Electronic Supplementary Material (ESI) for Dalton Transactions.


*Electronic Supplementary Information*

*for*

# A family of rhodium and iridium complexes with versatile semirigid benzylsilyl phosphines: from bidentate to tetradentate coordination

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# Index

# 1. Characterization of compound **1**

## 1.1 $^{1}$H NMR

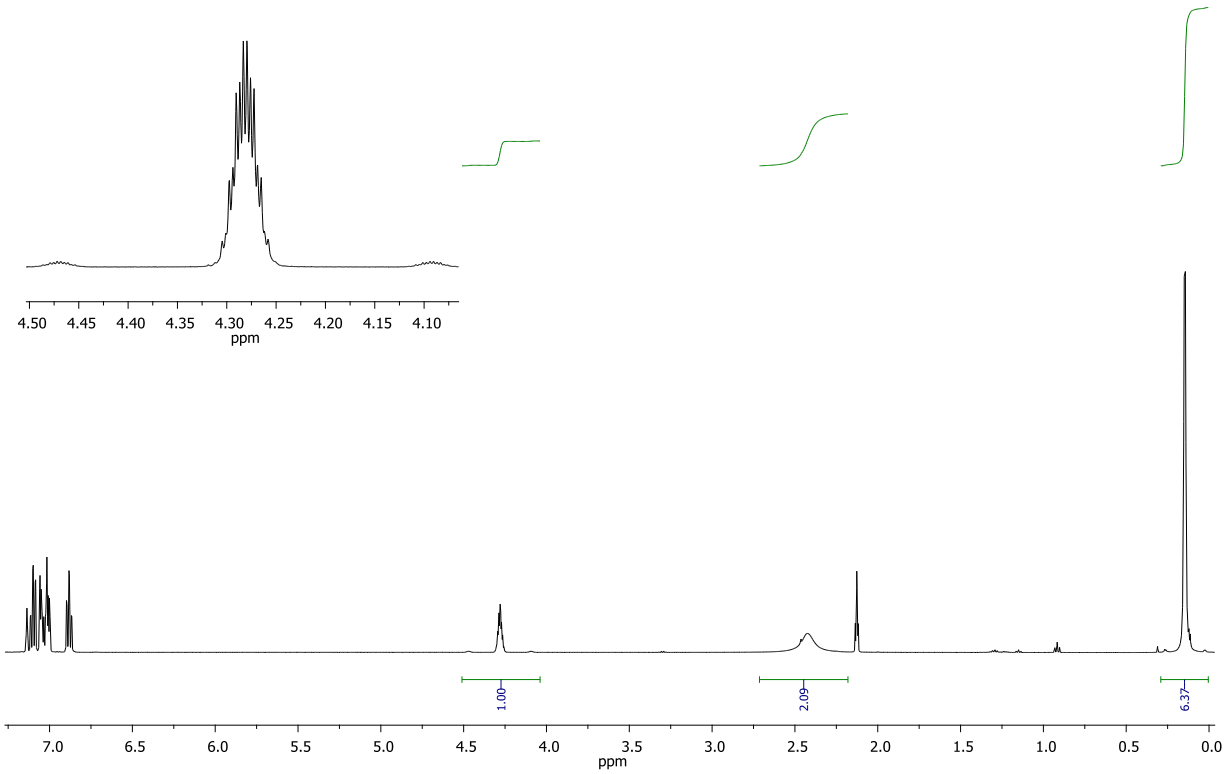



Figure S 1. $^{1}$H NMR spectrum (400 MHz, toluene-$d_8$) of compound **1** at room temperature.

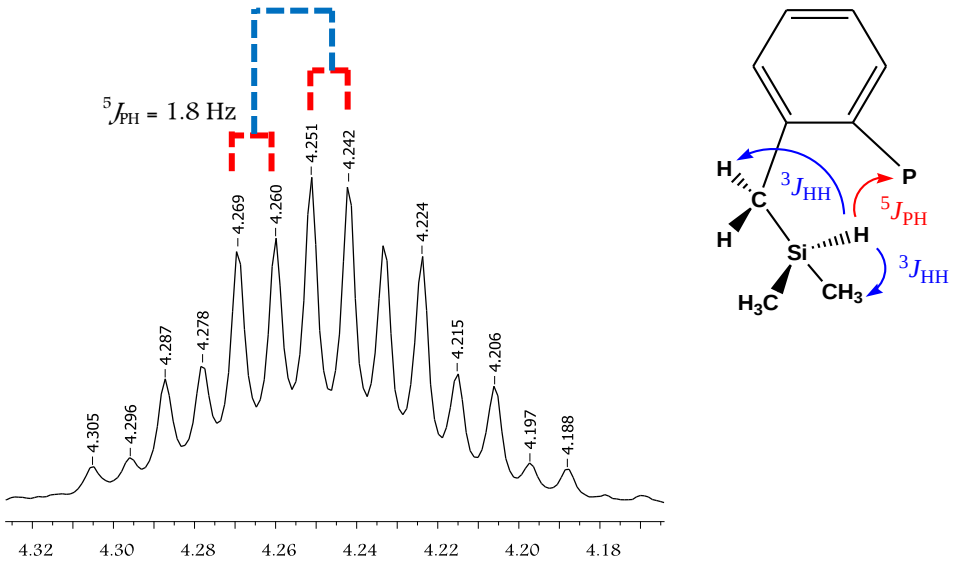



**Figure S 2**. Expansion of the signal of the $^1$H NMR spectrum at δ = 4.25 ppm due to the silicon-bonded hydrogen in compound **1**.

## 1.2 $^{13}$C NMR

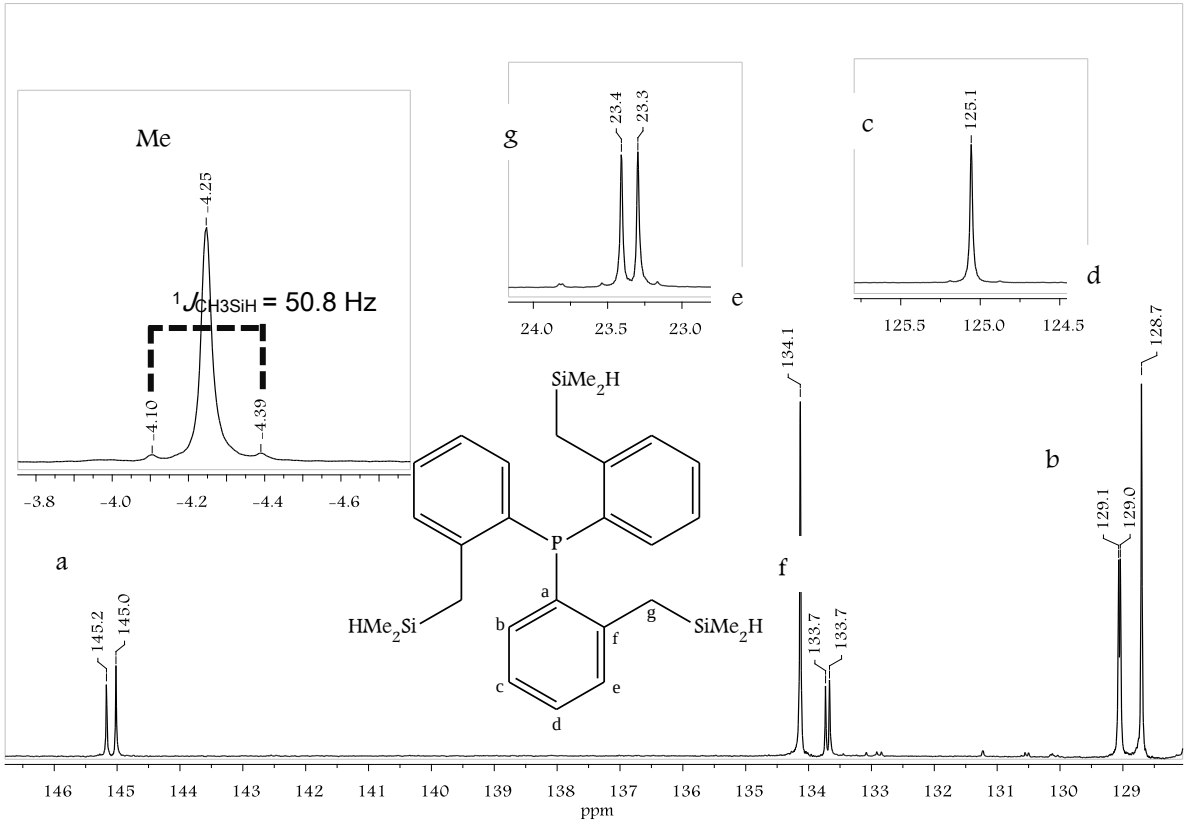



**Figure S 3**. $^{13}$C{$^1$H} NMR spectrum of compound **1** (176.008 MHz, toluene-$d_8$).

## 1.3 $^{31}$P NMR

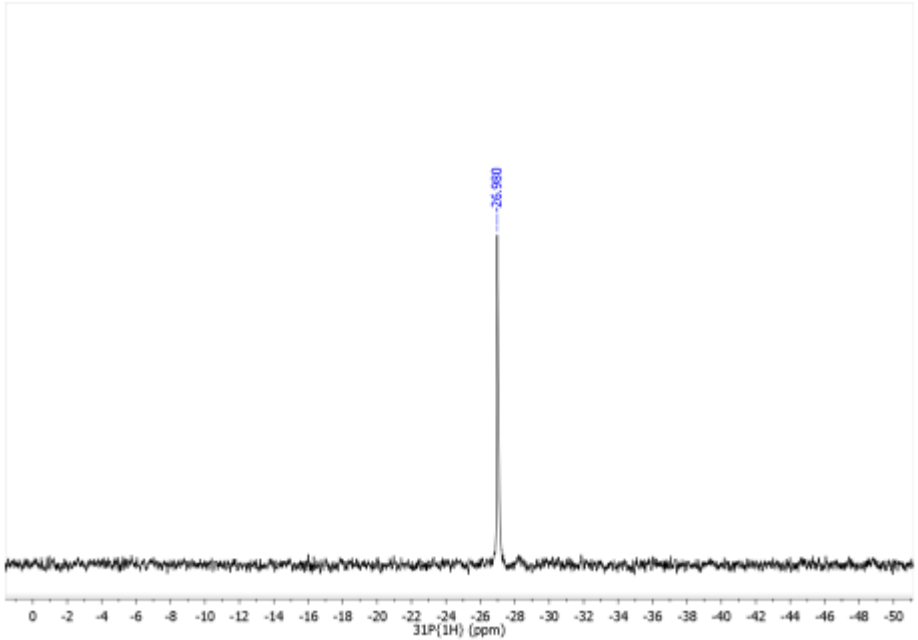



**Figure S 4**. $^{31}P\{^{1}H\}$ (161.9MHz, benzene-$d_6$) NMR spectrum of compound **1** at room temperature.

## 1.4 $^{29}$Si NMR

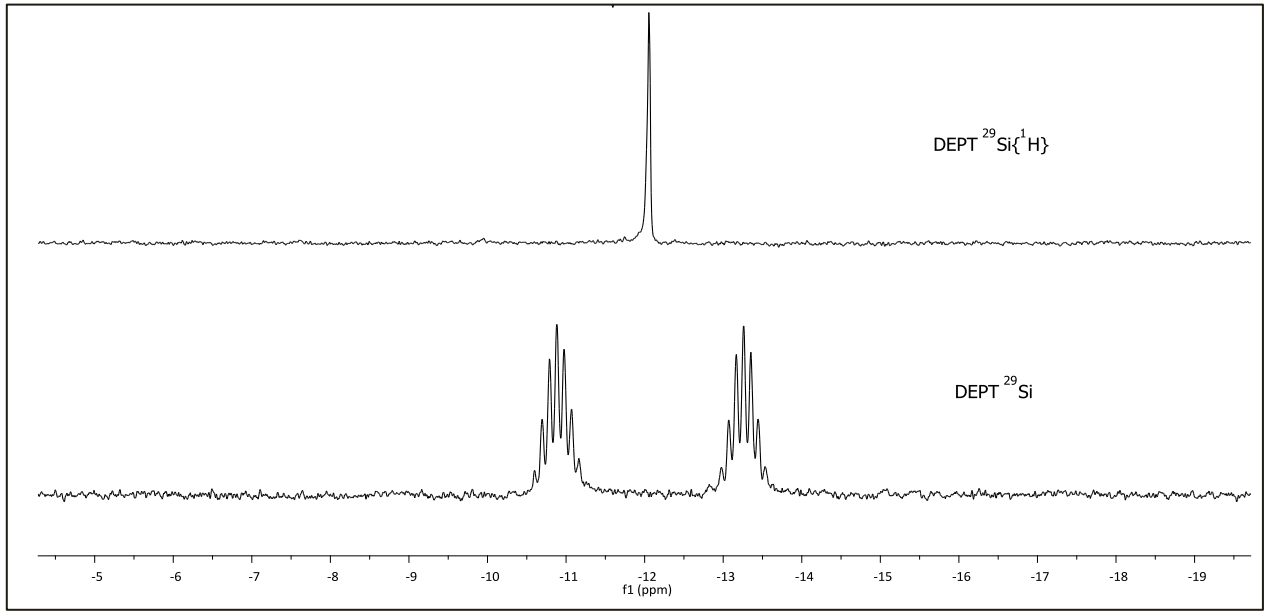



**Figure S 5.** DEPT $^{29}$Si (75.54 MHz, benzene-$d_6$, bottom) and DEPT $^{29}$Si $\{^1$H$\}$ spectra of compound **1**.

## 1.5 FT-IR

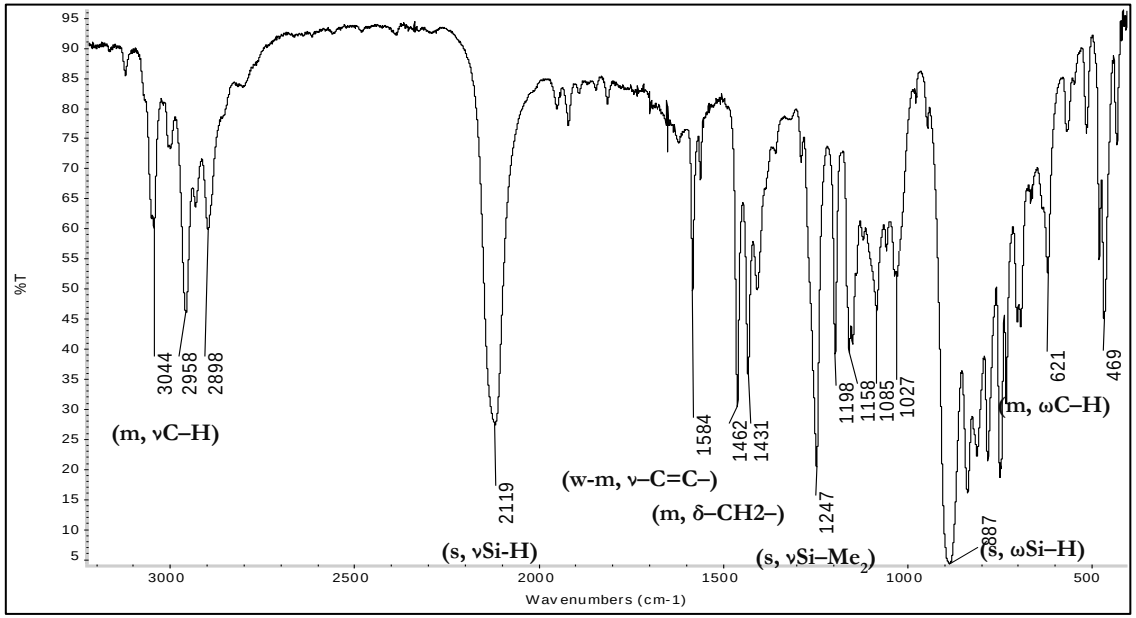



**Figure S 6**. FT- IR spectrum (KBr) of compound **1**.

## 1.6 X-Ray Diffraction structure and tables

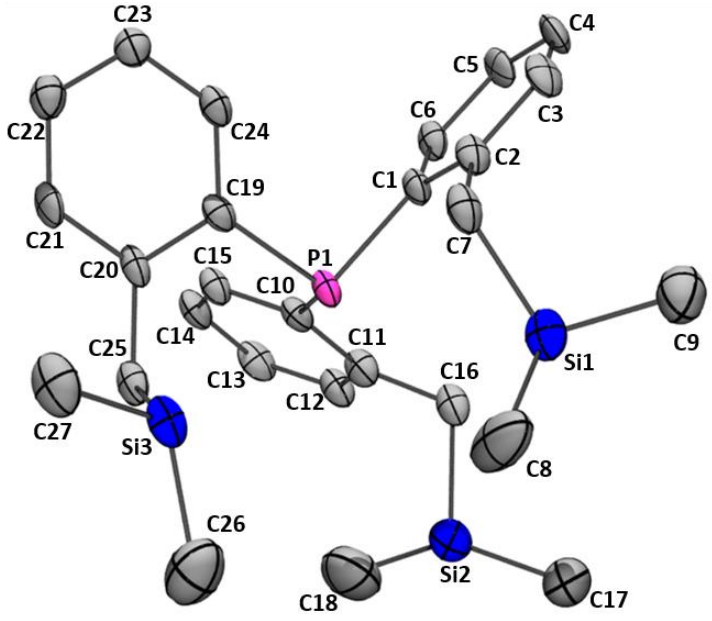



**Figure S 7**. ORTEP drawings of compound **1** showing ellipsoids at 50% probability level.

## X-Ray diffaction tables for compound **1**

Table S1 - Bond Distances (Angstrom)
for: mm104 P 1 21/c 1 R = 0.10

| | | | | | |
|---|---|---|---|---|---|
| P1 | -C1 | 1.834(6) | C14 | -C15 | 1.387(9) |
| P1 | -C10 | 1.853(6) | C19 | -C20 | 1.414(8) |
| P1 | -C19 | 1.841(6) | C19 | -C24 | 1.387(8) |
| Si1 | -C7 | 1.896(7) | C20 | -C25 | 1.505(8) |
| Si1 | -C8 | 1.856(9) | C20 | -C21 | 1.413(8) |
| Si1 | -C9 | 1.852(8) | C21 | -C22 | 1.374(9) |
| Si2 | -C16 | 1.873(7) | C22 | -C23 | 1.383(9) |
| Si2 | -C17 | 1.863(8) | C23 | -C24 | 1.389(8) |
| Si2 | -C18 | 1.857(10) | C3 | -H3A | 0.9300 |
| Si3 | -C25 | 1.890(6) | C4 | -H4 | 0.9300 |
| Si3 | -C26 | 1.863(10) | C5 | -H5 | 0.9300 |
| Si3 | -C27 | 1.871(8) | C6 | -H6 | 0.9300 |
| Si1 | -H1 | 0.9800 | C7 | -H7A | 0.9700 |
| Si2 | -H2 | 0.9800 | C7 | -H7B | 0.9700 |
| Si3 | -H3 | 0.9800 | C8 | -H8A | 0.9600 |
| C1 | -C6 | 1.404(8) | C8 | -H8B | 0.9600 |
| C1 | -C2 | 1.415(9) | C8 | -H8C | 0.9600 |
| C2 | -C3 | 1.413(9) | C9 | -H9A | 0.9600 |
| C2 | -C7 | 1.510(10) | C9 | -H9B | 0.9600 |
| C3 | -C4 | 1.387(10) | C9 | -H9C | 0.9600 |
| C4 | -C5 | 1.377(9) | C12 | -H12 | 0.9300 |
| C5 | -C6 | 1.383(8) | C13 | -H13 | 0.9300 |

| | | | | | |
|---|---|---|---|---|---|
| C10 | -C15 | 1.381(8) | C14 | -H14 | 0.9300 |
| C10 | -C11 | 1.428(8) | C15 | -H15 | 0.9300 |
| C11 | -C16 | 1.504(9) | C16 | -H16A | 0.9700 |
| C11 | -C12 | 1.384(9) | C16 | -H16B | 0.9700 |
| C12 | -C13 | 1.389(9) | C17 | -H17A | 0.9600 |
| C13 | -C14 | 1.387(9) | C17 | -H17B | 0.9600 |
| C17 | -H17C | 0.9600 | C25 | -H25A | 0.9700 |
| C18 | -H18A | 0.9600 | C25 | -H25B | 0.9700 |
| C18 | -H18B | 0.9600 | C26 | -H26A | 0.9600 |
| C18 | -H18C | 0.9600 | C26 | -H26B | 0.9600 |
| C21 | -H21 | 0.9300 | C26 | -H26C | 0.9600 |
| C22 | -H22 | 0.9300 | C27 | -H27A | 0.9600 |
| C23 | -H23 | 0.9300 | C27 | -H27B | 0.9600 |
| C24 | -H24 | 0.9300 | C27 | -H27C | 0.9600 |

Table S2 - Bond Angles (Degrees)
for: mm104 P 1 21/c 1 R = 0.10

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C1 | -P1 | -C10 | 102.5(3) | C3 | -C4 | -C5 | 120.5(6) |
| C1 | -P1 | -C19 | 100.7(2) | C4 | -C5 | -C6 | 119.7(6) |
| C10 | -P1 | -C19 | 101.2(2) | C1 | -C6 | -C5 | 121.4(6) |
| C7 | -Si1 | -C8 | 112.4(3) | Si1 | -C7 | -C2 | 110.3(4) |
| C7 | -Si1 | -C9 | 108.3(3) | C11 | -C10 | -C15 | 119.0(5) |
| C8 | -Si1 | -C9 | 111.5(4) | P1 | -C10 | -C15 | 122.6(4) |
| C16 | -Si2 | -C17 | 109.9(3) | P1 | -C10 | -C11 | 118.4(4) |
| C16 | -Si2 | -C18 | 110.6(4) | C10 | -C11 | -C12 | 117.9(5) |
| C17 | -Si2 | -C18 | 111.2(4) | C10 | -C11 | -C16 | 122.5(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C25 | -Si3 | -C26 | 110.0(4) | C12 | -C11 | -C16 | 119.5(6) |
| C25 | -Si3 | -C27 | 110.7(3) | C11 | -C12 | -C13 | 122.4(6) |
| C26 | -Si3 | -C27 | 109.9(4) | C12 | -C13 | -C14 | 119.4(6) |
| C8 | -Si1 | -H1 | 108.00 | C13 | -C14 | -C15 | 119.2(6) |
| C9 | -Si1 | -H1 | 108.00 | C10 | -C15 | -C14 | 122.1(5) |
| C7 | -Si1 | -H1 | 108.00 | Si2 | -C16 | -C11 | 112.2(4) |
| C18 | -Si2 | -H2 | 108.00 | P1 | -C19 | -C24 | 122.0(4) |
| C16 | -Si2 | -H2 | 108.00 | C20 | -C19 | -C24 | 119.2(5) |
| C17 | -Si2 | -H2 | 108.00 | P1 | -C19 | -C20 | 118.8(4) |
| C25 | -Si3 | -H3 | 109.00 | C21 | -C20 | -C25 | 119.1(5) |
| C27 | -Si3 | -H3 | 109.00 | C19 | -C20 | -C25 | 123.2(5) |
| C26 | -Si3 | -H3 | 109.00 | C19 | -C20 | -C21 | 117.6(5) |
| P1 | -C1 | -C6 | 122.2(5) | C20 | -C21 | -C22 | 122.1(5) |
| P1 | -C1 | -C2 | 118.6(4) | C21 | -C22 | -C23 | 119.9(5) |
| C2 | -C1 | -C6 | 119.2(5) | C22 | -C23 | -C24 | 119.3(5) |
| C1 | -C2 | -C3 | 118.2(6) | C19 | -C24 | -C23 | 122.0(5) |
| C1 | -C2 | -C7 | 121.8(5) | Si3 | -C25 | -C20 | 111.0(4) |
| C3 | -C2 | -C7 | 119.9(6) | C2 | -C3 | -H3A | 120.00 |
| C2 | -C3 | -C4 | 121.0(6) | C4 | -C3 | -H3A | 120.00 |
| C3 | -C4 | -H4 | 120.00 | C15 | -C14 | -H14 | 120.00 |
| C5 | -C4 | -H4 | 120.00 | C10 | -C15 | -H15 | 119.00 |
| C4 | -C5 | -H5 | 120.00 | C14 | -C15 | -H15 | 119.00 |
| C6 | -C5 | -H5 | 120.00 | Si2 | -C16 | -H16A | 109.00 |
| C1 | -C6 | -H6 | 119.00 | Si2 | -C16 | -H16B | 109.00 |
| C5 | -C6 | -H6 | 119.00 | C11 | -C16 | -H16A | 109.00 |
| Si1 | -C7 | -H7A | 110.00 | C11 | -C16 | -H16B | 109.00 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si1 | -C7 | -H7B | 110.00 | H16A | -C16 | -H16B | 108.00 |
| C2 | -C7 | -H7A | 110.00 | Si2 | -C17 | -H17A | 109.00 |
| C2 | -C7 | -H7B | 110.00 | Si2 | -C17 | -H17B | 109.00 |
| H7A | -C7 | -H7B | 108.00 | Si2 | -C17 | -H17C | 109.00 |
| Si1 | -C8 | -H8A | 109.00 | H17A | -C17 | -H17B | 110.00 |
| Si1 | -C8 | -H8B | 109.00 | H17A | -C17 | -H17C | 109.00 |
| Si1 | -C8 | -H8C | 109.00 | H17B | -C17 | -H17C | 109.00 |
| H8A | -C8 | -H8B | 109.00 | Si2 | -C18 | -H18A | 109.00 |
| H8A | -C8 | -H8C | 109.00 | Si2 | -C18 | -H18B | 109.00 |
| H8B | -C8 | -H8C | 110.00 | Si2 | -C18 | -H18C | 109.00 |
| Si1 | -C9 | -H9A | 109.00 | H18A | -C18 | -H18B | 109.00 |
| Si1 | -C9 | -H9B | 109.00 | H18A | -C18 | -H18C | 110.00 |
| Si1 | -C9 | -H9C | 109.00 | H18B | -C18 | -H18C | 109.00 |
| H9A | -C9 | -H9B | 109.00 | C20 | -C21 | -H21 | 119.00 |
| H9A | -C9 | -H9C | 109.00 | C22 | -C21 | -H21 | 119.00 |
| H9B | -C9 | -H9C | 110.00 | C21 | -C22 | -H22 | 120.00 |
| C11 | -C12 | -H12 | 119.00 | C23 | -C22 | -H22 | 120.00 |
| C13 | -C12 | -H12 | 119.00 | C22 | -C23 | -H23 | 120.00 |
| C12 | -C13 | -H13 | 120.00 | C24 | -C23 | -H23 | 120.00 |
| C14 | -C13 | -H13 | 120.00 | C19 | -C24 | -H24 | 119.00 |
| C13 | -C14 | -H14 | 120.00 | C23 | -C24 | -H24 | 119.00 |

Table S2 - Bond Angles (Degrees) (continued)
for: mm104 P 1 21/c 1 R = 0.10

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si3 | -C25 | -H25A | 109.00 | H26A | -C26 | -H26C | 109.00 |
| Si3 | -C25 | -H25B | 109.00 | H26B | -C26 | -H26C | 109.00 |
| C20 | -C25 | -H25A | 109.00 | Si3 | -C27 | -H27A | 110.00 |
| C20 | -C25 | -H25B | 109.00 | Si3 | -C27 | -H27B | 110.00 |
| H25A | -C25 | -H25B | 108.00 | Si3 | -C27 | -H27C | 109.00 |
| Si3 | -C26 | -H26A | 109.00 | H27A | -C27 | -H27B | 109.00 |
| Si3 | -C26 | -H26B | 110.00 | H27A | -C27 | -H27C | 109.00 |
| Si3 | -C26 | -H26C | 109.00 | H27B | -C27 | -H27C | 109.00 |
| H26A | -C26 | -H26B | 109.00 | | | | |

Translation of Symmetry Code to Equiv.Pos

a =[ 3666.00] = [ 3_666] =1-x,1-y,1-z
b =[ 4554.00] = [ 4_565] =x,1/2-y,-1/2+z
c =[ 1556.00] = [ 1_556] =x,y,1+z
d =[ 4555.00] = [ 4_566] =x,1/2-y,1/2+z
e =[ 1554.00] = [ 1_554] =x,y,-1+z
f =[ 2545.00] = [ 2_545] =-x,-1/2+y,1/2-z
g =[ 2656.00] = [ 2_656] =1-x,1/2+y,3/2-z
h =[ 2555.00] = [ 2_555] =-x,1/2+y,1/2-z
i =[ 3566.00] = [ 3_566] =-x,1-y,1-z
j =[ 2646.00] = [ 2_646] =1-x,-1/2+y,3/2-z

# 2 Spectroscopic characterization of compound **2Rh**

## 2.1 $^{1}$H NMR

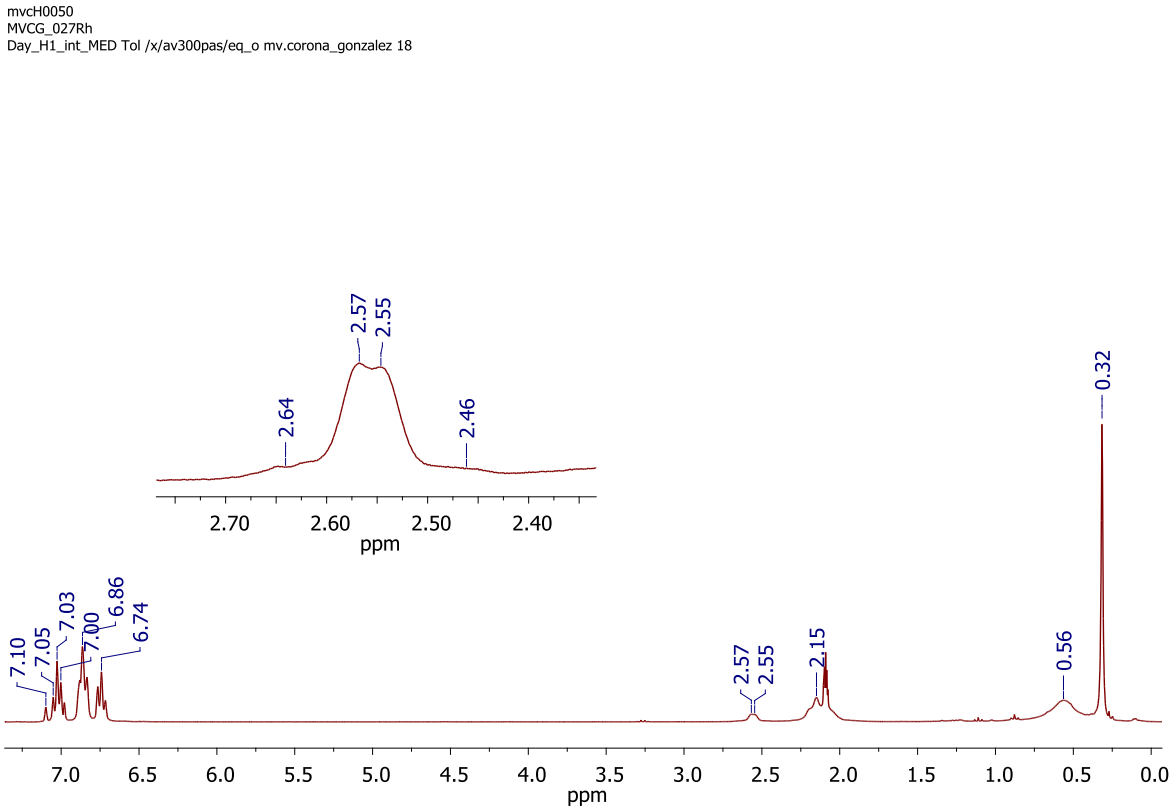



**Figure S 8**. $^{1}$H NMR spectrum (300 MHz, told-$d_8$) of complex **2Rh** at room temperature. Inset showing the signal due to $\eta^2$-(Si-H) with an average value of 51 Hz.

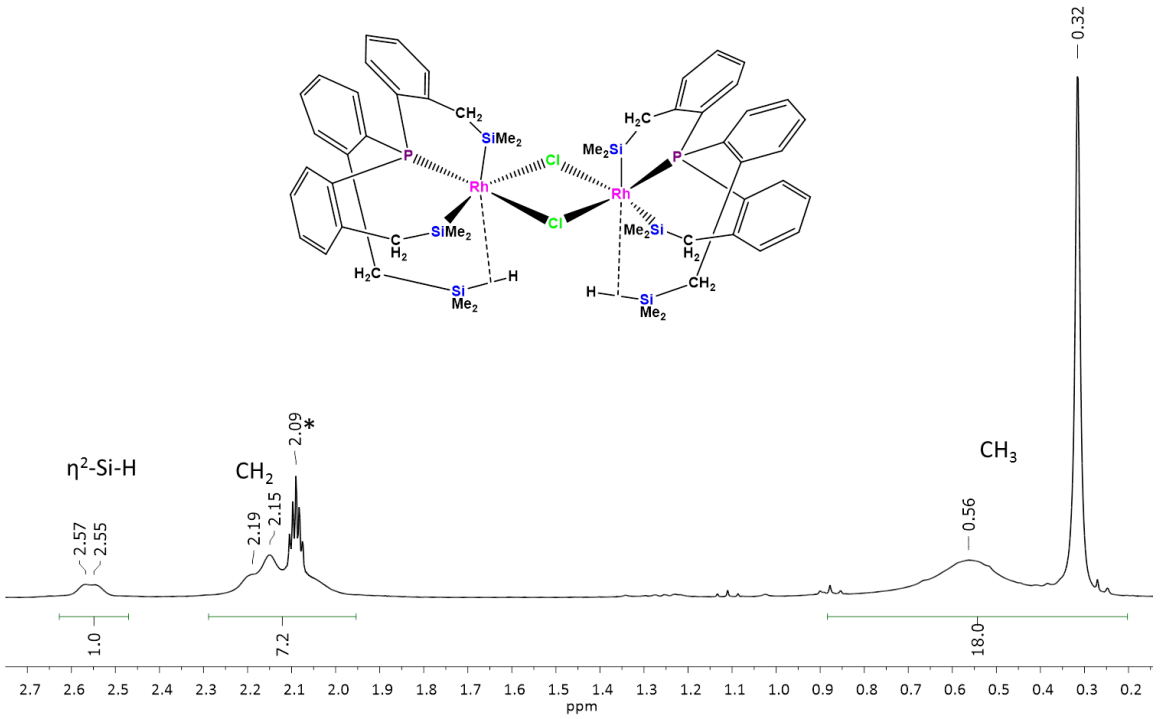



**Figure S 9.** High field region of the $^{1}H$ NMR spectrum (300 MHz, Tol-$d_8$) of **2Rh** at room temperature. Signal at δ 2.09 corresponds to residual solvent.

