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Supporting Information

C–H and C–F bond activation reactions of pentafluorostyrene at rhodium complexes

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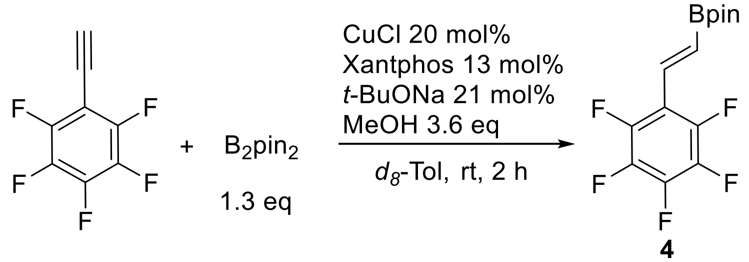
General information

Unless otherwise noted, all experiments were carried out under an atmosphere of argon by Schlenk or glovebox techniques. All solvents, except hexane and diethyl ether used for eluting, were purified and dried by conventional methods and distilled under argon before use. The rhodium complexes [Rh(Bpin)(PEt$_3$)$_3$] (**1**)[1] and [Rh(H)(PEt$_3$)$_3$] (**5**)[2] were prepared as reported in the literature. All reagents used were commercially available. Unless stated, NMR spectra were recorded at room temperature on a Bruker DPX 300 or a Bruker Advance 300 spectrometer using the solvent as an internal lock. ^{1}H and ^{13}C signals are referred to residual solvent peaks, those of ^{31}P{^{1}H} to 85% H$_3$PO$_4$, the ^{19}F NMR spectra to external CFCl$_3$. NMR assignments were supported by ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC, ^{1}H{^{19}F}, ^{1}H{^{31}P} and ^{19}F-^{19}F COSY experiments. Mass spectra were measured with a Micromass Q-Tof-2 instrument equipped with a Linden LIFDI source (Linden CMS GmbH). GC-MS analyses were performed with an Agilent 6890N gas-phase chromatograph equipped with an Agilent 5973 Network mass selective detector at 70eV. Infrared spectra were recorded with a Bruker Vertex 70 spectrometer equipped with an ATR unit (diamond).

General procedures

Synthesis of *E*-BpinCH=CHC$_6$F$_5$ (4)

The synthetic procedure to access compound **4** resembles a literature known method.[3] In a NMR tube, a solution of pentafluorophenylacetylene (26.6 mg, 0.14 mmol), MeOH (20 µL, 3.6 equiv) and *d$_8$*-toluene (0.5 mL) was added to the mixture of B$_2$pin$_2$ (44.9 mg, 0.18 mmol), *t*BuONa (2.8 mg, 0.029 mmol), Xantphos (10.2 mg, 0.018 mmol) and CuCl (2.7 mg, 0.027 mmol). The reaction was monitored by NMR spectroscopy and stopped when nearly full conversion of pentafluorophenylacetylene was observed (between 1.5-2h) and the formation of compound **4** completed. Then the reaction solution was purified by flash column chromatography on silica gel using a mixture of hexane and diethyl ether (2:1) as eluent to give the pure borylated pentafluorostyrene **4** (20 mg, 0.063 mmol, Yield: 45 %) after removing the solvents by vacuum evaporation.



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Analytical data for **4**: **^{1}H NMR** (300.1 MHz, C_6D_6): δ = 7.48 (d, ^3J(H,H) = 18.8 Hz, 1H, C*H*C_6F_5); 6.70 (d, ^3J(H,H) = 18.8 Hz, 1H, C*H*Bpin); 1.08 (s, 12H, C*H*$_3$ on Bpin group) ppm. **^{19}F NMR** (282.4 MHz, C_6D_6): δ = –144.0 (m, ^3J(F,F) = 22 Hz, 2F, *o*-F); –155.5 (tm, ^3J(F,F) = 22 Hz, 1F, *p*-F); –163.5 (m, ^3J(F,F) = 22 Hz, 2F, *m*-F) ppm. **GC-MS** (*d$_8$*-Tol): Calculated (*m/z*) for $[M]^+$: 320; found: 320.

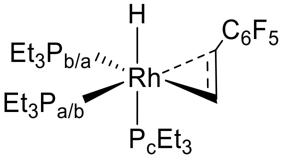
Reaction of an excess amount of pentafluorostyrene with [Rh(Bpin)(PEt$_3$)$_3$] (1)

In a NMR tube equipped with a PFA inliner [Rh(Bpin)(PEt$_3$)$_3$] (**1**) (63 mg, 0.107 mmol) was dissolved in 0.3 mL *d$_{14}$*-methylcyclohexane. Pentafluorostyrene (24 mg, 0.124 mmol) was added to the solution. After 5 min at room temperature, NMR spectra were measured at 213 K. The two complexes *fac*-[Rh(H)(η^2-$CH_2CHC_6F_5$)(PEt$_3$)$_3$] (**2**) and *fac*-[Rh(H)(η^2-CH(Bpin)CHC_6F_5)(PEt$_3$)$_3$] (**3**) were identified as well as dehydrogenative borylation product **4** in a ratio of 1.8:1:0.6.

Reaction of pentafluorostyrene with an excess amount of [Rh(Bpin)(PEt$_3$)$_3$] (1)

In a NMR tube equipped with a PFA inliner [Rh(Bpin)(PEt$_3$)$_3$] (**1**) (50 mg, 0.085 mmol) was dissolved in 0.3 mL *d$_{14}$*-methylcyclohexane. Pentafluorostyrene (6.6 mg, 0.034 mmol) was added to the solution. After 5 min at room temperature, NMR spectra were measured at 233 K. Complex *fac*-[Rh(H)(η^2-CH(Bpin)CHC_6F_5)(PEt$_3$)$_3$] (**3**) was identified together with [Rh(H)(PEt$_3$)$_3$] (**5**) in a ratio of 1:2 as well as traces of dehydrogenative borylation product **4**.

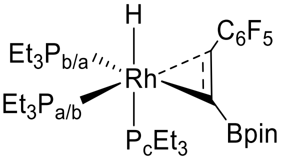
Formation of *fac*-[Rh(H)(η^2-$CH_2CHC_6F_5$)($(PEt_3)_3$)] (2)



In a NMR tube [Rh(H)($(PEt_3)_3$)] (**5**) (40 mg, 0.087 mmol) was dissolved in 0.5 mL of d_8-toluene. Pentafluorostyrene (12 mg, 0.062 mmol) was added to the solution. After 5 min at room temperature, NMR spectra were measured at room temperature and at 213 K revealing the full conversion of pentafluorostyrene and the formation of complex **2**.

Analytical data for **2**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol, 213 K): δ = 20.3 (ddd, $^1J(P_{a/b},Rh)$ = 139.8 Hz, $^2J(P_a,P_b)$ = 42.6 Hz, $^2J(P_{a/b},P_c)$ = 24.2 Hz, $P_{a/b}$); 13.7 (ddd, $^1J(P_{b/a},Rh)$ = 134.0 Hz, $^2J(P_b,P_a)$ = 42.9 Hz, $^2J(P_{b/a},P_c)$ = 28.8 Hz, $P_{b/a}$); 5.8 (dm, br, $^1J(P_c,Rh)$ = 95.8 Hz, P_c) ppm. **^{1}H NMR** (300.1 MHz, d_8-Tol, 213 K): δ = 3.32 (br, pseudo t in the ^{1}H{^{31}P} NMR spectrum, $^3J(H,H)$ ≈ 8 Hz, 1H, $C\mathit{H}C_6F_5$); 3.05 (br, d in the ^{1}H{^{31}P} NMR spectrum, $^3J(H,H)$ = 9.5 Hz, 1H, $C\mathit{H}_2CHC_6F_5$); 1.83 (br, d in ^{1}H{^{31}P} NMR spectrum, $^3J(H,H)$ = 8.1 Hz, 1H, $C\mathit{H}_2CHC_6F_5$); 1.59–1.43 (m, $PC\mathit{H}_2CH_3$, overlapping with signals for the rhodium complex **5**); 1.20–1.03 (m, $PC\mathit{H}_2CH_3$, overlapping with signals for **5**); 0.95–0.86 (m, t in the ^{1}H{^{31}P} NMR spectrum $^3J(H,H)$ = 7.2 Hz, 9H, $PCH_2C\mathit{H}_3$); 0.83–0.74 (m, t in the ^{1}H{^{31}P} NMR spectrum, $^3J(H,H)$ = 7.2 Hz, 9H, $PCH_2C\mathit{H}_3$); 0.72–0.63 (m, t in the ^{1}H{^{31}P} NMR spectrum, $^3J(H,H)$ = 7.2 Hz, 9H, $PCH_2C\mathit{H}_3$); –14.64 (dtd, $^2J(H,P_c)$ = 161.8 Hz, $^2J(H,P_a)$ = $^2J(H,P_b)$ = 19.8 Hz, $^1J(H,Rh)$ = 9.2 Hz, 1H, Rh*H*) ppm. **^{19}F NMR** (282.4 MHz, d_8-Tol, 213 K): δ = –146.0 (d br, $^3J(F,F)$ = 21 Hz, 1F, *o*-F); –146.7 (d br, $^3J(F,F)$ = 21 Hz, 1F, *o*-F); –166.3 (t, $^3J(F,F)$ = 21 Hz, 1F, *m*-F); –167.0 (t, $^3J(F,F)$ = 21 Hz, 1F, *m*-F); –170.9 (t, $^3J(F,F)$ = 21 Hz, 1F, *p*-F) ppm. **^{1}H-^{13}C HMQC NMR** (300.1/75.5 MHz, d_8-Tol, 213 K) δ = 29.2 (m, $\mathit{C}HC_6F_5$); 23.9 (m, $\mathit{C}H_2CHC_6F_5$) ppm.

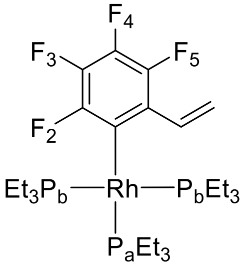
Formation of *fac*-[Rh(H)(η^2-CH(Bpin)CHC$_6$F$_5$)(PEt$_3$)$_3$] (3)



In a NMR tube [Rh(H)(PEt$_3$)$_3$] (**5**) (48 mg, 0.105 mmol) was dissolved in 0.3 mL *d*$_8$-toluene and the mixture was cooled in a 193 K bath. Borylated pentafluorostyrene **4** (20 mg, 0.062 mmol) was dissolved in 0.3 mL *d*$_8$-toluene and the mixture was cooled down to 193 K. Then, both solutions were combined via cannula. After 5 min at 193 K, the reaction solution was warmed up to 213 K revealing the formation of complex **3** with a 40 % consumption of compound **4**.

Analytical data for **3**: **^{31}P{^{1}H} NMR** (121.5 MHz, *d*$_8$-Tol, 213 K): δ = 18.2 (ddd, ^1J(P$_{a/b}$,Rh) = 142.9 Hz, ^2J(P$_a$,P$_b$) = 37.6 Hz, ^2J(P$_{a/b}$,P$_c$) = 28.3 Hz, P$_{a/b}$); 15.3 (ddd, ^1J(P$_{b/a}$,Rh) = 134.3 Hz, ^2J(P$_b$,P$_a$) = 37.1 Hz, ^2J(P$_{b/a}$,P$_c$) = 25.3 Hz, P$_{b/a}$); 3.3 (dm, ^1J(Rh,P$_c$) = 96.7 Hz, P$_c$) ppm. Selected **^{1}H NMR** (300.1 MHz, *d*$_8$-Tol, 213 K): δ = 3.97 (br, d in ^{1}H{^{31}P} NMR spectrum, ^3J(H,H) = 12.0 Hz, 1H, C*H*C$_6$F$_5$); 3.10 (br, d in ^{1}H{^{31}P} NMR spectrum, ^3J(H,H) = 12.0 Hz, 1H, C*H*Bpin); –14.87 (dtd, ^2J(H,P$_c$) = 163.0 Hz, ^2J(H,P$_a$) = ^2J(H,P$_b$) = 18.2 Hz, ^1J(H,Rh) = 5.5 Hz, 1H, Rh*H*) ppm. **^{19}F NMR** (282.4 MHz, *d*$_8$-Tol, 213 K): δ = –144.2 (d, ^3J(F,F) = 21 Hz, 1F, *o*-F) (overlapping with a signal of compound **4**); –145.0 (d, ^3J(F,F) = 21 Hz, 1F, *o*-F); –166.5 (t, ^3J(F,F) = 21 Hz, 1F, *m*-F); –167.1 (t, ^3J(F,F) = 21 Hz, 1F, *m*-F); –170.4 (t, ^3J(F,F) = 21 Hz, 1F, *p*-F) ppm. **^{1}H-^{13}C HMQC NMR** (300.1/75.5 MHz, *d*$_8$-Tol, 213 K) δ = 37.4 (m, *C*HC$_6$F$_5$); 15.8 (m, *C*HBpin) ppm.

Formation of [Rh(2-$C_6F_4CHCH_2$)(PEt_3)$_3$] (6)



In a NMR tube [Rh(H)(PEt_3)$_3$] (**5**) (36 mg, 0.078 mmol) was dissolved in 0.5 mL of *d_8*-toluene. Borylated pentafluorostyrene **4** (34 mg, 0.106 mmol) was added to the solution. After 30 min at room temperature, the NMR spectra revealed a full conversion of complex **5** to give complex **6** as well as another unidentified complex (ratio 13.5:1, based on the $^{31}P\{^1H\}$ NMR spectrum). The ^{31}P and ^{19}F NMR data given below were confirmed by simulation using gNMR software.[4]

Analytical data for **6**: **$^{31}P\{^1H\}$ NMR** (121.5 MHz, *d_8*-Tol): δ = 15.8 (dtddd, $^1J(P_a,Rh)$ = 123.3 Hz, $^2J(P_a,P_b)$ = 38.0 Hz, $^4J(P_a,F_2)$ = 14.6 Hz, $^5J(P_a,F_5)$ = 9.8 Hz, $^5J(P_a,F_3)$ = 6.6 Hz, 1P, P_a); 10.5 (dd, $^1J(P_b,Rh)$ = 143.3 Hz, $^2J(P_b,P_a)$ = 38.0 Hz, 2P, P_b) ppm. **^{19}F NMR** (282.4 MHz, *d_8*-Tol): δ = –105.7 (dq, $^5J(F_2,F_5)$ = 43.8 Hz, $^3J(F_2,F_3)$ ≈ $^3J(F_2,Rh)$ ≈ $^4J(F_2,P_a)$ = 14.6 Hz, 1F, F_2); –143.4 (dddd, $^3J(F_3,F_4)$ = 20.3 Hz, $^3J(F_3,F_2)$ = 14.6 Hz, $^5J(F_3,P_a)$ = 6.6 Hz, $^4J(F_3,Rh)$ = 4.0 Hz, 1F, F_3); –160.5 (dddd, $^5J(F_5,F_2)$ = 43.8 Hz, $^3J(F_5,F_4)$ = 20.3 Hz, $^5J(F_5,P_a)$ = 9.8 Hz, $^4J(F_5,Rh)$ = 5.2 Hz, 1F, F_5); –165.7 (t, $^3J(F_4,F_3)$ = $^3J(F_4,F_5)$ = 20.3 Hz, 1F, F_4) ppm. **LIFDI-TOF-MS** (Toluene): Calculated (*m/z*) for $[M]^+$: 632; found: 632. Selected **^1H NMR** data (300.1 MHz, *d_8*-Tol): δ = 8.16 (dd, $^3J(H,H)$ = 18.4 Hz, $^3J(H,H)$ = 11.8 Hz, 1H, CHC_6F_4); 6.38 (d, $^3J(H,H)$ = 18.1 Hz, 1H, $CH_2=CHC_6F_4$); 5.40 (d, $^3J(H,H)$ = 11.5 Hz, 1H, $CH_2=CHC_6F_4$) ppm.

Formation of *trans*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_2$] (7) and *mer*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_3$] (8)

In a NMR tube [Rh(H)(PEt$_3$)$_3$] (**5**) (23 mg, 0.050 mmol) was dissolved in 0.5 mL d_8-toluene. Pentafluorostyrene (13 mg, 0.067 mmol) was added to the solution. After 1 d at room temperature, NMR spectra were measured at room temperature and at 233 K revealing the full conversion of complex **5**.

The NMR spectra at room temperature showed the formation of complex **7**, free PEt$_3$, traces of complex *mer*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_3$] (**8**), unreacted complex **2** (36 %), minor amounts of the C–H bond activation complex [Rh(*E*-CHCHC$_6$F$_5$)(PEt$_3$)$_3$] (**15**) as well as of the hydrogenation product ethylpentafluorobenzene **9**. When the sample was cooled down to 233 K, complex **7** converted into complex **8** completely. The low temperature ^{19}F NMR spectrum shows a ratio of 1:0.18:0.07 for **8**:**9**:**15**. Treatment of the same NMR tube with KPF$_6$ (30 mg, 0.163 mmol) gave after 14 d a full conversion of complexes **7** and **8** into complex **6** as well as a product of C–D bond activation [Rh(4-C$_6$D$_4$CD$_3$)(PEt$_3$)$_3$].[5] In the absence of KPF$_6$, complex **6** can also be formed very slowly within weeks.

Analytical data for **7**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol): δ = 18.4 (dd, ^1J(P,Rh) = 114.2 Hz, ^2J(P,F) = 16.6 Hz, 2P) ppm. Selected **^{1}H NMR** data (300.1 MHz, d_8-Tol): δ = 3.20 (br, 2H, RhC*H*$_2$CH$_2$); 2.45 (br, 2H, C$_6$F$_4$C*H*$_2$CH$_2$) ppm. **^{19}F NMR** (282.4 MHz, d_8-Tol): δ = –130.6 (m, 1F), –142.0 (dd, ^3J(F,F) = 20 Hz, J = 16 Hz, 1F); –162.5 (dd, ^5J(F,F) = 29 Hz, ^3J(F,F) = 20 Hz, 1F); –167.3 (t, ^3J(F,F) = 20 Hz, 1F); –290.6 (m, 1F, RhF) ppm. Selected **^{13}C{^{1}H} NMR** data (75.5 MHz, d_8-Tol): δ = 37.3 (s br, C$_6$F$_4$*C*H$_2$CH$_2$); 23.2 (dm br, ^2J(C,Rh) = 32.6 Hz, Rh*C*H$_2$CH$_2$) ppm.

Analytical data for **8**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol, 233 K): δ = 7.9 (ddd, ^1J(P,Rh) = 103.8 Hz, ^2J(P,P) = 29.7 Hz, ^2J(P,F) = 17.9 Hz, 2P); -2.8 (apparent dm, ^1J(P,Rh) ≈ 90 Hz, 1P) ppm. Selected **^{1}H NMR** data (300.1 MHz, d_8-Tol, 233 K): δ = 3.04 (br, 2H, C$_6$F$_4$C*H*$_2$CH$_2$); 1.42 (br, 2H, RhC*H*$_2$CH$_2$, observed in the ^{1}H-^{1}H COSY NMR spectrum, overlapping with signals for PEt$_3$) ppm. **^{19}F NMR** (282.4 MHz, d_8-Tol, 233 K): δ = –122.6 (m, 1F), –140.6 (m, 1F); –161.2 (m, 1F); –165.7 (t, ^3J(F,F) = 21 Hz, 1F); –385.1 (m, 1F, RhF) ppm. **APT NMR** (75.5 MHz, d_8-Tol, 213 K) δ = 37.8 (m, $C_6F_4CH_2CH_2$); 23.7 (dm, ^2J(C,Rh) = 16.4 Hz, RhCH_2CH_2) ppm.

Formation of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(CO)(PEt_3)$_2$] (10) and *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(^{13}CO)(PEt_3)$_2$] (10')

After isolation of complex **7** and applying vacuum, the residue was dissolved in 0.5 mL d_8-toluene. Then CO (or ^{13}CO) was bubbled into the solution for 15 s. The NMR spectra were measured after 5 min at room temperature revealing the full conversion of complex **7** and the formation of complex **10** (or **10'**) as well as [Rh(H)(CO)(PEt_3)$_3$] (**11**)[6] (ratio 3.9:1) (or the isotopologue [Rh(H)(^{13}CO)(PEt_3)$_3$] (**11'**) (ratio 4.4:1)).

Analytical data for **10**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol): δ = 16.9 (dd, ^1J(P,Rh) = 98.5 Hz, ^2J(P,F) = 17.3 Hz, 2P) ppm. Selected **^{1}H NMR** (300.1 MHz, d_8-Tol): δ = 3.15 (br t, tt in the ^{1}H{^{19}F} NMR spectrum decoupled at -140 ppm, ^3J(H,H) = 7.5 Hz, ^3J(H,Rh) ≈ ^4J(H,F) = 1.9 Hz, 2H, $C_6F_4CH_2CH_2$); 2.56 (m, ttd in ^{1}H{^{19}F} NMR spectrum decoupled at -400 ppm, ^3J(H,P) = 9.3 Hz, ^3J(H,H) = 7.5 Hz, ^2J(H,Rh) = 2.1 Hz, 2H, $C_6F_4CH_2CH_2$) ppm. **^{19}F NMR** (282.4 MHz, d_8-Tol, 243 K): δ = –116.3 (dd, ^5J(F,F) = 27 Hz, J = 14 Hz, 1F); –139.8 (dd, ^3J(F,F) = 21 Hz; J = 16 Hz, 1F); –161.7 (dd, ^5J(F,F) = 27 Hz, ^3J(F,F) = 21 Hz, 1F); –165.0 (t, ^3J(F,F) = 21 Hz, 1F); –425.3 (m, 1F) ppm. Selected **^{13}C{^{1}H} NMR** data (75.5 MHz, d_8-Tol): δ = 33.4 (s br, $C_6F_4CH_2CH_2$); 24.0 (dq, ^1J(C,Rh) = 19.9 Hz, ^2J(C,P) ≈ ^2J(C,F) = 6.6 Hz, RhCH_2CH_2) ppm. **LIFDI-TOF-MS** (toluene): Calculated (*m/z*) for [M-CO]$^+$: 534; found: 534. **IR** (ATR): $\tilde{\nu}$ (CO) 2056 cm^{-1}.

Analytical data for **10'**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol): δ = 16.9 (ddd, ^1J(P,Rh) = 98.5 Hz, ^2J(P,F) = 17.3 Hz, ^2J(P,C) = 10.9 Hz, 2P) ppm. Selected **^{1}H NMR** (300.1 MHz, d_8-Tol): δ = 3.09 (br t, tq in ^{1}H{^{19}F} NMR spectrum decoupled at -140 ppm, ^3J(H,H) = 7.5 Hz, ^3J(H,Rh) ≈ ^4J(H,F) ≈ ^4J(H,C) = 1.9 Hz, 2H, $C_6F_4CH_2CH_2$); 2.50 (m, ttt in ^{1}H{^{19}F} NMR spectrum decoupled at -400 ppm, ^3J(H,P) = 9.3 Hz, ^3J(H,H) = 7.5 Hz, ^2J(H,Rh) ≈ ^3J(H,C) = 2.1 Hz, 2H, $C_6F_4CH_2CH_2$) ppm. **^{19}F NMR** (282.4 MHz, d_8-Tol): δ = –116.5 (m, 1F); –140.1 (dd, ^3J(F,F) = 20 Hz, J = 15 Hz, 1F); –162.0 (dd, ^5J(F,F) = 26 Hz, ^3J(F,F) = 20 Hz, 1F); –165.3 (t, ^3J(F,F) = 20 Hz, 1F); –418.2 (m, 1F) ppm. Selected **^{13}C{^{1}H} NMR** (75.5 MHz, d_8-Tol): δ = 189.5 (ddt, ^1J(C,Rh) = 41.3 Hz, ^2J(C,F) = 14.8 Hz,

${}^{2}J$(C,P) = 10.9 Hz, ${}^{13}C$O) ppm. **LIFDI-TOF-MS** (Toluene): Calculated (*m/z*) for [M-^{13}CO]$^+$: 534; found: 534. **IR** (ATR): $\tilde{\nu}$ (^{13}CO) 2002 cm^{-1}.

