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Electronic Supporting Information

C-H and C-O Oxidative Addition in Reactions of Aryl Carboxylates with a PNP Pincer-Ligated Rh(I) Fragment

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I. General Considerations.

Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Ethyl ether, C_6D_6, and pentane were dried over Na/K/Ph_2CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene was dried with and then distilled from CaH_2. (PNP)Rh(Me)(Cl),[1] (PNP)Rh(Ph)(Cl),[2] PhO_2CBu^t,[3] PhO_2CNEt_2[4] were prepared according to the published procedures. All other chemicals were used as received from commercial vendors (PhLi, 1.8 M/Bu_2O; BnMgCl, 1.0 M/Et_2O; MeMgCl, 3.0 M/THF). NMR spectra were recorded on a Varian iNova 300, Varian iNova 400, and Mercury 300 spectrometer. Chemical shifts are reported in δ (ppm). For ^1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced externally using CF_3COOH at δ -78.5 ppm. Elemental analyses were performed by CALI, Inc. (Parsippany, NJ).

II. Synthesis of precursors to (PNP)Rh (6).

(PNP)Rh(Me)(Ph) (3). **1** (15 mg, 0.026 mmol) was treated with PhLi (15 μL, 0.026 mmol) in C_6D_6 in a J. Young NMR tube. After 10 min, $^{31}P\{^1H\}$ NMR spectroscopic analysis revealed complete disappearance of the starting material and only the doublet for **3** was detected (35.9 ppm, J = 118 Hz). Complex **3** is unstable and thus was only characterized in situ in solution. Selected NMR spectroscopic data collected at the early stage of the reaction (10 min after the addition of PhLi) fits our previously reported data for complex **3**.[2]

(PNP)Rh(Me)(CH_2Ph) (**4**). **1** (15 mg, 0.026 mmol) was treated with $PhCH_2MgCl$ (26 μL, 0.026 mmol) in C_6D_6 in a J. Young NMR tube. After 10 min, $^{31}P\{^1H\}$ NMR spectroscopic analysis revealed complete disappearance of the starting material and only the doublet for **4** was detected (32.2 ppm, J = 120 Hz). ^1H NMR spectroscopic analysis revealed >98% conversion of (PNP)Rh(Me)(Cl) to (PNP)Rh(Me)(CH_2Ph) by using TMS as an internal integration standard. Complex **4** was not stable enough for isolation in pure solid form, and thus was only characterized in situ in solution. NMR data collected at the early stage of the reaction (10 min after the addition of BnMgCl). $^{31}P\{^1H\}$NMR (C_6D_6): δ 32.2 (d, J = 120 Hz). ^1H NMR (C_6D_6): δ 7.84 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 7.50 (d, J = 8 Hz, 2H, Bn-*H*), 7.09 (d, J = 8 Hz, 2H, Bn-*H*), 7.01 (t, J = 6 Hz,1H, Bn-*H*), 6.92 (br, 2H, (PNP)Aryl-*H*), 6.86 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 3.56 (td, J = 6, 3 Hz, 2H, Bn-*H*), 2.36 (m, 2H, C*H*Me_2), 2.22 (s, 6H, Ar-CH_3), 2.16 (m, 2H, C*H*Me_2), 1.57 (td, J = 6, 2 Hz, 3H, Rh-CH_3), 1.26 (app. q(dvt), J = 7 Hz, 6H, CHMe_2), 1.05 (app. q(dvt), J = 7 Hz, 6H, CHMe_2), 0.94 (app. q(dvt), J = 7 Hz, 6H, CHMe_2), 0.72 (app. q(dvt), J = 7 Hz, 6H, CHMe_2).

(PNP)Rh(Ph)(CH_2Ph) (5). **2** (82 mg, 0.13 mmol) was treated with BnMgCl (140 μL, 0.14 mmol) in PhF. After 10 min, the reaction mixture was passed through Celite and silica. The

volatiles were removed under vacuum. The residue was dissolved in pentane and placed in a -35 °C freezer. The green precipitate was collected the next day and dried in vacuum. Yield: 64 mg (72%). ^{31}P NMR{^{1}H} (C_6D_6): δ 34.2 (d, *J* = 121 Hz). ^{1}H NMR (C_6D_6): δ 8.01 (d, *J* = 8 Hz, 2H), 7.64 (d, *J* = 7 Hz, 2H), 7.47 (d, *J* = 8 Hz, 2H), 7.14 (m, 2H, overlapping with C_6D_6), 7.03 (d, *J* = 7 Hz, 1H), 6.96 (d, *J* = 6 Hz, 2H), 6.94 (br, 2H), 6.91 (d, *J* = 5 Hz, 2H), 6.87 (t, *J* = 7 H, 1H), 4.16 (q, *J* = 4 Hz, Rh-C*H*$_2$), 2.21 (m, 8H, Ar-C*H*$_3$+C*H*Me$_2$), 1.75 (m, 2H, C*H*Me$_2$), 0.90 (m, 12H, CH*Me*$_2$), 0.82 (app. q(dvt), *J* = 7 Hz, 6H, CH*Me*$_2$), 0.71 (app. q(dvt), *J* = 7 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.7 (vt, *J* = 9 Hz, *C*-N), 151.5, 151.4, 150.8 (dt, *J* = 34, 10 Hz, Rh-*C*), 136.7, 133.3, 131.9, 129.7, 128.5, 126.5, 125.1, 124.3 (vt, *J* = 3 Hz), 122.1, 121.9 (vt, *J* = 18 Hz), 117.1 (t, *J* = 5 Hz), 25.0 (vt, *J* = 11 Hz), 24.5 (vt, *J* = 10 Hz), 21.2 (dt, *J* = 29, 5 Hz, Rh-*C*H$_2$), 20.6, 19.4, 19.1, 18.8, 18.5.

(PNP)Rh(C_6H_5F) (7). To a stirred solution of C_6H_5F (3 mL) of **2** (25 mg, 0.039 mmol) was added MeMgCl (13 µL, 0.039 mmol). After 5 minutes the solution was filtered through Celite, the volatile components removed *in vacuo* and C_6H_5F (1 mL) added. After standing for 24 h a color change was noted for the solution from dark green to brown and removal of the volatile components gave an orange-brown solid (16.9 mg, 69 %). Brown block-like crystals suitable for an X-ray diffraction study were grown by slow evaporation of a solution prepared by the method above but using $PhCH_2MgCl$ (39 µL, 0.039 mmol) as the transmetallation reagent. ^{1}H NMR (C_6H_5F, 239 K) δ: -25.71, -29.31, -40.68 (all br), referenced to trace poly(dimethylsiloxane) grease as 0 ppm. ^{19}F NMR (C_6H_5F, 255 K) δ: -54.03 (br), -85.29 (br, overlapping) -85.50 (br, overlapping), -90.85 (br), -95.50 (br). ^{31}P{^{1}H} NMR (C_6H_5F, 293 K) δ: 52.4 (d, *J* = 113 Hz). Elem. An.. Found (Calculated) for $C_{32}H_{45}NFP_2Rh$: C 61.08 (61.24); H 7.16 (7.23).

Thermolysis of 7. **7** (10 mg, 0.016 mmol) was dissolved in 0.6 mL PhF in a J. Young NMR tube and was heated at 95 ^{o}C for 18 h. ^{31}P NMR spectroscopic analysis indicated no observable changes.

III. Reactions with PhO_2CPh.

(PNP)Rh(H)($C_6H_4COOC_6H_5$) (8). **1** (41 mg, 0.070 mmol) was dissolved in 1 mL of PhF followed by the addition of $PhCH_2MgCl$ (78 μL, 0.078 mmol). The mixture was passed through Celite and silica gel after stirring at ambient temperature for 10 min. The volatiles were removed under vacuum. The residue was redissolved in about 0.6 mL of PhF and heated at 60 °C for 3 h. The green solution gradually turned brown. $^{31}P\{^1H\}$ NMR spectroscopic analysis indicated full conversion to **7**. PhO_2CPh (13 mg, 0.065 mmol) was added to the solution and the reaction mixture was left at room temperature for overnight. The brown color of the solution changed to green-yellow. The volatiles were removed under vacuum and the residue was recrystallized from PhF/pentane at -35 °C to produce a yellow solid. Yield: 21 mg (43%). $^{31}P\{^1H\}$NMR (C_6D_6): δ 52.6 (d, J = 110 Hz). ^1H NMR (C_6D_6): δ 8.12 (d, J = 8 Hz, 1H), 7.94 (d, J = 7 Hz, 1H), 7.70 (d, J = 8 Hz, 2H), 7.09 (d, J = 7 Hz, 2H), 7.05 (t, J = 2 Hz, 1H), 6.80-6.93 (m, 5H), 6.73 (m, 3H), 2.16 (s, 6H), 2.07 (m, 4H), 1.09 (app. q(dvt), J = 8 Hz, 6H), 0.94 (m, 12H), 0.85 (app. q(dvt), J = 8 Hz, 6H), -19.9 (dt, J = 35 Hz, J = 14 Hz, 1H). $^{13}C\{^1H\}$NMR (C_6D_6): δ 181.0 (dt, J = 28, 10 Hz, Rh-*C*), 173.7 (C=O), 161.1 (vt, J = 9 Hz, C-N), 151.4 (C-O), 144.6, 133.6, 131.8, 131.1, 130.2, 129.5, 126.0, 122.8 (vt, J = 4 Hz), 122.3 (vt, J = 20 Hz), 121.5, 120.6, 115.9 (vt, J = 5 Hz), 115.6, 25.3 (vt, J = 12 Hz), 24.1 (vt, J = 11 Hz), 20.6, 18.3, 17.8 (two signals overlapping), 17.7. Elem. An.. Found (Calculated) for $C_{39}H_{50}NO_2P_2Rh$: C 64.11 (64.20); H 6.84 (6.91).

Thermolysis of complex 8. Complex **8** (10 mg, 0.014 mmol) was dissolved in 0.6 mL C_6D_6 in a J. Young NMR tube and was heated at 100 °C for 18 h. Both ^{31}P and ^1H NMR spectroscopic analyses indicated no observable changes.

NMR tube synthesis of 8 from 5. 5 (10 mg, 0.014 mmol) and $C_6H_5OC(O)C_6H_5$ (3.0 mg, 0.015 mmol) were dissolved in 0.60 mL of C_6D_6 in a J. Young NMR tube. The reaction mixture

was placed in a 60 °C oil bath for 100 min. ^{1}H NMR spectroscopic analysis indicated >98% conversion to **8** by using $(Me_3Si)_2O$ as an internal integration standard.

