}, \mathrm{F}}=4.5 \mathrm{~Hz}, \mathrm{P}_{\text {cis }}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}\left(75.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=221\left(\mathrm{dm}\right.$ in the ${ }^{13} \mathrm{C}$ domain, ${ }^{1} J_{\mathrm{C}, \mathrm{F}}=363 \mathrm{~Hz}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, $=C \mathrm{~F}$ ); 124 (qm in the ${ }^{13} \mathrm{C}$ domain, ${ }^{1} J_{\mathrm{C}, \mathrm{F}}=264 \mathrm{~Hz}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, $C^{2}$ ); 106 (m, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $=\mathrm{CH}$ ); 19 (m, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, ${ }^{\text {trans }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); 18 (m, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $\mathrm{P}^{\text {cis }} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ); 9 (m, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $\mathrm{PCH}_{2} \mathrm{CH}_{3}$ ) ppm.


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Analytical data for 9: ${ }^{1} \mathbf{H}$ NMR ( $300.1 \mathrm{MHz}, 238 \mathrm{~K}$, toluene-d ${ }^{8}$ ): $\delta=5.28$ (dd br, ddd in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, $\left.{ }^{2} J_{\mathrm{H}, \mathrm{F}}=67.9,{ }^{3} J_{\mathrm{H}, \mathrm{H}}=5.4,{ }^{2} J_{\mathrm{H}, \mathrm{Rh}}=2.3 \mathrm{~Hz}, \mathrm{CHF}\right) ; 1.95(\mathrm{~m}$ br, 1 H , $\mathrm{CHCF}_{3}$ ); 1.49-1.76 (m, 18H, $\mathrm{PCH}_{2} \mathrm{CH}_{3}$ ); 0.86-1.24 (m, 27H, $\mathrm{PCH}_{2} \mathrm{CH}_{3}$ );-0.74 (td, ${ }^{2} J_{\mathrm{H}, \mathrm{Pa}} \approx$ $\left.{ }^{2} J_{\mathrm{H}, \mathrm{Pc}}=7.9,{ }^{2} J_{\mathrm{H}, \mathrm{Pb}}=4.6 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{RhCH}_{3}\right) \mathrm{ppm} .{ }^{19} \mathbf{F} \mathbf{N M R}\left(282.4 \mathrm{MHz}, 238 \mathrm{~K}\right.$, toluene-d $\left.{ }^{8}\right): \delta$ $=-49.1\left(\mathrm{dt} \mathrm{br},{ }^{4} J_{\mathrm{F}, \mathrm{Pc}}=19,{ }^{3} J_{\mathrm{F}, \mathrm{H}} \approx{ }^{3} J_{\mathrm{F}, \mathrm{Rh}}=9 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right) ;-182.6\left(\mathrm{~m}, \mathrm{t}\right.$ br in ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum, $J \approx 35 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{~F}) \mathrm{ppm} .{ }^{31} \mathbf{P}\left\{{ }^{\mathbf{1}} \mathbf{H}\right\} \mathbf{N M R}\left(121.4 \mathrm{MHz}, 238 \mathrm{~K}\right.$, toluene-d ${ }^{8}$ ): $\delta=8.269$ (dddqd, ${ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=130.1,{ }^{3} J_{\mathrm{P}, \mathrm{Pa}}=30.62,{ }^{2} J_{\mathrm{P}, \mathrm{Pb}}=24.65,{ }^{4} J_{\mathrm{P}, \mathrm{F}}=20.10,{ }^{3} J_{\mathrm{P}, \mathrm{F}}=3.40 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}^{\mathrm{c}}$ ); 6.176 (ddddq, ${ }^{1} J_{P, R h}=91.97,{ }^{3} J_{P, F}=28.88,{ }^{2} J_{P, P a}=26.28,{ }^{2} J_{P, P \mathrm{Pc}}=24.65,{ }^{4} J_{P, F}=0.97 \mathrm{~Hz}, 1 \mathrm{P}$, $\mathrm{P}^{\mathrm{b}}$ ); -5.335 (ddddq, ${ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=102.98,{ }^{3} J_{\mathrm{P}, \mathrm{F}}=42.27,{ }^{2} J_{\mathrm{P}, \mathrm{Pc}}=30.62,{ }^{2} J_{\mathrm{P}, \mathrm{Pb}}=26.28,{ }^{4} J_{\mathrm{P}, \mathrm{F}}=-1.11$ $\left.\mathrm{Hz}, 1 \mathrm{P}, \mathrm{P}^{\mathrm{a}}\right) \mathrm{ppm} .{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR shifts and coupling constants were determined by $g N M R$ software. ${ }^{6}$

## Reaction of $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](3)$ with $\mathrm{BF}_{3}$

In a PFA tube $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](3)(20 \mathrm{mg}, 0.035 \mathrm{mmol})$ was dissolved in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(0.3 \mathrm{~mL})$. The reaction mixture was frozen to 77 K , the PFA tube was degassed in vacuo, and a defined amount of $\mathrm{BF}_{3}(0.04 \mathrm{mmol})$ 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 $\left[\mathrm{Rh}_{\left.\left(\mathrm{PEt}_{3}\right)_{4}\right] \mathrm{BF}_{4} \text {, a }}\right.$ $\left[\mathrm{Rh}\left(\mathrm{PEt}_{3}\right)_{2}\right] \mathrm{BF}_{4}$ derivative and $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](6)$ in a 1:2:2 ratio.

## Reaction of $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](3)$ with $\mathrm{LiBF}_{4}$

In an NMR tube equipped with a PFA inliner $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})(20 \mathrm{mg}, 0.035$ mmol ) was dissolved in THF-d ${ }^{8}(0.3 \mathrm{~mL})$. Then, $\mathrm{LiBF}_{4}(4 \mathrm{mg}, 0.043 \mathrm{mmol})$ 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 $\left[\mathrm{Rh}_{\left.\left(\mathrm{PEt}_{3}\right)_{4}\right] \mathrm{BF}_{4},[\mathrm{Rh}(\mathrm{THF}-1 .}\right.$ $\left.\left.\mathrm{d}^{8}\right)\left(\mathrm{PEt}_{3}\right)_{2}\right] \mathrm{BF}_{4}$ and $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](6)$ in a 5:2.3:1 ratio.

## Reaction of $\left[\operatorname{Rh}(E-C F=C H C F 3)\left(\mathrm{PEt}_{3}\right) 3\right](3)$ with $\mathbf{C O}$ or ${ }^{13} \mathrm{CO}$

Complex $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})(60 \mathrm{mg}, 0.10 \mathrm{mmol})$ was dissolved in toluene-d ${ }^{8}$ $(0.4 \mathrm{~mL})$ 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- $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})_{2}\left(\mathrm{PEt}_{3}\right)_{2}\right](\mathbf{1 0})$ 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-$\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{2}\right](\mathbf{1 1})$, was obtained. Yield: $48 \mathrm{mg}(95 \%)$.

