Electronic Supplementary Information (ESI)

# Tuning the Potential in Redox-active Diphosphine Ligands Based on the Alkyne Complexes [Tp*W(CO)L{$\eta^2$-$C_2(PPh_2)$}$_2$]

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Content

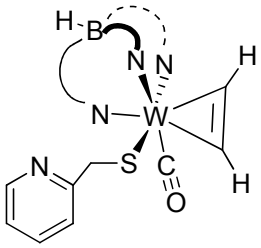
# 1 Syntheses and Analytical Data

## 1.1 General

All operations were carried out in an atmosphere of dry argon using Schlenk and glove box techniques. Solvents for reactions were dried and saturated with argon by standard methods and freshly distilled prior to use. Solvents for chromatography were used as purchased from commercial sources. NMR spectra were recorded at 300 K using Bruker Avance 250, 300 or 500 MHz spectrometers. In $^{1}$H and $^{13}$C NMR, the chemical shifts were internally referenced to the solvent residual peak and in $^{31}$P NMR, $H_3PO_4$ was used as external standard. IR spectroscopy was conducted on a Bruker ALPHA-T for solid-state measurements as well as those in solution. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series. CV experiments were performed using a Princeton Applied Research VersaSTAT 3 potentiostat. A three-electrode arrangement with a glassy carbon working electrode, a platinum wire counter electrode and a $Ag/AgBF_4$ in $CH_3CN$ reference electrode was employed. A 0.1 M $n$-$Bu_4N^+PF_6^-$ solution was used as supporting electrolyte. The $Fc/Fc^+$ redox couple was used as internal standard. The starting materials [Tp*W(CO)$_3$], **1**,[S1] and $Fc^+PF_6^-$[S2] were synthesized according to literature procedures. We have described the syntheses of iodide complexes **3**$^{I}$, **4**$^{I}$ and **5**$^{I}$ as well as cyanide complexes **3**$^{CN}$, **4**$^{CN}$ and **5**$^{CN}$ elsewhere.[S1] All other reagents were used as purchased from commercial sources.

## 1.2 [Tp*W(CO)L($\eta^2$-$C_2H_2$)] 3$^{L}$

### 1.2.1 3$^{SCPy}$

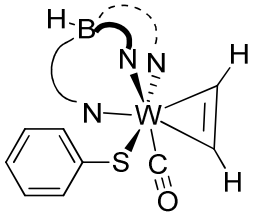



In a 100 mL Schlenk flask, 1488 mg (2.05 mmol) **3**$^{OTf}$ and 392 mg (2.66 mmol) sodium 2-pyridylmethanethiolate were dissolved in 50 mL of THF. After 90 min, the color had changed from blue to purple and the progress of the reaction was checked by IR spectroscopy. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using pure $Et_2O$ as eluent. After drying in vacuo, the solid product was obtained as a light purple foam. Yield: 1269 mg (88 %).

**$^{1}$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 12.02 (s, br, 1 H, alkyne-*H*), 10.93 (s, 1 H, alkyne-*H*), 8.47 (bd, 1 H, Py-*H*), 7.48 (s, br, 1 H, Py-*H*), 7.02 (m, br, 1 H, Py-*H*), 2.70 (s, 3 H, C*H*$_3$), 2.54 (s, 3 H, C*H*$_3$), 2.47 (s, 3 H, C*H*$_3$), 2.28 (s, 3 H, C*H*$_3$) , 2.25 (s, 3 H, C*H*$_3$), 2.00 (s, 3 H, C*H*$_3$) , 1.84 (s, 3 H, C*H*$_3$) , 1.75 (s, 3 H, C*H*$_3$) , 1.70 (s, 3 H, C*H*$_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298 K): $\delta$ (ppm) = 228.9 (*C*O), 185.8 (b, W*C*H), 176.1 (b, W*C*H), 151.7, 147.5, 142.0, 140.1, 123.0 ($^{3,5}$*C*CH$_3$), 163.2 (Py-*C*-Me), 152.4 (b, Py-*C*-H), 148.7, 135.8, 120.6 (Py-*C*-H), 113.7, 112.6, 112.1 ($^{4}$*C*CH$_3$), 85.9 (C*H*$_2$), 15.2 (C*C*H$_3$), 14.8 (C*C*H$_3$), 14.3 (C*C*H$_3$), 13.6

(C*C*H$_3$), 11.0 (C*C*H$_3$), 10.9 (C*C*H$_3$), 8.4 (C*C*H$_3$), 8.2 (C*C*H$_3$). **IR** (ATR, cm$^{-1}$): 2543 (w, BH), 1875 (s, CO). **IR** (THF, cm$^{-1}$): 2549 (w, BH), 1889 (s, CO). **Anal.** Calc. for $C_{27}H_{36}BN_7OSW$ (701.34 g/mol)·0.5 $C_4H_{10}O$: C, 47.17; H, 5.60; N, 13.28; S, 4.34. Found: C, 47.79; H, 5.57; N, 13.39; S, 4.18.

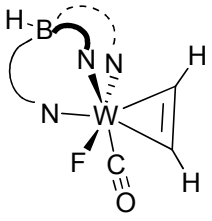
### 1.2.2 3$^{SPh}$




In a 100 mL Schlenk flask, 1165 mg (1.60 mmol) **3**$^{OTf}$ and 276 mg (2.09 mmol) sodium thiophenolate were suspended in 40 mL of THF. After 30 min of stirring in a warm water bath, the colour changed from light blue to deep blue, while the progress of the reaction was checked by IR spectroscopy. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using $CH_2Cl_2$/petroleum ether 1:1 as eluent. The blue fraction was collected and dried *in vacuo*. Yield 738 mg (67 %).

**$^1$H NMR** ($CDCl_3$, 500 MHz, 298 K): $\delta$ (ppm) = 12.66 (s, 1 H, alkyne-*H*), 11.30 (d, 1 H, alkyne-*H*,), 7.32-7.07 (m, 5 H, Ph-*H*), 2.53 (s, 3 H, C*H*$_3$), 2.50 (s, br, 3 H, C*H*$_3$), 2.32 (s, 3 H, C*H*$_3$), 2.30 (s, 3 H, C*H*$_3$), 2.27 (s, br, 3 H, C*H*$_3$), 2.01 (s, 3 H, C*H*$_3$), 1.82 (s, 3 H, C*H*$_3$) , 1.80 (s, 3 H, C*H*$_3$) , 1.74 (s, 3 H, C*H*$_3$). **$^{13}$C NMR** ($CDCl_3$, 63 MHz, 299 K): $\delta$ (ppm) = 232.7 (*C*O), 188.9 (W*C*H), 179.3 (W*C*H), 152.6, 152.2, 150.0, 147.4, 142.1, 141.0 ($^{3,5}$*C*CH$_3$), 131.7, 127.5, 124.6 (Ph-*C*), 113.8, 112.7, 111.2 ($^4$*C*CH$_3$), 14.6, 14.3, 13.6, 11.0, 11.0, 11.0, 8.4, 8.2, 8.0 (C*C*H$_3$). **IR** (ATR, cm$^{-1}$): 2543 (w, BH), 1890 (s, CO). **IR** (THF, cm$^{-1}$): 2548 (w, BH), 1902 (s, CO). **Anal.** Calc. for $C_{27}H_{35}BN_6OSW$ (686.32 g/mol)·0.5 $C_5H_{12}$: C, 49.05; H, 5.72; N, 11.63; S, 4.44. Found: C, 49.52; H, 5.88; N, 11.25; S, 3.97.

### 1.2.3 3$^{F}$

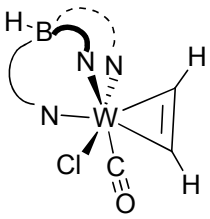



A solution of 2.00 g (3.30 mmol) **1** in 60 mL $CH_2Cl_2$ was saturated with acetylene by a vigorous gas stream for ten minutes. Then, with further purging with acetylene, a total of 1.09 g (3.30 mmol) of ferrocenium hexafluorophosphate was added in eight portions every four minutes. A few minutes after the addition of the last portion, the progress of the reaction was checked by IR spectroscopy. The intermediate was dried *in vacuo* and most of the ferrocene formed was removed by washing eight times with 10 mL of $Et_2O$. The green solid was dissolved in 40 mL of THF, and the solution was cooled to –60 °C. A solution of 1.35 g (4.29 mmol) *n*-$NBu_4F$ in 10 mL THF was then added. After about twenty minutes, the progress of the reaction was checked again by IR. At full conversion, the solution was warmed to room temperature using a water bath and the solvent was removed *in vacuo*. The

crude product was purified by column chromatography using an eluent mixture of $CH_2Cl_2$, $Et_2O$ and petroleum ether in the ratio 5:1:1. Removal of the solvent in vacuum resulted in a light blue powder. Yield: 1.27 g (65 %).

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 13.29 (s, 1 H, alkyne-*H*), 11.80 (s, 1 H, alkyne-*H*), 2.65 (s, 3 H, C*H*$_3$), 2.41 (s, 3 H, C*H*$_3$), 2.37 (s, 3 H, C*H*$_3$), 2.29 (s, 3 H, C*H*$_3$), 2.24 (s, 3 H, C*H*$_3$), 1.97 (s, 3 H, C*H*$_3$), 1.89 (s, 3 H, C*H*$_3$), 1.75 (s, 3 H, C*H*$_3$), 1.72 (s, 3 H, C*H*$_3$). **$^{13}$C NMR** ($CDCl_3$, 63 MHz, 298 K): $\delta$ (ppm) =238.2 (*C*O), 195.7 (W*C*H), 191.3 (W*C*H), 150.3, 150.3, 147.5, 143.4, 141.2, 140.4 ($^{3,5}$*C*CH$_3$), 113.0, 112.7, 112.6 ($^4$*C*CH$_3$), 14.1, 12.8 (d, $J_{CF}$ = 4.5 Hz), 12.1 (d, $J_{CF}$ = 6.4 Hz), 11.0, 10.6, 10.5, 8.3, 8.0, 7.8 (C*C*H$_3$). **$^{19}$F NMR** ($CDCl_3$, 282 MHz, 298 K): $\delta$ (ppm) = -95.8 (W*F*). **IR** (ATR, cm$^{-1}$): 2532 (w, BH), 1875 (s, CO). **IR** (THF, cm$^{-1}$): 2543 (w, BH), 1887 (s, CO). **Anal.** Calc. for $C_{21}H_{30}BFN_6OW$ (596.15 g/mol): C, 42.31; H, 5.07; N, 14.10. Found: C, 42.35; H, 5.25; N, 14.00.

### 1.2.4 $3^{Cl}$

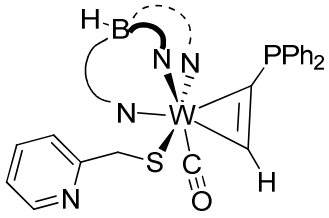



In a 500 mL Schlenk flask, 12.00 g (19.76 mmol) **1** were dissolved in 200 mL $CH_2Cl_2$. Acetylene was introduced into the flask from an acetylene gas cylinder, ensuring pressure equalization via syringe and septum. 6.54 g (19.76 mmol) of $FcPF_6$ were added in 5 portions every 5 minutes. The solvent was removed from the green solution *in vacuo*. 100 mL of $Et_2O$ was added and after one hour of vigorous stirring the orange solution was decanted. After dissolving in 120 mL of THF, 11 g (39.58 mmol) of *n*-$NBu_4Cl$ was added. After checking the reaction progress by IR and removing the solvent *in vacuo*, the mixture was treated with 100 mL methanol and **$3^{Cl}$** was filtered off over a G3 frit. The light blue product was washed with 20 mL methanol and 10 mL $Et_2O$ and dried overnight. Yield: 7.07 g (58 %).

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) =13.41 (s, 1H, alkyne-*H*), 12.12 (s, 1H, alkyne-*H*), 2.72 (s, 3H, C*H*$_3$), 2.48 (s, 3H, C*H*$_3$), 2.46 (s, 3H, C*H*$_3$), 2.37 (s, 3H, C*H*$_3$), 2.28 (s, 3H, C*H*$_3$), 2.00 (s, 3H, C*H*$_3$), 1.86 (s, 3H, C*H*$_3$), 1.75 (s, 3H, C*H*$_3$), 1.72 (s, 3H, $CH_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298 K): $\delta$ (ppm) = 232.9 (*C*O), 202.9 (W*C*H), 195.2 (W*C*H), 152.3, 151.8, 147.5, 143.3, 141.5, 140.6 ($^{3,5}$*C*CH$_3$), 113.6, 113.0, 112.7 ($^4$*C*CH$_3$), 14.4, 14.1, 13.7, 11.0, 10.9, 10.8, 8.3, 8.3, 8.0 (C*C*H$_3$). **IR** (ATR, cm$^{-1}$): 2541 (w, BH), 1883 (s, CO). **IR** (THF, cm$^{-1}$): 2551 (w, BH), 1907 (s, CO). **Anal.** Calc. for $C_{21}H_{31}BClN_6OW$ (613.61 g/mol): C, 41.10; H, 5.09; N, 13.70. Found: C, 42.03; H, 5.04; N, 12.42.

## 1.3 [Tp*W(CO)L($\eta^2$-$C_2${H}{$PPh_3$})] $4^L$

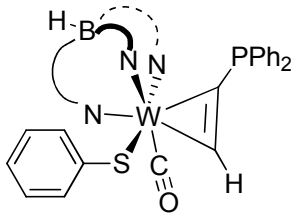
### 1.3.1 $4^{SCPy}$



In a 100 mL Schlenk flask, 663 mg (903 µmol) $\mathbf{3}^{SCPy}$ dissolved in 40 mL THF were cooled to –80 °C and 0.47 mL (1.18 mmol) of 2.5 M n-BuLi solution in hexane was added. After 15 min, 0.27 mL (1.46 mmol) $Ph_2PCl$ was added. After warming to room temperature, the solvent was removed under reduced pressure and the residue was transferred on top of a chromatography column packed with $CH_2Cl_2$. After all by-products elutable with $CH_2Cl_2$ passed the column, the blue product was collected with a mixture of $CH_2Cl_2$ and MeCN in a 10:1 ratio and dried *in vacuo*. Yield: 526 mg (66 %).

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 11.89 (s, br, 1 H, alkyne-*H*), 8.55 (d, 1 H, Py-*H*), 7.61 (m, 1 H, Py-*H*), 7.47-7.09 (m, 8 H, Ph-*H*, Py-*H*), 6.88 (m, 2 H, Ph-*H*), 8.38 (m, 2 H, Ph-*H*), 5.50 (s, br, 1 H, C$H_2$), 4.99 (s, br, 1 H, C$H_2$), 2.70 (s, 3 H, C$H_3$), 2.46 (s, 6 H, C$H_3$), 2.21 (d, 3 H, C$H_3$), 2.20 (s, 6 H, C$H_3$), 1.82 (s, 3 H, C$H_3$) , 1.74 (s, 3 H, C$H_3$), 1.52 (s, 3 H, C$H_3$), 1.3 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 63 MHz, 300 K): $\delta$ (ppm) = 191.2 (d, $^1J_{CP}$ = 52.2 Hz, W*C*P)), 189.4 (br, W*C*H), 163.1 (Py-*C*), 152.2, 151.6, 148.4, 147.2, 141.6, 141.1, 140.7, 140.4 ($^{3,5}$*C*$CH_3$, Py-*C*), 135.8, 134.6, 134.3, 131.4, 131.1, 128.1-127.8, 127.4, 127.2, 127.1 (Ph-*C*), 123.2, 120.5 (Py-*C*), 113.0, 112.5, 112.4 ($^4$*C*H), 51.3 (b, *C*$H_2$), 16.6, 16.3, 14.6, 13.0, 11.0, 10.8, 8.3, 8.1 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 298 K): $\delta$ (ppm) = 12.4 (WC*P*). **IR** (ATR, $cm^{-1}$): 2545 (w, BH), 1879 (s, CO). **IR** (THF, $cm^{-1}$): 2550 (w, BH), 1892 (s, CO). **Anal.** Calc. for $C_{39}H_{45}BN_7OPSW$ (885.51 g/mol): C, 52.90; H, 5.12; N, 11.07; S, 3.62. Found: C, 53.00; H, 4.95; N, 10.42; S, 3.31.

### 1.3.2 $4^{SPh}$

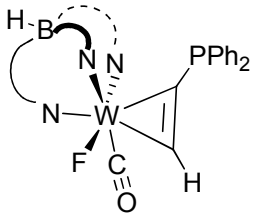


In a 100 mL Schlenk flask, 720 mg (1.05 mmol) $\mathbf{3}^{SPh}$ dissolved in 50 mL THF were cooled to –80 °C and 0.55 mL (1.38 mmol) of 2.5 M *n*-BuLi solution in hexane were added. After 10 min, 0.31 mL (1.68 mmol) $Ph_2PCl$ were added. After coming to room temperature, the solvent was removed *in vacuo* and the residue was purified by column chromatography with pure $Et_2O$. A second chromatography step using an eluent mixture of $CH_2Cl_2$/petroleum ether 1/1 followed. The product $\mathbf{4}^{SPh}$ was obtained as a blue solid after removal of the solvents *in vacuo*. Yield: 410 mg (45 %).