IV. Reactions with MeO_2CPh.

(PNP)Rh(H)($C_6H_4COOCH_3$) (9). **1** (30 mg, 0.052 mmol) was dissolved in about 0.6 mL of PhF followed by the addition of PhLi (31 μL, 0.057 mmol). The reaction mixture was stirred for about 10 min and passed through Celite and silica. The volatiles were removed under vacuum. The residue was redissolved in about 0.6 mL of PhF and heated at 60 °C for 3 h. The green solution gradually turned brown. $^{31}P\{^1H\}$ NMR spectroscopic analysis indicated full conversion to **7**. MeO_2CPh (9.0 μL, 0.068 mmol) was added to the solution and the reaction mixture was left at room temperature overnight. The brown color of the solution changed to green-yellow. The volatiles were removed under vacuum. The residue was redissolved in C_6D_6. **9** was not isolated and only characterized in solution by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 52.1 (d, J = 110 Hz). ^1H NMR (C_6D_6): δ 7.91 (d, J = 7 Hz, 1H), 7.83 (m, 3H), 7.04 (t, J = 6 Hz, 1H), 6.91 (br, 2H), 6.85 (m, 3H), 3.32 (s, 3H), 2.22 (s, 6H), 2.09 (m, 2H), 2.00 (m, 2H), 1.08 (app. q(dvt), J = 8 Hz, 6H), 0.94 (app. q(dvt), J = 8 Hz, 6H), 0.88 (m, 12H), -19.5 (dt, J = 35 Hz, J = 14 Hz, 1H). Thermolysis of complex **9** at 100 °C for 18 h did not lead to any observable changes by NMR spectroscopy.

NMR tube synthesis of 9 from 5. **5** (10 mg, 0.014 mmol) and MeO_2CPh (4.0 μL, 0.030 mmol) were dissolved in 0.60 mL of C_6D_6 in a J. Young NMR tube. The reaction mixture was placed in a 60 °C oil bath for 100 min. ^1H NMR spectroscopic analysis indicated >98% conversion to **9** by using $(Me_3Si)_2O$ as internal standard .

V. Reactions with PhO_2CCF_3.

(PNP)Rh(OPh)(C(O)CF_3) (10). **1** (119 mg, 0.205 mmol) was dissolved in 3 mL of PhF followed by the addition of BnMgCl (225 μL, 0.225 mmol). The mixture was passed through Celite and silica after stirring at ambient temperature for 10 min. The volatiles were removed under vacuum. The residue was redissolved in about 3 mL of PhF and heated at 60 °C oil bath for 3 h. $^{31}P\{^1H\}$ NMR spectroscopic analysis indicated full conversion to **7**. After that, PhO_2CCF_3 (305 μL, 2.05 mmol) was added to the solution and the reaction mixture was left at ambient temperature for 4 h. The volatiles were removed under vacuum and the residue was recrystallized from PhF/pentane at -35 °C to give a green solid. Yield: 81 mg (55%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 50.4 (d, J = 110 Hz). ^1H NMR (C_6D_6): δ 7.46 (d, J = 8 Hz, 2H), 7.16-7.20 (m, 2H), 6.81 (s, 1H), 6.77 (d, J = 5 Hz, 2H), 6.67-6.74 (m, 4 Hz), 2.28 (m, 4H), 2.09 (s, 6H), 1.28 (app. q(dvt), J = 8 Hz, 6H), 0.94 (app. q(dvt), J = 8 Hz, 6H), 0.84 (m, 12H). $^{13}C\{^{19}F, ^1H\}$ NMR (C_6D_6): δ 191.9 (dt, $J_{C\text{-}Rh}$ = 44 Hz, $J_{C\text{-}P}$ = 9 Hz, *C*=O), 172.9, 159.9 (t, J = 9 Hz, N-*C*), 132.7, 132.0, 131.2, 129.2, 126.1, 120.3, 118.1, 115.1, 105.6, 25.6 (br), 23.8 (br), 20.5, 18.0, 17.4, 16.8. ^{19}F NMR (C_6D_6): δ -66.9. IR (solid): 1701 cm^{-1}. Elem. An.. Found (Calculated) for $C_{34}H_{45}NO_2F_3P_2Rh$: C 56.72 (56.59); H 6.46 (6.29); N 1.90 (1.94).

NMR tube synthesis of 10. **5** (10 mg, 0.014 mmol) was dissolved in 0.6 mL of PhF in a J. Young NMR tube. A capillary with a PPh_3 solution as standard was inserted in the same NMR tube. The reaction mixture was placed in a 60 °C oil bath for 3 h. $^{31}P\{^1H\}$ NMR indicated complete conversion to **7**. After that, PhO_2CCF_3 (21 μL, 0.14 mmol) was added to the solution and the reaction mixture was left at ambient temperature for 4 h. $^{31}P\{^1H\}$ NMR spectroscopic analysis indicated 85% conversion to product **10** and 15% of an unidentified product (singlet at δ 30.6 ppm).

NMR tube synthesis of (PNP)Rh(I)(C(O)CF$_3$). 10 (11 mg, 0.015 mmol) was treated with Me_3SiI (7.0 μL, 0.045 mmol) in a J. Young NMR tube in 0.60 mL of C_6D_6. After 1 h at room temperature, $^{31}P\{^1H\}$ NMR spectroscopic analysis indicated >97% conversion to (PNP)Rh(I)(C(O)CF$_3$). No NMR detectable changes were observed after overnight. ^1H NMR (C_6D_6): δ 7.57 (d, *J* = 8 Hz, 2H), 6.80 (br, 2H), 6.76 (d, *J* = 8 Hz, 2H), 2.69 (m, 2H), 2.39 (m, 2H), 2.09 (s, 6H), 1.37 (app. q(dvt), *J* = 8 Hz, 6H), 1.17 (app. q(dvt), *J* = 8 Hz, 6H), 1.06 (app. q(dvt), *J* = 8 Hz, 6H), 0.99 (app. q(dvt), *J* = 8 Hz, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 192.5~191.5 (m, *C*=O), 160.0 9 (vt, *J* = 9 Hz, N-*C*), 132.7, 132.1, 126.8, 119.6 (vt, *J* = 19 Hz), 118.6, 103.3 (q, *J* = 301 Hz), 25.9 (vt, *J* = 12 Hz), 25.3 (vt, *J* = 12 Hz), 20.5, 19.0, 181., 17.8, 17.7. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 51 (d(br), J = 100 Hz). ^{19}F NMR (C_6D_6): δ -68.9. IR (C_6D_6): 1693 cm^{-1}.

In another J. Young NMR tube, **10** (11 mg, 0.015 mmol) was treated with Me_3SiI (7.0 μL, 0.045 mmol) in 0.60 mL of $CDCl_3$. After 1h at room temperature, $^{31}P\{^1H\}$ NMR analysis indicated >97% conversion to (PNP)Rh(I)(C(O)CF$_3$). ^1H NMR ($CDCl_3$): 7.45 (d, J = 8 Hz, 2H), 6.98 (br, 2H), 6.92(d, J = 9 Hz, 2H), 2.98 (m, 2H), 2.74 (m, 2H), 2.26 (s, 6H), 1.44 (app. q(dvt), *J* = 8 Hz, 6H), 1.29 (app. q(dvt), J = 8 Hz, 6H), 1.16 (app. q(dvt), *J* = 8 Hz, 12H). Me_3SiOPh was also observed by NMR matching the data from a literature source.[5]

Thermolysis of complex 10. In a J. Young NMR tube, **10** (10 mg, 0.014 mmol) was dissolved in about 0.6 mL of C_6D_6 and placed in a 60 °C oil bath for 15 h. Based on ^{31}P NMR spectroscopic analysis, (PNP)Rh(CO) (~20%) was observed together with another new broad doublet at δ 57.0 ppm (*J* = 88 Hz) (~70%) and a broad signal δ 53 ppm . Interestingly, free PhO_2CCF_3 (-75.5 ppm) was detected by ^{19}F NMR. A quartet δ 3.5 ppm (*J* = 11 Hz) together with another small signal at ca. -4 ppm were also observed by ^{19}F NMR. Although the Rh complexes are unidentified in this reaction, the formation of (PNP)Rh(CO) as well as the apparent quartet in

the ^{19}F NMR spectrum (Rh-CF_3) suggest that CO deinserted from the acyl complex. The IR spectrum of this mixture revealed two CO stretching bands (2062 and 1942 cm^{-1}). We have not been able to isolate analytically pure compounds from this reaction mixture. We tentatively assign the signal δ 57.0 ppm observed by ^{31}P NMR to complex (PNP)Rh(CF_3)(CO)(OPh) (IR: 2062 cm^{-1}).

VI. Reactions with PhO_2CCH_3.

Reaction with PhO_2CCH_3. **1** (15 mg, 0.026 mmol) was dissolved in about 0.6 mL of PhF, followed by the addition of PhLi (15 μL, 0.027 mmol). The reaction mixture was stirred for about 10 min and passed through Celite and silica. The volatiles were removed under vacuum. The residue was redissolved in about 0.6 mL of PhF and heated at 60 °C for 3 h. The green solution turned to brown gradually. $^{31}P\{^1H\}$ NMR indicated full conversion to **7**. PhO_2CCH_3 (5.0 μL, 0.039 mmol) was added to the solution and the reaction mixture was allowed to stand at room temperature. After 2 h, $^{31}P\{^1H\}$ NMR spectroscopic analysis revealed two doublets δ 49.9 ppm (J = 108 Hz) (57%) and 47.1 ppm (J = 131 Hz) (43%). Unfortunately, we were not able to isolate pure compounds out of this reaction mixture. Due to the similarity in the $^{31}P\{^1H\}$ NMR (δ 49.9 ppm (J = 108 Hz)) and the Rh-*H* ^1H NMR signals (δ -19.6 ppm (dt, J = 33, 12 Hz)) to compounds **8** and **9**, we tentatively assigned the ^{31}P signal δ 49.9 ppm (J = 108 Hz) to the compound **11**.

NMR tube reaction of 5 with PhO_2CCH_3. **5** (15 mg, 0.021 mmol) and PhO_2CCH_3 (3.0 μL, 0.025 mmol) were dissolved in 0.60 mL of C_6D_6 in a J. Young NMR tube. The reaction mixture was heated at 60 ^oC for 100 min. $^{31}P\{^1H\}$ NMR spectroscopic analysis revealed the formation of (PNP)Rh(CO) (30%), the possible C-H activation product **11** (30%) and two other unidentified species (40%). Continued thermolysis of this reaction mixture at 95^oC for 2 days resulted in (PNP)Rh(CO) as the only observable compound by ^{31}P NMR. However, ^1H NMR spectroscopic analysis revealed that (PNP)Rh(CO) can only account for ~50% percent of the total organometallic Rh by using $(Me_3Si)_2O$ as internal standard. Free ethane was also observed by ^1H NMR.