The synthesis of the labeled derivatives trans,cis- $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left({ }^{13} \mathrm{CO}\right)_{2}\left(\mathrm{PEt}_{3}\right)_{2}\right]\left(\mathbf{1 0}{ }^{\boldsymbol{\prime}}\right)$ and trans- $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left({ }^{13} \mathrm{CO}\right)\left(\mathrm{PEt}_{3}\right)_{2}\right](11 ')$ was performed following the same procedure using ${ }^{13} \mathrm{CO}$.

Analytical data for the main unknown product: ${ }^{1} \mathbf{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 213 \mathrm{~K}$ ): $\delta=$ $5.40\left(\mathrm{dq},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{F}}=47.9,{ }^{3} J_{\mathrm{H}, \mathrm{F}}=6.7 \mathrm{~Hz}, 1 \mathrm{H},=\mathrm{CH}\right) \mathrm{ppm} .{ }^{19} \mathbf{F} \mathbf{N M R}\left(282.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 213 \mathrm{~K}\right)$ : $\delta=-19.4$ (br, 1F, F); -55.2 (br, 3F, CF $F_{3}$ ) ppm. ${ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}\left(121.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 201 \mathrm{~K}\right.$ ): $\delta$ $=24.9\left(\mathrm{~d} \mathrm{br},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=121 \mathrm{~Hz}, \mathrm{PEt}_{3}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}\left\{{ }^{\mathbf{1}} \mathbf{H}\right\} \mathbf{N M R}\left(75.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 213 \mathrm{~K}\right): \delta=111$ ( m , observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $=C \mathrm{H}$ ) ppm.

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

Analytical data for 11: IR $\left(\mathrm{cm}^{-1}\right): \tilde{v}=1959(\mathrm{~s}, \mathrm{CO}), 1597(\mathrm{~m}, \mathrm{C}=\mathrm{C}) .{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}(300.1 \mathrm{MHz}$, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=5.02\left(\mathrm{dqtd},{ }^{3} \mathrm{~J}_{\mathrm{H}, \mathrm{F}}=53.8,{ }^{3} J_{\mathrm{H}, \mathrm{F}}=8.4,{ }^{4} J_{\mathrm{H}, \mathrm{P}}=2.4,{ }^{3} J_{\mathrm{H}, \mathrm{Rh}}=0.5 \mathrm{~Hz}, 1 \mathrm{H},=\mathrm{CH}\right) ; 1.63$ (m, q in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.6,12 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{CH}_{3}\right) ; 0.99\left(\mathrm{dt},{ }^{3} J_{\mathrm{H}, \mathrm{P}}=16.1,{ }^{3} J_{\mathrm{H}, \mathrm{H}}=\right.$ $7.6,18 \mathrm{H}, \mathrm{PCH}_{2} \mathrm{CH}_{3}$ ) ppm. ${ }^{19} \mathbf{F}$ NMR $\left(282.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right.$ ): $\delta=-43.5$ (dquint, ${ }^{3} J_{\mathrm{F}, \mathrm{H}}=54,{ }^{4} J_{\mathrm{F}, \mathrm{F}}$ $\left.\approx{ }^{2} J_{\mathrm{F}, \mathrm{Rh}}=13 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{~F}\right) ;-55.1\left(\mathrm{ddt},{ }^{4} J_{\mathrm{F}, \mathrm{F}}=13,{ }^{3} J_{\mathrm{F}, \mathrm{H}}=9,{ }^{5} J_{\mathrm{F}, \mathrm{P}}=4 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right) \mathrm{ppm} .{ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\}$ NMR ( $121.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=22.2\left(\mathrm{dq},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=131.5,{ }^{5} J_{\mathrm{P}, \mathrm{F}}=4.3 \mathrm{~Hz}, \mathrm{PEt}_{3}\right) \mathrm{ppm} .{ }^{\mathbf{1 3}} \mathbf{C}\left\{{ }^{1} \mathbf{H}\right\}$ NMR ( $75.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=214\left(\mathrm{~m}\right.$ in the ${ }^{13} \mathrm{C}$ domain, ${ }^{1} J_{\mathrm{C}, \mathrm{F}}=340,{ }^{1} J_{\mathrm{C}, \mathrm{Rh}}=57,{ }^{3} J_{\mathrm{C}, \mathrm{F}}=17$ Hz observed in a ${ }^{19} \mathrm{~F},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, $=C \mathrm{~F}$ ); $197\left(\mathrm{dm}\right.$ in the ${ }^{13} \mathrm{C}$ domain, ${ }^{1} J_{\mathrm{C}, \mathrm{Rh}}=$ 58 Hz , observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, CO); 123.2 (qm in the ${ }^{13} \mathrm{C}$ domain, ${ }^{1} J_{\mathrm{C}, \mathrm{F}}$ $=272,{ }^{3} J_{\mathrm{C}, \mathrm{F}}=18 \mathrm{~Hz}$, confirmed by a ${ }^{19} \mathrm{~F},{ }^{13} \mathrm{C} \mathrm{HMBC}$ NMR spectrum, $C \mathrm{~F}_{3}$ ); $108.0\left(\mathrm{qqm},{ }^{2} J_{\mathrm{C}, \mathrm{F}}\right.$ $\left.=30,{ }^{2} J_{\mathrm{C}, \mathrm{F}} \approx{ }^{3} J_{\mathrm{C}, \mathrm{P}}=5 \mathrm{~Hz},=C \mathrm{H}\right) ; 8.2\left(\mathrm{~s}, \mathrm{PCH}_{2} C \mathrm{H}_{3}\right) ; 17.6\left(\mathrm{vt} \mathrm{d}, N=\left.\right|^{1} J_{\mathrm{C}, \mathrm{P}}+{ }^{3} J_{\mathrm{C}, \mathrm{P}}=13 \mid,{ }^{2} J_{\mathrm{C}, \mathrm{Rh}}\right.$ $\left.=1.3 \mathrm{~Hz}, \mathrm{PCH}_{2} \mathrm{CH}_{3}\right) \mathrm{ppm}$.