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 12.73 (s, 1 H, alkyne-*H*), 7.40-7.07 (m, 11 H, Ph-*H*), 6.88 (m, 2 H, Ph-*H*), 6.40 (m, 2 H, Ph-*H*), 2.46 (s, 3 H, C$H_3$), 2.40 (d, 3 H, C$H_3$,

$J_{HP}$ = 1.13 Hz), 2.22 (s, 3 H, C$H_3$), 2.18 (s, 3 H, C$H_3$), 2.17 (s, 3 H, C$H_3$), 1.74 (s, 3 H, C$H_3$), 1.72 (s, 3 H, C$H_3$), 1.51 (s, 3 H, C$H_3$) , 1.36 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298 K): $\delta$ (ppm) = 233.9 (*C*O), 194.3 (d, W*C*P, $^1J_{CP}$ = 53.6 Hz), 191.8 (d, W*C*H, $^2J_{CP}$ = 3.7 Hz), 152.2, 150.1, 147.3, 141.7, 140.9, 140.7, ($^{3,5}$*C*CH$_3$), 134.9, 134.5, 131.9, 131.6, 131.4, 128.2-127.2, 124.7 (Ph-*C*), 113.3, 112.7, 112.6 ($^4$*C*CH$_3$), 14.7 (C*C*H$_3$), 13.0 (C*C*H$_3$), 11.4, (C*C*H$_3$), 11.1 (C*C*H$_3$), 11.0 (C*C*H$_3$), 10.8 (C*C*H$_3$), 8.3 (C*C*H$_3$), 8.2 (C*C*H$_3$), 8.1 (C*C*H$_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 298 K): $\delta$ (ppm) = 12.9 (s, WC*P).* **IR** (ATR, cm$^{-1}$): 2549 (w, BH), 1892 (s, CO). **IR** (THF, cm$^{-1}$): 2550 (w, BH), 1907 (s, CO). **Anal.** Calc. for $C_{39}H_{44}BN_6OPSW$ (870.50 g/mol)·0.33 $CH_2Cl_2$: C, 52.56; H, 5.01; N, 9.35; S, 3.57. Found: C, 52.54, H, 4.97, N, 9.18, S, 3.21.

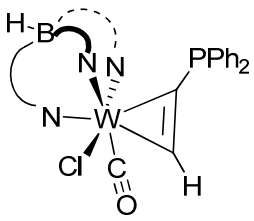
### 1.3.3 4$^F$




In a 100 mL Schlenk flask, 332 mg (557 µmol) **3$^F$** dissolved in 40 mL THF were cooled to –80 °C and 0.30 mL (740 µmol) of 2.5 M n-BuLi solution in hexane were added. After 15 min, 0.15 mL (840 µmol) $Ph_2PCl$ were added. After coming to room temperature, the solvent was removed under reduced pressure. The residue was recrystallized several times from $CH_2Cl_2$/n-pentane, first separating lithium chloride and sus, brequently the product **4$^F$**. A chromatographic purification is not applicable due to complex decomposition. This sequence yielded solely a small sample of crystalline material.

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 13.27 (s, 1 H, alkyne-*H*), 7.31-7.09 (m, 6 H, Ph-*H*), 6.84 (m, 2 H, Ph-*H*), 6.38 (m, 2 H, Ph-*H*), 2.59 (s, 3 H, C$H_3$), 2.46 (s, 3 H, C$H_3$), 2.19 (s, 3 H, C$H_3$), 2.11 (s, 6 H, C$H_3$), 1.82 (s, 3 H, C$H_3$), 1.76 (s, 3 H, C$H_3$), 1.52 (s, 3 H, C$H_3$), 1.36 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298 K): $\delta$ (ppm) = 239.2 (s, *C*O), 201.1 (d, $^1J_{CP}$ = 52.7 Hz, W*C*P), 200.0 ((d, $^2J_{CP}$ = 5.5 Hz, W*C*H), 150.1, 150.0, 147.2, 143.0, 141.1, 139.8 ($^{3,5}$*C*CH$_3$), 135.4-127.1 (m, Ph-*C*), 112.7, 112.6, 112.4 ($^4$*C*CH$_3$), 13.6, 13.0, 12.9, 11.2, 10.7, 10.3, 8.4, 7.8, 7.8 (C*C*H$_3$). **$^{19}$F NMR** ($CDCl_3$, 282 MHz, 298 K): $\delta$ (ppm) = -93.6 (s, W*F*). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 298 K): $\delta$ (ppm) = 12.5 (WC*P*). **IR** (THF, cm$^{-1}$): 2545 (w, BH), 1893 (s, CO).

### 1.3.4 4$^{Cl}$



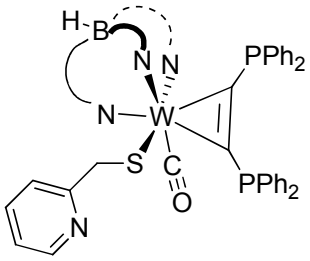

In a 250 mL Schlenk flask, 2.00 g (3.26 mmol) **3$^{Cl}$** dissolved in 120 mL THF were cooled to –80 °C and 1.70 mL (4.24 mmol) of 2.5 M n-BuLi solution in hexane were added. After 15 min, 0.96 mL (5.22 mmol) $Ph_2PCl$ were added. After coming to room temperature, the solvent is

removed *in vacuo*. The residue was suspended in 50 mL MeOH and **4$^{Cl}$** was filtered off through a G3 frit. The blue product was washed with 10 mL MeOH and dried overnight in air. Yield 1.59 g (61 %).

**$^{1}$H NMR** ($CDCl_3$, 300 MHz, 300 K): $\delta$ (ppm) = 13.34 (s, 1H, alkyne-*H*), 7.28-7.12 (m, 6H, Ph-*H*), 6.87 (m, 2H, Ph-*H*), 6.38 (m, 2H, Ph-*H*), 2.68 (s, 3H, C$H_3$), 2.51 (s, 3H, C$H_3$), 2.28 (d, 3H, C$H_3$, $J_{HP}$ = 1.32 Hz), 2.20 (s, 3H, C$H_3$), 2.18 (s, 3H, C$H_3$), 1.80 (s, 3H, C$H_3$), 1.75 (s, 3H, C$H_3$), 1.50 (s, 3H, C$H_3$), 1.25 (s, 3H, $CH_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 300 K): $\delta$ (ppm) = 234.0 (*C*O), 208.3 (W*C*H), 204.7 (d, W*C*P, $^{1}J_{CP}$ = 4.5 Hz), 152.0, 151.8, 147.2, 142.9, 141.4, 140.1 ($^{3,5}$*C*$CH_3$), 134.9, 134.6, 133.5, 131.4, 131.2, 128.4, 128.3, 128.3, 128.1, 127.4, 127.3 (Ph-*C*), 113.0, 113.0, 112.9 ($^{4}$*C*$CH_3$), 15.3, 15.1, 14.1, 13.6, 11.1, 11.0, 10.6, 8.5, 8.1 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 301 K): $\delta$ (ppm) = 16.4 (s, WC*P*). **IR** (ATR, $cm^{-1}$): 2545 (w, BH), 1896 (s, CO). **IR** (THF, $cm^{-1}$): 2550 (w, BH), 1911 (s, CO). **Anal.** Calc. for $C_{33}H_{39}BClN_6OPW$ (796.78 g/mol): C, 49.74; H, 4.93; N, 10.55. Found: C, 49.56; H, 5.21; N, 9.80.

## 1.4 [Tp*W(CO)L($\eta^2$-$C_2${$PPh_3$}$_2$)] 5$^{L}$

### 1.4.1 5$^{SCPy}$

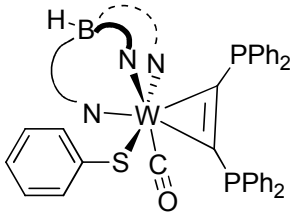



In a 100 mL Schlenk flask, 526 mg (594 µmol) **4$^{SCPy}$** dissolved in 30 mL THF were cooled to –80 °C and 0.31 mL (775 µmol) of a 2.5 M n-BuLi solution in hexane were added. After ten minutes, 0.18 mL (976 µmol) $Ph_2PCl$ were added. After warming to ambient temperature and removing the solvent *in vacuo*, the crude product was purified by column chromatography using an eluent mixture of $CH_2Cl_2$/MeCN 10/1. The product was obtained as a blue-green solid after drying *in vacuo*. Yield 363 mg (57 %).

**$^{1}$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 8.45 (bd, 1 H, Py-*H*), 7.72 (s, br, 2 H, Py-*H*), 7.44 (s, br, 1H, Py-*H*), 7.36-7.14 (m, 8 H, Ph-*H*), 7.02 (m, 6 H, Ph-*H*), 6.82 (m, 2 H, Ph-*H*), 6.66 (m, 2 H, Ph-*H*), 6.49 (m, 2 H, Ph-*H*), 2.56 (d, 3 H, C$H_3$, $J_{HP}$ = 2.08 Hz), 2.52 (s, 3 H, C$H_3$), 2.45 (s, 3 H, C$H_3$), 2.25 (s, 3 H, C$H_3$), 2.18 (s, 3 H, C$H_3$), 2.12 (s, 3 H, C$H_3$), 1.97 (s, 3 H, C$H_3$), 1.72 (s, 3 H, C$H_3$), 1.51 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 63 MHz, 300 K): $\delta$ (ppm) = 205.0 (m, W*C*P), 204.2 (m, W*C*P), 163.9, 151.6, 151.4, 148.6, 142.4, 140.2, 138.9, 137.3 (Py-*C*, $^{3,5}$*C*$CH_3$), 133.3-126.9 (Ph-*C*), 122.7, 120.5 (Py-*C*), 113.1, 113.1, 112.3 ($^{4}$*C*H), 16.9 (d, $J_{CP}$ = 19.5 Hz), 15.1 (d, $J_{CP}$ = 12.2 Hz) 14.9, 11.3, 11.0, 10.8, 8.5, 8.3, 8.2 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 298 K): $\delta$ (ppm) = 13.4 (d, WCP, $^{3}J_{PP}$ = 10.4 Hz), 11.5 (s, br, WCP). **IR** (ATR, $cm^{-1}$): 2531 (w, BH), 1914 (s, CO). **IR** ($CDCl_3$, $cm^{-1}$): 2553 (w, BH), 1919 (s, CO).

**Anal.** Calc. for $C_{51}H_{54}BN_7OP_2SW$ (1069.69 g/mol): C, 57.26; H, 5.09; N, 9.17; S, 3.00. Found: C, 57.30; H, 4.96; N, 8.90; S, 2.79.

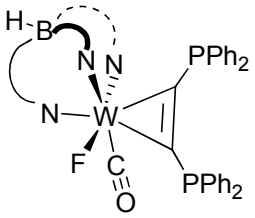
### 1.4.2 $5^{SPh}$



In a 50 mL Schlenk flask, 280 mg (322 µmol) of **$4^{SPh}$** dissolved in 15 mL of THF were cooled to –80 °C and 0.17 mL (425 µmol) of a 2.5 M n-BuLi solution in hexane were added. After ten minutes, 0.10 mL (542 µmol) $Ph_2PCl$ were added. After warming to room temperature, the crude product was transferred on top of a chromatography column packed with $Et_2O$ and all non-polar by-products were eluted first with n-pentane before the product is eluted as a green band with pure $Et_2O$. After drying *in vacuo*, the product is obtained as a green solid. Yield: 308 mg (91 %).

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 7.76 (m, 2 H, Ph-*H*), 7.44 (m, 4 H, Ph-*H*), 7.26 (m, 5 H, Ph-*H*), 7.04 (m, 5 H, Ph-*H*), 6.88 (m, 4 H, Ph-*H*), 6.80 (m, 2 H, Ph-*H*), 6.70 (m, 2 H, Ph-*H*), 6.48 (m, 2 H, Ph-*H*), 2.54 (s, 3 H, C$H_3$), 2.35 (s, 3 H, C$H_3$), 2.22 (s, 3 H, C$H_3$), 2.20 (s, br, 3 H, C$H_3$), 2.14 (s, 3 H, C$H_3$), 2.10 (s, br, 3 H, C$H_3$), 1.98 (s, 3 H, C$H_3$), 1.70 (s, 3 H, C$H_3$), 1.35 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 299 K): $\delta$ (ppm) = 233.8 (*C*O), 151.1, 151.9, 150.1, 142.6, 140.4, 140.2 ($^{3,5}$*C*$CH_3$), 138.4, 138.3, 137.1 (d), 136.5, 136.2, 134.9, 134.6, 134.3, 133.4, 133.1, 131.5, 129.2, 128.9, 128.6, 128.3, 128.2, 128.0, 127.9, 127.6, 127.5, 127.2, 127.0, 126.9 (Ph-*C*), 113.2, 113.0, 112.5 ($^4$*C*H), 16.7 (d, $J_{CP}$ = 18.5 Hz), 15.5 (d, $J_{CP}$ = 12.1 Hz), 14.7, 11.4, 11.1, 10.8, 8.6, 8.2, 8.2 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 299 K): $\delta$ (ppm) = 14.3 (d, WCP, $^3J_{PP}$ = 10.4 Hz), 13.6 (bd, WCP). **IR** (THF, $cm^{-1}$): 2550 (w, BH), 1926 (s, CO).

### 1.4.3 $5^{F}$

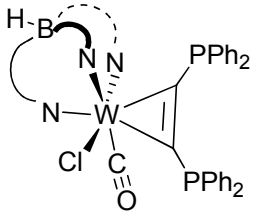


In a 50 mL Schlenk flask, 175 mg (163 µmol) **$5^{I}$** were dissolved in 20 mL THF and cooled to –80 °C. Sus, brequently, 0.40 mL (200 µmol) of a 0.5 M *n*-$NBu_4F$ solution in THF was added and the reaction solution was stirred for one hour. After removing the cooling bath, the mixture was heated to 80 °C for two hours under reflux. The solvent was then removed *in vacuo* and the crude product was subjected to column chromatographic work-up using an eluent mixture of $CH_2Cl_2$, $Et_2O$ and petroleum ether in the ratio 5/1/1. Care must be taken to use both degassed solvents and deoxygenated silica and to carry out the procedure under inert gas. In the next step, the product obtained is further purified by crystallisation from $CH_2Cl_2$/*n*-pentane. The product and a by-product that cannot be

separated in bulk were obtained in a ratio of 2/1 in a combined amount of 64 mg. A purer sample for analysis was obtained by picking crystals.

**$^{1}$H NMR** ($CDCl_3$, 300 MHz, 297 K): $\delta$ (ppm) = 7.78 (m, 2 H, Ph-*H*), 7.40 (m, 4 H, Ph-*H*), 7.15 (m, 6 H, Ph-*H*), 6.97 (m, 2 H, Ph-*H*), 6.76 (m, 2 H, Ph-*H*), 6.63 (m, 2 H, Ph-*H*), 6.47 (m, 2 H, Ph-*H*), 2.48 (s, 3 H, C$H_3$), 2.40 (s, 3 H, C$H_3$), 2.33 (s, 3 H, $J_{HP}$ = 1.32 Hz, C$H_3$), 2.25 (s, 3 H, C$H_3$), 2.16 (s, 3 H, C$H_3$), 2.05 (s, 3 H, C$H_3$), 1.93 (s, 3 H, C$H_3$), 1.76 (s, 3 H, C$H_3$), 1.54 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298K): $\delta$ (ppm) = 150.0, 149.4, 148.9, 142.9, 140.6, 140.1 ($^{3,5}$*C*$CH_3$), 137.8-126.8 (Ph-*C*), 113.2, 112.7, 112.4 ($^{4}$*C*H), 15.0 (d, $J_{CP}$ = 10.4 Hz), 14.1 (d, $J_{CP}$ = 16.7 Hz), 13.7, 11.4, 10.8, 10.5, 8.6, 8.1, 8.0 (C*C*$H_3$). **$^{19}$F NMR** ($CDCl_3$, 282 MHz, 298 K): $\delta$ (ppm) = –99.6 (WF). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 298 K): $\delta$ (ppm) = 11.2 (s, br, WC*P*), 8.2 (s, br, WC*P*). **IR** (ATR, $cm^{-1}$): 2524 (w, BH), 1884 (s, CO). **IR** (THF, $cm^{-1}$): 2546 (w, BH), 1896 (s, CO). **Anal.** Calc. for $C_{45}H_{48}BFN_6OP_2W$ (964.50 g/mol): C, 56.04; H, 5.02; N, 8.71. Found: C, 54.32; H, 5.85; N, 8.38.

