Supporting Information

Activation of Perfluoro(methyl vinyl ether) at Rh(I) Complexes: Metal-Centered versus Phosphine Mediated Decarbonylation

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1. Synthesis and characterization of all compounds

1.1 General Procedures, Methods and Materials

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by conventional methods¹ and, prior to use, distilled under argon. The rhodium complexes $[Rh(H)(PEt_3)_3]$ (1)², $[Rh(F)(CO)(PEt_3)_2]$ (4)³ $[Rh(F)(PEt_3)_3]$ (6)⁴ were prepared as described in the literature. All other reagents were obtained from commercial sources. The mass of gaseous compounds such as perfluoro(methyl vinyl ether), difluorophosgene or trifluoroethylene was determined by condensation into a dried Young NMR tube. The NMR tube was weighed before and after the condensation procedure. The gas was then condensed into a second tube containing the reaction solution by trap-to-trap condensation. In addition, the obtained partial pressure of the gas relates to a certain amount of compound for a given gas volume. It can be used for further experiments. Unless stated, NMR spectra were recorded at room temperature on a Bruker DPX 300 or a Bruker Avance 300 spectrometer. ¹H and ${}^{13}C{}^{1}H{}$ signals are referred to residual solvent signals, those of ${}^{31}P{}^{1}H{}$ to 85% H₃PO₄ and the ${}^{19}FNMR$ spectra to external CFCl₃. ¹H, ¹⁹F and ³¹P{¹H} signal assignments were confirmed by ¹H{³¹P}, ¹H{¹⁹F}, ¹⁹F{¹H}, ¹H, ¹H COSY, ¹⁹F, ¹⁹F COSY or ³¹P, ³¹P COSY, ¹H, ³¹P HSQC NMR experiments. The determined coupling constant values of the higher order spectra were confirmed by gNMR software simulations. Infrared spectra were recorded inside a glovebox on a Bruker ALPHA II spectrometer equipped with an ATR-module (diamond). The Shimadzu GC-2014 gas chromatograph with a thermal conductivity detector and a Resteks ShinCarbon packed column ST 80/100 (2 m, 1/8" outer diameter, 2 mm inner diameter) was used for CO detection.

1.2 Reaction of PMVE with [Rh(H)(PEt₃)₃] (1)

In a Young NMR tube $[Rh(H)(PEt_3)_3]$ (1) (40 mg, 0.087 mmol) was dissolved in tol-d₈ (0.4 mL). The tube was cooled to 77 K, degassed *in vacuo*, and pressurized with PMVE to 0.2 bar (36 mg, 0.218 mmol). The reaction was monitored by NMR spectroscopy at variable temperature from 233K to 298K. The formation of intermediate 2 and an isomer of it 2' in a ratio of 1.7:1 was observed at 273 K. Additionally, the generation of *Z*-(F₃CO)CF=CF(PFEt₃) at this temperature was identified. After warming up the NMR tube to 298 K, conversion of 2, 2' and *Z*-(OCF₃)CF=CF(PFEt₃) into complex 3 and complex 4 in a ratio of 1.3:1, as well as

trifluoroethylene (C₂F₃H:4 in a 0.4:1 ratio), Et₃PF₂ and 1,2,2,2-tetrafluoroethyl trifluoromethyl ether OCF₃CF₃CFH was observed. A solution of the complexes **3** and **4** was not stable at 298 K and a slow transformation into complex [Rh(CO)(CF(OCF₃)CF₃)(PEt₃)₂] (**5**) after 30 minutes was observed. Monitoring the reaction at 298 K at various times revealed the evolution of **3** into **4**, while **4** converts into **5**. When the reaction was completed after a day, organic products were separated from the organometallic product **5** by a trap-to-trap distillation under inert atmosphere.



Analytical data for **2 and 2':** ¹**H NMR** (600 MHz, Toluene-*d*₈) $\delta = 1.34-1.68$ (m, PCH₂CH₃), 0.86-1.10 (m, PCH₂CH₃), -11.94 (dm, ²*J*_{H,Pc}= 152.8, dt in ¹H{³¹P} NMR spectrum, ¹*J*_{H,Rh}=17.3 Hz, ³*J*_{H,Fa/c} = 26.2, 1H, Rh*H* for **2'**), -12.12 (dm, ²*J*_{H,Pc}=152.3, dd in ¹H{³¹P} NMR spectrum, ³*J*_{H,Fa}= 26.2, ¹*J*_{H,Rh}=17.3, 1H, RhH for **2**) ppm, part of the resonances corresponding for the phosphine ligands are overlapping. ³¹P{¹H} NMR (273 K, 202 MHz, Toluene-*d*₈) δ 13.98-12.78 (dm, ¹*J*_{P,Rh}= 100.7, 1P, P^a/P^b), 11.16-9.39 (m, 1P, P^a/P^b), 4.85-2.64 (dm, ¹*J*_{P,Rh}= 91.3 Hz, 1P, P^c) ppm, the resonances corresponding to the phosphine ligands of **2** and **2'** are overlapping. ¹⁹F NMR (253 K, 282.4 MHz, Toluene-*d*₈, isomer **2**) δ = -54.7 (t br, *J* = 8 Hz, 3F, OCF₃), -96.2 (dm, ²*J*_{Fa,Fb} = 155 Hz, CF^bF^a), -112.5 (ddd br, ²*J*_{Fb,Fa} = 154, ³*J*_{Fb,Pb} =74, ³*J*_{Fb,Pc} = 21 Hz, 1F, C*F*^bF^a), -129.8 (dt br, ³*J*_{Fc,Pc} \approx ³*J*_{Fc,Fa} = 29 Hz, 1F, C*F*^cOCF₃) ppm. ¹⁹F NMR (253 K, 282.4 MHz, Toluene-*d*₈, isomer **2'**) δ = -54.8 (t br, *J*_{E,F} = 8 Hz, 3F, OCF₃), -101.3 (dm, ddm br in ¹⁹F{¹H} NMR spectrum, ²*J*_{Fa,Fb} = 152, ³*J*_{Fa,Pa} = 52, 1F, CF^bF^a), -108.2 (dm, ddm in ¹⁹F{¹H} NMR spectrum, ²*J*_{Fa,Fa} = 154, ³*J*_{Fb,Pc} = 32 Hz, 1F, C*F*^bF^a), -119.4 (m, 1F, C*F*^cOCF₃) ppm.