Analytical data for **11**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol): δ = 26.5 (d, ${}^{1}J$(P,Rh) = 146.7 Hz) ppm. Selected **^{1}H NMR** (300.1 MHz, d_8-Tol, 243 K): δ = –11.11 (qd, d in ^{1}H{^{31}P} NMR spectrum, ${}^{2}J$(H,P) = 17.1 Hz, ${}^{1}J$(H,Rh) = 4.4 Hz, 1H) ppm. **IR** (ATR): $\tilde{\nu}$ (CO) 1950 cm^{-1}.

Analytical data for **11'**: **^{31}P{^{1}H} NMR** (121.5 MHz, d_8-Tol): δ = 26.5 (ddm, ${}^{1}J$(P,Rh) = 146.0 Hz, ${}^{2}J$(P,C) = 11.1 Hz) ppm. Selected **^{1}H NMR** (300.1 MHz, d_8-Tol): δ = –11.17 (m, dd in ^{1}H{^{31}P} NMR spectrum, ${}^{2}J$(H,C) = 36.3 Hz, ${}^{1}J$(H,Rh) = 4.4 Hz, 1H) ppm. **IR** (ATR): $\tilde{\nu}$ (^{13}CO) 1902 cm^{-1}.

Formation of [Rh(4-$C_6F_4CHCH_2$)(PEt_3)$_3$] (12)

In a NMR tube [Rh(H)(PEt_3)$_3$] (**5**) (15 mg, 0.033 mmol) was dissolved in 0.5 mL of C_6D_6. Pentafluorostyrene (8.4 mg, 0.043 mmol) was added to the solution. The reaction was monitored by NMR spectroscopy and after 1 d at 333 K, full conversion of complex **5** was observed. Formation of complex [Rh(4-$C_6F_4CHCH_2$)(PEt_3)$_3$] (**12**) and the fluorido complex [Rh(F)(PEt_3)$_3$] (**13**)[7] as well as the hydrogenation product ethylpentafluorobenzene **9**[8] in a ratio of 1.5:1.6:1 (determined by ^{19}F NMR spectroscopy) was obtained.

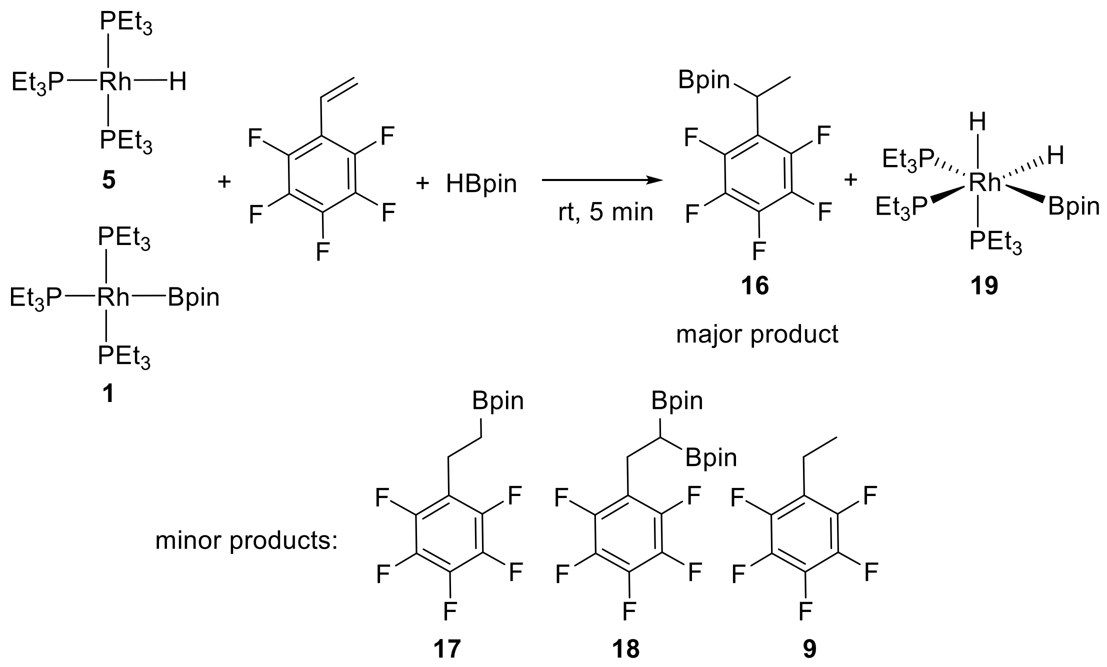
Analytical data for **12**: **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = 18.4 (dm, ${}^{1}J$(P,Rh) = 138.1 Hz, 1P, P_{trans} to C_6F_4); 14.0 (dd, ${}^{1}J$(P,Rh) = 141.1 Hz, ${}^{2}J$(P,P) = 40.1 Hz, 2P) ppm. Selected **^{1}H NMR** data (300.1 MHz, C_6D_6): δ = 6.98 (dd, ${}^{3}J$(H,H) = 18.1 Hz, ${}^{3}J$(H,H) = 12.1 Hz, 1H, C_6F_4CH); 6.20 (d, ${}^{3}J$(H,H) = 18.1 Hz, 1H, H_{cis} to C_6F_4); 5.33 (d, ${}^{3}J$(H,H) = 12.1 Hz, 1H, H_{trans} to C_6F_4) ppm. **^{19}F NMR** (282.4 MHz, C_6D_6): δ = –110.7 (m, 2F); –147.3 (m, 2F) ppm.

Synthesis of [Rh(*E*-$CHCHC_6F_5$)(PEt_3)$_3$] (15)

In a Schlenk tube [Rh(Me)(PEt_3)$_3$] (**14**) (44 mg, 0.093 mmol) was dissolved in 0.7 mL of THF. Pentafluorostyrene (14.2 µl, 0.10 mmol) was added to the solution. After 30 min at room temperature the volatiles were removed in vacuum, and complex **15** as a brown oil was obtained. Yield: 87% (54 mg).

Analytical data for **15**: **^{31}P{^{1}H} NMR** (202.5 MHz, d_8-THF): δ = 19.4 (dt, ^{1}J(P,Rh) = 115.7 Hz, ^{2}J(P,P) = 36.1 Hz, 1P, P_{trans}); 16.6 (dd, ^{1}J(P,Rh) = 156.7 Hz, ^{2}J(P,P) = 36.1 Hz, 2P, P_{cis}) ppm. **^{1}H NMR** data (300.1 MHz, d_8-THF): δ = 9.18 (dt br, d br in the ^{1}H{^{31}P} NMR spectrum, dtt in the ^{1}H{^{19}F} NMR spectrum, ^{3}J(H,H) = 18.6 Hz, ^{3}J(H,P_{cis}) = 4.4 Hz, ^{3}J(H,P_{trans}) ≈ ^{2}J(H,Rh) = 1.9 Hz, 1H, C*H*Rh); 6.42 (ddq br, d br in the ^{1}H{^{31}P} NMR spectrum, ddq in the ^{1}H{^{19}F} NMR spectrum, ^{3}J(H,H) = 18.6 Hz, ^{3}J(H,P_{trans}) = 6.7 Hz, ^{3}J(H,P_{cis}) ≈ ^{2}J(H,Rh) = 1.7 Hz, 1H, C*H*C_6F_5); 1.70-1.53 (m, 18H, PCH_2CH_3); 1.21-1.05 (m, 27H, PCH_2CH_3) ppm. **^{19}F NMR** (282.4 MHz, d_8-THF): δ = −155.3 (dm, ^{3}J(F,F) = 22 Hz, 2F, *o*-F); −171.0 (m, 2F, *m*-F); −172.1 (tm, ^{3}J(F,F) = 22 Hz, 1F, *p*-F) ppm. **APT NMR** (75.5 MHz, d_8-THF): δ = 198.0 (dqm, ^{1}J(C,Rh) = 75.7 Hz, ^{2}J(C,P) = 27 Hz, Rh*C*H); 144.3 (dm, ^{1}J(C,F) = 242.7 Hz, *o-C*F); 138.7 (dm, ^{1}J(C,F) = 246.9 Hz, *m-C*F); 137.3 (dm, ^{1}J(C,F) = 245.1 Hz, *p-C*F); 117.4 (m, C_{ipso}F); 115.7 (s br, *C*HC_6F_5); 21.5 (dt, ^{1}J(C,P_{trans}) = 15.8 Hz, ^{1}J(C,P_{cis}) = 2.9 Hz, $P_{trans}CH_2CH_3$); 19.1 (t br, ^{1}J(C,P) = 11.5 Hz, $P_{cis}CH_2CH_3$); 9.7 (s, $P_{trans}CH_2CH_3$); 9.3 (s, $P_{cis}CH_2CH_3$) ppm **LIFDI-TOF-MS** (Toluene): Calculated (*m/z*) for $[M]^+$: 650; found: 650.

Stoichiometric hydroboration reactions with $[Rh(H)(PEt_3)_3]$ (5) or $[Rh(Bpin)(PEt_3)_3]$ (1)



In a NMR tube [Rh(H)(PEt$_3$)$_3$] (**5**) (51.0 mg, 0.111 mmol) was dissolved in 0.5 mL of *d$_8$*-toluene. HBpin (41 µl, 0.269 mmol) was introduced into the solution. After 30 s, pentafluorostyrene (21.1 mg, 0.109 mmol) was added into the solution. The ^{19}F NMR spectroscopic data revealed after 5 min the full conversion of pentafluorostyrene as well as the formation of Markovnikov hydroboration compound [$C_6F_5CH(Bpin)CH_3$] (**16**),[9] small amounts of the *anti*-Markovnikov product [$C_6F_5CH_2CH_2(Bpin)$] (**17**),[9] the diboryl compound [$C_6F_5CH_2CH(Bpin)_2$] (**18**)[9] as well as the hydrogenation compound **9** in a ratio of 92:2:4:2. The rhodium (III) complex *fac*-[Rh(H)$_2$(Bpin)(PEt$_3$)$_3$] (**19**)[10] was formed as the only rhodium complex.

Alternatively, in a NMR tube equipped with a PFA tube [Rh(Bpin)(PEt$_3$)$_3$] (**1**) (36.7 mg, 0.063 mmol) was dissolved in *d$_{14}$*-methylcyclohexane (0.3 mL). Pentafluorostyrene (12.7 mg, 0.065 mmol) was added to the solution. After 30 s, HBpin (12 µl, 0.079 mmol) was introduced to the solution. The ^{19}F NMR spectroscopic data revealed after 5 min the full conversion of pentafluorostyrene as well as the formation of the same organic products in a ratio of 49:14:22:15 as well as the rhodium (III) complex **19**.

Analytical data for **16**: **^{1}H NMR** data (300.1 MHz, C_6D_6): δ = 2.63 (q, ^3J(H,H) = 7.7 Hz, 1H, C*H*Bpin); 1.28 (d, ^3J(H,H) = 7.7 Hz, 3H, C*H*$_3$); 1.05 (s, 12H, *Bpin*) ppm. **^{19}F NMR** (282.4 MHz, C_6D_6): δ = –144.8 (dm, ^3J(F,F) = 22 Hz, 2F, *o*-F); –160.3 (t, ^3J(F,F) = 22 Hz, 1F, *p*-F); –164.4 (tm, ^3J(F,F) = 22 Hz, 2F, *m*-F) ppm. **GC-MS** (*d$_8$*-Tol): Calculated (*m/z*) for [M]$^+$: 322; found: 322.

Analytical data for **17**: **^{19}F NMR** (282.4 MHz, C_6D_6): δ = –145.5 (dm, ^3J(F,F) = 22 Hz, 2F, *o*-F); –160.2 (t, ^3J(F,F) = 22 Hz, 1F, *p*-F); –164.6 (tm, ^3J(F,F) = 22 Hz, 2F, *m*-F) ppm. The signals for **17** in the ^{1}H NMR spectrum might overlap with these for compound **16**, **18** and **9**. **GC-MS** (*d$_8$*-Tol): Calculated (*m/z*) for [M]$^+$: 322; found: 322. This compound is proposed based on the GC-MS data and literature.[9]

Analytical data for **18**: **^{1}H NMR** data (300.1 MHz, C_6D_6): δ = 3.01 (d, ^3J(H,H) = 7.7 Hz, 2H, C*H*$_2$); 1.39 (br, observed in the ^{1}H-^{1}H COSY NMR spectrum, overlapping with signals for compound **16** and unknown compound) ppm. **^{19}F NMR** (282.4 MHz, C_6D_6): δ = –143.5 (dm,

^3J(F,F) = 22 Hz, 2F, *o*-F); (the other two signals are overlapped with signals for compound **16**, **17** and **9**) ppm. **GC-MS** (d_8-Tol): Calculated (*m/z*) for $[M]^+$: 448; found: 448.

General procedure for the catalytic conversion of pentafluorostyrene

In a NMR tube, the catalyst (mol% based on the amount of pentafluorostyrene) was dissolved in the corresponding solvent (0.5 mL) and HBpin. Then pentafluorostyrene was added to the solution stepwise. After 5 min at room temperature, the ^{1}H and ^{19}F NMR spectroscopic data revealed full conversion of pentafluorostyrene as well as the formation of the Markovnikov hydroboration compound **16**, small amounts of the anti-Markovnikov product **17**, the diboryl compound **18** as well as the hydrogenation compound **9**.

Entry 1: $[Rh(H)(PEt_3)_3]$ (**5**) (5 mg, 0.011 mmol, 3 mol%) was dissolved in C_6D_6. Then HBpin (70 µl, 0.46 mmol) and pentafluorostyrene (70.3 mg, 0.36 mmol) were added. The mixture of products **16**:**17**:**18**:**9** was obtained in a ratio of 91:6:1:2.

Entry 2: $[Rh(Bpin)(PEt_3)_3]$ (**1**) (7.8 mg, 0.013 mmol, 3.7 mol%) was dissolved in Me_6Si_2 in a PFA tube. HBpin (70 µl, 0.46 mmol) and pentafluorostyrene (70.3 mg, 0.36 mmol) were added afterwards. The mixture of products **16**:**17**:**18**:**9** was obtained in a ratio of 81:9:3:3.

Entry 3: $[Rh(H)(PEt_3)_3]$ (**5**) (10 mg, 0.022 mmol, 1.5 mol%) was added to a mixture of HBpin (273 µl, 1.79 mmol) and pentafluorostyrene (281.2 mg, 1.42 mmol). The mixture of products **16**:**17**:**18**:**9** was obtained in a ratio of 75:13:4:8.

NMR Spectra

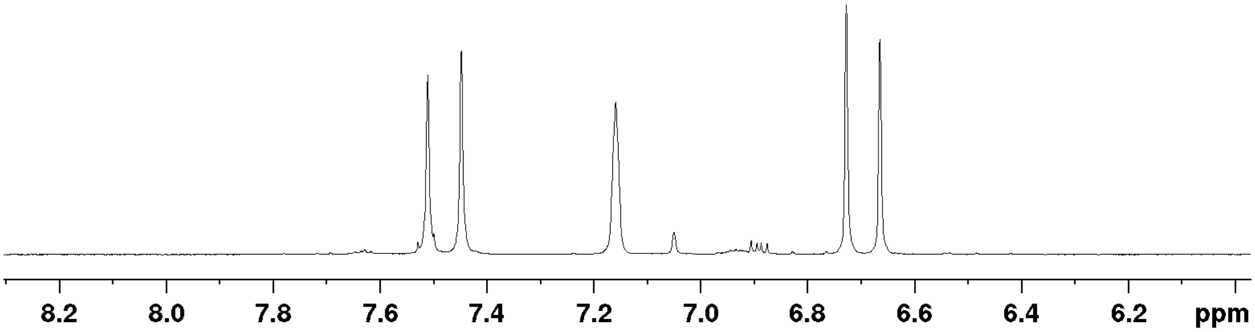


Figure S1 Part of the ^1H NMR (300.1 MHz, C_6D_6) spectrum of *E*-BpinCH=CHC$_6$F$_5$ (**4**).

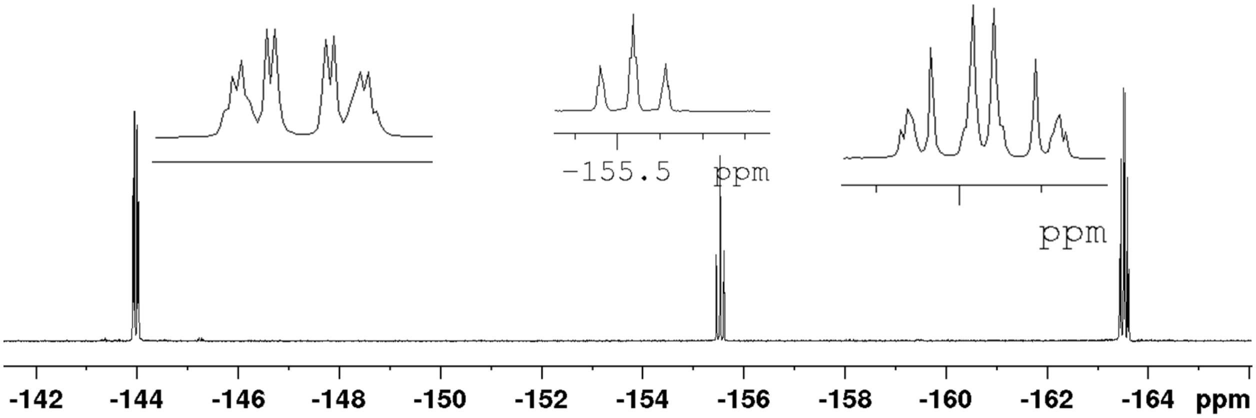


Figure S2 ^{19}F NMR (282.4 MHz, C_6D_6) spectrum of *E*-BpinCH=CHC$_6$F$_5$ (**4**).

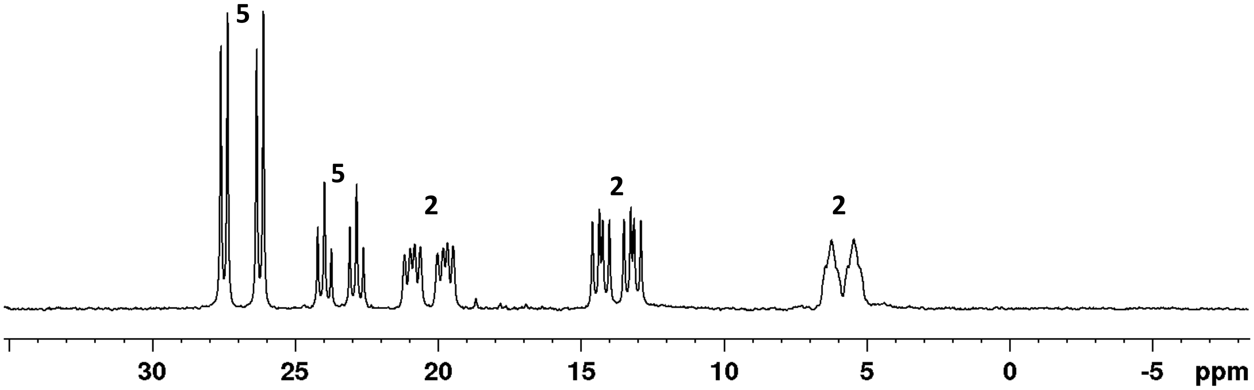


Figure S3 $^{31}P\{^1H\}$ NMR (121.5 MHz, d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH$_2$CHC$_6$F$_5$)(PEt$_3$)$_3$] (**2**).

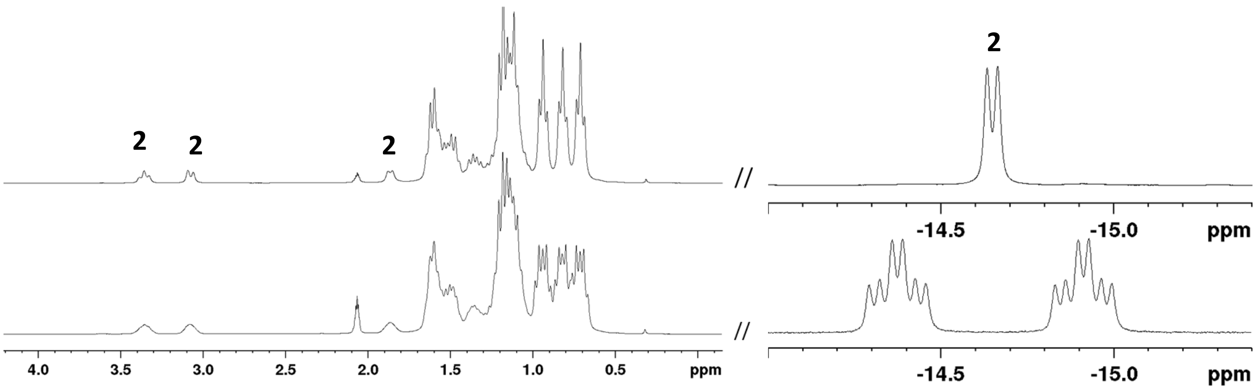


Figure S4 $^{1}H\{^{31}P\}$ (top) and ^{1}H (bottom) NMR (300.1 MHz, d_8-Tol, 213 K) spectra of *fac*-[Rh(H)(η^2-$CH_2CHC_6F_5$)(PEt_3)$_3$] (**2**).

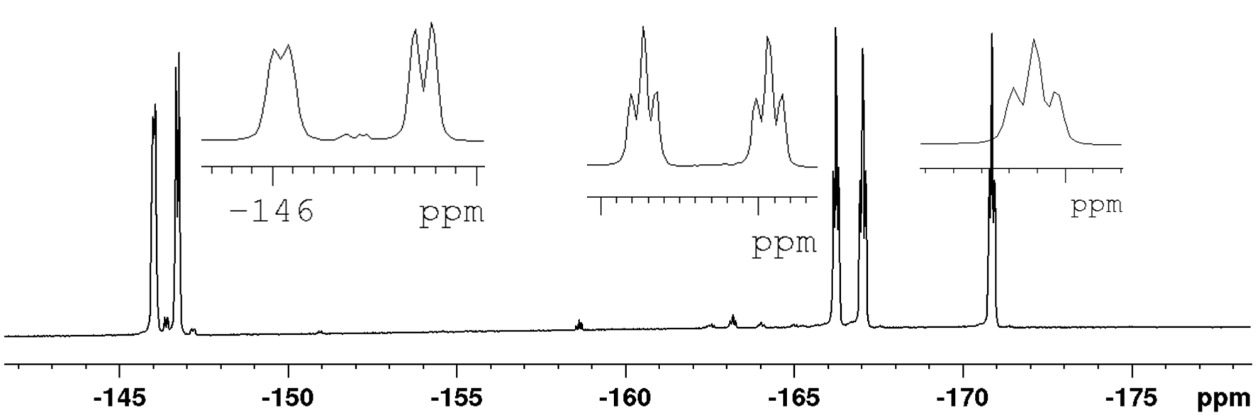


Figure S5 ^{19}F NMR (282.4 MHz, d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-$CH_2CHC_6F_5$)(PEt_3)$_3$] (**2**).