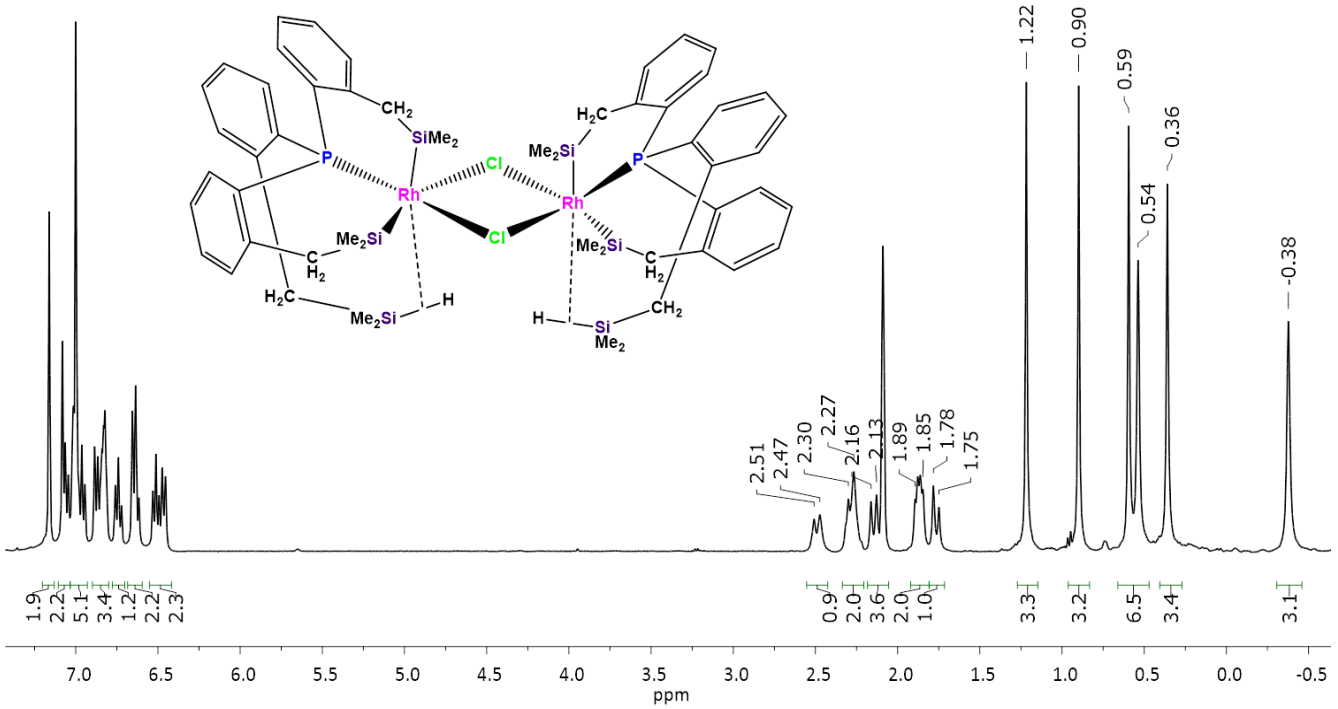



**Figure S 10**. $^{1}$H NMR spectrum (400 MHz, tol-$d_8$) at 223K of compound **2Rh**.

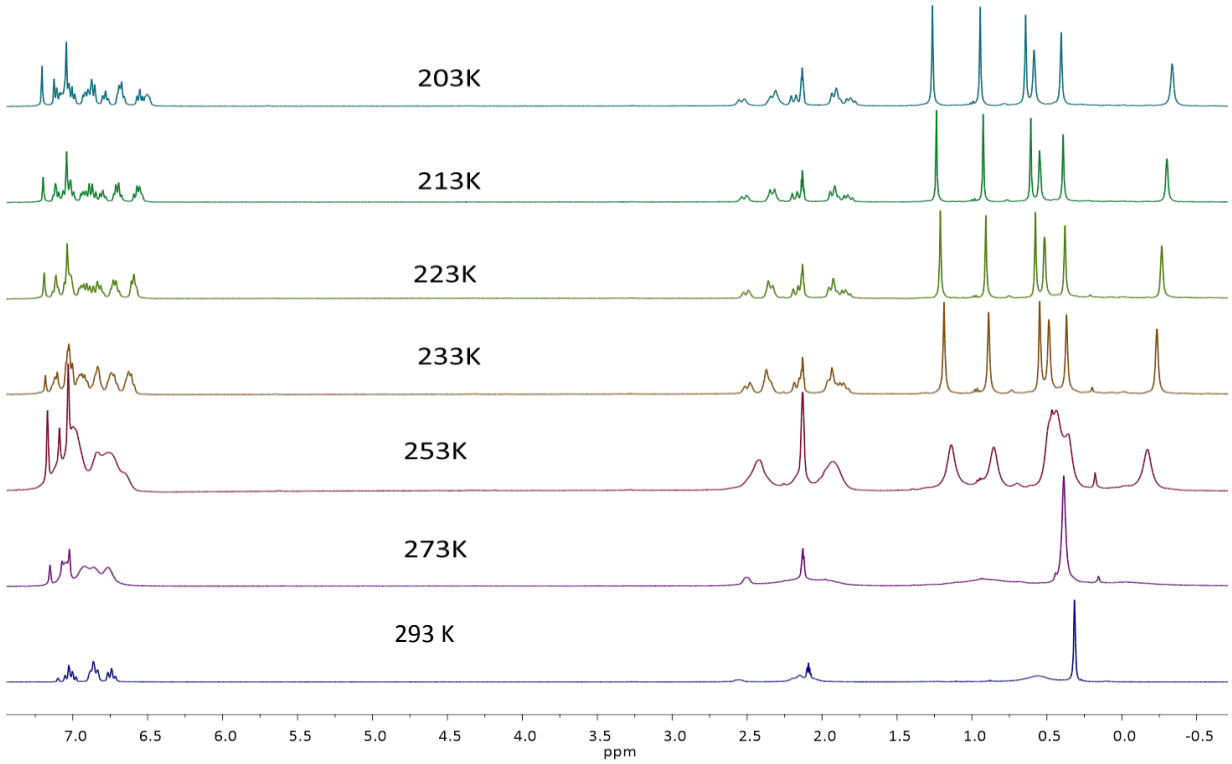



**Figure S 11.** Variable temperature $^{1}H$ NMR spectra (400 MHz, Tol-$d_8$) of complex **2Rh**.

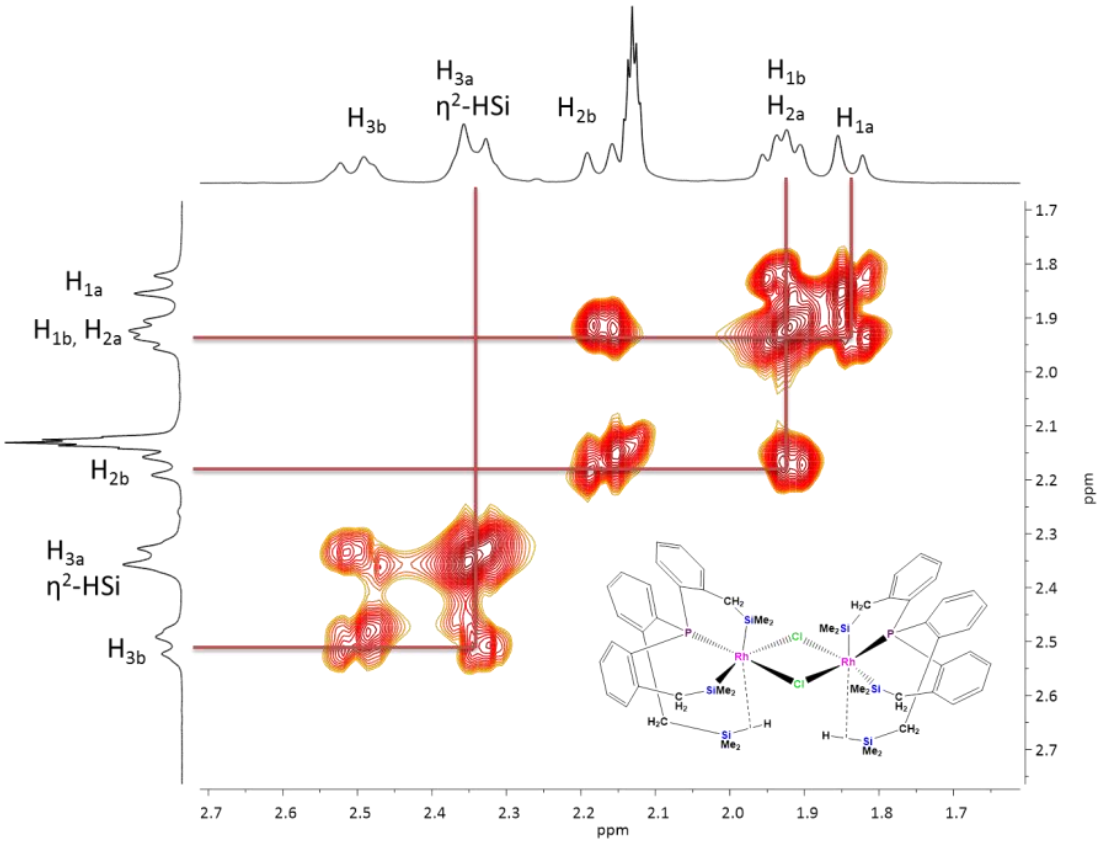



**Figure S 12.** COSY $^{1}H$-$^{1}H$ $\{^{31}P\}$ (400MHz, tol-$d_8$, 223 K) spectrum of compound **2Rh.**

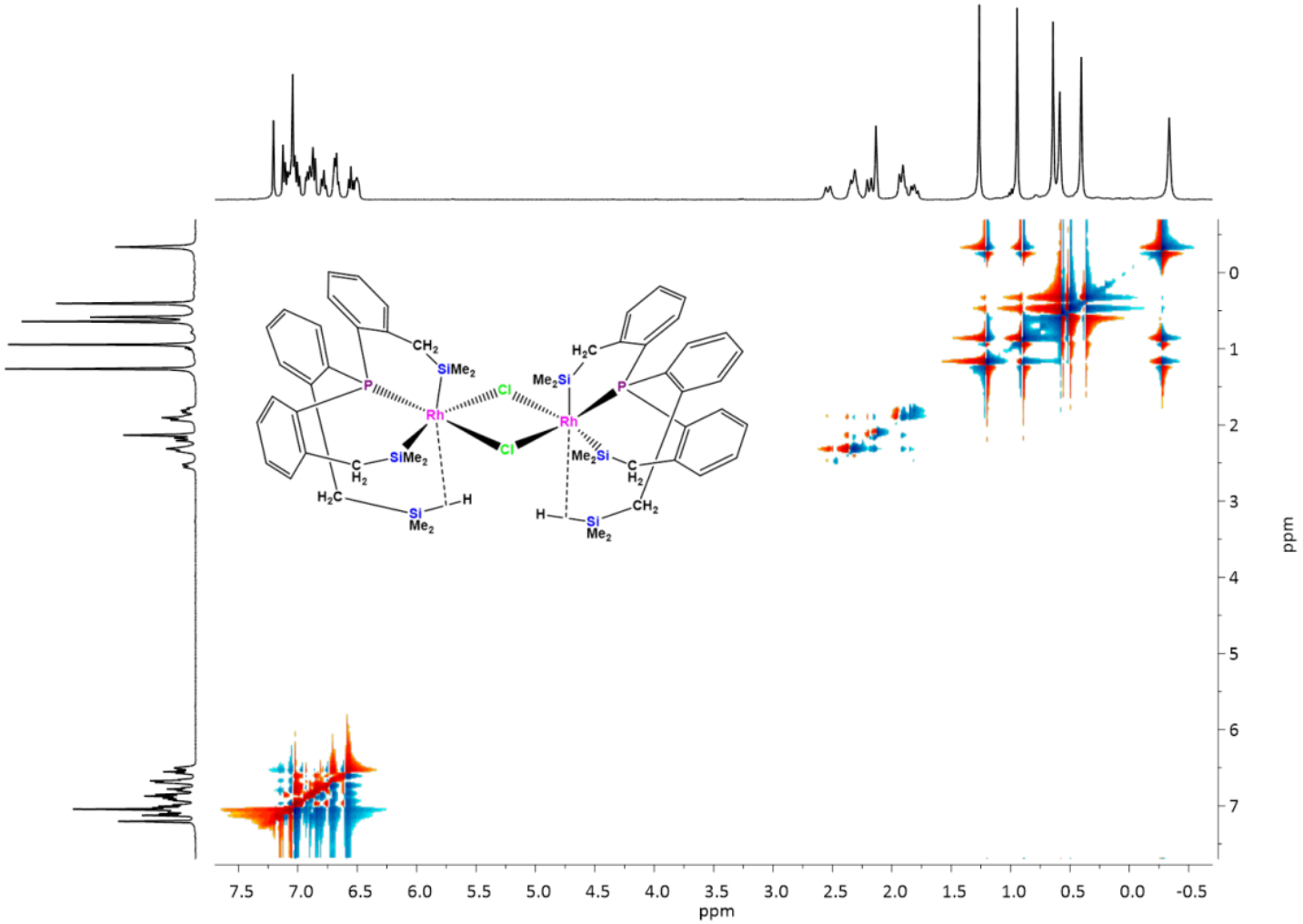



**Figure S 13.** NOESY $^{1}H$-$^{1}H$ NMR spectrum (400 MHz, tol-$d_8$) at 223 K of compound **2Rh**.

## 2.2 $^{13}$C NMR

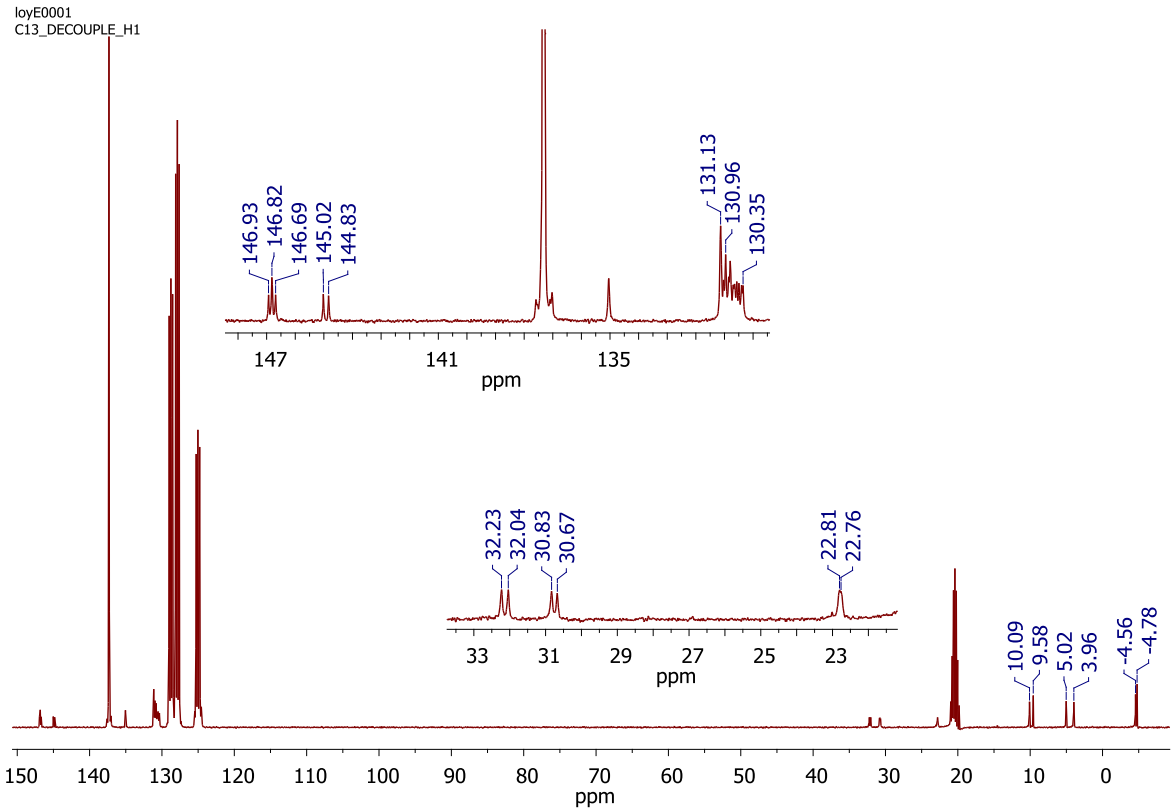



**Figure S 14**. $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, toluene-$d_8$) of complex **2Rh** at 223 K.

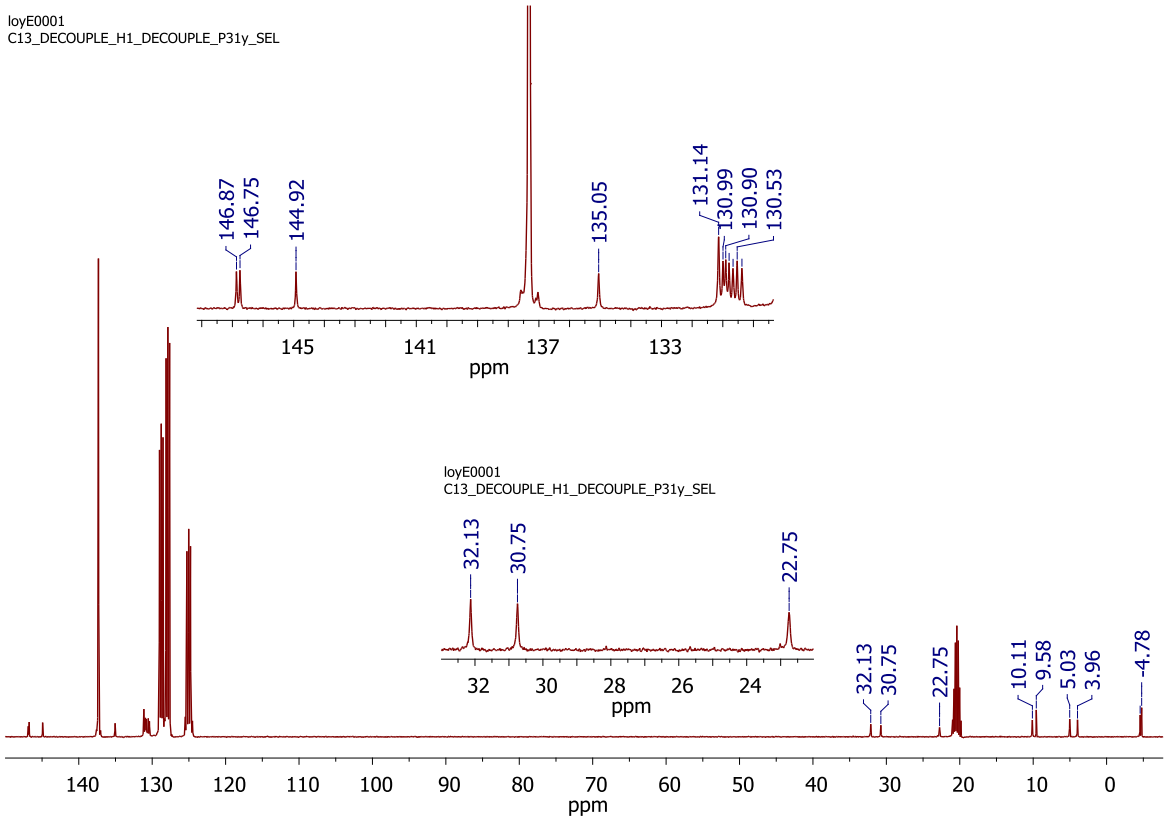



**Figure S 15.** $^{13}C\{^{1}H\}$ NMR spectrum (100.61 MHz, toluene-$d_8$) of complex **2Rh** with $^{31}P$ decoupling (δ 27.7) at 223 K.