The isomers have been assigned comparing the P,F and F,F, and Rh,F coupling constants with data for other rhodium olefin complexes.^{5,6}

Analytical data for **3**: ¹**H NMR** (300.1 MHz, Toluene-d₈) $\delta = 5.81$ (ddd, ²*J*_{H,F} = 57.4, ³*J*_{H,F} = 9.4 ³*J*_{H,F} = 8.6 Hz, 1H, CFH, s in ¹H{¹⁹F} NMR spectrum), 1.72-1.48 (m, PCH₂CH₃), 1.06-0.81 (m, PCH₂CH₃) ppm, the resonances corresponding to the phosphine ligands are overlapped with

the signals of other products. ³¹P{¹H} NMR (121.5 MHz, Toluene-*d*₈) $\delta = 22.33$ (dt br, $J_{P,Rh} = 138.3$, ${}^{3}J_{P,F} = 24.4$ Hz) ppm. ¹⁹F NMR (282.4 MHz, Toluene-d8) $\delta = -58.4$ (d br, $J_{F,F} = 4$ Hz, 3F, OCF₃), -92.4 (dm, ${}^{2}J_{F,F} = 295$ Hz, 1F, CFF), -94.0 (dm, ${}^{2}J_{F,F} = 296$ Hz, dt br at 213K, ${}^{2}J_{F,F} = 296$, ${}^{3}J_{F,P} = 24$ Hz ,1F, CFF), -134.9 (dm, ${}^{2}J_{F,H} = 57$ Hz, 1F, CFH in ${}^{19}F{}^{1}H{}$ NMR spectrum appears as a br signal) ppm. **IR** (ATR, diamond): IR (cm⁻¹): $\tilde{v} = 1945$ (CO).

Analytical data for **4**: ¹**H NMR** (300.1 MHz, Toluene-d₈): $\delta = 1.61$ (qm, ³ $J_{H,H} = 7.6$ Hz, 12 H, PC H_2 CH₃), 1.08 (dt, ³ $J_{H,P} = 15.8$, ³ $J_{H,H} = 7.6$ Hz, 18 H, PCH₂CH₃) ppm. ³¹P{¹H} NMR (243 MHz, Toluene-d₈) $\delta = 25.31$ (dd, ¹ $J_{P,Rh} = 127.8$, ² $J_{P,F} = 26.1$ Hz) ppm. ¹⁹F NMR (282.4 MHz, Toluene-d₈) $\delta = -272.6$ (dt, ¹ $J_{F,Rh} = 48$, ² $J_{F,P} = 26$ Hz) ppm.

The values are in accordance to the literature.³

Analytical data for **5**: ¹**H NMR** (300.1 MHz, C₆D₆) $\delta = 1.57 \cdot 1.50$ (m, q in ¹H{³¹P}, ³*J*_{H,H} = 7.43, 6H, P*CH*₂CH₃), 0.99 – 0.89 (m, t in ¹H{³¹P}, ³*J*_{H,H} = 7.43, 9H, PCH₂CH₃) ppm. ³¹P{¹H} **NMR** (122 MHz, C₆D₆) $\delta = 24.36$ (d, ¹*J*_{P,Rh} = 120.9 Hz) ppm. ¹⁹F **NMR** (282.4 MHz, C₆D₆) $\delta = -53.7$ (dq, ³*J*_{F,F} = 10, ⁵*J*_{F,F} = 1 Hz, 3F, CF₃), -81.5 (dq, ⁴*J*_{F,F} = 3, ⁵*J*_{F,F} = 1 Hz, 3F, O*CF*₃), -129.5 (qq, ³*J*_{F,F} = 10, ⁴*J*_{F,F} = 3 Hz, 1F, CF) ppm. **IR** (ATR, diamond): IR (cm⁻¹): $\tilde{v} = 1938$ (CO).

Analytical data for **CF**₂=**CFH:** ¹**H NMR** (300.1 MHz, Toluene-d₈) $\delta = 5.63$ (ddd, ²*J*_{F,H} = 70.4, ³*J*_{F,H} = 13.2, ³*J*_{F,H} = 4.3 Hz, s in ¹H{¹⁹F} NMR spectrum, 1H, CF*H*) ppm, ¹⁹**F NMR** (282.4 MHz, Toluene-d₈) $\delta = -100.7$ (ddd, ²*J*_{F,F} = 84, ³*J*_{F,F} =33, ³*J*_{F,H} =13 Hz, dd in ¹⁹F{¹H} NMR spectrum, 1F, CFF), -126.5 (ddd, ³*J*_{F,F} = 118, ²*J*_{F,F} = 83, ³*J*_{F,H} = 4 Hz, dd in ¹⁹F{¹H} NMR spectrum, 1F, CF*F*), -204.3 (ddd, ³*J*_{F,F} = 118, ²*J*_{F,H} = 70, ³*J*_{F,F} = 33 Hz, dd in ¹⁹F{¹H} NMR spectrum, 1F, C*F*H) ppm.