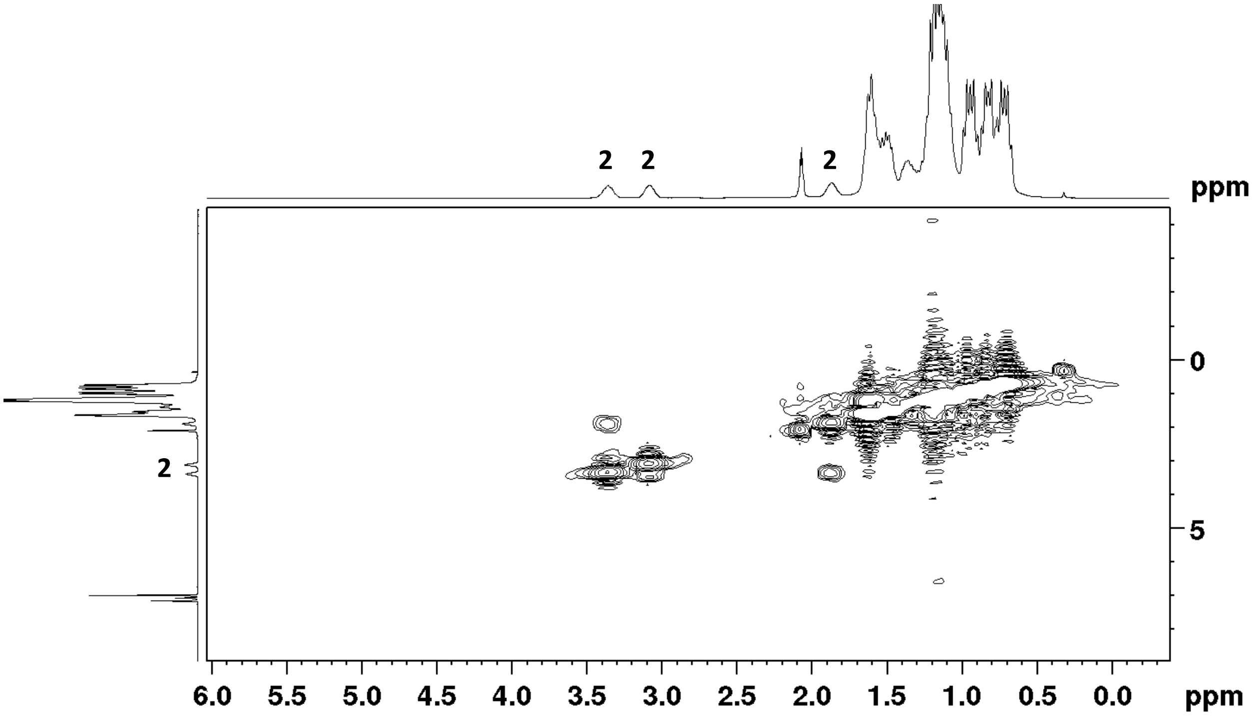


Figure S6 ^{1}H-^{1}H COSY NMR (d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH$_2$CHC$_6$F$_5$)(PEt$_3$)$_3$] (**2**).

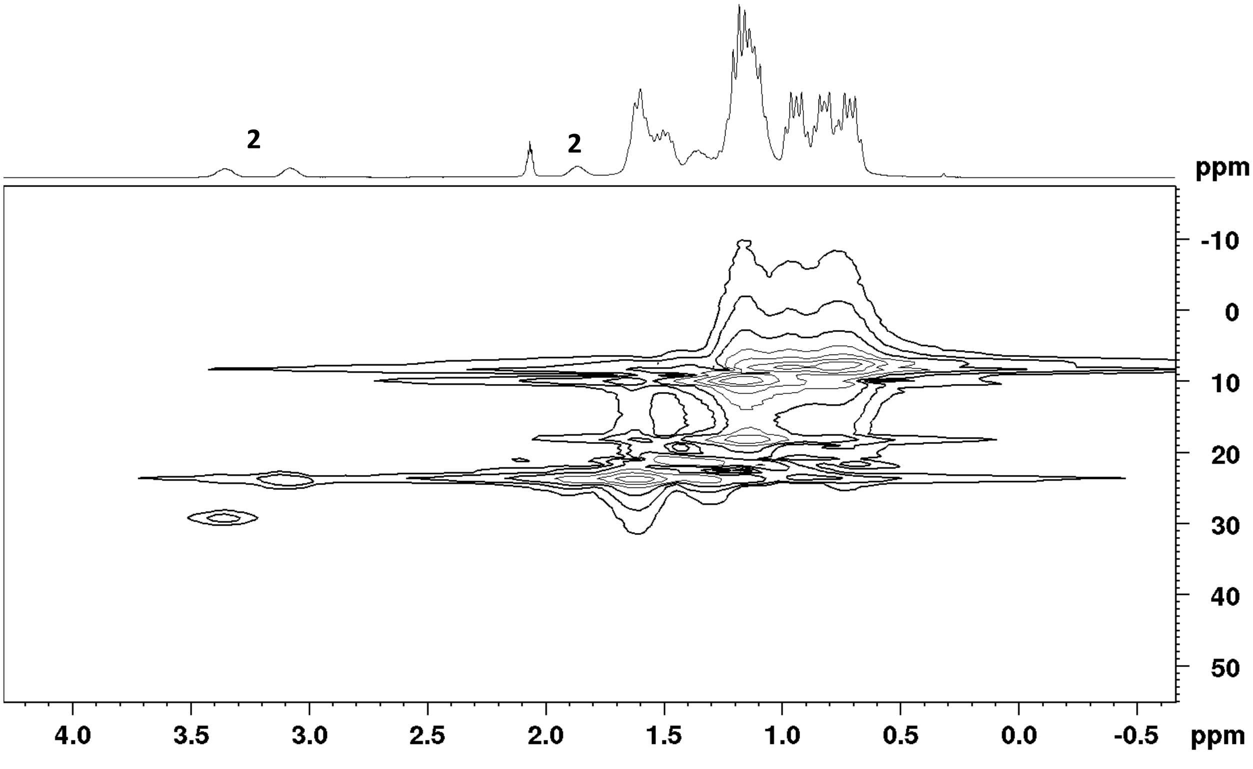


Figure S7 ^{1}H-^{13}C HMQC NMR (d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH$_2$CHC$_6$F$_5$)(PEt$_3$)$_3$] (**2**).

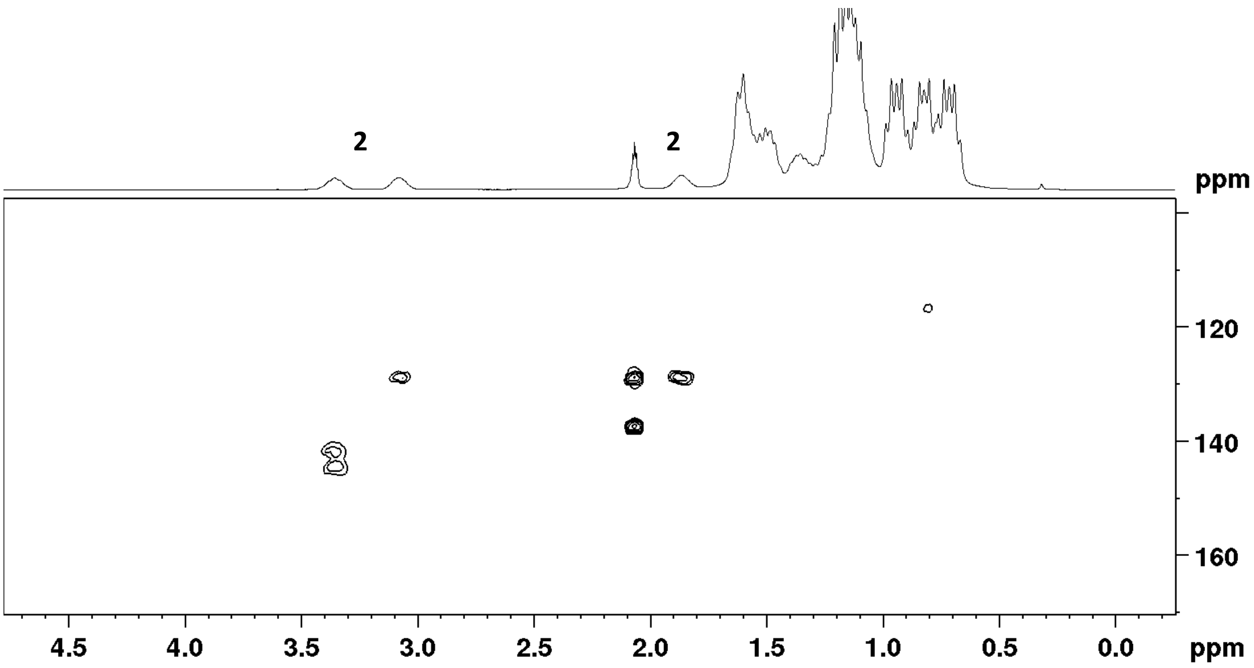


Figure S8 ^{1}H-^{13}C HMBC NMR (d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-$CH_2CHC_6F_5$)(PEt_3)$_3$] (**2**).

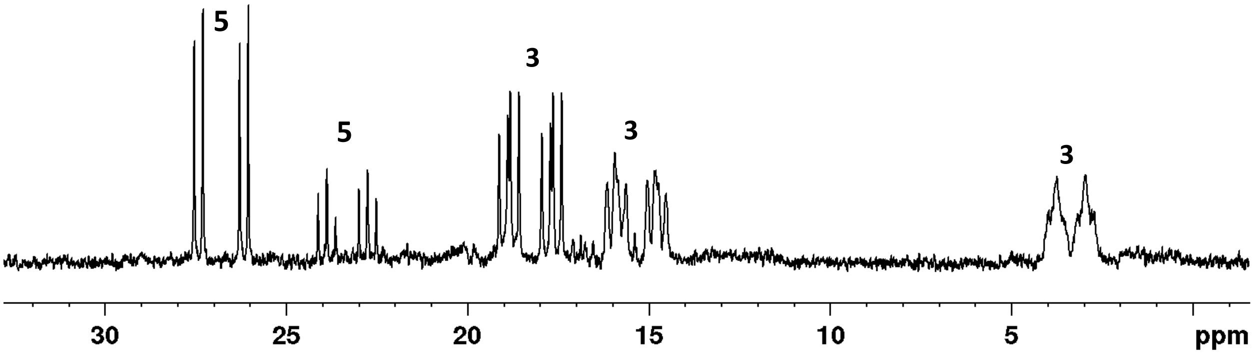


Figure S9 ^{31}P{^{1}H} NMR (121.5 MHz, d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH(Bpin)CHC_6F_5)(PEt_3)$_3$] (**3**).

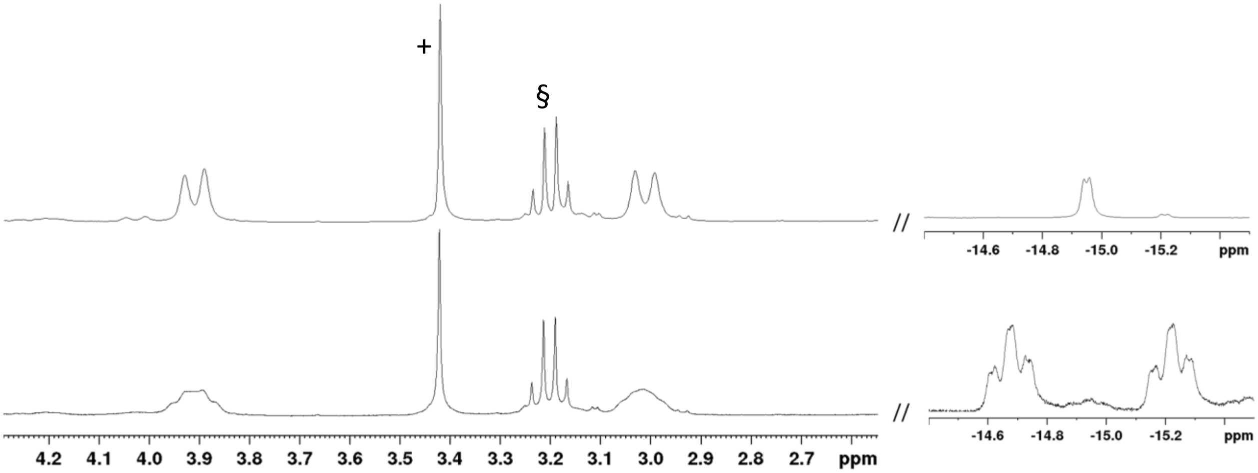


Figure S10 Part of the $^1H\{^{31}P\}$ (top) and ^1H (bottom) NMR (300.1 MHz, d_8-Tol, 213 K) spectra of *fac*-[Rh(H)(η^2-CH(Bpin)CHC$_6$F$_5$)(PEt$_3$)$_3$] (**3**). + MeOH; § Et$_2$O. Both are left from starting material.

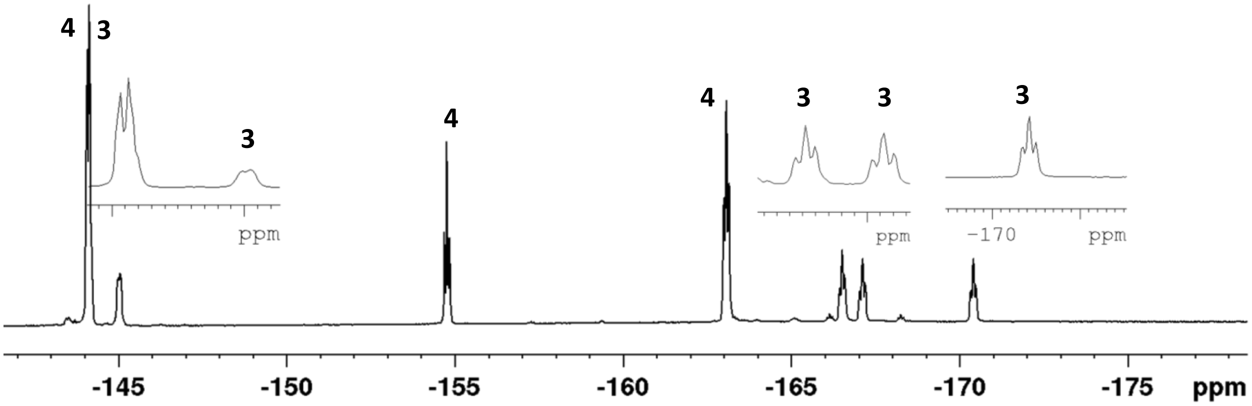


Figure S11 ^{19}F NMR (282.4 MHz, d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH(Bpin)CHC$_6$F$_5$)(PEt$_3$)$_3$] (**3**).

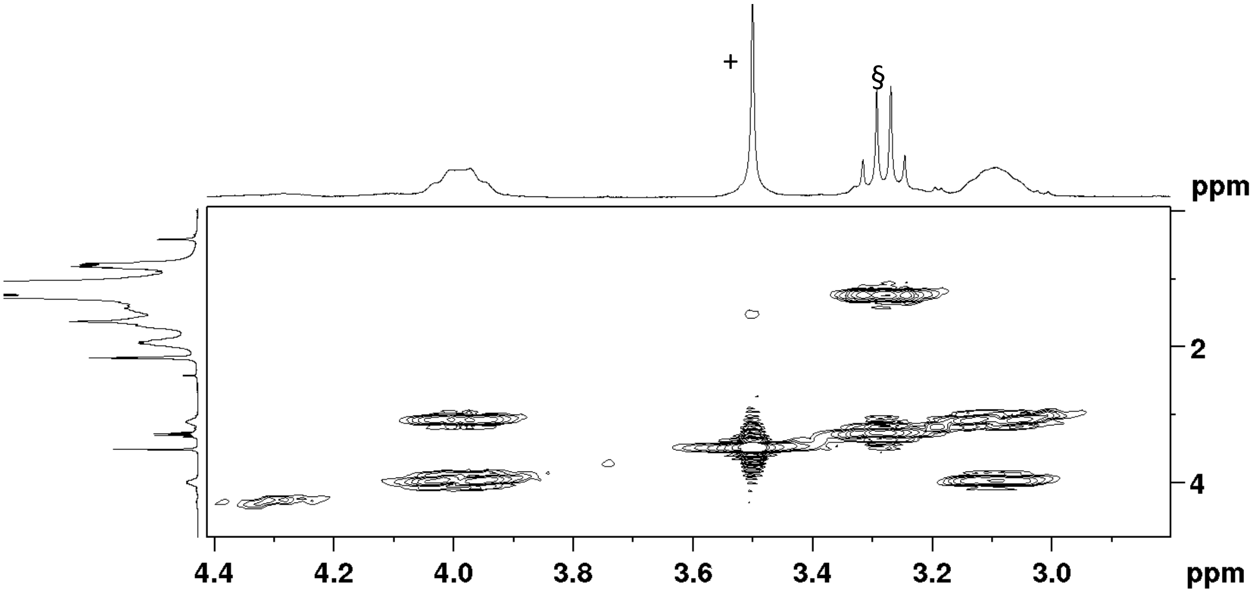


Figure S12 Part of the ^{1}H-^{1}H COSY NMR (*d$_8$*-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH(Bpin)CHC$_6$F$_5$)(PEt$_3$)$_3$] (**3**). + MeOH; § Et$_2$O. Both are left from starting material.

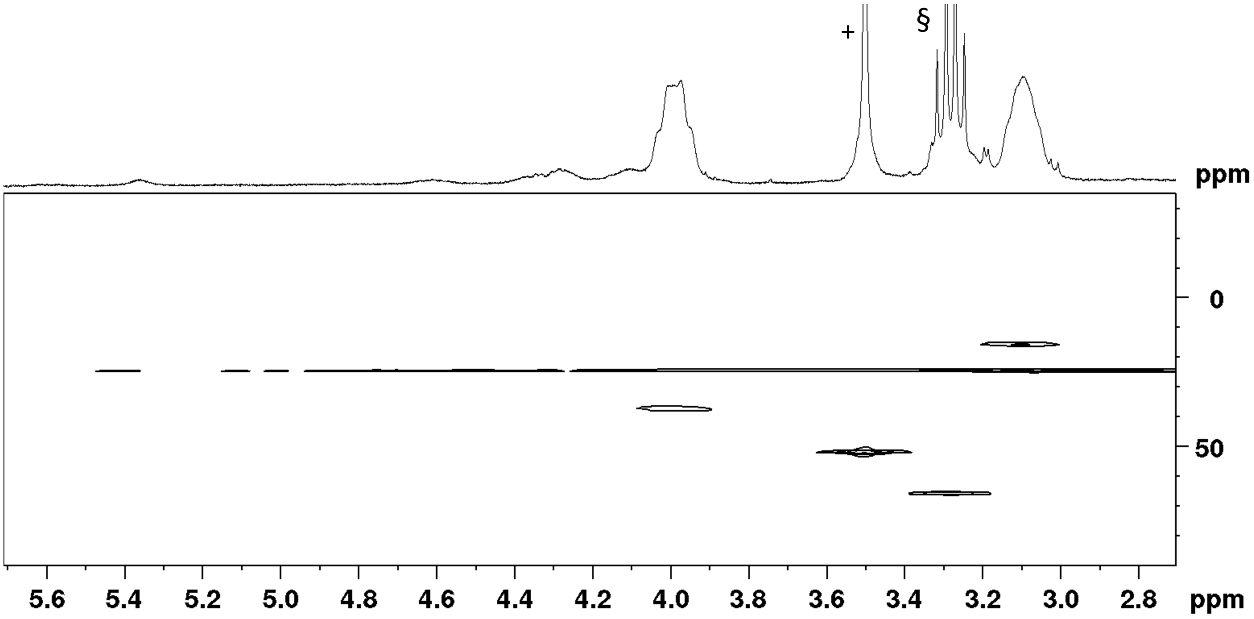


Figure S13 Part of the ^{1}H-^{13}C HMQC NMR (*d$_8$*-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH(Bpin)CHC$_6$F$_5$)(PEt$_3$)$_3$] (**3**). + MeOH; § Et$_2$O. Both are left from starting material.

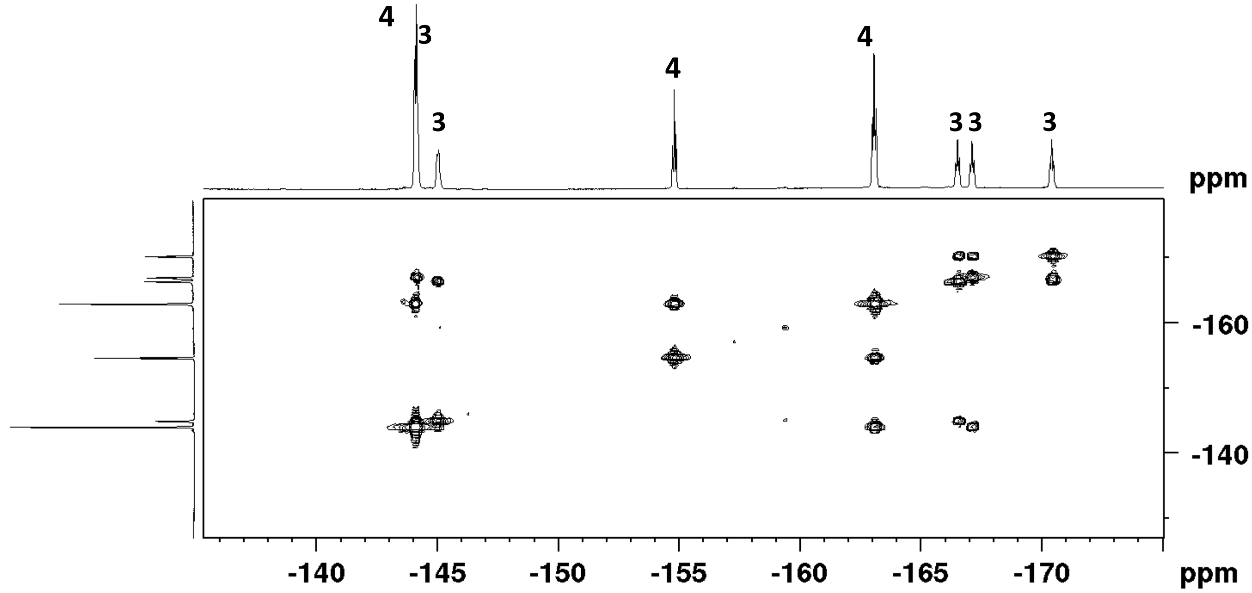


Figure S14 ^{19}F-^{19}F COSY NMR (d_8-Tol, 213 K) spectrum of *fac*-[Rh(H)(η^2-CH(Bpin)CHC$_6$F$_5$)(PEt$_3$)$_3$] (**3**).

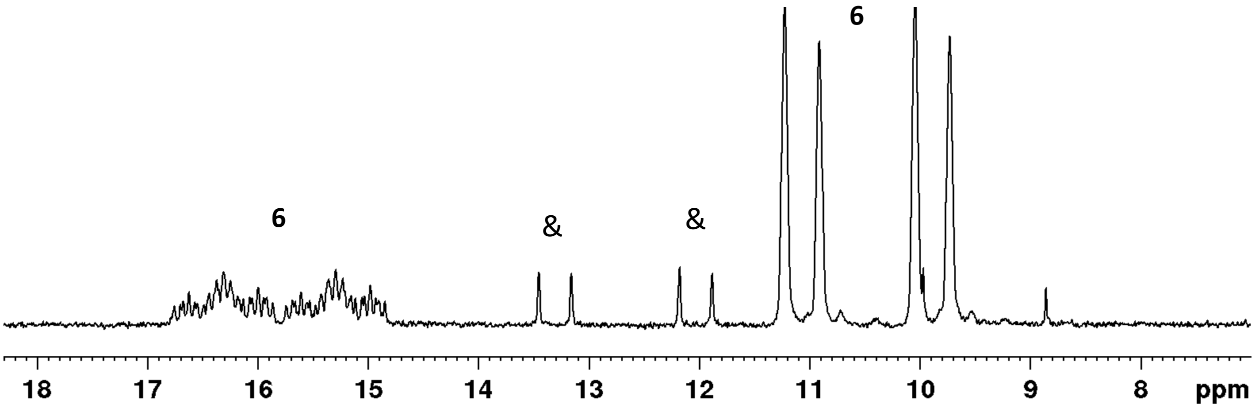


Figure S15 $^{31}P\{^1H\}$ NMR (121.5 MHz, d_8-Tol, 253 K) spectrum of [Rh(2-C$_6$F$_4$CHCH$_2$)(PEt$_3$)$_3$] (**6**); & unidentified complex.