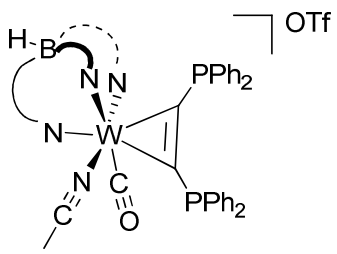
### 1.4.4 $5^{Cl}$




In a 100 mL Schlenk flask, 760 mg (954 µmol) **$4^{Cl}$** dissolved in 60 mL THF were cooled to –80 °C and 0.50 mL (1.25 mmol) of a 2.5 M n-BuLi solution in hexane were added. After ten minutes, 0.28 mL (1.52 mmol) $Ph_2PCl$ was added. After coming to room temperature and removing the solvent *in vacuo*, the crude product was purified by column chromatography with $CH_2Cl_2$/petroleum ether 1/1 as eluent. After drying *in vacuo*, the target compound **$5^{Cl}$** was obtained as a green powder. Yield: 817 mg (87 %).

**$^{1}$H NMR** ($CDCl_3$, 300 MHz, 298 K): $\delta$ (ppm) = 8.10 (m, 2 H, Ph-*H*), 7.43 (m, 3 H, Ph-*H*), 7.28-7.02 (m, 9 H, Ph-*H*), 6.79 (m, 2 H, Ph-*H*), 6.65 (m, 2 H, Ph-*H*), 6.50 (m, 2 H, Ph-*H*), 2.57 (s, 3 H, C$H_3$), 2.57 (s, 3 H, C$H_3$), 2.42 (d, 3 H, C$H_3$, $J_{HP}$ = 1.70 Hz), 2.20 (s, 3 H, C$H_3$), 2.15 (s, 3 H, C$H_3$), 2.12 (s, 3 H, C$H_3$), 1.95 (s, 3 H, C$H_3$), 1.78 (s, 3 H, C$H_3$), 1.54 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298 K): $\delta$ (ppm) = 235.4 (*C*O), 217.0 (dd, W*C*P, $^{1}J_{CP}$ = 50.0 Hz, $^{3}J_{CP}$ = 6.4 Hz), 211.3 (dd, W*C*P, $^{1}J_{CP}$ = 45.4 Hz, $^{3}J_{CP}$ = 4.5 Hz), 151.7, 151.6, 150.3, 143.6, 141.3, 140.0 ($^{3,5}$*C*$CH_3$), 138.8-133.2, 129.3-126.9 (Ph-*C*), 113.6, 113.1, 113.0 ($^{4}$*C*H), 15.9 (d, $J_{CP}$ = 18.2 Hz), 15.1 (d, $J_{CP}$ = 10.0 Hz), 14.3, 11.3, 11.0, 10.5, 8.6, 8.2, 8.1 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 299 K): $\delta$ (ppm) = 17.3 (d, WCP, $^{3}J_{PP}$ = 10.4 Hz), 16.7 (d, WCP, $^{3}J_{PP}$ = 10.4 Hz). **IR** (ATR, $cm^{-1}$): 2547 (w, BH), 1909 (s, CO). **IR** (THF, $cm^{-1}$): 2551 (w, BH), 1922 (s, CO). **Anal.** Calc. for $C_{45}H_{48}BClN_6OP_2W$ (980.95 g/mol): C, 55.10; H, 4.93; N, 8.57. Found: C, 54.67; H, 4.95; N, 8.37.

### 1.4.5 $5^{NCMe}$-OTf

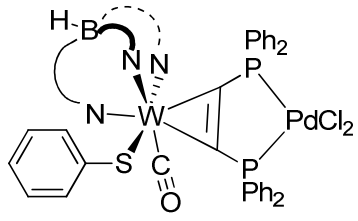



In a 100 mL Schlenk flask, 500 mg (457 µmol) **$5^{OTf}$** were dissolved in 50 mL MeCN. The reaction solution was heated for 30 min under reflux, while a colour change from turquoise to a deep green was os, brerved. After checking the progress of the conversion by IR, the solvent was removed *in vacuo*. The green residue was dissolved in 5 mL $CH_2Cl_2$, layered with 30 mL *n*-pentane and then crystallised overnight. The supernatant was discarded and the crystals were dried *in vacuo*. Yield: 460 mg (89 %).

**$^1$H NMR** ($CDCl_3$, 300 MHz, 298 K): *δ* (ppm) = 7.74 (m, 2 H, Ph-*H*), 7.48 (m, 3 H, Ph-*H*), 7.34 (m, 3 H, Ph-*H*), 7.23-7.00 (m, 6 H, Ph-*H*), 6.80 (m, 2 H, Ph-*H*), 6.56 (m, 2 H, Ph-*H*), 6.46 (m, 2 H, Ph-*H*), 3.03 (s, 3 H, NCC*H*$_3$), 2.54 (s, 3 H, C*H*$_3$), 2.23 (s, 3 H,), 2.19 (s, 3 H, C*H*$_3$), 2.15 (d, 3 H, C*H*$_3$, $J_{HP}$ = 2.08 Hz), 2.13 (s, 3 H, C*H*$_3$), 1.96 (s, 3 H, C*H*$_3$), 1.94 (s, 3 H, C*H*$_3$), 1.81 (s, 3 H, C*H*$_3$), 1.62 (s, 3 H, C*H*$_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 298 K): *δ* (ppm) = 224.7 (m, *C*O), 214.9 (d, W*C*P, $^1J_{CP}$ = 6.4 Hz), 214.3 (d, W*C*P, $^1J_{CP}$ = 5.6 Hz), 152.4, 150.9, 150.5 ($^{3,5}$*C*CH$_3$), 150.3 (d, N*C*CH$_3$), 145.3, 144.1, 141.7 ($^{3,5}$*C*CH$_3$), 136.0-127.4 (Ph-*C*), 114.4, 114.4, 113.9 ($^4$*C*H), 95.3 (q, *C*F$_3$, $^1J_{CF}$ = 485 Hz), 14.8, 14.7 (d, $J_{CP}$ = 8.8 Hz), 14.0, 11.2, 11.0, 10.4, 8.4, 8.1, 7.9 (C*C*H$_3$), 4.8 (NCC*C*H$_3$). **$^{19}$F NMR** ($CDCl_3$, 282 MHz, 298 K): *δ* (ppm) = –78.2 (C*F*$_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 298 K): *δ* (ppm) = 20.9, 20.1 (WC*P*). **IR** (ATR, cm$^{-1}$): 2562 (w, BH), 2276 (w, MeCN), 1927 (s, CO). **IR** ($CH_2Cl_2$, cm$^{-1}$): 2562 (w, BH), 1953 (s, CO). **Anal.** Calc. for $C_{48}H_{51}BF_3N_7O_4P_2SW$ (1135.62 g/mol): C, 50.77; H, 4.53; N, 8.63; S, 2.82. Found: C, 50.89; H, 4.56; N, 8.23; S, 2.93.

## 1.5 Dinuclear Complexes [($5^L$)$PdCl_2$]

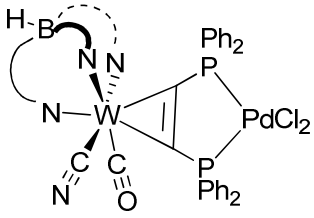
### 1.5.1 [($5^{SPh}$)$PdCl_2$]




In a 100 mL Schlenk flask, a solution of 97 mg (340 µmol) [(cod)$PdCl_2$] in 20 mL $CH_2Cl_2$ was added to a stirred solution of 358 mg (340 µmol) **$5^{SPh}$** in 50 mL $CH_2Cl_2$. After one hour, the solvent was removed under reduced pressure and the residue was purified by column chromatography using an eluent mixture of THF/petroleum ether 1/1. The brown product band was collected and dried *in vacuo*. Yield 208 mg (50 %).

**$^{1}$H NMR** ($CDCl_3$, 300 MHz, 299 K): $\delta$ (ppm) = 8.35 (m, br, 2 H, Ph-*H*), 7.62-6.98 (m, br, 23 H, Ph-*H*), 2.60 (s, 3 H, C$H_3$), 2.27 (s, 3 H, C$H_3$), 2.14 (s, 3 H, C$H_3$), 1.87 (s, br, 3 H, C$H_3$), 1.80 (s, br, 3 H, C$H_3$), 1.67 (s, br, 3 H, C$H_3$), 1.59 (s, 3 H, C$H_3$), 1.30 (s, 3 H, C$H_3$), 1.23 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 75 MHz, 299 K): $\delta$ (ppm) = 152.9, 152.9, 147.2, 142.3, 142.0, 142.0 ($^{3,5}$*C*$CH_3$), 137.1-125.3 (Ph-*C*), 116.8, 113.6, 112.4 ($^{4}$*C*H), 16.2, 14.9, 14.9, 11.2, 11.1, 11.0, 8.3, 8.2, 7.9 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 121 MHz, 299 K): $\delta$ (ppm) = 52.1 (d, WC*P*, $^{2}J_{PP}$ = 31.2 Hz), 43.2 (d, WC*P*, $^{2}J_{PP}$ = 31.2 Hz). **IR** (ATR, $cm^{-1}$): 2558 (w, BH), 1926 (s, CO). **IR** ($CH_2Cl_2$, $cm^{-1}$): 2562 (w, BH), 1949 (s, CO). **Anal.** Calc. for $C_{51}H_{53}BCl_2N_6OP_2PdSW$ (1232.00 g/mol)·0.5 $CH_2Cl_2$: C, 48.53; H, 4.27; N, 6.59; S, 2.52. Found: C, 48.86; H, 4.54; N, 6.28; S, 2.24.

### **1.5.2** [(5$^{CN}$)$PdCl_2$]




In a 50 mL Schlenk flask, a solution of 29 mg (102 µmol) [(cod)$PdCl_2$] in 5 mL $CH_2Cl_2$ was slowly added to a stirred solution of 100 mg (103 µmol) **5$^{CN}$** in 5 mL $CH_2Cl_2$. A colour change from green to yellow-brown was observed immediately. After one hour, the solvent was removed *in vacuo*, the residue was dissolved in 2 mL $CH_2Cl_2$ and layered with 40 mL $Et_2O$. The supernatant was separated from the precipitating ochre-coloured powder and the solid is dried *in vacuo*. Yield 112 mg (94 %).

**$^{1}$H NMR** ($CDCl_3$, 250 MHz, 300 K): $\delta$ (ppm) = 8.27-8.07 (m, 4 H, Ph-*H*), 7.70 (m, 3 H, Ph-*H*), 7.56-7.41 (m, 6 H, Ph-*H*), 7.29-7.19 (m, 5 H, Ph-*H*), 6.96 (m, 2 H, Ph-*H*), 2.66 (s, 3 H, C$H_3$), 2.53 (s, 3 H, C$H_3$), 2.39 (s, 3 H, C$H_3$), 2.16 (s, 3 H, C$H_3$), 1.76 (s, 3 H, C$H_3$), 1.75 (s, 3 H, C$H_3$), 1.42 (s, 3 H, C$H_3$), 1.38 (s, 3 H, C$H_3$), 0.92 (s, 3 H, C$H_3$). **$^{13}$C NMR** ($CDCl_3$, 63 MHz, 298 K): $\delta$ (ppm) = 243.2 (m, *C*O), 233.4 (m, W*C*P), 222.9 (m, W*C*P), 153.5, 152.4 ($^{3,5}$*C*$CH_3$), 150.6 (*C*N), 146.6, 143.9, 143.9, 141.9 ($^{3,5}$*C*$CH_3$), 136.6-121.9 (Ph-*C*), 114.0, 113.9, 113.0 ($^{4}$*C*H), 16.3, 15.3, 15.2, 11.3, 10.8, 10.8, 8.2, 8.1, 8.1 (C*C*$H_3$). **$^{31}$P NMR** ($CDCl_3$, 101 MHz, 298 K): $\delta$ (ppm) = 54.7 (d, WC*P*, $^{2}J_{PP}$ = 36.3 Hz), 46.1 (d, WC*P*, $^{2}J_{PP}$ = 32.7 Hz). **IR** (ATR, $cm^{-1}$): 2558 (w, BH), 2118 (w, CN), 1962 (s, CO). **IR** ($CH_2Cl_2$, $cm^{-1}$): 2562 (w, BH), 2114 (w, CN), 1976 (s, CO). **Anal.** Calc. for $C_{46}H_{48}BCl_2N_7OP_2PdW$ (1148.84 g/mol)·$CH_2Cl_2$·$CH_3CN$: C, 46.16; H, 4.19; N, 8.79, Found: C, 46.48; H, 4.11; N, 8.26.

## 2 $^{13}$C NMR shift / CO vibration correlations

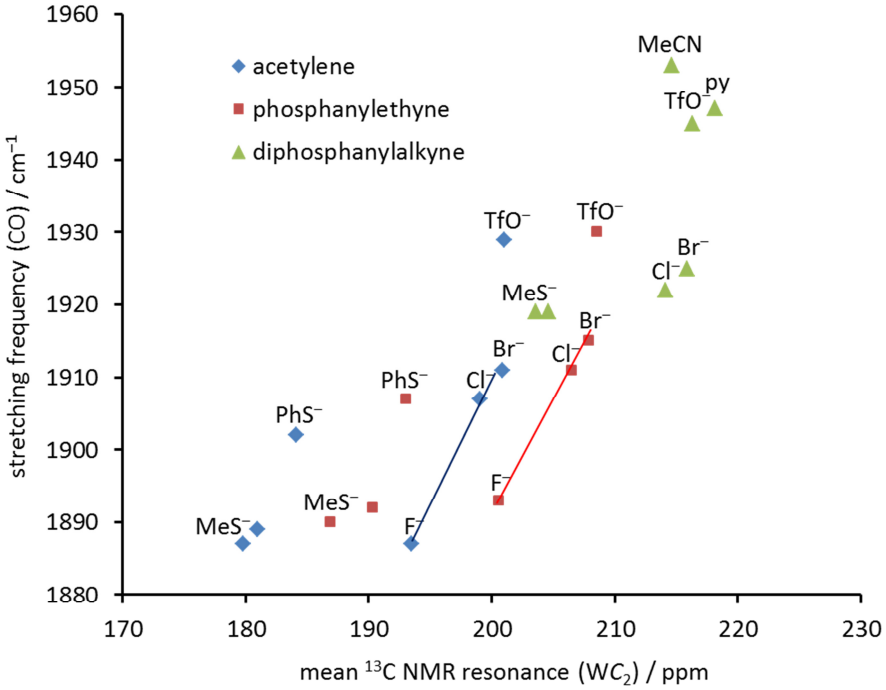



**Figure S1.** Correlation of the stretching frequency of the CO valence vibration with the mean $^{13}$C NMR shifts of the two W-bound alkyne carbon atoms.

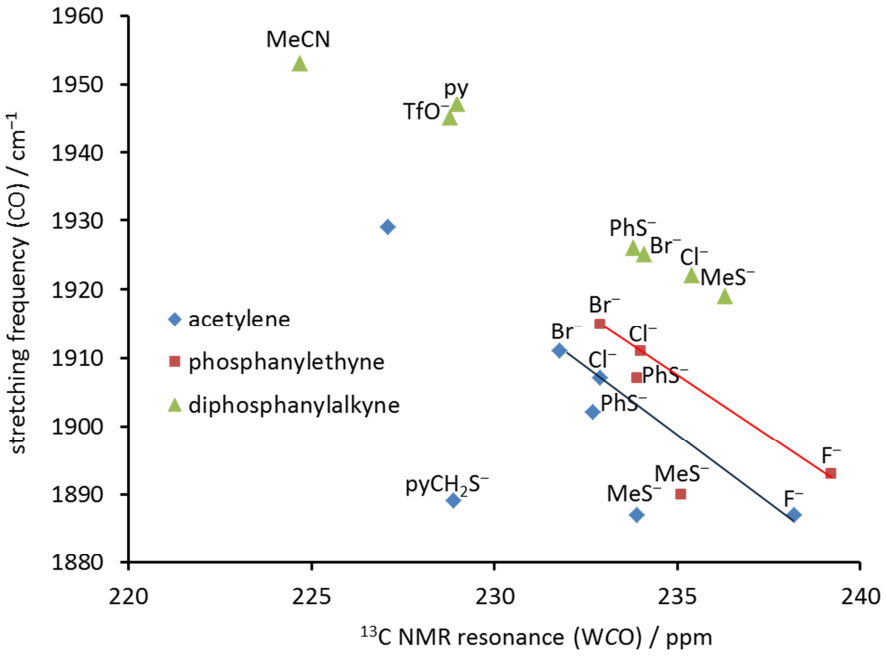



**Figure S2.** Correlation of the stretching frequency of the CO valence vibration with the $^{13}$C NMR shifts of the W-bound CO ligand.

# 3 X-Ray Analysis

## 3.1 General information

In all figures, ellipsoids have been set at 50 % probability. Co-crystallized solvents, partial P-oxidation and hydrogen atoms have been omitted while Ph-carbon atoms are depicted as ball-and-stick-models for clarity. Where multiple layers exist in the same structure, the one with the highest probability is depicted. Single crystals suitable for X-ray diffraction analysis were selected in Fomblin YR-1800 perfluoropolyether oil (Alfa Aesar) at ambient temperature and mounted on a glass fiber. During the measurement, the samples were cooled to 123(2) K. Diffraction data were collected on a Bruker D8 QUEST diffractometer and a Bruker Kappa Apex II diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Structure solutions were found by direct methods (SHELXS-97 or SHELXS-2013)[S3] and were refined by full-matrix least-squares procedures on $F^2$ (SHELXL-2013)[S4] All non-hydrogen atoms were anisotropically refined unless stated otherwise. Hydrogen atoms were included at calculated positions with fixed thermal parameters unless stated otherwise.