The values are in accordance to the literature.⁷

Analytical data for **CHF(OCF₃)(CF₃):** ¹**H NMR** (300.1 MHz, C₆D₆) $\delta = 4.96$ (dq, ²*J*_{H,F} = 53.1, ³*J*_{H,F} = 2.8 Hz, s in ¹H{¹⁹F}, 1H, CH) ppm. ¹⁹F **NMR** (282.4 MHz, C₆D₆) $\delta = -60.0$ (d, ⁴*J*_{F,F} = 4 Hz, 3F, OCF₃), -84.1 (dd, ³*J*_{F,F} = 6, ³*J*_{F,H} = 3 Hz, d in ¹⁹F{¹H} NMR spectrum, 3F, CF₃), -146.0 (dqq, ²*J*_{F,H} = 53, *J*_{F,F} = 6, ⁴*J*_{F,F} = 4 Hz, qq in ¹⁹F{¹H} NMR spectrum, 1F, CF) ppm.

The values are in accordance to the literature.⁸

1.3 Independent reaction of PMVE with [Rh(F)(CO)(PEt₃)₂] (4)

In a Young NMR tube $[Rh(F)(CO)(PEt_3)_2]$ (4) (40 mg, 0.104 mmol) was dissolved in C₆D₆ (0.4 mL). The reaction mixture was cooled to 77 K, degassed *in vacuo*, and pressurized with PMVE to 0.2 bar. NMR studies show at 298K the formation of **5**.

1.4 Reaction of PMVE with triethylphosphine PEt₃

In a in a PFA inliner tube triethylphosphine (25 μ l, 0.169 mmol) was dissolved in C₆D₆ (0.4 mL). The tube was cooled to 77 K, degassed *in vacuo*, and pressurized with PMVE to 0.2 bar (36 mg, 0.220 mmol). The tube was sealed by melting, right after the addition of the PMVE gas. NMR spectroscopy after 10 minutes shows at 298K the formation of fluorophosphoranes *Z/E*-(OCF₃)CF=CF(PFEt₃) in a 10:1 ratio. At 298K, after 30 minutes, the colour of the solution changed from yellow to red. Based on the ³¹P{¹H} NMR spectrum, a full conversion into Et₃PF₂ was observed. In the ¹⁹F NMR spectrum in addition to the formation of Et₃PF₂ some unidentified decomposition products, presumably due to the further reactivity of the C₂F₄, were observed. The ¹³C{¹H} NMR spectrum reveals the formation of CO. Using a gas tight syringe, 250 μ L of the gas phase was injected into the gas chromatograph (GC) the CO with a retention time of 2.8 min⁻¹ could be detected at an oven temperature of 40°C.

Analytical data for Z/E -(F^d₃CO)CF^a=CF^b(PF^cEt₃):

¹**H** NMR (300.1 MHz, C₆D₆, *Z* isomer) $\delta = 1.82$ (dq, ²*J*_{H,P}= 16.6, ³*J*_{H,H}= 7.8 Hz, 6H, P*C*H₂CH₃), 1.03 (dt, ³*J*_{H,P} = 23.4, ³*J*_{H,H} = 7.8 Hz, 9H, PCH₂CH₃) ppm, the resonances corresponding to the *E* isomer are overlapped with these signals. ³¹P{¹H} NMR (121.5 MHz, C₆D₆) $\delta = -63.57$ (dt br, ¹*J*_{P,Fc} = 598.8, ²*J*_{P,F} = 2.4 Hz, For the *Z* isomer), -63.76 (ddd br, ¹*J*_{P,Fc} = 592.2, ²*J*_{P,Fa} = 15.4, ²*J*_{P,Fb} = 1.4 Hz, For the *E* isomer) ppm. ¹⁹F NMR (282.4 MHz, C₆D₆, *Z* isomer) $\delta = -19.6$ (dm, ¹*J*_{Fc,P} = 599 Hz, dd br in ¹⁹F{¹H} NMR spectrum ¹*J*_{Fc,P} = 599, ³*J*_{Fc,Fb} = 14 Hz, F^c), -59.9 (dd br, ⁵*J*_{Fd,Fb} = 6, ⁴*J*_{Fd,Fa} = 4 Hz, 3F, OC*F*^{*d*}₃), -118.9 (d br, ³*J*_{Fa,Fb} = 116 Hz dm in ¹⁹F{¹H} ³*J*_{Fa,Fb} = 116, ⁴*J*_{Fa,Fd} = 4 Hz, 1F, F^a), -156.3 (dm, ³*J*_{Fb,Fa} = 115 Hz ddqd in ¹⁹F{¹H} NMR spectrum, ³*J*_{Fb,Fa} = 115, ³*J*_{Fb,Fc} = 14, ⁴*J*_{Fb,Fd} = 6, ²*J*_{Fb,P} = 2 Hz, 1F, F^b) ppm. ¹⁹F NMR (282.4 MHz, C₆D₆, *E* isomer) $\delta = -22.3$ (dm, ¹*J*_{Fc,P} = 592, ddd in ¹⁹F{¹H} NMR spectrum, ¹*J*_{Fc,P} = 592, ³*J*_{Fc,Fb} = 12, ⁴*J*_{Fc,Fa} = 11 Hz, 1F, F^c), -58.9 (d br, ⁴*J*_{Fd,Fa} = 6 Hz, 3F, OCF^d₃), -105.4 (m, dm in ¹⁹F{¹H} NMR spectrum, ³*J*_{Fa,Fb} = 25, 1F, F^a), -152.5 (ddm, ddd in ¹⁹F{¹H} NMR spectrum, ³*J*_{Fb,Fa} = 25, ³*J*_{Fb,Fc} = 12, ²*J*_{Fb,P} = 2 Hz, 1F, F^b) ppm.