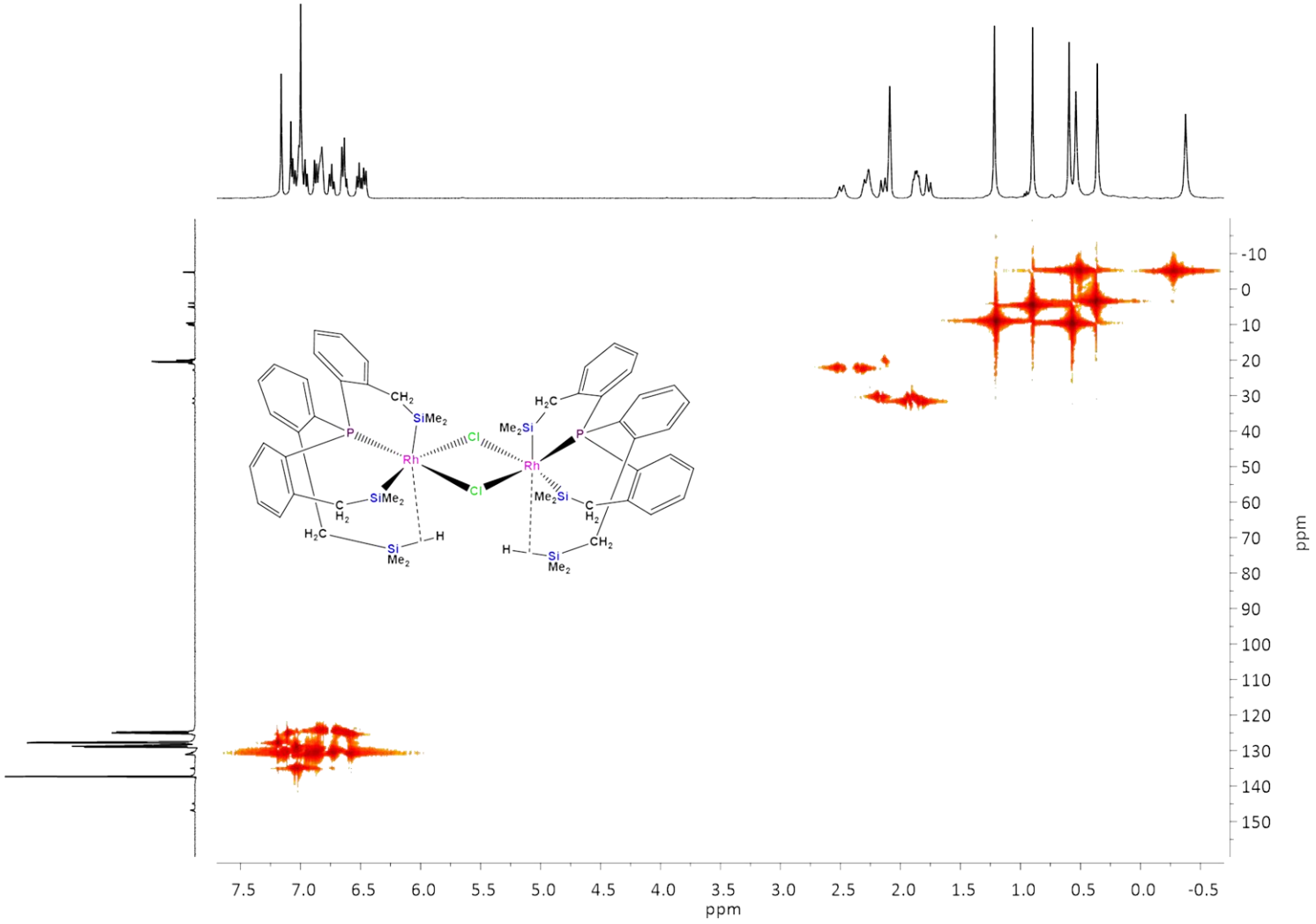



**Figure S 16.** HMQC $^{1}H$-$^{13}C$ (400 MHz, tol-$d_8$) NMR spectrum of compound **2Rh**.

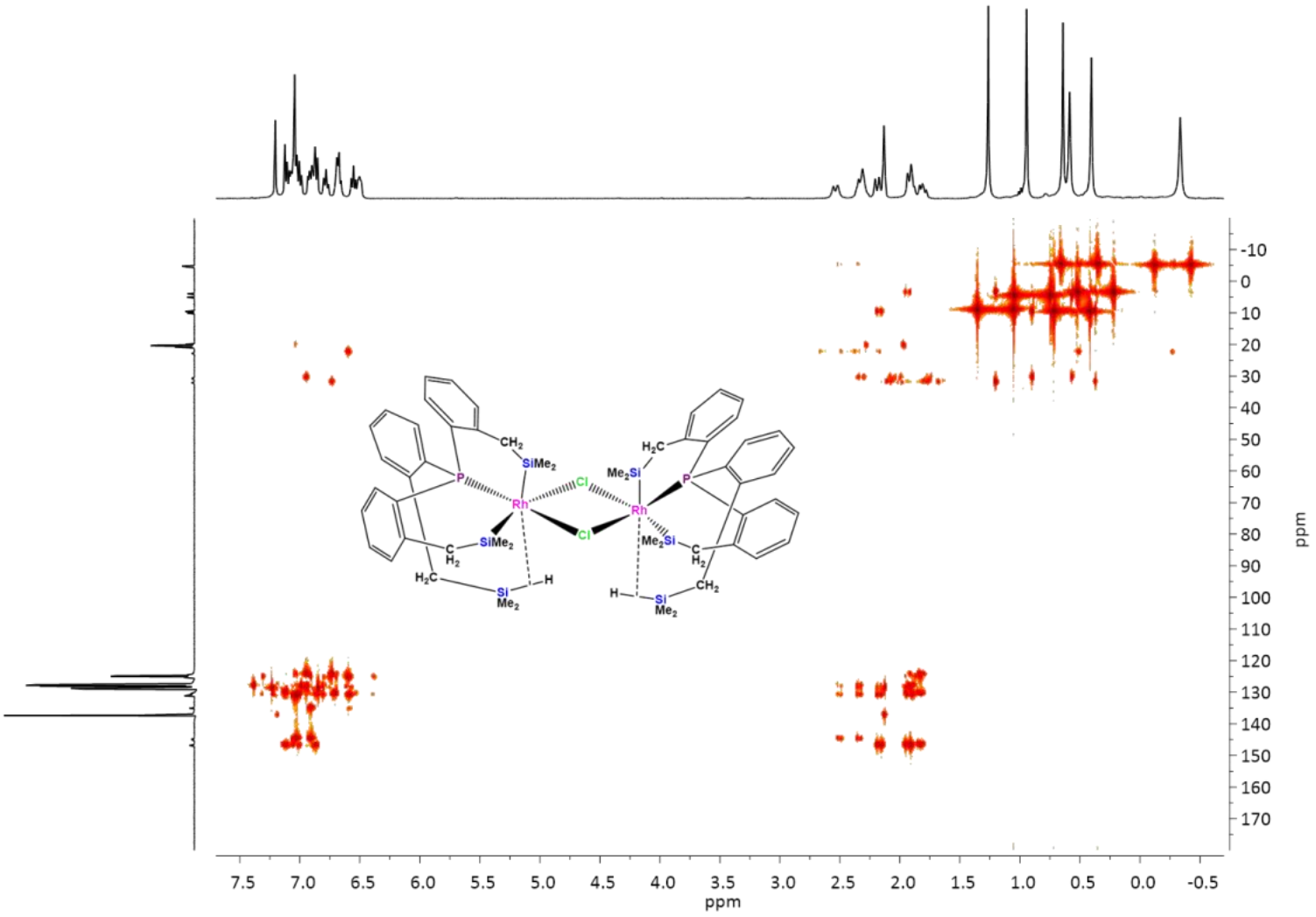



**Figure S 17**. HMBC $^{1}H$-$^{13}C$ (400 MHz, tol-$d_8$) NMR spectrum at 223 K of compound **2Rh**.

## 2.3 $^{31}$P NMR

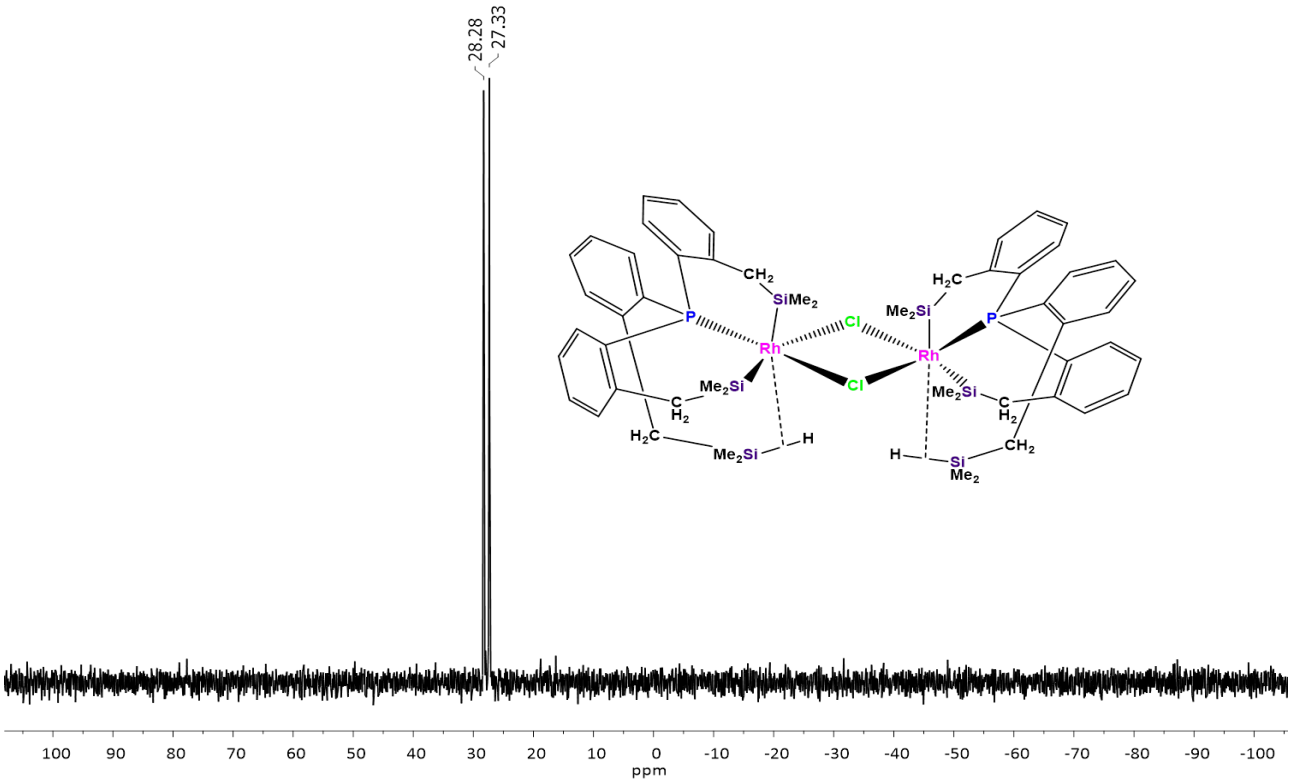



**Figure S 18.** $^{31}P\{^{1}H\}$ NMR spectrum (161.92 MHz, toluene-$d_8$) of complex **2Rh** at 223 K.

## 2.4 $^{29}$Si NMR

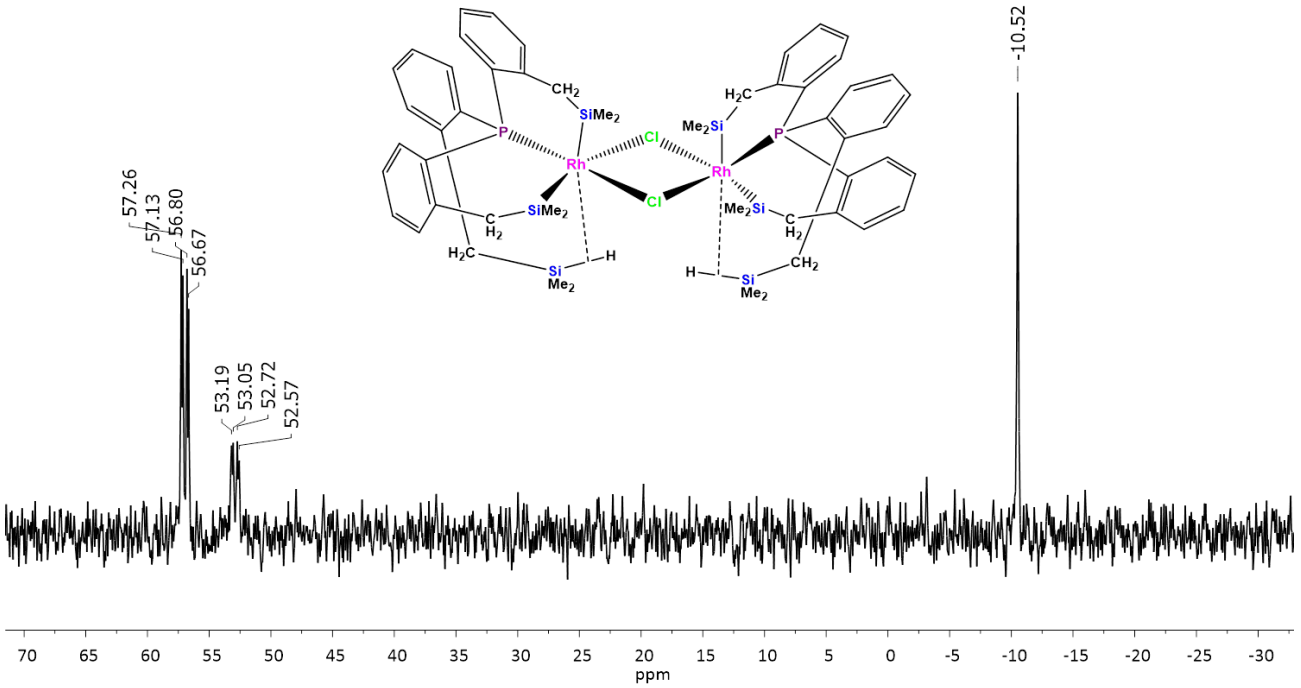



**Figure S 19.** DEPT $^{29}$Si{$^{1}$H}NMR spectrum (79.46 MHz, toluene-d$_8$) at 223 K of complex **2Rh**.

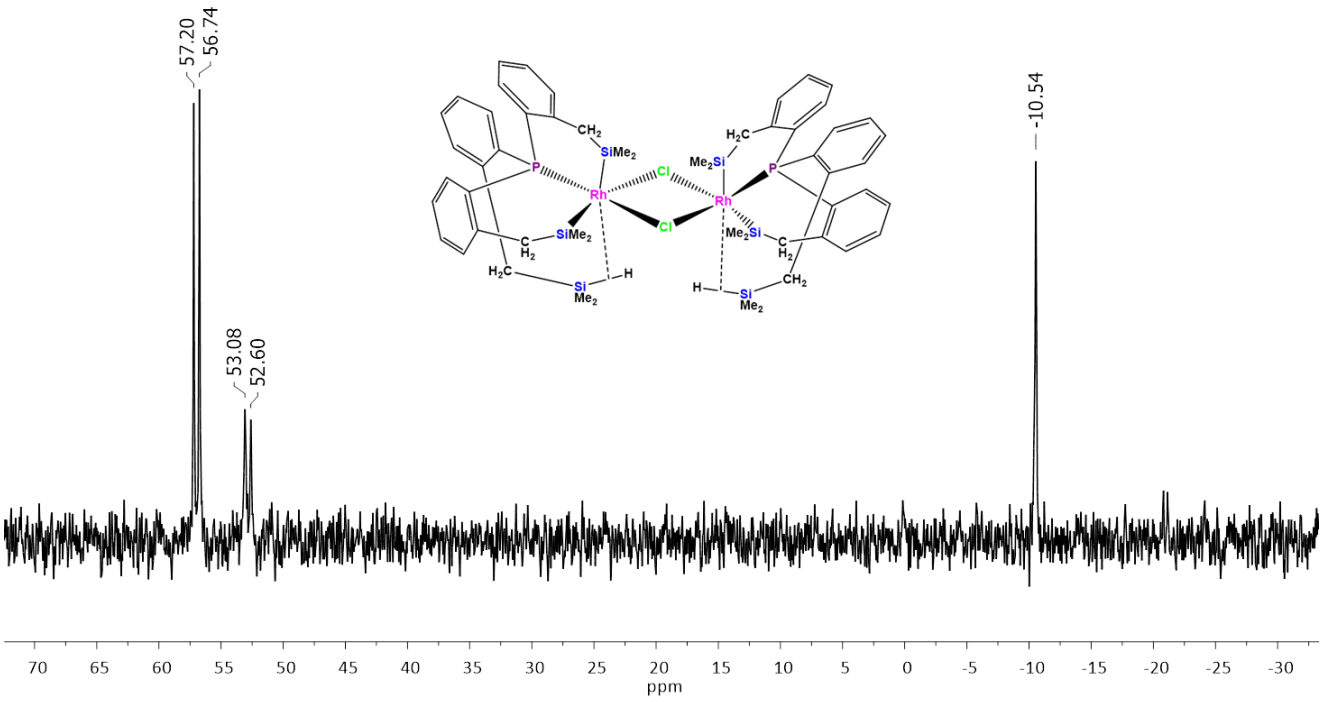



**Figure S 20.** DEPT $^{29}Si\{^{1}H\}\{^{31}P\}$ NMR spectrum (79.46 MHz, toluene-$d_8$) at 223 K of compound **2Rh**.

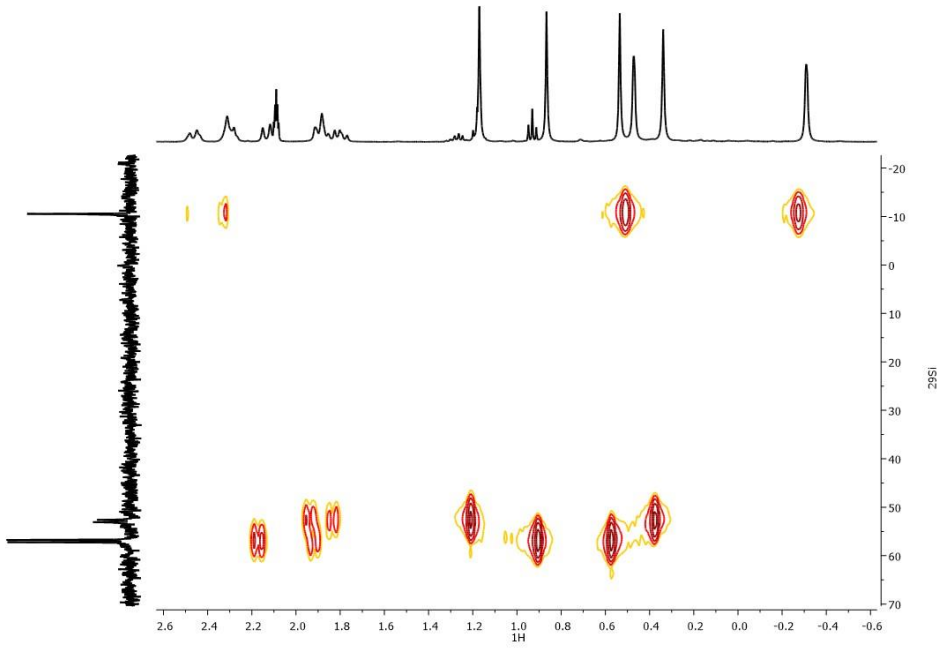



**Figure S 21.** HMQC $^{29}Si$-$^{1}H$ (79.46 MHz, toluene-$d_8$) NMR spectrum of compound **2Rh** at 223 K.

## 2.5 $^{103}Rh$ NMR

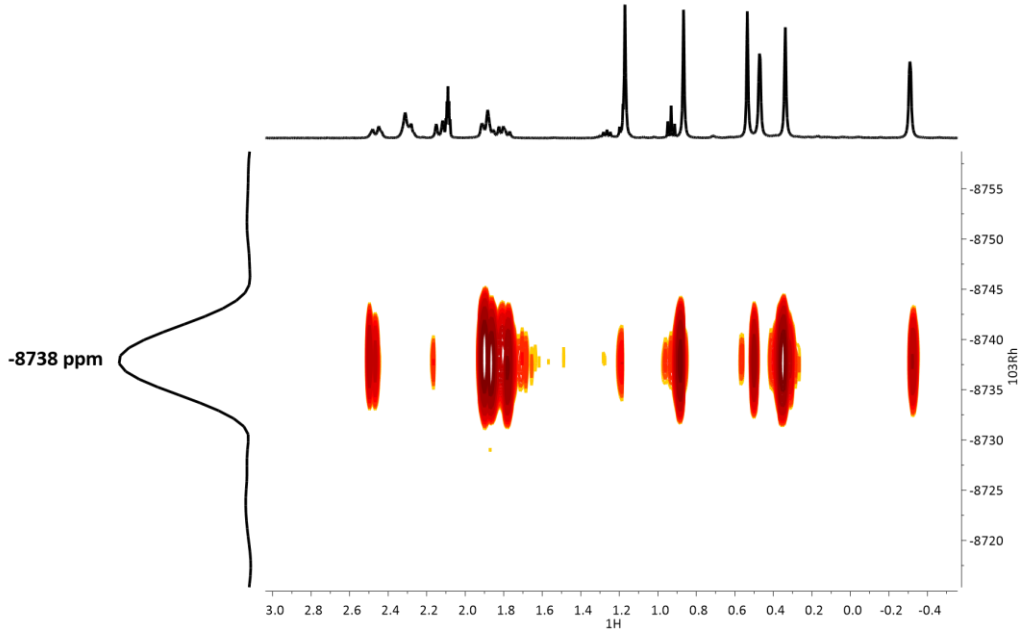



**Figure S 22**. Partial region of the HMQC $^{103}Rh$-$^{1}H$ {$^{31}P$} (400 MHz, Tol- $d_8$) at 223 K of compound **2Rh.**

# 3. Characterization of compound **3Rh**

## 3.1 $^{1}$H NMR

At ambient temperature the $^{1}$H NMR spectrum of **3Rh** in $C_6D_6$ shows six singlet signals at δ –0.22, 0.05, 0.49, 0.59, 0.65 and 1.28 for the methyl groups each accounting for six hydrogens. If the solid state structure is to be preserved, the observation of six methyl signals is indicative of hindered rotation around the Si-O-Si bridge which makes the two methyl groups on each Si inequivalent. In addition, six methylene hydrogen signals are observed between δ 1.8 and 3.7. The diastereotopic hydrogens of each methylene give rise to a doublet and a doublet of doublet, the latter one due to additional coupling with phosphorous. The most shielded signal at δ 1.91 also features an additional small coupling with rhodium ($^{3}J_{H\text{-}Rh}$ 2 Hz).

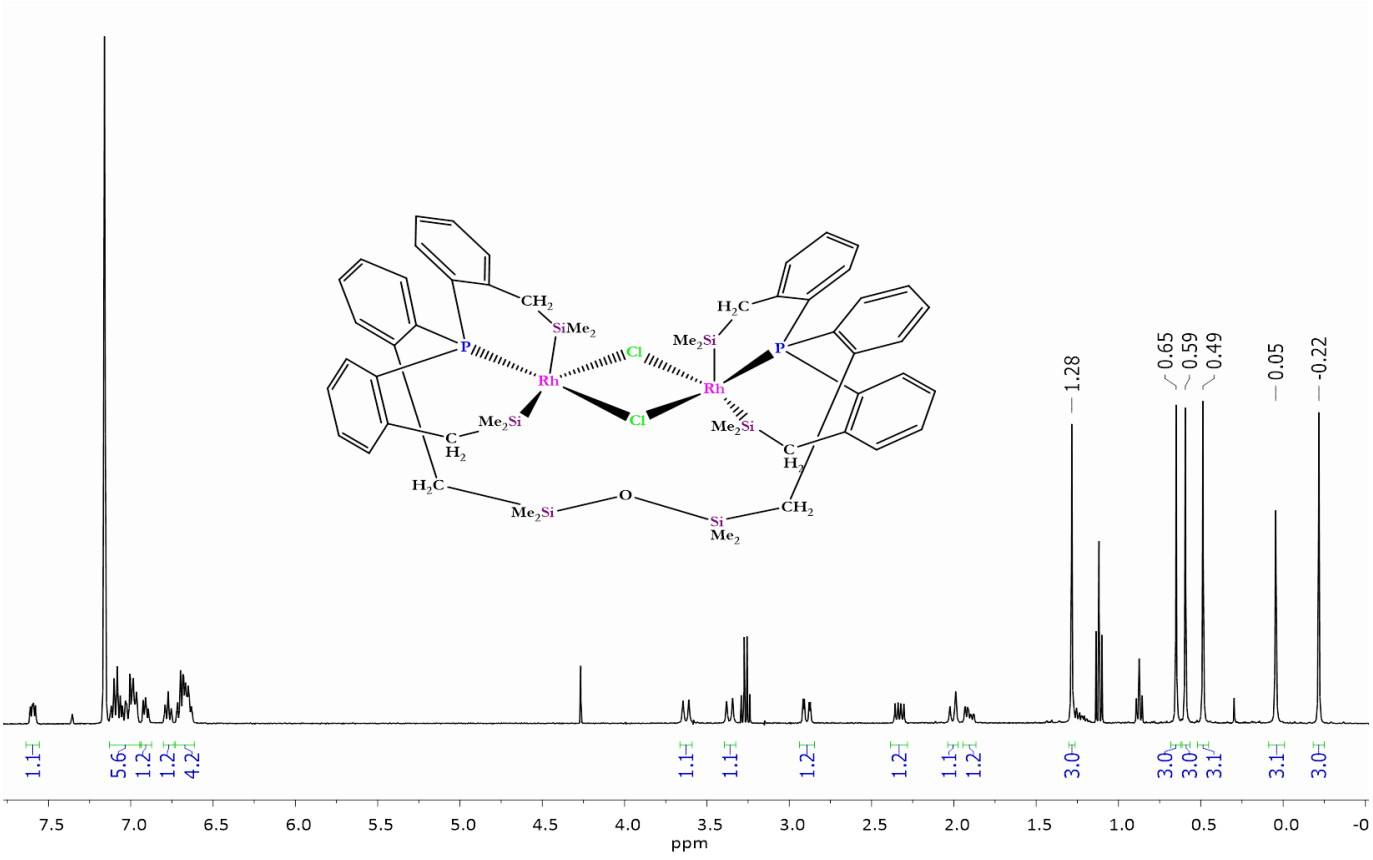



**Figure S 23.** $^{1}$H NMR (400 Hz, $C_6D_6$) spectrum of complex **3Rh** at room temperature.

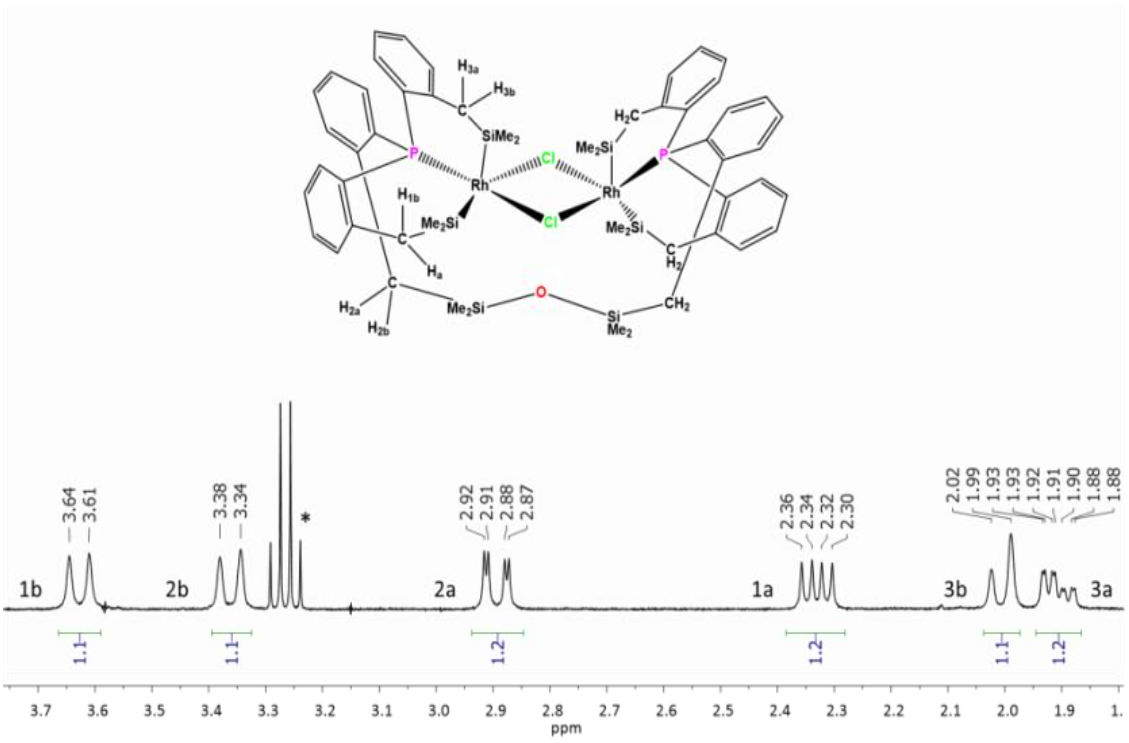



**Figure S 24**. Partial region of the $^{1}H$ NMR (400 Hz, $C_6D_6$) of complex **3Rh**. * $Et_2O$.

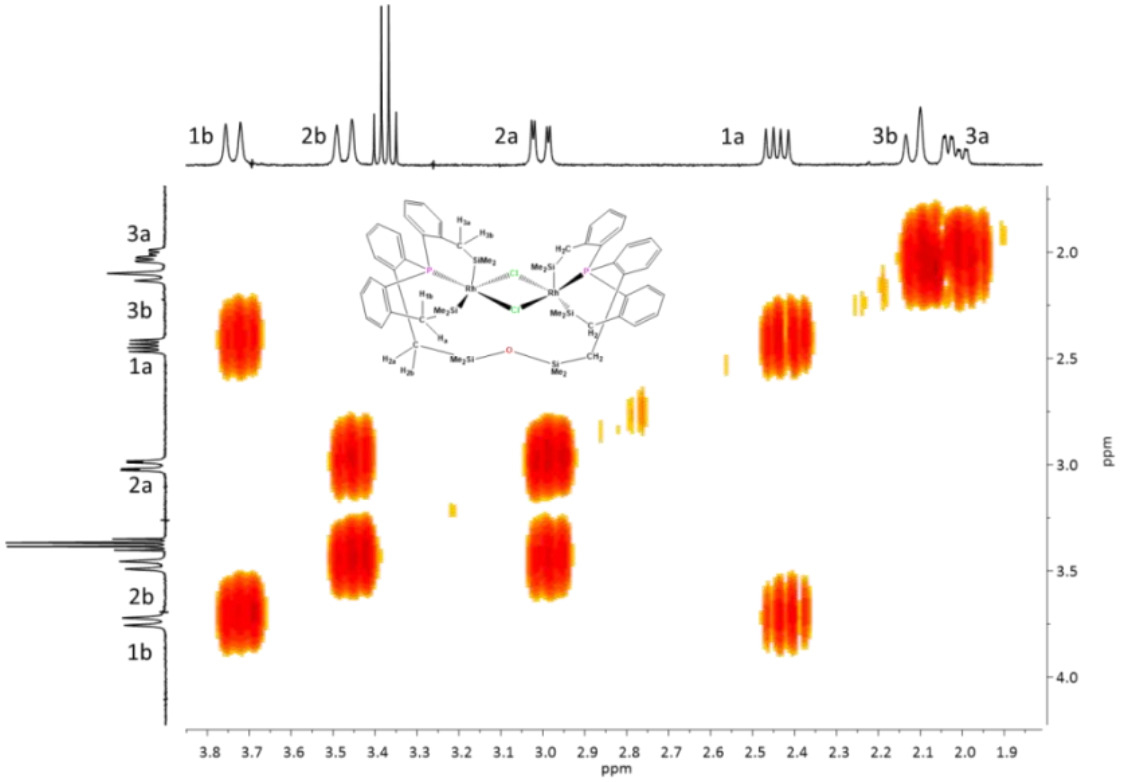



**Figure S 25**. COSY $^{1}H$-$^{1}H$ (400 Hz, $C_6D_6$) NMR spectrum of complex **3Rh**.

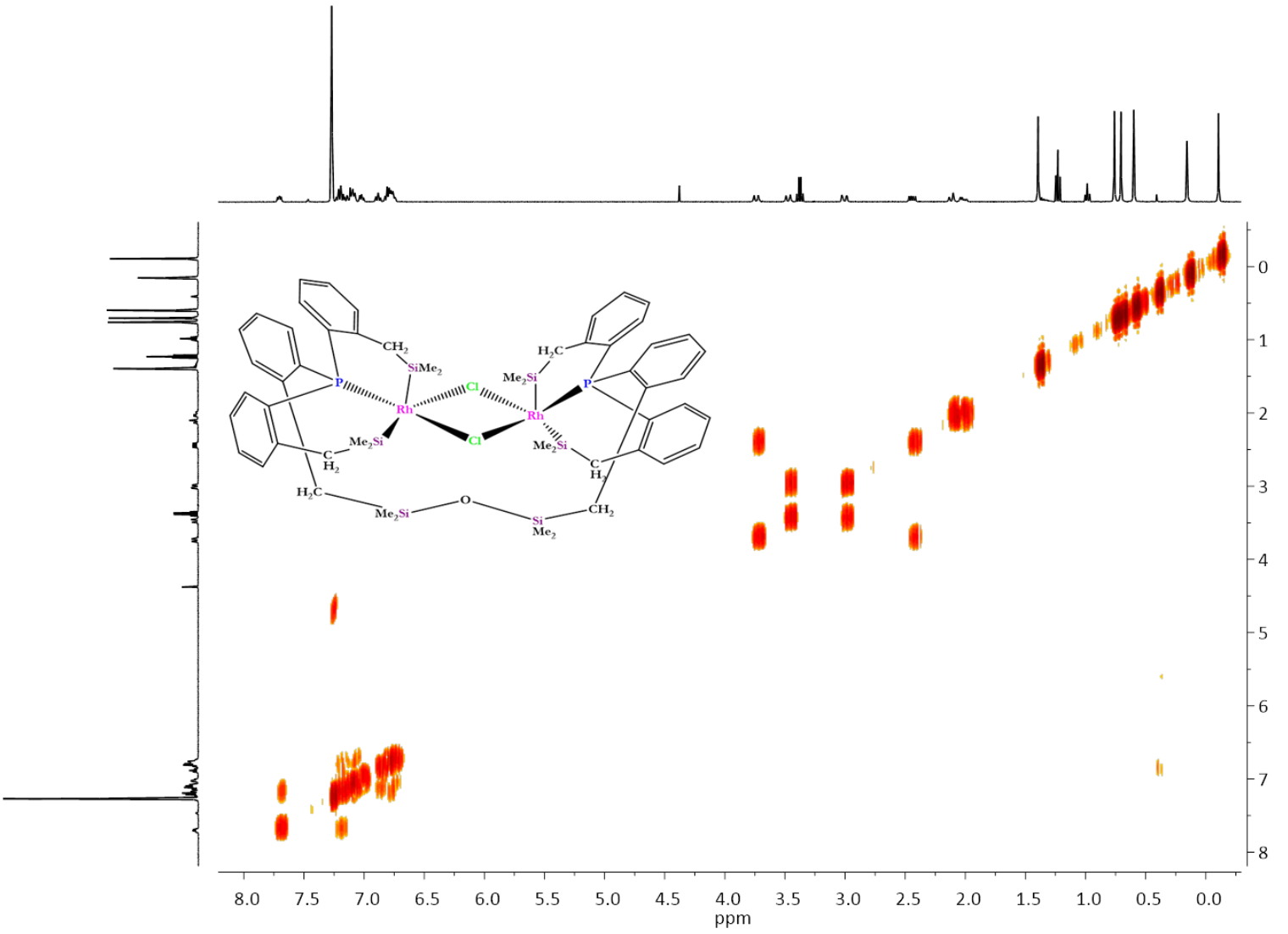



**Figure S 26.** COSY $^{1}H$-$^{1}H$ (400 Hz, $C_6D_6$) of complex **3Rh**.

## 3.2 $^{13}$C NMR

Six carbon methyl singlet signals between 2.95 < δ < 9.55 were observed while three carbon benzyl doublets between 28.7 < δ < 33.3 with $^{3}J_{C\text{-}P}$ coupling constants of 13 Hz are present in the $^{13}C\{^{1}H\}$ NMR spectrum.