## 3.2 Crystallographic Details, Figures and Selected Structural Parameters

### 3.2.1 [Tp*W(CO)L($\eta^2$-$C_2H_2$)] $3^L$

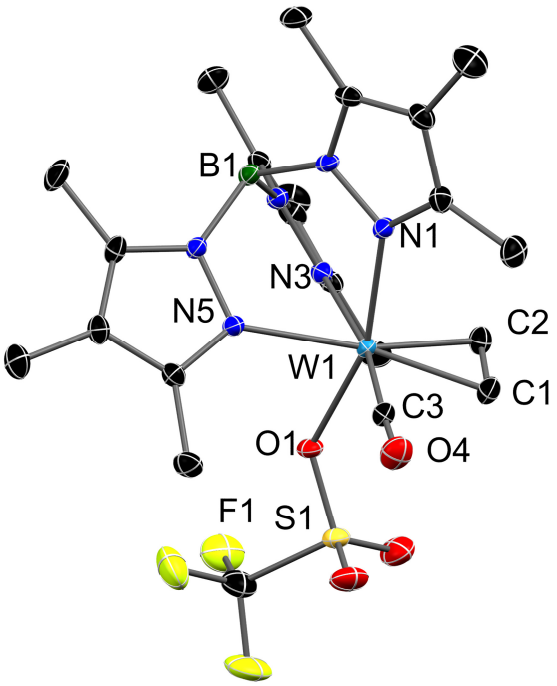



**Figure S3**. Molecular structure of $\mathbf{3}^{OTF}$ in the crystal. Selected bond lengths (Å): W1–N1 2.1453(14), W1–N3 2.2270(15), W1–N5 2.2266(14), W1–O1 2.1309(12), W1–C3 1.9707(19), W1–C1 2.0440(18), W1–C2 2.0221(18), C1–C2 1.293(3).

| compound | $3^{OTf}$ |
|---|---|
| empirical formula | $C_{22}H_{30}BF_3N_6O_4SW \cdot 0.5CH_2Cl_2$ |
| fw (g mol$^{-1}$) | 768.70 |
| crystal size (mm) | 0.50 × 0.16 × 0.03 |
| crystal system | monoclinic |
| space group | $P2_1/c$ |
| $a$ (Å) | 12.8417(5) |
| $b$ (Å) | 22.0759(8) |
| $c$ (Å) | 11.0925(4) |
| $\alpha$ (deg) | |
| $\beta$ (deg) | 115.227(1) |
| $\gamma$ (deg) | |
| V (Å$^3$) | 2844.02(18) |
| Z | 4 |
| $\mu$ (mm$^{-1}$) | 4.29 |
| measured reflections | 90884 |
| independent reflections | 10316 |
| reflections with $I>2\sigma(I)$ | 8893 |
| $R_{int}$ | 0.042 |
| $R1$ (F[$I>2\sigma(I)$]) | 0.021 |
| w$R2$ (F$^2$[all data]) | 0.043 |
| GOF | 1.017 |
| parameters | 379 |
| restraints | 0 |
| CCDC no. | 2202261 |

### 3.2.2 [Tp*W(CO)L($\eta^2$-C$_2${H}{PPh$_3$})] $4^L$

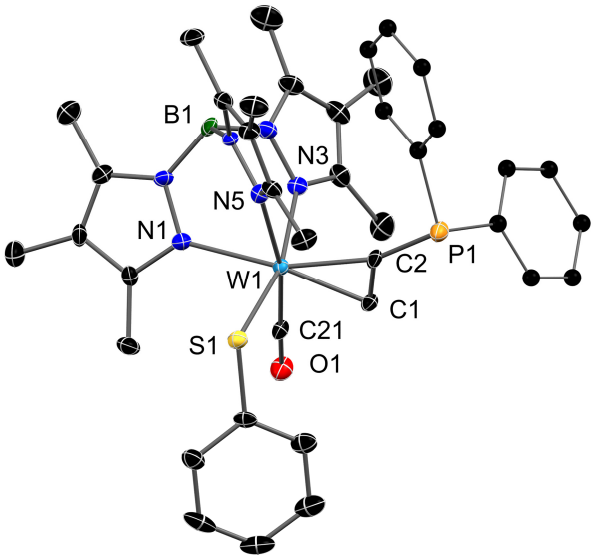



**Figure S4**. Molecular structure of $4^{SPh}$ in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.251(5), W1–N3 2.224(4), W1–N5 2.238(4), W1–S1 2.3884(14), W1–C21 1.946(4), W1–C1 2.043(5), W1–C2 2.069(5), C1–C2 1.311(7), P1–C2 1.787(5), C1–C2–P1 132.6(4).

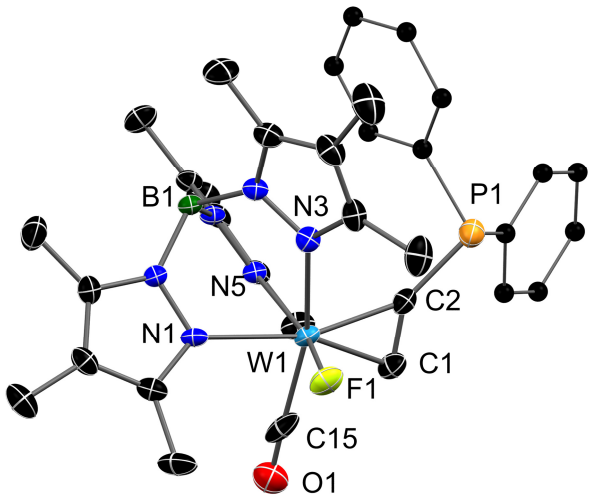



**Figure S5**. Molecular structure of $4^F$ in the crystal. Selected bond lengths (Å) and -angles (°): N1–W1 2.233(2), N3–W1 2.214(2), N5–W1 2.184(2), F1–W1 1.9636(19), C15–W1 2.001(4), C1–W1 2.030(3), C2–W1 2.059(3), C1–C2 1.310(5), C2–P1 1.793(3), C1–C2–P1 141.1(3).

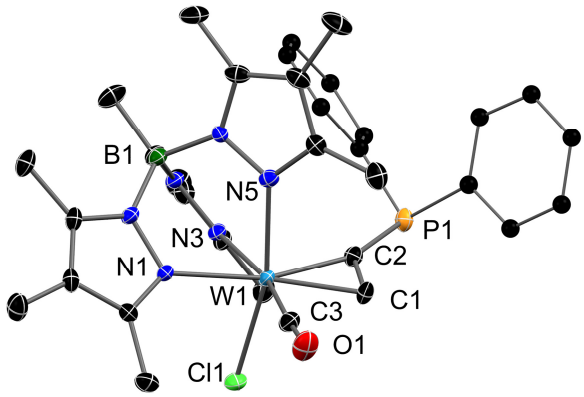



**Figure S6**. Molecular structure of $\mathbf{4}^{\mathbf{Cl}}$ in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.220(3), W1–N3 2.235(3), W1–N5 2.207(3), W1–Cl1 2.4249(9), W1–C3 1.964(4), W1–C1 2.030(4), W1–C2 2.052(4), C1–C2 1.327(6), P1–C2 1.782(4), C1–C2–P1 133.9(3).

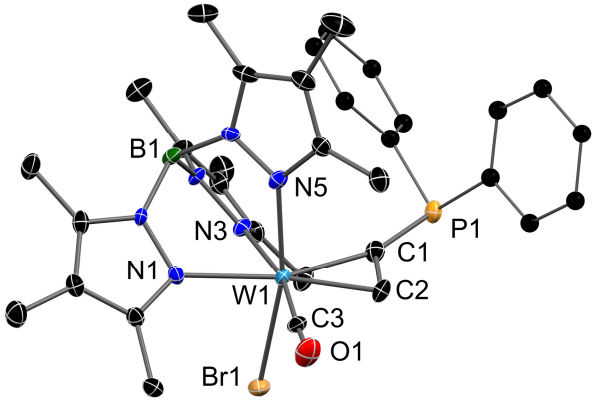
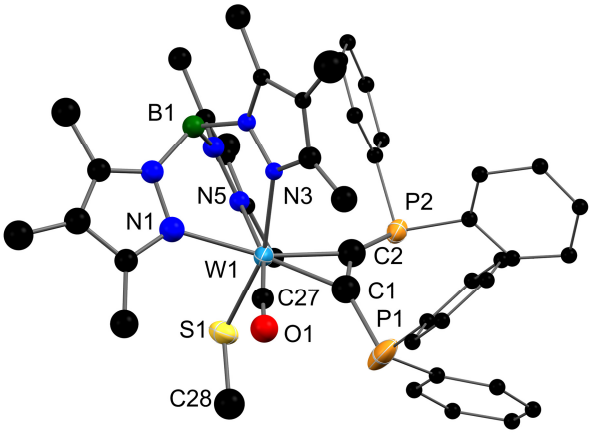



**Figure S7**. Molecular structure of $\mathbf{4}^{\mathbf{Br}}$ in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.217(5), W1–N3 2.229(4), W1–N5 2.196(5), W1–Br1 2.5788(6), W1–C3 1.951(6), W1–C1 2.050(6), W1–C2 2.032(6), C1–C2 1.326(9), P1–C1 1.787(6), C2–C1–P1 133.3(5).

| compound | $\mathbf{4}^{\mathbf{SPh}}$ | $\mathbf{4}^{\mathbf{F}}$ |
|---|---|---|
| empirical formula | $C_{39}H_{44}BN_6OPSW$ | $C_{33}H_{39}BFN_6OPW$ |
| fw (g mol$^{-1}$) | 870.49 | 780.33 |
| crystal size (mm) | 0.08 × 0.06 × 0.05 | 0.12 × 0.11 × 0.03 |
| crystal system | Orthorhombic | Triclinic |
| space group | $P2_12_12_1$ | $P\bar{1}$ |
| *a* (Å) | 11.0623(9) | 9.0234(8) |
| *b* (Å) | 17.4935(17) | 10.1907(9) |
| *c* (Å) | 19.5062(19) | 19.5548(18) |
| *α* (deg) | | 88.570(4) |
| *β* (deg) | | 77.444(5) |
| *γ* (deg) | | 69.035(4) |
| V (Å$^3$) | 3818.0(6) | 1636.2(3) |
| *Z* | 4 | 2 |
| *μ* (mm$^{-1}$) | 3.16 | 3.621 |
| measured reflections | 7553 | 53800 |
| independent reflections | 7553 | 11718 |
| reflections with $I>2\sigma(I)$ | 6533 | 10164 |
| $R_{int}$ | 0.077 | 0.0454 |
| $R1$ (F[$I>2\sigma(I)$]) | 0.037 | 0.0355 |
| w$R2$ (F$^2$[all data]) | 0.073 | 0.0836 |
| GOF | 1.083 | 1.044 |
| parameters | 465 | 415 |
| restraints | 0 | 0 |
| CCDC no. | 2202262 | 2202263 |

| compound | $\mathbf{4^{Cl}}$ | $\mathbf{4^{Br}}$ |
|---|---|---|
| empirical formula | $C_{33}H_{39}BClN_6OPW \cdot 4CH_2Cl_2$ | $C_{33}H_{39}BBrN_6OPW \cdot C_5H_{12}$ |
| fw (g mol$^{-1}$) | 1136.48 | 913.38 |
| crystal size (mm) | 0.45 × 0.14 × 0.09 | 0.21 × 0.12 × 0.11 |
| crystal system | orthorhombic | Orthorhombic |
| space group | *Pca*2$_1$ | *Pca*2$_1$ |
| *a* (Å) | 16.460(3) | 16.5493(5) |
| *b* (Å) | 10.3892(18) | 10.3618(2) |
| *c* (Å) | 22.022(4) | 22.0549(6) |
| *α* (deg) | | |
| *β* (deg) | | |
| *γ* (deg) | | |
| V (Å$^3$) | 3765.9(11) | 3781.99(17) |
| Z | 4 | 4 |
| *μ* (mm$^{-1}$) | 3.79 | 4.19 |
| measured reflections | 75214 | 41114 |
| independent reflections | 15292 | 11985 |
| reflections with $I>2\sigma(I)$ | 13754 | 9887 |
| $R_{int}$ | 0.033 | 0.057 |
| $R1$ (F[$I>2\sigma(I)$]) | 0.025 | 0.035 |
| w$R2$ (F$^2$[all data]) | 0.066 | 0.068 |
| GOF | 1.066 | 1.001 |
| parameters | 407 | 397 |
| restraints | 1 | 0 |
| CCDC no. | 2203102 | 2202390 |

### 3.2.3 [Tp*W(CO)L($\eta^2$-C$_2${PPh$_3$}$_2$)] 5$^L$



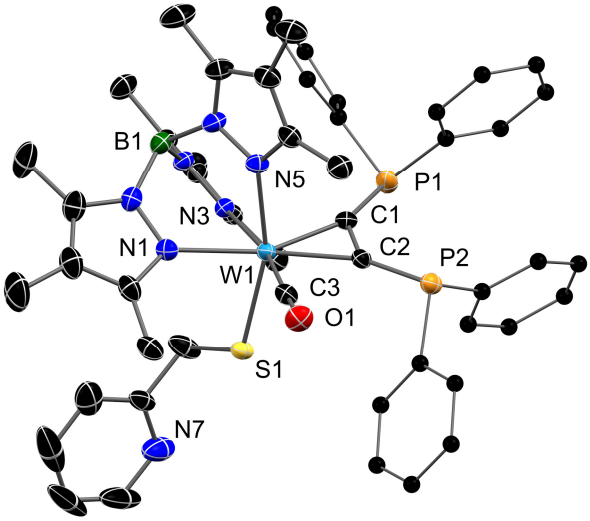




**Figure S8**. Lower-quality refinement of the molecular structure of **5$^{SMe}$**. Selected bond lengths (Å) and -angles (°): W1–N1 2.231, W1–N3 2.237, W1–N5 2.280, W1–S1 2.383, W1–C27 1,885, W1–C1 2.042, W1–C2 2.100, C1–C2 1.231, P1–C1 1.889, P2–C2 1.817, C2–C1–P1 142.71, C1–C2–P2 144.27.

**Figure S9**. Molecular structure of **5$^{SCPy}$** in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.272(2), W1–N3 2.228(2), W1–N5 2.202(2), W1–S1 2.3790(7), W1–C3 1.962(3), W1–C1 2.060(3), W1–C2 2.085(3), C1–C2 1.325(4), P1–C1 1.798(3), P2–C2 1.793(3), C2–C1–P1 135.2(2), C1–C2–P2 136.6(2).

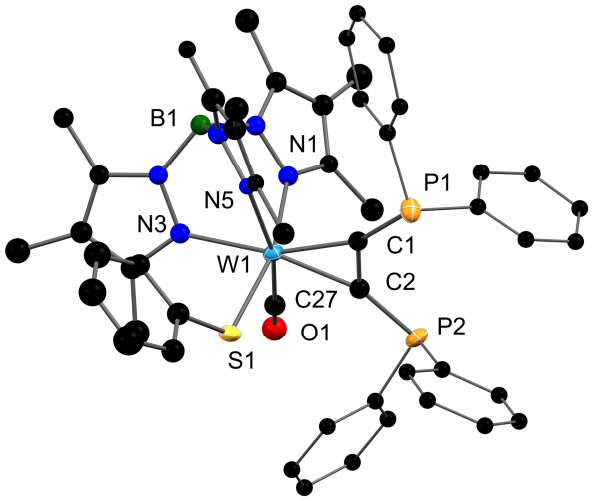



**Figure S10**. Lower-quality refinement of the molecular structure of $\mathbf{5}^{SPh}$. Selected bond lengths (Å) and -angles (°): W1–N1 2.197, W1–N3 2.248, W1–N5 2.247, W1–S1 2.397, W1–C27 2,015, W1–C1 2.077, W1–C2 2.082, C1–C2 1.382, P1–C1 1.769, P2–C2 1.786, C2–C1–P1 133.84, C1–C2–P2 134.65.