The values are in accordancee to the literature for other olefins.⁹⁻¹¹

Selected analytical data for **Et₃PF₂**: ¹**H NMR** (300.1 MHz, C₆D₆) $\delta = 1.83$ (dtq, ²*J*_{H,P} = 15.8, ³*J*_{H,F} = 10.9, ²*J*_{H,H} = 7.8 Hz, 6H, P*CH*₂CH₃), 1.05 (dtt, ³*J*_{H,P} = 22.7, ³*J*_{H,H} = 7.8, ⁴*J*_{H,F} = 1.1 Hz, 9H, PCH₂*CH*₃) ppm. ³¹P{¹H} **NMR** (121.5 MHz, C₆D₆) $\delta = -11.00$ (t, ¹*J*_{P,F} = 584.9 Hz) ppm. ¹⁹F **NMR** (282.4 MHz, C₆D₆) $\delta = -39.5$ (ddm, ¹*J*_{F,P} = 585, ³*J*_{F,H} = 11 Hz) ppm.

The values are in accordance to the literature.¹²

Analytical data for **CO**:

¹³C{¹H} NMR (75.5 MHz, C₆D₆) δ = -184.1 (s, CO) ppm.

This value are in accordance to the literature.¹³

1.5 Independent reaction of fluorophosgene with triethylphosphine PEt₃

In a Young NMR tube triethylphosphine (25 μ l, 0.169 mmol) was dissolved in C₆D₆ (0.4 mL). The tube was cooled to 77 K, degassed *in vacuo*, and pressurized with COF₂ to 0.2 bar. NMR spectroscopy after 10 minutes shows at 273K the formation Et₃PF₂.

1.6 Reaction of 1 equivalent of the PMVE with [Rh(H)(PEt₃)₃] (1)

In a Young NMR tube $[Rh(H)(PEt_3)_3]$ (1) (50 mg, 0.109 mmol) was dissolved in C₆D₆ (0.4 mL). The reaction mixture was cooled to 77 K, degassed *in vacuo*, and pressurized with PMVE to 0.1 bar (18 mg, 0.109 mmol). NMR studies reveal the formation of **7** at 298K, as well as fluorophosphoranes F₂PEt₃, and phosphine oxide.

1.7 Independent reaction of trifluoroethylene with [Rh(F)(PEt₃)₃] (6)

In a Young NMR tube $[Rh(F)(PEt_3)_3]$ (4) (22 mg, 0.046 mmol) was dissolved in C₆D₆ (0.4 mL). The reaction mixture was cooled to 77 K, degassed *in vacuo*, and pressurized with trifluoroethylene to 0.2 bar (14 mg, 0.171 mmol). NMR studies show at 298K the formation of 7, as well as free phosphine PEt₃.

Analytical data for 7: ¹**H** NMR (300.1 MHz, C₆D₆): $\delta = 5.50$ (ddd, ²*J*_{H,Fc} = 73.3 Hz, ³*J*_{H,Pb} = 8.8, ³*J*_{H,F} = 2.7 Hz, dd in the ¹H{³¹P} NMR spectrum, CF*H*), 1.66 (m, ³*J*_{H,H} = 7.59 Hz, 6H, P*CH*₂CH₃), 1.25 (m, quint br, ²*J*_{H,P} \approx ³*J*_{H,H} = 7.7 Hz, 6H, P*CH*₂CH₃), 1.08 (m, t in ¹H{³¹P} NMR spectrum, ³*J*_{H,H} = 7.6 Hz, 9H, PCH₂CH₃), 0.96 (m, dt in ¹H{³¹P} NMR spectrum, ³*J*_{H,F} = 11.4, ³*J*_{H,H} = 7.7 Hz, 9H, PCH₂CH₃) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): $\delta = 32.3$ (ddt br, ²*J*_{Pa,Pb} = 368.2 Hz, ¹*J*_{Pa,Rh} = 138.9 Hz, ³*J*_{Pa,Fb} \approx ³*J*_{Pa,Fc} = 47.9 Hz, 1P, P^a), 25.9 (dddd, ²*J*_{Pb,Pa} = 368.2 Hz, ${}^{1}J_{Pb,Rh} = 133.3 \text{ Hz}, {}^{3}J_{Pb,Fa} = 44.2 \text{ Hz}, {}^{2}J_{P,F} = 14.8 \text{ Hz}, 1P, P^{b}) \text{ ppm. }{}^{19}\text{F NMR}$ (282.4 MHz, C₆D₆): $\delta = -89.4 \text{ (dddd, }{}^{2}J_{Fa,Fb} = 109, {}^{3}J_{Fa,Pb} = 46, {}^{3}J_{Fa,Fc} = 33, {}^{2}J_{Fa,Rh} = 13 \text{ Hz}, 1F, CF^{a}F), -90.8 \text{ (dddd,}$ ${}^{2}J_{Fb,Fa} = 109 \text{ Hz}, {}^{3}J_{Fb,Fc} = 69 \text{ Hz}, {}^{3}J_{Fb,Pa} = 44, {}^{2}J_{Fb,Rh} = 4 \text{ Hz}, CFF^{b}), -194.9 \text{ (m, dddm in }{}^{19}F{}^{1}H}$ NMR spectrum, ${}^{3}J_{Fc,Fb} = 69, {}^{3}J_{Fc,Pa} = 48, {}^{3}J_{Fc,Fa} = 32, 1F, CF^{c}H), -218.3 \text{ (m, Rh}F) \text{ ppm. NMR}$ assignments of the CF₂CFH moiety are consistent with previously reported η^{2} -coordinated trifluoroethylene at a nickel complex.¹⁷