VII. Reactions with PhO_2CBu^t.

(PNP)Rh(H)($C_6H_4O(O)CCMe_3$) (12). **1** (138 mg, 0.238 mmol) was dissolved in 1 mL of toluene followed by the addition of PhLi (138 μL, 0.248 mmol). The mixture was passed through Celite and silica after stirring at ambient temperature for 10 min. The volatiles were removed under vacuum. The residue was redissolved in about 3 mL of toluene. PhO_2CBu^t (47 μL, 0.26 mmol) was added to the solution and the reaction mixture was heated at 60 °C for 100 min. The volatiles were removed under vacuum and the residue was recrystallized from toluene/pentane at -35 °C. Yield: 73 mg (45%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 50.4 (d, J = 110 Hz). ^1H NMR (C_6D_6): 7.76 (d, J = 8 Hz, (PNP)Aryl-*H*), 7.67 (d, J = 6 Hz, 1H), 6.90 (br, 2H, (PNP)Aryl-*H*), 6.79-6.86 (m, 5H), 2.21 (s, 6H, Ar-C*H*$_3$), 2.15 (m, 4H, C*H*Me$_2$), 1.10 (app. q(dvt), 6H, J = 7 Hz, CH*Me*$_2$), 1.01 (m, 15H, CH*Me*$_2$ + C*Me*$_3$), 0.91 (m, 12H, CH*Me*$_2$), -19.41(dt, J = 31 Hz, 14 Hz, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 177.3, 160.7 (vt, J = 10 Hz, *C*-N), 155.5, 149.0, 139.9 (dt, J = 29 Hz, 9 Hz, ipso-*C*), 131.6, 131.2, 123.9, 123.2 (vt, J = 10 Hz), 122.5 (vt, J = 3 Hz), 122.2, 116.1, 115.7 (t, J = 5 Hz), 39.9, 26.7, 25.2 (vt, J = 14 Hz), 24.6 (vt, J = 9 Hz), 20.7, 18.3, 18.2, 17.9. Elem. An.. Found (Calculated) for $C_{37}H_{54}NO_2P_2Rh$: C 62.49 (62.62); H 7.61 (7.67).

NMR tube synthesis of 12. **5** (10 mg, 0.014 mmol) and PhO_2CBu^t (3.5 μL, 0.015 mmol) were dissolved in 0.60 mL of C_6D_6 in a J. Young NMR tube. The reaction mixture was placed in a 60 °C oil bath for 100 min. ^1H NMR spectroscopic analysis indicated >98% conversion to complex **12** by using $(Me_3Si)_2O$ as internal standard.

(PNP)Rh(C_6H_5)(OC(O)CMe$_3$) (14). **12** (40 mg, 0.056 mmol) and PhO_2CBu^t (30 μL, 0.16 mmol) were dissolved in about 0.6 mL C_6D_6 in a sealed NMR tube and the NMR tube was heated in a 90 °C oil bath. The yellow-greenish solution changed to red gradually. After 53 h, ^{31}P NMR spectroscopic analysis revealed complete consumption of **12** and the appearance of a new

dominant doublet of **14**. The reaction mixture was passed through Celite. The volatiles were removed under vacuum and the residue was recrystalized from toluene/pentane at -35°. Yield: 19 mg (48%). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 40.0 (d, J = 107 Hz). ^{1}H (C_6D_6): δ 8.08 (d, J = 8 Hz, 1H), 7.92 (d, J = 9 Hz, 2H), 6.68-6.99 (m, 8H), 2.47 (m, 2H), 2.24 (m, 2H), 2.12 (s, 6H), 1.35 (s, 9H), 1.22 (app. q(dvt), J = 8 Hz, 6H), 1.15 (app. q(dvt), J = 8 Hz, 6H), 1.07 (app. q(dvt), J = 8 Hz, 6H), 0.40 (app. q(dvt), J = 8 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 189.2 (C=O), 161.3 (t, J = 10 Hz, *C*-N), 138.7 (dt, J = 29 Hz, 9 Hz, ipso-*C*), 136.0, 132.5, 131.5, 127.3, 125.4 (vt, J = 3 Hz), 123.0, 119.0, 118.8 (vt, J = 6 Hz), 118.7, 118.5, 39.3, 30.0, 24.1 (vt, J = 11 Hz), 23.5 (vt, J = 12 Hz), 20.5, 19.2, 17.6, 17.5, 17.3. Elem. An.. Found (Calculated) for $C_{37}H_{54}NO_2P_2Rh$: C 62.61 (62.62); H 7.77 (7.67).

NMR tube thermolysis of 12 in the absence of PhO_2CBu^t. **12** (10 mg, 0.014 mmol) was dissolved in about 0.6 mL C_6D_6 in a sealed NMR tube and heated in a 90 °C oil bath for two days. $^{31}P\{^{1}H\}$ NMR spectroscopic analysis revealed that there are several other unidentified species in the reaction mixture in addition to **14** (50%).

NMR tube thermolysis of 12 in the presence of excess PhO_2CBu^t. The NMR sample of complex **12** generated from the reaction of **5** with PhO_2CBu^t, as described above, was treated with 3 equiv of PhO_2CBu^t. The reaction mixture was heated at 90 °C for 2 d. ^{31}P NMR spectroscopic analysis indicated disappearance of the C-H activation product **12** and the formation of one doublet corresponding the C-O activation product **14**. However, the ^{1}H NMR spectroscopic analysis indicated only ca. 82% formation of the desired product. Some small amounts of impurities remain unidentified.

NMR tube thermolysis of 12 in the presence of excess PhO_2CNEt_2. **12** (10 mg, 0.014 mmol) and PhO_2CNEt_2 (10 μL, 0.060mmol) were dissolved in about 0.6 mL C_6D_6 in a sealed

NMR tube and heated in a 90 °C oil bath. After 5 d, ^{1}H NMR spectroscopic analysis indicated the formation of compounds **14** and **15** in a ca. 1:2 ratio.

VIII. Reactions with PhO_2CNEt_2.

(PNP)Rh(H)($C_6H_4O(O)CNEt_2$) (13). **1** (57 mg, 0.098 mmol) was dissolved in 1 mL of toluene followed by the addition of PhLi (57 μL, 0.10 mmol). The mixture was passed through Celite and silica after stirring at ambient temperature for 10 min. The volatiles were removed under vacuum. The residue was redissolved in about 3 mL of toluene. PhO_2CNEt_2 (22 μL, 0.12 mmol) was added to the solution and the reaction mixture was heated at 60 °C for 100 min. The volatiles were removed under vacuum and the residue was recrystallized from pentane/hexamethyldisiloxane at -35°. Yield: 30 mg (42%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 49.7 (d, J = 111 Hz). ^1H (C_6D_6): 7.80 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 7.77 (br, 1H), 6.95 (br, 2H, (PNP)Aryl-*H*), 6.92 (d, J = 8 Hz, 1H), 6.89 (d, J = 3 Hz, 1H), 6.86 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 6.77 (d, J = 7 Hz, 1H, (PNP)Aryl-*H*), 2.93 (q, J = 7 Hz, 2H, CH_2CH_3), 2.79(q, J = 7 Hz, 2H, CH_2CH_3), 2.34 (m, 2H, $CHMe_2$), 2.23 (s, 6H, Ar-CH_3), 2.18 (m, 2H, $CHMe_2$), 1.15 (app. q(dvt), J = 8 Hz, 6H, $CHMe_2$), 1.03 (m, 18H, $CHMe_2$), 0.84 (t, J = 6 Hz, 3H, CH_2CH_3), 0.57 (t, J = 6 Hz, 3H, CH_2CH_3), -19.53 (dt, J = 31 Hz, 14 Hz, 1H, Rh-*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.9 (vt, J = 8 Hz, *C*-N), 155.7, 155.1, 148.5, 141.7 (dt, J = 30 Hz, 10 Hz), 131.5, 131.4, 123.6 (vt, J = 20 Hz), 123.4, 122.2 (vt, J = 3 Hz), 122.0, 115.9, 115.6 (vt, J = 6 Hz), 41.9, 25.1 (vt, J = 10 Hz), 24.9 (vt, J = 10 Hz), 20.7, 18.2, 17.9, 14.0, 13.2. Elem. An.. Found (Calculated) for $C_{37}H_{55}N_2O_2P_2Rh$: C 61.25 (61.32); H 7.58 (7.65); N 3.81 (3.87).

NMR tube synthesis of 13. **5** (10 mg, 0.014 mmol) and PhO_2CNEt_2 (4.0 μL, 0.015 mmol) were dissolved in 0.60 mL of C_6D_6 in a J. Young NMR tube. The reaction mixture was placed in a 60 °C oil bath for 100 min. ^1H NMR spectroscopic analysis indicated >98% conversion to complex **13** by using $(Me_3Si)_2O$ as an internal integration standard.

(PNP)Rh(C_6H_5)(OC(O)NEt_2) (15). **13** (48 mg, 0.066 mmol) and PhO_2CNEt_2 (37 μL, 0.20 mmol) were dissolved in about 0.6 mL C_6D_6 in a sealed NMR tube and the NMR tube was heated in a 90 °C oil bath. The yellow-greenish solution changed to red gradually. After 9 d, the ^{31}P NMR spectroscopic analysis showed complete consumption of **13** and the appearance of a new dominant doublet of **15**. The reaction mixture was passed through Celite. The volatiles were removed under vacuum and the residue was recrystalized from pentane/hexamethyldisiloxane at -35°. Yield: 22 mg (46%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 39.9 (d, J = 108 Hz). ^1H NMR (C_6D_6): δ8.10 (d, J = 9 Hz, 1H), 7.88 (d, J = 8 Hz, 2H, (PNP)Aryl-*H*), 7.01 (d, J = 7 Hz, 2H), 6.87 (m, 3H), 6.82 (d, J = 8 Hz, 1H), 6.78 (br, 1H), 6.75 (br, 1H), 3.32 (q, J = 7 Hz, 2H, C*H*$_2$CH$_3$), 3.24 (q, J = 7 Hz, 2H, C*H*$_2$CH$_3$), 2.52 (m, 2H, C*H*Me$_2$), 2.20 (m, 2H, C*H*Me$_2$), 2.14 (s, 6H, Ar-CH$_3$), 1.34 (app. q(dvt), J = 8 Hz, 6H, CH*Me*$_2$), 1.01-1.21 (m, 18H), 0.55 (app. q(dvt), J = 8 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 165.1 (*C*=O), 161.1 (vt, J = 9 Hz, *C*-N), 140.2 (dt, J = 34 Hz, 9 Hz), 136.5, 133.7, 132.3, 131.3, 127.1, 125.4, 125.0 (vt, J = 3 Hz), 122.8, 120.2 (vt, J = 20 Hz), 118.7 (t, J = 5 Hz), 40.4, 40.3, 24.6 (vt, J = 10 Hz), 24.0 (vt, J = 11 Hz), 20.5, 19.2, 18.2, 17.9, 17.6, 14.8, 14.6. Elem. An.. Found (Calculated) for $C_{37}H_{55}N_2O_2P_2Rh$: C 61.35 (61.32); H 7.78 (7.65); N 3.79 (3.87).