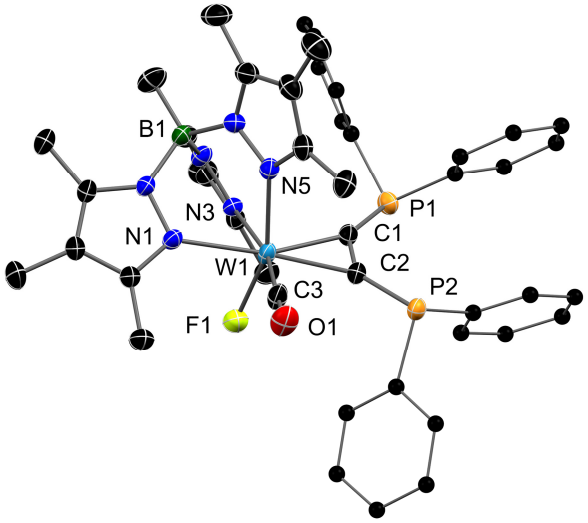



**Figure S11**. Molecular structure of $\mathbf{5}^{F}$ in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.2376(18), W1–N3 2.2231(18), W1–N5 2.1954(19), W1–F1 1.9618(15), W1–C3 1.958(2), W1–C1 2.048(2), W1–C2 2.076(2), C1–C2 1.327(3), P1–C1 1.786(2), P2–C2 1.795(2), C2–C1–P1 139.25(17), C1–C2–P2 139.35(17).

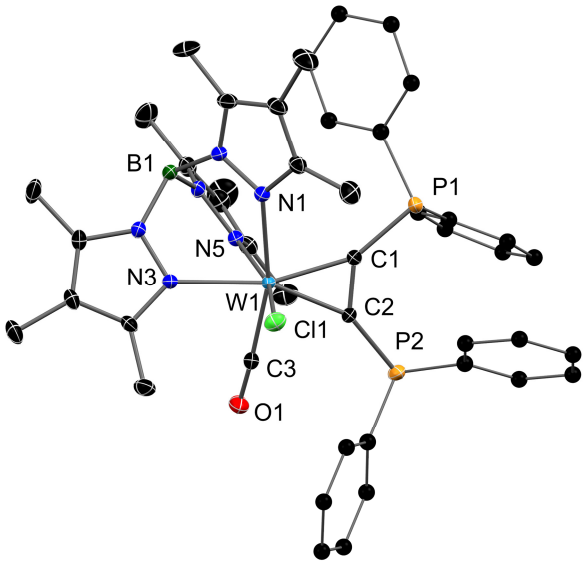



**Figure S12**. Molecular structure of $\mathbf{5}^{Cl}$ in the crystal. Selected bond lengths (Å) and -angles (°): N1–W1 2.2291(15), N3–W1 2.2278(16), N5–W1 2.1778(16), W1–Cl1 2.4265(5), W1–C3 1.9641(19), W1–C1 2.0402(18), W1–C2 2.0595(18), C1–C2 1.331(2), P1–C1 1.7943(18), P2–C2 1.8001(18), C2–C1–P1 134.50(15), C1–C2–P2 136.01(15).

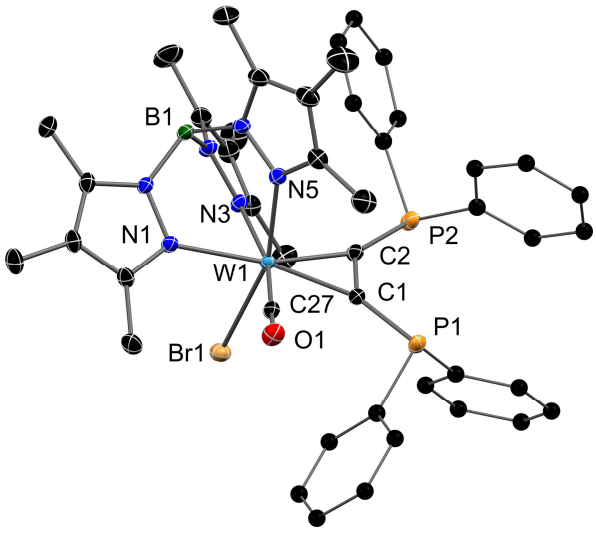



**Figure S13**. Molecular structure of $\mathbf{5}^{Br}$ in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.2345(11), W1–N3 2.2340(11), W1–N5 2.1788(11), W1–Br1 2.58686(15), W1–C27 1.9667(13), W1–C1 2.0617(13), W1–C2 2.0405(13), C1–C2 1.3340(18), P1–C1 1.8010(13), P2–C2 1.7955(13), C2–C1–P1 135.17(10), C1–C2–P2 134.47(10).

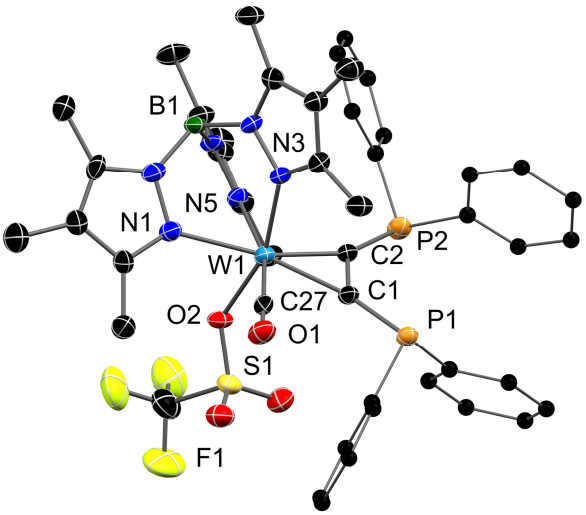



**Figure S14**. Molecular structure of $\mathbf{5^{OTf}}$ in the crystal. Shown is one individual molecule of the asymmetric unit. Selected bond lengths (Å) and -angles (°): W1–N1 2.254(5), W1–N3 2.160(5), W1–N5 2.223(6), W1–O2 2.146(4), W1–C27 1.963(8), W1–C1 2.076(6), W1–C2 2.039(7), C1–C2 1.342(9), P1–C1 1.791(7), P2–C2 1.785(7), C2–C1–P1 133.8(6), C1–C2–P2 134.6(5).

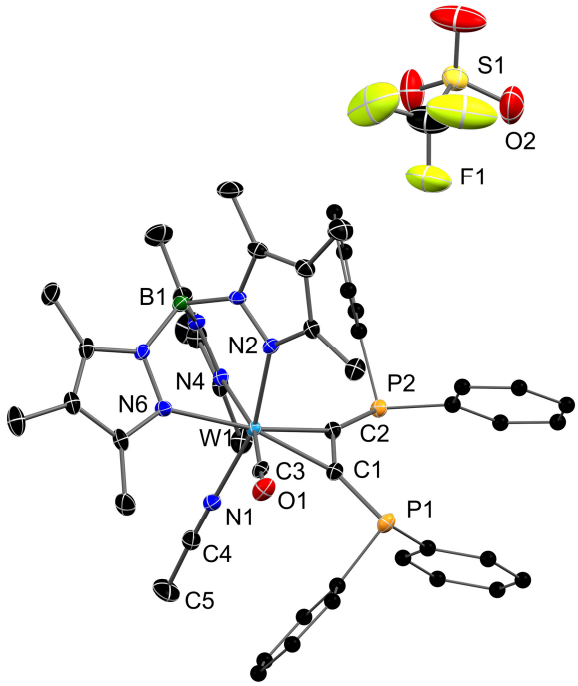



**Figure S15**. Molecular structure of $\mathbf{5^{MeCN}}$**-OTf** in the crystal. Selected bond lengths (Å) and -angles (°): W1–N2 2.164(3), W1–N4 2.233(3), W1–N6 2.201(3), W1–N1 2.126(3), W1–C3 1.976(3), W1–C1 2.057(3), W1–C2 2.034(3), C1–C2 1.330(5), P1–C1 1.793(3), P2–C2 1.790(3), C2–C1–P1 139.6(3), C1–C2–P2 136.3(3).

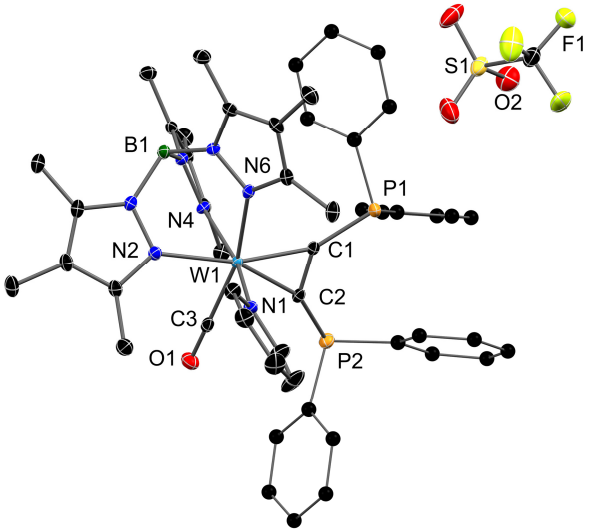



**Figure S16**. Molecular structure of $\mathbf{5^{Py}}$**-OTf** in the crystal. Selected bond lengths (Å) and -angles (°): W1–N2 2.217(2), W1–N4 2.1733(19), W1–N6 2.224(2), W1–N1 2.193(2), W1–C3 1.977(3), W1–C1 2.026(2), W1–C2 2.061(2), C1–C2 1.337(3), P1–C1 1.795(2), P2–C2 1.797(2), C2–C1–P1 135.02(19), C1–C2–P2 134.23(19).

| compound | $\mathbf{5}^{\mathbf{SCPy}}$ | $\mathbf{5}^{\mathbf{F}}$ | $\mathbf{5}^{\mathbf{Cl}}$ |
|---|---|---|---|
| empirical formula | $C_{51}H_{54}BN_7OP_2SW \cdot 2CH_2Cl_2$ | $C_{45}H_{48}BFN_6OP_2W \cdot 2CHCl_3$ | $C_{45}H_{48}BClN_6OP_2W \cdot 0.893C_5H_{12} \cdot 0.107CH_2Cl_2$ |
| fw (g mol$^{-1}$) | 1239.52 | 1203.23 | 1054.46 |
| crystal size (mm) | 0.13 × 0.12 × 0.11 | 0.26 × 0.06 × 0.04 | 0.60 × 0.21 × 0.13 |
| crystal system | triclinic | Triclinic | monoclinic |
| space group | P$\bar{1}$ | P$\bar{1}$ | $P2_1/n$ |
| *a* (Å) | 13.4082(13) | 11.5877(10) | 13.1334(6) |
| *b* (Å) | 13.6770(13) | 13.9252(12) | 19.3491(8) |
| *c* (Å) | 16.9058(16) | 16.8414(15) | 19.7000(8) |
| *α* (deg) | 100.820(3) | 86.448(4) | |
| *β* (deg) | 94.524(4) | 78.987(4) | 99.355(2) |
| *γ* (deg) | 113.869(3) | 68.149(4) | |
| V (Å$^3$) | 2743.0(5) | 2475.7(4) | 4939.6(4) |
| *Z* | 2 | 2 | 4 |
| *μ* (mm$^{-1}$) | 2.44 | 2.77 | 2.51 |
| measured reflections | 132596 | 80268 | 129485 |
| independent reflections | 19014 | 17837 | 17834 |
| reflections with $I>2\sigma(I)$ | 15414 | 15081 | 15411 |
| $R_{int}$ | 0.076 | 0.050 | 0.032 |
| $R1$ (F[$I>2\sigma(I)$]) | 0.040 | 0.032 | 0.025 |
| w$R2$ (F$^2$[all data]) | 0.089 | 0.076 | 0.063 |
| GOF | 1.052 | 1.027 | 1.093 |
| Parameters | 587 | 515 | 558 |
| Restraints | 0 | 0 | 5 |
| CCDC no. | 2203103 | 2202267 | 2202268 |

| compound | $\mathbf{5}^{\mathbf{Br}}$ | $\mathbf{5}^{\mathbf{OTf}}$ |
|---|---|---|
| empirical formula | $C_{45}H_{48}BBrN_6OP_2W \cdot C_5H_{12}$ | $C_{46}H_{48}BF_3N_6O_4P_2SW \cdot 0.333\ C_5H_{12} \cdot 1.333$ THF |
| fw (g mol$^{-1}$) | 1097.55 | 1217.01 |
| crystal size (mm) | 0.26 × 0.22 × 0.18 | 0.19 × 0.09 × 0.08 |
| crystal system | monoclinic | Triclinic |
| space group | $P2_1/c$ | P1 |
| *a* (Å) | 13.1304(4) | 15.1651(9) |
| *b* (Å) | 19.4822(6) | 21.3862(12) |
| *c* (Å) | 19.7195(6) | 25.7029(16) |
| *α* (deg) | | 98.383(3) |
| *β* (deg) | 99.166(1) | 104.409(4) |
| *γ* (deg) | | 93.786(3) |
| V (Å$^3$) | 4980.0(3) | 7941.9(8) |
| *Z* | 4 | 6 |
| *μ* (mm$^{-1}$) | 3.23 | 2.346 |
| measured reflections | 219003 | 212014 |
| independent reflections | 18111 | 69859 |
| reflections with $I>2\sigma(I)$ | 16485 | 56838 |
| $R_{int}$ | 0.032 | 0.0679 |
| $R1$ (F[$I>2\sigma(I)$]) | 0.020 | 0.0419 |
| w$R2$ (F$^2$[all data]) | 0.044 | 0.0888 |
| GOF | 1.066 | 0.985 |
| parameters | 523 | 3610 |
| restraints | 0 | 1449 |
| CCDC no. | 2221973 | 2203161 |

| compound | $5^{MeCN}$-OTf | $5^{Py}$-OTf |
|---|---|---|
| empirical formula | $C_{48}H_{51}BF_3N_7O_4P_2SW$ | $C_{51}H_{53}BF_3N_7O_4P_2SW \cdot 2CH_2Cl_2$ |
| fw (g mol$^{-1}$) | 1135.61 | 1344.39 |
| crystal size (mm) | 0.16 × 0.10 × 0.07 | 0.99 × 0.05 × 0.04 |
| crystal system | monoclinic | Triclinic |
| space group | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 12.9737(6) | 10.7634(5) |
| $b$ (Å) | 20.0730(8) | 15.6372(8) |
| $c$ (Å) | 18.6793(9) | 17.1562(9) |
| $\alpha$ (deg) | 90.0 | 81.843(2) |
| $\beta$ (deg) | 92.342(2) | 86.429(2) |
| $\gamma$ (deg) | 90.0 | 81.767(2) |
| V (Å$^3$) | 4860.4(4) | 2826.3(2) |
| Z | 4 | 2 |
| $\mu$ (mm$^{-1}$) | 2.548 | 2.379 |
| measured reflections | 146718 | 136805 |
| independent reflections | 14187 | 16463 |
| reflections with $I>2\sigma(I)$ | 11090 | 13958 |
| $R_{int}$ | 0.084 | 0.0723 |
| $R1$ (F[$I>2\sigma(I)$]) | 0.0355 | 0.0303 |
| w$R2$ (F$^2$[all data]) | 0.0620 | 0.056 |
| GOF | 1.057 | 1.043 |
| parameters | 668 | 741 |
| restraints | 294 | 59 |
| CCDC no. | 2203105 | 2202269 |

### 3.2.4 Dinuclear Complexes with Pd

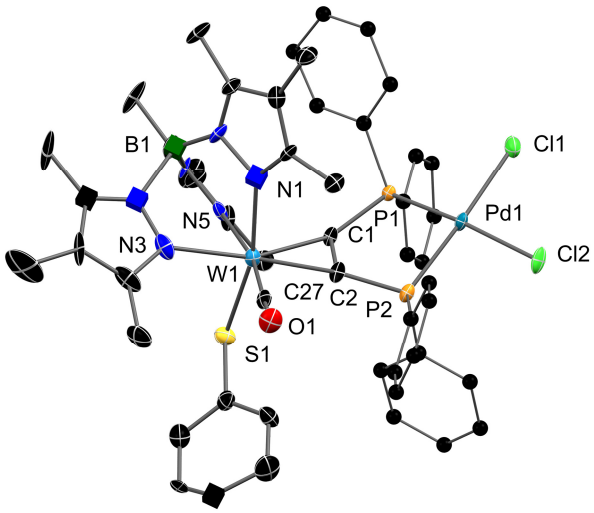



**Figure S17**. Lower-quality refinement of the molecular structure of the molecular structure of **($5^{SPh}$)PdCl$_2$** in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.207, W1–N3 2.237, W1–N5 2.238, W1–S1 2.358, W1–C27 1.997, W1–C1 2.063, W1–C2 2.078, P1–C1 1.804, P2–C2 1.804, Pd1–P1 2.247, Pd1–P2 2.246, Pd1–Cl1 2.349, Pd1–Cl2 2.369, C2–C1 P1 117.9, C1–C2–P2 119.0, P2–Pd1–P1 86.98, P1–Pd1–Cl1 88.26, Cl1–Pd1–Cl2 93.79, P2–Pd1–Cl2 90.77.