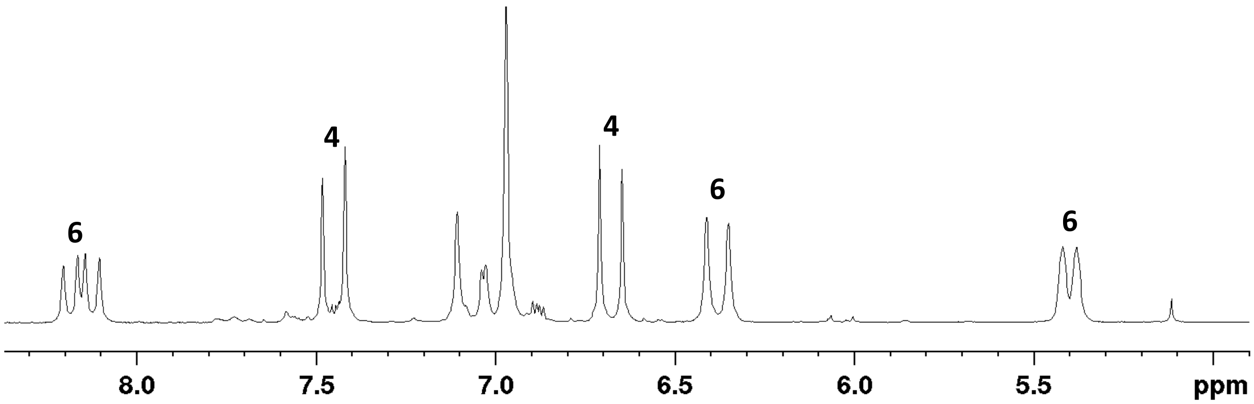


Figure S16 Part of the ^{1}H NMR (300.1 MHz, d_8-Tol, 253 K) spectrum of [Rh(2-$C_6F_4CHCH_2$)$(PEt_3)_3$] (**6**).

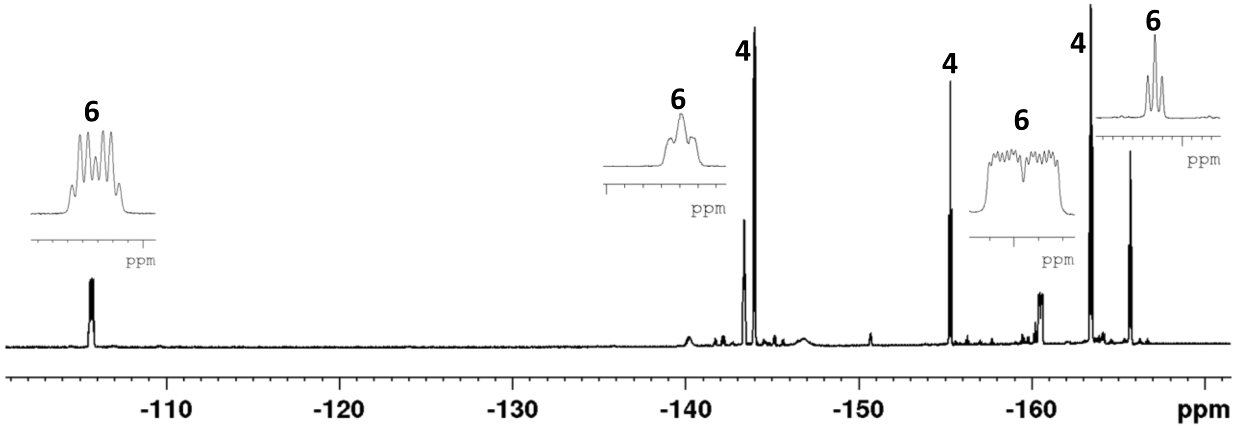


Figure S17 ^{19}F NMR (282.4 MHz, d_8-Tol, 253 K) spectrum of [Rh(2-$C_6F_4CHCH_2$)$(PEt_3)_3$] (**6**).

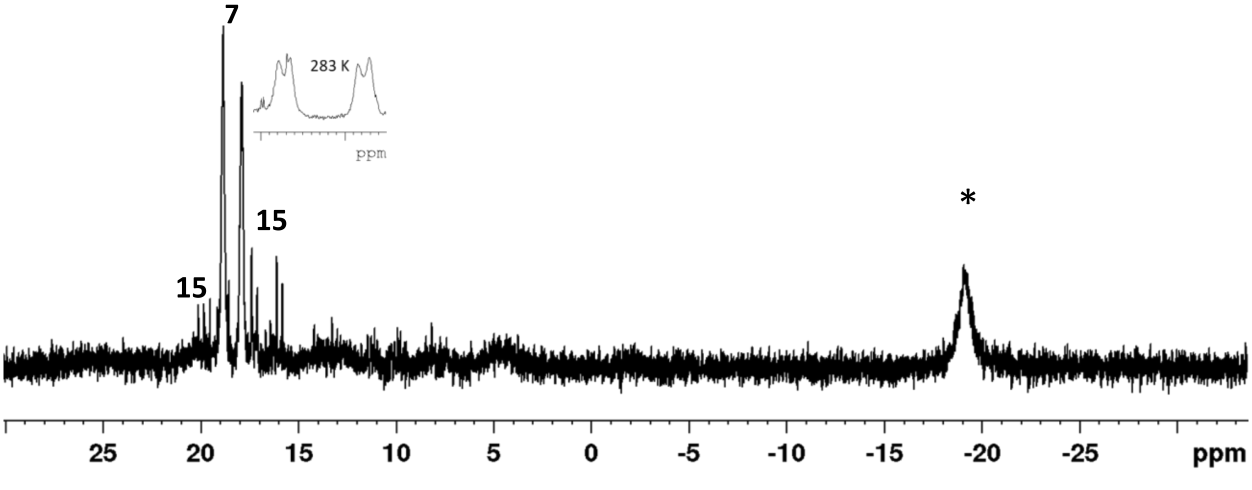


Figure S18 ^{31}P{^{1}H} NMR (121.5 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)(CH_2CH_2(2-C_6F_4))$(PEt_3)_2$] (**7**). * PEt_3

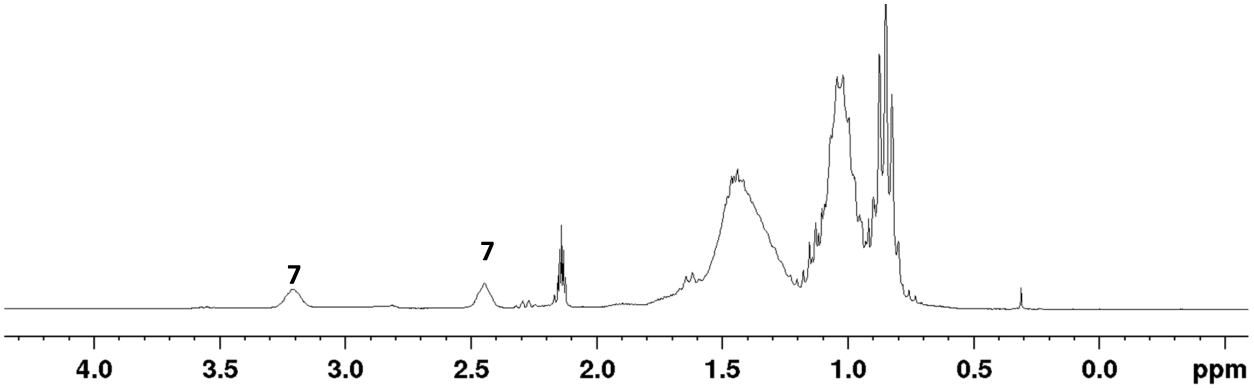


Figure S19 ^{1}H NMR (300.1 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_2$] (**7**).

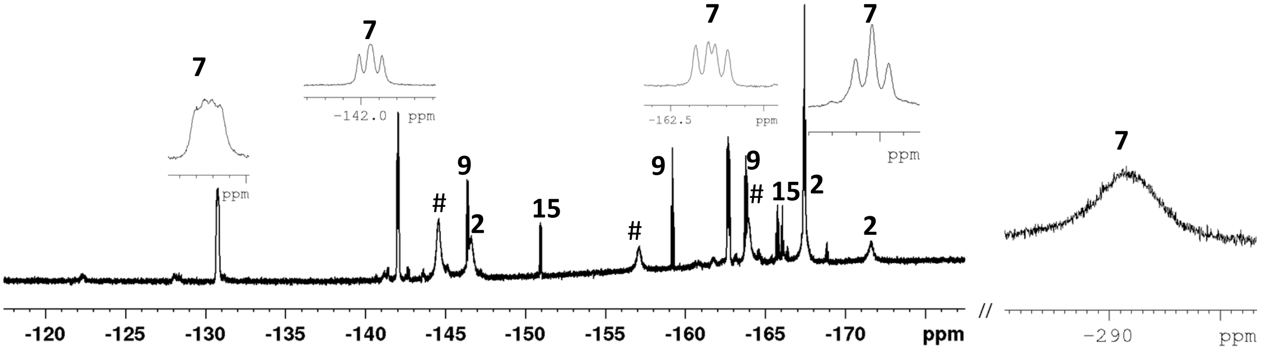


Figure S20 ^{19}F NMR (282.4 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_2$] (**7**).

free pentafluorostyrene

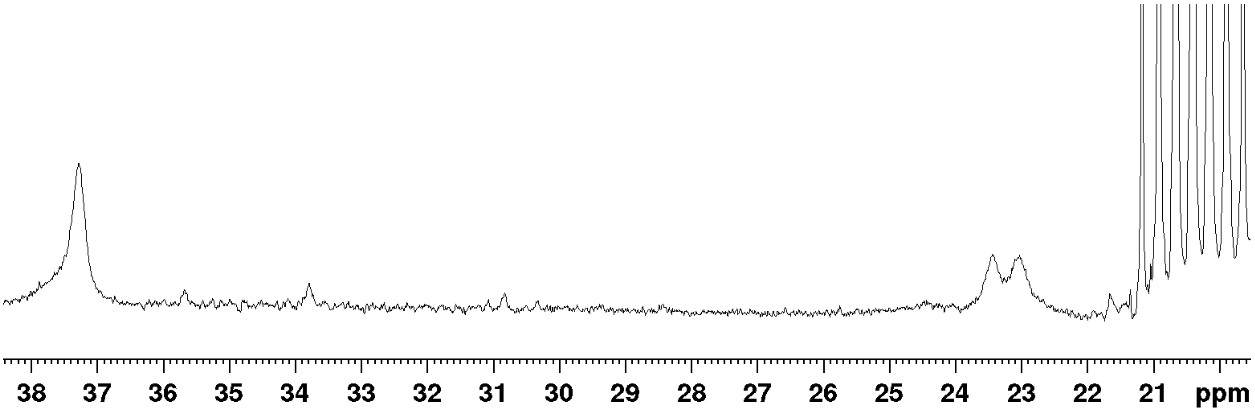


Figure S21 Part of the ^{13}C{^{1}H} NMR (75.5 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_2$] (**7**).

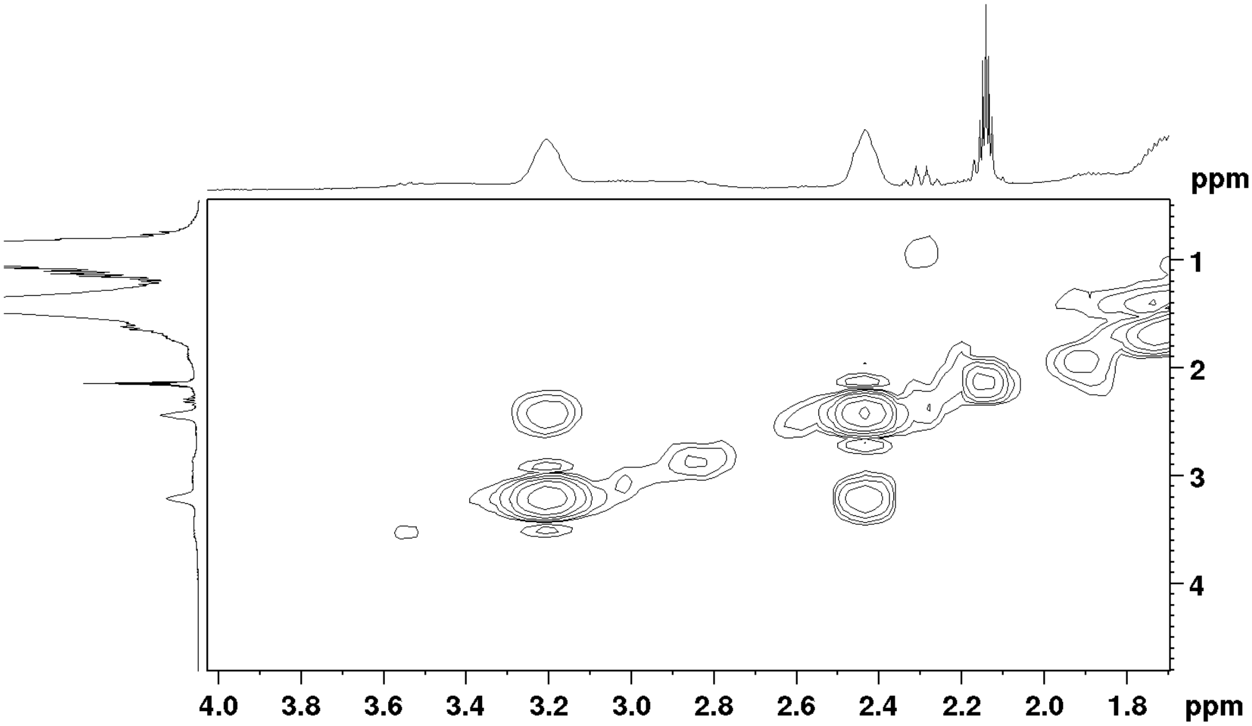


Figure S22 Part of the ^{1}H-^{1}H COSY NMR (d_8-Tol) spectrum of *trans*-[Rh(F)(CH_2CH_2(2-C_6F_4))(PEt_3)$_2$] (**7**).

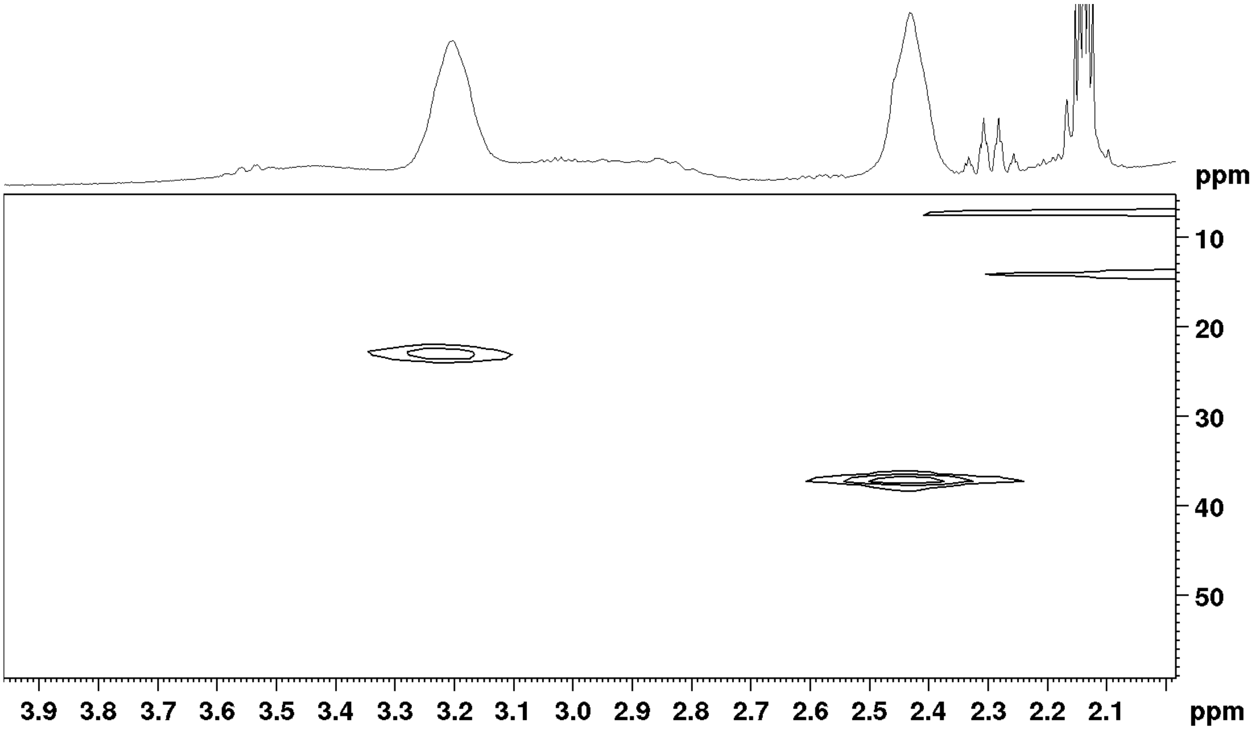


Figure S23 Part of the ^{1}H-^{13}C HMQC NMR (d_8-Tol) spectrum of *trans*-[Rh(F)(CH_2CH_2(2-C_6F_4))(PEt_3)$_2$] (**7**).

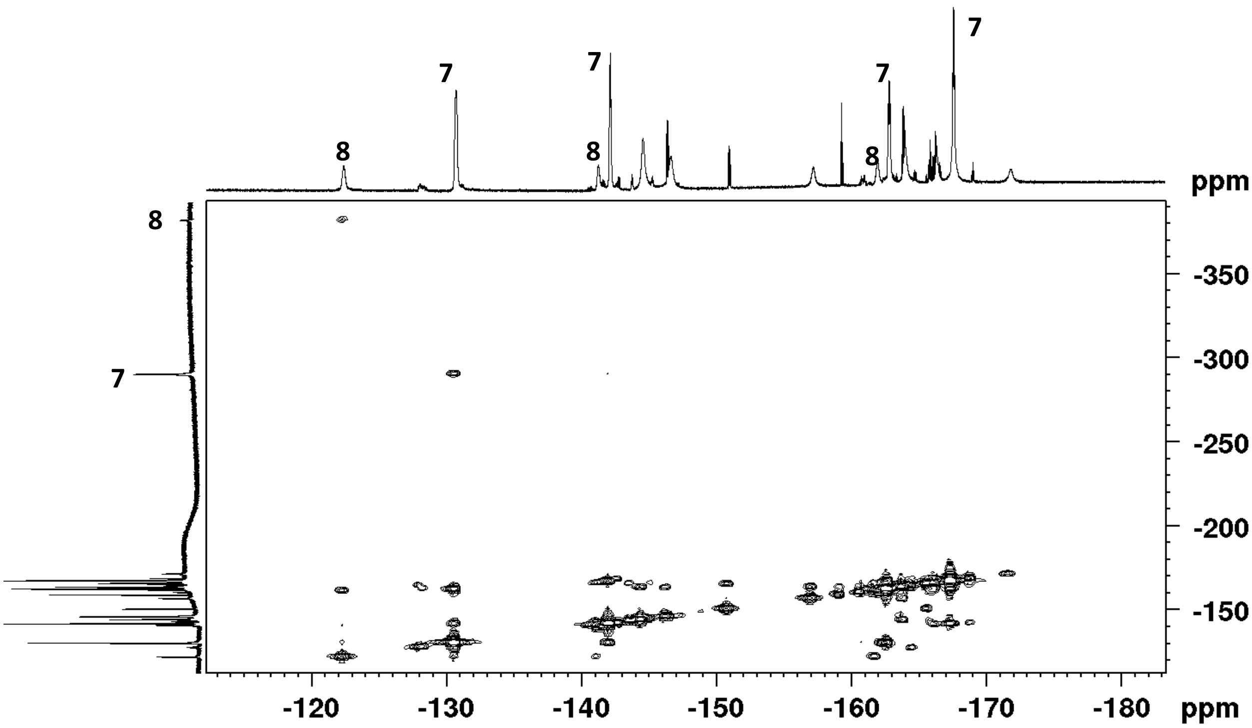


Figure S24 ^{19}F-^{19}F COSY NMR (d_8-Tol) spectrum of *trans*-[Rh(F)(CH$_2$CH$_2$-(2-C$_6$F$_4$))(PEt$_3$)$_2$] (**7**) and *mer*-[Rh(F)(CH$_2$CH$_2$(2-C$_6$F$_4$))(PEt$_3$)$_3$] (**8**).

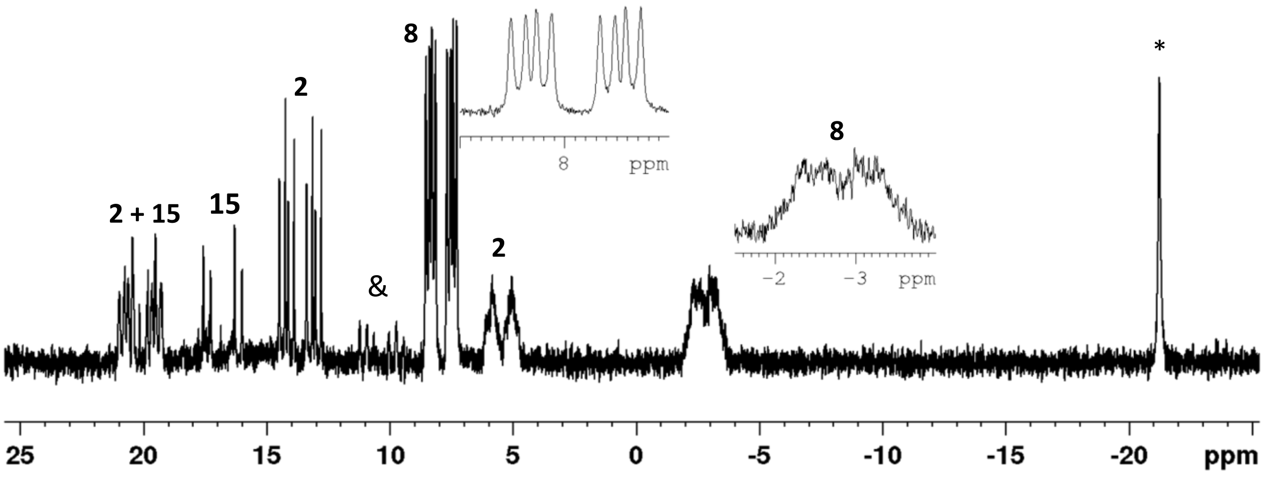


Figure S25 ^{31}P{^{1}H} NMR (121.5 MHz, d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH$_2$CH$_2$-(2-C$_6$F$_4$))(PEt$_3$)$_3$] (**8**).* PEt$_3$, & unidentified complex.

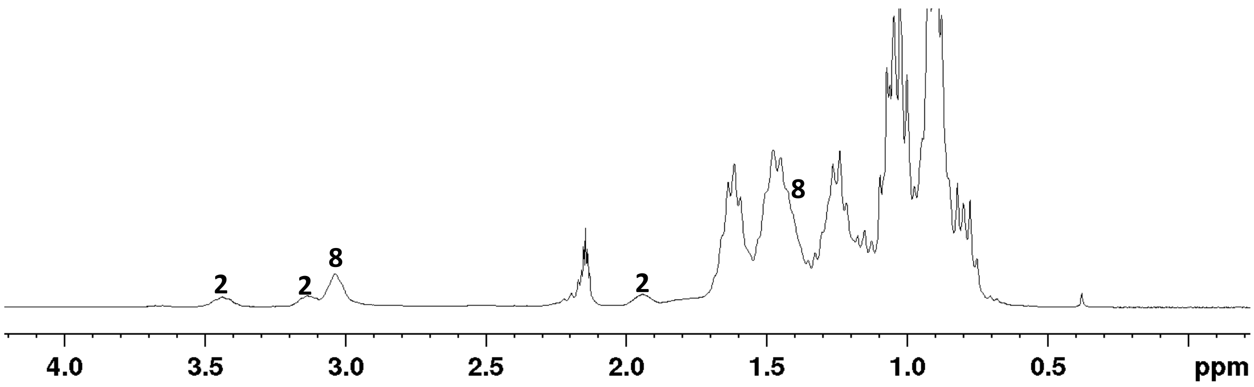


Figure S26 ^{1}H NMR (300.1 MHz, d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH_2CH_2-(2-C_6F_4))(PEt_3)$_3$] (**8**).