Selected analytical data for $\mathbf{1 0}{ }^{\prime}:{ }^{31} \mathbf{P}\left\{{ }^{\mathbf{1}} \mathbf{H}\right\} \mathbf{N M R}\left(121.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 201 \mathrm{~K}\right): ~ \delta=26.3$ (dddt, $\left.{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=74.2,{ }^{3} J_{\mathrm{P}, \mathrm{F}}=51.3,{ }^{2} J_{\mathrm{P}, \mathrm{P}}=32.0,{ }^{2} J_{\mathrm{P}, \mathrm{C}}=17.5 \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{\text {trans }}\right) ; 5.34\left(\mathrm{dq} \mathrm{br},{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=121.4\right.$, $\left.{ }^{2} J_{\mathrm{P}, \mathrm{P}} \approx{ }^{2} J_{\mathrm{P}, \mathrm{C}}=30.0, \mathrm{~Hz}, 1 \mathrm{P}, \mathrm{P}_{\text {cis }}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}\left\{{ }^{\mathbf{1}} \mathbf{H}\right\} \mathbf{N M R}\left(75.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, 201 \mathrm{~K}\right): \delta=198.3$ (ddt, $\left.{ }^{1} J_{\mathrm{C}, \mathrm{Rh}}=69.0,{ }^{2} J_{\mathrm{C}, \mathrm{Pc}}=28.7,{ }^{2} J_{\mathrm{C}, \mathrm{Pt}}={ }^{3} J_{\mathrm{C}, \mathrm{F}}=17.7 \mathrm{~Hz}, C \mathrm{C}\right) \mathrm{ppm}$.

Selected analytical data for 11': IR $\left(\mathrm{cm}^{-1}\right): \tilde{v}=1917\left(\mathrm{~s},{ }^{13} \mathrm{CO}\right), 1599(\mathrm{~m}, \mathrm{C}=\mathrm{C}) .{ }^{\mathbf{1 9}} \mathbf{F}$ NMR ( $282.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta=-43.5$ (dsext, ${ }^{3} J_{\mathrm{F}, \mathrm{H}}=54,{ }^{4} J_{\mathrm{F}, \mathrm{F}} \approx{ }^{3} J_{\mathrm{F}, \mathrm{C}} \approx{ }^{2} J_{\mathrm{F}, \mathrm{Rh}}=13 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{~F}$ ); -55.1 (ddt, ${ }^{4} J_{\mathrm{F}, \mathrm{F}}=13,{ }^{3} \mathrm{~J}_{\mathrm{F}, \mathrm{H}}=9,{ }^{5} J_{\mathrm{F}, \mathrm{P}}=4 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}$ ) ppm. ${ }^{31} \mathbf{P}\left\{{ }^{\mathbf{1}} \mathbf{H}\right\} \mathbf{N M R}\left(121.4 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=$ 22.2 (ddq, $\left.{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=131.5,{ }^{2} J_{\mathrm{P}, \mathrm{C}}=14.2,{ }^{5} J_{\mathrm{P}, \mathrm{F}}=4.3 \mathrm{~Hz}, \mathrm{PEt}_{3}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}(75.5 \mathrm{MHz}$, $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 201 \mathrm{~K}\right): \delta=196.6\left(\mathrm{dtd},{ }^{1} J_{\mathrm{C}, \mathrm{Rh}}=55.6,{ }^{2} J_{\mathrm{C}, \mathrm{P}}=13.9,{ }^{3} J_{\mathrm{C}, \mathrm{F}}=12.5 \mathrm{~Hz}, C \mathrm{O}\right.$ ); 17.6 (vt t, $N=$ $\left.\left|{ }^{1} J_{\mathrm{C}, \mathrm{P}}+{ }^{3} J_{\mathrm{C}, \mathrm{P}}=13\right|,{ }^{2} J_{\mathrm{C}, \mathrm{Rh}} \approx{ }^{3} J_{\mathrm{C}, \mathrm{C}}=1.3 \mathrm{~Hz}, \mathrm{PCH}_{2} \mathrm{CH}_{3}\right) \mathrm{ppm}$.

## Reaction of $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{3}\right](12)$ with $\mathrm{NEt}_{3} \cdot 3 \mathrm{HF}$ or $\mathrm{HBF}_{4} \cdot \mathrm{Et}_{2} \mathrm{O}$

Complex $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1 2})(0.06 \mathrm{mmol})$ was dissolved in $\mathrm{CD}_{2} \mathrm{Cl}_{2}(0.4 \mathrm{~mL})$ and excess of $\mathrm{NEt}_{3} \cdot 3 \mathrm{HF}(7 \mu \mathrm{~L}, 0.04 \mathrm{mmol})$ or $\mathrm{HBF}_{4} \cdot \mathrm{Et}_{2} \mathrm{O}(12 \mu \mathrm{~L}, 0.08 \mathrm{mmol})$ was added at around 243 K . The reaction mixture was slowly warmed up to room temperature. After 1 day $85 \%$ conversion of complex $\mathbf{1 2}$ to yield mainly $\left[\operatorname{Rh}\left\{(Z)-\mathrm{C}\left(\mathrm{PEt}_{3}\right)=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{2}\right] \mathrm{BF}_{4}$ (13•BF4) with $\mathrm{HBF}_{4} \cdot \mathrm{Et}_{2} \mathrm{O}$ was observed, while for HF , an $80 \%$ conversion to $\mathbf{1 3} \cdot \mathbf{F H F}$ as the main product was obtained. When $\mathrm{HBF}_{4}$ is used, another complex, which might be $\left[\mathrm{Rh}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{3}\right] \mathrm{BF}_{4}$ was detected. Note that the reaction with $\mathrm{NEt}_{3} \cdot 3 \mathrm{HF}$ was performed in a PFA inliner.

Analytical data for 13: IR $\left(\mathrm{cm}^{-1}\right): \tilde{v} 1950(\mathrm{~s}, \mathrm{CO}) .{ }^{\mathbf{1}} \mathbf{H}$ NMR $\left(300.1 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta=6.63$ (dqq, ${ }^{3} J_{\mathrm{H}, \mathrm{P}}=36.4,{ }^{3} J_{\mathrm{H}, \mathrm{F}}=6.3,{ }^{4} J_{\mathrm{H}, \mathrm{P}} \approx{ }^{3} J_{\mathrm{H}, \mathrm{Rh}}=3.9 \mathrm{~Hz}, 1 \mathrm{H},=\mathrm{CH}$ ) ppm; the resonances corresponding to the phosphine ligands are overlapped with the signals for the other products. ${ }^{19} \mathbf{F}$ NMR ( $282.4 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta=-63.3\left(\mathrm{q} \mathrm{br},{ }^{3} \mathrm{~J}_{\mathrm{F}, \mathrm{H}} \approx{ }^{5} \mathrm{~J}_{\mathrm{F}, \text { Pcis }}=4 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{C} F_{3}\right) \mathrm{ppm} .{ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\}$ NMR ( $121.4 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta=37.1\left(\mathrm{dt},{ }^{2} J_{\mathrm{P}, \mathrm{Rh}}=4.8,{ }^{3} J_{\mathrm{P}, \mathrm{P}}=2.4 \mathrm{~Hz}, 1 \mathrm{P},=\mathrm{CPEt} 3\right) ; 14.5(\mathrm{dqd}$, $\left.{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=125.0,{ }^{5} J_{\mathrm{P}, \mathrm{F}}=5.2,{ }^{3} J_{\mathrm{P}, \mathrm{P}}=2.6 \mathrm{~Hz}, 2 \mathrm{P}, \mathrm{Rh} P E t^{2}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}(75.5 \mathrm{MHz}$, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta=192\left(\mathrm{~m}\right.$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, CO ); $166(\mathrm{~m}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, $=C \mathrm{PEt}_{3}$ ); 122 (qm in the ${ }^{13} \mathrm{C}$ domain, ${ }^{1} J_{\mathrm{C}, \mathrm{F}}=260 \mathrm{~Hz}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, $C \mathrm{~F}_{3}$ ); 136 ( qm in the ${ }^{13} \mathrm{C}$ domain, ${ }^{2} J_{\mathrm{C}, \mathrm{F}}=37 \mathrm{~Hz}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $=C \mathrm{H}$ ) ppm.