1.8 Reaction of PMVE with [Rh(F)(PEt₃)₃] (6)

In a Young NMR tube $[Rh(F)(PEt_3)_3]$ (6) (40 mg, 0.084 mmol) was dissolved in C₆D₆ (0.4 mL). The solution was cooled to 77 K, degassed *in vacuo*, and pressurized with PMVE to 0.2 bar (36 mg, 0.218 mmol). NMR studies show at 298K the formation of **8** and **4** and **5**, as well as fluorophosphoranes F₂PEt₃, and traces of $[Rh(PEt_3)_4]^+$. At the beginning of the reaction, *Z*-(OCF₃)CF=CF(PFEt₃) was formed with no indications for the formation of **4** or **5**. However, after 3 hours, as the fluorophosphorane decomposed, a mixture of complexes **8** and **4** in a 2.4:1 ratio, and the Et₃PF₂ were observed. Additionally, the formation of complex **5** slowly took place. A similar reaction was conducted in non-dried C₆D₆, and only **8** along with phosphine oxide Et₃P=O were formed.

Analytical data for **8**: ¹**H NMR** (500.1 MHz, C₆D₆) $\delta = 1.66 - 1.34$ (m, overlapped with signals of other Et groups, 12H, PCH₂CH₃), 1.13 - 0.91 (m, overlapped with signals of other Et groups, 18H, PCH₂CH₃) ppm. ³¹P{¹H} **NMR** (242 MHz, C₆D₆) $\delta = 34.09$ (ddtd, ²*J*_{P,Pa} = 366.7, ¹*J*_{P,Rh} = 133.4, ³*J*_{P,Fa} \approx ³*J*_{P,Fc} = 45.0, ²*J*_{P,Fd} = 17.3 Hz, 1P, P^b), 30.52 (dddd, ²*J*_{P,Pb} = 366.7, ¹*J*_{P,Rh} = 134.1, ³*J*_{P,Fb} = 45.3, ²*J*_{P,Fd} = 18.6 Hz, 1P, P^a) ppm, the spectrum is of higher order an coupling constants have been simulated. ¹⁹**F NMR** (282.4 MHz, C₆D₆) $\delta = -57.1$ (t br, ⁴*J*_{F,Fb} \approx ⁵*J*_{F,Fc} = 6 Hz, 3F, OCF₃), -96.8 (dmq, ²*J*_{Fb,Fa} = 109, ³*J*_{Fb,Pa} = 45, ⁵*J*_{Fb,F} = 6 Hz, 1F, C*F*^bF^a), -98.2 (dddd, ²*J*_{Fa,Fb} = 109, ³*J*_{Fa,Pb} = 46, ³*J*_{Fa,Fd} = 18, ²*J*_{F,Rh} = 12 Hz, 1F, CF^b*F*^a), -116.1 (m, ⁴*J*_{Fc,F} = 6 Hz, 1F, C*F*^cOCF₃), -206.35 (m, Rh*F*^d) ppm. The correlation of the olefinic fluorine atoms and the fluoride ligand was confirmed by ¹⁹F, ¹⁹F COSY NMR spectrum.





S1. ³¹P{¹H} NMR spectrum of the reaction of complex 1 with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at variable temperature showing the evolution of 2, 2' and (F_3CO)CF=CF(PFEt₃) to complex 3, 4 and Et₃PF₂.



S2. ${}^{31}P{}^{1}H$ NMR spectrum of the reaction of complex 1 with excess of perfluoro (methyl vinyl ether) in C₆D₆ at room temperature at different time showing the evolution complex 3 to 4 and complex 4 to 5.



S3. ¹⁹F NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at variable temperature showing the evolution of **2**, **2**' and (F₃CO)CF=CF(PFEt₃) to complex **3**, CF₂CFH (#), and OCF₃CF₃CFH (+), and Et₃PF₂. * = *PMVE*.



S4. ${}^{31}P{}^{1}H$ NMR spectrum (202 MHz) of the reaction of complex 1 with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at 273 K.



S5. Section of the ³¹P{¹H} NMR spectrum (202 MHz) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at 273 K showing the formation of **2** and **2**'.



S6. Section of the ¹⁹F NMR spectrum (below) and ¹⁹F{¹H} NMR spectrum (top) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at 273 K showing the formation of **2** and **2'**. * = *PMVE*.



S7. ¹⁹F NMR NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at 273 K showing the formation of **2** (zoomed in section a) and **2'** (zoomed in section b). * = PMVE.



S8. ¹H NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene- d_8 at 273 K showing the formation of **2** and **2'**: Zoomed in for the Metal-*H* region.



S9. Section of the ¹H NMR spectrum (bottom) and ¹H{³¹P} NMR spectrum (top) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene- d_8 at 273 K showing the formation of **2** and **2'** at 300 MHz (right) and 600 MHz (left) NMR spectrometers.



S10. Section of the ¹H-³¹P HSQC NMR spectrum (600 MHz) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at 273 K showing the formation of **2** and **2**'. ¹ $H_{1}^{31}P_{1}$ (*X axis*) and ³¹ $P_{1}^{1}H_{1}$ (*Y axis*) are externally projected for clarity.



S11. ${}^{19}F-{}^{19}F$ COSY NMR spectrum of the reaction of complex 1 with excess of perfluoro (methyl vinyl ether) in toluene-d₈ at 273 K showing the formation of 2 and 2'.



a)

S12. Section of the ¹H NMR spectrum (bottom) and ¹H{¹⁹F} NMR spectrum (top) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ showing the formation of **3**. The overlapping peak could belong to the probable isomer of **3** *trans*-[Rh(CF(OCF₃)CF₂H)(CO)(PEt₃)₂].