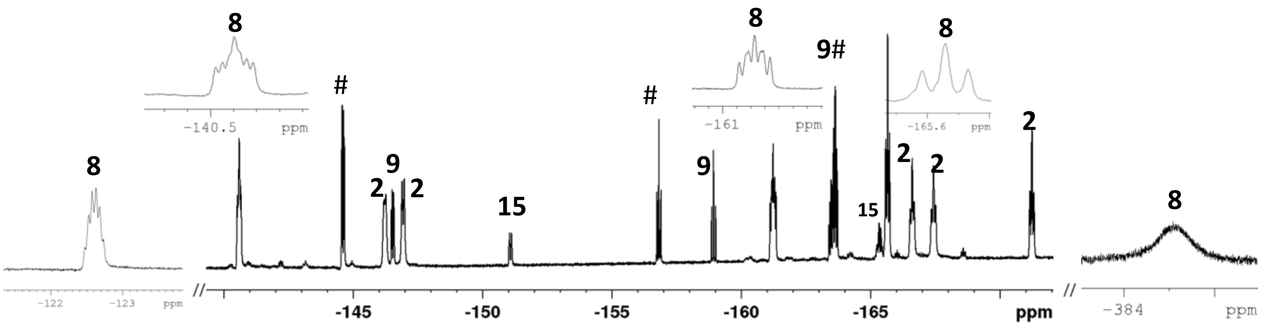


Figure S27 ^{19}F NMR (282.4 MHz, d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH_2CH_2-(2-C_6F_4))(PEt_3)$_3$] (**8**), # free pentafluorostyrene.

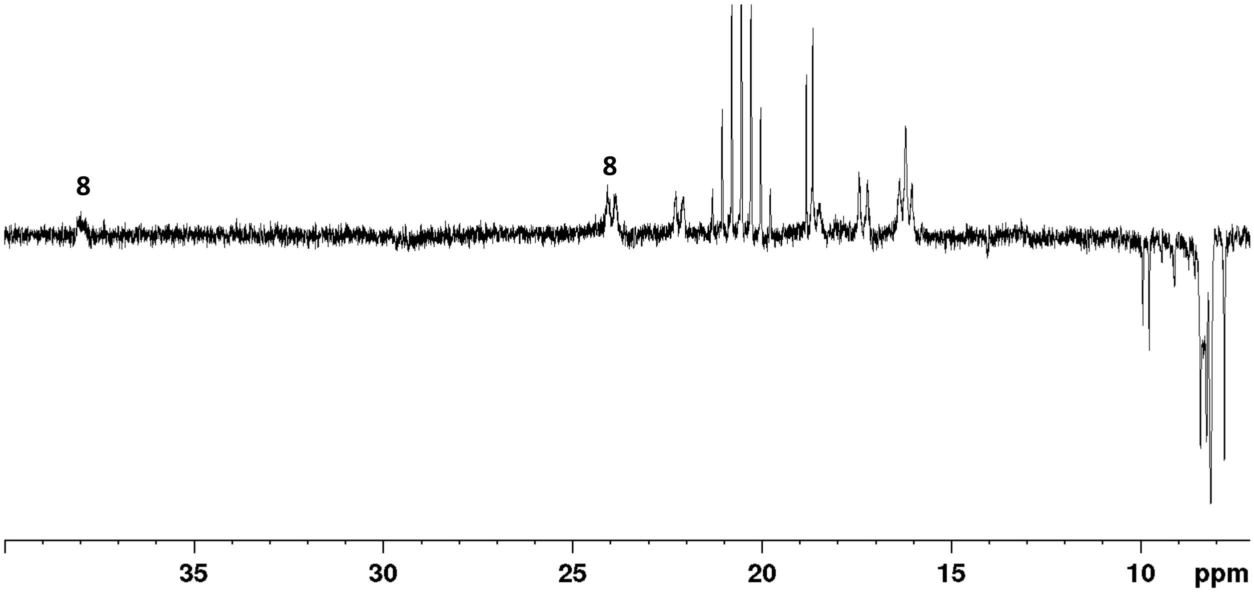


Figure S28 Part of the APT NMR (d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH_2CH_2(2-C_6F_4))(PEt_3)$_3$] (**8**).

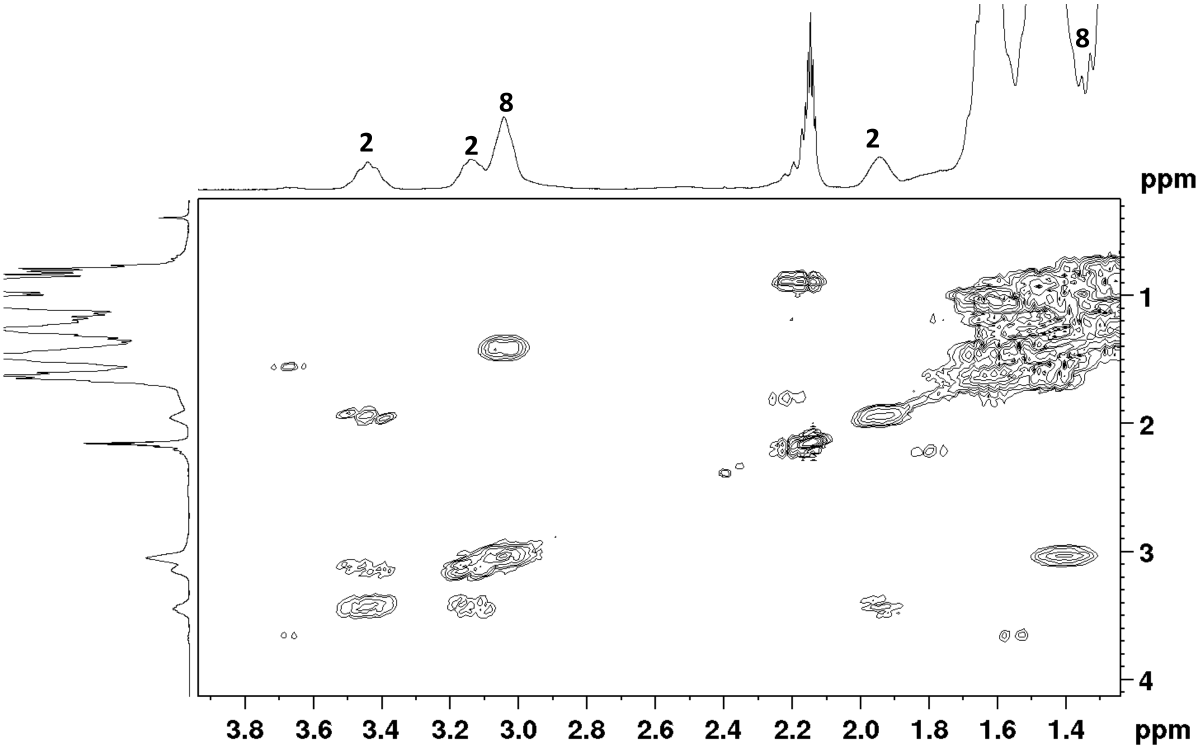


Figure S29 Part of the ^1H-^1H COSY NMR (d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH_2CH_2-(2-C_6F_4))(PEt_3)$_3$] (**8**).

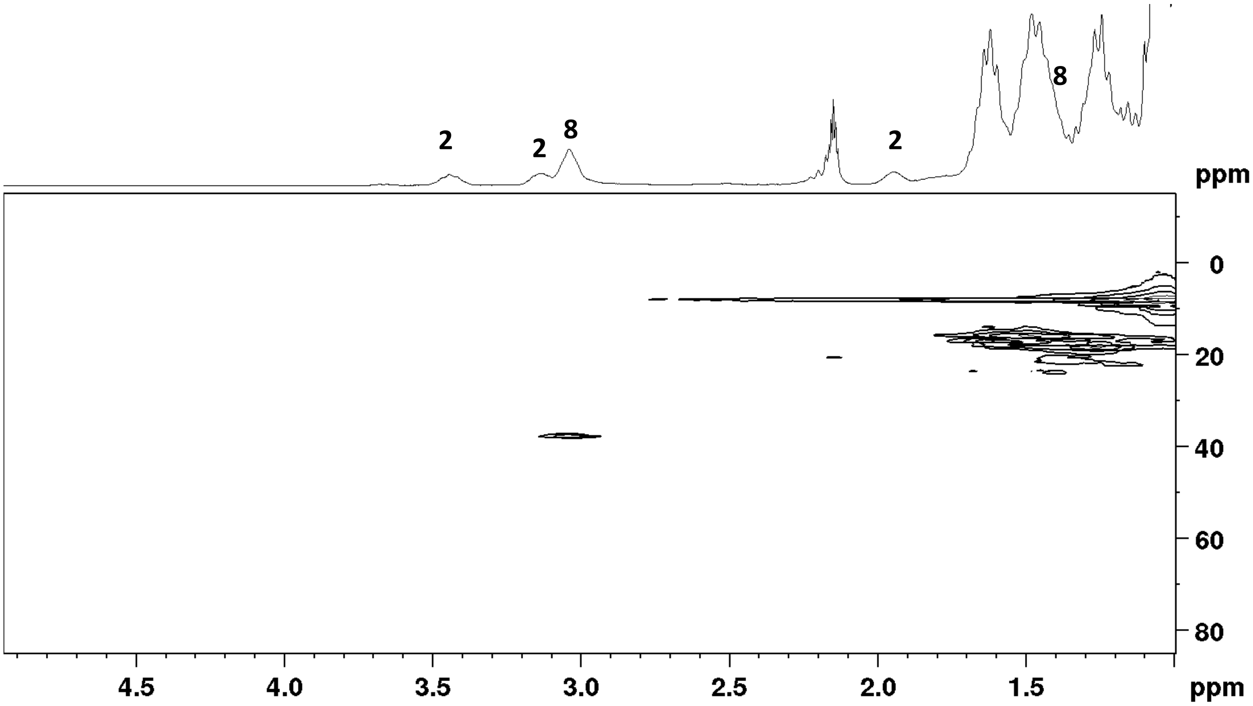


Figure S30 Part of the ^1H-^{13}C HMQC NMR (d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH_2CH_2-(2-C_6F_4))(PEt_3)$_3$] (**8**).

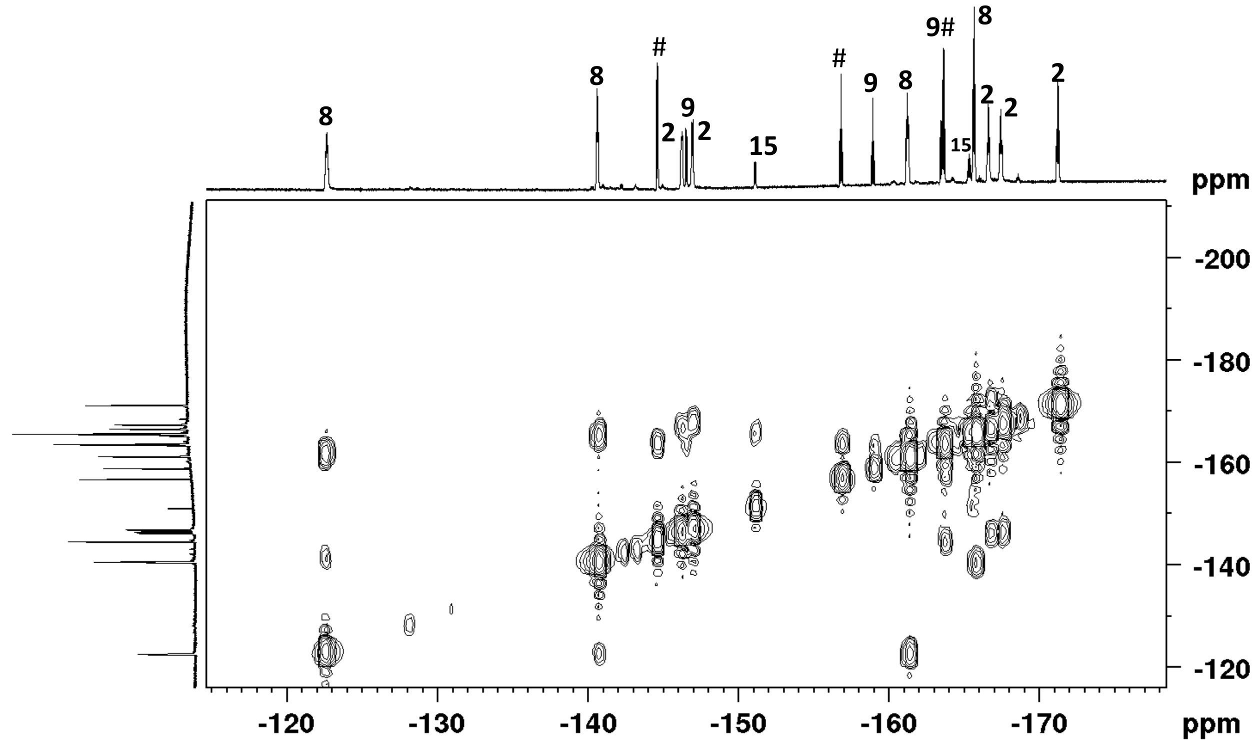


Figure S31 Part of the ^{19}F-^{19}F COSY NMR (d_8-Tol, 233 K) spectrum of *mer*-[Rh(F)(CH_2CH_2-(2-C_6F_4))(PEt_3)$_3$] (**8**); # free pentafluorostyrene.

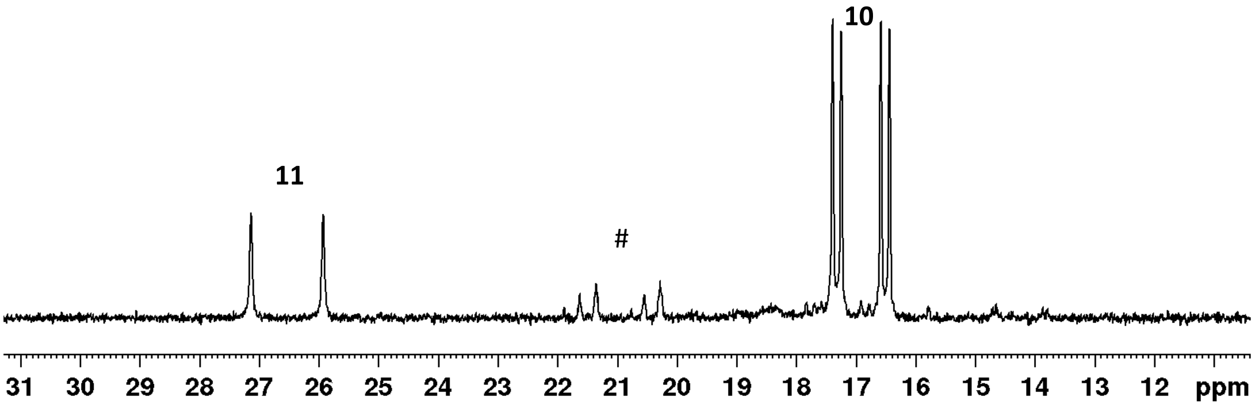


Figure S32 $^{31}P\{^1H\}$ NMR (121.5 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(CO)(PEt_3)$_2$] (**10**) and [Rh(H)(CO)(PEt_3)$_3$] (**11**); # unidentified complex.

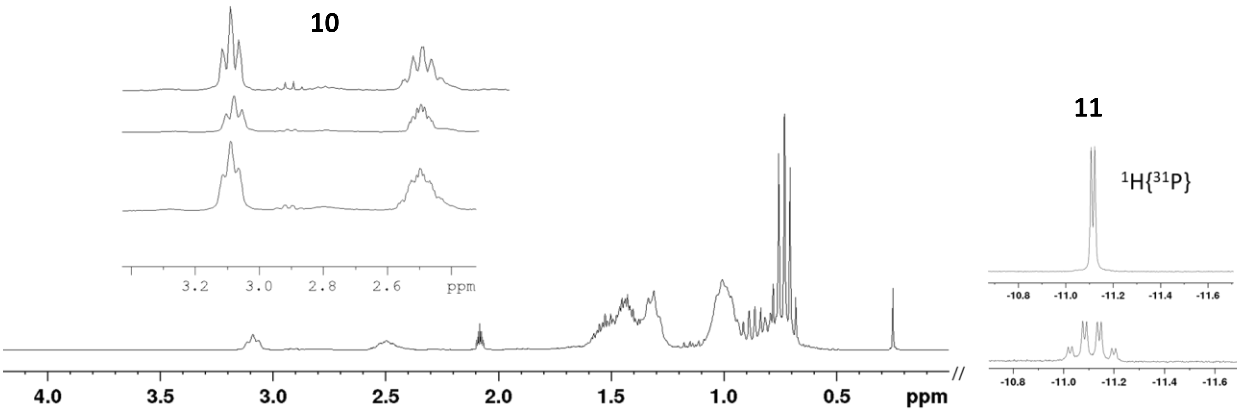


Figure S33 ^{1}H{^{19}F}, ^{1}H{^{31}P} and ^{1}H (top to bottom) NMR (300.1 MHz, d_8-Tol) spectra of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(CO)(PEt_3)$_2$] (**10**) and [Rh(H)(^{13}CO)(PEt_3)$_3$] (**11**) (243 K).

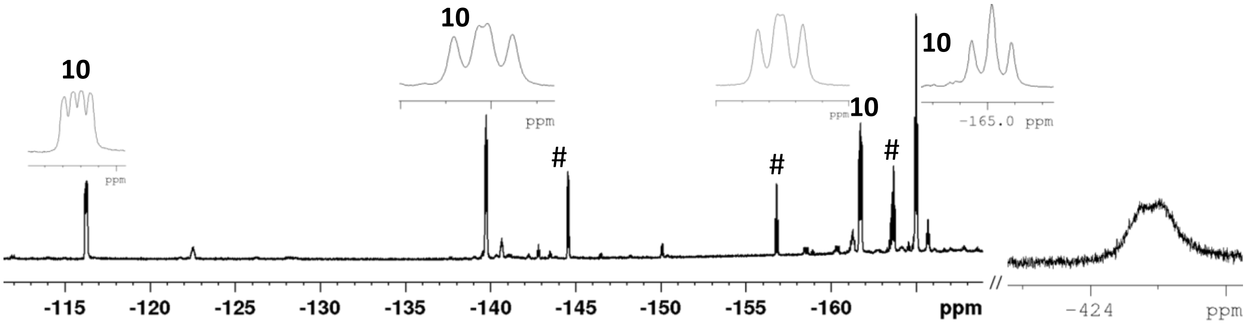


Figure S34 ^{19}F NMR (282.4 MHz, d_8-Tol, 243 K) spectrum of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(CO)(PEt_3)$_2$] (**10**); # free pentafluorostyrene.

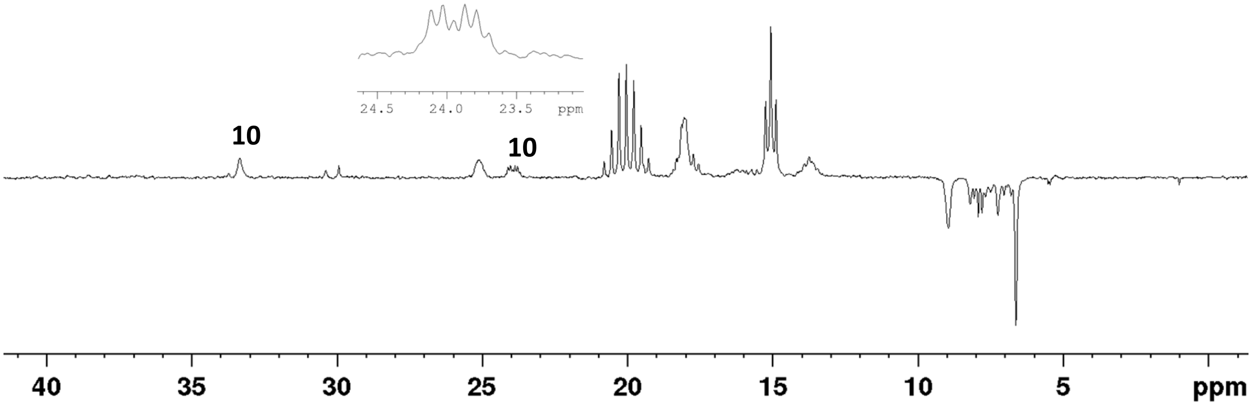


Figure S35 Part of the APT NMR (75.5 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(CO)(PEt_3)$_2$] (**10**).

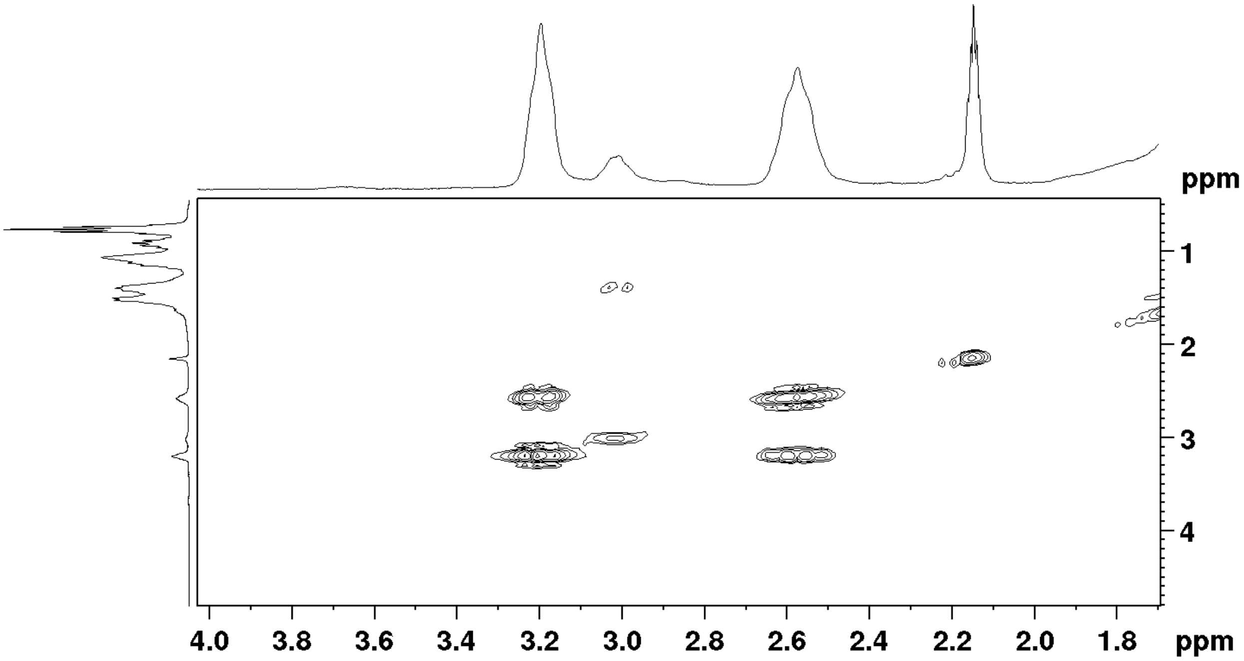


Figure S36 Part of the ^{1}H-^{1}H COSY NMR (d_8-Tol) spectrum of *trans*-[Rh(F)(CH$_2$CH$_2$C$_6$F$_4$)(CO)(PEt$_3$)$_2$] (**10**).

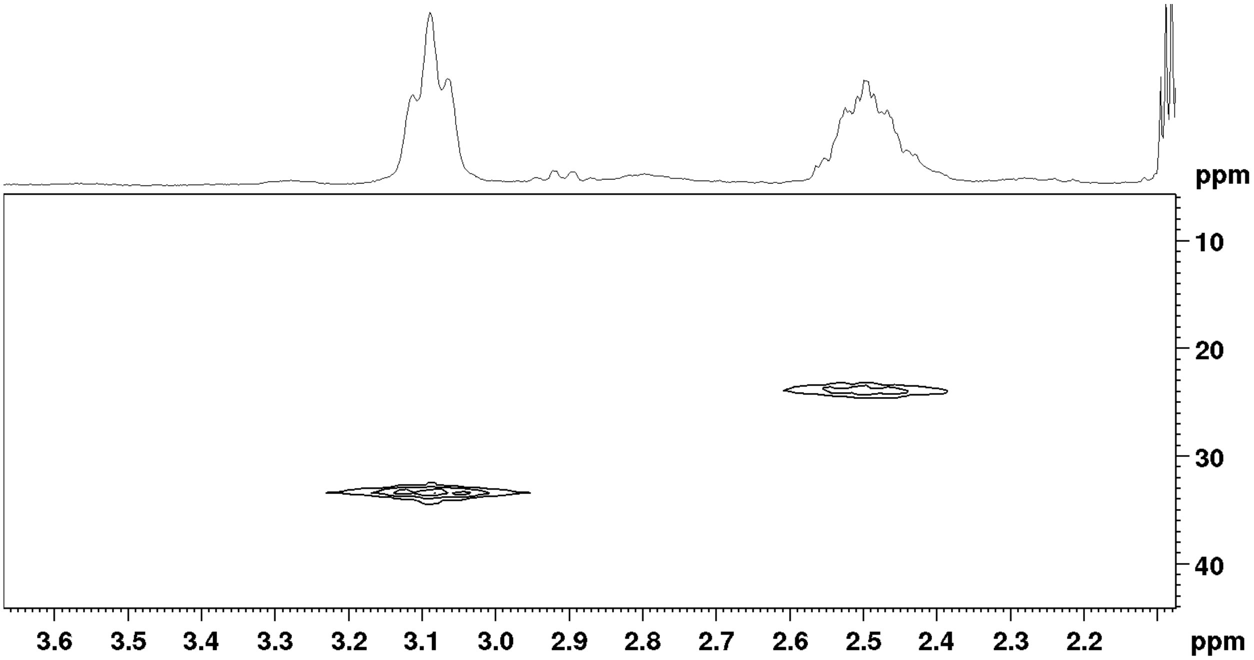


Figure S37 Part of the ^{1}H-^{13}C HMQC NMR (d_8-Tol) spectrum of *trans*-[Rh(F)(CH$_2$CH$_2$C$_6$F$_4$)(CO)(PEt$_3$)$_2$] (**10**).