## Reaction of $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (6) with $\mathrm{Et}_{3} \mathrm{~N} \cdot 3 \mathrm{HF}$

In an NMR tube equipped with a PFA inliner $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{6})(23 \mathrm{mg}, 0.042 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}(0.3 \mathrm{~mL})$. Then, excess of $\mathrm{NEt}_{3} \cdot 3 \mathrm{HF}(15 \mu \mathrm{~L}, 0.092 \mathrm{mmol})$ was added to the solution. After 5 minutes at room temperature, the NMR spectroscopic data of the reaction mixture revealed $36 \%$ conversion of $\mathbf{6}$ into $\left[\mathrm{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (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 $\left[\mathbf{R h}(\mathbf{F})\left(\mathbf{P R}_{3}\right)_{2}\right]_{2}(14) \mathbf{R}=i \operatorname{Pr}(\mathbf{a}), E t(b)$

$\left[\mathrm{Rh}(\mathrm{F})(\text { cyclooctene })_{2}\right]_{2}(150 \mathrm{mg}, 0.22 \mathrm{mmol})$ was dissolved in THF $(10 \mathrm{~mL})$ and the corresponding phosphine was added ( 4 eq., 0.88 mmol ). The dark red solution was stirred for 1 h and then the volatiles were removed under vacuum. The obtained product was washed with cold pentane ( $2 \times 5 \mathrm{~mL}$ ) and dried under vacuum. Complex 14a was obtained as a dark red solid while $\mathbf{1 4 b}$ 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 $\left[\mathbf{R h}(\mathbf{F})\left(\mathbf{P i P r}_{3}\right)_{2}\right]_{2}$ (14a) with 3,3,3-trifluoropropyne

In a Young NMR tube $\left[\mathrm{Rh}(\mathrm{F})\left(\mathrm{PiPr}_{3}\right)_{2}\right]_{2}(\mathbf{1 4 a})(50 \mathrm{mg}, 0.056 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ $(0.4 \mathrm{~mL})$. The reaction mixture was frozen to 77 K , the NMR tube was degassed in vacuo, and pressurized with 3,3,3-tetrafluoropropyne ( $13 \mathrm{mg}, 0.14 \mathrm{mmol}$ ). After warming up to room temperature the NMR spectroscopic data of the reaction mixture revealed after 5 min the full conversion of $\mathbf{1 4 a}$ into $\left[\mathrm{Rh}(\mathrm{F})\left(\mathrm{CH} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 5})$ together with small unknown impurities.

Analytical data of 15: IR $\left(\mathrm{cm}^{-1}\right): \tilde{v} 1810(\mathrm{~m}, \mathrm{C} \equiv \mathrm{C}) .{ }^{\mathbf{1}} \mathbf{H}$ NMR (300.1 MHz, $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=4.52$ (qd, $\left.{ }^{4} J_{\mathrm{H}, \mathrm{F}}=4.0,{ }^{2} J_{\mathrm{H}, \mathrm{Rh}}=1.5 \mathrm{~Hz}, 1 \mathrm{H}, \equiv \mathrm{C} H\right) ; 2.11\left(\mathrm{~m}\right.$, sept in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, ${ }^{3} J_{\mathrm{H}, \mathrm{H}}=$ $\left.7.2 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) ; 1.32\left(\mathrm{~m}, \mathrm{~d}\right.$ in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, ${ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.0 \mathrm{~Hz}, 18 \mathrm{H}$, $\left.\mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) ; 1.17\left(\mathrm{~m}, \mathrm{~d}\right.$ in ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR spectrum, $\left.{ }^{3} J_{\mathrm{H}, \mathrm{H}}=7.0 \mathrm{~Hz}, 18 \mathrm{H}, \mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) \mathrm{ppm}$. ${ }^{19}$ F NMR ( 282.4 MHz, Tol-d 8 ): $\delta=-47.7\left(\mathrm{dq},{ }^{4} J_{\mathrm{F}, \mathrm{H}}=4,{ }^{4} J_{\mathrm{F}, \mathrm{P}} \approx{ }^{3} J_{\mathrm{F}, \mathrm{Rh}}=2 \mathrm{~Hz}, 3 \mathrm{~F}, \mathrm{CF} F_{3}\right.$ );-242.9 (m br, d br at $233 \mathrm{~K},{ }^{1} J_{\mathrm{F}, \mathrm{Rh}}=87 \mathrm{~Hz}, 1 \mathrm{~F}, \mathrm{RhF}$ ) ppm. ${ }^{31} \mathbf{P}\left\{{ }^{1} \mathbf{H}\right\}$ NMR ( 121.4 MHz, Tol- $\mathrm{d}_{8}$ ): $\delta=$ 36.4 (d, ${ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=119.0 \mathrm{~Hz}, \mathrm{PiPr}_{3}$ ) ppm. $\left.{ }^{\mathbf{3 1}} \mathbf{P} \mathbf{~}{ }^{\mathbf{1}} \mathbf{H}\right\} \mathbf{N M R}(121.4 \mathrm{MHz}$, Tol-d $8,233 \mathrm{~K}$ ): $\delta=36.4$ (dd, $\left.{ }^{1} J_{\mathrm{P}, \mathrm{Rh}}=119.0,{ }^{3} \mathrm{~J}_{\mathrm{P}, \mathrm{F}}=10.3 \mathrm{~Hz}, \mathrm{PiPr}_{3}\right) \mathrm{ppm} .{ }^{13} \mathbf{C}\left\{{ }^{1} \mathbf{H}\right\} \mathbf{N M R}\left(75.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta=83(\mathrm{~m}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $\left.\equiv \mathrm{CH}\right) ; 61\left(\mathrm{dm}\right.$ in the ${ }^{13} \mathrm{C}$ domain, ${ }^{2} J_{\mathrm{C}, \mathrm{F}}=40 \mathrm{~Hz}$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMBC NMR spectrum, $\equiv \mathrm{CCF}_{3}$ ); 21 ( m , observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $\left.\mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) ; 19.3$ (m, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $\left.\operatorname{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) ; 18.9\left(\mathrm{~m}\right.$, observed in a ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$ HMQC NMR spectrum, $\left.\mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) \mathrm{ppm}$.