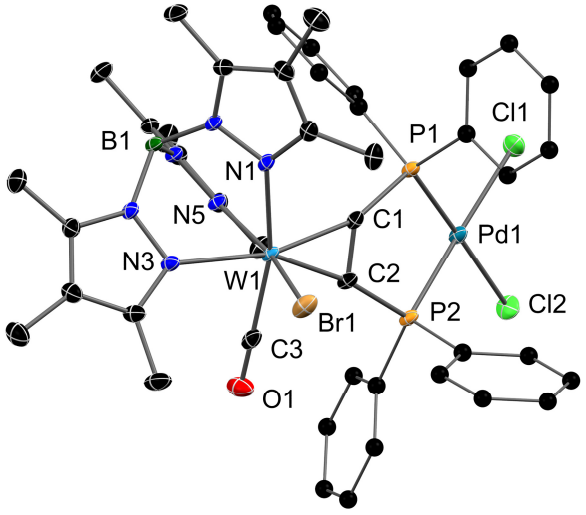



**Figure S18**. Molecular structure of **($5^{Br}$)PdCl$_2$** in the crystal. Selected bond lengths (Å) and -angles (°): N1–W1 2.225(2), N3–W1 2.218(2), N5–W1 2.175(2), Br1–W1 2.5551(4), W1–C3 1.988(3), W1–C1 2.035(3), W1–C2 2.043(2), P1–C1 1.805(3), P2–C2 1.805(3), P1–Pd1 2.2477(7), P2–Pd1 2.2406(7), Cl1–Pd1 2.3363(8), Cl2–Pd1 2.3355(7), C2–C1–P1 118.16(19), C1–C2–P2 119.1(2), P2–Pd1–P1 87.77(3), P2–Pd1–Cl2 89.38(3), Cl2–Pd1–Cl1 93.35(3), P1–Pd1–Cl1 89.32(3).

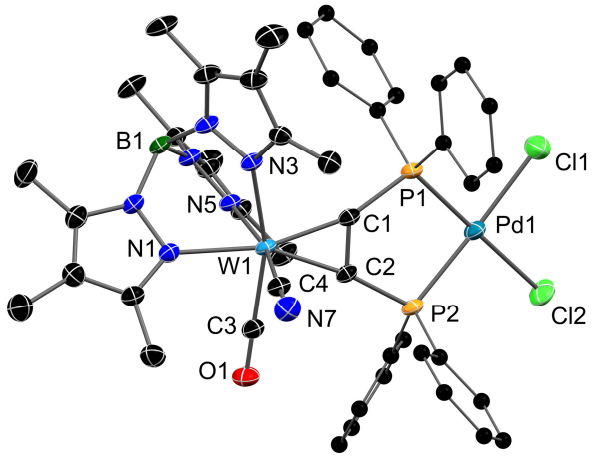



**Figure S19**. Molecular structure of **(5$^{CN}$)PdCl$_2$** in the crystal. Selected bond lengths (Å) and -angles (°): W1–N1 2.215(3), W1–N3 2.218(2), W1–N5 2.180(3), W1–C4 2.143(3), W1–C3 2.000(3), W1–C1 2.020(3), W1–C2 2.057(3), P1–C1 1.807(3), P2–C2 1.819(3), Pd1–P1 2.2335(8), Pd1–P2 2.2556(9), Pd1–Cl1 2.3407(11), Pd1–Cl2 2.3454(9), C2–C1–P1 120.2(2), C1–C2–P2 119.1(3), P1–Pd1–P2 88.82(3), P1–Pd1–Cl1 86.08(4), Cl1–Pd1–Cl2 93.33(4), P2–Pd1–Cl2 91.71(4).

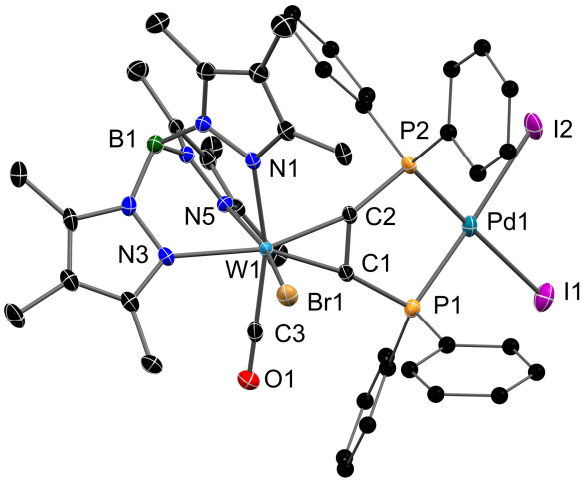



**Figure S20**. Molecular structure of **(5$^{Br}$)PdI$_2$** in the crystal. Selected bond lengths (Å) and -angles (°): N1–W1 2.231(3), N3–W1 2.222(3), N5–W1 2.164(2), Br1–W1 2.5396(4), W1–C3 1.981(3), W1–C1 2.051(3), W1–C2 2.036(3), P1–C1 1.825(3), P2–C2 1.803(3), P1–Pd1 2.2853(9), P2–Pd1 2.2730(9), Pd1–I1 2.6670(4), Pd1–I2 2.6320(4), C2–C1–P1 119.5(2), C1–C2–P2 119.9(2), P2–Pd1–P1 87.74(3), P1–Pd1–I1 92.95(2), I2–Pd1–I1 93.137(12), P2–Pd1–I2 86.01(2).

| compound | **(5$^{Br}$)PdCl$_2$** | **(5$^{CN}$)PdCl$_2$** | **(5$^{Br}$)PdI$_2$** |
|---|---|---|---|
| empirical formula | $C_{45}H_{48}BBrCl_2N_6OP_2PdW$ ·3 $CH_2Cl_2$ | $C_{46}H_{48}BCl_2N_7OP_2PdW$ ·$C_2H_3N$·$CH_2Cl_2$ | $C_{45}H_{48}BBrI_2N_6OP_2PdW$ ·2 $CH_2Cl_2$ |
| fw (g mol$^{-1}$) | 1457.48 | 1222.36 | 1555.45 |
| crystal size (mm) | 0.21 × 0.10 × 0.03 | 0.10 × 0.10 × 0.03 | 0.36 × 0.13 × 0.07 |
| crystal system | monoclinic | Triclinic | monoclinic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ |
| *a* (Å) | 15.3742(16) | 13.5408(11) | 12.7620(7) |
| *b* (Å) | 16.4883(18) | 13.7166(11) | 15.7369(10) |
| *c* (Å) | 21.753(2) | 16.4682(12) | 27.1915(16) |
| *α* (deg) | | 92.352(4) | 90.0 |
| *β* (deg) | 91.629(3) | 92.815(4) | 100.596(2) |
| *γ* (deg) | | 119.240(4) | 90.0 |
| V (Å$^3$) | 5512.0(10) | 2658.3(4) | 5367.9(6) |
| Z | 4 | 2 | 4 |
| *μ* (mm$^{-1}$) | 3.63 | 2.81 | 4.671 |
| measured reflections | 141896 | 85217 | 119210 |
| independent reflections | 19918 | 19133 | 17711 |
| reflections with *I*>2σ(*I*) | 15751 | 15229 | 13826 |
| $R_{int}$ | 0.068 | 0.047 | 0.0498 |
| *R*1 (F[*I*>2σ(*I*)]) | 0.032 | 0.038 | 0.0331 |
| w*R*2 (F$^2$[all data]) | 0.076 | 0.095 | 0.0736 |
| GOF | 1.052 | 0.929 | 1.032 |
| parameters | 631 | 582 | 604 |
| restraints | 0 | 0 | 0 |
| CCDC no. | 2202264 | 2202265 | 2203104 |

# 4 NMR spectra of selected compounds

## 4.1 [Tp*W(CO)L($\eta^2$-$C_2H_2$)] $3^L$

### 4.1.1 $3^{SMePy}$

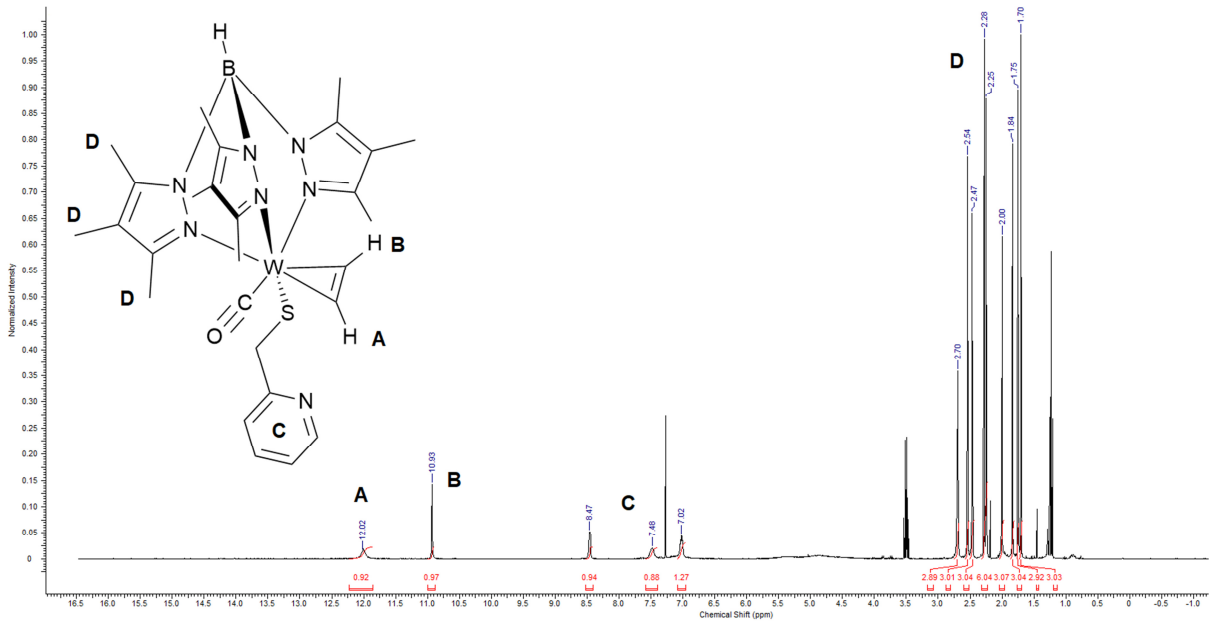



**Figure S21.** $^1$H NMR of $\mathbf{3}^{\mathbf{SMePy}}$ ($CDCl_3$, 500 MHz, 298 K). Note very broad $CH_2$ protons at ca. 5 ppm.