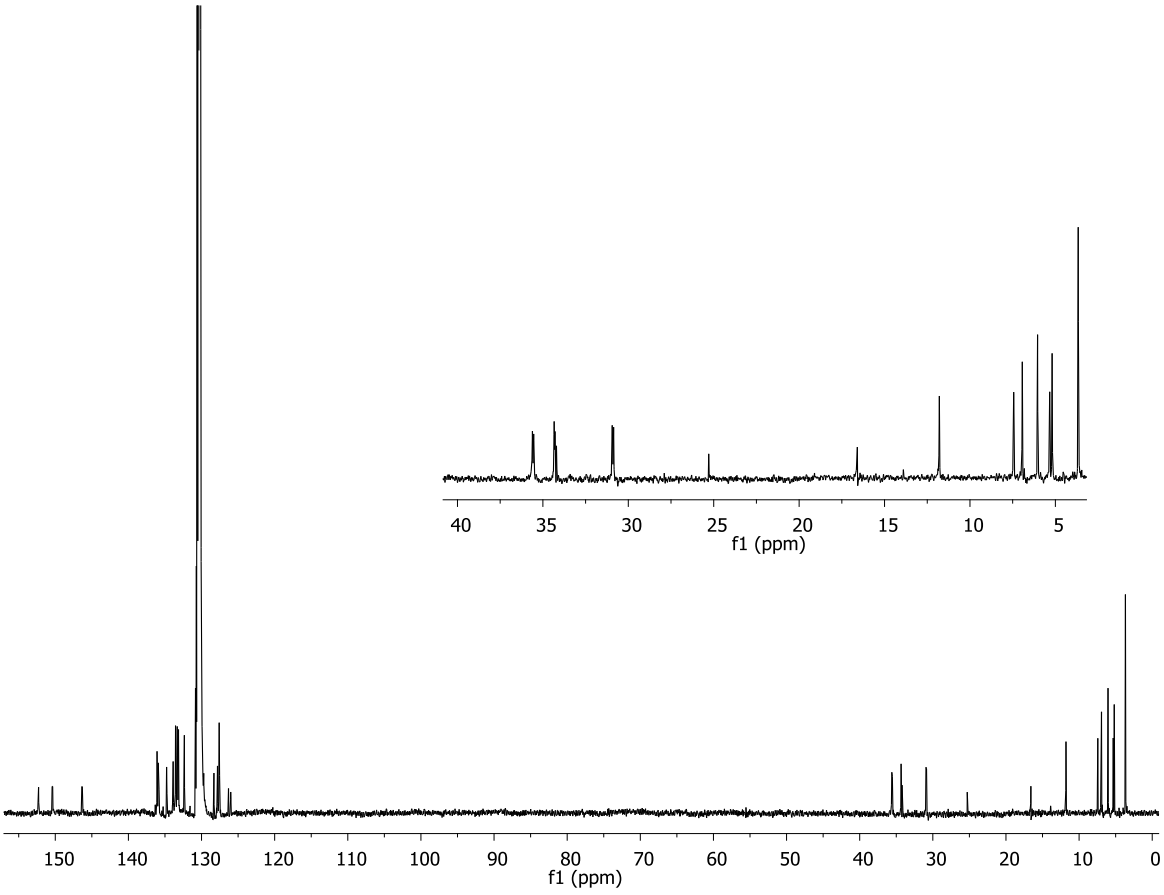



**Figure S 27.** $^{13}C\{^{1}H\}$ (100.58 MHz, $C_6D_6$) NMR spectrum of complex **3Rh** at room temperature.

## 3.3 $^{31}$P NMR

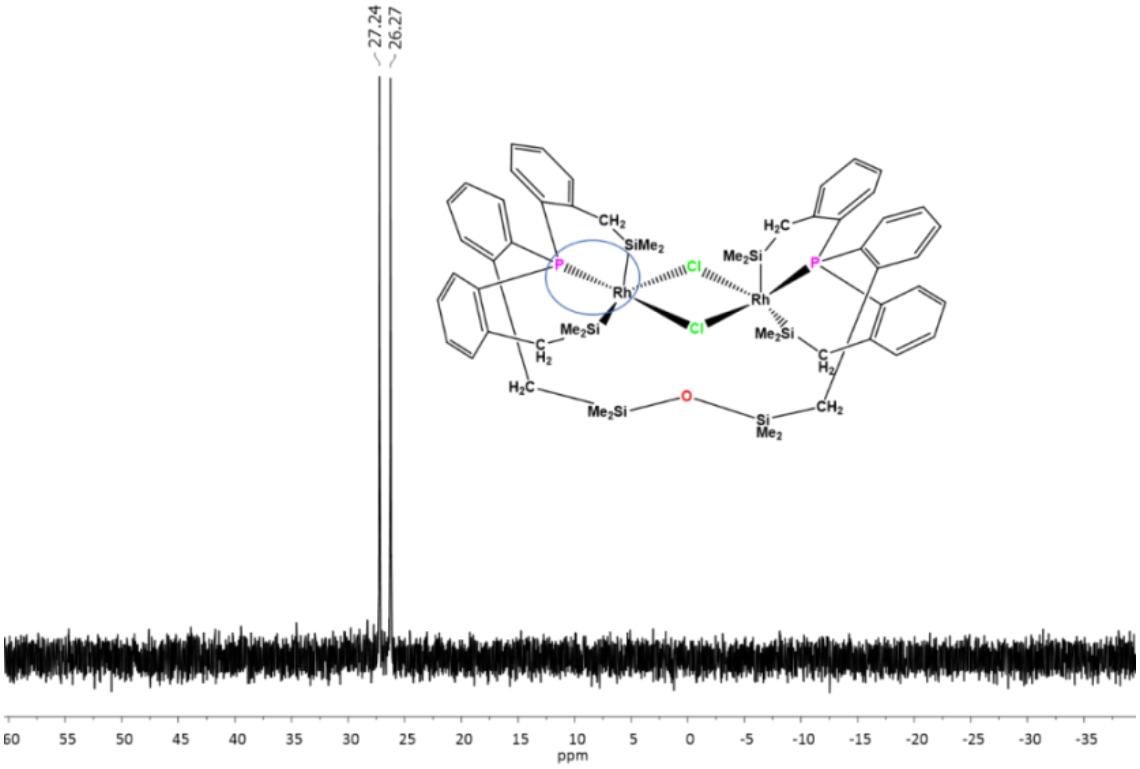



**Figure S 28**. $^{31}$P($^{1}$H) (161.92 MHz, $C_6D_6$) NMR spectrum at ambient temperature of complex **3Rh.**

## 3.4 $^{29}$Si NMR

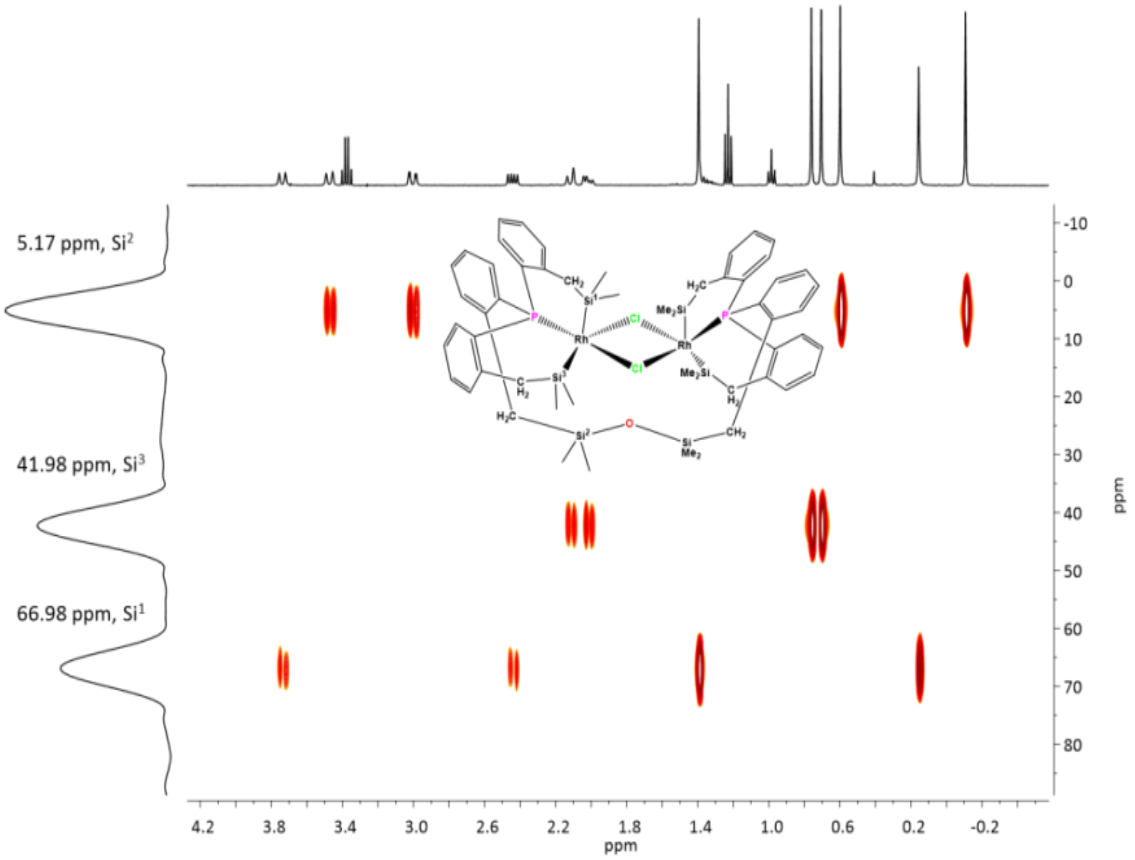



**Figure S 29.** HMQC $^{29}$Si-$^{1}$H{$^{31}$P} ($C_6D_6$) at ambient temperature for complex **3Rh**.

## 3.5 $^{103}$Rh NMR

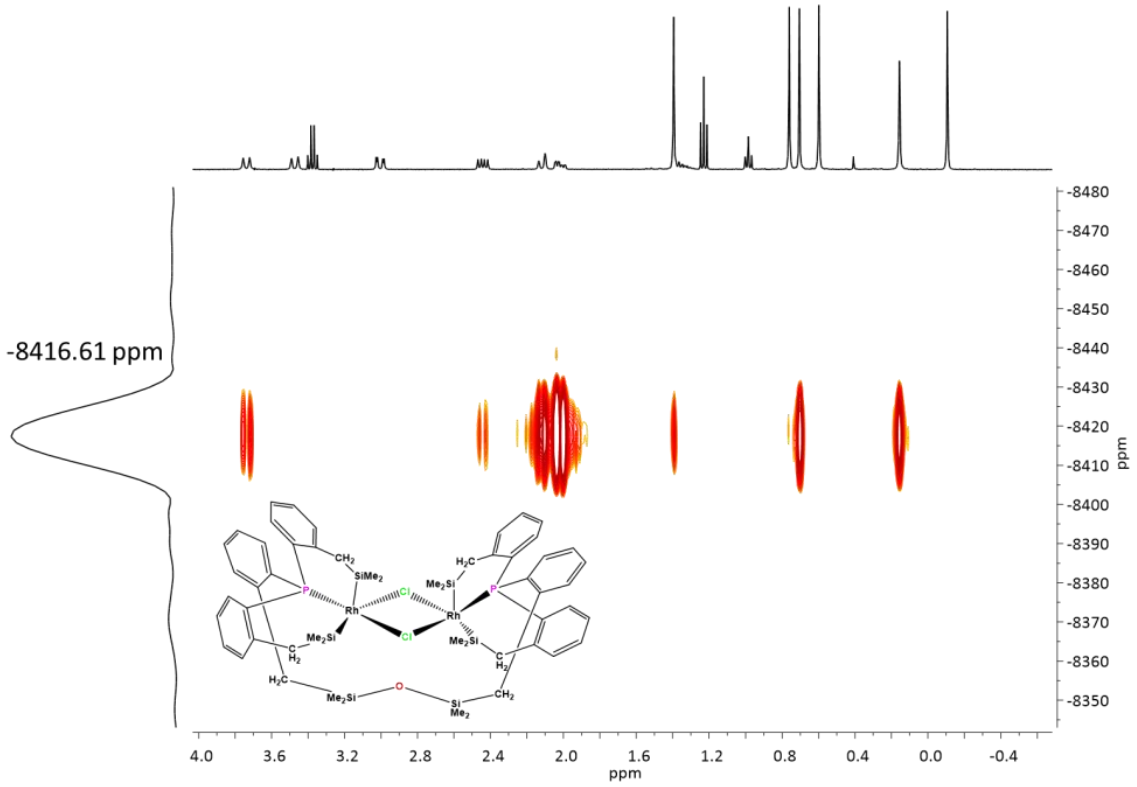



**Figure S 30.** HMQC $^{103}$Rh-$^{1}$H{$^{31}$P} (12.59 MHz, $C_6D_6$) of compound **3Rh**

## 3.6 FT-IR

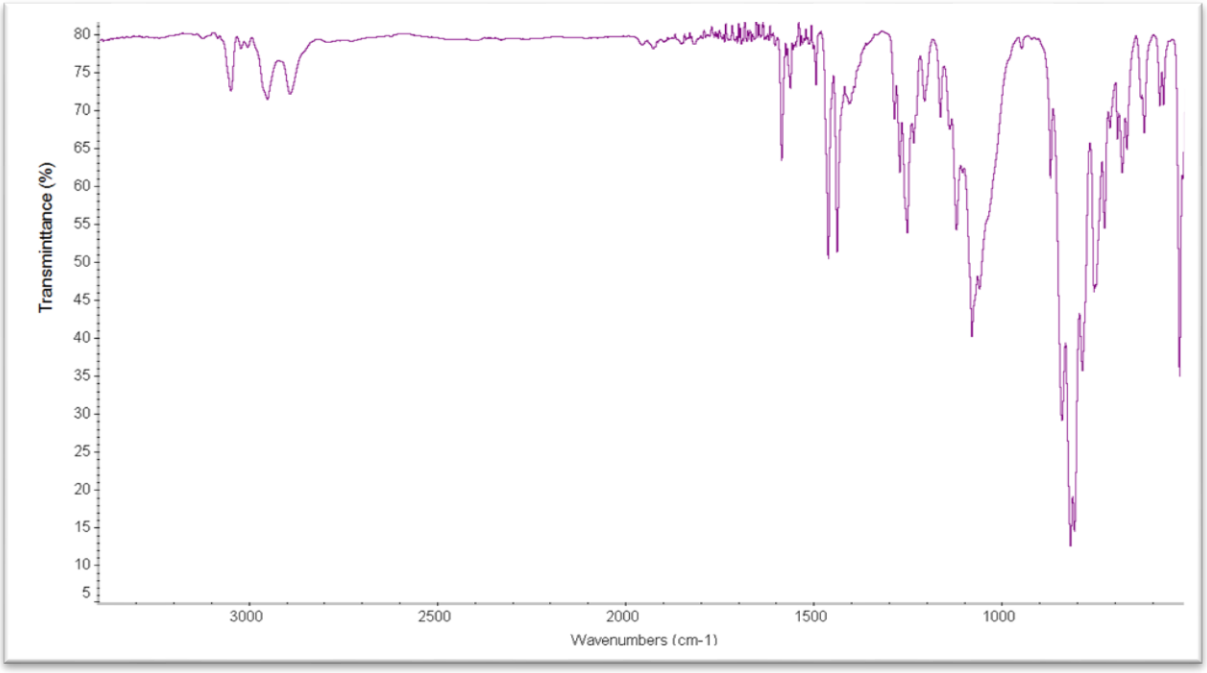



**Figure S 31**. FT- IR (ATR) spectrum of complex **3Rh**.

## 3.7 X-Ray Diffraction structure and tables

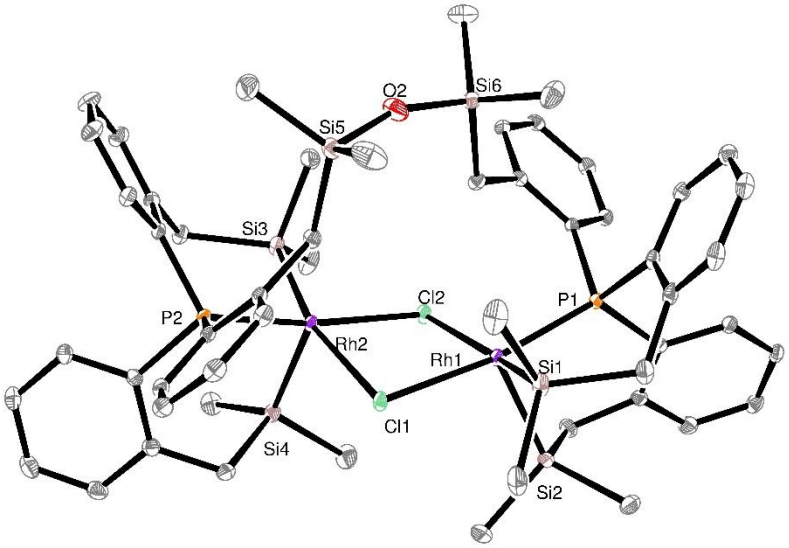



**Figure S 32**. ORTEP drawing of compound **3Rh** with thermal ellipsoids at 30% probability. Hydrogen atoms and methyl groups on silicon have been removed for clarity.

### Tables for complex 3Rh

Table S3. Bond lengths [A] and angles [deg] for vicky261115.

| | |
|---|---|
| C(1)-C(2) | 1.401(4) |
| C(1)-C(6) | 1.414(4) |
| C(1)-P(1) | 1.837(3) |
| C(2)-C(3) | 1.385(4) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.380(4) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.382(5) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.390(5) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.502(4) |

| | |
|---|---|
| C(7)-Si(1) | 1.896(3) |
| C(7)-H(7A) | 0.9900 |
| C(7)-H(7B) | 0.9900 |
| C(8)-Si(1) | 1.887(3) |
| C(8)-H(8A) | 0.9800 |
| C(8)-H(8B) | 0.9800 |
| C(8)-H(8C) | 0.9800 |
| C(9)-Si(1) | 1.873(4) |
| C(9)-H(9A) | 0.9800 |
| C(9)-H(9B) | 0.9800 |
| C(9)-H(9C) | 0.9800 |
| C(10)-C(15) | 1.399(4) |
| C(10)-C(11) | 1.405(4) |
| C(10)-P(1) | 1.840(3) |
| C(11)-C(12) | 1.394(4) |
| C(11)-C(16) | 1.510(4) |
| C(12)-C(13) | 1.384(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.377(4) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.389(4) |
| C(14)-H(14) | 0.9500 |
| C(15)-H(15) | 0.9500 |
| C(16)-Si(2) | 1.912(3) |
| C(16)-H(16A) | 0.9900 |
| C(16)-H(16B) | 0.9900 |
| C(17)-Si(2) | 1.886(3) |
| C(17)-H(17A) | 0.9800 |
| C(17)-H(17B) | 0.9800 |
| C(17)-H(17C) | 0.9800 |
| C(18)-Si(2) | 1.868(3) |
| C(18)-H(18A) | 0.9800 |
| C(18)-H(18B) | 0.9800 |
| C(18)-H(18C) | 0.9800 |
| C(19)-C(54) | 1.399(4) |
| C(19)-C(20) | 1.411(4) |
| C(19)-P(1) | 1.848(3) |
| C(20)-C(51) | 1.402(4) |
| C(20)-C(21) | 1.510(4) |
| C(21)-Si(6) | 1.889(3) |
| C(21)-H(21A) | 0.9900 |
| C(21)-H(21B) | 0.9900 |
| C(22)-Si(6) | 1.850(3) |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-Si(6) | 1.847(3) |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-C(25) | 1.520(4) |
| C(24)-Si(5) | 1.885(3) |
| C(24)-H(24A) | 0.9900 |
| C(24)-H(24B) | 0.9900 |

| | |
|---|---|
| C(25)-C(48) | 1.402(4) |
| C(25)-C(26) | 1.408(4) |
| C(26)-C(45) | 1.404(4) |
| C(26)-P(2) | 1.845(3) |
| C(27)-C(44) | 1.397(4) |
| C(27)-C(28) | 1.409(4) |
| C(27)-P(2) | 1.835(3) |
| C(28)-C(41) | 1.393(4) |
| C(28)-C(29) | 1.501(4) |
| C(29)-Si(4) | 1.904(3) |
| C(29)-H(29A) | 0.9900 |
| C(29)-H(29B) | 0.9900 |
| C(30)-Si(3) | 1.886(3) |
| C(30)-H(30A) | 0.9800 |
| C(30)-H(30B) | 0.9800 |
| C(30)-H(30C) | 0.9800 |
| C(31)-Si(3) | 1.891(3) |
| C(31)-H(31A) | 0.9800 |
| C(31)-H(31B) | 0.9800 |
| C(31)-H(31C) | 0.9800 |
| C(32)-C(33) | 1.497(4) |
| C(32)-Si(3) | 1.904(3) |
| C(32)-H(32A) | 0.9900 |
| C(32)-H(32B) | 0.9900 |
| C(33)-C(38) | 1.389(4) |
| C(33)-C(34) | 1.413(4) |
| C(34)-C(35) | 1.395(4) |
| C(34)-P(2) | 1.835(3) |
| C(35)-C(36) | 1.390(4) |
| C(35)-H(35) | 0.9500 |
| C(36)-C(37) | 1.383(5) |
| C(36)-H(36) | 0.9500 |
| C(37)-C(38) | 1.382(5) |
| C(37)-H(37) | 0.9500 |
| C(38)-H(38) | 0.9500 |
| C(39)-Si(4) | 1.883(3) |
| C(39)-H(39A) | 0.9800 |
| C(39)-H(39B) | 0.9800 |
| C(39)-H(39C) | 0.9800 |
| C(40)-Si(4) | 1.874(3) |
| C(40)-H(40A) | 0.9800 |
| C(40)-H(40B) | 0.9800 |
| C(40)-H(40C) | 0.9800 |
| C(41)-C(42) | 1.384(5) |
| C(41)-H(41) | 0.9500 |
| C(42)-C(43) | 1.378(5) |
| C(42)-H(42) | 0.9500 |
| C(43)-C(44) | 1.381(4) |
| C(43)-H(43) | 0.9500 |
| C(44)-H(44) | 0.9500 |
| C(45)-C(46) | 1.385(4) |
| C(45)-H(45) | 0.9500 |
| C(46)-C(47) | 1.379(5) |
| C(46)-H(46) | 0.9500 |

| | |
|---|---|
| C(47)-C(48) | 1.381(4) |
| C(47)-H(47) | 0.9500 |
| C(48)-H(48) | 0.9500 |
| C(49)-Si(5) | 1.850(4) |
| C(49)-H(49A) | 0.9800 |
| C(49)-H(49B) | 0.9800 |
| C(49)-H(49C) | 0.9800 |
| C(50)-Si(5) | 1.867(4) |
| C(50)-H(50A) | 0.9800 |
| C(50)-H(50B) | 0.9800 |
| C(50)-H(50C) | 0.9800 |
| C(51)-C(52) | 1.388(4) |
| C(51)-H(51) | 0.9500 |
| C(52)-C(53) | 1.379(4) |
| C(52)-H(52) | 0.9500 |
| C(53)-C(54) | 1.385(4) |
| C(53)-H(53) | 0.9500 |
| C(54)-H(54) | 0.9500 |
| C(55)-C(56) | 1.462(7) |
| C(55)-H(55A) | 0.9800 |
| C(55)-H(55B) | 0.9800 |
| C(55)-H(55C) | 0.9800 |
| C(56)-O(1) | 1.454(6) |
| C(56)-H(56A) | 0.9900 |
| C(56)-H(56B) | 0.9900 |
| C(58)-O(1) | 1.411(5) |
| C(58)-C(59) | 1.499(6) |
| C(58)-H(58A) | 0.9900 |
| C(58)-H(58B) | 0.9900 |
| C(59)-H(59A) | 0.9800 |
| C(59)-H(59B) | 0.9800 |
| C(59)-H(59C) | 0.9800 |
| Si(1)-Rh(1) | 2.2922(8) |
| Si(2)-Rh(1) | 2.2879(9) |
| Si(3)-Rh(2) | 2.2948(8) |
| Si(4)-Rh(2) | 2.2887(9) |
| Si(5)-O(2) | 1.623(2) |
| Si(6)-O(2) | 1.624(2) |
| P(1)-Rh(1) | 2.2330(7) |
| P(2)-Rh(2) | 2.2425(7) |
| Cl(1)-Rh(1) | 2.4161(7) |
| Cl(1)-Rh(2) | 2.6037(7) |
| Cl(2)-Rh(2) | 2.3994(7) |
| Cl(2)-Rh(1) | 2.5970(7) |

| | |
|---|---|
| C(2)-C(1)-C(6) | 118.8(3) |
| C(2)-C(1)-P(1) | 118.4(2) |
| C(6)-C(1)-P(1) | 122.7(2) |
| C(3)-C(2)-C(1) | 121.6(3) |
| C(3)-C(2)-H(2) | 119.2 |
| C(1)-C(2)-H(2) | 119.2 |
| C(4)-C(3)-C(2) | 119.4(3) |
| C(4)-C(3)-H(3) | 120.3 |
| C(2)-C(3)-H(3) | 120.3 |

| | |
|---|---|
| C(3)-C(4)-C(5) | 119.6(3) |
| C(3)-C(4)-H(4) | 120.2 |
| C(5)-C(4)-H(4) | 120.2 |
| C(4)-C(5)-C(6) | 122.4(3) |
| C(4)-C(5)-H(5) | 118.8 |
| C(6)-C(5)-H(5) | 118.8 |
| C(5)-C(6)-C(1) | 118.0(3) |
| C(5)-C(6)-C(7) | 119.7(3) |
| C(1)-C(6)-C(7) | 122.2(3) |
| C(6)-C(7)-Si(1) | 114.5(2) |
| C(6)-C(7)-H(7A) | 108.6 |
| Si(1)-C(7)-H(7A) | 108.6 |
| C(6)-C(7)-H(7B) | 108.6 |
| Si(1)-C(7)-H(7B) | 108.6 |
| H(7A)-C(7)-H(7B) | 107.6 |
| Si(1)-C(8)-H(8A) | 109.5 |
| Si(1)-C(8)-H(8B) | 109.5 |
| H(8A)-C(8)-H(8B) | 109.5 |
| Si(1)-C(8)-H(8C) | 109.5 |
| H(8A)-C(8)-H(8C) | 109.5 |
| H(8B)-C(8)-H(8C) | 109.5 |
| Si(1)-C(9)-H(9A) | 109.5 |
| Si(1)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 109.5 |
| Si(1)-C(9)-H(9C) | 109.5 |
| H(9A)-C(9)-H(9C) | 109.5 |
| H(9B)-C(9)-H(9C) | 109.5 |
| C(15)-C(10)-C(11) | 119.4(2) |
| C(15)-C(10)-P(1) | 119.0(2) |
| C(11)-C(10)-P(1) | 121.6(2) |
| C(12)-C(11)-C(10) | 118.0(3) |
| C(12)-C(11)-C(16) | 119.1(3) |
| C(10)-C(11)-C(16) | 122.7(3) |
| C(13)-C(12)-C(11) | 122.3(3) |
| C(13)-C(12)-H(12) | 118.9 |
| C(11)-C(12)-H(12) | 118.9 |
| C(14)-C(13)-C(12) | 119.5(3) |
| C(14)-C(13)-H(13) | 120.2 |
| C(12)-C(13)-H(13) | 120.2 |
| C(13)-C(14)-C(15) | 119.6(3) |
| C(13)-C(14)-H(14) | 120.2 |
| C(15)-C(14)-H(14) | 120.2 |
| C(14)-C(15)-C(10) | 121.2(3) |
| C(14)-C(15)-H(15) | 119.4 |
| C(10)-C(15)-H(15) | 119.4 |
| C(11)-C(16)-Si(2) | 107.7(2) |
| C(11)-C(16)-H(16A) | 110.2 |
| Si(2)-C(16)-H(16A) | 110.2 |
| C(11)-C(16)-H(16B) | 110.2 |
| Si(2)-C(16)-H(16B) | 110.2 |
| H(16A)-C(16)-H(16B) | 108.5 |
| Si(2)-C(17)-H(17A) | 109.5 |
| Si(2)-C(17)-H(17B) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 |

| | |
|---|---|
| Si(2)-C(17)-H(17C) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 |
| Si(2)-C(18)-H(18A) | 109.5 |
| Si(2)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| Si(2)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| C(54)-C(19)-C(20) | 119.3(2) |
| C(54)-C(19)-P(1) | 119.4(2) |
| C(20)-C(19)-P(1) | 121.3(2) |
| C(51)-C(20)-C(19) | 117.6(2) |
| C(51)-C(20)-C(21) | 118.2(2) |
| C(19)-C(20)-C(21) | 124.1(2) |
| C(20)-C(21)-Si(6) | 120.6(2) |
| C(20)-C(21)-H(21A) | 107.2 |
| Si(6)-C(21)-H(21A) | 107.2 |
| C(20)-C(21)-H(21B) | 107.2 |
| Si(6)-C(21)-H(21B) | 107.2 |
| H(21A)-C(21)-H(21B) | 106.8 |
| Si(6)-C(22)-H(22A) | 109.5 |
| Si(6)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| Si(6)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| Si(6)-C(23)-H(23A) | 109.5 |
| Si(6)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| Si(6)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(25)-C(24)-Si(5) | 120.9(2) |
| C(25)-C(24)-H(24A) | 107.1 |
| Si(5)-C(24)-H(24A) | 107.1 |
| C(25)-C(24)-H(24B) | 107.1 |
| Si(5)-C(24)-H(24B) | 107.1 |
| H(24A)-C(24)-H(24B) | 106.8 |
| C(48)-C(25)-C(26) | 117.7(3) |
| C(48)-C(25)-C(24) | 118.7(3) |
| C(26)-C(25)-C(24) | 123.6(2) |
| C(45)-C(26)-C(25) | 119.6(3) |
| C(45)-C(26)-P(2) | 119.1(2) |
| C(25)-C(26)-P(2) | 121.3(2) |
| C(44)-C(27)-C(28) | 119.4(3) |
| C(44)-C(27)-P(2) | 120.3(2) |
| C(28)-C(27)-P(2) | 120.3(2) |
| C(41)-C(28)-C(27) | 118.0(3) |
| C(41)-C(28)-C(29) | 120.2(3) |
| C(27)-C(28)-C(29) | 121.5(3) |
| C(28)-C(29)-Si(4) | 107.4(2) |
| C(28)-C(29)-H(29A) | 110.2 |
| Si(4)-C(29)-H(29A) | 110.2 |

| | |
|---|---|
| C(28)-C(29)-H(29B) | 110.2 |
| Si(4)-C(29)-H(29B) | 110.2 |
| H(29A)-C(29)-H(29B) | 108.5 |
| Si(3)-C(30)-H(30A) | 109.5 |
| Si(3)-C(30)-H(30B) | 109.5 |
| H(30A)-C(30)-H(30B) | 109.5 |
| Si(3)-C(30)-H(30C) | 109.5 |
| H(30A)-C(30)-H(30C) | 109.5 |
| H(30B)-C(30)-H(30C) | 109.5 |
| Si(3)-C(31)-H(31A) | 109.5 |
| Si(3)-C(31)-H(31B) | 109.5 |
| H(31A)-C(31)-H(31B) | 109.5 |
| Si(3)-C(31)-H(31C) | 109.5 |
| H(31A)-C(31)-H(31C) | 109.5 |
| H(31B)-C(31)-H(31C) | 109.5 |
| C(33)-C(32)-Si(3) | 110.3(2) |
| C(33)-C(32)-H(32A) | 109.6 |
| Si(3)-C(32)-H(32A) | 109.6 |
| C(33)-C(32)-H(32B) | 109.6 |
| Si(3)-C(32)-H(32B) | 109.6 |
| H(32A)-C(32)-H(32B) | 108.1 |
| C(38)-C(33)-C(34) | 118.0(3) |
| C(38)-C(33)-C(32) | 120.2(3) |
| C(34)-C(33)-C(32) | 121.8(2) |
| C(35)-C(34)-C(33) | 119.6(3) |
| C(35)-C(34)-P(2) | 120.4(2) |
| C(33)-C(34)-P(2) | 120.0(2) |
| C(36)-C(35)-C(34) | 121.1(3) |
| C(36)-C(35)-H(35) | 119.4 |
| C(34)-C(35)-H(35) | 119.4 |
| C(37)-C(36)-C(35) | 119.1(3) |
| C(37)-C(36)-H(36) | 120.4 |
| C(35)-C(36)-H(36) | 120.4 |
| C(38)-C(37)-C(36) | 120.2(3) |
| C(38)-C(37)-H(37) | 119.9 |
| C(36)-C(37)-H(37) | 119.9 |
| C(37)-C(38)-C(33) | 121.8(3) |
| C(37)-C(38)-H(38) | 119.1 |
| C(33)-C(38)-H(38) | 119.1 |
| Si(4)-C(39)-H(39A) | 109.5 |
| Si(4)-C(39)-H(39B) | 109.5 |
| H(39A)-C(39)-H(39B) | 109.5 |
| Si(4)-C(39)-H(39C) | 109.5 |
| H(39A)-C(39)-H(39C) | 109.5 |
| H(39B)-C(39)-H(39C) | 109.5 |
| Si(4)-C(40)-H(40A) | 109.5 |
| Si(4)-C(40)-H(40B) | 109.5 |
| H(40A)-C(40)-H(40B) | 109.5 |
| Si(4)-C(40)-H(40C) | 109.5 |
| H(40A)-C(40)-H(40C) | 109.5 |
| H(40B)-C(40)-H(40C) | 109.5 |
| C(42)-C(41)-C(28) | 121.8(3) |
| C(42)-C(41)-H(41) | 119.1 |
| C(28)-C(41)-H(41) | 119.1 |

| | |
|---|---|
| C(43)-C(42)-C(41) | 120.0(3) |
| C(43)-C(42)-H(42) | 120.0 |
| C(41)-C(42)-H(42) | 120.0 |
| C(42)-C(43)-C(44) | 119.5(3) |
| C(42)-C(43)-H(43) | 120.2 |
| C(44)-C(43)-H(43) | 120.2 |
| C(43)-C(44)-C(27) | 121.2(3) |
| C(43)-C(44)-H(44) | 119.4 |
| C(27)-C(44)-H(44) | 119.4 |
| C(46)-C(45)-C(26) | 121.2(3) |
| C(46)-C(45)-H(45) | 119.4 |
| C(26)-C(45)-H(45) | 119.4 |
| C(47)-C(46)-C(45) | 119.4(3) |
| C(47)-C(46)-H(46) | 120.3 |
| C(45)-C(46)-H(46) | 120.3 |
| C(46)-C(47)-C(48) | 120.2(3) |
| C(46)-C(47)-H(47) | 119.9 |
| C(48)-C(47)-H(47) | 119.9 |
| C(47)-C(48)-C(25) | 121.9(3) |
| C(47)-C(48)-H(48) | 119.0 |
| C(25)-C(48)-H(48) | 119.0 |
| Si(5)-C(49)-H(49A) | 109.5 |
| Si(5)-C(49)-H(49B) | 109.5 |
| H(49A)-C(49)-H(49B) | 109.5 |
| Si(5)-C(49)-H(49C) | 109.5 |
| H(49A)-C(49)-H(49C) | 109.5 |
| H(49B)-C(49)-H(49C) | 109.5 |
| Si(5)-C(50)-H(50A) | 109.5 |
| Si(5)-C(50)-H(50B) | 109.5 |
| H(50A)-C(50)-H(50B) | 109.5 |
| Si(5)-C(50)-H(50C) | 109.5 |
| H(50A)-C(50)-H(50C) | 109.5 |
| H(50B)-C(50)-H(50C) | 109.5 |
| C(52)-C(51)-C(20) | 122.5(3) |
| C(52)-C(51)-H(51) | 118.8 |
| C(20)-C(51)-H(51) | 118.8 |
| C(53)-C(52)-C(51) | 119.3(3) |
| C(53)-C(52)-H(52) | 120.4 |
| C(51)-C(52)-H(52) | 120.4 |
| C(52)-C(53)-C(54) | 119.7(3) |
| C(52)-C(53)-H(53) | 120.2 |
| C(54)-C(53)-H(53) | 120.2 |
| C(53)-C(54)-C(19) | 121.6(3) |
| C(53)-C(54)-H(54) | 119.2 |
| C(19)-C(54)-H(54) | 119.2 |
| C(56)-C(55)-H(55A) | 109.5 |
| C(56)-C(55)-H(55B) | 109.5 |
| H(55A)-C(55)-H(55B) | 109.5 |
| C(56)-C(55)-H(55C) | 109.5 |
| H(55A)-C(55)-H(55C) | 109.5 |
| H(55B)-C(55)-H(55C) | 109.5 |
| O(1)-C(56)-C(55) | 109.5(5) |
| O(1)-C(56)-H(56A) | 109.8 |
| C(55)-C(56)-H(56A) | 109.8 |

| | |
|---|---|
| O(1)-C(56)-H(56B) | 109.8 |
| C(55)-C(56)-H(56B) | 109.8 |
| H(56A)-C(56)-H(56B) | 108.2 |
| O(1)-C(58)-C(59) | 108.2(3) |
| O(1)-C(58)-H(58A) | 110.1 |
| C(59)-C(58)-H(58A) | 110.1 |
| O(1)-C(58)-H(58B) | 110.1 |
| C(59)-C(58)-H(58B) | 110.1 |
| H(58A)-C(58)-H(58B) | 108.4 |
| C(58)-C(59)-H(59A) | 109.5 |
| C(58)-C(59)-H(59B) | 109.5 |
| H(59A)-C(59)-H(59B) | 109.5 |
| C(58)-C(59)-H(59C) | 109.5 |
| H(59A)-C(59)-H(59C) | 109.5 |
| H(59B)-C(59)-H(59C) | 109.5 |
| C(9)-Si(1)-C(8) | 104.92(18) |
| C(9)-Si(1)-C(7) | 105.98(17) |
| C(8)-Si(1)-C(7) | 107.42(14) |
| C(9)-Si(1)-Rh(1) | 106.03(11) |
| C(8)-Si(1)-Rh(1) | 116.72(13) |
| C(7)-Si(1)-Rh(1) | 114.78(10) |
| C(18)-Si(2)-C(17) | 102.05(16) |
| C(18)-Si(2)-C(16) | 114.45(17) |
| C(17)-Si(2)-C(16) | 104.43(15) |
| C(18)-Si(2)-Rh(1) | 111.00(12) |
| C(17)-Si(2)-Rh(1) | 126.45(13) |
| C(16)-Si(2)-Rh(1) | 98.78(10) |
| C(30)-Si(3)-C(31) | 106.01(17) |
| C(30)-Si(3)-C(32) | 105.04(14) |
| C(31)-Si(3)-C(32) | 108.56(14) |
| C(30)-Si(3)-Rh(2) | 106.96(11) |
| C(31)-Si(3)-Rh(2) | 116.44(11) |
| C(32)-Si(3)-Rh(2) | 112.97(9) |
| C(40)-Si(4)-C(39) | 104.01(16) |
| C(40)-Si(4)-C(29) | 111.26(16) |
| C(39)-Si(4)-C(29) | 104.90(15) |
| C(40)-Si(4)-Rh(2) | 109.45(12) |
| C(39)-Si(4)-Rh(2) | 124.99(11) |
| C(29)-Si(4)-Rh(2) | 101.99(10) |
| O(2)-Si(5)-C(49) | 109.09(18) |
| O(2)-Si(5)-C(50) | 106.59(17) |
| C(49)-Si(5)-C(50) | 108.5(2) |
| O(2)-Si(5)-C(24) | 105.11(12) |
| C(49)-Si(5)-C(24) | 111.05(16) |
| C(50)-Si(5)-C(24) | 116.23(16) |
| O(2)-Si(6)-C(23) | 110.65(17) |
| O(2)-Si(6)-C(22) | 105.69(16) |
| C(23)-Si(6)-C(22) | 108.63(18) |
| O(2)-Si(6)-C(21) | 105.82(12) |
| C(23)-Si(6)-C(21) | 111.33(14) |
| C(22)-Si(6)-C(21) | 114.53(14) |
| C(1)-P(1)-C(10) | 103.19(13) |
| C(1)-P(1)-C(19) | 102.40(13) |
| C(10)-P(1)-C(19) | 102.28(12) |

| | |
|---|---|
| C(1)-P(1)-Rh(1) | 118.91(9) |
| C(10)-P(1)-Rh(1) | 119.09(9) |
| C(19)-P(1)-Rh(1) | 108.58(9) |
| C(34)-P(2)-C(27) | 101.44(13) |
| C(34)-P(2)-C(26) | 103.83(13) |
| C(27)-P(2)-C(26) | 103.02(13) |
| C(34)-P(2)-Rh(2) | 116.40(9) |
| C(27)-P(2)-Rh(2) | 119.45(9) |
| C(26)-P(2)-Rh(2) | 110.79(9) |
| Rh(1)-Cl(1)-Rh(2) | 96.49(2) |
| Rh(2)-Cl(2)-Rh(1) | 97.08(2) |
| P(1)-Rh(1)-Si(2) | 89.26(3) |
| P(1)-Rh(1)-Si(1) | 91.36(3) |
| Si(2)-Rh(1)-Si(1) | 88.37(4) |
| P(1)-Rh(1)-Cl(1) | 170.66(3) |
| Si(2)-Rh(1)-Cl(1) | 100.08(3) |
| Si(1)-Rh(1)-Cl(1) | 88.69(3) |
| P(1)-Rh(1)-Cl(2) | 97.29(2) |
| Si(2)-Rh(1)-Cl(2) | 104.33(3) |
| Si(1)-Rh(1)-Cl(2) | 164.66(3) |
| Cl(1)-Rh(1)-Cl(2) | 80.73(2) |
| P(2)-Rh(2)-Si(4) | 89.62(3) |
| P(2)-Rh(2)-Si(3) | 90.07(3) |
| Si(4)-Rh(2)-Si(3) | 92.06(3) |
| P(2)-Rh(2)-Cl(2) | 171.71(3) |
| Si(4)-Rh(2)-Cl(2) | 98.36(3) |
| Si(3)-Rh(2)-Cl(2) | 87.43(3) |
| P(2)-Rh(2)-Cl(1) | 100.54(2) |
| Si(4)-Rh(2)-Cl(1) | 96.26(3) |
| Si(3)-Rh(2)-Cl(1) | 166.52(3) |
| Cl(2)-Rh(2)-Cl(1) | 80.90(2) |
| C(58)-O(1)-C(56) | 113.3(3) |
| Si(5)-O(2)-Si(6) | 159.01(18) |