## Rearrangement of $\left[\operatorname{Rh}(\mathrm{F})\left(\mathrm{CH}_{\mathrm{E}} \mathrm{CCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](15)$ in the presence of phosphine

In an NMR tube $\left[\mathrm{Rh}(\mathrm{F})\left(\mathrm{CH} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 5})(30 \mathrm{mg}, 0.055 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}$ $(0.4 \mathrm{~mL})$. Then, excess of $\operatorname{PiPr}_{3}(23 \mu \mathrm{~L}, 0.12 \mathrm{mmol})$ was added to the solution. Complex 15
slowly converted into complex $\left[\mathrm{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right]$ (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 $\mathrm{NEt}_{3}$ instead of the phosphine did not reduce the reaction time.

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

## Reaction of $\left[\operatorname{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](16)$ with $\mathrm{PEt}_{3}$

In a NMR tube $\left[\mathrm{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](16)(20 \mathrm{mg}, 0.037 \mathrm{mmol})$ was dissolved in $\mathrm{C}_{6} \mathrm{D}_{6}(0.4 \mathrm{~mL})$. Then, excess of $\mathrm{PEt}_{3}(37 \mu \mathrm{~L}, 0.25 \mathrm{mmol})$ 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 $\left[\mathrm{Rh}\left\{\mathrm{F}(\mathrm{HF})_{2}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](5)$ and $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (6) (1:1 ratio) as well as the release of $\mathrm{PiPr}_{3}$ and small amounts of 3,3,3-trifluoropropene.

## NMR Spectra



S1. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of $Z-1,3,3,3$-tetrafluoropropene with $\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ at different times.


S2. ${ }^{19} \mathrm{~F}$ NMR spectrum of the reaction of Z-1,3,3,3-tetrafluoropropene with $\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ at different times.


S3. Section of the ${ }^{19} \mathrm{~F}$ NMR (bottom) and ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra corresponding to complex $[\mathrm{Rh}\{(\mathrm{Z})$ $\left.\left.\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](4)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S4. Parts of the ${ }^{1} \mathrm{H}$ (bottom), ${ }^{1} \mathrm{H}\left\{{ }^{19} \mathrm{~F}\right\}$ (middle) and ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ (top) NMR spectra corresponding to complex $\left[\mathrm{Rh}\left\{(\mathrm{Z})-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](4)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


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


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


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


S8. Parts of the ${ }^{1} \mathrm{H}$ (bottom), ${ }^{1} \mathrm{H}\left\{{ }^{19} \mathrm{~F}\right\}$ (middle) and ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ (top) NMR spectra corresponding to complex fac-[Rh(H)( $\left.\left.\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (7) in toluene-d ${ }_{8}$.


S9. ${ }^{1} \mathrm{H}^{1} \mathrm{H}$ COSY NMR spectrum of the reaction of $Z-1,3,3,3$-tetrafluoropropene with $\left[\mathrm{Rh}(\mathrm{H})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1})$ in toluene- $\mathrm{d}^{8}$ at 223 K .


S10. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S11. ${ }^{19} \mathrm{~F}$ NMR spectrum of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S12. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S13. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (2) with $Z$ -1,3,3,3-tetrafluoropropene in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S14. ${ }^{19}$ F NMR spectrum of the reaction of complex $\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ with Z-1,3,3,3-tetrafluoropropene in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S15. ${ }^{1} \mathrm{H}$ NMR spectrum of the reaction of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CH}^{2}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ with Z-1,3,3,3-tetrafluoropropene in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S16. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of complex $\left[\operatorname{Rh}\left\{(E)-\mathrm{CH}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{2})$ with $\mathrm{Et}_{3} \mathrm{~N} \cdot 3 \mathrm{HF}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S17. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.




S18. ${ }^{19} \mathrm{~F}$ (bottom) and ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ (top) NMR spectrum of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](3)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S19. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S20. Section of ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra of the reaction of $Z-1,3,3,3$-tetrafluoropropene with $\left[\mathrm{Rh}\left(\mathrm{CH}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](8)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ at different times with and without presence of base.


S21. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of complex $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ with $\mathrm{BF}_{3}$ at 263 K in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.


S22. ${ }^{19} \mathrm{~F}$ NMR spectrum of the reaction of complex $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\boldsymbol{3})$ with $\mathrm{BF}_{3}$ at 263 K in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.


S23. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of complex $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ with $\mathrm{LiBF}_{4}$ in THF-d ${ }^{8}$.


S24. ${ }^{19} \mathrm{~F}$ NMR spectrum of the reaction of complex $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ with $\mathrm{LiBF}_{4}$ in THF-d ${ }^{8}$.


S25. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex $\left.\mathrm{fac}-\left[\mathrm{Rh}_{\left(\mathrm{CH}_{3}\right)}\right)\left(\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{9})$ in toluene- $\mathrm{d}^{8}$ at 213 K : experimental (bottom), simulated (top). ${ }^{6}$


S26. ${ }^{19} \mathrm{~F}$ NMR spectrum of complex $\left.\mathrm{fac}-\left[\mathrm{Rh}_{\left(\mathrm{CH}_{3}\right)}\right)\left(\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](9)$ in toluene-d ${ }^{8}$ at 238 K .


S27. ${ }^{1} \mathrm{H}$ NMR spectrum of complex fac- $\left[\mathrm{Rh}_{( }\left(\mathrm{CH}_{3}\right)\left(\mathrm{CF}_{3} \mathrm{CHCHF}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right](9)$ in toluene- $\mathrm{d}^{8}$ at 238 K .


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


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


S30. ${ }^{19} \mathrm{~F}$ NMR spectrum of the reaction of $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{3})$ with CO in toluene-d ${ }^{8}$ at 213 K .


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


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


S33. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex trans- $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{2}\right](\mathbf{1 1})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$. The signals for $\mathbf{1 1}$ (bottom) and $\mathbf{1 1}^{\prime}$ (top) are shown for comparison.


S34. ${ }^{19} \mathrm{~F}$ NMR spectrum of complex trans- $\left[\operatorname{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{2}\right](\mathbf{1 1})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$. The signals for $\mathbf{1 1}$ (bottom) and $\mathbf{1 1}^{\prime}$ (top) are shown for comparison.


S35. ${ }^{1} \mathrm{H}$ NMR spectrum of complex trans- $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{2}\right](\mathbf{1 1})$ in $\mathrm{C}_{6} \mathrm{D}_{6}(\mathrm{no}$ changes in complex $\mathbf{1 1}^{\prime}$ ).