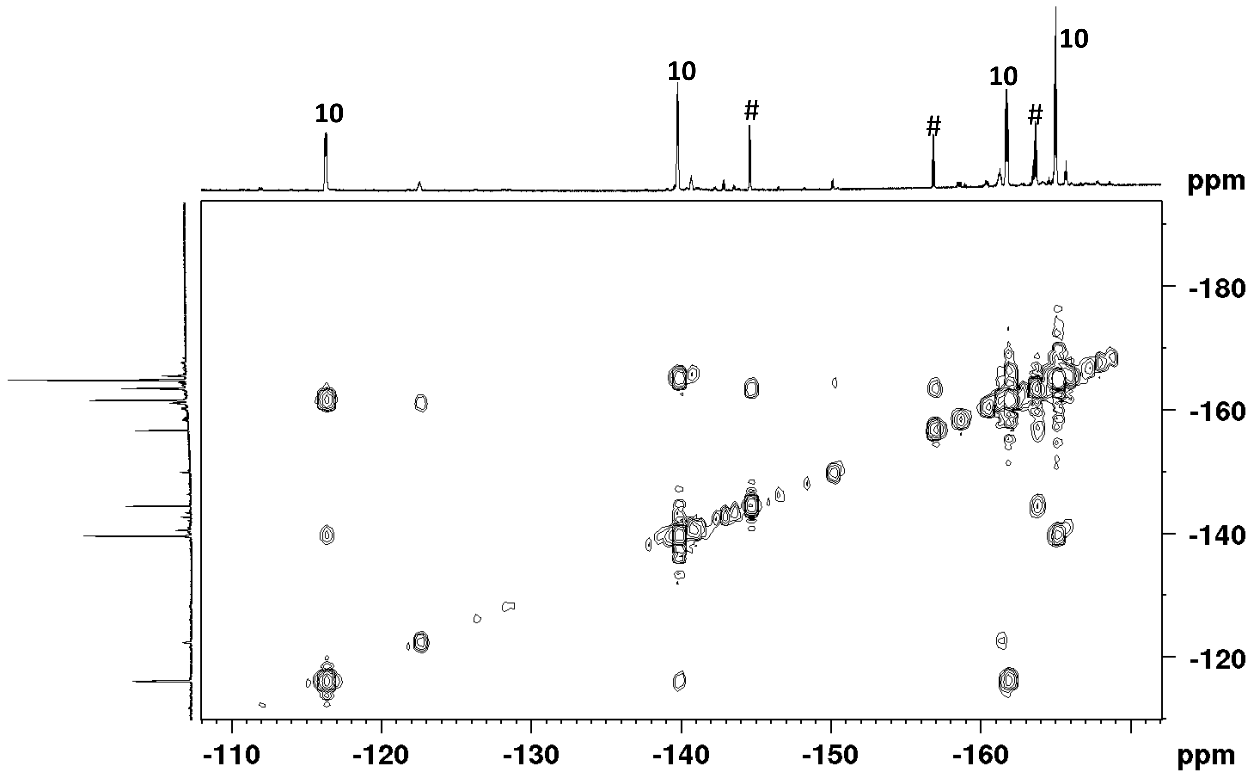


Figure S38 Part of the ^{19}F-^{19}F COSY NMR (d_8-Tol) spectrum of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(CO)(PEt_3)$_2$] (**10**); # free pentafluorostyrene.

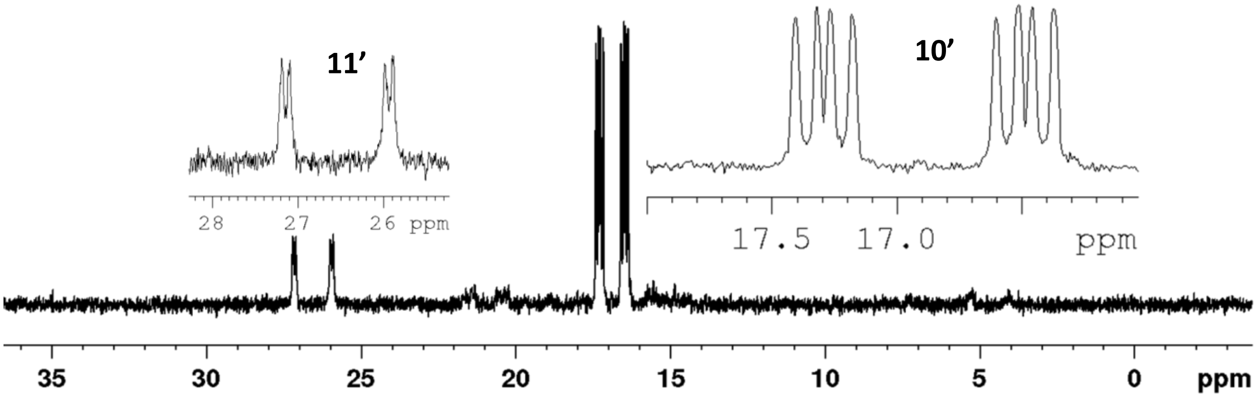


Figure S39 $^{31}P\{^1H\}$ NMR (121.5 MHz, d_8-Tol) spectrum of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(^{13}CO)(PEt_3)$_2$] (**10'**) and [Rh(H)(^{13}CO)(PEt_3)$_3$] (**11'**).

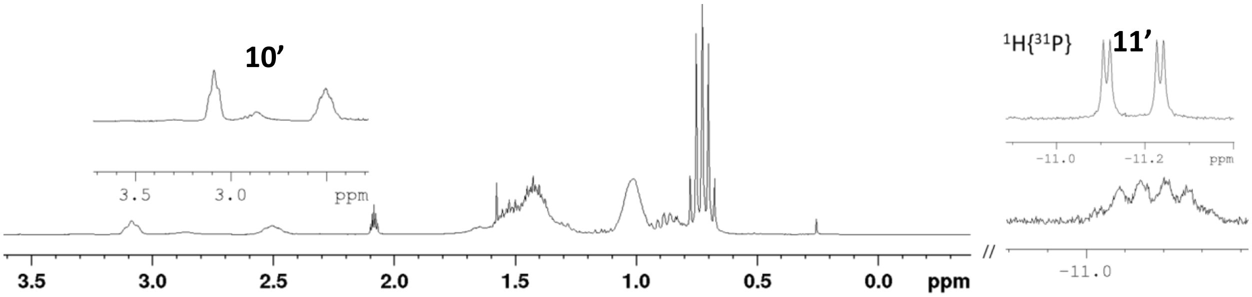


Figure S40 ^1H NMR (300.1 MHz, d_8-Tol) spectra of *trans*-[Rh(F)($CH_2CH_2C_6F_4$)(^{13}CO)(PEt_3)$_2$] (**10’**). [Rh(H)(^{13}CO)(PEt_3)$_3$] (**11’**)

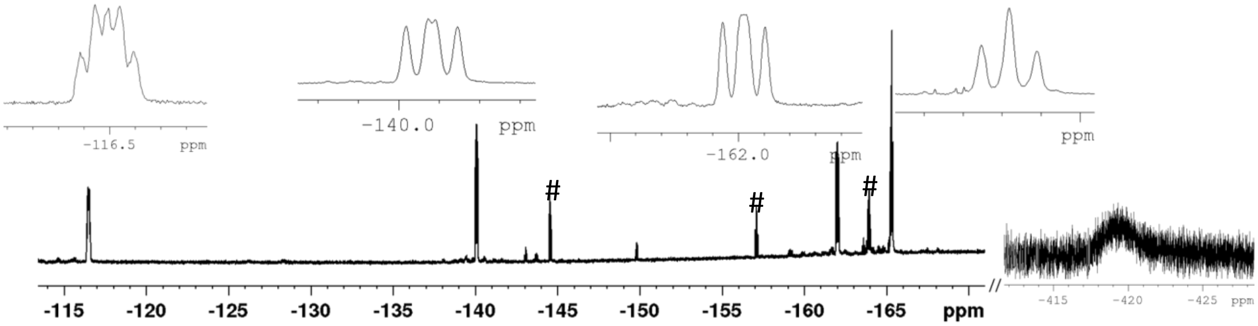


Figure S41 ^{19}F NMR (282.4 MHz, d_8-Tol) spectrum of *trans*- [Rh(F)($CH_2CH_2C_6F_4$)(^{13}CO)(PEt_3)$_2$] (**10’**); # free pentafluorostyrene.

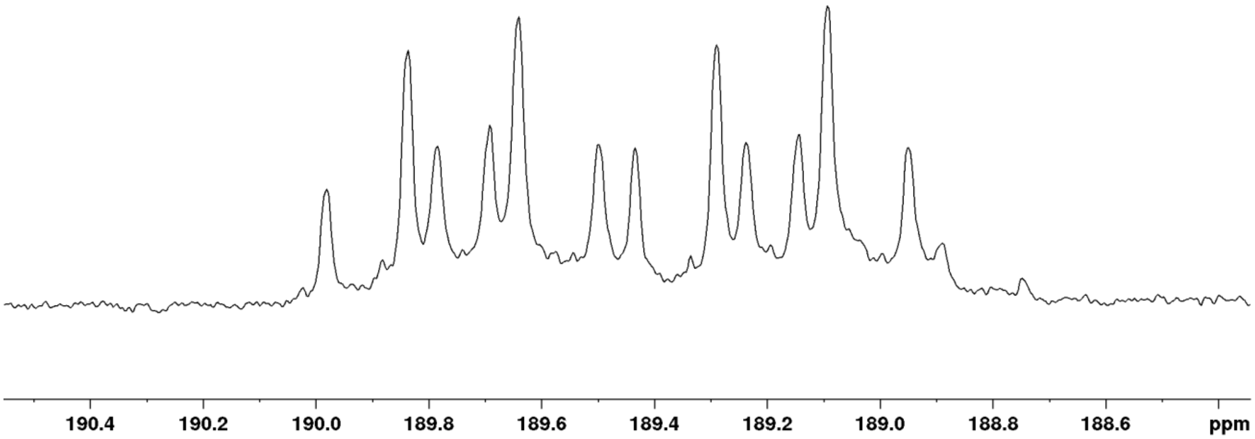


Figure S42 The signal for the ^{13}CO ligand of *trans*- [Rh(F)($CH_2CH_2C_6F_4$)(^{13}CO)(PEt_3)$_2$] (**10’**) in the APT ^{13}C NMR (75.5 MHz, d_8-Tol) spectrum.

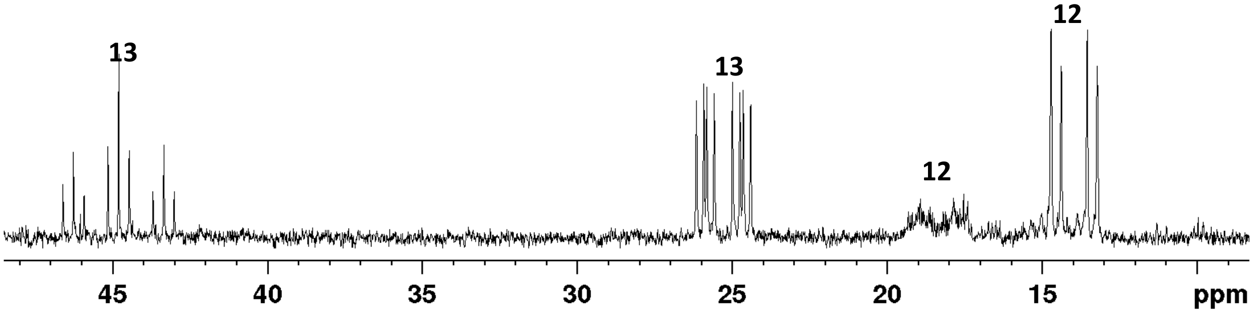


Figure S43 $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6) spectrum of [Rh(4-$C_6F_4CHCH_2$)(PEt_3)$_3$] (**12**). [Rh(F)(PEt_3)$_3$] (**13**)[7]

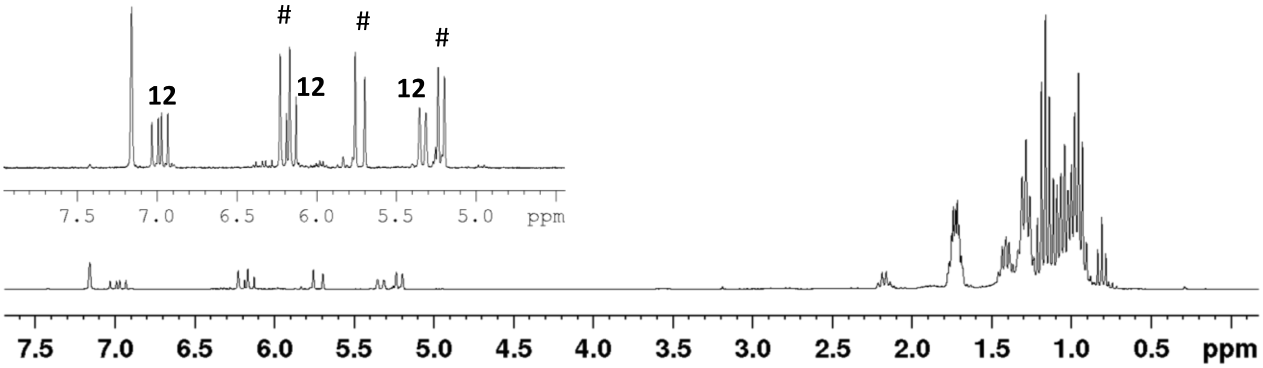


Figure S44 ^1H NMR (300.1 MHz, C_6D_6) spectrum of [Rh(4-$C_6F_4CHCH_2$)(PEt_3)$_3$] (**12**). # free pentafluorostyrene

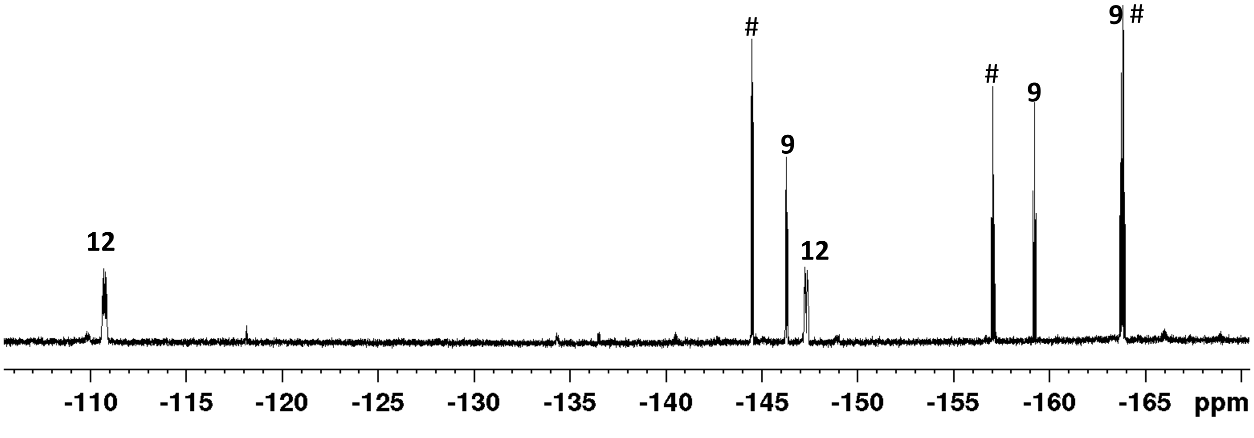


Figure S45 ^{19}F NMR (282.4 MHz, C_6D_6) spectrum of [Rh(4-$C_6F_4CHCH_2$)(PEt_3)$_3$] (**12**); # free pentafluorostyrene.

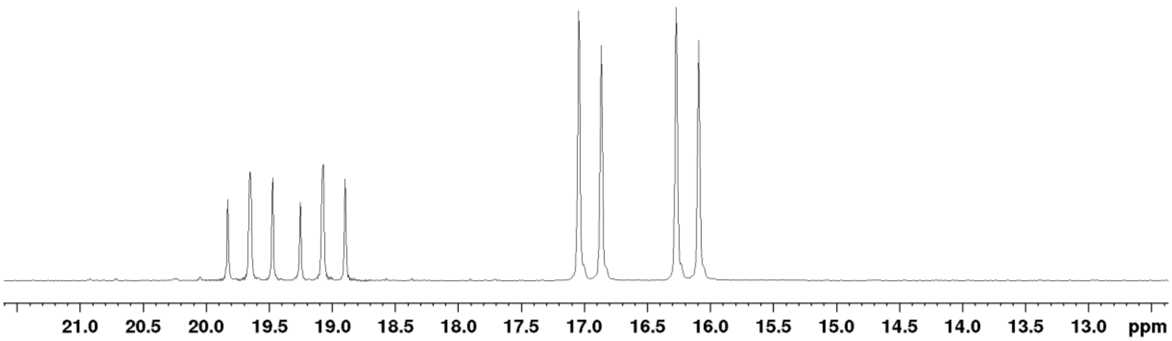


Figure S46 $^{31}P\{^1H\}$ NMR (202.5 MHz, d_8-THF) spectrum of [Rh(*E*-CHCHC$_6$F$_5$)(PEt$_3$)$_3$] (**15**).

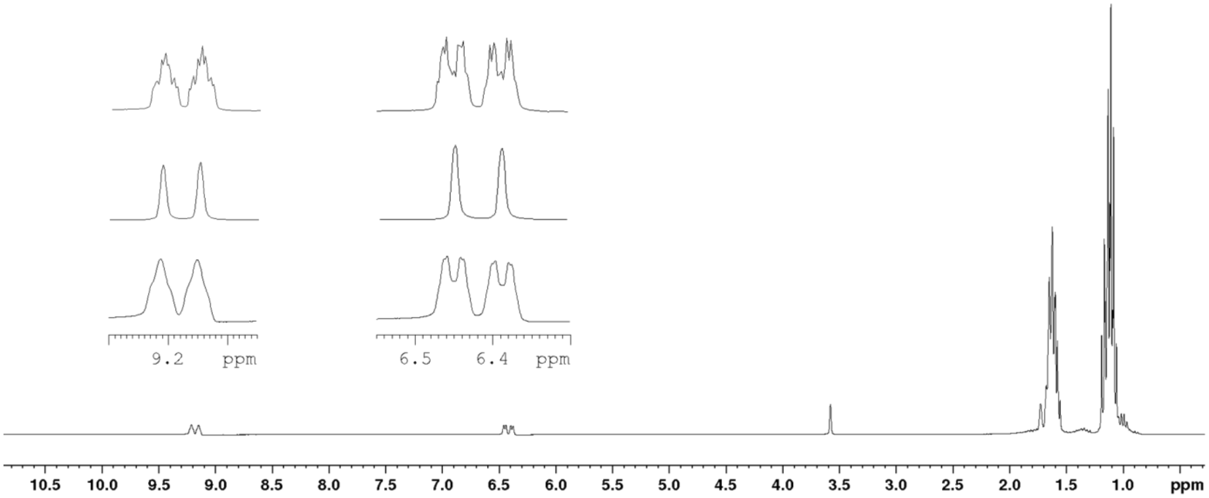


Figure S47 ^1H NMR (300.1 MHz, d_8-THF) spectrum of [Rh(*E*-CHCHC$_6$F$_5$)(PEt$_3$)$_3$] (**15**) showing the vinylic signals in the ^1H (bottom), $^1H\{^{31}P\}$ (middle) and $^1H\{^{19}F\}$ (top) spectra.

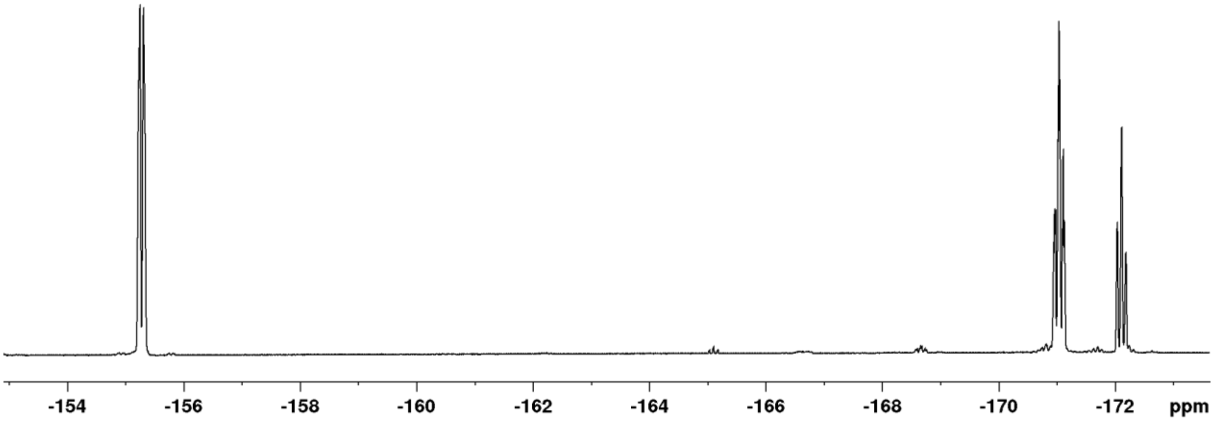


Figure S48 ^{19}F NMR (282.4 MHz, d_8-THF) spectrum of [Rh(*E*-CHCHC$_6$F$_5$)(PEt$_3$)$_3$] (**15**).

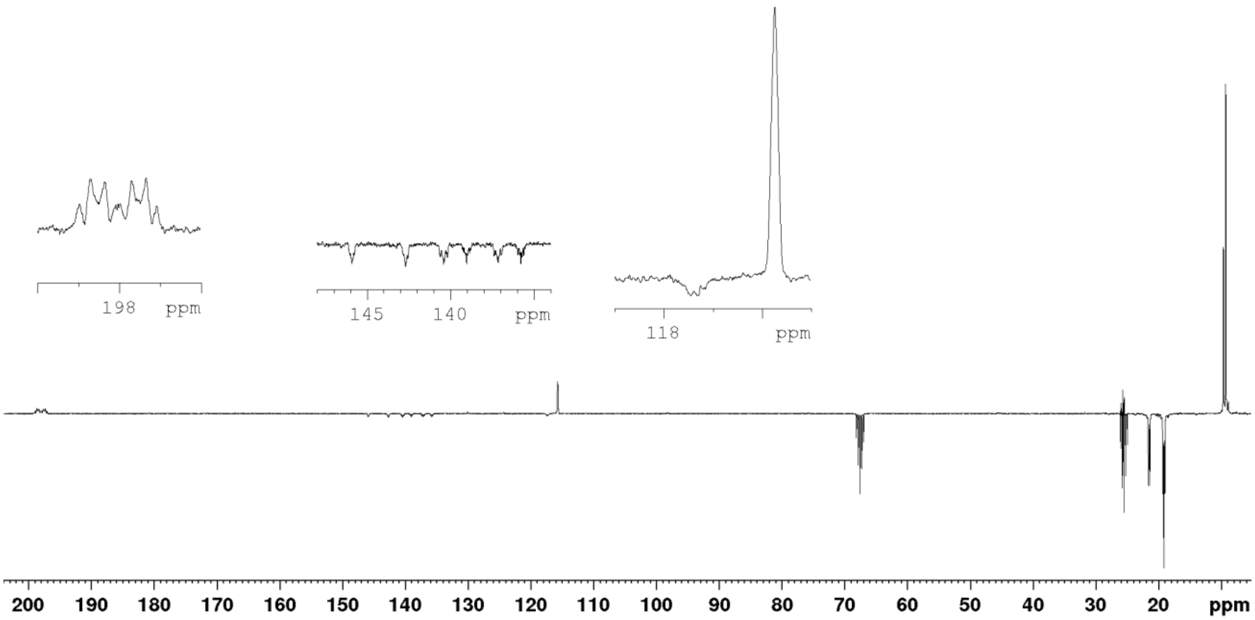


Figure S49 APT $^{13}C\{1H\}$ NMR (75.5 MHz, d_8-THF) spectrum of [Rh(*E*-$CHCHC_6F_5$)(PEt_3)$_3$] (**15**).