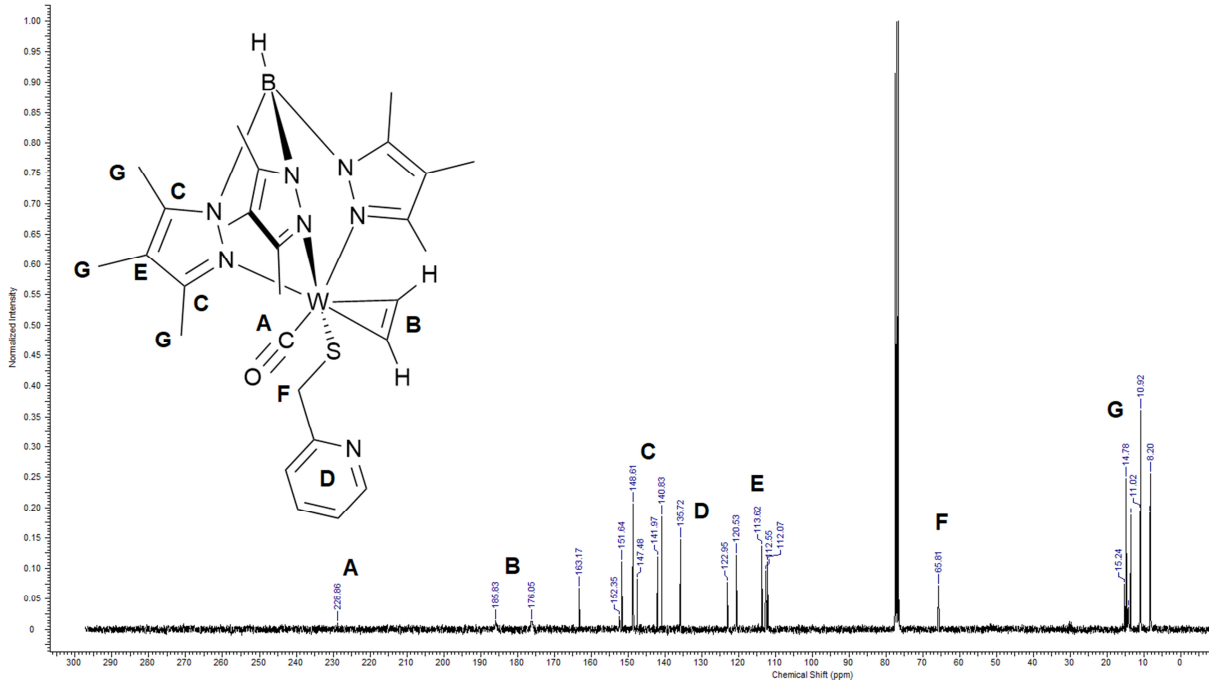



**Figure S22.** $^{13}$C NMR of $\mathbf{3}^{\mathbf{SMePy}}$ ($CDCl_3$, 63 MHz, 299 K).

### 4.1.2 $3^{Br}$

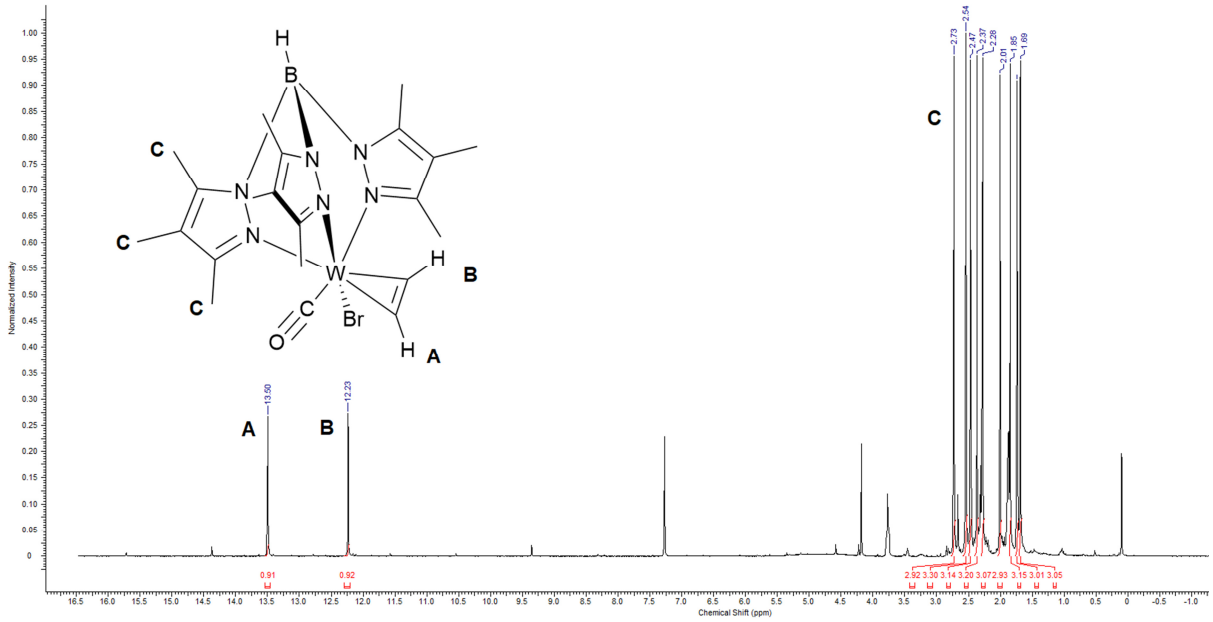



**Figure S23.** $^{1}$H NMR of $\mathbf{3^{Br}}$ ($CDCl_3$, 300 MHz, 298 K).

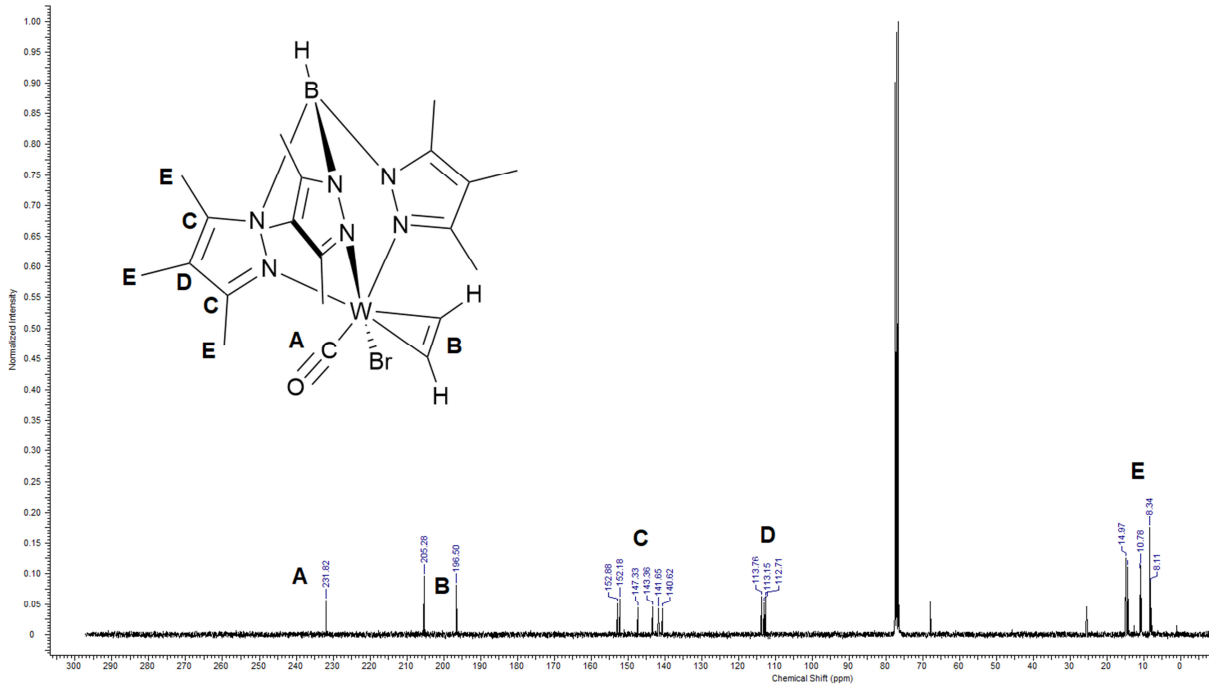



**Figure S24.** $^{13}$C NMR of $\mathbf{3^{Br}}$ ($CDCl_3$, 75 MHz, 298 K).

### 4.1.3 $3^{OTf}$

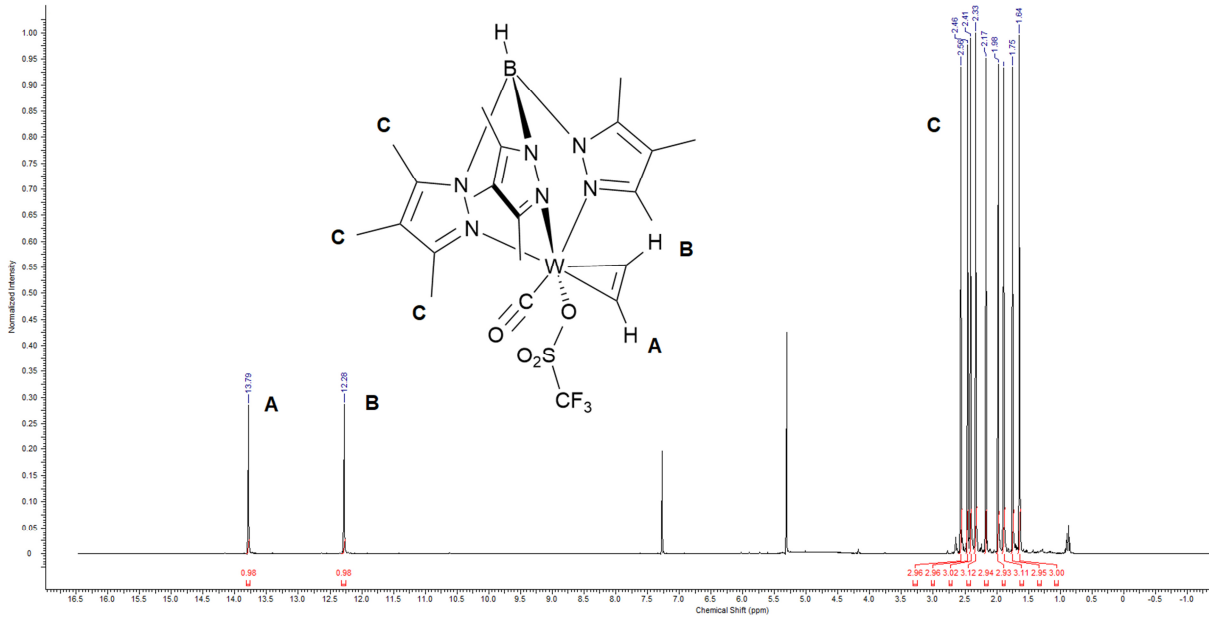



**Figure S25.** $^{1}$H NMR of $\mathbf{3^{OTf}}$ ($CDCl_3$, 300 MHz, 298 K).

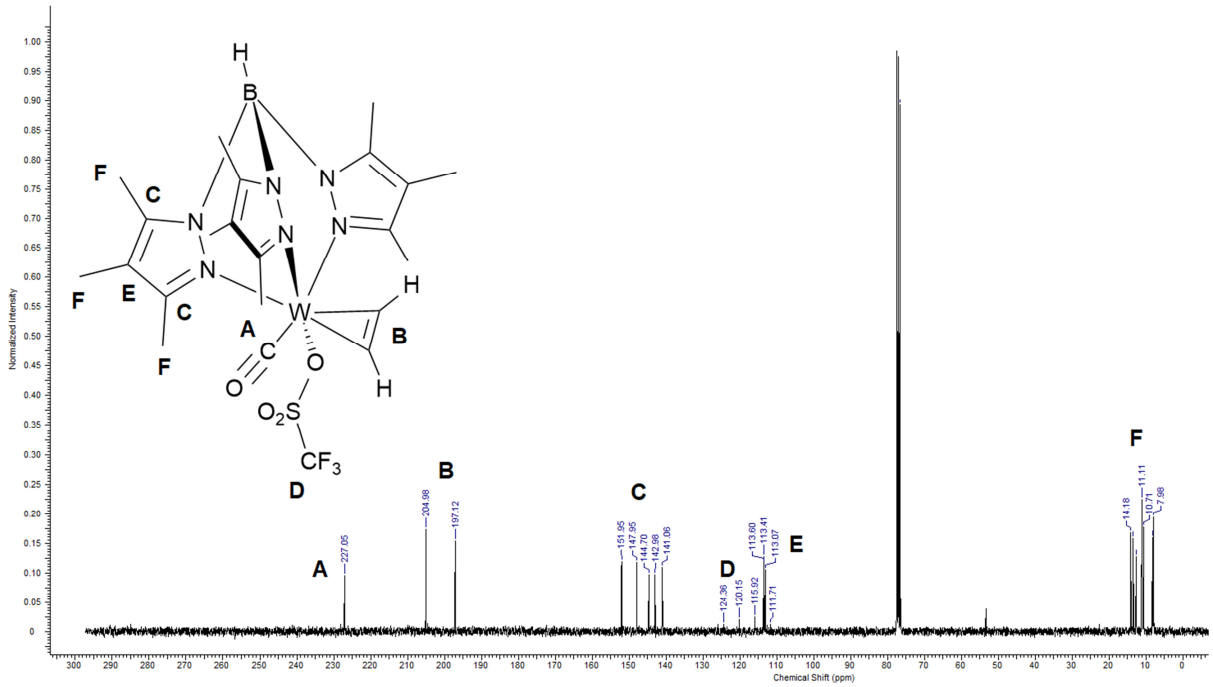



**Figure S26.** $^{13}$C NMR of $\mathbf{3^{OTf}}$ ($CDCl_3$, 75 MHz, 298 K).

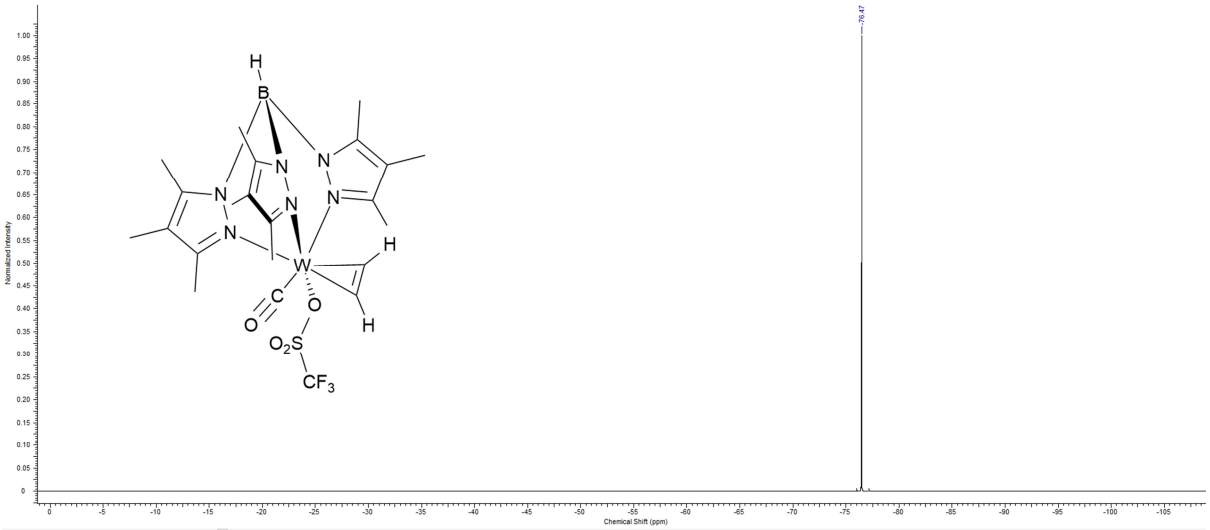



**Figure S27.** $^{19}F$ NMR of $\mathbf{3^{OTf}}$ ($CDCl_3$, 282 MHz, 298 K).

## 4.2 [Tp*W(CO)L($\eta^2$-$C_2${H}{$PPh_3$})] $\mathbf{4^L}$

### 4.2.1 $\mathbf{4^{SMePy}}$

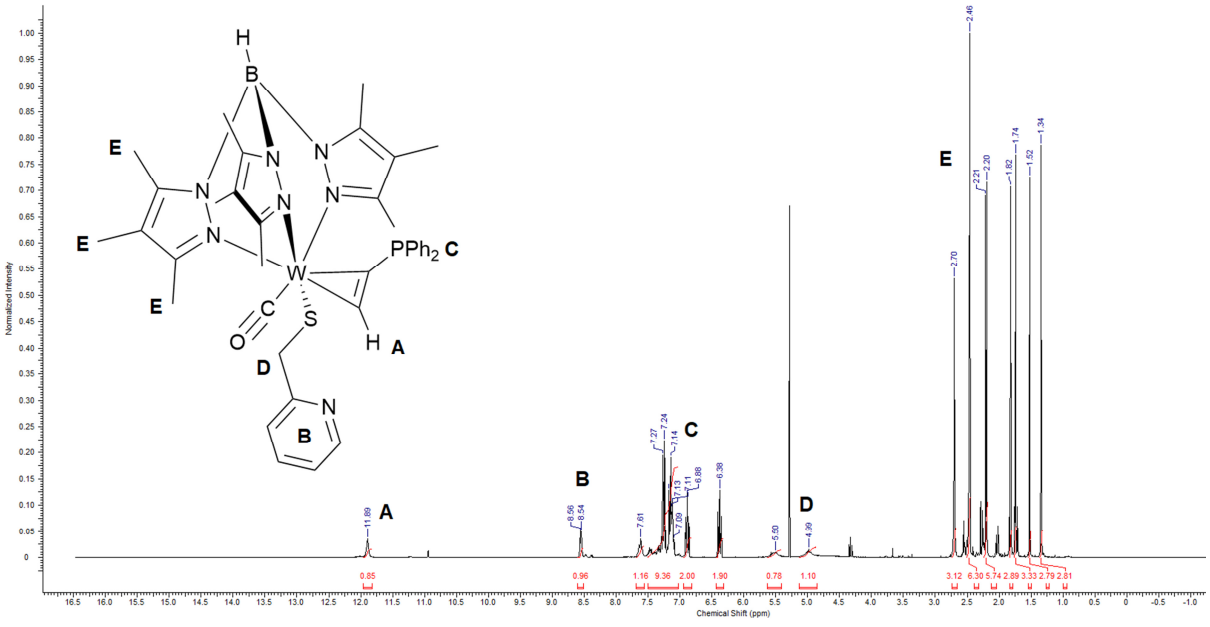



**Figure S28.** $^1H$ NMR of $\mathbf{4^{SMePy}}$ ($CDCl_3$, 300 MHz, 298 K).

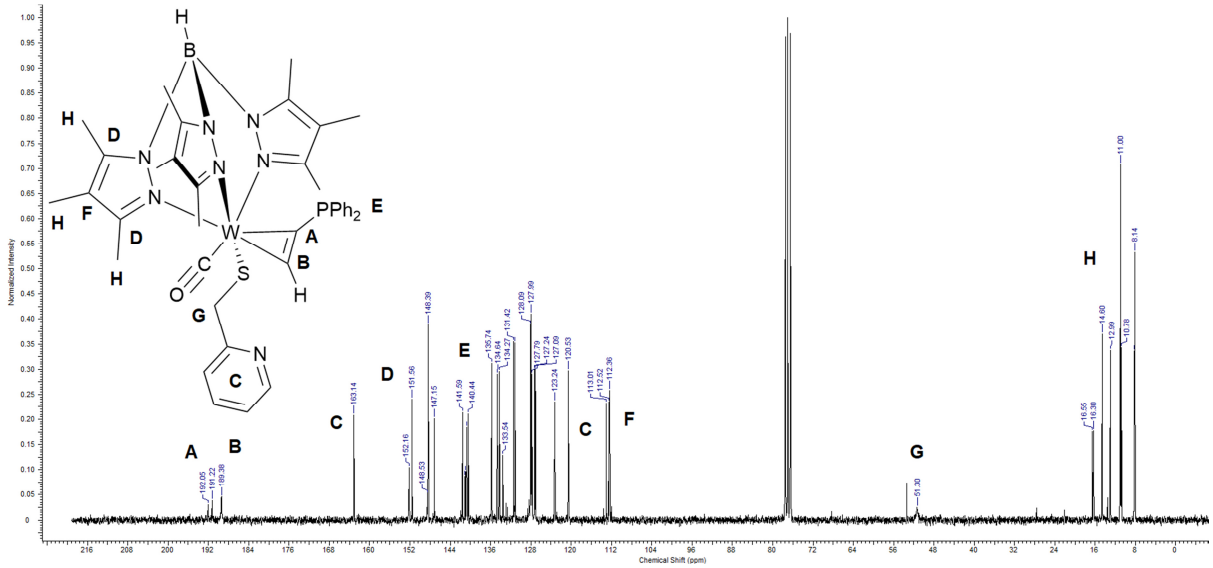


**Figure S29.** $^{13}$C NMR of **4**$^{\mathbf{SMePy}}$ ($CDCl_3$, 63 MHz, 300 K). $^{13}$CO not resolved.

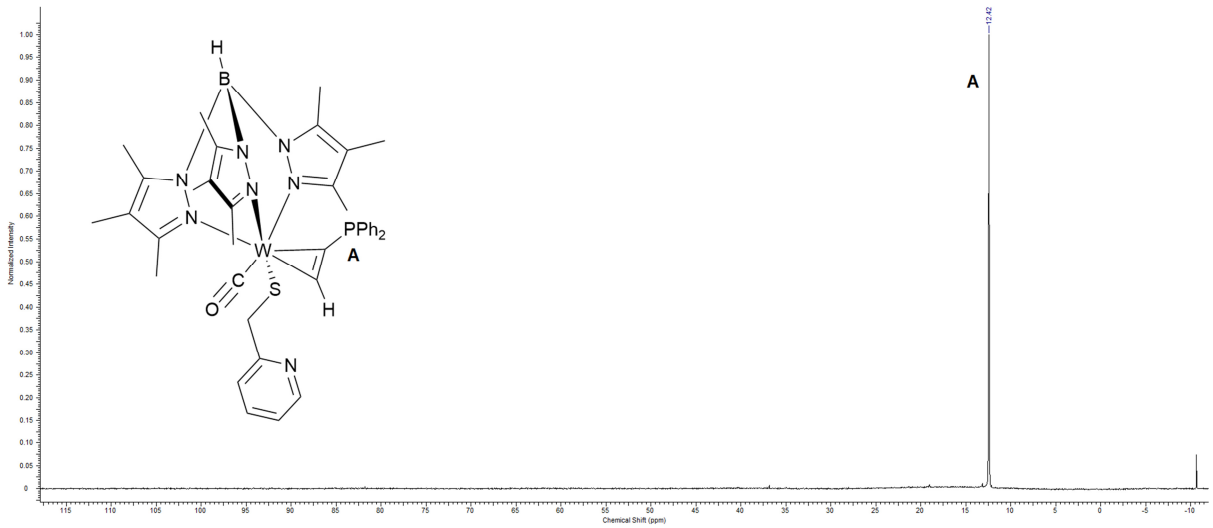