S36. Section of the ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex trans- $\left[\mathrm{Rh}\left\{(E)-\mathrm{CF}=\mathrm{CHCF}_{3}\right\}\left({ }^{13} \mathrm{CO}\right)\left(\mathrm{PEt}_{3}\right)_{2}\right]$ $\left(\mathbf{1 1}^{\prime}\right)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S37. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{3}\right](\mathbf{1 2})$ with HF (top) or $\mathrm{HBF}_{4}$ (bottom) in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.


S38. ${ }^{19} \mathrm{~F}$ NMR spectrum of the reaction of $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (12) with HF (top) or $\mathrm{HBF}_{4}$ (bottom) in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.


S39. Section of the ${ }^{1} \mathrm{H}$ NMR (bottom), ${ }^{1} \mathrm{H}\left\{{ }^{19} \mathrm{~F}\right\}$ NMR (middle) and ${ }^{1} \mathrm{H}\left\{{ }^{31} \mathrm{P}\right\}$ NMR (top) of complex $\left[\mathrm{Rh}\left\{(\mathrm{Z})-\mathrm{C}\left(\mathrm{PEt}_{3}\right)=\mathrm{CHCF}_{3}\right\}(\mathrm{CO})\left(\mathrm{PEt}_{3}\right)_{2}\right]^{+}(\mathbf{1 3})$ corresponding to the vinyl proton of the phosphonioalkenyl ligand in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.


S40. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of $\left[\mathrm{Rh}\left(\mathrm{C} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PEt}_{3}\right)_{3}\right]$ (6) with $\mathrm{Et}_{3} \mathrm{~N} \cdot 3 \mathrm{HF}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S41. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex $\left[\mathrm{Rh}(\mathrm{F})\left(\mathrm{CH} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 5})$ in Tol- $\mathrm{d}_{8}$ at 233 K .


S42. ${ }^{19} \mathrm{~F}$ NMR spectrum of complex $\left[\mathrm{Rh}(\mathrm{F})\left(\mathrm{CH} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](15)$ in Tol- $\mathrm{d}_{8}$ showing the Rh-F ligand resonance at 233 K .


S43. ${ }^{1} \mathrm{H}$ NMR spectrum of complex $\left[\mathrm{Rh}(\mathrm{F})\left(\mathrm{CH} \equiv \mathrm{CCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](15)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S44. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of complex $\left[\mathrm{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 6})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.





S45. Sections of the ${ }^{19} \mathrm{~F}$ NMR (bottom) and the ${ }^{19} \mathrm{~F}\left\{{ }^{1} \mathrm{H}\right\}$ NMR (top) spectra of complex $\left[\operatorname{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 6})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S46. ${ }^{19} \mathrm{~F},{ }^{13} \mathrm{C}$ HMBC NMR spectrum of complex $\left[\mathrm{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 6})$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S47. ${ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectrum of the reaction of complex $\left[\mathrm{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right](\mathbf{1 6})$ with $\mathrm{PEt}_{3}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


S48. ${ }^{19} \mathrm{~F}$ NMR spectrum of the reaction of complex $\left[\mathrm{Rh}(\mathrm{F})\left(=\mathrm{C}=\mathrm{CHCF}_{3}\right)\left(\mathrm{PiPr}_{3}\right)_{2}\right]$ (16) with $\mathrm{PEt}_{3}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.

## 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



7

Complex 7a


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 $5.7 \mathrm{~kJ} / \mathrm{mol}$.


9

Complex 9a


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 $0.2 \mathrm{~kJ} / \mathrm{mol}$.