NMR tube thermolysis of 13 in the absence of PhO_2CNEt_2. **13** (10 mg, 0.015 mmol) was dissolved in about 0.6 mL C_6D_6 in a sealed NMR tube and heated in a 90 °C oil bath for 7 days. $^{31}P\{^1H\}$ NMR spectroscopic analysis revealed that there were several unidentified species in the reaction mixture in addition to **15** (50%). It is worth noting that the by-products observed by this reaction are similar to the by-products observed in the thermolysis of **12** in the absence of phenyl pivalate.

NMR tube thermolysis of 13 in the presence of excess PhO_2CNEt_2. The NMR sample of complex **13** generated from reaction of **5** with PhO_2CNEt_2as described above was treated with excess (10 eq) of PhO_2CNEt_2. The reaction mixture was heated at 90 °C for 9 d. ^{31}P NMR spectroscopic analysis indicated disappearance of the C-H activation product **13** and the formation of one doublet corresponding the C-O activation product **15**. However, the ^{1}H NMR spectroscopic analysis indicated only ca. 90% formation of the desired product. Some small amounts of impurities remian unidentified.

NMR tube thermolysis of 13 in the presence of excess PhO_2CBu^t. **13** (10 mg, 0.015 mmol) together with PhO_2CBu^t (11μL, 0.060 mmol) were dissolved in about 0.6 mL C_6D_6 in a sealed NMR tube and heated in a 90 °C oil bath. After 5 d, ^{1}H NMR spectroscopic analysis indicated >98% conversion to compounds **14** and **15** in a ca. 5:2 ratio.

IX. Graphical NMR spectra.

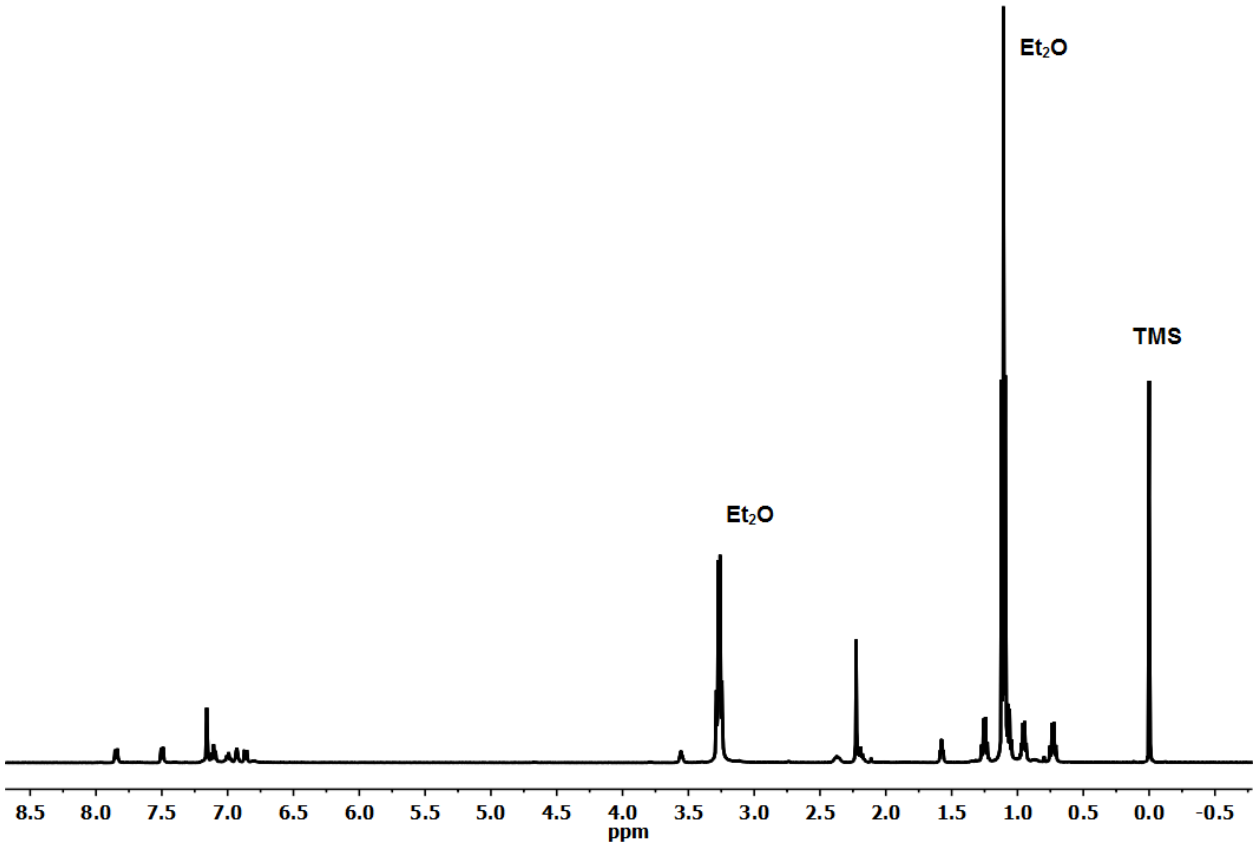

Figure S1 ^{1}H NMR spectrum of **4** generated in situ in C_6D_6 at 23 °C.

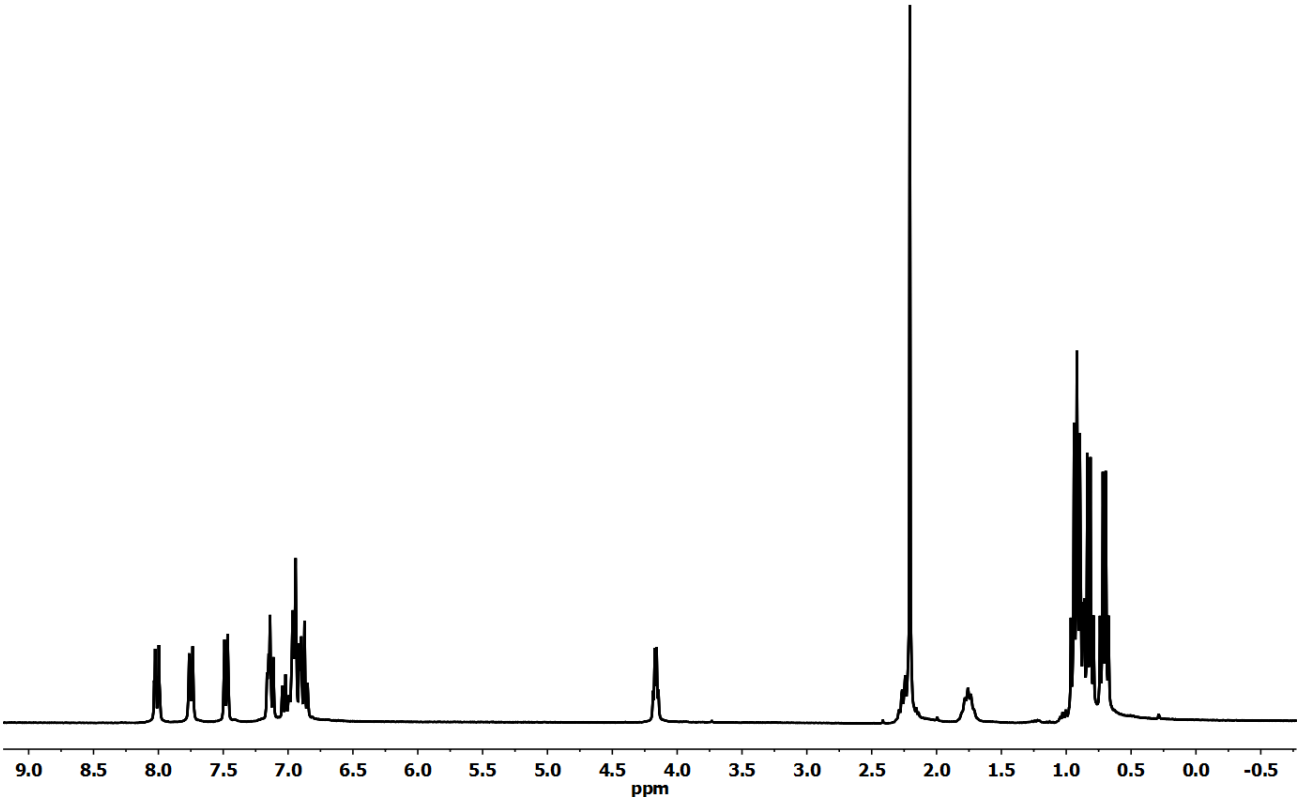

Figure S2 ^{1}H NMR spectrum of **5** in C_6D_6 at 23 °C.

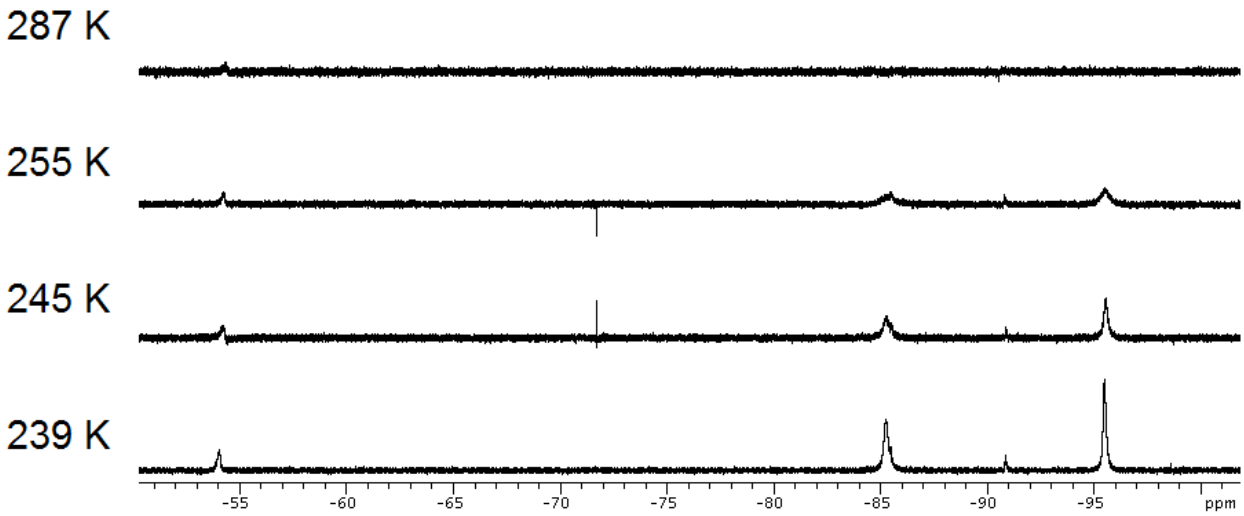

Figure S3 Variable temperature ^{19}F NMR spectra of **7** in PhF (Referenced to C_6H_5F, -113.5 ppm).