S13. Section of the ¹⁹F NMR spectrum (bottom) and ¹⁹F{¹H} NMR spectrum (top for the CFH group) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ showing the formation of **3**. The overlapping peak in the middle of the signal for the CF₂ group could belong to the probable isomer of **3** *trans*-[Rh(CF(OCF₃)CF₂H)(CO)(PEt₃)₂].



S14. Section of the ${}^{31}P{}^{1}H$ NMR spectrum of the reaction of complex 1 with excess of perfluoro (methyl vinyl ether) in toluene-d₈ showing the formation of 3.



S15. Section of the ³¹P{¹H} NMR spectrum (left) and the ¹⁹F NMR spectrum (right) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in toluene-d₈ showing the formation of **4**.



S16. Section of the ¹⁹F NMR spectrum (bottom) and ¹H NMR spectrum (top) of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in C_6D_6 showing the formation of trifluoroethylene CF₂=CFH.



S17. ³¹P{¹H} NMR spectrum of the reaction of PEt₃ with excess of perfluoro (methyl vinyl ether) in C_6D_6 showing the formation of (F₃CO)CF=CF(PFEt₃) after 10 minutes (bottom) and Et₃PF₂ after 30 minutes (top).



S18. ¹⁹F NMR spectrum of the reaction of PEt₃ with excess of perfluoro (methyl vinyl ether) in C₆D₆ showing the formation of Z/E-(F₃CO)CF=CF(PFEt₃). Zoomed in for each isomer with ¹⁹F{¹H} NMR spectrum on the top.



S19. ¹³C{¹H} NMR spectrum of the reaction of PEt₃ with excess of perfluoro (methyl vinyl ether) in C₆D₆ showing the formation CO upon the decomposition of Z/E-(F₃CO)CF=CF(PFEt₃).



S20. ¹⁹F NMR spectrum of the reaction of PEt₃ with excess of perfluoro (methyl vinyl ether) in C_6D_6 highlighting the formation Et_3PF_2 .



S21. ³¹P{¹H} NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in C_6D_6 after the separation showing the formation of complex **5**.



S22. ¹⁹F NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in C_6D_6 after the separation showing the formation of complex **5**.



S23. ¹⁹F NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in C₆D₆ after the separation highlighting the formation of OCF₃CF₃CFH (+) and ¹⁹F{¹H} NMR spectrum (top) of it. * = *PMVE*, # = trifluoroethylene.



S24. ¹H NMR spectrum of the reaction of complex **1** with excess of perfluoro (methyl vinyl ether) in C_6D_6 after the separation highlighting the formation of OCF₃CF₃CFH.



S25. ³¹P{¹H} NMR spectrum of the reaction of complex **6** with excess of perfluoro (methyl vinyl ether) in C_6D_6 in presence of oxygen (bottom), and under inert condition (top) showing the formation of complex **8** and triethylphosphine oxide, and complexes **8**, **4**, **5** and difluorophosphorane, respectively.



S26. ³¹P{¹H} NMR spectrum of the reaction of complex **6** with excess of perfluoro (methyl vinyl ether) in C₆D₆ showing the formation of complex **8** and Z-(F₃CO)CF=CF(PFEt₃) at the beginning of the reaction.



S27. ³¹P{¹H} NMR spectrum (202.4 MHz) of the reaction of complex **6** with excess of perfluoro (methyl vinyl ether) in C_6D_6 showing the formation of complex **8**, as well as complexes **4** and **5** upon the decomposition of *Z*-(F₃CO)CF=CF(PFEt₃).



S28. Section of the ¹⁹F NMR spectrum (470.6 MHz) of the reaction of complex **6** with excess of perfluoro (methyl vinyl ether) in C_6D_6 showing the formation of complex **8**.



S29. ¹⁹F-¹⁹F COSY NMR spectrum of the reaction of complex **6** with excess of perfluoro (methyl vinyl ether) in C_6D_6 showing the formation of complex **8**.



S30. ³¹P{¹H} NMR spectrum of the reaction of complex **6** with excess of trifluoroethylene in C_6D_6 showing the formation of complex **7** and dissociation of the PEt₃.



S31. ¹⁹F NMR spectrum (470.6 MHz) of the reaction of complex 6 with excess of trifluoroethylene in C_6D_6 showing the formation of complex 7.



S32. Section of the ¹⁹F-¹⁹F COSY NMR spectrum of the reaction of complex **6** with excess of trifluoroethylene in C₆D₆ showing the formation of complex **7**. # = trifluoroethylene.



S33. ¹H NMR spectrum of the reaction of complex 1 with excess of trifluoroethylene in C_6D_6 showing the formation of complex 7.

2. DFT Calculations

2.1 Computational details for geometry optimization of all the calculated complexes

DFT calculations for compounds **2***, **2**'* and **8** were performed using the Gaussian 16 (Revision A.03) program package¹⁴ and the B3LYP functional, Rh was described on using a RECP with the associated cc-pvdz basis set.¹⁵ For **8**, cc-pvtz basis sets were employed for all the other atoms. For **2*** and **2**'*, cc-pvdz basis sets were employed for all C, P and O atoms, while cc-pvtz basis sets were employed for H and F atoms. For all calculations, dispersion effects were taken into account using the Grimme D3 dispersion correction with Becke-Johnson damping.¹⁶ Frequency calculations were run for all stationary points to identify them as minima (no negative eigenvalues). Energies were corrected for zero-point energy.