## 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 | 0.00120 | $-0.33758$ | -0.29248 | Rh | -0.04779 | -0.01759 | -0.61464 | Rh | 0.01560 | 0.36287 | 0.28874 | Rh | -0.06148 | -0.05461 | -0.62865 |
| P | -0.48702 | -1.14701 | 1.89623 | P | 0.19895 | -1.39818 | 1.33096 | P | -0.41829 | 0.67572 | -2.04124 | P | 0.04096 | -1.29836 | 1.42632 |
| P | -2.00863 | 0.62015 | -0.99287 | P | -2.30591 | 0.49626 | -0.54785 | P | -2.12801 | -0.26839 | 0.99321 | P | -2.31285 | 0.57719 | -0.55883 |
| P | 1.46053 | 1.45544 | 0.16797 | P | 1.13121 | 1.90216 | 0.06169 | P | 1.36624 | -1.59695 | 0.16678 | P | 1.33286 | 1.76797 | 0.05215 |
| C | -3.57202 | -0.00729 | -0.15998 | C | -3.47985 | -0.90852 | -0.11525 | C | -3.58906 | 0.07639 | -0.14179 | C | -3.54620 | -0.49279 | 0.37561 |
| C | -2.26430 | 0.17089 | -2.79023 | C | -2.86731 | 0.91828 | $-2.28698$ | C | -2.59833 | 0.71986 | 2.51237 | C | -3.07227 | 0.49458 | -2.27239 |
| C | -2.32658 | 2.46719 | -1.12409 | C | -2.98882 | 2.00674 | 0.33932 | C | -2.47284 | -1.99739 | 1.63181 | C | -2.75578 | 2.34680 | -0.11974 |
| C | 3.27893 | 1.00174 | 0.10126 | C | 2.85276 | 1.88571 | -0.68696 | C | 3.18305 | -1.16016 | 0.30805 | C | 3.02652 | 1.52545 | -0.72232 |
| C | 1.30343 | 2.75654 | -1.17552 | C | 0.36295 | 3.43829 | -0.70250 | C | 1.12749 | -2.80587 | 1.59062 | C | 0.79680 | 3.44662 | -0.61793 |
| C | 1.33916 | 2.39925 | 1.78862 | C | 1.35452 | 2.41668 | 1.85868 | C | 1.30279 | -2.69174 | -1.35701 | C | 1.69463 | 2.17224 | 1.85080 |
| C | -0.90265 | -0.02711 | 3.33592 | C | -0.49730 | -0.75120 | 2.95790 | C | -0.89572 | -0.69414 | -3.23422 | C | -0.44696 | -0.50234 | 3.06365 |
| C | -1.86248 | -2.42138 | 1.97380 | C | -0.56400 | -3.10228 | 1.23381 | C | -1.69287 | 2.01532 | -2.40042 | C | -0.94956 | -2.88872 | 1.44974 |
| C | 0.89156 | -2.13168 | 2.70093 | C | 1.91856 | -1.85135 | 1.92816 | C | 0.99605 | 1.37656 | -3.06765 | C | 1.68455 | -2.00509 | 2.00222 |
| C | 1.11147 | -2.12483 | -0.69681 | C | 1.20398 | -1.12987 | -1.96162 | C | 1.20005 | 2.16881 | 0.17881 | C | 1.11199 | -1.41639 | -1.82168 |
| C | -0.27097 | -2.23490 | -1.13434 | C | -0.20114 | -1.48811 | -2.08486 | C | -0.17166 | 2.43340 | 0.58233 | C | -0.31835 | -1.66919 | -1.91282 |
| H | -0.94492 | -2.94765 | -0.62270 | F | -0.60706 | $-2.78735$ | -1.78321 | H | -0.84266 | 2.97817 | $-0.10576$ | F | -0.82876 | -2.88870 | -1.48004 |
| F | -0.50912 | -2.34245 | $-2.50501$ | H | -0.74345 | -1.16844 | -2.99482 | F | -0.40200 | 2.93962 | 1.86137 | H | -0.84384 | -1.39833 | -2.84831 |
| H | 1.86874 | 2.33449 | -2.03448 | H | 0.60013 | 3.36417 | -1.78609 | H | 1.69512 | -2.37503 | 2.44012 | H | 1.06037 | 3.44034 | -1.69445 |
| C | 1.68978 | 4.21252 | -0.90476 | C | 0.69653 | 4.82538 | -0.14587 | C | 1.47364 | -4.28484 | 1.40226 | C | 1.29522 | 4.73267 | 0.04689 |
| H | 0.24351 | 2.70091 | -1.48486 | H | -0.72902 | 3.26003 | -0.63611 | H | 0.06482 | -2.70888 | 1.88027 | H | -0.30987 | 3.42052 | -0.59020 |
| H | 1.12938 | 1.60272 | 2.53003 | H | 1.27239 | 1.47584 | 2.43514 | H | 1.09646 | -1.97810 | $-2.17546$ | H | 1.58765 | 1.20891 | 2.37814 |
| H | 0.40034 | 2.99039 | 1.73251 | H | 0.44234 | 2.99823 | 2.11205 | H | 0.37598 | -3.29801 | -1.26247 | H | 0.84061 | 2.79482 | 2.19485 |
| C | 2.50330 | 3.25804 | 2.29371 | C | 2.61645 | 3.16897 | 2.28970 | C | 2.49924 | -3.56270 | -1.75411 | C | 3.03424 | 2.79838 | 2.24950 |
| H | 3.32011 | 0.10856 | -0.54856 | H | 2.70929 | 1.29078 | -1.61163 | H | 3.19336 | -0.22066 | 0.89199 | H | 2.81375 | 0.92565 | -1.62994 |
| H | 3.53039 | 0.63371 | 1.11835 | H | 3.46507 | 1.23072 | -0.03226 | H | 3.49058 | -0.85909 | -0.71520 | H | 3.56513 | 0.82496 | -0.05034 |
| C | 4.30924 | 2.03253 | -0.37342 | C | 3.59191 | 3.18735 | -1.01338 | C | 4.17711 | -2.16019 | 0.90699 | C | 3.90154 | 2.72955 | -1.08364 |
| C | -2.04848 | 0.94666 | 3.07586 | C | -1.99252 | -0.97836 | 3.18407 | C | -1.94344 | -1.69240 | -2.75227 | C | -1.91463 | -0.16000 | 3.30420 |
| H | 0.03068 | 0.52929 | 3.56154 | H | -0.27292 | 0.33468 | 2.98090 | H | 0.05608 | -1.22021 | -3.45309 | H | 0.16049 | 0.41954 | 3.15033 |
| H | -1.10118 | -0.66179 | 4.22558 | H | 0.08500 | -1.21230 | 3.78524 | H | -1.19570 | -0.22007 | -4.19179 | H | -0.08184 | -1.18755 | 3.85900 |
| C | 2.25601 | -1.44240 | 2.65727 | C | 2.85790 | $-0.68778$ | 2.23262 | c | 2.34196 | 0.67693 | -2.87433 | C | 2.83844 | -1.03673 | 2.24794 |
| H | 0.93681 | -3.10675 | 2.16928 | H | 2.35476 | -2.49522 | 1.14319 | H | 1.08404 | 2.45134 | -2.80150 | H | 1.97363 | -2.74271 | 1.23441 |
| H | 0.59225 | -2.36155 | 3.74598 | H | 1.78950 | -2.48332 | 2.83231 | H | 0.68200 | 1.35097 | -4.13352 | H | 1.46946 | $-2.57868$ | 2.92902 |
| H | -2.72777 | -1.97852 | 1.44199 | H | -1.64715 | -2.93498 | 1.05693 | H | -2.50308 | 1.89314 | -1.65664 | H | -1.94648 | -2.64384 | 1.03393 |
| C | -2.28239 | -2.96257 | 3.34303 | C | -0.34128 | -4.06715 | 2.40192 | C | -2.26538 | 2.12032 | -3.81565 | C | -1.07727 | $-3.65363$ | 2.76997 |
| H | -1.51079 | -3.24889 | 1.32064 | H | -0.18269 | -3.51876 | 0.28296 | H | -1.17792 | 2.96055 | -2.12548 | H | -0.46560 | $-3.50646$ | 0.66891 |
| H | -2.00264 | -0.90292 | -2.85608 | H | -2.46202 | 0.10209 | -2.92116 | H | -2.27449 | 1.75659 | 2.29019 | H | -2.79098 | -0.50833 | -2.65776 |