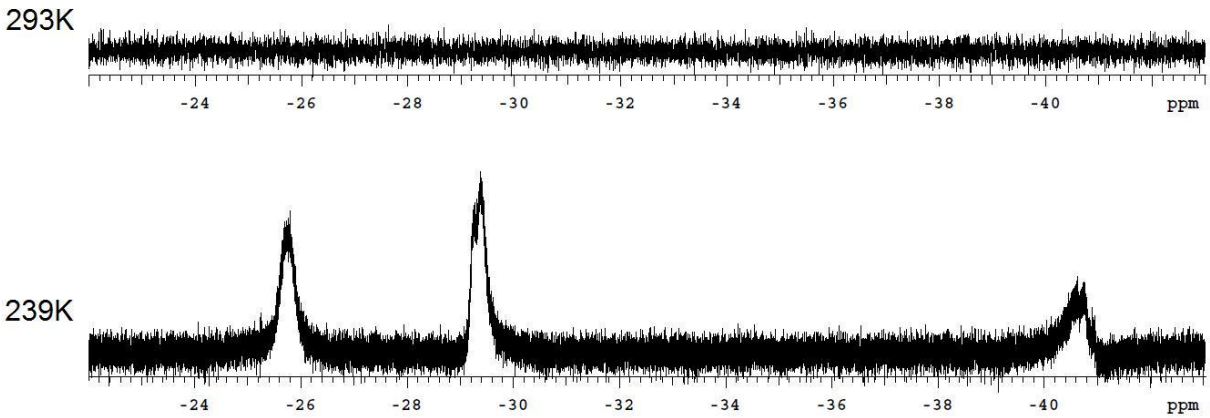

Figure S4 Variable temperature ^{1}H NMR spectra of **7** in PhF (Referenced to trace poly(dimethylsiloxane) as 0 ppm and only hydride region was shown).

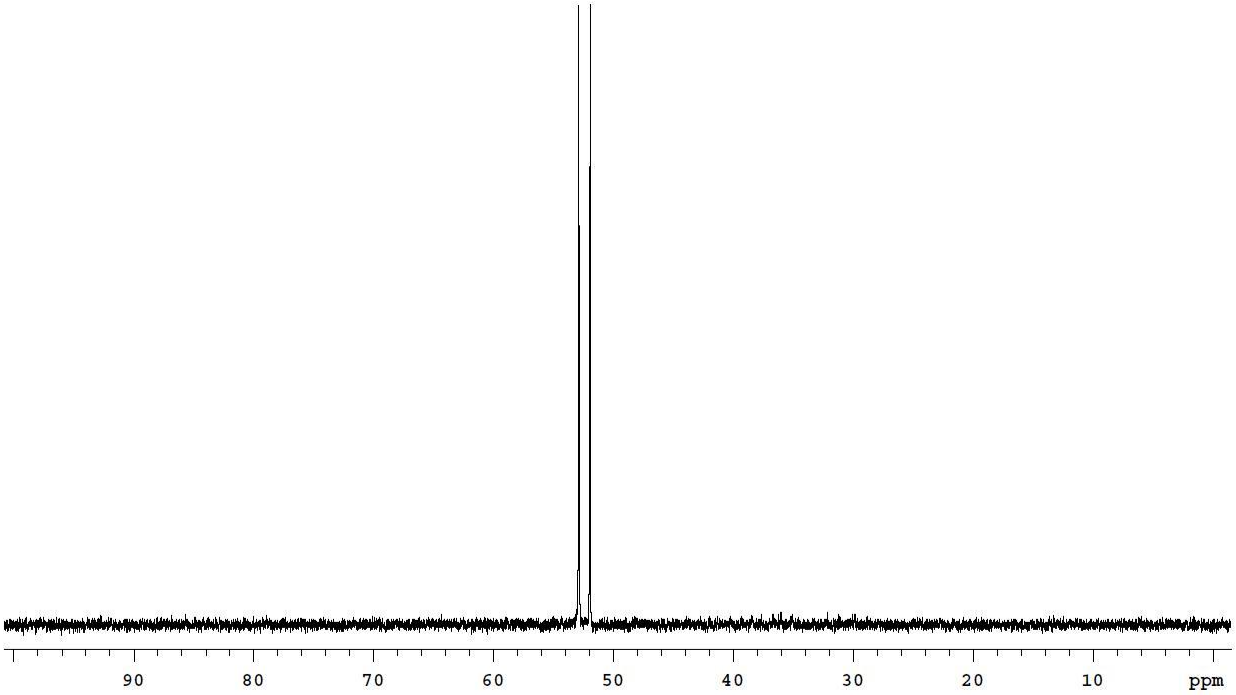

Figure S5 $^{31}P\{^{1}H\}$ NMR spectrum of **7** in PhF at 23 °C.

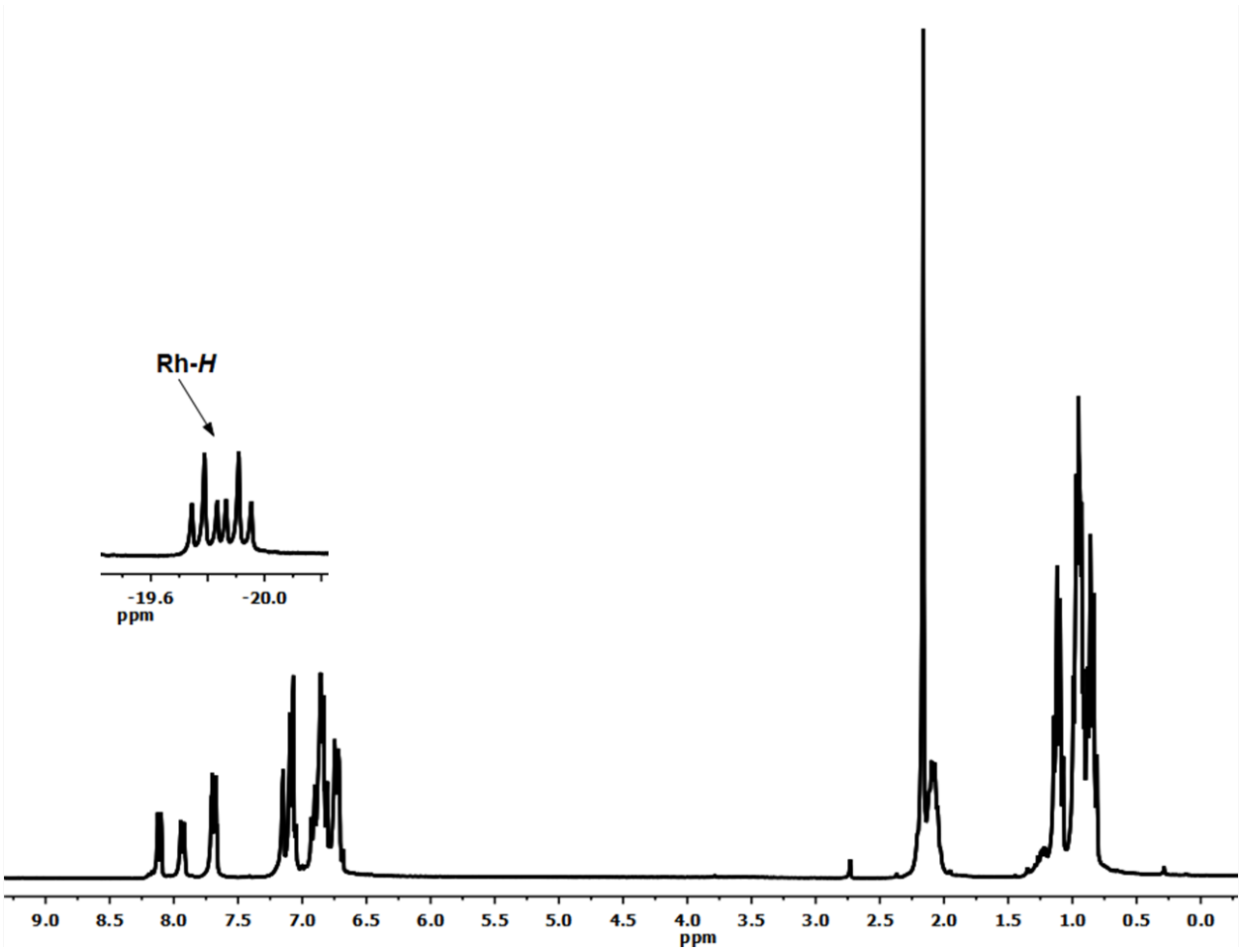

Figure S6 ^{1}H NMR observation of **8** in C_6D_6 at 23 °C.