2.2 Structure optimization of complexes 2*, 2'* and 8

Cartesian coordinates of all optimized structures:

Complex 2*: Energy: -2282.956007 [Hartree/Particle]

| Rh | 0.23755 | -0.06301 | -0.23642 |
|----|----------|----------|----------|
| Р | -0.04946 | 2.26744 | 0.14086 |
| С | 1.26947 | 3.26699 | 0.99298 |
| С | -1.54097 | 2.86360 | 1.06426 |
| Р | 2.25096 | -0.09172 | -1.41316 |
| С | 3.23037 | -1.63471 | -1.11285 |
| С | 3.57119 | 1.21090 | -1.29817 |
| С | 1.98269 | -0.18037 | -3.23880 |
| С | -0.21329 | 3.20952 | -1.44413 |
| С | -0.38861 | -1.94500 | -0.63917 |
| С | -1.44843 | -1.23186 | 0.09227 |
| 0 | -2.69024 | -1.18702 | -0.58627 |

| F | -1.70187 | -1.74112 | 1.37312 |
|---|----------|----------|----------|
| F | 0.15281 | -3.05926 | -0.02765 |
| F | -0.64675 | -2.32407 | -1.93428 |
| С | -3.45750 | -0.09401 | -0.45231 |
| F | -3.55153 | 0.35219 | 0.82228 |
| F | -4.69317 | -0.39938 | -0.87673 |
| F | -3.03307 | 0.96075 | -1.19720 |
| Р | 1.13054 | -0.50868 | 1.95667 |
| С | 2.80361 | 0.18231 | 2.37372 |
| С | 1.34745 | -2.25835 | 2.51415 |
| С | 0.09405 | 0.17806 | 3.32769 |
| Η | -0.41351 | 0.28210 | -1.62921 |
| Η | 1.29590 | -1.00317 | -3.43581 |
| Η | 2.91924 | -0.33168 | -3.78008 |
| Η | 1.50777 | 0.74289 | -3.57082 |
| Η | 2.56843 | -2.48940 | -1.24985 |
| Η | 3.59249 | -1.64636 | -0.08492 |
| Η | 4.08096 | -1.70850 | -1.79392 |
| Η | 3.91601 | 1.29250 | -0.26729 |
| Η | 3.15422 | 2.17231 | -1.60105 |
| Η | 4.42015 | 0.97303 | -1.94328 |
| Η | 3.55937 | -0.30845 | 1.76018 |
| Η | 3.04316 | 0.01382 | 3.42575 |
| Η | 2.83087 | 1.24989 | 2.16496 |

| Η | 0.38023 | -2.75481 | 2.49115 |
|---|----------|----------|----------|
| Н | 1.76286 | -2.28516 | 3.52379 |
| Н | 2.01110 | -2.77836 | 1.82510 |
| Н | -0.92004 | -0.19766 | 3.19875 |
| Н | 0.07642 | 1.26587 | 3.26509 |
| Η | 0.48026 | -0.11793 | 4.30525 |
| Н | -2.43499 | 2.56751 | 0.52265 |
| Н | -1.51876 | 3.95035 | 1.17283 |
| Η | -1.57240 | 2.39846 | 2.04853 |
| Н | -1.06098 | 2.80405 | -1.99484 |
| Н | 0.68618 | 3.06043 | -2.04217 |
| Н | -0.36006 | 4.27698 | -1.26569 |
| Н | 1.34709 | 2.96099 | 2.03649 |
| Н | 1.03057 | 4.33225 | 0.95903 |
| Н | 2.23114 | 3.09940 | 0.50930 |

Complex 2'*: Energy: -2282.951980 [Hartree/Particle]

| Rh | -0.40366 | -0.02814 | -0.36724 |
|----|----------|----------|----------|
| Р | -2.69901 | -0.49135 | -0.44245 |
| С | -3.89340 | -0.18913 | 0.95179 |
| С | -3.02616 | -2.26918 | -0.83237 |
| Р | -0.46971 | 2.32877 | -0.07042 |
| С | 0.83498 | 3.20421 | 0.91399 |
| С | -1.99598 | 3.12289 | 0.63787 |
| С | -0.32606 | 3.21660 | -1.68671 |
| С | -3.58745 | 0.35024 | -1.83195 |
| С | 1.42853 | -0.63475 | -1.13875 |
| С | 0.43429 | -1.71950 | -1.10319 |
| F | 0.04769 | -2.26177 | -2.30348 |
| F | 0.73024 | -2.79625 | -0.27884 |
| 0 | 2.62296 | -0.95442 | -0.41910 |
| F | 1.79754 | -0.20965 | -2.40201 |
| Р | -0.11511 | -0.67911 | 1.93050 |
| С | -0.84358 | 0.44945 | 3.21138 |
| С | 1.57069 | -0.96864 | 2.63226 |
| С | -0.93207 | -2.28428 | 2.36930 |
| Н | -0.66790 | 0.34390 | -1.87752 |
| С | 3.48076 | 0.02641 | -0.10386 |
| F | 4.44320 | -0.50612 | 0.67151 |