# 4. Characterization of compound **4Rh**

## 4.1 Solid state $^{1}$H NMR

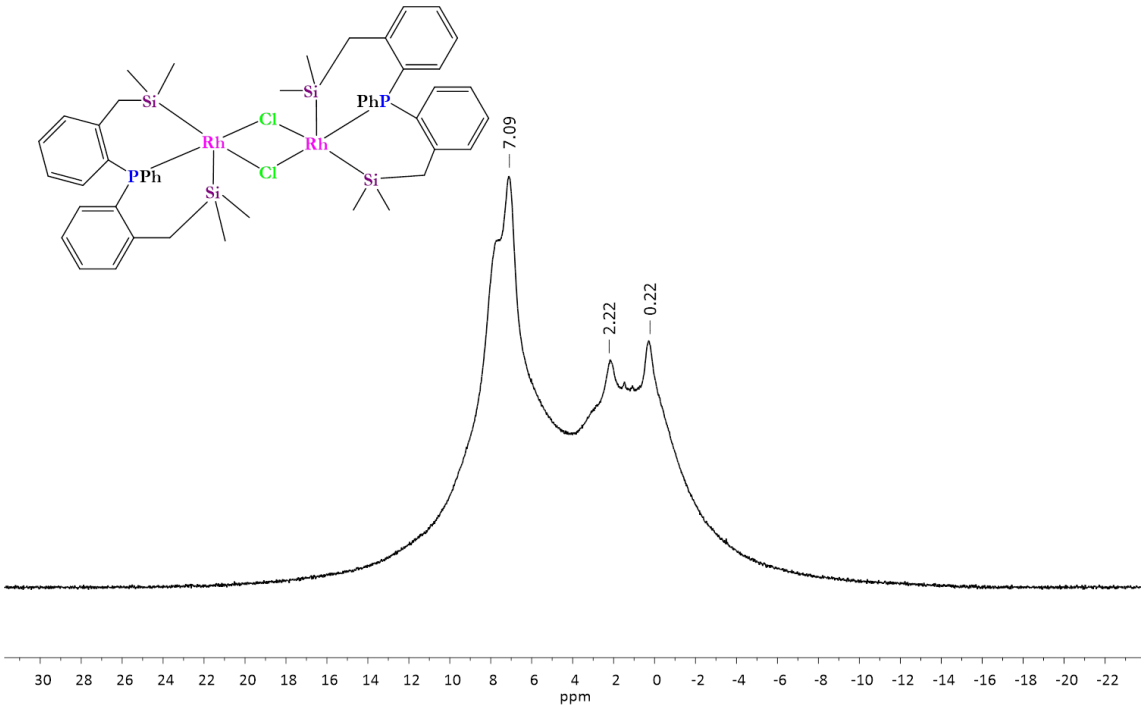



**Figure S 33**. $^{1}$H NMR (CP MAS, Vr=16 kHz) of complex **4Rh**.

## 4.2 Solid state $^{13}C$ NMR

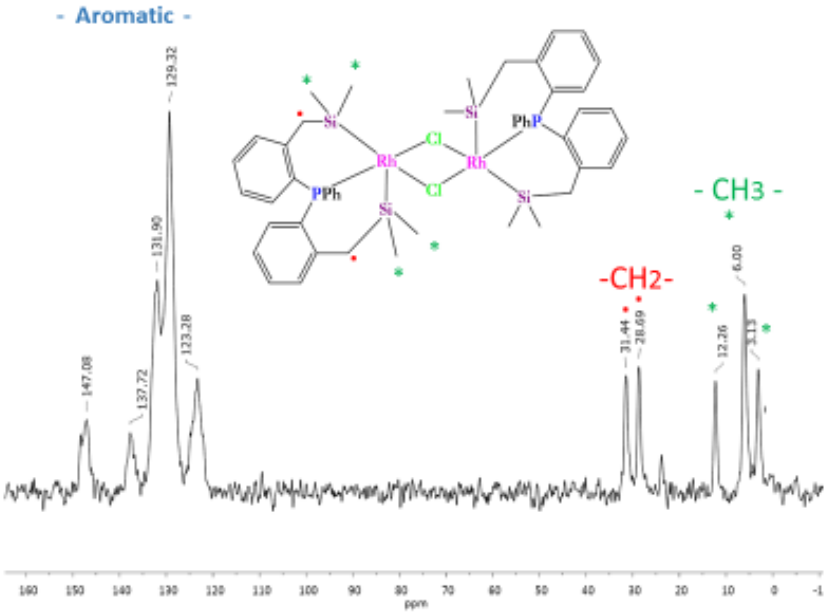



**Figure S 34**. $^{13}C$ (CP MAS, Vr=16 kHz) NMR spectrum of complex **4Rh**.

## 4.3 Solid state $^{31}$P NMR

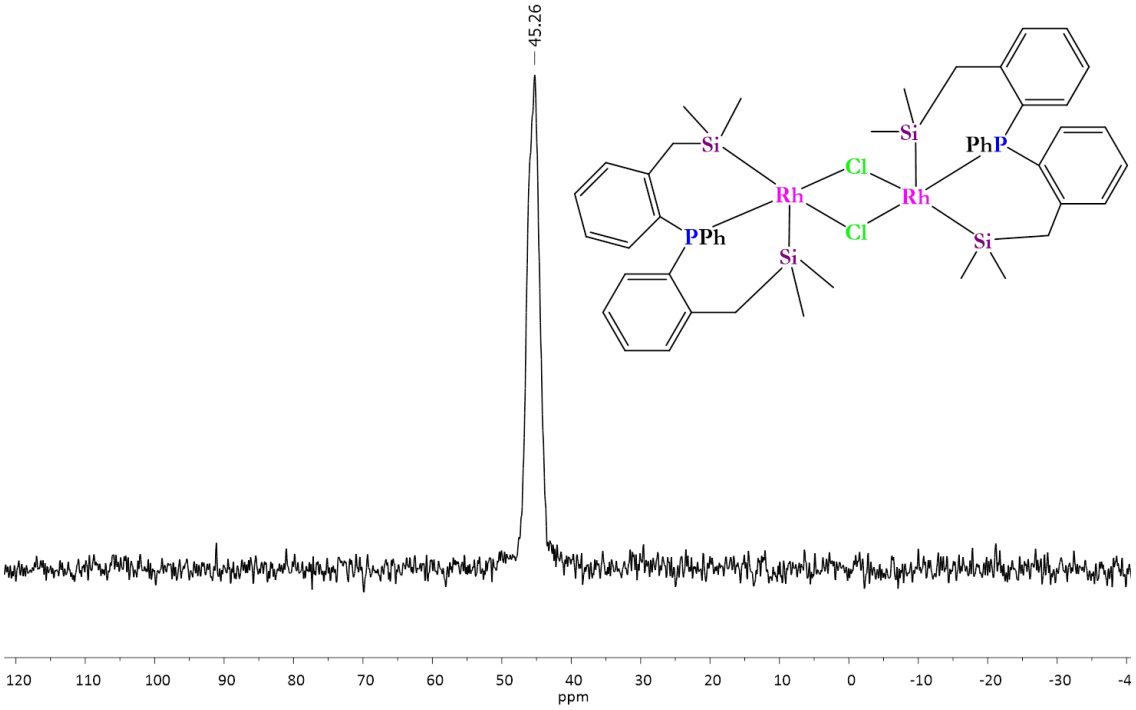



**Figure S 35**. $^{31}$P (CP MAS, Vr=16 kHz) NMR spectrum of complex **4Rh**.

## 4.4 Solid state $^{29}$Si NMR

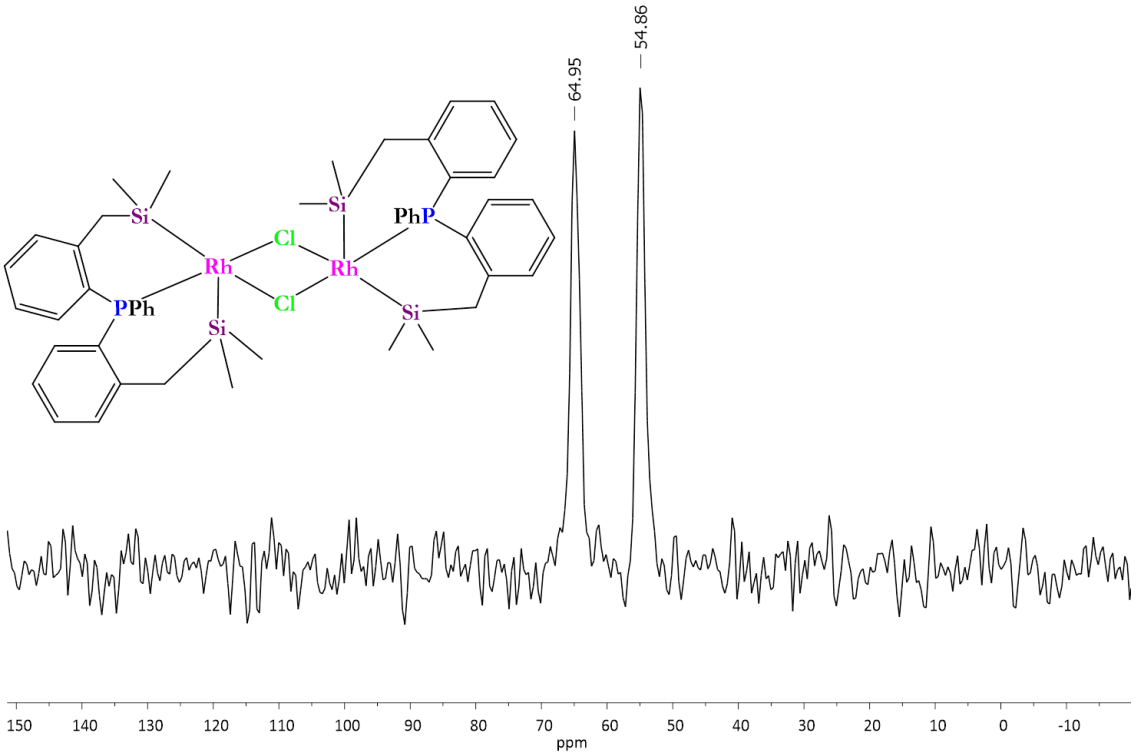



**Figure S 36.** $^{29}$Si (CP MAS, Vr=16 kHz) NMR spectrum of complex **4Rh**.

## 4.5 FT-IR

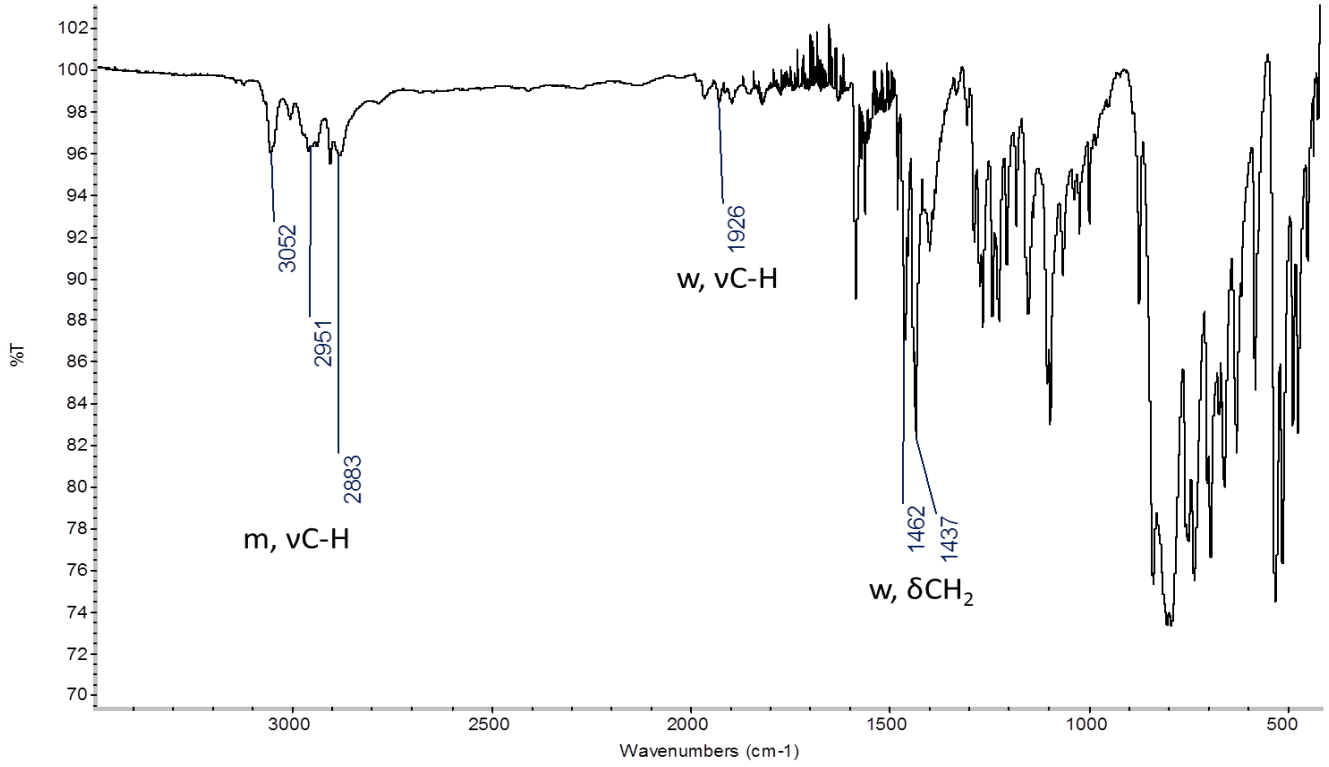



**Figure S 37.** FT- IR (KBr) of compound **4Rh.**

## 4.6 X-Ray Diffraction structure and tables

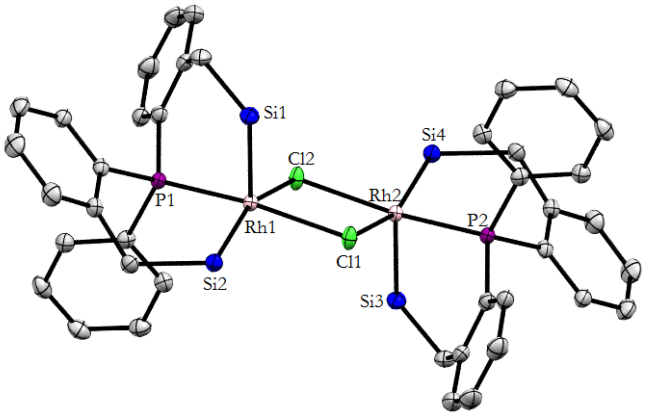



**Figure S 38**. ORTEP drawing of complex **4Rh** with thermal ellipsoids at 50% probability- Hydrogen atoms as well as methyl groups on silicon were omitted for clarity.

Table S4 - Bond Distances (Angstrom)
for: mm69 P 1 21/c 1 R = 0.03

| | | | | | |
|---|---|---|---|---|---|
| Rh1 | -Cl1 | 2.4160(5) | C15 | -C16 | 1.395(3) |
| Rh1 | -P1 | 2.2075(5) | C15 | -C20 | 1.393(3) |
| Rh1 | -Si1 | 2.2824(8) | C16 | -C17 | 1.392(3) |
| Rh1 | -Si2 | 2.2959(7) | C17 | -C18 | 1.392(3) |
| Rh1 | -Cl1_a | 2.5591(6) | C18 | -C19 | 1.382(3) |
| P1 | -C1 | 1.822(2) | C19 | -C20 | 1.386(3) |
| P1 | -C8 | 1.823(2) | C0AA | -H0AA | 0.9600 |
| P1 | -C15 | 1.829(2) | C0AA | -H0AB | 0.9600 |
| Si1 | -C0AA | 1.882(3) | C0AA | -H0AC | 0.9600 |
| Si1 | -C7 | 1.912(3) | C2 | -H2 | 0.9300 |
| Si1 | -C21 | 1.875(2) | C3 | -H3 | 0.9300 |
| Si2 | -C14 | 1.903(2) | C4 | -H4 | 0.9300 |
| Si2 | -C22 | 1.881(3) | C5 | -H5 | 0.9300 |
| Si2 | -C23 | 1.892(2) | C7 | -H7A | 0.9700 |
| C1 | -C2 | 1.395(3) | C7 | -H7B | 0.9700 |
| C1 | -C6 | 1.410(3) | C9 | -H9 | 0.9300 |
| C2 | -C3 | 1.393(3) | C10 | -H10 | 0.9300 |
| C3 | -C4 | 1.385(4) | C11 | -H11 | 0.9300 |
| C4 | -C5 | 1.387(4) | C12 | -H12 | 0.9300 |
| C5 | -C6 | 1.399(3) | C14 | -H14A | 0.9700 |
| C6 | -C7 | 1.498(3) | C14 | -H14B | 0.9700 |
| C8 | -C9 | 1.404(3) | C16 | -H16 | 0.9300 |
| C8 | -C13 | 1.407(3) | C17 | -H17 | 0.9300 |
| C9 | -C10 | 1.391(3) | C18 | -H18 | 0.9300 |
| C10 | -C11 | 1.391(3) | C19 | -H19 | 0.9300 |
| C11 | -C12 | 1.383(3) | C20 | -H20 | 0.9300 |
| C12 | -C13 | 1.403(3) | C21 | -H21A | 0.9600 |
| C13 | -C14 | 1.495(3) | C21 | -H21B | 0.9600 |
| C21 | -H21C | 0.9600 | C26 | -C27 | 1.374(4) |
| C22 | -H22A | 0.9600 | C27 | -C28 | 1.383(3) |
| C22 | -H22B | 0.9600 | C28 | -C29 | 1.382(4) |
| C22 | -H22C | 0.9600 | C24 | -H24 | 0.9300 |
| C23 | -H23A | 0.9600 | C25 | -H25 | 0.9300 |

| | | | | | |
|---|---|---|---|---|---|
| C23 | -H23B | 0.9600 | C26 | -H26 | 0.9300 |
| C23 | -H23C | 0.9600 | C27 | -H27 | 0.9300 |
| C24 | -C25 | 1.377(4) | C28 | -H28 | 0.9300 |
| C24 | -C29 | 1.389(4) | C29 | -H29 | 0.9300 |
| C25 | -C26 | 1.382(4) | | | |

Table S5 - Bond Angles (Degrees)
for: mm69 P 1 21/c 1 R = 0.03

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cl1 | -Rh1 | -P1 | 173.42(3) | C22 | -Si2 | -C23 | 107.53(11) |
| Cl1 | -Rh1 | -Si1 | 100.12(2) | P1 | -C1 | -C2 | 121.49(17) |
| Cl1 | -Rh1 | -Si2 | 88.71(2) | P1 | -C1 | -C6 | 117.73(17) |
| Cl1 | -Rh1 | -Cl1_a | 83.92(2) | C2 | -C1 | -C6 | 120.4(2) |
| P1 | -Rh1 | -Si1 | 86.37(2) | C1 | -C2 | -C3 | 120.8(2) |
| P1 | -Rh1 | -Si2 | 89.41(2) | C2 | -C3 | -C4 | 119.2(2) |
| Cl1_a | -Rh1 | -P1 | 95.37(2) | C3 | -C4 | -C5 | 120.4(2) |
| Si1 | -Rh1 | -Si2 | 96.92(3) | C4 | -C5 | -C6 | 121.7(2) |
| Cl1_a | -Rh1 | -Si1 | 106.44(2) | C1 | -C6 | -C5 | 117.6(2) |
| Cl1_a | -Rh1 | -Si2 | 156.39(3) | C1 | -C6 | -C7 | 121.5(2) |
| Rh1 | -Cl1 | -Rh1_a | 96.08(2) | C5 | -C6 | -C7 | 120.9(2) |
| Rh1 | -P1 | -C1 | 109.31(7) | Si1 | -C7 | -C6 | 121.20(16) |
| Rh1 | -P1 | -C8 | 121.22(7) | P1 | -C8 | -C9 | 120.43(16) |
| Rh1 | -P1 | -C15 | 111.20(7) | P1 | -C8 | -C13 | 119.50(16) |
| C1 | -P1 | -C8 | 105.68(10) | C9 | -C8 | -C13 | 120.07(19) |
| C1 | -P1 | -C15 | 105.45(10) | C8 | -C9 | -C10 | 120.8(2) |
| C8 | -P1 | -C15 | 102.75(9) | C9 | -C10 | -C11 | 119.3(2) |
| Rh1 | -Si1 | -C0AA | 122.43(11) | C10 | -C11 | -C12 | 120.1(2) |
| Rh1 | -Si1 | -C7 | 111.22(7) | C11 | -C12 | -C13 | 121.8(2) |
| Rh1 | -Si1 | -C21 | 106.91(9) | C8 | -C13 | -C12 | 117.8(2) |
| C0AA | -Si1 | -C7 | 102.42(13) | C8 | -C13 | -C14 | 121.30(19) |
| C0AA | -Si1 | -C21 | 106.62(14) | C12 | -C13 | -C14 | 120.7(2) |
| C7 | -Si1 | -C21 | 106.16(11) | Si2 | -C14 | -C13 | 120.41(15) |
| Rh1 | -Si2 | -C14 | 114.55(7) | P1 | -C15 | -C16 | 118.89(16) |
| Rh1 | -Si2 | -C22 | 119.29(8) | P1 | -C15 | -C20 | 121.78(16) |
| Rh1 | -Si2 | -C23 | 101.74(8) | C16 | -C15 | -C20 | 119.33(19) |
| C14 | -Si2 | -C22 | 109.16(10) | C15 | -C16 | -C17 | 120.2(2) |
| C14 | -Si2 | -C23 | 102.67(10) | C16 | -C17 | -C18 | 119.9(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C17 | -C18 | -C19 | 119.9(2) | C11 | -C12 | -H12 | 119.00 |
| C18 | -C19 | -C20 | 120.4(2) | C13 | -C12 | -H12 | 119.00 |
| C15 | -C20 | -C19 | 120.2(2) | Si2 | -C14 | -H14A | 107.00 |
| Si1 | -C0AA | -H0AA | 110.00 | Si2 | -C14 | -H14B | 107.00 |
| Si1 | -C0AA | -H0AB | 109.00 | C13 | -C14 | -H14A | 107.00 |
| Si1 | -C0AA | -H0AC | 109.00 | C13 | -C14 | -H14B | 107.00 |
| H0AA | -C0AA | -H0AB | 110.00 | H14A | -C14 | -H14B | 107.00 |
| H0AA | -C0AA | -H0AC | 109.00 | C15 | -C16 | -H16 | 120.00 |
| H0AB | -C0AA | -H0AC | 109.00 | C17 | -C16 | -H16 | 120.00 |
| C1 | -C2 | -H2 | 120.00 | C16 | -C17 | -H17 | 120.00 |
| C3 | -C2 | -H2 | 120.00 | C18 | -C17 | -H17 | 120.00 |
| C2 | -C3 | -H3 | 120.00 | C17 | -C18 | -H18 | 120.00 |
| C4 | -C3 | -H3 | 120.00 | C19 | -C18 | -H18 | 120.00 |
| C3 | -C4 | -H4 | 120.00 | C18 | -C19 | -H19 | 120.00 |
| C5 | -C4 | -H4 | 120.00 | C20 | -C19 | -H19 | 120.00 |
| C4 | -C5 | -H5 | 119.00 | C15 | -C20 | -H20 | 120.00 |
| C6 | -C5 | -H5 | 119.00 | C19 | -C20 | -H20 | 120.00 |
| Si1 | -C7 | -H7A | 107.00 | Si1 | -C21 | -H21A | 109.00 |
| Si1 | -C7 | -H7B | 107.00 | Si1 | -C21 | -H21B | 109.00 |
| C6 | -C7 | -H7A | 107.00 | Si1 | -C21 | -H21C | 110.00 |
| C6 | -C7 | -H7B | 107.00 | H21A | -C21 | -H21B | 109.00 |
| H7A | -C7 | -H7B | 107.00 | H21A | -C21 | -H21C | 110.00 |
| C8 | -C9 | -H9 | 120.00 | H21B | -C21 | -H21C | 109.00 |
| C10 | -C9 | -H9 | 120.00 | Si2 | -C22 | -H22A | 110.00 |
| C9 | -C10 | -H10 | 120.00 | Si2 | -C22 | -H22B | 109.00 |
| C11 | -C10 | -H10 | 120.00 | Si2 | -C22 | -H22C | 110.00 |
| C10 | -C11 | -H11 | 120.00 | H22A | -C22 | -H22B | 109.00 |
| C12 | -C11 | -H11 | 120.00 | H22A | -C22 | -H22C | 109.00 |

Table S5 - Bond Angles (Degrees) (continued)
for: mm69 P 1 21/c 1 R = 0.03

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H22B | -C22 | -H22C | 109.00 | C25 | -C24 | -H24 | 120.00 |
| Si2 | -C23 | -H23A | 109.00 | C29 | -C24 | -H24 | 120.00 |
| Si2 | -C23 | -H23B | 109.00 | C24 | -C25 | -H25 | 120.00 |
| Si2 | -C23 | -H23C | 109.00 | C26 | -C25 | -H25 | 120.00 |
| H23A | -C23 | -H23B | 109.00 | C25 | -C26 | -H26 | 120.00 |
| H23A | -C23 | -H23C | 109.00 | C27 | -C26 | -H26 | 120.00 |
| H23B | -C23 | -H23C | 109.00 | C26 | -C27 | -H27 | 120.00 |
| C25 | -C24 | -C29 | 120.3(2) | C28 | -C27 | -H27 | 120.00 |
| C24 | -C25 | -C26 | 119.7(2) | C27 | -C28 | -H28 | 120.00 |
| C25 | -C26 | -C27 | 120.1(2) | C29 | -C28 | -H28 | 120.00 |
| C26 | -C27 | -C28 | 120.6(2) | C24 | -C29 | -H29 | 120.00 |
| C27 | -C28 | -C29 | 119.5(2) | C28 | -C29 | -H29 | 120.00 |
| C24 | -C29 | -C28 | 119.9(2) | | | | |

Translation of Symmetry Code to Equiv.Pos

a =[ 3667.00] = [ 3_667] =1-x,1-y,2-z
b =[ 3667.00] = [ 3_667] =1-x,1-y,2-z
c =[ 3567.00] = [ 3_567] =-x,1-y,2-z
d =[ 2556.00] = [ 2_556] =-x,1/2+y,3/2-z
e =[ 3666.00] = [ 3_666] =1-x,1-y,1-z
f =[ 4554.00] = [ 4_565] =x,1/2-y,-1/2+z
g =[ 4565.00] = [ 4_576] =x,3/2-y,1/2+z
h =[ 1455.00] = [ 1_455] =-1+x,y,z
i =[ 3567.00] = [ 3_567] =-x,1-y,2-z
j =[ 3566.00] = [ 3_566] =-x,1-y,1-z
k =[ 4564.00] = [ 4_575] =x,3/2-y,-1/2+z
l =[ 1655.00] = [ 1_655] =1+x,y,z
m =[ 2546.00] = [ 2_546] =-x,-1/2+y,3/2-z
n =[ 3566.00] = [ 3_566] =-x,1-y,1-z
o =[ 4555.00] = [ 4_566] =x,1/2-y,1/2+z

# 5. Characterization of compound **5Rh**

## 5.1 $^{1}$H NMR

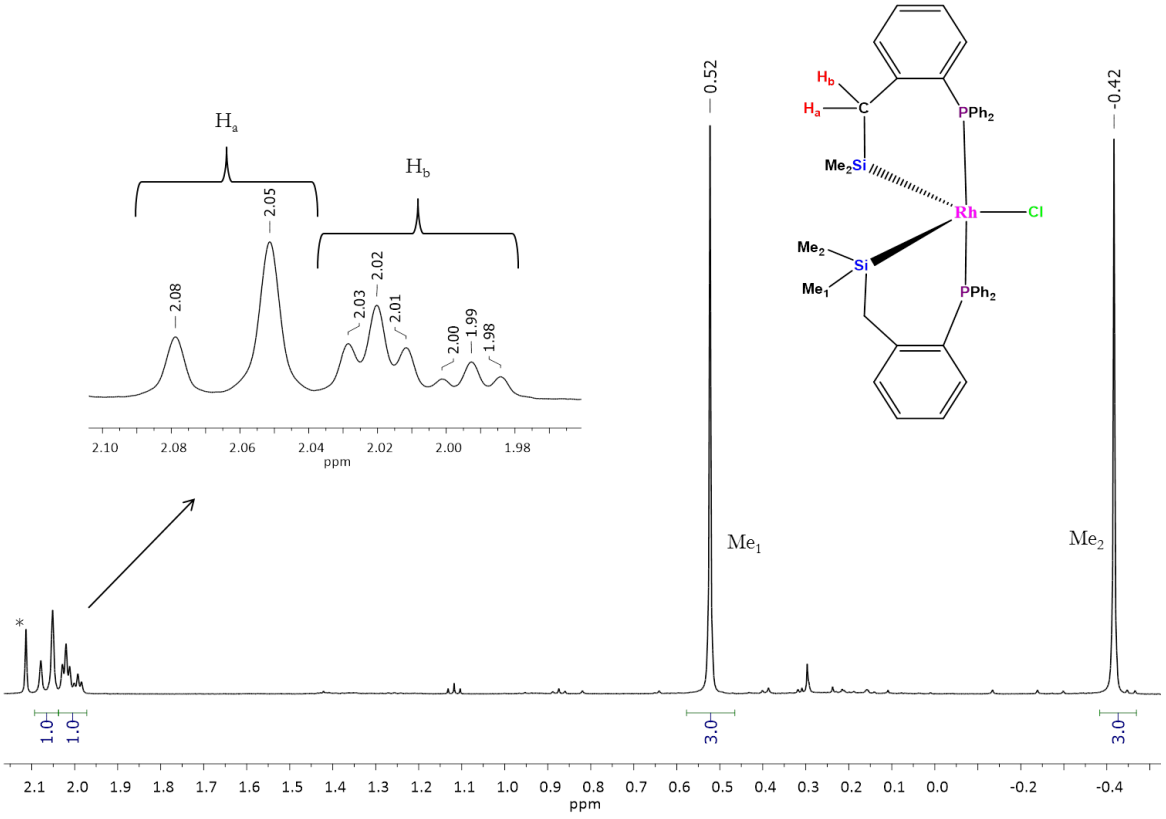



**Figure S 39**. Partial $^{1}$H (500 MHz, $C_6D_6$) NMR spectrum of complex **5Rh**. *Residual toluene

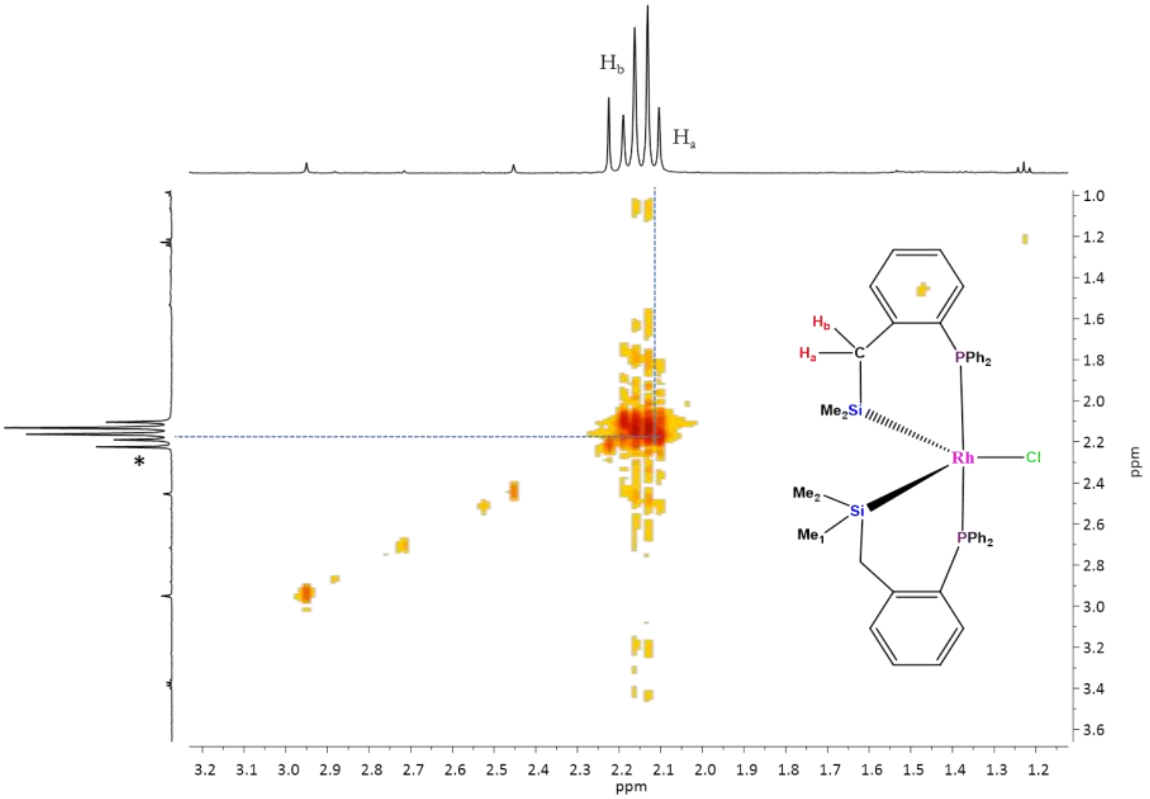



**Figure S 40.** COSY $^{1}H$-$^{1}H$ $\{^{31}P\}$(500 MHz, $C_6D_6$) of complex **5Rh**. * Residual toluene

## 5.2 $^{13}$C NMR

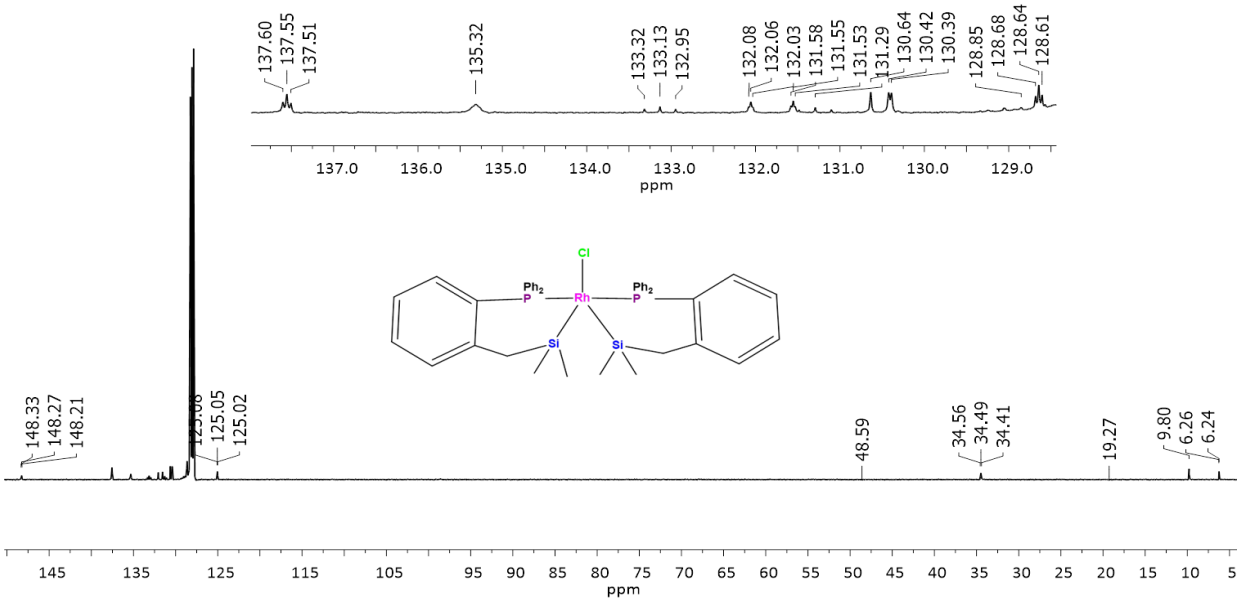



**Figure S 41.** Room temperature $^{13}C\{^{1}H\}$ (125.76 MHz, $C_6D_6$) NMR spectrum of complex **5Rh.**

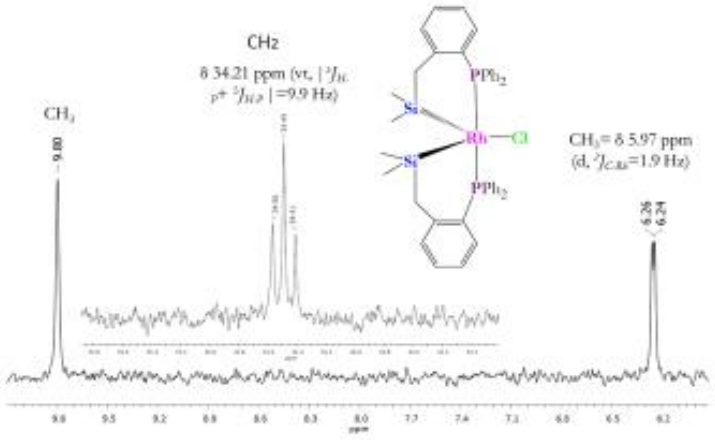



**Figure S 42**. Partial region of the $^{13}C\{^{1}H\}$ (125.72 MHz, $C_6D_6$) NMR spectrum of complex **5Rh** at room temperature.