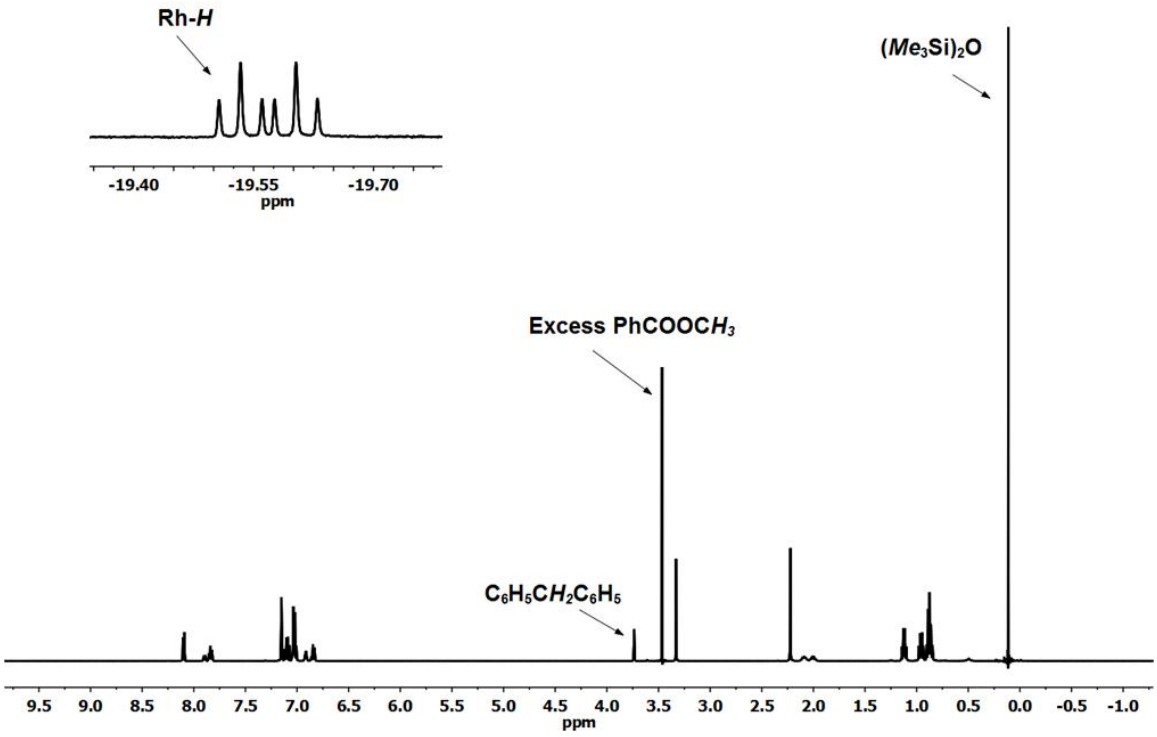

Figure S7 ^{1}H NMR observation of **9** in C_6D_6 (internal standard $(Me_3Si)_2O$) at 23 °C.

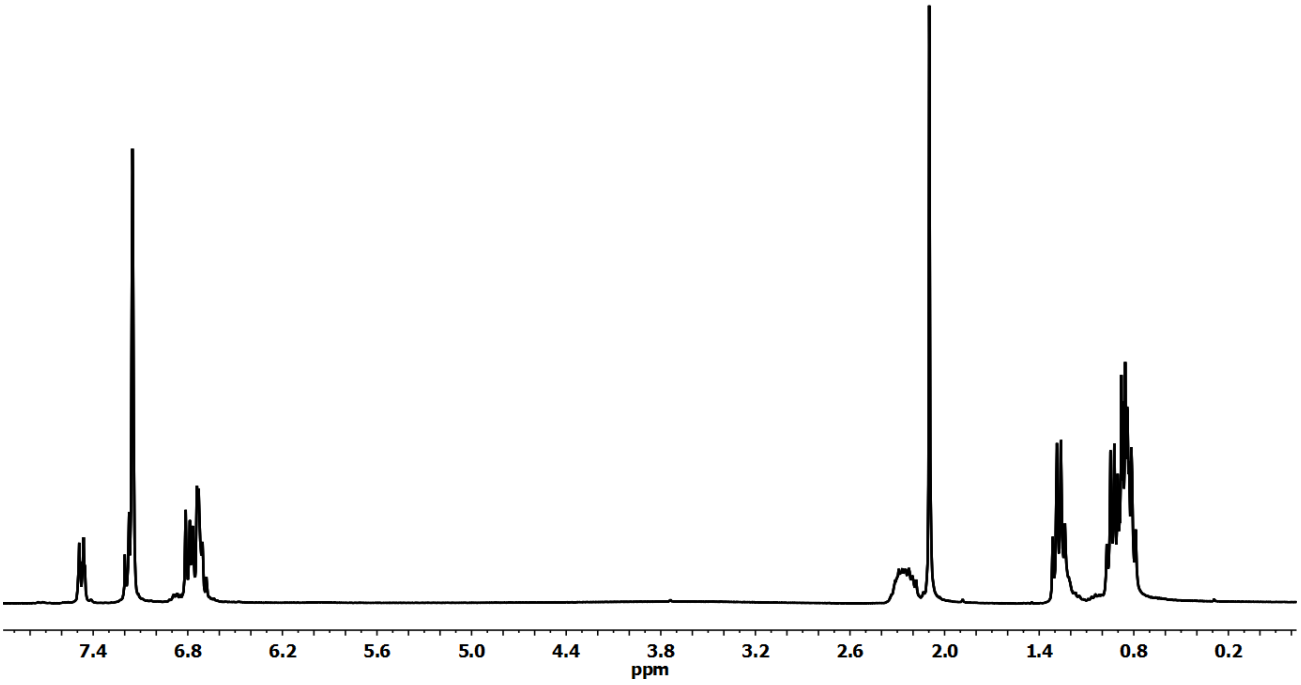

Figure S8 ^{1}H NMR spectrum of **10** in C_6D_6 at 23 °C.

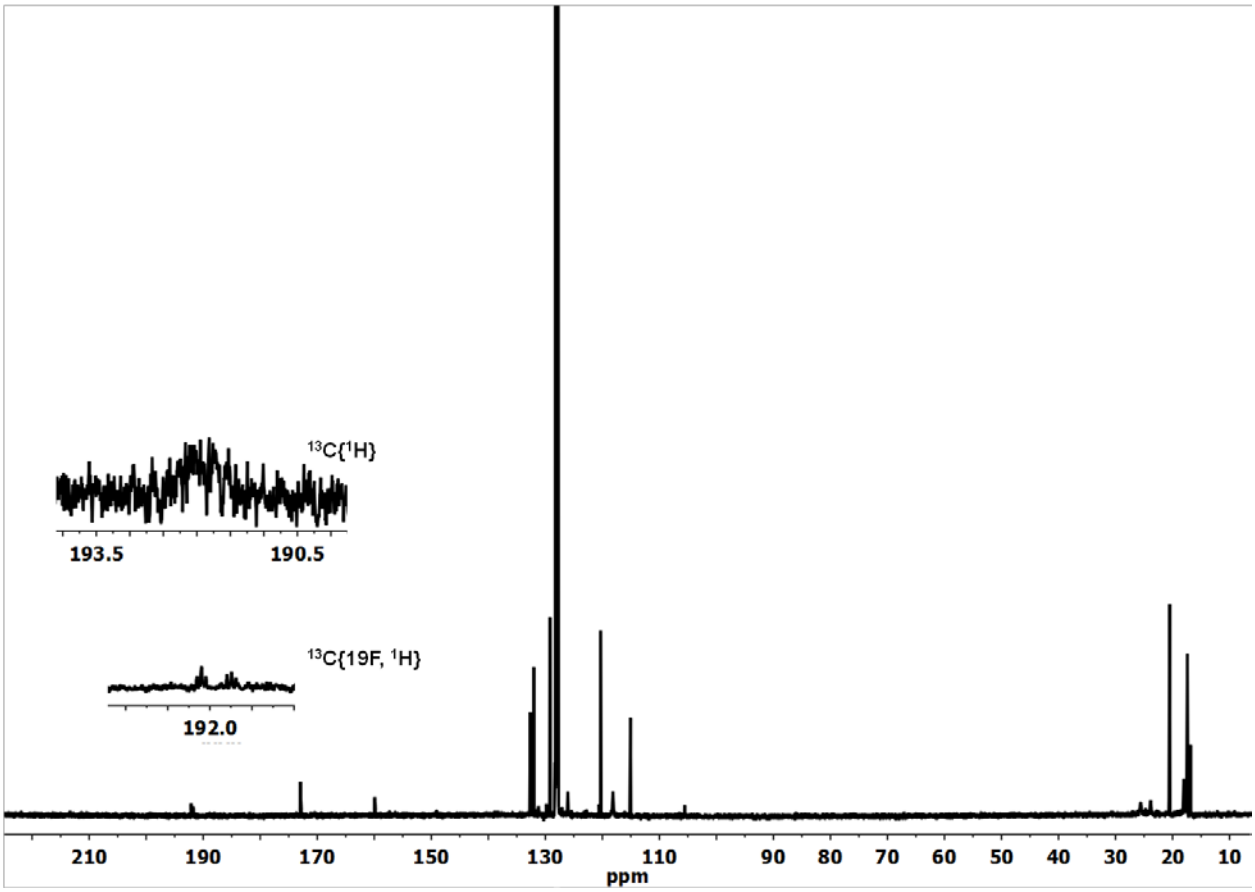

Figure S9 $^{13}C\{^{19}F, ^{1}H\}$ NMR spectrum of **10** in C_6D_6 at 23 °C (on top showing the *C*=O signal without ^{19}F decoupling).

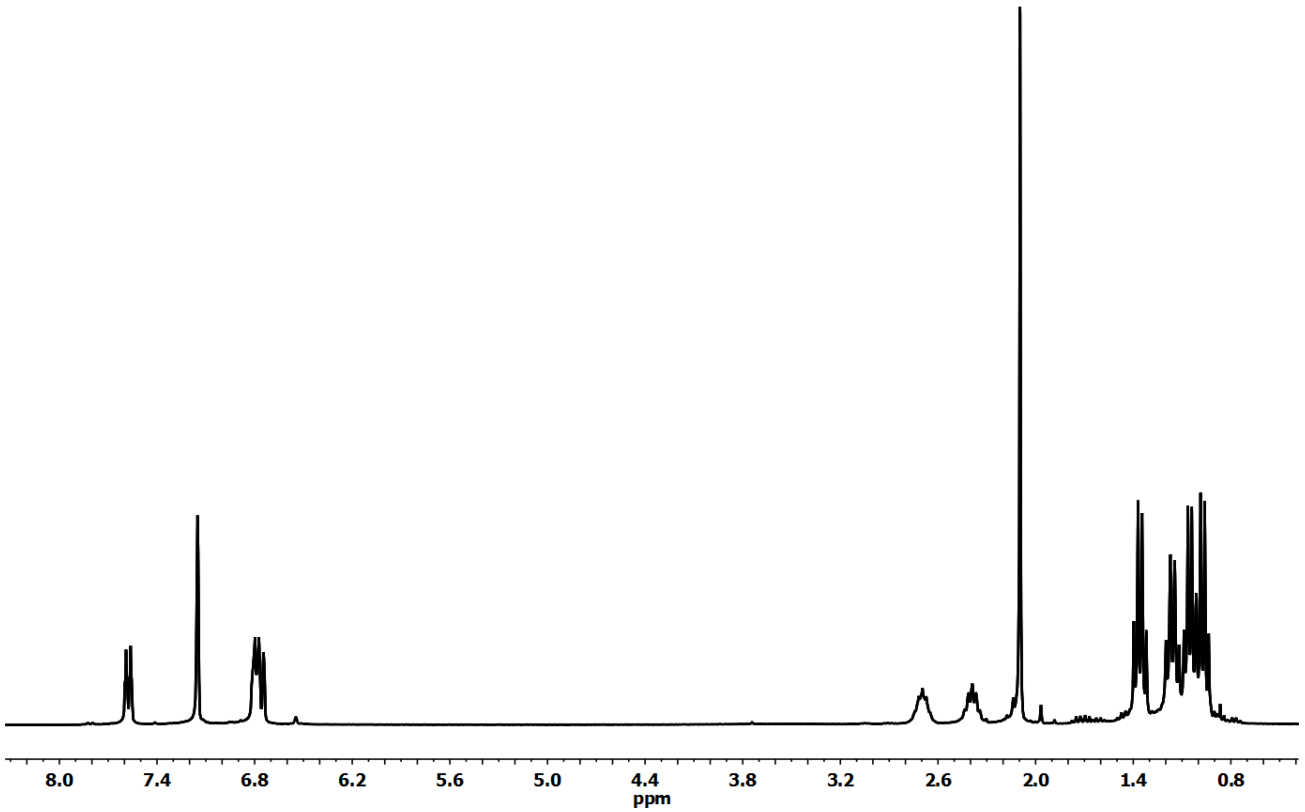

Figure S10 ^{1}H NMR observation of (PNP)Rh(I)(C(O)CF_3) in C_6D_6 at 23 °C.