| F | 2.91623 | 1.04513 | 0.60304 |
|---|----------|----------|----------|
| F | 4.07904 | 0.59788 | -1.16748 |
| Н | 1.80160 | 3.03618 | 0.44546 |
| Н | 0.87532 | 2.80511 | 1.92692 |
| Н | 0.62805 | 4.27576 | 0.95620 |
| Н | -2.86486 | 2.82859 | 0.04921 |
| Н | -1.91608 | 4.21232 | 0.63277 |
| Н | -2.14080 | 2.78046 | 1.66289 |
| Н | -1.15928 | 2.92251 | -2.32466 |
| Н | 0.59621 | 2.89420 | -2.16986 |
| Н | -0.32151 | 4.30102 | -1.55603 |
| Н | -1.89446 | 0.62619 | 2.98528 |
| Н | -0.32054 | 1.40521 | 3.19184 |
| Н | -0.75701 | 0.01905 | 4.21125 |
| Н | 2.08224 | -1.70907 | 2.02001 |
| Н | 1.49586 | -1.32528 | 3.66150 |
| Н | 2.14229 | -0.04344 | 2.60535 |
| Н | -3.58834 | -0.75014 | 1.83452 |
| Н | -4.90401 | -0.49504 | 0.67187 |
| Н | -3.89739 | 0.87161 | 1.20246 |
| Н | -2.46687 | -2.52525 | -1.73160 |
| Н | -4.09119 | -2.45893 | -0.98293 |
| Η | -2.65362 | -2.89033 | -0.01886 |
| Н | -3.07355 | 0.10451 | -2.76051 |

| Η | -3.54447 | 1.43064 | -1.69368 |
|---|----------|----------|----------|
| Н | -4.63131 | 0.03414 | -1.88897 |
| Н | -0.53000 | -3.05766 | 1.71746 |
| Н | -2.00672 | -2.21378 | 2.20753 |
| Н | -0.74588 | -2.54432 | 3.41328 |

Complex 8

| С | -0.02122 | 0.24713 | 1.81876 |
|----|----------|----------|----------|
| С | -0.14944 | 1.37847 | 0.93991 |
| F | 1.06475 | 0.16874 | 2.64492 |
| F | -1.10309 | -0.17473 | 2.54739 |
| F | 0.87134 | 2.31067 | 0.96098 |
| 0 | -1.38122 | 2.05908 | 0.93551 |
| С | -1.70588 | 2.76964 | -0.17470 |
| F | -2.96564 | 3.19458 | -0.01524 |
| F | -1.65576 | 2.04053 | -1.31161 |
| F | -0.91920 | 3.83972 | -0.36259 |
| Rh | 0.15471 | -0.33898 | -0.06630 |
| F | 0.48180 | -1.68605 | -1.53254 |
| Р | -2.06718 | -1.16765 | -0.17121 |
| С | -3.54765 | -0.17142 | 0.33636 |
| С | -2.19580 | -2.71028 | 0.85310 |
| Р | 2.48533 | -0.07116 | -0.32336 |
| С | 3.51137 | 1.09897 | 0.69188 |

| С | 2.75236 | 0.36399 | -2.10422 |
|---|----------|----------|----------|
| С | 5.00843 | 0.79624 | 0.79579 |
| С | 4.18190 | 0.39526 | -2.64591 |
| С | -0.94534 | -3.58977 | 0.77540 |
| С | -4.87803 | -0.92556 | 0.38149 |
| С | 3.23838 | -1.74629 | -0.10978 |
| С | 3.07431 | -2.28302 | 1.31442 |
| С | -2.43990 | -1.75746 | -1.88440 |
| С | -2.35653 | -0.65063 | -2.93624 |

3. References

- 1. D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Butterworth/Heinemann, London/Oxford, 3rd edn., 1988.
- 2. T. Braun, D. Noveski, M. Ahijado and F. Wehmeier, *Dalton Transactions*, 2007, 3820-3825.
- 3. N. Pfister, T. Braun, P. Wittwer and M. Ahrens, Z. Anorg. Allg. Chem., 2018, 644, 1064-1070.
- 4. M. Talavera, C. N. von Hahmann, R. Müller, M. Ahrens, M. Kaupp and T. Braun, *Angew. Chem. Int. Ed.*, 2019, **58**, 10688-10692.
- 5. M. Talavera, C. N. von Hahmann, R. Muller, M. Ahrens, M. Kaupp and T. Braun, *Angew. Chem. Int. Ed. Engl.*, 2019, **58**, 10688-10692.
- 6. M. Talavera and T. Braun, *Chem. Eur. J.*, 2021, **27**, 11926-11934.
- 7. P. K. Sazonov, G. A. Artamkina, V. N. Khrustalev, M. Y. Antipin and I. P. Beletskaya, *J. Organomet. Chem.*, 2003, **681**, 59-69.
- 8. A. Foris, *Magn. Reson. Chem.*, 2004, **42**, 534-555.
- 9. U. Allwörden and G. V. Röschenthaler, *Chemiker-Zeitung*, 1988, **112**, 69-76.
- 10. A. L. Raza, M. F. Kuehnel, M. Talavera, M. Teltewskoi, M. Ahrens, P. Kläring, T. Braun and D. Lentz, *J. Fluorine Chem.*, 2018, **214**, 80-85.
- 11. D. Noveski, T. Braun, M. Schulte, B. Neumann and H.-G. Stammler, *Dalton Trans.*, 2003, DOI: 10.1039/b306635e, 4075-4083.
- 12. A. A. Facundo, A. Arévalo, G. Fundora-Galano, M. Flores-Álamo, E. Orgaz and J. J. García, *New J. Chem.*, 2019, **43**, 6897-6908.
- 13. J. Seravalli and S. W. Ragsdale, *Biochem.*, 2008, **47**, 6770-6781.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
- 15. K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, J. Chem. Phys., 2007, **126**, 124101.
- 16. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
- 17. K. A. Giffin, L. A. Pua, S. Piotrkowski, B. M. Gabidullin, I. Korobkov, R. P. Hughes, and R. T. Baker, *J. Am.Chem. Soc.*, 2017, **139**, 4075-4086.