## 5.3 $^{31}$P NMR

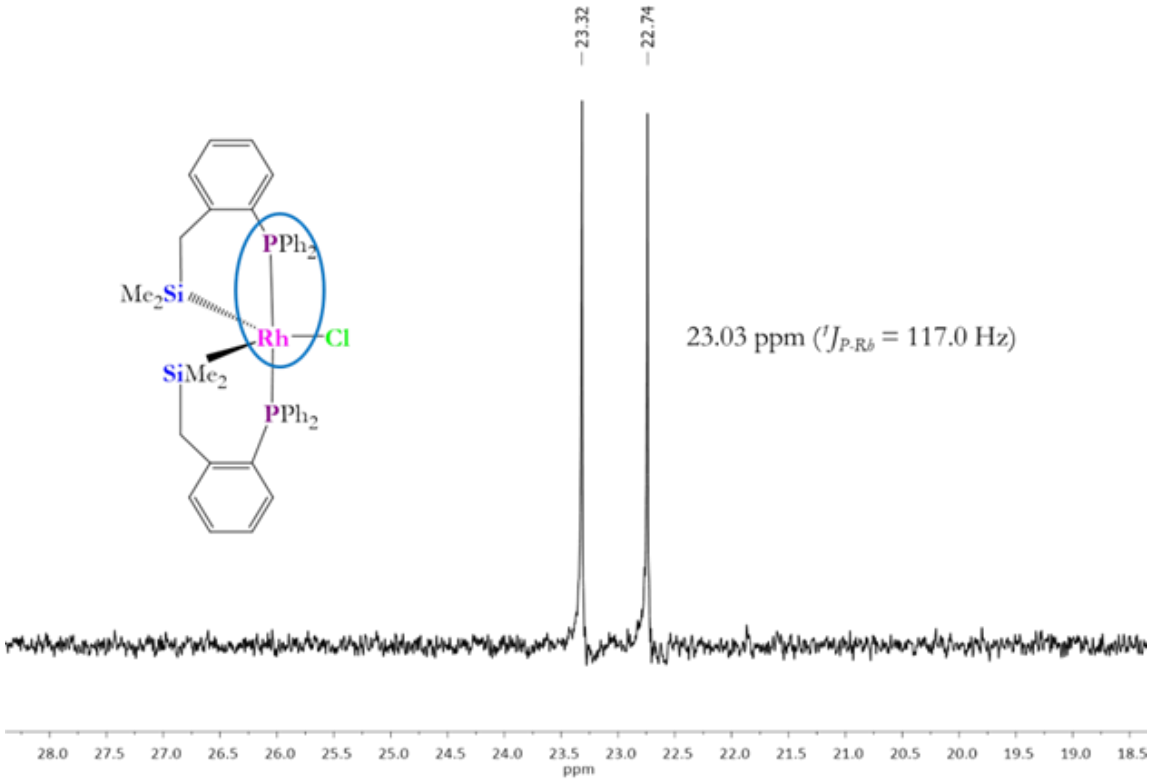



**Figure S 43**. $^{31}P\{^{1}H\}$ NMR spectrum (202.40 MHz, $C_6D_6$) at room temperature of complex **5Rh**.

## 5.4 $^{29}$Si NMR

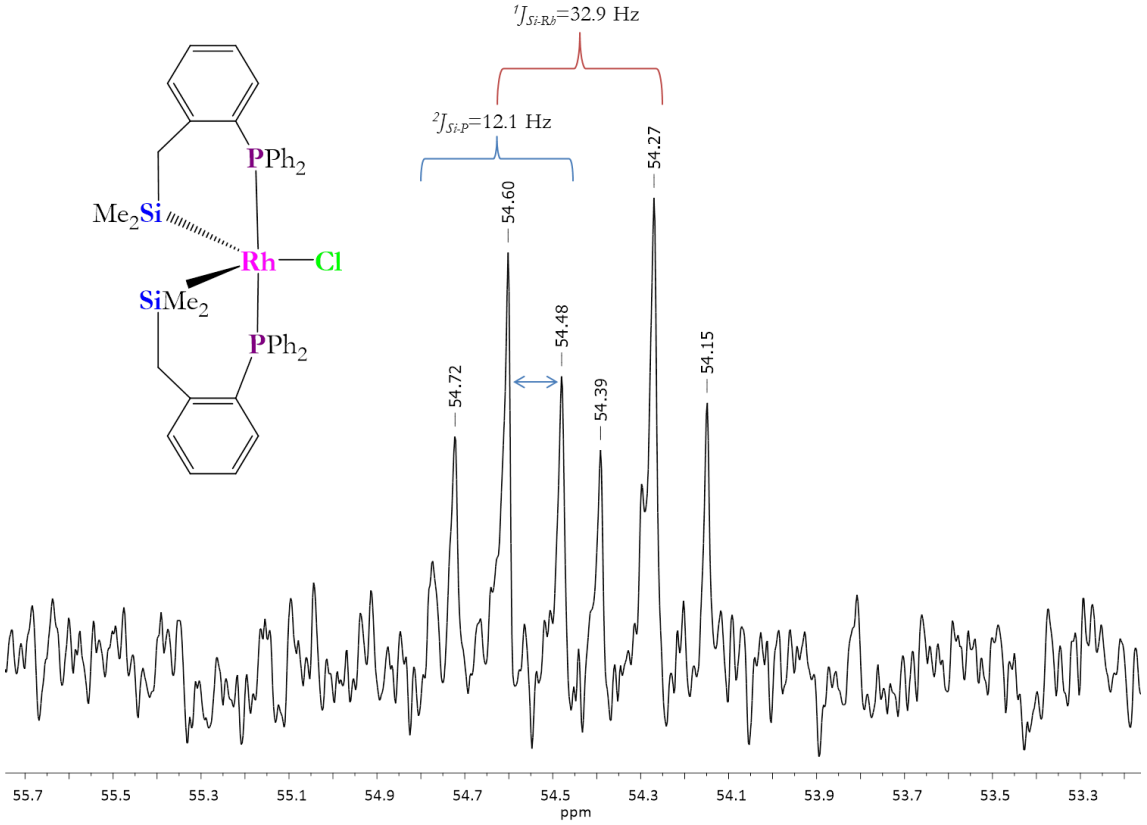



**Figure S 44**. $^{29}$Si{$^{1}$H} (99.36 MHz, $C_6D_6$) NMR spectrum of complex **5Rh**.

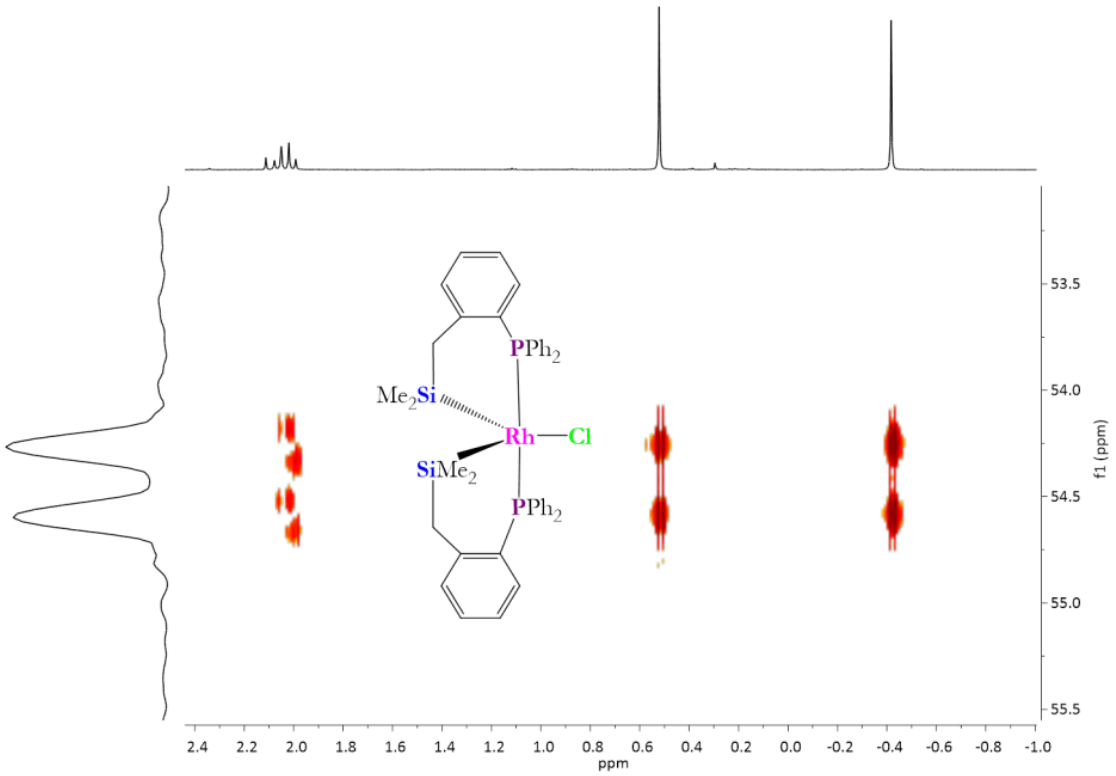



**Figure S 45**. HMBC $^{29}Si$-$^{1}H\{^{31}P\}$ (500 MHz-99.36 MHz, $C_6D_6$) of complex **5Rh**.

## 5.5 FT-IR

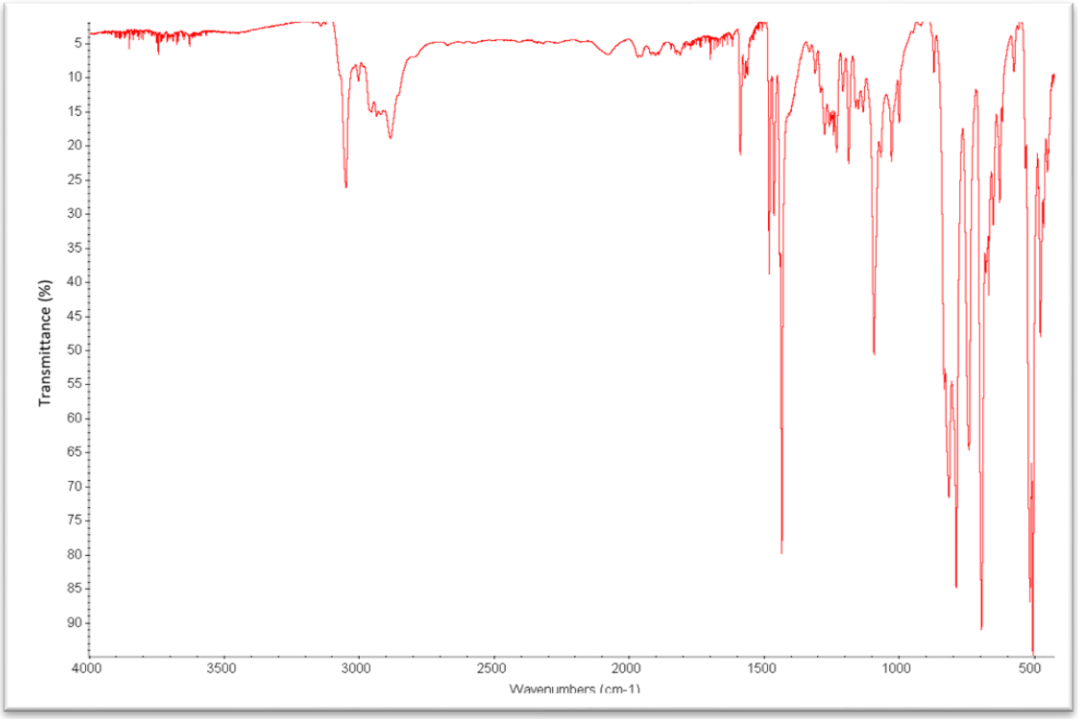



**Figure S 46.** FT-IR spectrum (ATR) of complex **5Rh**.

## 5.6 X-Ray Diffraction structure and tables

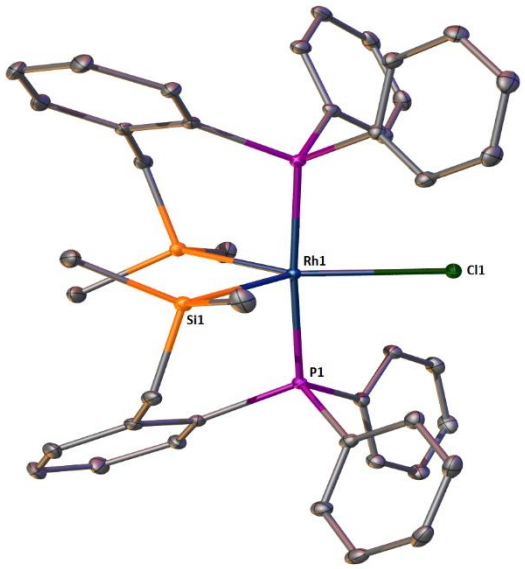



**Figure S 47**. ORTEP diagram of complex **5Rh** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

## Tables for complex **5Rh**

Table S6 - Bond Distances (Angstrom)
for: mm75 C 1 2/c 1 R = 0.03

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Rh1 | -Cl1 | 2.4579(8) | C15 | -C16 | 1.395(3) | | |
| Rh1 | -P1 | 2.3478(5) | C16 | -C17 | 1.387(3) | | |
| Rh1 | -Si1 | 2.3415(6) | C17 | -C18 | 1.391(3) | | |
| Rh1 | -P1_a | 2.3478(5) | C18 | -C19 | 1.392(3) | | |
| Rh1 | -Si1_a | 2.3415(6) | C2AA | -H2AA | 0.9300 | | |
| P1 | -C0AA | 1.820(2) | C1AA | -H1AA | 0.9300 | | |
| P1 | -C8 | 1.847(2) | C4 | -H4 | 0.9300 | | |
| P1 | -C14 | 1.839(2) | C5 | -H5 | 0.9300 | | |
| Si1 | -C7 | 1.915(2) | C7 | -H7A | 0.9700 | | |
| Si1 | -C20 | 1.888(2) | C7 | -H7B | 0.9700 | | |
| Si1 | -C21 | 1.889(2) | C9 | -H9 | 0.9300 | | |
| O1 | -C22 | 1.426(3) | C10 | -H10 | 0.9300 | | |
| O1 | -C25 | 1.436(3) | C11 | -H11 | 0.9300 | | |
| C0AA | -C2AA | 1.398(3) | C12 | -H12 | 0.9300 | | |
| C0AA | -C6 | 1.417(3) | C13 | -H13 | 0.9300 | | |
| C2AA | -C1AA | 1.392(3) | C15 | -H15 | 0.9300 | | |
| C1AA | -C4 | 1.393(3) | C16 | -H16 | 0.9300 | | |
| C4 | -C5 | 1.384(4) | C17 | -H17 | 0.9300 | | |
| C5 | -C6 | 1.399(3) | C18 | -H18 | 0.9300 | | |
| C6 | -C7 | 1.497(3) | C19 | -H19 | 0.9300 | | |
| C8 | -C9 | 1.395(3) | C20 | -H20B | 0.9600 | | |
| C8 | -C13 | 1.407(3) | C20 | -H20C | 0.9600 | | |
| C9 | -C10 | 1.393(3) | C20 | -H20A | 0.9600 | | |
| C10 | -C11 | 1.392(3) | C21 | -H21C | 0.9600 | | |
| C11 | -C12 | 1.382(3) | C21 | -H21A | 0.9600 | | |
| C12 | -C13 | 1.386(3) | C21 | -H21B | 0.9600 | | |
| C14 | -C19 | 1.406(3) | O2 | -C26 | 1.443(7) | | |
| C14 | -C15 | 1.396(3) | O2 | -C29 | 1.502(8) | | |

Table S6 - Bond Distances (Angstrom) (continued)
for: mm75 C 1 2/c 1 R = 0.03

| | | | | | |
|---|---|---|---|---|---|
| C22 | -C23 | 1.513(4) | C26 | -C27 | 1.372(8) |
| C23 | -C24 | 1.519(4) | C27 | -C28 | 1.559(8) |
| C24 | -C25 | 1.534(4) | C28 | -C29 | 1.342(9) |
| C22 | -H22A | 0.9700 | C26 | -H26A | 0.9700 |
| C22 | -H22B | 0.9700 | C26 | -H26B | 0.9700 |
| C23 | -H23B | 0.9700 | C27 | -H27A | 0.9700 |
| C23 | -H23A | 0.9700 | C27 | -H27B | 0.9700 |
| C24 | -H24A | 0.9700 | C28 | -H28A | 0.9700 |
| C24 | -H24B | 0.9700 | C28 | -H28B | 0.9700 |
| C25 | -H25B | 0.9700 | C29 | -H29A | 0.9700 |
| C25 | -H25A | 0.9700 | C29 | -H29B | 0.9700 |

Table S7 - Bond Angles (Degrees)
for: mm75 C 1 2/c 1 R = 0.03

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cl1 | -Rh1 | -P1 | 87.96(2) | C1AA | -C4 | -C5 | 119.9(2) |
| Cl1 | -Rh1 | -Si1 | 137.62(2) | C4 | -C5 | -C6 | 122.1(2) |
| Cl1 | -Rh1 | -P1_a | 87.96(2) | C0AA | -C6 | -C5 | 117.8(2) |
| Cl1 | -Rh1 | -Si1_a | 137.62(2) | C0AA | -C6 | -C7 | 121.27(18) |
| P1 | -Rh1 | -Si1 | 87.82(2) | C5 | -C6 | -C7 | 121.0(2) |
| P1 | -Rh1 | -P1_a | 175.93(2) | Si1 | -C7 | -C6 | 119.50(15) |
| P1 | -Rh1 | -Si1_a | 95.19(2) | P1 | -C8 | -C13 | 120.26(16) |
| P1_a | -Rh1 | -Si1 | 95.19(2) | C9 | -C8 | -C13 | 118.9(2) |
| Si1 | -Rh1 | -Si1_a | 84.76(2) | P1 | -C8 | -C9 | 120.86(16) |
| P1_a | -Rh1 | -Si1_a | 87.82(2) | C8 | -C9 | -C10 | 120.3(2) |
| Rh1 | -P1 | -C0AA | 115.51(7) | C9 | -C10 | -C11 | 120.1(2) |
| Rh1 | -P1 | -C8 | 113.94(7) | C10 | -C11 | -C12 | 120.2(2) |
| Rh1 | -P1 | -C14 | 117.63(7) | C11 | -C12 | -C13 | 120.1(2) |
| C0AA | -P1 | -C8 | 101.67(9) | C8 | -C13 | -C12 | 120.6(2) |
| C0AA | -P1 | -C14 | 104.16(9) | P1 | -C14 | -C19 | 120.20(16) |
| C8 | -P1 | -C14 | 101.83(9) | C15 | -C14 | -C19 | 118.65(19) |
| Rh1 | -Si1 | -C7 | 112.52(7) | P1 | -C14 | -C15 | 121.16(16) |
| Rh1 | -Si1 | -C20 | 104.29(8) | C14 | -C15 | -C16 | 120.42(19) |
| Rh1 | -Si1 | -C21 | 127.45(8) | C15 | -C16 | -C17 | 120.1(2) |

C7 -Si1 -C20 101.69(11) C16 -C17 -C18 120.5(2)

C7 -Si1 -C21 104.51(10) C17 -C18 -C19 119.4(2)

C20 -Si1 -C21 103.14(11) C14 -C19 -C18 121.0(2)

C22 -O1 -C25 107.14(19) C1AA -C2AA -H2AA 119.00

P1 -C0AA -C2AA 122.92(16) C0AA -C2AA -H2AA 119.00

P1 -C0AA -C6 117.15(16) C2AA -C1AA -H1AA 120.00

C2AA -C0AA -C6 119.83(19) C4 -C1AA -H1AA 120.00

C0AA -C2AA -C1AA 121.1(2) C5 -C4 -H4 120.00

C2AA -C1AA -C4 119.3(2) C1AA -C4 -H4 120.00

Table S7 - Bond Angles (Degrees) (continued)
for: mm75 C 1 2/c 1 R = 0.03

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4 | -C5 | -H5 | 119.00 | Si1 | -C20 | -H20B | 109.00 |
| C6 | -C5 | -H5 | 119.00 | H20A | -C20 | -H20B | 110.00 |
| Si1 | -C7 | -H7B | 107.00 | H20A | -C20 | -H20C | 109.00 |
| C6 | -C7 | -H7A | 107.00 | Si1 | -C20 | -H20C | 110.00 |
| Si1 | -C7 | -H7A | 107.00 | H20B | -C20 | -H20C | 109.00 |
| H7A | -C7 | -H7B | 107.00 | Si1 | -C21 | -H21B | 110.00 |
| C6 | -C7 | -H7B | 107.00 | Si1 | -C21 | -H21C | 110.00 |
| C8 | -C9 | -H9 | 120.00 | Si1 | -C21 | -H21A | 110.00 |
| C10 | -C9 | -H9 | 120.00 | H21A | -C21 | -H21C | 109.00 |
| C11 | -C10 | -H10 | 120.00 | H21B | -C21 | -H21C | 109.00 |
| C9 | -C10 | -H10 | 120.00 | H21A | -C21 | -H21B | 109.00 |
| C12 | -C11 | -H11 | 120.00 | C26 | -O2 | -C29 | 108.7(5) |
| C10 | -C11 | -H11 | 120.00 | O1 | -C22 | -C23 | 105.3(2) |
| C11 | -C12 | -H12 | 120.00 | C22 | -C23 | -C24 | 101.1(2) |
| C13 | -C12 | -H12 | 120.00 | C23 | -C24 | -C25 | 104.6(2) |
| C8 | -C13 | -H13 | 120.00 | O1 | -C25 | -C24 | 106.7(2) |
| C12 | -C13 | -H13 | 120.00 | O1 | -C22 | -H22A | 111.00 |
| C16 | -C15 | -H15 | 120.00 | O1 | -C22 | -H22B | 111.00 |
| C14 | -C15 | -H15 | 120.00 | C23 | -C22 | -H22B | 111.00 |
| C15 | -C16 | -H16 | 120.00 | H22A | -C22 | -H22B | 109.00 |
| C17 | -C16 | -H16 | 120.00 | C23 | -C22 | -H22A | 111.00 |
| C18 | -C17 | -H17 | 120.00 | C22 | -C23 | -H23B | 112.00 |
| C16 | -C17 | -H17 | 120.00 | C24 | -C23 | -H23A | 112.00 |
| C17 | -C18 | -H18 | 120.00 | C24 | -C23 | -H23B | 112.00 |
| C19 | -C18 | -H18 | 120.00 | H23A | -C23 | -H23B | 109.00 |
| C18 | -C19 | -H19 | 120.00 | C22 | -C23 | -H23A | 112.00 |
| C14 | -C19 | -H19 | 119.00 | C23 | -C24 | -H24B | 111.00 |
| Si1 | -C20 | -H20A | 109.00 | C25 | -C24 | -H24A | 111.00 |

Table S7 - Bond Angles (Degrees) (continued)
for: mm75 C 1 2/c 1 R = 0.03

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C23 | -C24 | -H24A | 111.00 | H26A | -C26 | -H26B | 109.00 |
| H24A | -C24 | -H24B | 109.00 | C26 | -C27 | -H27A | 109.00 |
| C25 | -C24 | -H24B | 111.00 | C26 | -C27 | -H27B | 109.00 |
| O1 | -C25 | -H25A | 110.00 | C28 | -C27 | -H27A | 109.00 |
| O1 | -C25 | -H25B | 110.00 | C28 | -C27 | -H27B | 109.00 |
| C24 | -C25 | -H25B | 110.00 | H27A | -C27 | -H27B | 108.00 |
| H25A | -C25 | -H25B | 109.00 | C27 | -C28 | -H28A | 111.00 |
| C24 | -C25 | -H25A | 110.00 | C27 | -C28 | -H28B | 111.00 |
| O2 | -C26 | -C27 | 103.5(4) | C29 | -C28 | -H28A | 111.00 |
| C26 | -C27 | -C28 | 112.5(4) | C29 | -C28 | -H28B | 111.00 |
| C27 | -C28 | -C29 | 102.8(5) | H28A | -C28 | -H28B | 109.00 |
| O2 | -C29 | -C28 | 110.2(4) | O2 | -C29 | -H29A | 110.00 |
| O2 | -C26 | -H26A | 111.00 | O2 | -C29 | -H29B | 110.00 |
| O2 | -C26 | -H26B | 111.00 | C28 | -C29 | -H29A | 110.00 |
| C27 | -C26 | -H26A | 111.00 | C28 | -C29 | -H29B | 110.00 |
| C27 | -C26 | -H26B | 111.00 | H29A | -C29 | -H29B | 108.00 |

# 6. Characterization of compound **2Ir**

## 6.1 $^{1}$H NMR

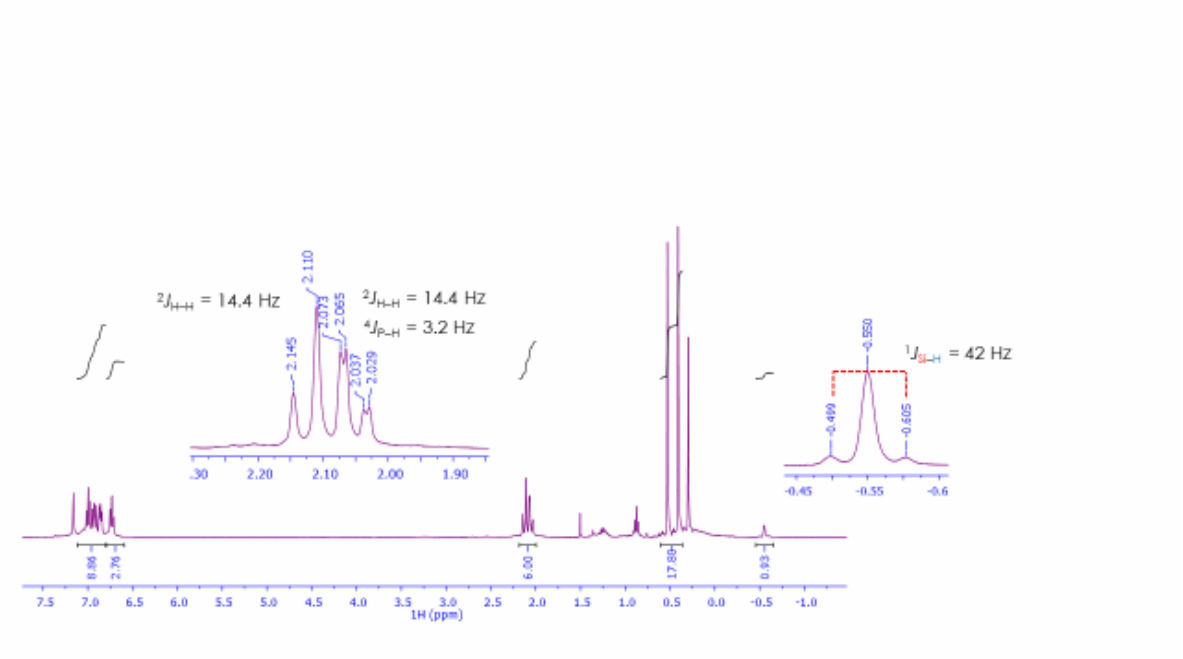



**Figure S 48.** $^{1}$H NMR spectrum (400 MHz) in $C_6D_6$ of complex **2Ir.**

## 6.2 $^{13}$C NMR

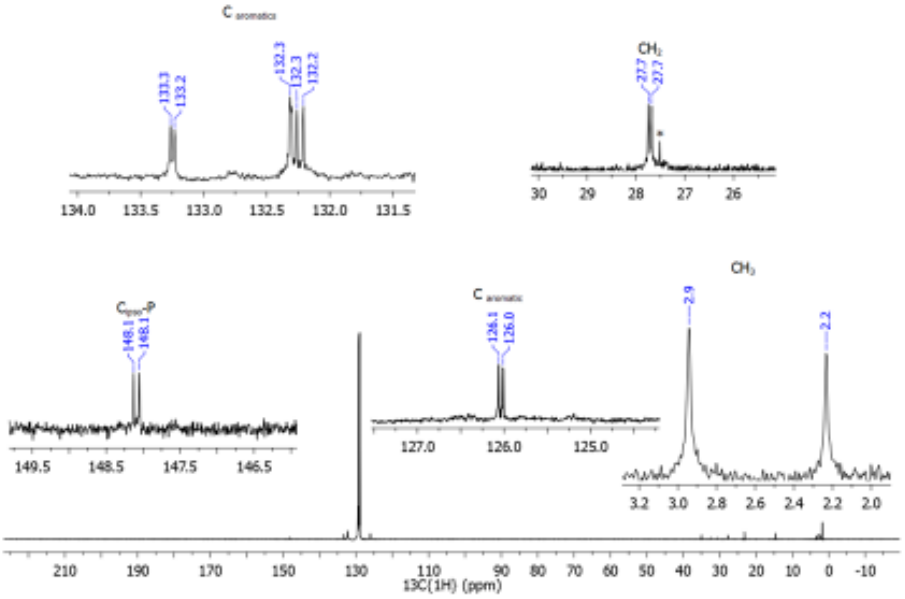



**Figure S 49.** $^{13}$C{$^{1}$H} NMR spectrum (176.008 MHz) in $C_6D_6$ of complex **2Ir.**

## 6.3 $^{31}$P NMR

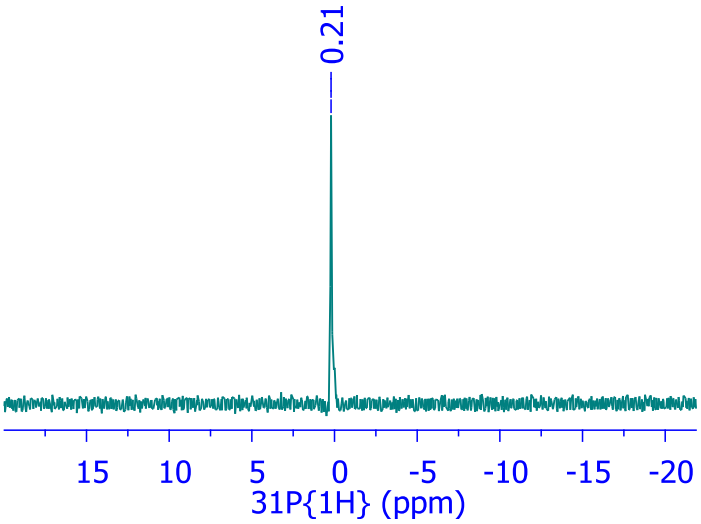



**Figure S 50.** $^{31}P\{^{1}H\}$ NMR spectrum of complex **2Ir** in $C_6D_6$.

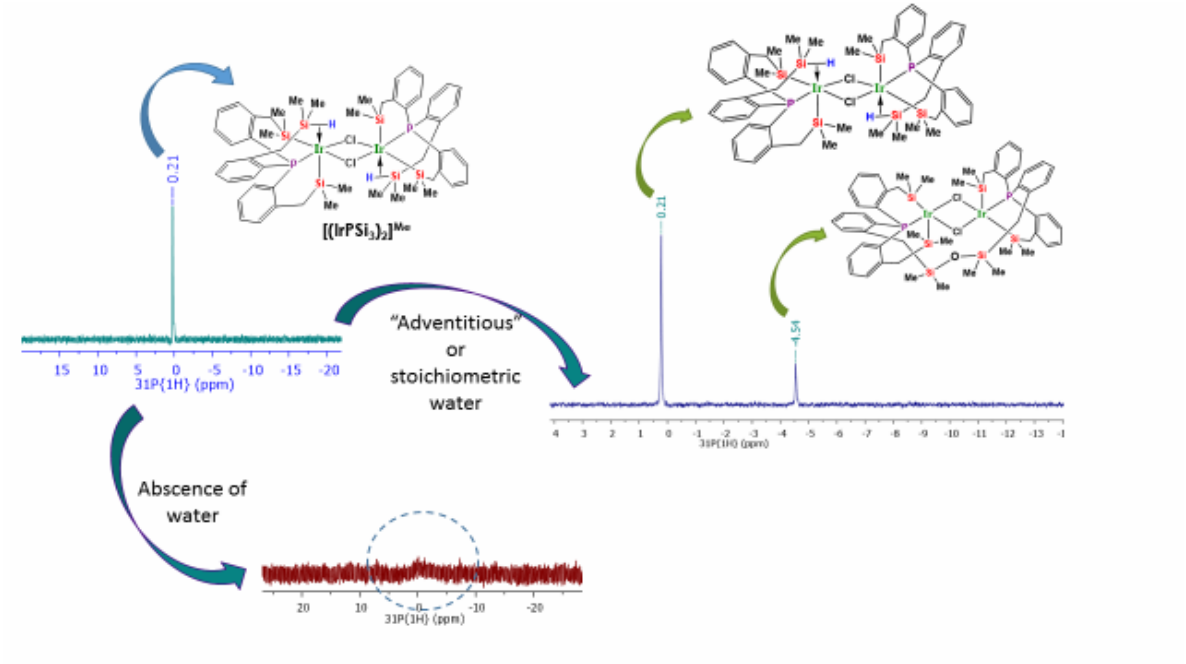
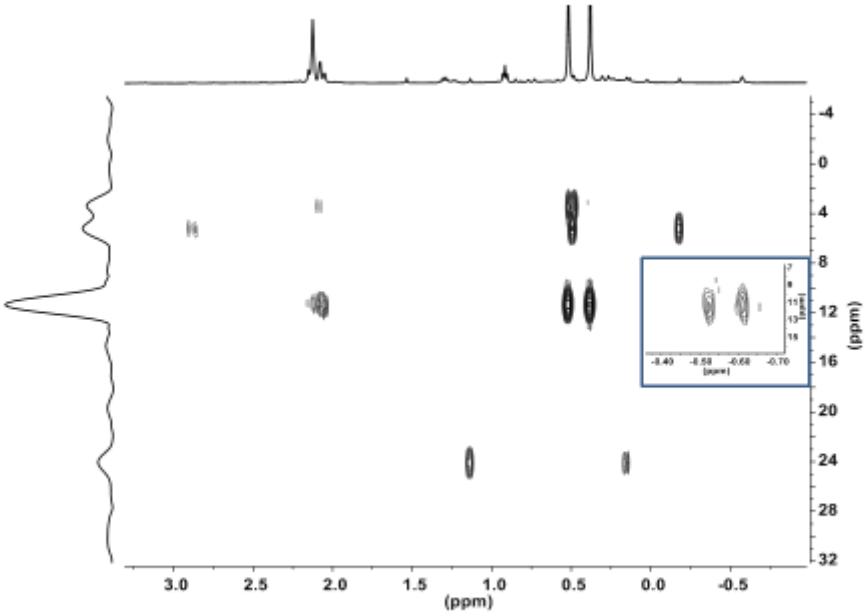



**Figure S 51.** $^{31}P\{^{1}H]$ NMR spectra showing conversion of complex **2Ir** (top left) to **3Ir** in the presence of adventitious water (top right) and to unknown compounds in very dried solvents.