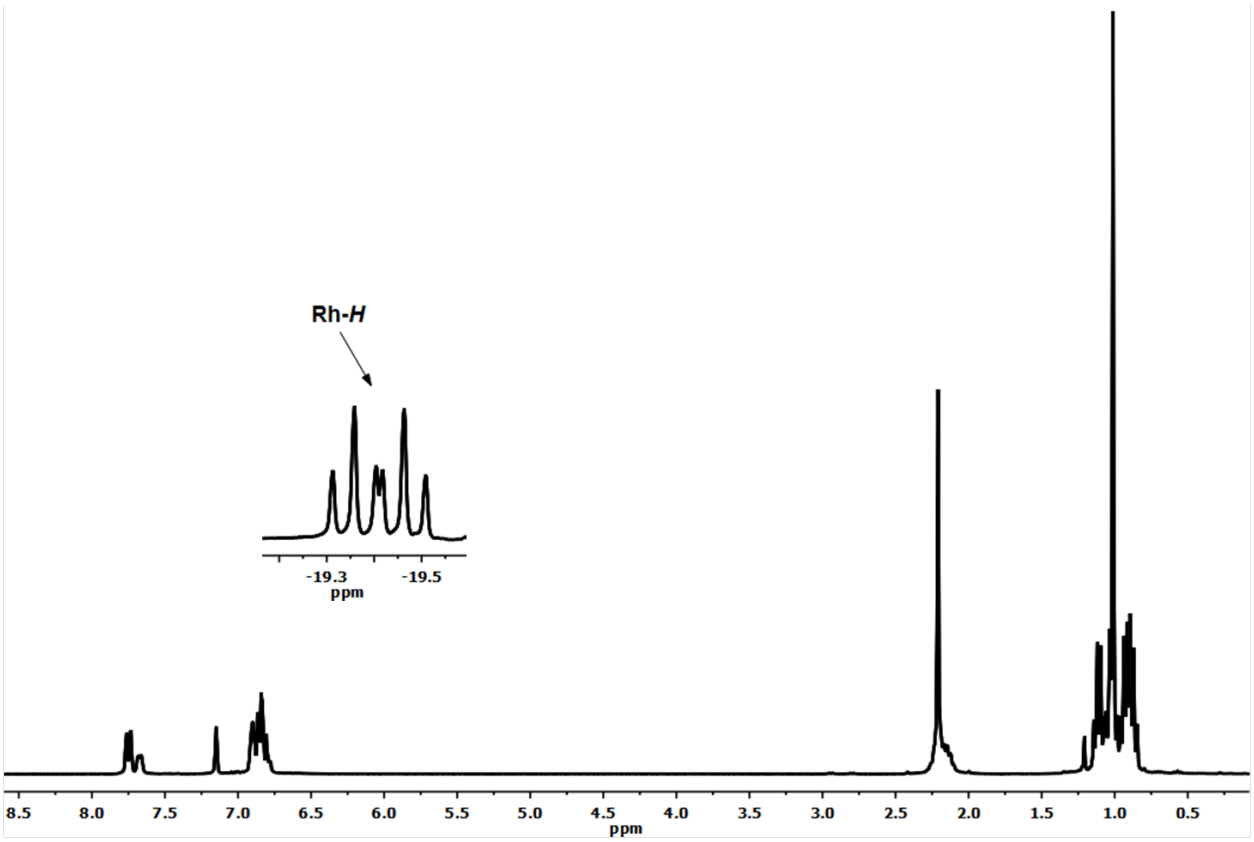

Figure S11 ^{1}H NMR spectrum of **12** in C_6D_6 at 23 °C.

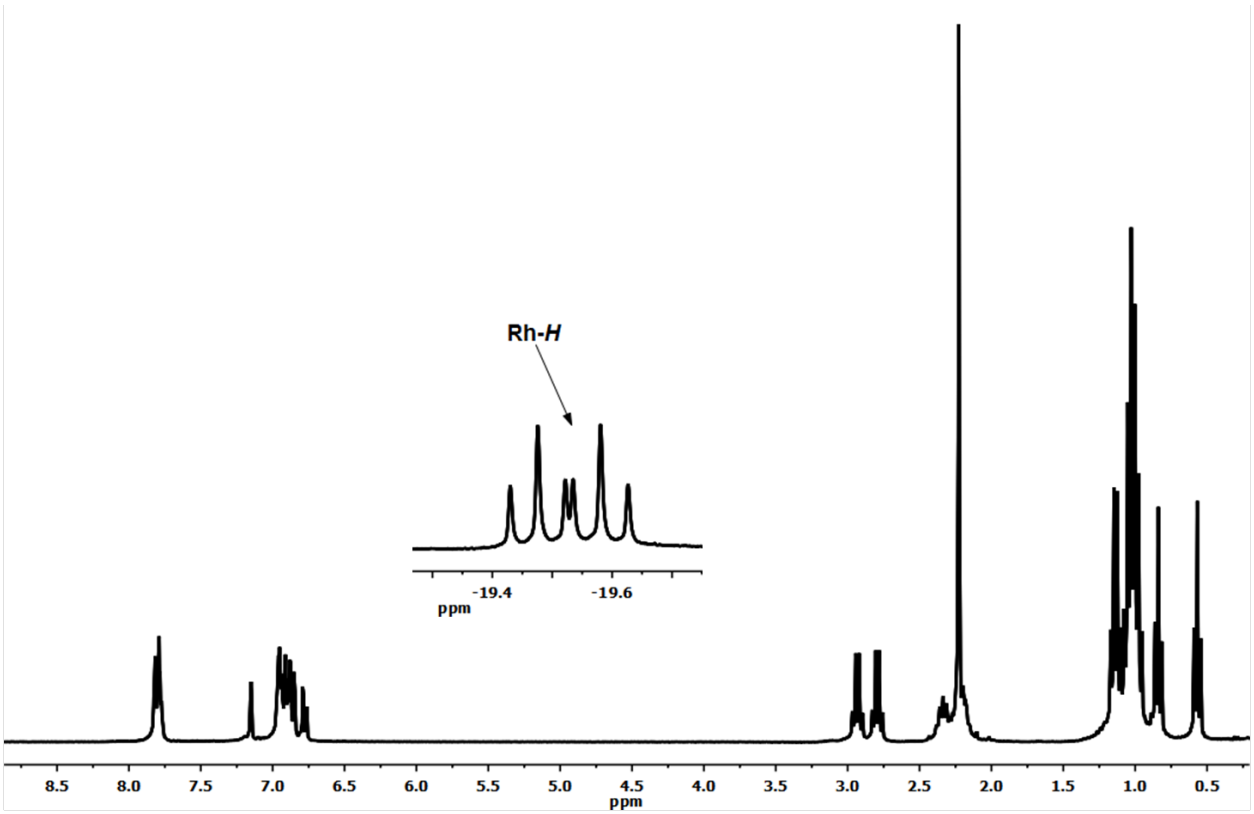

Figure S12 ^{1}H NMR spectrum of **13** in C_6D_6 at 23 °C.