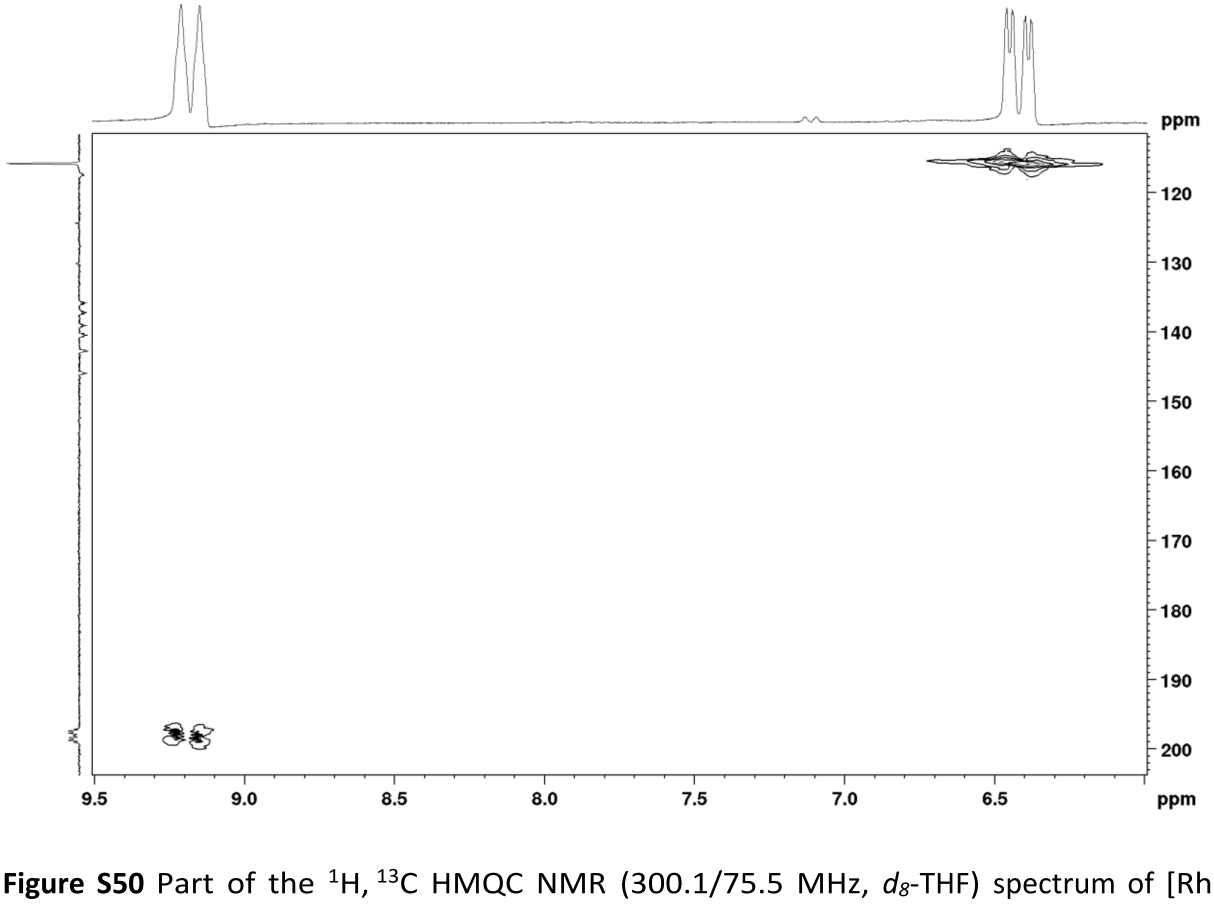


Figure S50 Part of the ^1H, ^{13}C HMQC NMR (300.1/75.5 MHz, d_8-THF) spectrum of [Rh(*E*-$CHCHC_6F_5$)(PEt_3)$_3$] (**15**).

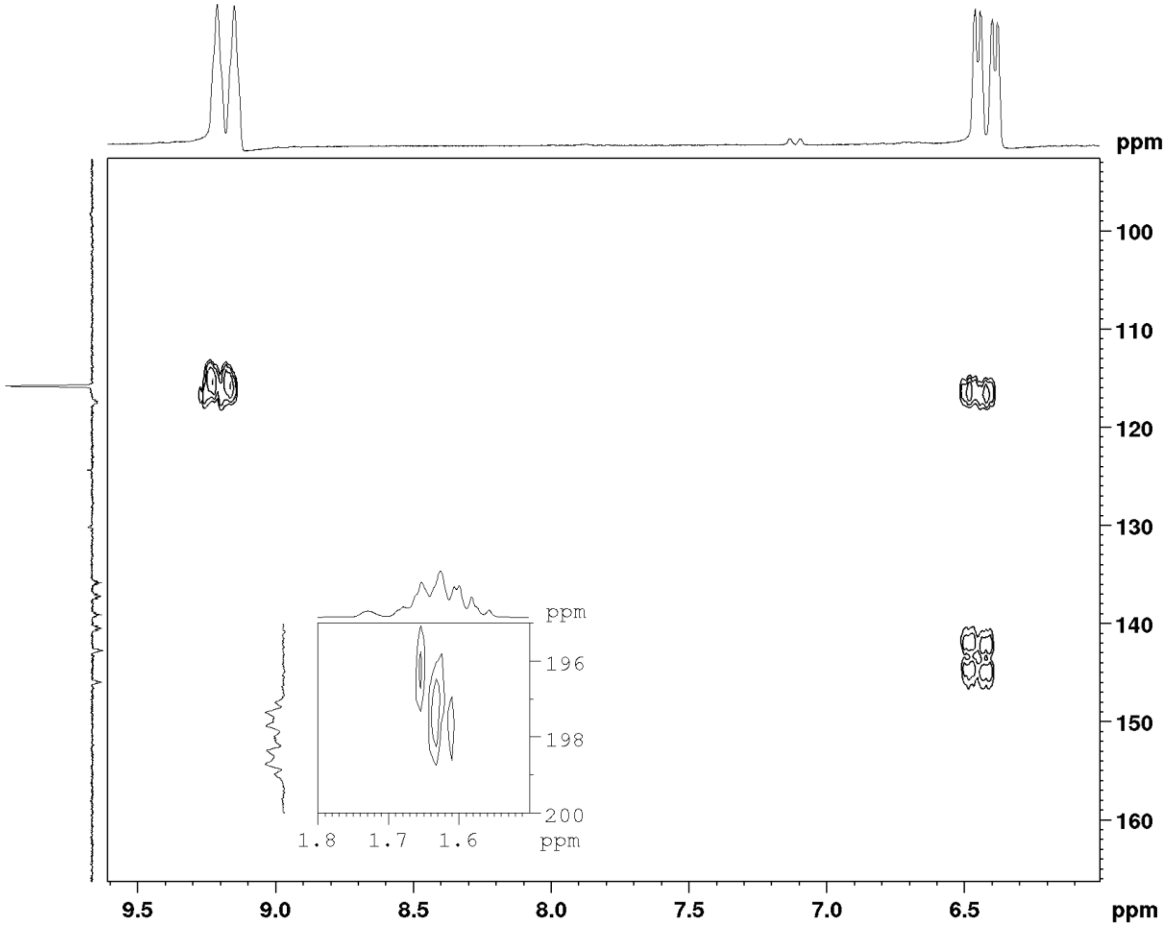


Figure S51 Part of the ^{1}H, ^{13}C HMBC NMR (300.1/75.5 MHz, d_8-THF) spectrum of [Rh(E-CHCHC$_6$F$_5$)(PEt$_3$)$_3$] (**15**).

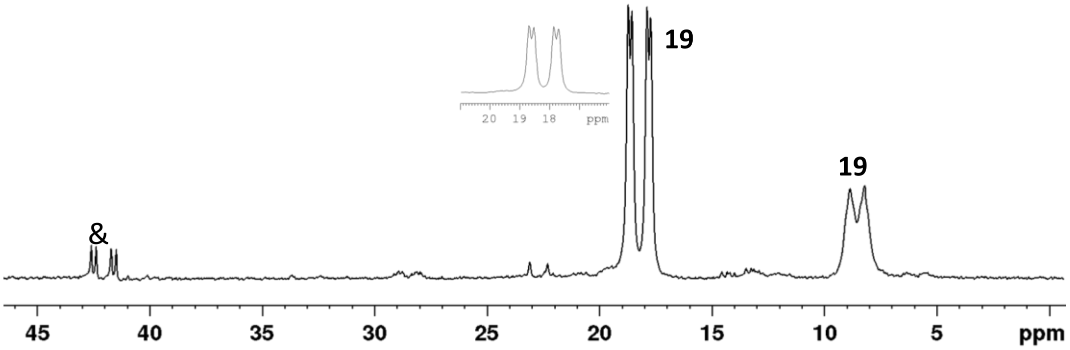


Figure S52 ^{31}P{^{1}H} NMR (121.5 MHz, d_8-Tol, 213 K) spectrum of fac-[Rh(H)$_2$(Bpin)(PEt$_3$)$_3$] (**19**);[11] & unidentified complex.

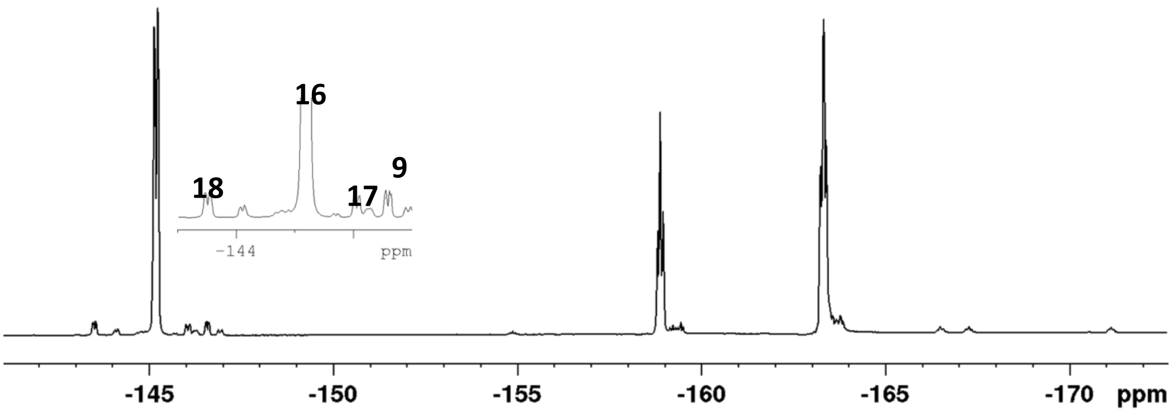


Figure S53 ^{19}F NMR (282.4 MHz, *d$_8$*-Tol, 213 K) spectrum of the stoichiometric hydroboration reaction with complex **5**.

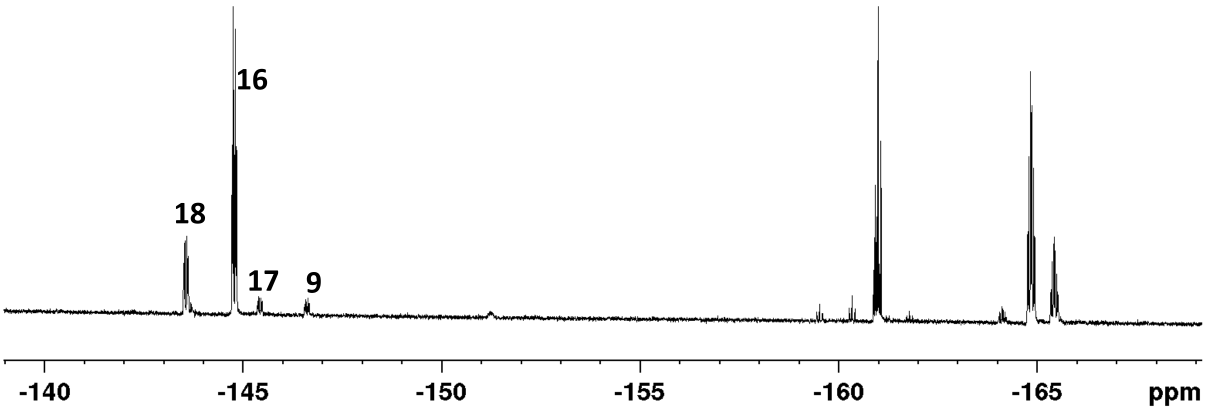


Figure S54 ^{19}F NMR (282.4 MHz, Me$_6$Si$_2$) spectrum of the stoichiometric hydroboration reaction of complex **1**.

16˜

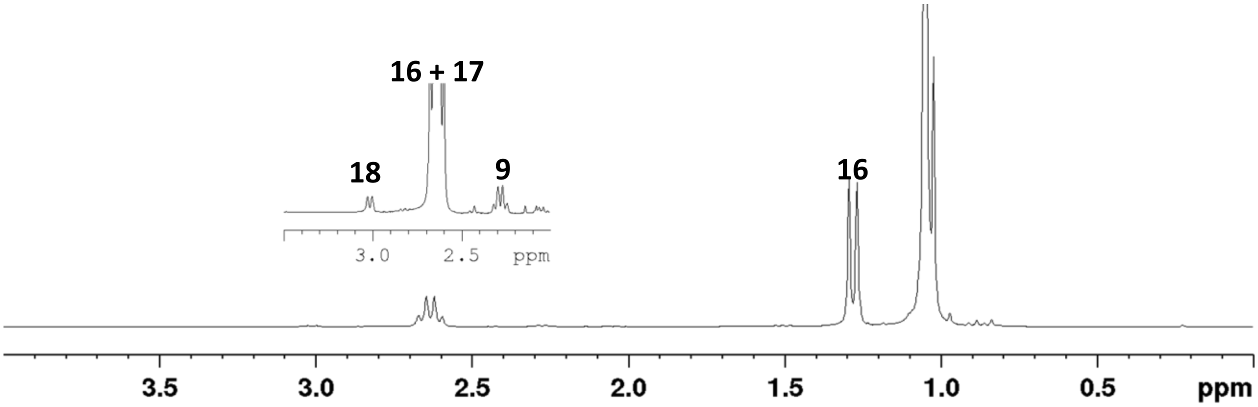


Figure S55 ^{1}H NMR (300.1 MHz, C_6D_6) spectrum of the catalytic hydroboration reaction with complex **5** as catalyst.

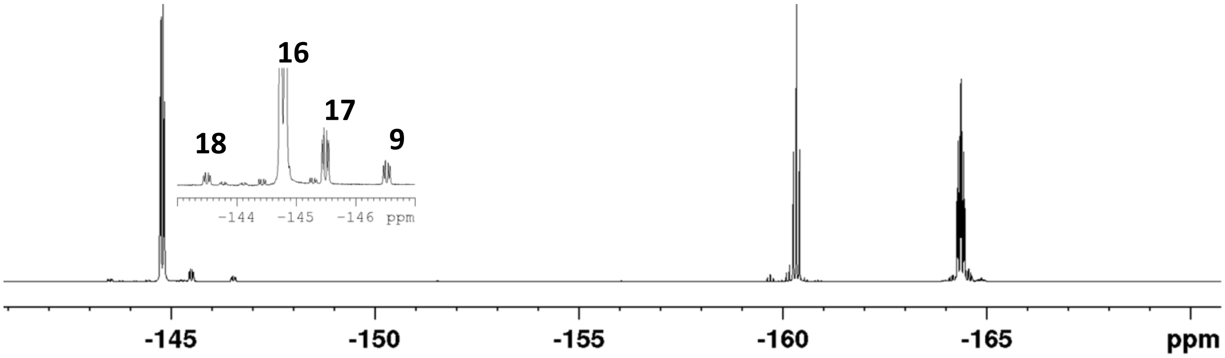


Figure S56 ^{19}F NMR (282.4 MHz, C_6D_6) spectrum of the catalytic hydroboration reaction with complex **5** as catalyst.

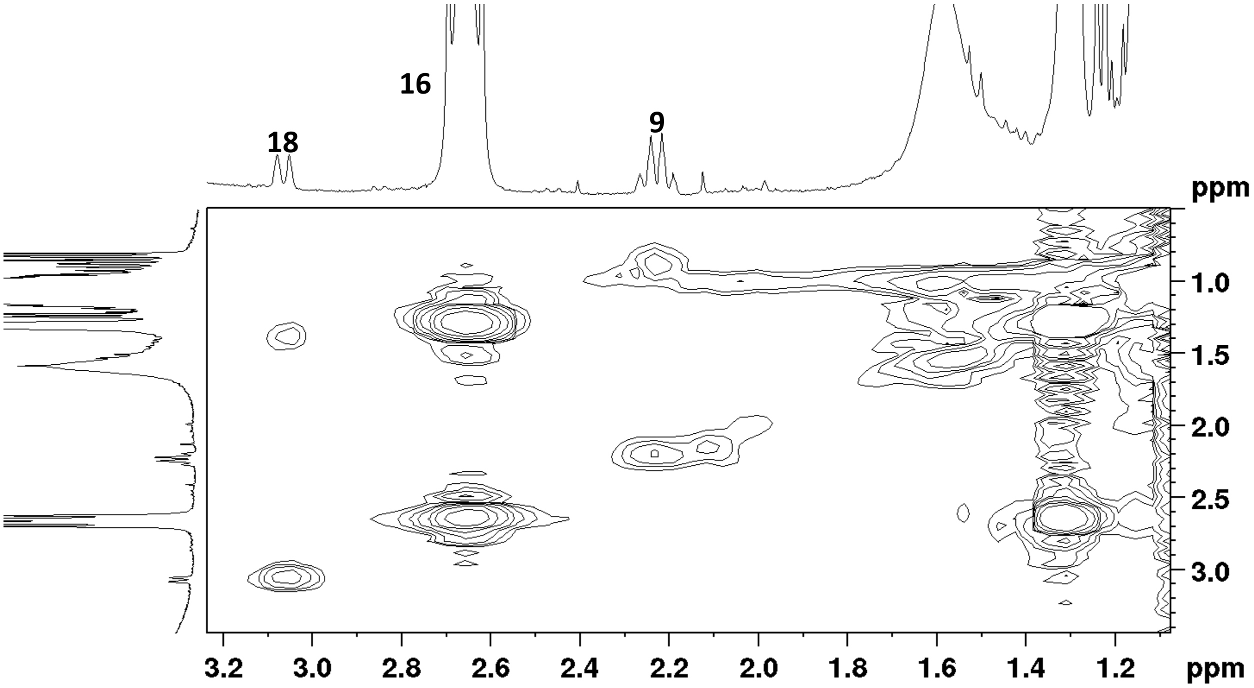


Figure S57 Part of the ^{1}H-^{1}H COSY NMR (C_6D_6) spectrum of the catalytic hydroboration reaction with complex **5** as catalyst.

X-ray diffraction analysis

Methodology

Suitable crystals for X-ray crystallography of *mer*-[Rh(F)(CH_2CH_2(2-C_6F_4))(PEt_3)$_3$] (**8**) were obtained from the reaction mixture by slow evaporation while letting the solution warm up from 193 K to 278 K of *trans*-[Rh(F)(CH_2CH_2(2-C_6F_4))(PEt_3)$_2$] (**7**), free PEt_3, traces of complex *mer*-[Rh(F)(CH_2CH_2(2-C_6F_4))(PEt_3)$_3$] (**8**) and [Rh(E-$CHCHC_6F_5$)(PEt_3)$_3$] (**15**). Note that at the crystallization temperature, formation of complex **8** from **7** and free phosphine takes place. Crystallographic data were collected on a Bruker D8 Venture diffractometer at 100 K. The structures were solved by intrinsic phasing (SHELXT-2014)[12] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-2016).[13] The SADABS program[14] was used for multi-scan absorption corrections. All non–hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined using a riding model. Crystal data and structural refinement details for complex **8** are given in Table S1. CCDC 1956127 contains the crystallographic data.

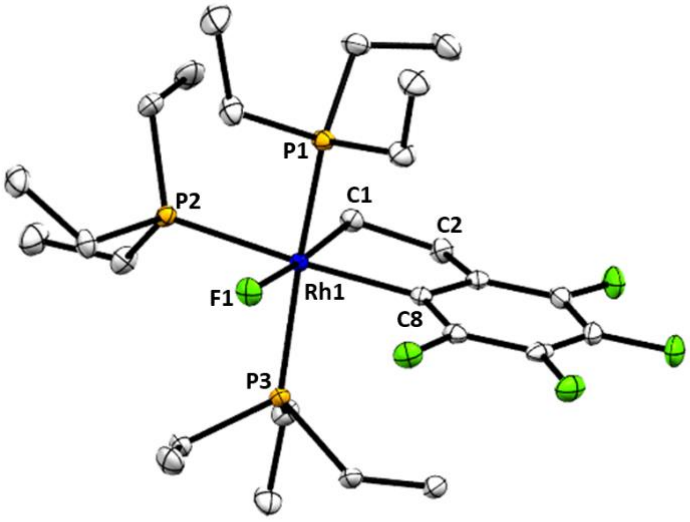


Figure S58 ORTEP diagram of complex **8**. Ellipsoids are drawn at 50% probability. Hydrogens are omitted for clarity. Selected distances [Å] and bond angles [°]:Rh1–C1 2.0775(15), Rh1–C8 2.0828(15), Rh1–F1 2.1360(9), Rh1–P3 2.3470(4), Rh1–P1 2.3502(4), Rh1–P2 2.3836(4), C1–C2 1.539(2), C1–Rh1–F1 173.53(5), C8–Rh1–F1 96.96(5), C1–Rh1–P3 93.56(4), C8–Rh1–P3 87.01(4), F1–Rh1–P3 92.84(3), P3–Rh1–P1 168.314(15), C1–Rh1–P2 90.47(4), C8–Rh1–P2 172.89(4), F1–Rh1–P2 90.08(3), P3–Rh1–P2 93.662(15), P1–Rh1–P2 92.732(16).

Table S1. Crystal data and structure refinement for complex **8**.

Empirical formula	$C_{26}H_{49}F_5P_3Rh$
Formula weight	652.47
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 19.5336(18) Å
	b = 13.3846(12) Å
	c = 22.1579(19) Å .
Volume	5793.2(9) $Å^3$
Z	8
Density (calculated)	1.496 Mg/m^3
Absorption coefficient	0.802 mm^{-1}
F(000)	2720
Crystal size	0.320 x 0.284 x 0.217 mm^3
Theta range for data collection	2.582 to 26.434°.
Index ranges	-24<=h<=24, -16<=k<=16, -27<=l<=27
Reflections collected	222646
Independent reflections	5956 [R(int) = 0.0554]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6695
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5956 / 0 / 325
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0199, wR2 = 0.0426
R indices (all data)	R1 = 0.0256, wR2 = 0.0446
Largest diff. peak and hole	0.395 and -0.339 e.$Å^{-3}$

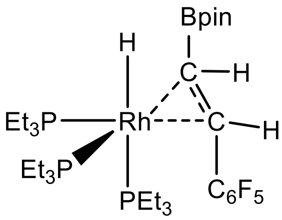
DFT calculations

Computational details for geometry optimization of all the calculated complexes

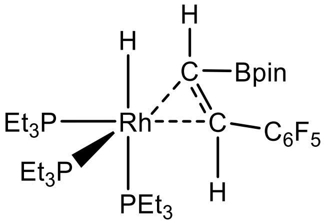
Calculations were run using the Gaussian 09 (Revision D.01) program package[15] and the BP86 functional. Rhodium was described with RECPs and the associated def2-SVP basis sets.[16,17] All the other atoms were described with def2-SVP basis sets. A Grimme D3 dispersion correction with Becke-Johnson damping was included.[18,19] All calculated structures were identified as minima (no negative eigenvalues).