## 6.4 $^{29}$Si NMR

**Figure S 51**. HMQC $^{29}$Si-$^{1}$H{$^{31}$P} (500 MHz-99.36 MHz, $C_6D_6$) of a mixture of complexes **2Ir and 3Ir**.



## 6.5 FT-IR

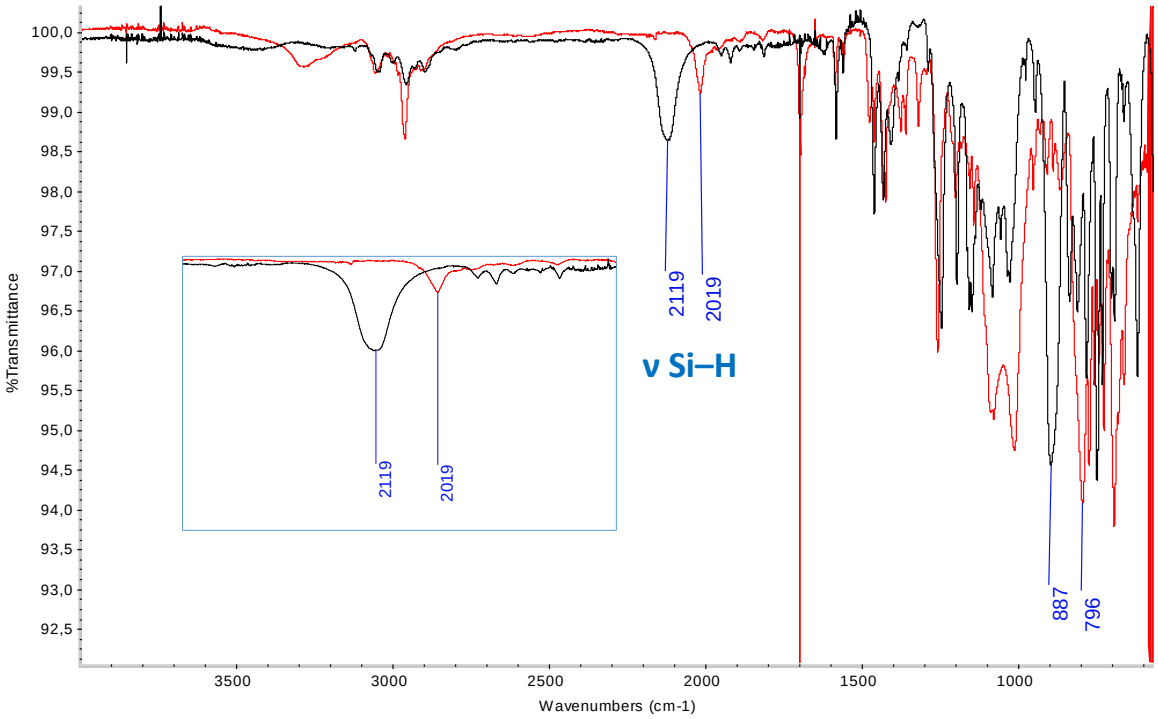



**Figure S 52.** FT-IR spectrum of complex **2Ir** (red) and its comparison with free ligand **1** (black). Inset: hydride region with same colour code.

# 7 Characterization of compound **3Ir**

## 7.1 $^{1}$H NMR

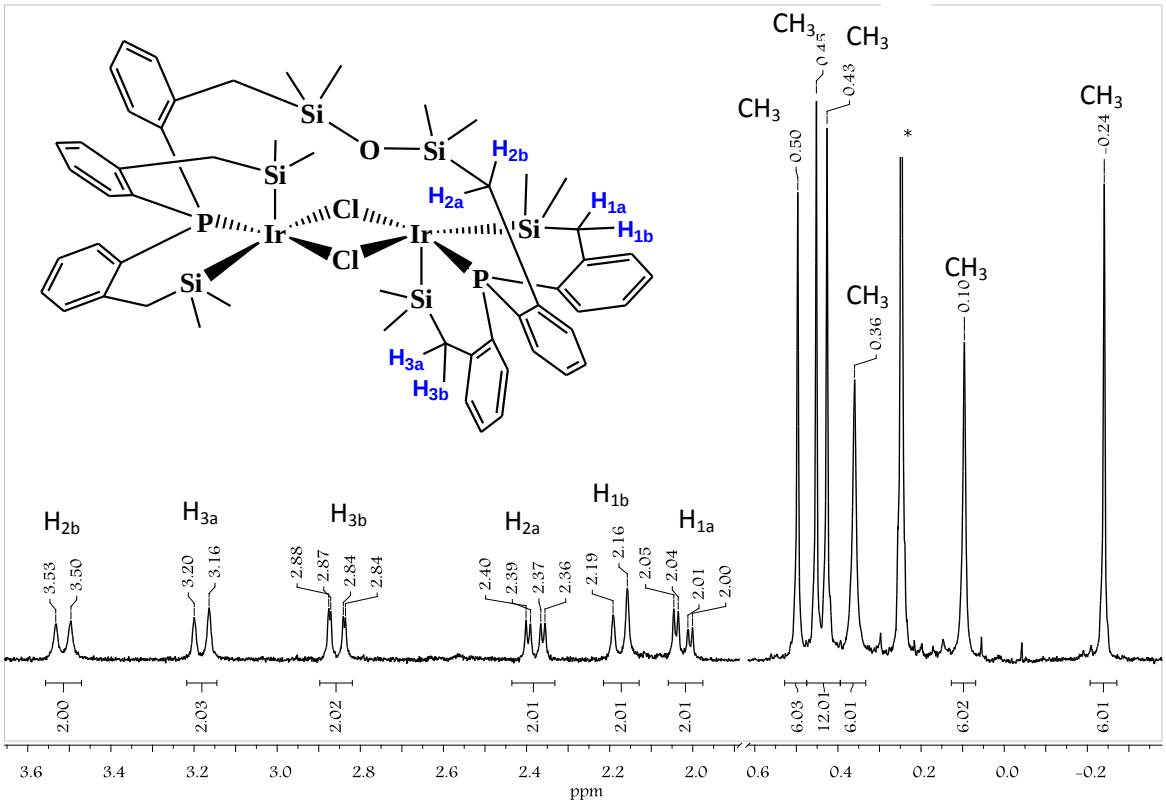



**Figure S 53.** Partial $^{1}$H (400 MHz, $C_6D_6$) NMR spectrum of complex **3Ir** at ambient temperature.

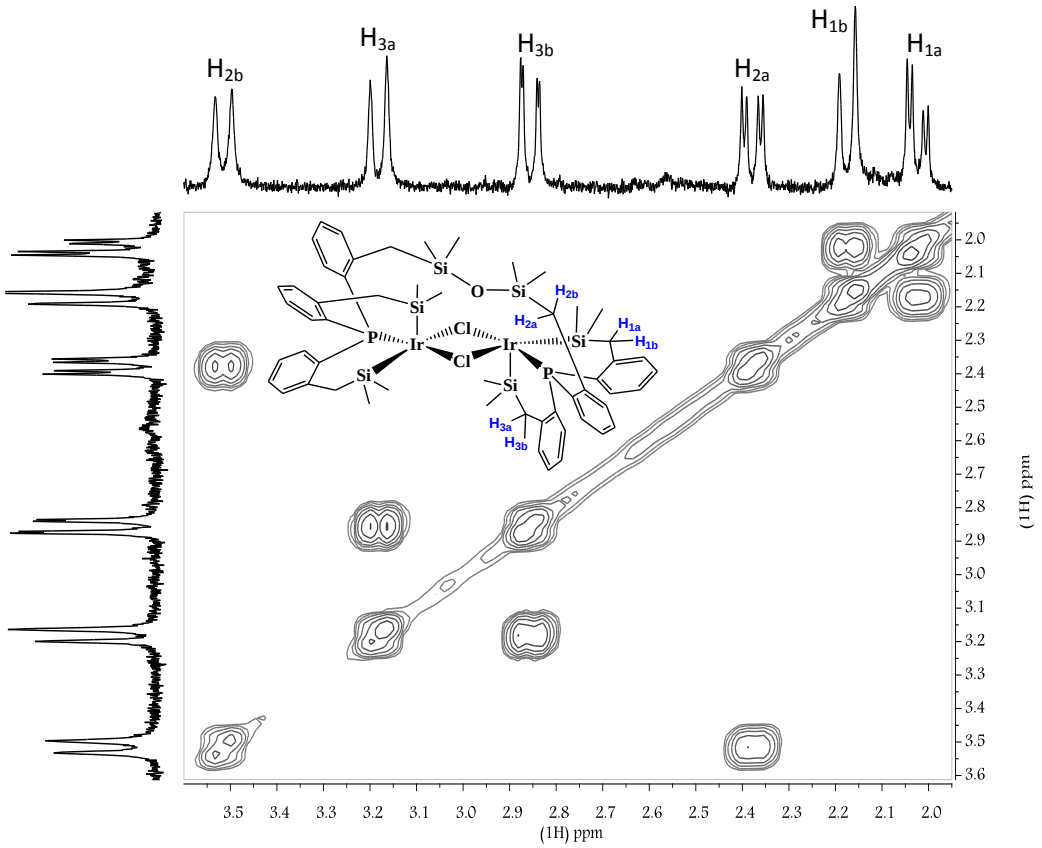



**Figure S 54.** COSY $^{1}H$–$^{1}H$ (400 MHz, $C_6D_6$) NMR spectrum of complex **3Ir**.

## 7.2 $^{13}$C NMR

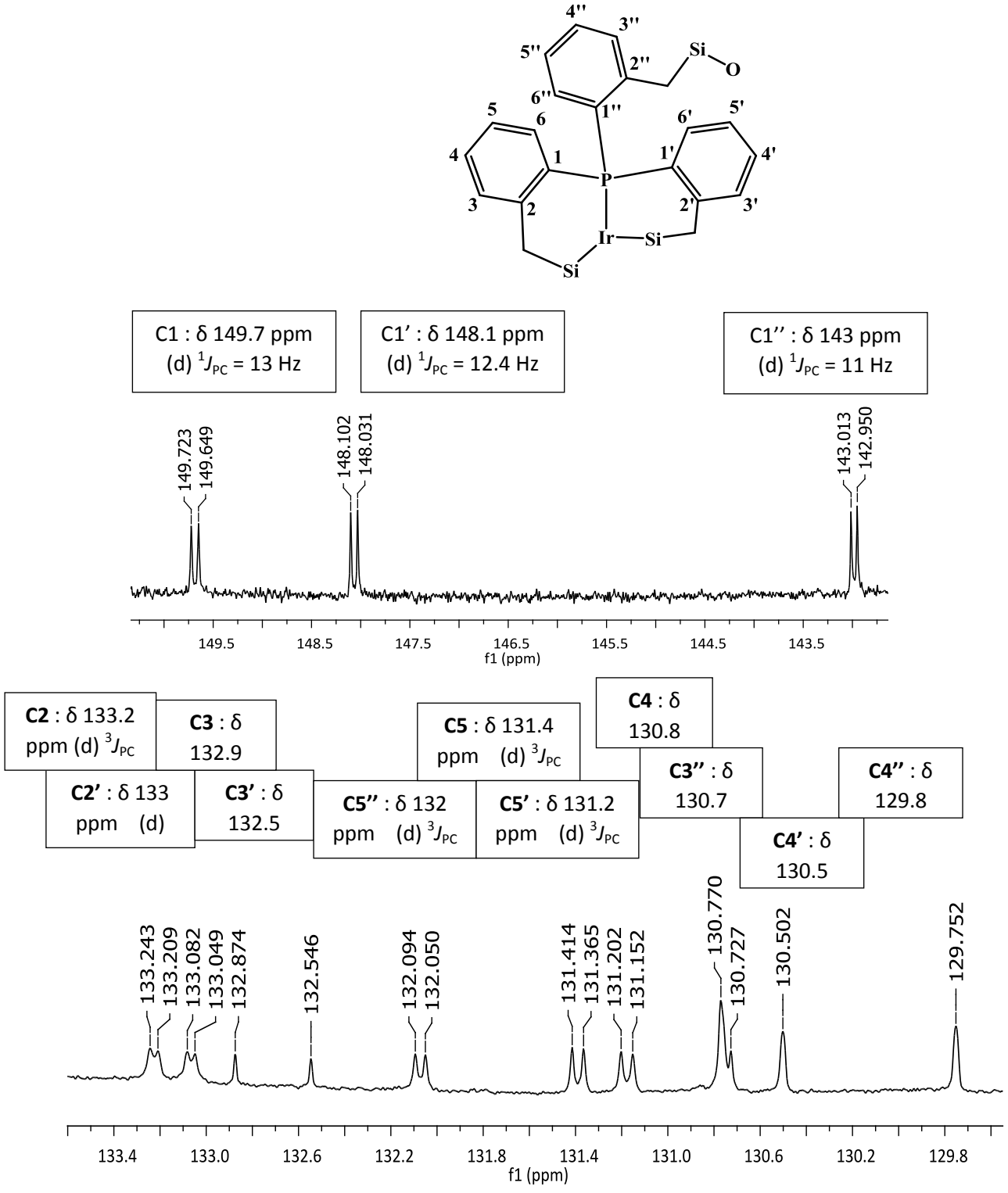



**Figure S 55.** Regions of $^{13}$C{$^{1}$H] NMR spectrum of complex **3Ir** and numbering for assignment.

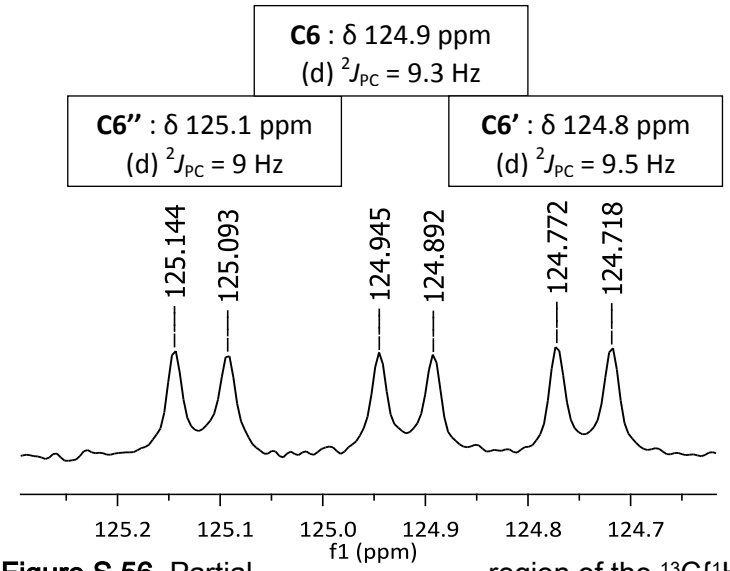



**Figure S 56.** Partial region of the $^{13}C\{^1H\}$ NMR (175 MHz) spectrum of complex **3Ir.** Numbering is shown in previous Figure.

## 7.3 $^{31}$P NMR

**Figure S 57.** $^{31}P\{^{1}H\}$ (161.9 MHz, $C_6D_6$) NMR spectrum of complex **3Ir**.

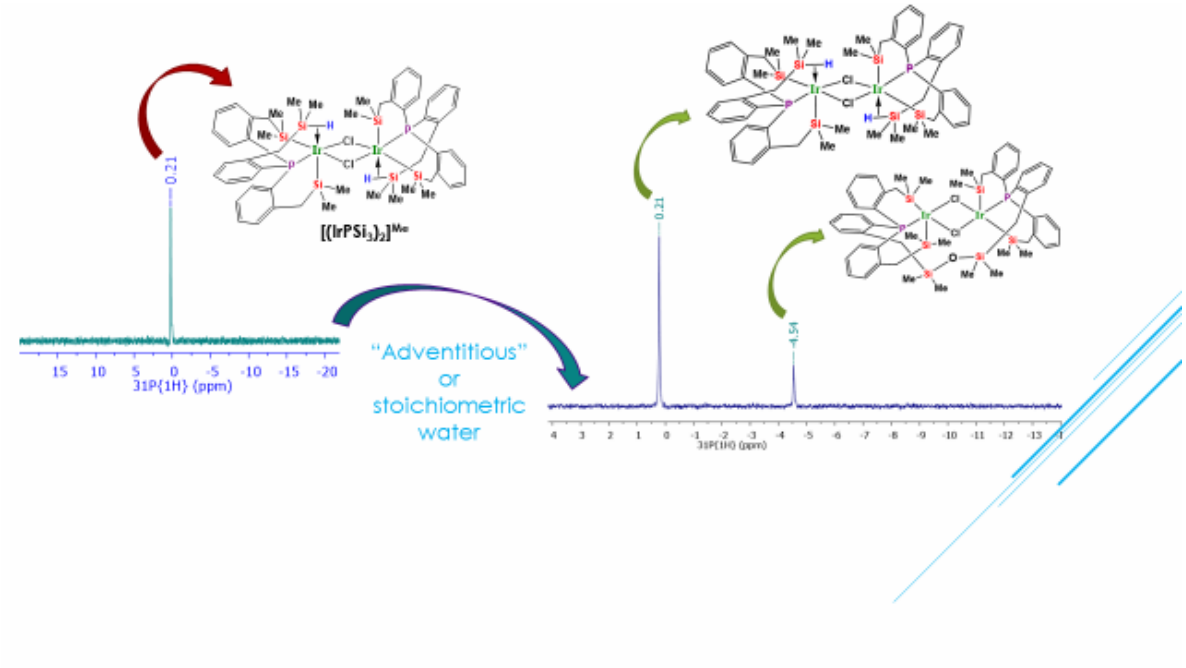



**Figure S 58.** $^{31}P\{^{1}H\}$ NMR spectrum of compound **2Ir** and its gradual conversion to **3Ir** in the presence of water.

## 7.6 X-Ray Diffraction structure and tables

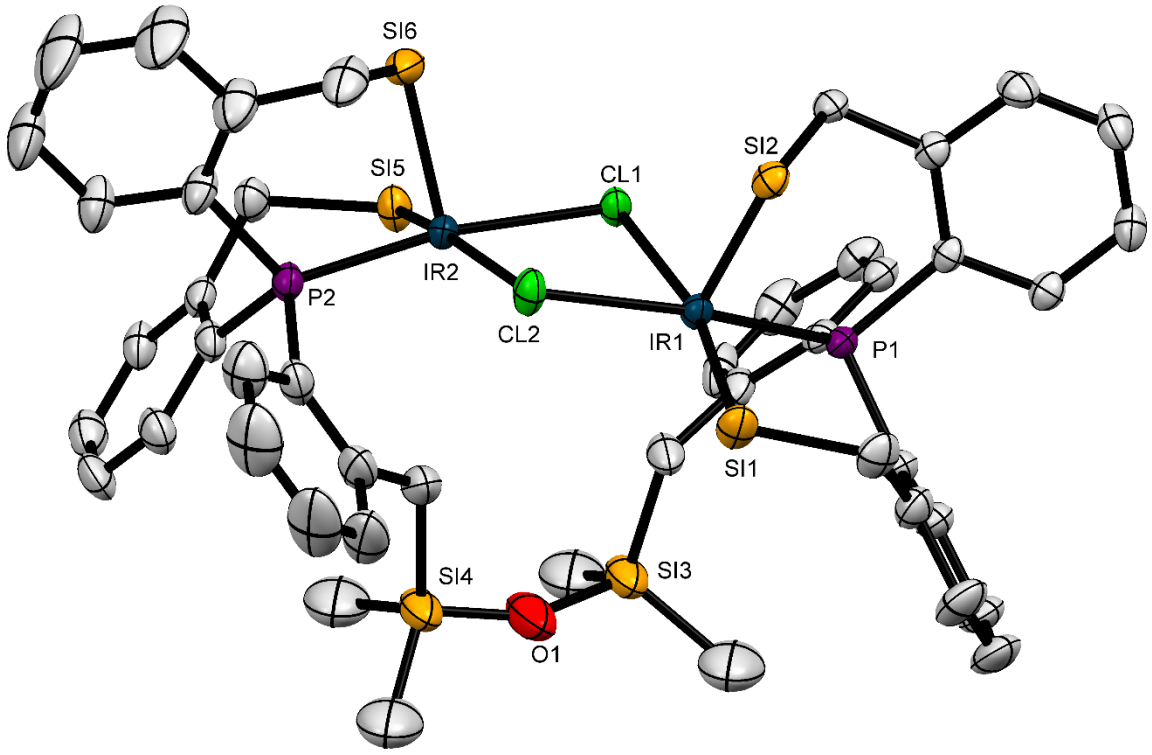



**Figure S 59.** X-ray diffraction structure of compound **3Ir** with thermal ellipsoids at the 50% probability level. Hydrogen atoms were removed for clarity.

## Tables for complex 3Ir

Table S8. Bond lengths [Å] and angles [°] for vm1_sq.

| | |
|---|---|
| C(1)-C(6) | 1.390(6) |
| C(1)-C(2) | 1.414(6) |
| C(1)-P(1) | 1.832(4) |
| C(2)-C(3) | 1.402(6) |
| C(2)-C(19) | 1.494(6) |
| C(3)-C(4) | 1.374(8) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.376(8) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.389(6) |
| C(5)-H(5) | 0.9500 |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.385(6) |
| C(7)-C(12) | 1.420(6) |
| C(7)-P(1) | 1.838(4) |
| C(8)-C(9) | 1.389(6) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.375(7) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.369(8) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.389(7) |
| C(11)-H(11) | 0.9500 |
| C(12)-C(21) | 1.508(7) |
| C(13)-C(18) | 1.399(5) |
| C(13)-C(14) | 1.415(5) |
| C(13)-P(1) | 1.833(4) |
| C(14)-C(15) | 1.388(6) |
| C(14)-C(20) | 1.498(5) |
| C(15)-C(16) | 1.380(6) |
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.369(6) |

| | |
|---|---|
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.386(6) |
| C(17)-H(17) | 0.9500 |
| C(18)-H(18) | 0.9500 |
| C(19)-Si(1) | 1.893(5) |
| C(19)-H(19A) | 0.8383 |
| C(19)-H(19B) | 0.8638 |
| C(20)-Si(2) | 1.903(4) |
| C(20)-H(20A) | 0.9900 |
| C(20)-H(20B) | 0.9900 |
| C(21)-Si(3P) | 1.894(7) |
| C(21)-Si(3) | 1.915(7) |
| C(21)-H(21A) | 1.1075 |
| C(21)-H(21B) | 1.0215 |
| C(22)-Si(1) | 1.884(6) |
| C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 |
| C(22)-H(22C) | 0.9800 |
| C(23)-Si(1) | 1.885(5) |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-Si(2) | 1.886(4) |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-Si(2) | 1.862(5) |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(28)-C(33) | 1.383(7) |
| C(28)-C(29) | 1.405(7) |
| C(28)-P(2) | 1.845(5) |
| C(29)-C(30) | 1.406(8) |
| C(29)-C(46) | 1.494(8) |
| C(30)-C(31) | 1.388(10) |

| | |
|---|---|
| C(30)-H(30) | 0.9500 |
| C(31)-C(32) | 1.347(10) |
| C(31)-H(31) | 0.9500 |
| C(32)-C(33) | 1.383(8) |
| C(32)-H(32) | 0.9500 |
| C(33)-H(33) | 0.9500 |
| C(34)-C(39) | 1.405(6) |
| C(34)-C(35) | 1.407(6) |
| C(34)-P(2) | 1.832(4) |
| C(35)-C(36) | 1.393(6) |
| C(35)-C(47) | 1.498(6) |
| C(36)-C(37) | 1.385(7) |
| C(36)-H(36) | 0.9500 |
| C(37)-C(38) | 1.373(8) |
| C(37)-H(37) | 0.9500 |
| C(38)-C(39) | 1.379(7) |
| C(38)-H(38) | 0.9500 |
| C(39)-H(39) | 0.9500 |
| C(40)-C(45) | 1.395(6) |
| C(40)-C(41) | 1.410(7) |
| C(40)-P(2) | 1.832(4) |
| C(41)-C(42) | 1.408(7) |
| C(41)-C(48) | 1.502(7) |
| C(42)-C(43) | 1.378(9) |
| C(42)-H(42) | 0.9500 |
| C(43)-C(44) | 1.369(10) |
| C(43)-H(43) | 0.9500 |
| C(44)-C(45) | 1.388(7) |
| C(44)-H(44) | 0.9500 |
| C(45)-H(45) | 0.9500 |
| C(46)-Si(4P) | 1.786(7) |
| C(46)-Si(4) | 2.032(7) |
| C(46)-H(46A) | 1.0078 |
| C(46)-H(46B) | 1.0227 |
| C(47)-Si(5) | 1.900(4) |
| C(47)-H(47A) | 0.9804 |

| | |
|---|---|
| C(47)-H(47B) | 0.9628 |
| C(48)-Si(6) | 1.898(6) |
| C(48)-H(48A) | 0.9900 |
| C(48)-H(48B) | 0.9900 |
| Si(3)-O(1) | 1.733(8) |
| Si(3)-C(27) | 1.81(2) |
| Si(3)-C(26) | 1.833(18) |
| Si(4)-O(1) | 1.533(7) |
| Si(4)-C(50) | 1.772(19) |
| Si(4)-C(49) | 1.83(2) |
| C(26)-H(26A) | 0.9800 |
| C(26)-H(26B) | 0.9800 |
| C(26)-H(26C) | 0.9800 |
| C(27)-H(27A) | 0.9800 |
| C(27)-H(27B) | 0.9800 |
| C(27)-H(27C) | 0.9800 |
| C(49)-H(49A) | 0.9800 |
| C(49)-H(49B) | 0.9800 |
| C(49)-H(49C) | 0.9800 |
| C(50)-H(50A) | 0.9800 |
| C(50)-H(50B) | 0.9800 |
| C(50)-H(50C) | 0.9800 |
| Si(3P)-O(1) | 1.503(7) |
| Si(3P)-C(26P) | 1.756(18) |
| Si(3P)-C(27P) | 1.96(2) |
| Si(4P)-O(1) | 1.714(7) |
| Si(4P)-C(49P) | 1.831(17) |
| Si(4P)-C(50P) | 1.836(19) |
| C(26P)-H(26D) | 0.9800 |
| C(26P)-H(26E) | 0.9800 |
| C(26P)-H(26F) | 0.9800 |
| C(27P)-H(27D) | 0.9800 |
| C(27P)-H(27E) | 0.9800 |
| C(27P)-H(27F) | 0.9800 |
| C(49P)-H(49D) | 0.9800 |
| C(49P)-H(49E) | 0.9800 |

| | |
|---|---|
| C(49P)-H(49F) | 0.9800 |
| C(50P)-H(50D) | 0.9800 |
| C(50P)-H(50E) | 0.9800 |
| C(50P)-H(50F) | 0.9800 |
| C(51)-Si(5) | 1.883(5) |
| C(51)-H(51A) | 0.9800 |
| C(51)-H(51B) | 0.9800 |
| C(51)-H(51C) | 0.9800 |
| C(52)-Si(5) | 1.884(5) |
| C(52)-H(52A) | 0.9800 |
| C(52)-H(52B) | 0.9800 |
| C(52)-H(52C) | 0.9800 |
| C(53)-Si(6) | 1.880(6) |
| C(53)-H(53A) | 0.9800 |
| C(53)-H(53B) | 0.9800 |
| C(53)-H(53C) | 0.9800 |
| C(54)-Si(6) | 1.874(5) |
| C(54)-H(54A) | 0.9800 |
| C(54)-H(54B) | 0.9800 |
| C(54)-H(54C) | 0.9800 |
| Cl(1)-Ir(2) | 2.3839(9) |
| Cl(1)-Ir(1) | 2.5958(9) |
| Cl(2)-Ir(1) | 2.3937(10) |
| Cl(2)-Ir(2) | 2.5801(10) |
| Ir(1)-P(1) | 2.2228(10) |
| Ir(1)-Si(2) | 2.2963(12) |
| Ir(1)-Si(1) | 2.3110(12) |
| Ir(2)-P(2) | 2.2300(10) |
| Ir(2)-Si(6) | 2.2935(13) |
| Ir(2)-Si(5) | 2.3145(13) |

| | |
|---|---|
| C(6)-C(1)-C(2) | 119.7(4) |
| C(6)-C(1)-P(1) | 119.3(3) |
| C(2)-C(1)-P(1) | 121.0(3) |
| C(3)-C(2)-C(1) | 117.5(4) |
| C(3)-C(2)-C(19) | 120.0(4) |

| | |
|---|---|
| C(1)-C(2)-C(19) | 122.5(4) |
| C(4)-C(3)-C(2) | 122.1(5) |
| C(4)-C(3)-H(3) | 119.0 |
| C(2)-C(3)-H(3) | 119.0 |
| C(3)-C(4)-C(5) | 120.0(5) |
| C(3)-C(4)-H(4) | 120.0 |
| C(5)-C(4)-H(4) | 120.0 |
| C(4)-C(5)-C(6) | 119.6(5) |
| C(4)-C(5)-H(5) | 120.2 |
| C(6)-C(5)-H(5) | 120.2 |
| C(5)-C(6)-C(1) | 121.1(5) |
| C(5)-C(6)-H(6) | 119.4 |
| C(1)-C(6)-H(6) | 119.4 |
| C(8)-C(7)-C(12) | 118.4(4) |
| C(8)-C(7)-P(1) | 120.0(3) |
| C(12)-C(7)-P(1) | 121.4(3) |
| C(7)-C(8)-C(9) | 122.3(4) |
| C(7)-C(8)-H(8) | 118.9 |
| C(9)-C(8)-H(8) | 118.9 |
| C(10)-C(9)-C(8) | 119.0(5) |
| C(10)-C(9)-H(9) | 120.5 |
| C(8)-C(9)-H(9) | 120.5 |
| C(11)-C(10)-C(9) | 119.6(4) |
| C(11)-C(10)-H(10) | 120.2 |
| C(9)-C(10)-H(10) | 120.2 |
| C(10)-C(11)-C(12) | 122.9(4) |
| C(10)-C(11)-H(11) | 118.6 |
| C(12)-C(11)-H(11) | 118.6 |
| C(11)-C(12)-C(7) | 117.8(4) |
| C(11)-C(12)-C(21) | 119.2(4) |
| C(7)-C(12)-C(21) | 122.9(4) |
| C(18)-C(13)-C(14) | 119.0(4) |
| C(18)-C(13)-P(1) | 119.0(3) |
| C(14)-C(13)-P(1) | 121.9(3) |
| C(15)-C(14)-C(13) | 117.6(4) |
| C(15)-C(14)-C(20) | 119.2(4) |