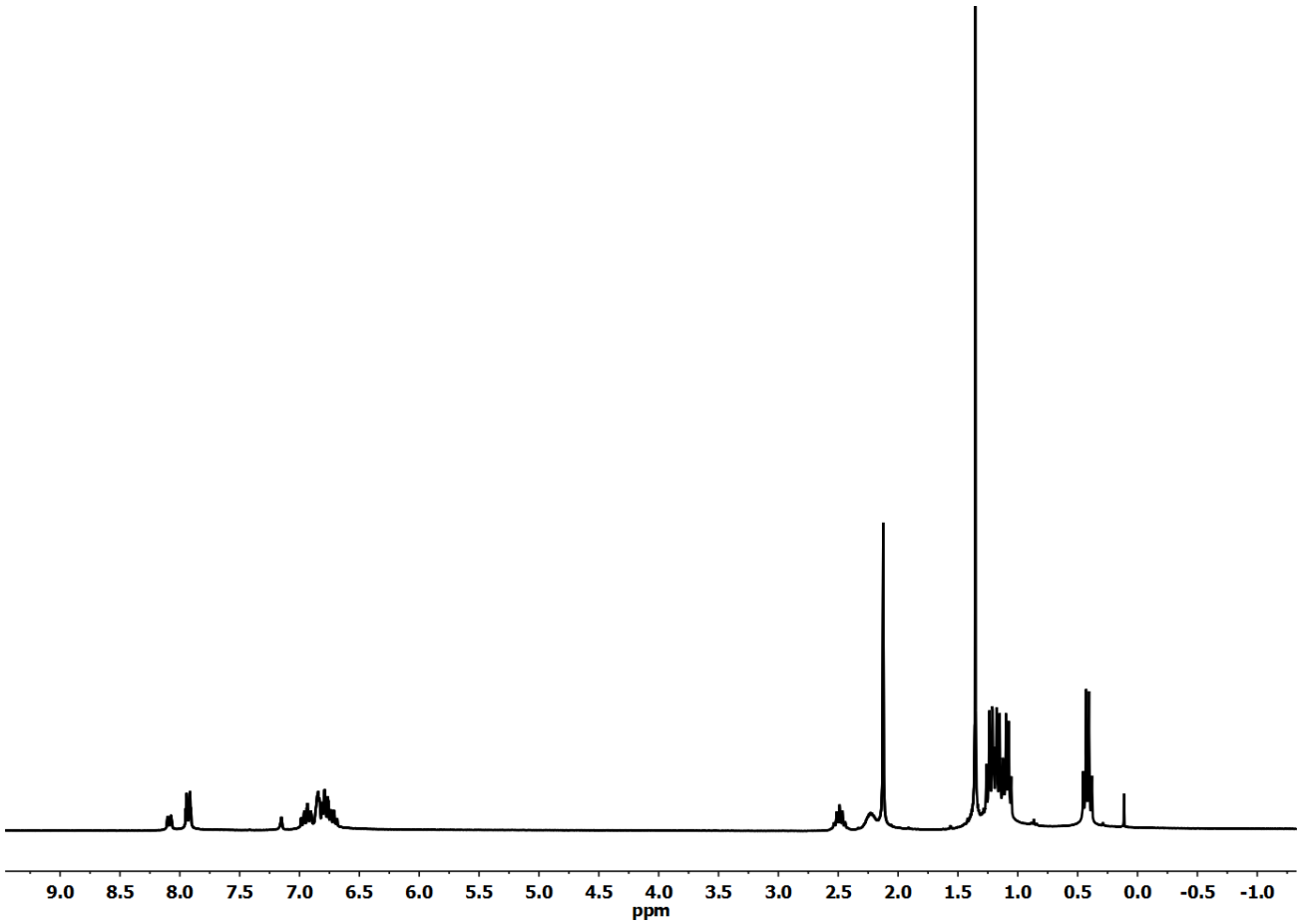

Figure S13 ^{1}H NMR spectrum of **14** in C_6D_6 at 23 °C.

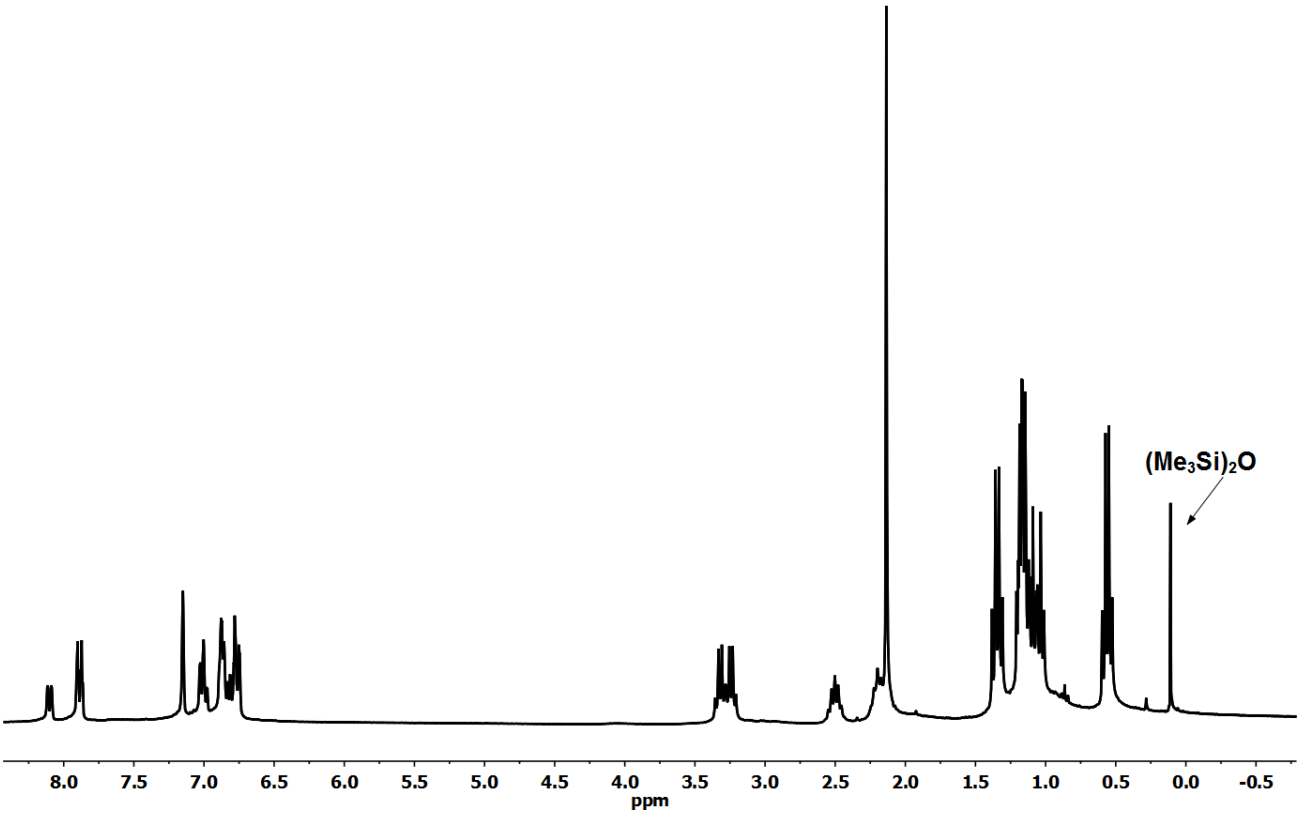

Figure S14 ^{1}H NMR spectrum of **15** in C_6D_6 at 23 °C.

X. Details of X-ray diffractometry studies.

X-Ray data collection, solution, and refinement for 7. A brown, multi-faceted crystal of suitable size (0.3 x 0.1 x 0.1 mm) and quality was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[6] An absorption correction was applied using SADABS.[7] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic $P2_1/c$ space group using XS[8] (incorporated in SHELXTL). No obvious missed symmetry was reported by PLATON.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model with the exception of the hydrogen bound to rhodium which was located from the difference map. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to R_1 = 0.0537 ($I > 2\sigma(I)$, 4907) and wR_2 = 0.1322 (F^2, 32901 data, 357 parameters). The fluorine atom on the fluorobenzene residue was found to reside with equal occupancy on C(34) and C(35) and was refined as such.

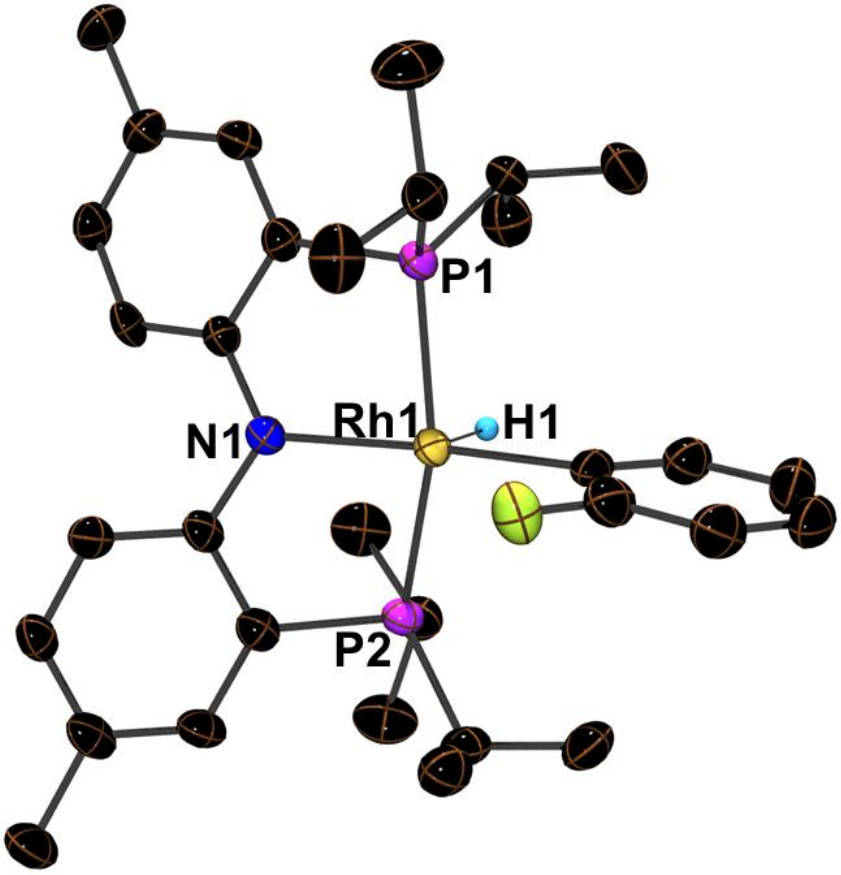

Figure S15. An ORTEP drawing[10] of **7** (50% thermal ellipsoids) showing selected atom labeling. Hydrogen atoms (except Rh-H) and disorder of the fluorophenyl group are omitted for clarity. Selected bond distances (Å) and angles (deg) for **7**: Rh1-P1, 2.2695(17); Rh1-P2, 2.2847(19); Rh1-N1, 2.059(4); Rh1-C33, 2.024(4); P1-Rh1-P2, 160.58(4).

X-Ray data collection, solution, and refinement for 8. An orange block (0.10 x 0.09 x 0.07 mm) was selected from a representative sample of crystals of the same habit using an optical microscope, mounted onto a nylon loop and placed in a cold stream of nitrogen (110 K). Low-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[6] An absorption correction was applied using SADABS.[7] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved in the monoclinic space group $P2_1/c$ by direct methods using XS[8] (incorporated in SHELXTL). and refined by full-matrix least squares on F^2. No obvious missed symmetry was reported by PLATON.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model with the exception of the hydrogen bound to rhodium which was located from the difference map. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to R_1 = 0.0596 ($I > 2\sigma(I)$, 8357 data) and wR_2 = 0.1602 (F^2, 38554 data, 420 parameters).

X-Ray data collection, solution, and refinement for 15. A brown, multi-faceted crystal of suitable size (0.25 x 0.05 x 0.03 mm) and quality was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Due to a fault with the cryostream, room-temperature X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[6] An absorption correction was applied using SADABS.[7] The space group was determined on the basis of systematic absences and intensity statistics and the structure was

solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic $P2_1/n$ space group using XS[8] (incorporated in SHELXTL). No obvious missed symmetry was reported by PLATON.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to $R_1 = 0.0397$ ($I > 2\sigma(I)$, 8517 data) and w$R_2 = 0.1045$ (F^2, 40598 data, 410 parameters).

XI. Supporting Information References.

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[10] Created using *Persistence of Vision Ray Tracer (POV-Ray)* and *Ortep-3 for Windows* (Farugia, L. *J. Appl. Crystallogr.* 1997, **30**, 565)