Geometry optimization of both possible isomers of complex 3

Complex **3**



Complex **3a**



Energy in Hartree (corrected for zero-point energy): -3062.695001 for complex **3** and -3062.686929 for complex **3a**. Accordingly, structure **3** is favored by 21.2 kJ/mol.

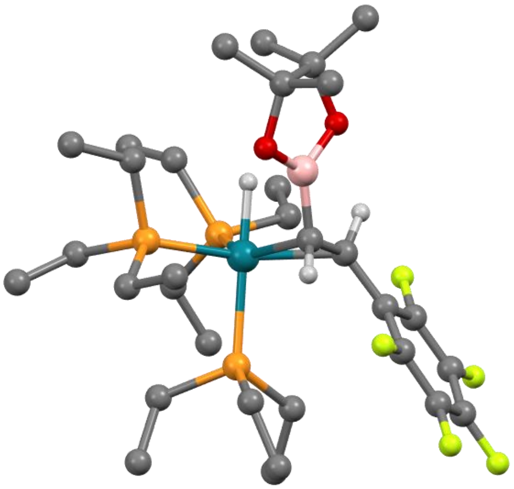


Figure S59 DFT optimized structure of complex **3**. Hydrogens of the phosphine ligands are omitted for clarity.

Geometry optimization of complex 7

Calculations predict a *trans* arrangement between the fluorido ligand and the aromatic ring. Energy (corrected for zero-point energy) = -2073.816153 Hartrees

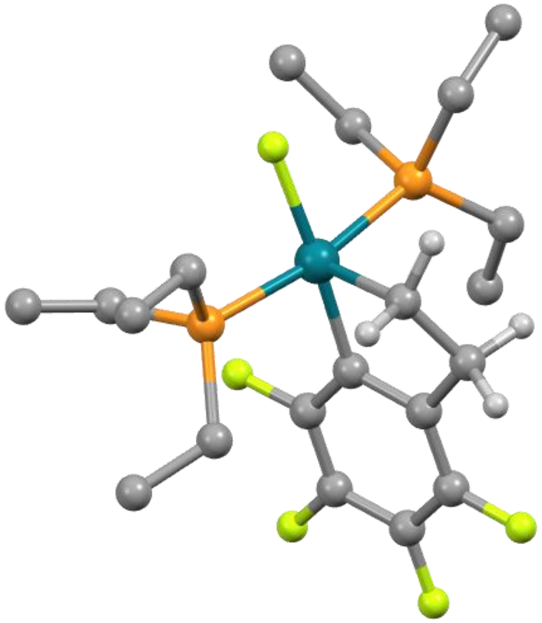
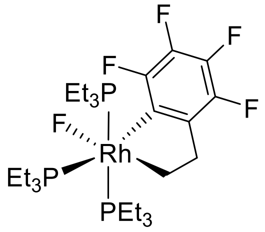


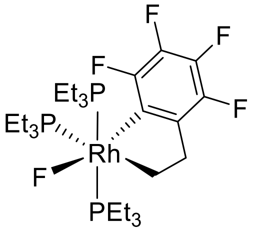
Figure S60 DFT optimized structure of complex **7**. Hydrogens of the phosphine ligands are omitted for clarity.

Geometry optimization of the possible isomers of complex 8

Complex **8**



Complex **8a**



Energy in Hartree (corrected for zero-point energy): -2652.473037 for complex **8a** and -2652.477736 for complex **8**. Thus, structure **8** is lower in energy, which is in agreement with the solid state structure obtained by X-ray analysis. However, the DFT data is not conclusive because the small energy difference of 12 kJ/mol could allow the observation of any of the isomers in the reaction.

Table S2. XYZ coordinates of all the calculated structures

Complex 3

Rh	0.37898	-0.38728	0.10645
P	-1.44686	-1.18400	-1.18770
P	0.35498	-1.81136	1.94261
P	1.98367	-1.45600	-1.17920
H	1.58315	0.13677	1.01629
C	-1.28917	-2.98364	-1.69816
C	-2.04879	-3.50631	-2.92143
C	-1.72197	-0.30046	-2.81863
C	-3.13465	-0.21073	-3.40340
C	-3.12520	-1.09594	-0.34972
C	-4.20724	-2.13222	-0.66319
C	2.13226	-2.13357	2.49258
C	2.49322	-3.42824	3.22499
C	-0.38468	-1.05604	3.48013
C	-0.19747	-1.77100	4.82091
C	-0.38071	-3.54049	1.98854
C	-1.90893	-3.57640	2.03854
C	3.71939	-0.85072	-0.88315
C	4.86118	-1.44187	-1.71086
C	2.19491	-3.32356	-0.94751
C	2.52491	-4.19432	-2.16418
C	1.84643	-1.28089	-3.03656
C	1.83481	0.18169	-3.48707
C	0.41237	1.69619	-0.51572
C	-0.55762	1.57917	0.55449
H	0.03646	-4.09367	2.85508
H	-0.00780	-4.05958	1.07965
H	-2.29921	-3.14063	2.98069
H	-2.28614	-4.61842	1.97498
H	-2.36021	-3.00581	1.20629
H	-0.58887	-2.80978	4.80298
H	-0.73740	-1.23290	5.62859
H	0.86952	-1.81958	5.11953
H	3.56575	-3.42097	3.51411
H	2.33608	-4.31926	2.58267
H	1.90450	-3.57717	4.15192
H	2.39415	-1.23792	3.09719
H	2.74275	-2.04230	1.57403
H	0.03682	-0.02943	3.50802
H	-1.45900	-0.91058	3.24971
H	0.90714	-1.79140	-3.33904
H	2.67276	-1.84004	-3.52330
H	0.99396	0.72870	-3.02172
H	1.73575	0.25520	-4.59004
H	2.75658	0.71722	-3.18483
H	5.82594	-0.96095	-1.44240
H	4.71310	-1.28008	-2.79842
H	4.98404	-2.53228	-1.54424
H	3.89305	-1.01168	0.20239
H	3.64528	0.24815	-1.01512
H	1.25657	-3.67655	-0.47498
H	2.97833	-3.43411	-0.16707
H	1.72349	-4.15156	-2.93000
H	2.63465	-5.25835	-1.86458
H	3.46936	-3.88974	-2.65720
H	-3.50676	-0.08227	-0.57115
H	-2.89364	-1.08909	0.73422
H	-4.54798	-2.07568	-1.71530
H	-5.09528	-1.95539	-0.02031
H	-3.86932	-3.17127	-0.47155
H	-3.12045	0.36057	-4.35518
H	-3.82095	0.32900	-2.72088
H	-3.57535	-1.20418	-3.61675
H	-1.02010	-0.77511	-3.53655
H	-1.32868	0.72044	-2.65437
H	-1.79767	-4.57282	-3.10397
H	-1.77581	-2.94722	-3.83956
H	-3.14693	-3.44099	-2.80308
H	-1.53383	-3.57534	-0.79094
H	-0.20353	-3.13316	-1.85334
H	-0.20056	1.81687	1.56978
C	-2.00054	1.82205	0.41281
C	-2.65561	2.33516	-0.73765
C	-4.05236	2.46630	-0.82616
C	-4.86702	2.15654	0.27533
C	-4.25398	1.71774	1.46404
C	-2.86164	1.58351	1.51566
F	-2.33288	1.13479	2.67276
F	-5.00770	1.42297	2.53520
F	-6.19979	2.28823	0.20113
F	-4.61333	2.91004	-1.96389
F	-1.96367	2.71845	-1.83517
H	0.05597	1.85756	-1.54236
B	1.80610	2.23425	-0.14342
O	2.08572	2.81117	1.09404
O	2.91641	2.28763	-0.99418
C	3.92048	3.12440	-0.35389
C	3.51469	3.02917	1.17333
C	3.75223	4.53812	-0.93042
C	5.31143	2.58202	-0.68236
C	3.77508	4.29999	1.98217
C	4.12280	1.81091	1.88509
H	3.62993	1.69479	2.87110
H	5.21345	1.92361	2.04873
H	3.93815	0.88447	1.30856
H	3.45089	4.14687	3.03125
H	4.85589	4.55125	1.98948
H	3.21177	5.16116	1.57681
H	5.42781	1.52725	-0.37198
H	6.09441	3.18358	-0.17643

Complex 3a

Rh	-0.11108	0.60239	-0.24349
P	0.64411	1.06689	1.95101
P	-2.23811	1.52987	-0.12848
P	1.03289	2.22893	-1.40769
H	-0.72570	0.28723	-1.67196
C	0.67402	2.89664	2.36905
C	1.54051	3.41208	3.52194
C	2.34617	0.47605	2.44192
C	2.67496	0.17756	3.90797
C	-0.47640	0.28198	3.23340
C	-0.59820	0.88831	4.63459
C	-2.83633	1.90359	-1.88092
C	-3.84684	3.02633	-2.12700
C	-3.58345	0.38102	0.46684
C	-5.05020	0.78974	0.30819
C	-2.65180	3.11009	0.80823
C	-2.96783	2.90834	2.29416
C	1.28167	1.70282	-3.18769
C	2.35043	2.38307	-4.04904
C	0.22132	3.91888	-1.49241
C	0.79490	5.02419	-2.38456
C	2.75743	2.71312	-0.87596
C	3.70207	1.51699	-0.78772
C	0.89206	-1.27949	-0.78401
C	-0.18222	-1.54819	0.15467
C	-1.47392	-2.17587	-0.15322
C	-2.05363	-2.32990	-1.43944
C	-3.34656	-2.84359	-1.63395
C	-4.10676	-3.29147	-0.53870
C	-3.55617	-3.19320	0.75128
C	-2.26854	-2.66551	0.91713
F	-1.40598	-1.91748	-2.54964
F	-3.85308	-2.93365	-2.87472
F	-5.33650	-3.79806	-0.72157
F	-4.26619	-3.60436	1.81492
F	-1.80936	-2.55505	2.18481
H	-3.50479	3.61906	0.31456
H	-1.77361	3.77654	0.68262
H	-3.93852	2.39491	2.44228
H	-3.02609	3.88301	2.82239
H	-2.20007	2.29884	2.80706
H	-5.28097	1.76266	0.78969
H	-5.71570	0.02772	0.76588
H	-5.33632	0.86756	-0.76006
H	-4.14471	3.04741	-3.19671
H	-3.41890	4.02281	-1.89007
H	-4.77308	2.91117	-1.52981
H	-3.22224	0.92462	-2.24022
H	-1.91908	2.07624	-2.47710
H	-3.38980	-0.55670	-0.08692
H	-3.33987	0.14589	1.52515
H	2.64931	3.20179	0.11692
H	3.15314	3.48855	-1.56662
H	3.28184	0.74775	-0.11387
H	4.70010	1.81651	-0.40407
H	3.84484	1.02065	-1.76747
H	2.36869	1.93257	-5.06391
H	3.36484	2.25139	-3.62071
H	2.17955	3.46979	-4.17291
H	0.27275	1.77585	-3.65014
H	1.48358	0.61448	-3.10905
H	0.19749	4.24894	-0.43019
H	-0.83717	3.72134	-1.75832
H	1.87046	5.21058	-2.18700
H	0.25922	5.98212	-2.21336
H	0.68711	4.77839	-3.45978
H	-0.15768	-0.78026	3.28445
H	-1.46924	0.24491	2.74141
H	0.36085	0.88077	5.18704
H	-1.33378	0.31555	5.23831
H	-0.95611	1.93817	4.60025
H	3.71679	-0.19894	3.99548
H	2.01410	-0.61311	4.31710
H	2.59179	1.06548	4.56443
H	3.05166	1.22352	2.02007
H	2.49092	-0.44501	1.84302
H	1.47209	4.51859	3.59307
H	2.61041	3.16107	3.37284
H	1.23117	2.99828	4.50110
H	-0.38467	3.19385	2.50509
H	0.98792	3.38002	1.42084
H	0.13424	-1.78465	1.18339
B	2.35491	-1.66604	-0.50730
H	0.65103	-1.41510	-1.84953
O	2.84504	-2.20964	0.67982
O	3.32844	-1.64691	-1.50222
C	4.43535	-2.47585	-1.06792
C	4.25910	-2.50844	0.51249
C	4.23890	-3.85214	-1.72294
C	5.74201	-1.84529	-1.55152
C	5.06978	-1.42308	1.23459
C	4.53590	-3.86793	1.15811
H	4.88836	-0.42213	0.80104
H	6.15679	-1.63426	1.18825
H	4.77165	-1.39573	2.30122
H	3.86394	-4.65165	0.76213
H	4.36879	-3.79960	2.25192
H	5.58697	-4.18054	0.98993
H	5.84315	-0.79941	-1.20637
H	5.76329	-1.84131	-2.65986

Complex 7

Rh	0.11089	-0.87771	-0.15760
F	0.08766	-2.94160	-0.13971
C	0.09642	1.10939	0.00718
C	0.40897	1.84987	-1.16728
C	0.40161	3.24942	-1.14310
C	0.07956	3.94988	0.03727
C	-0.23907	3.22791	1.20397
C	-0.22703	1.82170	1.16628
F	-0.53325	1.15054	2.31615
F	-0.54709	3.89192	2.33240
F	0.07073	5.29474	0.05686
F	0.70568	3.96493	-2.25011
C	0.76736	1.00706	-2.36461
C	0.16744	-0.39244	-2.15178
H	0.74015	-1.20052	-2.65311
H	-0.87574	-0.42449	-2.53078
H	1.87620	0.94013	-2.45269
H	0.42041	1.46413	-3.31803
P	-2.20099	-0.98982	-0.13761
C	-2.69724	-1.35364	1.61678
C	-4.04262	-2.03631	1.89021
C	-3.10905	0.53477	-0.68731
C	-4.53537	0.77069	-0.17922
C	-2.78519	-2.39925	-1.19147
C	-4.26083	-2.47064	-1.59678
P	2.41956	-1.04130	0.08415
C	3.61201	0.36670	-0.13867
C	3.42950	1.52857	0.84431
C	3.06416	-2.38910	-1.00786
C	4.49057	-2.88428	-0.75872
C	2.75521	-1.60411	1.82771
C	2.20199	-3.00438	2.13048
H	2.15903	-3.18179	3.22437
H	2.84557	-3.79258	1.68905
H	1.19318	-3.13822	1.68630
H	2.26836	-0.84115	2.47267
H	3.84822	-1.53512	2.02532
H	2.94300	-2.01032	-2.04649
H	2.29824	-3.18609	-0.88552
H	4.74363	-3.71198	-1.45380
H	4.61746	-3.27246	0.27263
H	5.24629	-2.08602	-0.91171
H	4.16363	2.33300	0.63402
H	3.58425	1.20590	1.89413
H	2.41532	1.96419	0.76929
H	3.49030	0.71571	-1.18579
H	4.63752	-0.05715	-0.06183
H	-2.43775	-3.30449	-0.65077
H	-2.13626	-2.35064	-2.09197
H	-4.93997	-2.54231	-0.72487
H	-4.44036	-3.36394	-2.23121
H	-4.56644	-1.58454	-2.19028
H	-2.44637	1.37334	-0.38566
H	-3.07213	0.51589	-1.79872
H	-4.93384	1.72363	-0.58609
H	-4.56023	0.85481	0.92684
H	-5.23353	-0.03662	-0.47582
H	-2.59925	-0.38702	2.15498
H	-1.86726	-1.99123	1.99210
H	-4.90296	-1.43757	1.53279
H	-4.17538	-2.19287	2.98120
H	-4.09574	-3.03331	1.40837

Complex 8a

Rh	-0.27579	-0.10629	-0.76952
F	-1.81750	-0.47379	-2.15214
C	1.40205	0.41210	0.24363
C	2.51416	0.78706	-0.57504
C	3.73352	1.16714	0.00512
C	3.91299	1.18955	1.39985
C	2.83811	0.81233	2.22032
C	1.61973	0.43676	1.62738
F	2.98430	0.81342	3.55850
F	5.08740	1.55607	1.94306
F	4.77783	1.52306	-0.77908
C	2.34143	0.74878	-2.07667
C	0.93824	0.23165	-2.45633
H	0.98637	-0.71262	-3.02710
H	0.40127	0.93046	-3.12114
H	3.14836	0.12647	-2.52693
H	2.52903	1.76579	-2.49264
P	-0.89736	2.16366	-0.87090
C	-0.43691	3.12684	0.67203
C	-1.30089	4.28626	1.17584
C	-2.68361	2.32134	-1.43096
C	-3.78344	2.93481	-0.56220
P	0.60008	-2.28835	-0.67206
C	1.27556	-2.78372	1.00635
C	2.09324	-2.61687	-1.74047
C	2.72363	-4.00894	-1.64980
C	-0.57623	-3.62385	-1.20377
C	-0.98970	-3.42675	-2.66893
H	-1.80506	-4.12845	-2.94076
H	-0.14319	-3.61944	-3.36042
H	-1.34523	-2.38405	-2.82124
H	-1.46429	-3.53809	-0.54537
H	-0.13106	-4.62479	-1.02126
H	2.82610	-1.83341	-1.45681
H	1.79672	-2.39503	-2.78492
H	3.56189	-4.09695	-2.37196
H	1.99928	-4.81409	-1.89044
H	3.13997	-4.21467	-0.64347
H	-1.02290	-1.77610	2.84211
H	-2.89908	1.26329	-1.70796
H	-2.63315	2.86735	-2.39617
H	-3.87629	2.44563	0.42803
H	-4.76360	2.81208	-1.06945
H	-3.63384	4.01821	-0.38846
H	-0.30345	2.37266	1.46802
H	0.59365	3.47230	0.43868
H	-0.77338	4.82070	1.99365
H	-2.26440	3.92985	1.58918
H	-1.52983	5.02810	0.38647
P	-1.96635	-0.55993	0.97802
C	-1.78768	-2.06170	2.09051
H	-1.31359	-2.84147	1.46433
C	-3.02941	-2.65791	2.76560
C	-3.66824	-0.81520	0.25780
C	-3.80616	-2.03691	-0.65314
H	-3.88753	0.10492	-0.32032
H	-4.39409	-0.84842	1.09887
H	-3.11462	-1.91107	-1.50829
H	-4.84435	-2.11988	-1.03770
H	-3.57811	-2.98506	-0.12260
C	-0.05713	3.20444	-2.17217
C	-0.41193	4.69409	-2.18475
H	-0.31156	2.73430	-3.14467
H	1.03362	3.06186	-2.03354
H	-1.50724	4.86368	-2.25079
H	0.04990	5.19306	-3.06243
H	-0.04127	5.21725	-1.28069
F	0.63776	0.06167	2.51027
C	1.09569	-4.23902	1.44995
H	1.55883	-4.96043	0.74889
H	0.02460	-4.51271	1.54514
H	1.56158	-4.39540	2.44521
H	-3.77163	-3.01369	2.02427
H	-3.54341	-1.94156	3.43208
H	-2.73855	-3.53336	3.38338
C	-2.30181	0.82521	2.19232
H	-2.50214	1.70072	1.54369
H	-1.32724	1.02349	2.67713
C	-3.40602	0.70922	3.24748
H	-4.38730	0.42775	2.81299
H	-3.54294	1.68523	3.75927
H	-3.15432	-0.03220	4.03101
H	0.82816	-2.09529	1.74409
H	2.35098	-2.50869	0.96838

Complex 8

Rh	-0.33544	-0.10114	-0.03620
P	-2.72587	-0.12351	-0.22975
C	1.72416	-0.02786	0.06354
C	2.36739	0.10539	-1.19978
C	3.76397	0.15082	-1.28631
C	4.56743	0.06724	-0.13429
C	3.94519	-0.04917	1.12001
C	2.53660	-0.08815	1.20271
F	2.02315	-0.19440	2.45185
F	4.70091	-0.12110	2.23032
F	5.90844	0.10710	-0.22332
F	4.37798	0.28765	-2.48583
C	1.48494	0.26792	-2.41188
C	0.04418	-0.18290	-2.09364
H	-0.11065	-1.22020	-2.45912
H	-0.67759	0.43829	-2.66614
H	1.91650	-0.25845	-3.29302
H	1.48990	1.34606	-2.70181
P	-0.19478	2.25696	-0.01624
C	-0.70612	2.87760	1.65873
C	-1.51809	4.16898	1.75822
C	1.49203	3.03212	-0.25808
C	1.71998	4.43876	0.30669
C	-1.22563	3.08569	-1.33745
C	-0.99453	4.55176	-1.71567
P	0.07814	-2.42545	0.13471
C	0.35434	-2.96435	1.88749
C	-0.90688	-2.92628	2.75613
C	1.66239	-2.96382	-0.70349
C	1.92672	-4.46781	-0.81308
C	-1.10406	-3.72585	-0.49015
C	-1.48143	-3.58223	-1.96572
H	2.47065	-2.46610	-0.13231
H	1.67535	-2.48623	-1.70434
H	2.94846	-4.64365	-1.20913
H	1.21987	-4.97549	-1.50044
H	1.86789	-4.97910	0.17033
H	-0.66011	-3.19364	3.80429
H	-1.68082	-3.64345	2.40907
H	-1.30477	-1.89056	2.74193
H	1.10433	-2.25279	2.28596
H	0.81651	-3.97610	1.86608
H	2.20555	2.32758	0.20954
H	1.70486	2.99346	-1.34685
H	2.76396	4.75638	0.10266
H	1.58692	4.46196	1.40673
H	1.04982	5.20285	-0.13014
H	0.24473	2.95198	2.22753
H	-1.21080	2.00400	2.11500
H	-0.95578	5.05768	1.40728
H	-1.80760	4.35573	2.81361
H	-2.45965	4.11626	1.17215
C	-3.64295	1.17762	0.74848
H	-3.18726	2.14992	0.47515
C	-3.56705	0.96593	2.26856
H	-4.69459	1.21929	0.39066
C	-3.31328	0.15312	-1.98181
C	-3.61727	-1.66899	0.32782
H	-3.07222	-1.97674	1.24375
H	-3.38853	-2.42967	-0.44372
C	-5.12805	-1.63620	0.59127
H	-5.40506	-0.89743	1.36758
H	-5.46597	-2.62971	0.95408
H	-5.71413	-1.40103	-0.31663
C	-4.80688	0.15407	-2.31924
H	-5.38707	0.83981	-1.66842
H	-5.25318	-0.85586	-2.22814
H	-4.96431	0.48545	-3.36725
F	-0.74117	-0.01916	2.05998
H	-1.68418	4.84411	-2.53554
H	0.03675	4.72365	-2.08238
H	-1.17617	5.24099	-0.86840
H	-2.85262	1.11860	-2.27481
H	-2.77672	-0.60882	-2.58586
H	-2.53920	0.65659	2.55432
H	-4.26109	0.17001	2.60524
H	-3.84543	1.89562	2.80662
H	-1.05446	2.43959	-2.22561
H	-2.28499	2.92153	-1.05322
H	-2.00104	-3.68120	0.15503
H	-0.63661	-4.71382	-0.29330
H	-1.93832	-2.59273	-2.16973
H	-2.20845	-4.36296	-2.27231
H	-0.59662	-3.67130	-2.62907

H	5.48865	2.63949	-1.77547	H	6.61872	-2.42332	-1.19375			
H	2.75393	4.95033	-0.68186	H	3.29185	-4.32057	-1.38869			
H	3.83377	4.48536	-2.03447	H	5.07536	-4.54401	-1.49847			
H	4.52769	5.23547	-0.55455	H	4.17969	-3.71813	-2.82139			

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