| | |
|---|---|
| C(13)-C(14)-C(20) | 123.0(4) |
| C(16)-C(15)-C(14) | 122.4(4) |
| C(16)-C(15)-H(15) | 118.8 |
| C(14)-C(15)-H(15) | 118.8 |
| C(17)-C(16)-C(15) | 120.3(4) |
| C(17)-C(16)-H(16) | 119.9 |
| C(15)-C(16)-H(16) | 119.9 |
| C(16)-C(17)-C(18) | 119.0(4) |
| C(16)-C(17)-H(17) | 120.5 |
| C(18)-C(17)-H(17) | 120.5 |
| C(17)-C(18)-C(13) | 121.7(4) |
| C(17)-C(18)-H(18) | 119.2 |
| C(13)-C(18)-H(18) | 119.2 |
| C(2)-C(19)-Si(1) | 112.4(3) |
| C(2)-C(19)-H(19A) | 113.8 |
| Si(1)-C(19)-H(19A) | 114.9 |
| C(2)-C(19)-H(19B) | 109.0 |
| Si(1)-C(19)-H(19B) | 111.1 |
| H(19A)-C(19)-H(19B) | 94.2 |
| C(14)-C(20)-Si(2) | 108.2(3) |
| C(14)-C(20)-H(20A) | 110.1 |
| Si(2)-C(20)-H(20A) | 110.1 |
| C(14)-C(20)-H(20B) | 110.1 |
| Si(2)-C(20)-H(20B) | 110.1 |
| H(20A)-C(20)-H(20B) | 108.4 |
| C(12)-C(21)-Si(3P) | 126.9(4) |
| C(12)-C(21)-Si(3) | 115.0(4) |
| C(12)-C(21)-H(21A) | 118.3 |
| Si(3P)-C(21)-H(21A) | 97.5 |
| Si(3)-C(21)-H(21A) | 115.2 |
| C(12)-C(21)-H(21B) | 111.6 |
| Si(3P)-C(21)-H(21B) | 105.7 |
| Si(3)-C(21)-H(21B) | 102.1 |
| H(21A)-C(21)-H(21B) | 90.3 |
| Si(1)-C(22)-H(22A) | 109.5 |
| Si(1)-C(22)-H(22B) | 109.5 |

| | |
|---|---|
| H(22A)-C(22)-H(22B) | 109.5 |
| Si(1)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| Si(1)-C(23)-H(23A) | 109.5 |
| Si(1)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| Si(1)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| Si(2)-C(24)-H(24A) | 109.5 |
| Si(2)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| Si(2)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| Si(2)-C(25)-H(25A) | 109.5 |
| Si(2)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| Si(2)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| C(33)-C(28)-C(29) | 120.1(5) |
| C(33)-C(28)-P(2) | 119.0(4) |
| C(29)-C(28)-P(2) | 120.9(4) |
| C(28)-C(29)-C(30) | 117.1(5) |
| C(28)-C(29)-C(46) | 124.2(5) |
| C(30)-C(29)-C(46) | 118.5(5) |
| C(31)-C(30)-C(29) | 121.4(6) |
| C(31)-C(30)-H(30) | 119.3 |
| C(29)-C(30)-H(30) | 119.3 |
| C(32)-C(31)-C(30) | 120.3(6) |
| C(32)-C(31)-H(31) | 119.8 |
| C(30)-C(31)-H(31) | 119.8 |
| C(31)-C(32)-C(33) | 120.0(6) |
| C(31)-C(32)-H(32) | 120.0 |

| | |
|---|---|
| C(33)-C(32)-H(32) | 120.0 |
| C(32)-C(33)-C(28) | 121.1(6) |
| C(32)-C(33)-H(33) | 119.5 |
| C(28)-C(33)-H(33) | 119.5 |
| C(39)-C(34)-C(35) | 119.3(4) |
| C(39)-C(34)-P(2) | 119.3(4) |
| C(35)-C(34)-P(2) | 121.4(3) |
| C(36)-C(35)-C(34) | 118.2(4) |
| C(36)-C(35)-C(47) | 118.9(4) |
| C(34)-C(35)-C(47) | 122.9(4) |
| C(37)-C(36)-C(35) | 121.6(5) |
| C(37)-C(36)-H(36) | 119.2 |
| C(35)-C(36)-H(36) | 119.2 |
| C(38)-C(37)-C(36) | 120.1(5) |
| C(38)-C(37)-H(37) | 119.9 |
| C(36)-C(37)-H(37) | 119.9 |
| C(37)-C(38)-C(39) | 119.7(5) |
| C(37)-C(38)-H(38) | 120.2 |
| C(39)-C(38)-H(38) | 120.2 |
| C(38)-C(39)-C(34) | 121.1(5) |
| C(38)-C(39)-H(39) | 119.5 |
| C(34)-C(39)-H(39) | 119.5 |
| C(45)-C(40)-C(41) | 120.2(4) |
| C(45)-C(40)-P(2) | 118.5(4) |
| C(41)-C(40)-P(2) | 121.3(3) |
| C(42)-C(41)-C(40) | 116.6(5) |
| C(42)-C(41)-C(48) | 119.8(5) |
| C(40)-C(41)-C(48) | 123.4(4) |
| C(43)-C(42)-C(41) | 122.2(6) |
| C(43)-C(42)-H(42) | 118.9 |
| C(41)-C(42)-H(42) | 118.9 |
| C(44)-C(43)-C(42) | 120.6(6) |
| C(44)-C(43)-H(43) | 119.7 |
| C(42)-C(43)-H(43) | 119.7 |
| C(43)-C(44)-C(45) | 119.0(5) |
| C(43)-C(44)-H(44) | 120.5 |

| | |
|---|---|
| C(45)-C(44)-H(44) | 120.5 |
| C(44)-C(45)-C(40) | 121.4(5) |
| C(44)-C(45)-H(45) | 119.3 |
| C(40)-C(45)-H(45) | 119.3 |
| C(29)-C(46)-Si(4P) | 117.1(4) |
| C(29)-C(46)-Si(4) | 127.4(4) |
| C(29)-C(46)-H(46A) | 106.7 |
| Si(4P)-C(46)-H(46A) | 98.3 |
| Si(4)-C(46)-H(46A) | 105.0 |
| C(29)-C(46)-H(46B) | 116.9 |
| Si(4P)-C(46)-H(46B) | 108.0 |
| Si(4)-C(46)-H(46B) | 91.1 |
| H(46A)-C(46)-H(46B) | 108.0 |
| C(35)-C(47)-Si(5) | 112.1(3) |
| C(35)-C(47)-H(47A) | 123.5 |
| Si(5)-C(47)-H(47A) | 95.7 |
| C(35)-C(47)-H(47B) | 120.1 |
| Si(5)-C(47)-H(47B) | 92.5 |
| H(47A)-C(47)-H(47B) | 105.9 |
| C(41)-C(48)-Si(6) | 108.0(4) |
| C(41)-C(48)-H(48A) | 110.1 |
| Si(6)-C(48)-H(48A) | 110.1 |
| C(41)-C(48)-H(48B) | 110.1 |
| Si(6)-C(48)-H(48B) | 110.1 |
| H(48A)-C(48)-H(48B) | 108.4 |
| O(1)-Si(3)-C(27) | 106.7(7) |
| O(1)-Si(3)-C(26) | 110.4(7) |
| C(27)-Si(3)-C(26) | 109.1(9) |
| O(1)-Si(3)-C(21) | 99.4(3) |
| C(27)-Si(3)-C(21) | 121.2(6) |
| C(26)-Si(3)-C(21) | 109.4(6) |
| O(1)-Si(4)-C(50) | 107.7(7) |
| O(1)-Si(4)-C(49) | 110.9(7) |
| C(50)-Si(4)-C(49) | 107.1(9) |
| O(1)-Si(4)-C(46) | 103.2(3) |
| C(50)-Si(4)-C(46) | 113.9(7) |

| | |
|---|---|
| C(49)-Si(4)-C(46) | 114.0(6) |
| Si(3)-C(26)-H(26A) | 109.5 |
| Si(3)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| Si(3)-C(26)-H(26C) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 |
| H(26B)-C(26)-H(26C) | 109.5 |
| Si(3)-C(27)-H(27A) | 109.5 |
| Si(3)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| Si(3)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| Si(4)-C(49)-H(49A) | 109.5 |
| Si(4)-C(49)-H(49B) | 109.5 |
| H(49A)-C(49)-H(49B) | 109.5 |
| Si(4)-C(49)-H(49C) | 109.5 |
| H(49A)-C(49)-H(49C) | 109.5 |
| H(49B)-C(49)-H(49C) | 109.5 |
| Si(4)-C(50)-H(50A) | 109.5 |
| Si(4)-C(50)-H(50B) | 109.5 |
| H(50A)-C(50)-H(50B) | 109.5 |
| Si(4)-C(50)-H(50C) | 109.5 |
| H(50A)-C(50)-H(50C) | 109.5 |
| H(50B)-C(50)-H(50C) | 109.5 |
| O(1)-Si(3P)-C(26P) | 115.4(8) |
| O(1)-Si(3P)-C(21) | 109.6(4) |
| C(26P)-Si(3P)-C(21) | 114.6(6) |
| O(1)-Si(3P)-C(27P) | 105.7(6) |
| C(26P)-Si(3P)-C(27P) | 103.1(8) |
| C(21)-Si(3P)-C(27P) | 107.5(6) |
| O(1)-Si(4P)-C(46) | 106.8(3) |
| O(1)-Si(4P)-C(49P) | 106.3(7) |
| C(46)-Si(4P)-C(49P) | 109.1(6) |
| O(1)-Si(4P)-C(50P) | 106.2(6) |
| C(46)-Si(4P)-C(50P) | 121.6(6) |

| | |
|---|---|
| C(49P)-Si(4P)-C(50P) | 105.9(8) |
| Si(3P)-C(26P)-H(26D) | 109.5 |
| Si(3P)-C(26P)-H(26E) | 109.5 |
| H(26D)-C(26P)-H(26E) | 109.5 |
| Si(3P)-C(26P)-H(26F) | 109.5 |
| H(26D)-C(26P)-H(26F) | 109.5 |
| H(26E)-C(26P)-H(26F) | 109.5 |
| Si(3P)-C(27P)-H(27D) | 109.5 |
| Si(3P)-C(27P)-H(27E) | 109.5 |
| H(27D)-C(27P)-H(27E) | 109.5 |
| Si(3P)-C(27P)-H(27F) | 109.5 |
| H(27D)-C(27P)-H(27F) | 109.5 |
| H(27E)-C(27P)-H(27F) | 109.5 |
| Si(4P)-C(49P)-H(49D) | 109.5 |
| Si(4P)-C(49P)-H(49E) | 109.5 |
| H(49D)-C(49P)-H(49E) | 109.5 |
| Si(4P)-C(49P)-H(49F) | 109.5 |
| H(49D)-C(49P)-H(49F) | 109.5 |
| H(49E)-C(49P)-H(49F) | 109.5 |
| Si(4P)-C(50P)-H(50D) | 109.5 |
| Si(4P)-C(50P)-H(50E) | 109.5 |
| H(50D)-C(50P)-H(50E) | 109.5 |
| Si(4P)-C(50P)-H(50F) | 109.5 |
| H(50D)-C(50P)-H(50F) | 109.5 |
| H(50E)-C(50P)-H(50F) | 109.5 |
| Si(5)-C(51)-H(51A) | 109.5 |
| Si(5)-C(51)-H(51B) | 109.5 |
| H(51A)-C(51)-H(51B) | 109.5 |
| Si(5)-C(51)-H(51C) | 109.5 |
| H(51A)-C(51)-H(51C) | 109.5 |
| H(51B)-C(51)-H(51C) | 109.5 |
| Si(5)-C(52)-H(52A) | 109.5 |
| Si(5)-C(52)-H(52B) | 109.5 |
| H(52A)-C(52)-H(52B) | 109.5 |
| Si(5)-C(52)-H(52C) | 109.5 |
| H(52A)-C(52)-H(52C) | 109.5 |

| | |
|---|---|
| H(52B)-C(52)-H(52C) | 109.5 |
| Si(6)-C(53)-H(53A) | 109.5 |
| Si(6)-C(53)-H(53B) | 109.5 |
| H(53A)-C(53)-H(53B) | 109.5 |
| Si(6)-C(53)-H(53C) | 109.5 |
| H(53A)-C(53)-H(53C) | 109.5 |
| H(53B)-C(53)-H(53C) | 109.5 |
| Si(6)-C(54)-H(54A) | 109.5 |
| Si(6)-C(54)-H(54B) | 109.5 |
| H(54A)-C(54)-H(54B) | 109.5 |
| Si(6)-C(54)-H(54C) | 109.5 |
| H(54A)-C(54)-H(54C) | 109.5 |
| H(54B)-C(54)-H(54C) | 109.5 |
| Ir(2)-Cl(1)-Ir(1) | 97.53(3) |
| Ir(1)-Cl(2)-Ir(2) | 97.70(3) |
| P(1)-Ir(1)-Si(2) | 90.71(4) |
| P(1)-Ir(1)-Si(1) | 90.97(4) |
| Si(2)-Ir(1)-Si(1) | 92.03(5) |
| P(1)-Ir(1)-Cl(2) | 171.67(4) |
| Si(2)-Ir(1)-Cl(2) | 97.21(4) |
| Si(1)-Ir(1)-Cl(2) | 91.35(4) |
| P(1)-Ir(1)-Cl(1) | 96.11(3) |
| Si(2)-Ir(1)-Cl(1) | 98.62(4) |
| Si(1)-Ir(1)-Cl(1) | 167.12(4) |
| Cl(2)-Ir(1)-Cl(1) | 80.18(3) |
| P(2)-Ir(2)-Si(6) | 91.09(5) |
| P(2)-Ir(2)-Si(5) | 91.95(4) |
| Si(6)-Ir(2)-Si(5) | 91.23(5) |
| P(2)-Ir(2)-Cl(1) | 170.80(4) |
| Si(6)-Ir(2)-Cl(1) | 97.89(4) |
| Si(5)-Ir(2)-Cl(1) | 89.85(4) |
| P(2)-Ir(2)-Cl(2) | 95.60(4) |
| Si(6)-Ir(2)-Cl(2) | 101.72(5) |
| Si(5)-Ir(2)-Cl(2) | 164.84(4) |
| Cl(1)-Ir(2)-Cl(2) | 80.68(3) |
| C(1)-P(1)-C(13) | 103.06(18) |

| | |
|---|---|
| C(1)-P(1)-C(7) | 103.41(18) |
| C(13)-P(1)-C(7) | 102.65(18) |
| C(1)-P(1)-Ir(1) | 117.90(14) |
| C(13)-P(1)-Ir(1) | 118.82(12) |
| C(7)-P(1)-Ir(1) | 108.97(13) |
| C(40)-P(2)-C(34) | 102.3(2) |
| C(40)-P(2)-C(28) | 103.9(2) |
| C(34)-P(2)-C(28) | 103.2(2) |
| C(40)-P(2)-Ir(2) | 119.33(17) |
| C(34)-P(2)-Ir(2) | 116.97(14) |
| C(28)-P(2)-Ir(2) | 109.35(14) |
| C(22)-Si(1)-C(23) | 105.2(3) |
| C(22)-Si(1)-C(19) | 105.6(3) |
| C(23)-Si(1)-C(19) | 108.5(2) |
| C(22)-Si(1)-Ir(1) | 108.61(19) |
| C(23)-Si(1)-Ir(1) | 115.94(18) |
| C(19)-Si(1)-Ir(1) | 112.33(15) |
| C(25)-Si(2)-C(24) | 103.3(2) |
| C(25)-Si(2)-C(20) | 103.6(2) |
| C(24)-Si(2)-C(20) | 114.1(2) |
| C(25)-Si(2)-Ir(1) | 124.58(17) |
| C(24)-Si(2)-Ir(1) | 110.64(17) |
| C(20)-Si(2)-Ir(1) | 100.73(13) |
| C(51)-Si(5)-C(52) | 104.2(3) |
| C(51)-Si(5)-C(47) | 109.1(2) |
| C(52)-Si(5)-C(47) | 104.8(2) |
| C(51)-Si(5)-Ir(2) | 117.37(19) |
| C(52)-Si(5)-Ir(2) | 108.48(18) |
| C(47)-Si(5)-Ir(2) | 111.80(15) |
| C(54)-Si(6)-C(53) | 102.4(3) |
| C(54)-Si(6)-C(48) | 111.9(3) |
| C(53)-Si(6)-C(48) | 104.4(3) |
| C(54)-Si(6)-Ir(2) | 112.13(18) |
| C(53)-Si(6)-Ir(2) | 124.7(2) |
| C(48)-Si(6)-Ir(2) | 101.12(18) |
| Si(3P)-O(1)-Si(4P) | 157.4(5) |

| | |
|---|---|
| Si(4)-O(1)-Si(3) | 149.5(5) |

# 8. Spectroscopic characterization of compound **4Ir**

## 8.1 $^{1}$H NMR

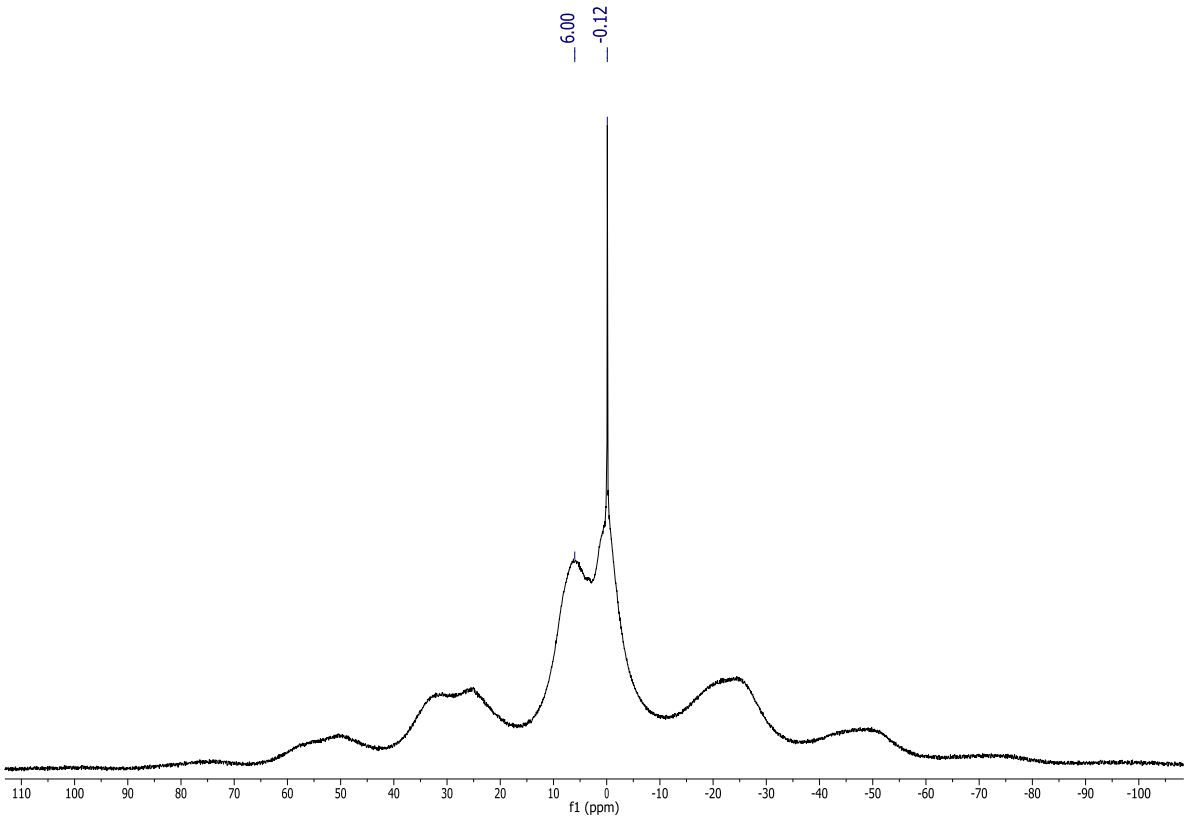



**Figure S 60**. $^{1}$H NMR (MAS, Vr=8 kHz) of complex **4Ir**.

## 8.2 $^{13}$C NMR

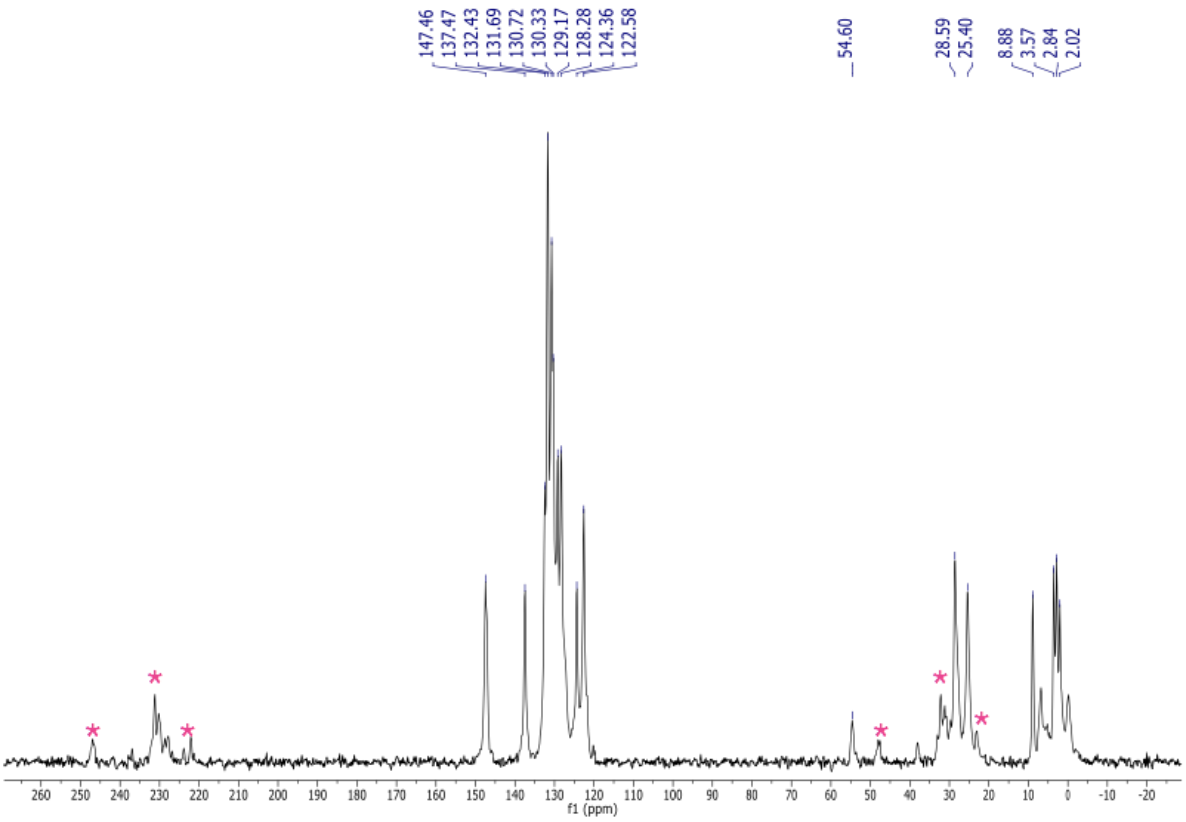



**Figure S 61**. $^{13}$C (CP MAS, Vr=10 kHz) NMR spectrum of complex **4Ir**. (* spinning side bands)

## 8.3 $^{31}$P NMR

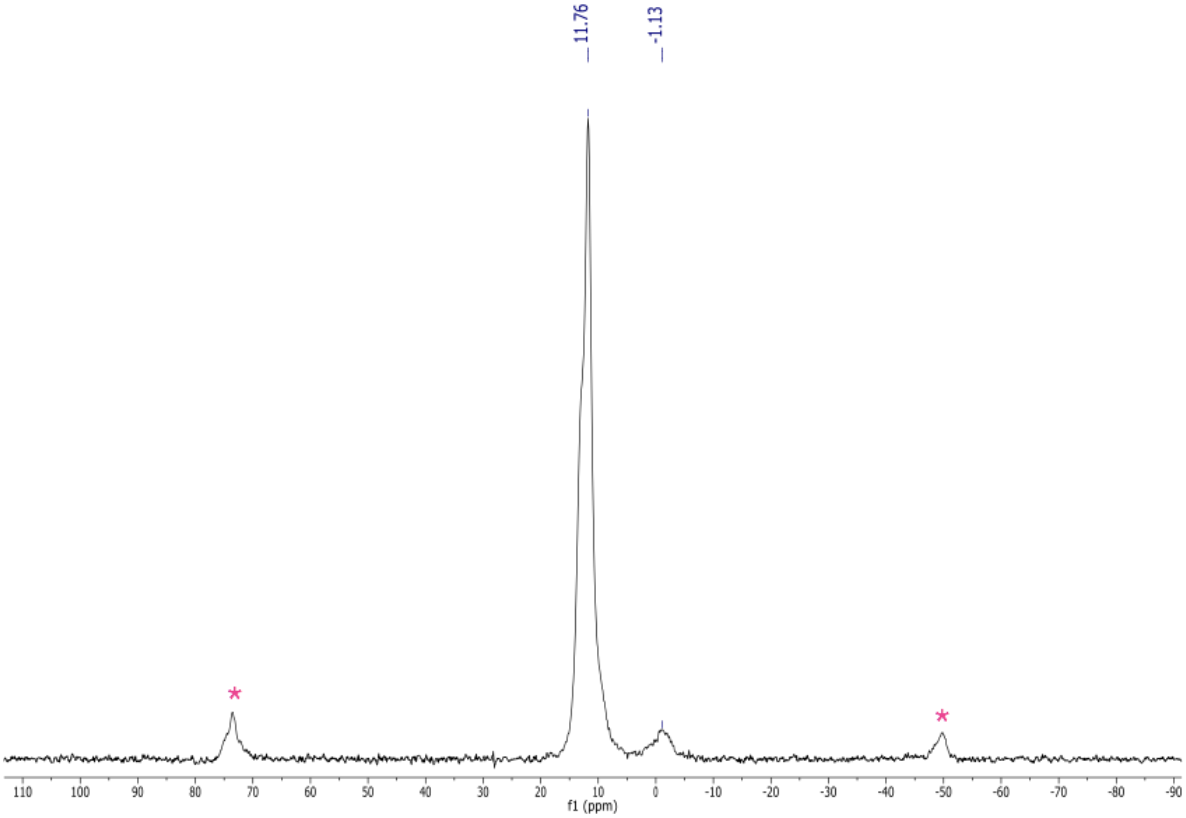



**Figure S 62**. $^{31}$P (CP MAS, Vr=10 kHz) NMR spectrum of complex **4Ir**. (* spinning side bands)

## 8.4 $^{29}$Si NMR

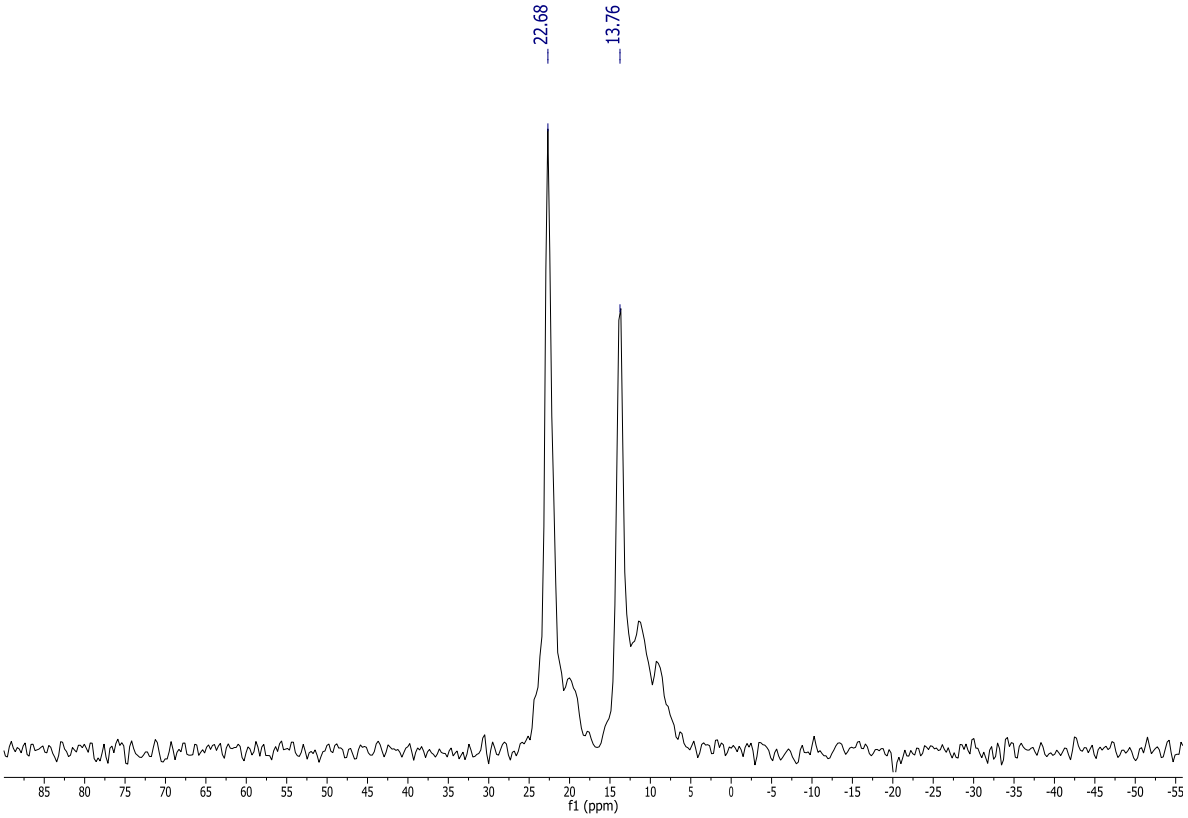



**Figure S 62.** $^{29}$Si (CP MAS, Vr=10 kHz) NMR spectrum of complex **4Ir.**

## 8.5 FT-IR

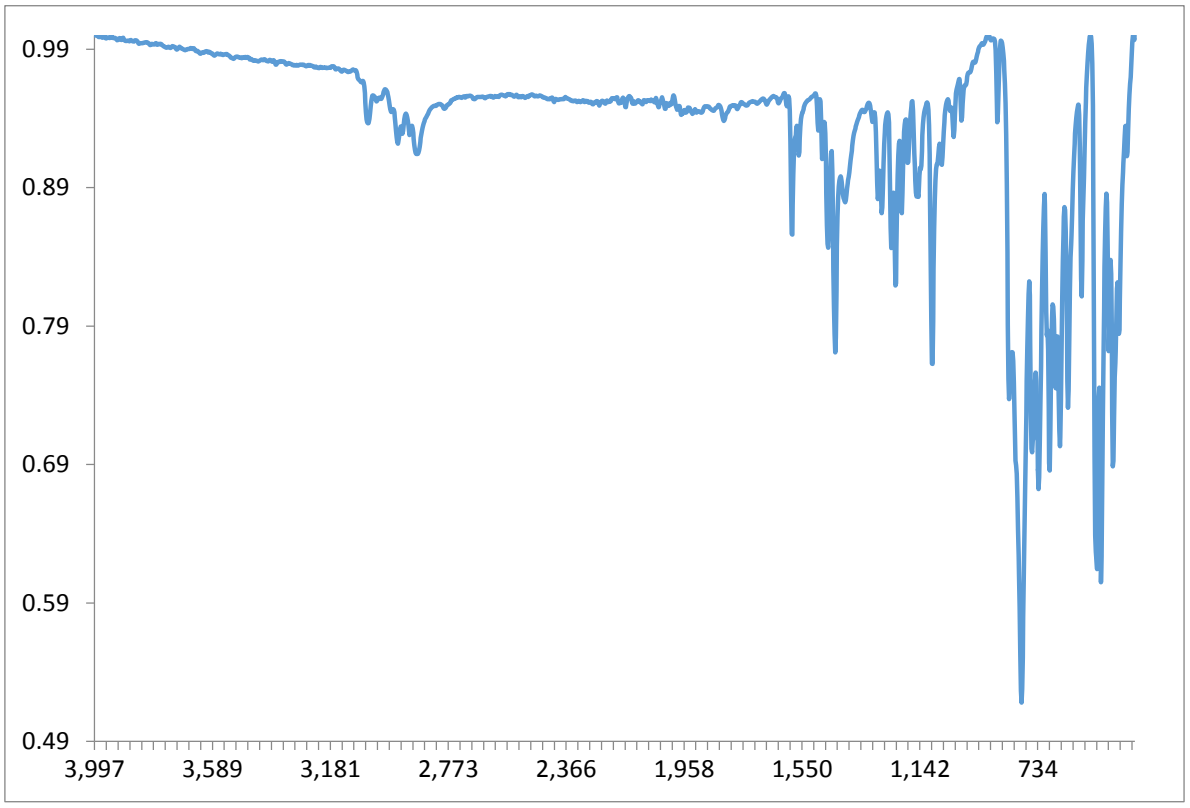



**Figure S 63.** FT-IR spectrum (ATR) of complex **4Ir**.