| H | -1.43100 | 0.69236 | -3.31009 | H | -2.27827 | 1.82066 | $-2.55868$ | H | -1.90140 | 0.37319 | 3.30241 | H | -2.50826 | 1.22070 | -2.89045 |
| C | -3.60449 | 0.45580 | -3.47263 | C | -4.35861 | 1.12553 | -2.56275 | C | -4.04124 | 0.68897 | 3.02170 | C | -4.57832 | 0.72005 | -2.43151 |
| C | $-2.15533$ | 3.27315 | 0.16020 | C | -2.51226 | 2.19644 | 1.77807 | C | -2.27393 | -3.13042 | 0.62516 | C | -2.24433 | 2.83125 | 1.23782 |
| H | -3.33923 | 2.62035 | -1.55206 | H | -4.09661 | 2.02219 | 0.27523 | H | -3.49339 | -2.03243 | 2.06766 | H | -3.84856 | 2.51300 | -0.21948 |
| H | -1.61508 | 2.82125 | -1.90071 | H | -2.63458 | 2.85216 | $-0.28983$ | H | -1.77175 | -2.11190 | 2.48711 | H | -2.27854 | 2.92963 | -0.93808 |
| H | $-3.69763$ | -1.03996 | -0.55340 | H | $-3.58738$ | $-1.48493$ | -1.05938 | H | -3.78691 | 1.16373 | -0.01715 | H | -3.82375 | -1.29389 | -0.34325 |
| C | -4.87249 | 0.79581 | -0.26984 | C | -4.84204 | -0.57049 | 0.49578 | C | -4.87939 | -0.73377 | 0.02196 | C | -4.78860 | 0.17162 | 0.97464 |
| H | -3.30284 | -0.12344 | 0.90725 | H | -2.91276 | -1.57603 | 0.56064 | H | -3.21080 | $-0.04243$ | -1.17361 | H | -2.97659 | -1.00126 | 1.17148 |
| H | 4.09698 | 2.37697 | -1.40588 | H | 3.02297 | 3.81259 | -1.73121 | H | 3.90291 | -2.43933 | 1.94466 | H | 3.38657 | 3.41322 | -1.78894 |
| H | 5.32110 | 1.57486 | -0.39055 | H | 4.56922 | 2.95905 | $-1.48945$ | H | 5.18930 | -1.70547 | 0.95403 | H | 4.83080 | 2.38749 | -1.58680 |
| H | 4.36222 | 2.92686 | 0.27769 | H | 3.79899 | 3.80323 | -0.11709 | H | 4.26159 | -3.09376 | 0.31742 | H | 4.20585 | 3.32251 | -0.19944 |
| H | 2.58126 | -1.28946 | 1.61051 | H | 2.96739 | -0.02978 | 1.35026 | H | 2.69010 | 0.77862 | -1.82802 | H | 3.03679 | -0.41891 | 1.35230 |
| H | 3.02654 | -2.05059 | 3.17484 | H | 3.86885 | -1.06193 | 2.49636 | H | 3.11463 | 1.11725 | $-3.53804$ | H | 3.76867 | -1.59906 | 2.47129 |
| H | 2.23268 | -0.44921 | 3.15341 | H | 2.50382 | -0.07057 | 3.08410 | H | 2.28598 | -0.40602 | -3.11124 | H | 2.65247 | -0.36024 | 3.10734 |
| H | -2.72048 | -2.17140 | 3.98580 | H | $-0.63413$ | -3.63286 | 3.38102 | H | -2.88368 | 1.23757 | -4.07904 | H | -1.59727 | -3.06728 | 3.55521 |
| H | -1.43240 | -3.41240 | 3.89621 | H | 0.71900 | -4.38052 | 2.48074 | H | -1.47221 | 2.21840 | -4.58577 | H | -0.09200 | -3.95841 | 3.17809 |
| H | -3.05352 | $-3.75350$ | 3.23079 | H | -0.94139 | -4.99075 | 2.26045 | H | -2.91897 | 3.01334 | -3.90608 | H | -1.66274 | -4.58461 | 2.61695 |
| H | -1.86820 | 1.51441 | 2.14310 | H | -2.59673 | -0.56041 | 2.35855 | H | -1.71578 | -2.02850 | -1.72291 | H | -2.28960 | 0.55552 | 2.55184 |
| H | -2.16088 | 1.67376 | 3.90661 | H | -2.32890 | -0.48734 | 4.12116 | H | -1.97847 | -2.58658 | -3.40844 | H | -2.04387 | 0.31104 | 4.30133 |
| H | -3.01862 | 0.41823 | 2.96645 | H | -2.24218 | -2.05511 | 3.26649 | H | -2.96136 | $-1.25220$ | -2.74413 | H | $-2.56709$ | -1.05632 | 3.27739 |
| H | -5.19121 | 0.95507 | -1.31763 | H | -5.45230 | 0.08199 | -0.15940 | H | -5.30447 | -0.66045 | 1.04081 | H | -5.40702 | 0.68655 | 0.21417 |
| H | -4.77649 | 1.79367 | 0.20478 | H | -4.73500 | -0.05235 | 1.47153 | H | -4.71609 | -1.80876 | -0.19373 | H | -4.51792 | 0.92199 | 1.74536 |
| H | -5.69896 | 0.26699 | 0.25095 | H | -5.42765 | -1.49577 | 0.68105 | H | $-5.65487$ | $-0.37359$ | -0.68712 | H | -5.43353 | -0.58492 | 1.46992 |
| H | -2.91969 | 3.00865 | 0.91890 | H | -3.02982 | 1.51379 | 2.47954 | H | $-3.04632$ | -3.11868 | -0.16975 | H | -2.88409 | 2.47669 | 2.07043 |
| H | -2.23993 | 4.36323 | -0.03121 | H | -2.69158 | 3.23331 | 2.13090 | H | -2.32000 | -4.12278 | 1.12002 | H | -2.21930 | 3.93939 | 1.29168 |
| H | -1.16221 | 3.08346 | 0.61332 | H | -1.42619 | 1.98580 | 1.85346 | H | -1.28835 | -3.04804 | 0.12516 | H | -1.21801 | 2.45182 | 1.42388 |
| H | -4.42617 | -0.15131 | -3.04055 | H | -4.94625 | 0.20409 | $-2.37383$ | H | -4.75355 | 1.12874 | 2.29390 | H | -5.17710 | -0.05331 | -1.90923 |
| H | -3.54616 | 0.19442 | -4.55042 | H | -4.52284 | 1.40092 | -3.62608 | H | -4.12751 | 1.28469 | 3.95501 | H | -4.86079 | 0.67596 | -3.50470 |
| H | -3.90345 | 1.52326 | -3.41360 | H | -4.79359 | 1.93801 | -1.94480 | H | -4.39042 | -0.33740 | 3.26072 | H | -4.90008 | 1.71221 | -2.05262 |
| H | 2.76271 | 4.33241 | -0.65959 | H | 1.77159 | 5.07408 | $-0.23353$ | H | 2.55067 | -4.44805 | 1.20427 | H | 2.39431 | 4.84809 | -0.02065 |
| H | 1.10048 | 4.64208 | -0.06852 | H | 0.41703 | 4.91528 | 0.92397 | H | 0.90230 | -4.74190 | 0.56840 | H | 1.01460 | 4.78423 | 1.11857 |
| H | 1.48418 | 4.83783 | $-1.79971$ | H | 0.13027 | 5.60863 | -0.69356 | H | 1.21792 | -4.85595 | 2.32021 | H | 0.84098 | 5.61738 | -0.44828 |
| H | 3.42697 | 2.65724 | 2.41700 | H | 3.53369 | 2.59518 | 2.04629 | H | 3.41021 | -2.94984 | -1.90956 | H | 3.88477 | 2.15501 | 1.94596 |
| H | 2.26048 | 3.68840 | 3.28892 | H | 2.61511 | 3.33175 | 3.38869 | H | 2.29189 | -4.08622 | -2.71196 | H | 3.09124 | 2.91290 | 3.35307 |
| H | 2.73762 | 4.10201 | 1.61762 | H | 2.70079 | 4.16267 | 1.80824 | H | 2.73818 | $-4.33636$ | -1.00029 | H | 3.19126 | 3.79931 | 1.80475 |


| 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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