**Figure S30.** $^{31}$P NMR of **4**$^{\mathbf{SMePy}}$ ($CDCl_3$, 121 MHz, 298 K).

### 4.2.2 $4^{Br}$

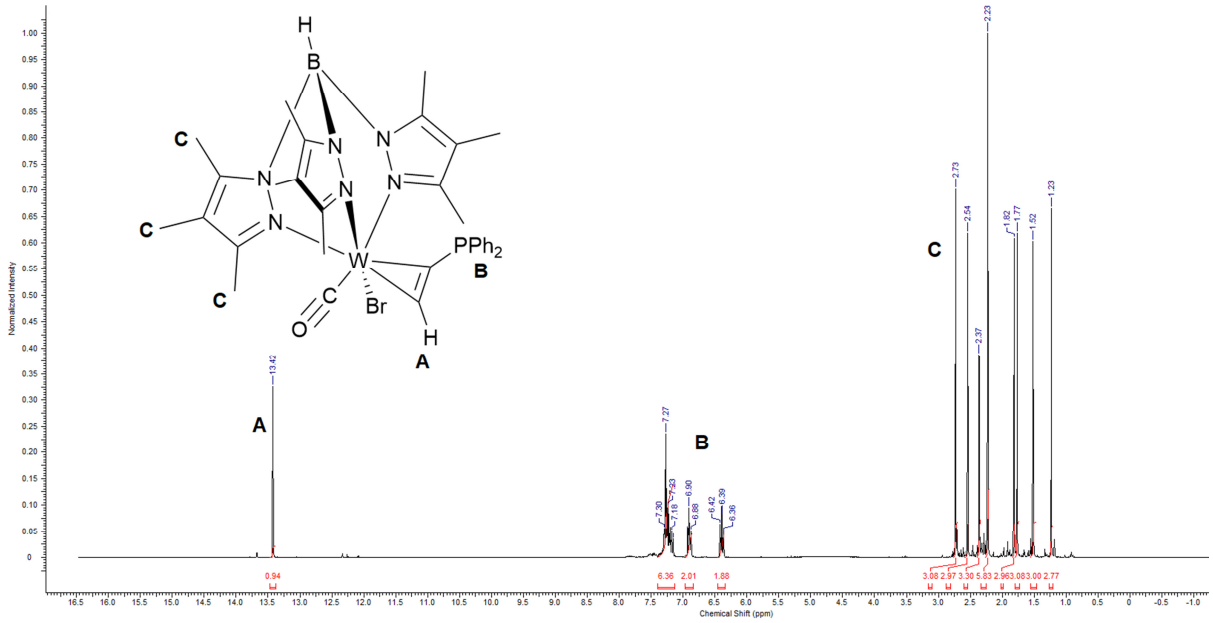



**Figure S31.** $^{1}$H NMR of $\mathbf{4}^{Br}$ ($CDCl_3$, 300 MHz, 298 K).

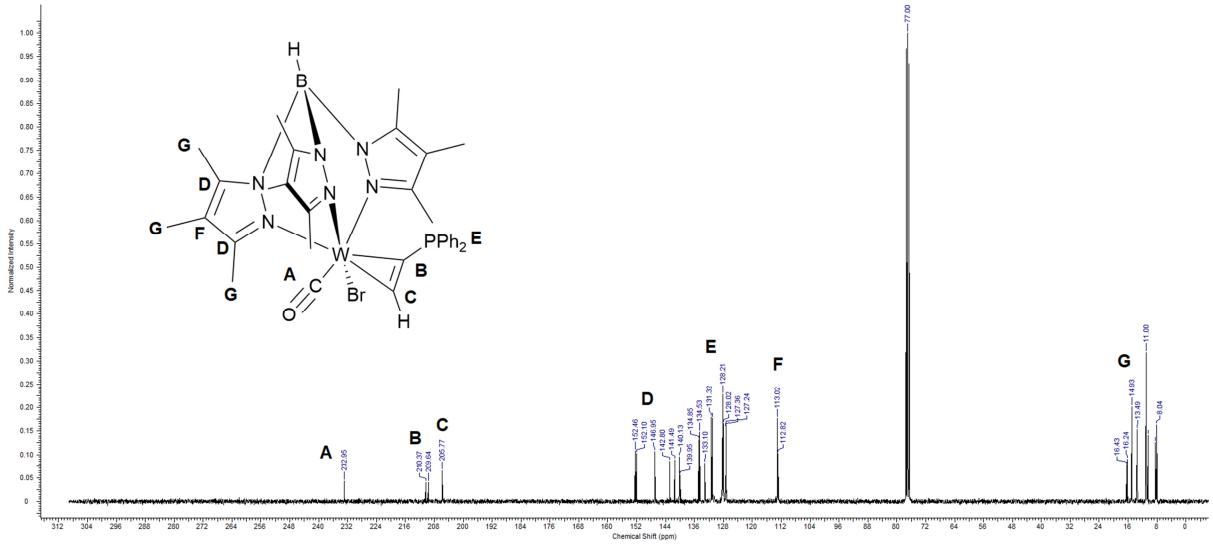



**Figure S32.** $^{13}$C NMR of $\mathbf{4}^{Br}$ ($CDCl_3$, 75 MHz, 298 K).

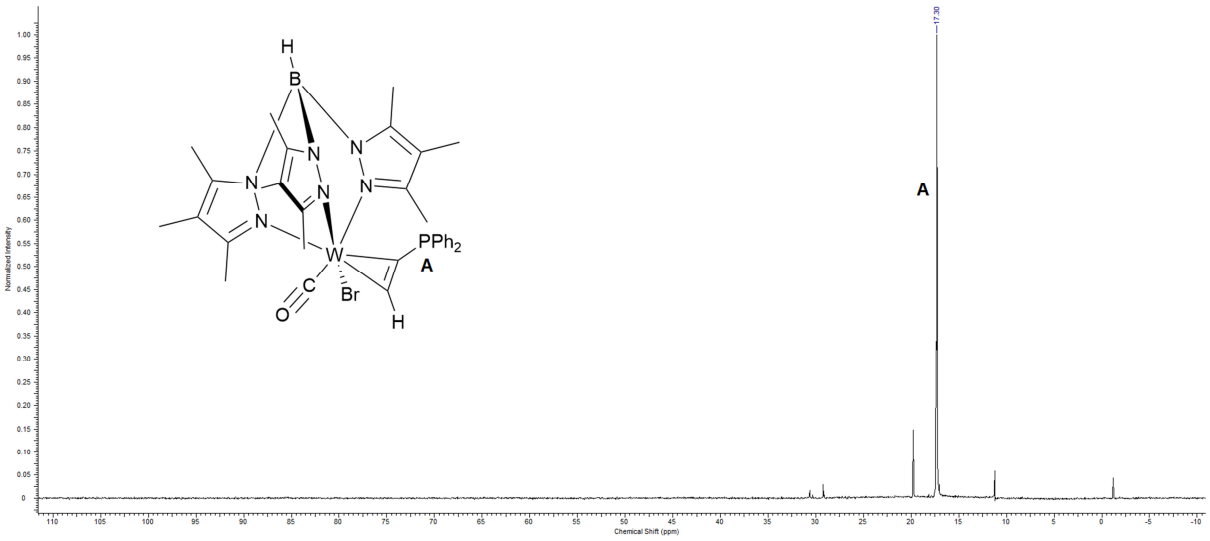



**Figure S33.** $^{31}$P NMR of **4$^{Br}$** ($CDCl_3$, 121 MHz, 299 K).

## 4.2.3 4$^{OTf}$

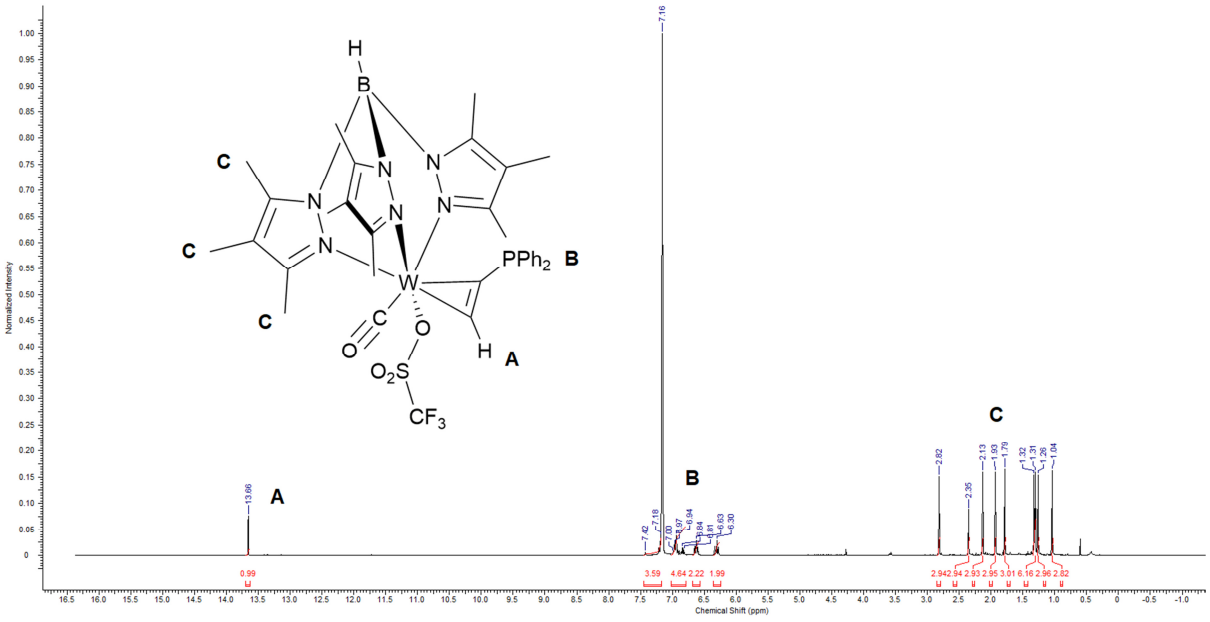



**Figure S34.** $^{1}$H NMR of **4$^{OTf}$** ($C_6D_6$, 300 MHz, 298 K). Low concentration due to low solubility.

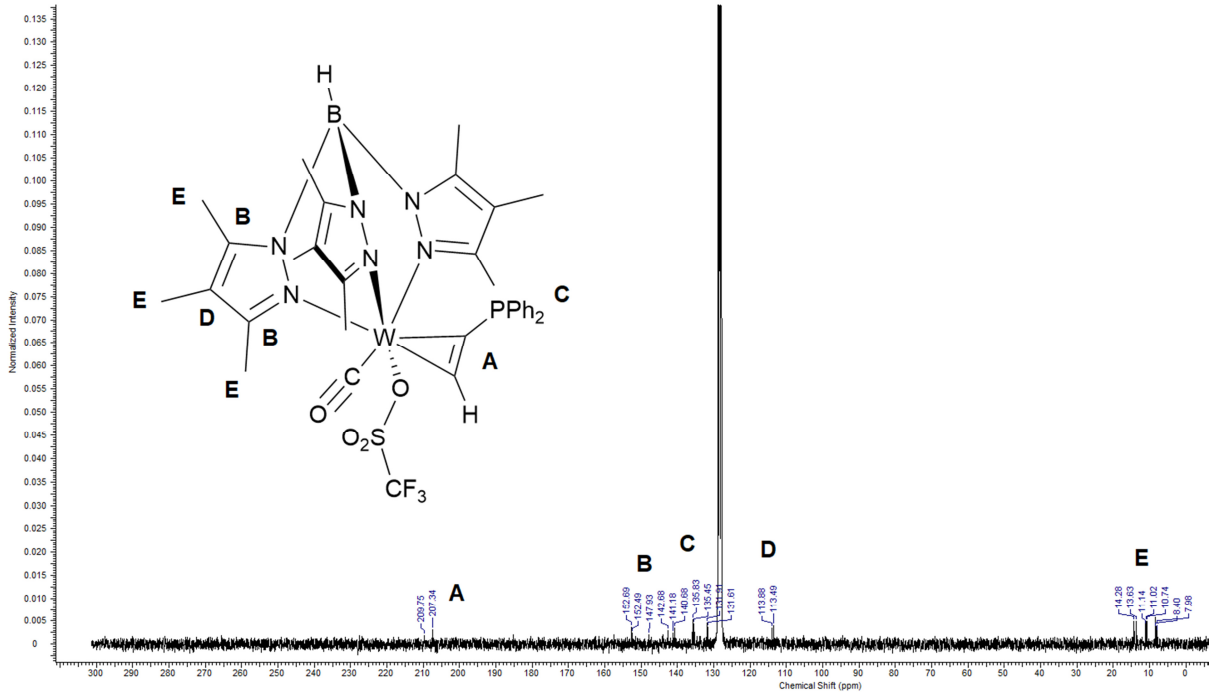



**Figure S35.** $^{13}C$ NMR of **4**$^{OTf}$ ($C_6D_6$, 63 MHz, 298 K). Low concentration due to low solubility.

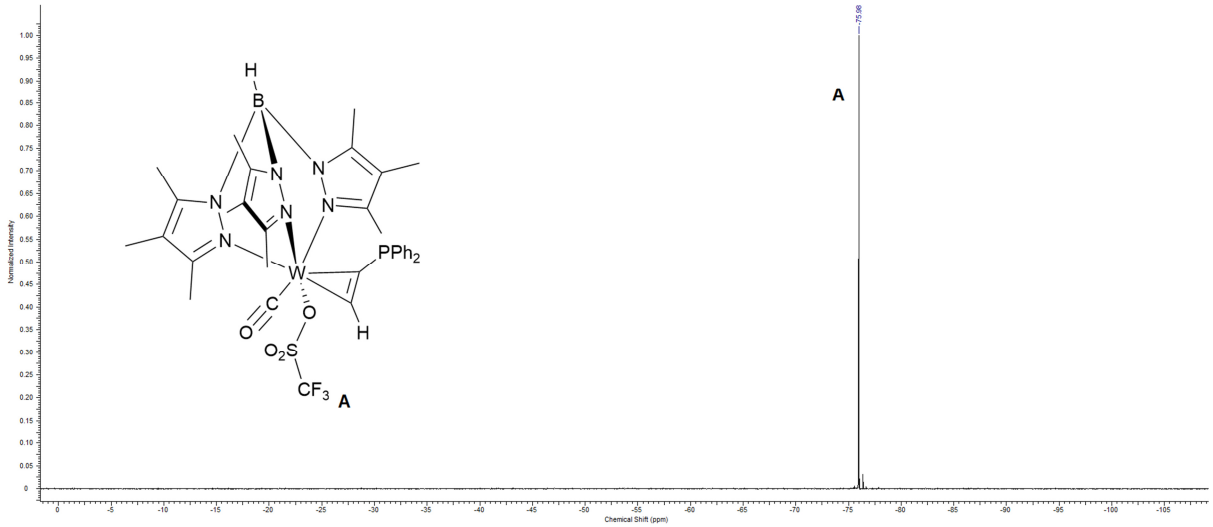



**Figure S36.** $^{19}F$ NMR of **4**$^{OTf}$ ($C_6D_6$, 282 MHz, 298 K). Low concentration due to low solubility.

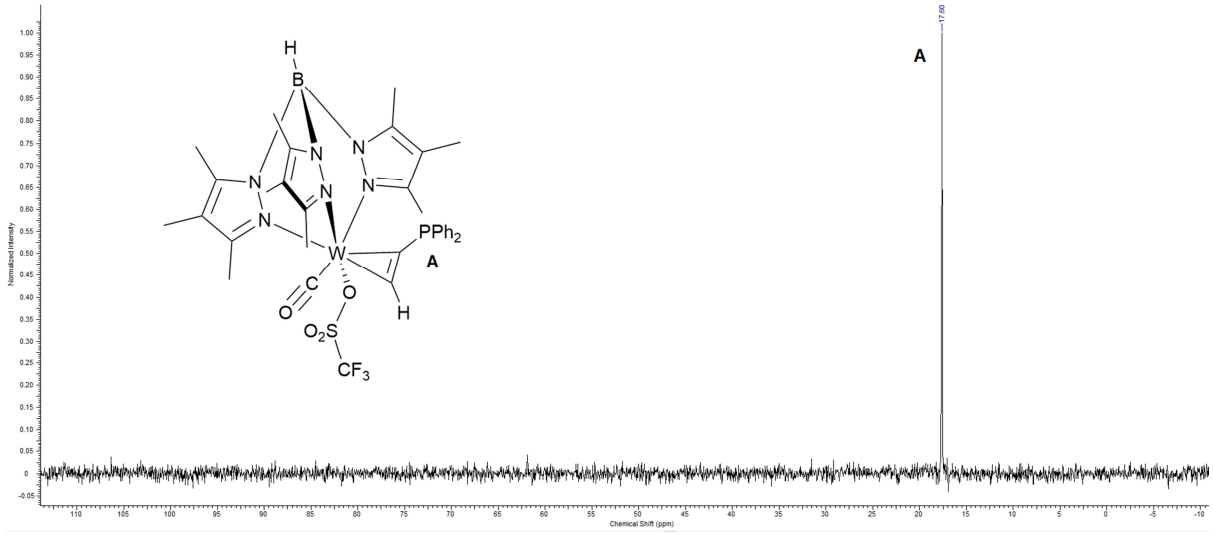



**Figure S37.** $^{31}P$ NMR of $\mathbf{4}^{\mathbf{OTf}}$ ($C_6D_6$, 121 MHz, 298 K). Low concentration due to low solubility.

## 4.3 [Tp*W(CO)L($\eta^2$-$C_2${$PPh_3$}$_2$)] $\mathbf{5}^{\mathbf{L}}$

### 4.3.1 $\mathbf{5}^{\mathbf{SMePy}}$

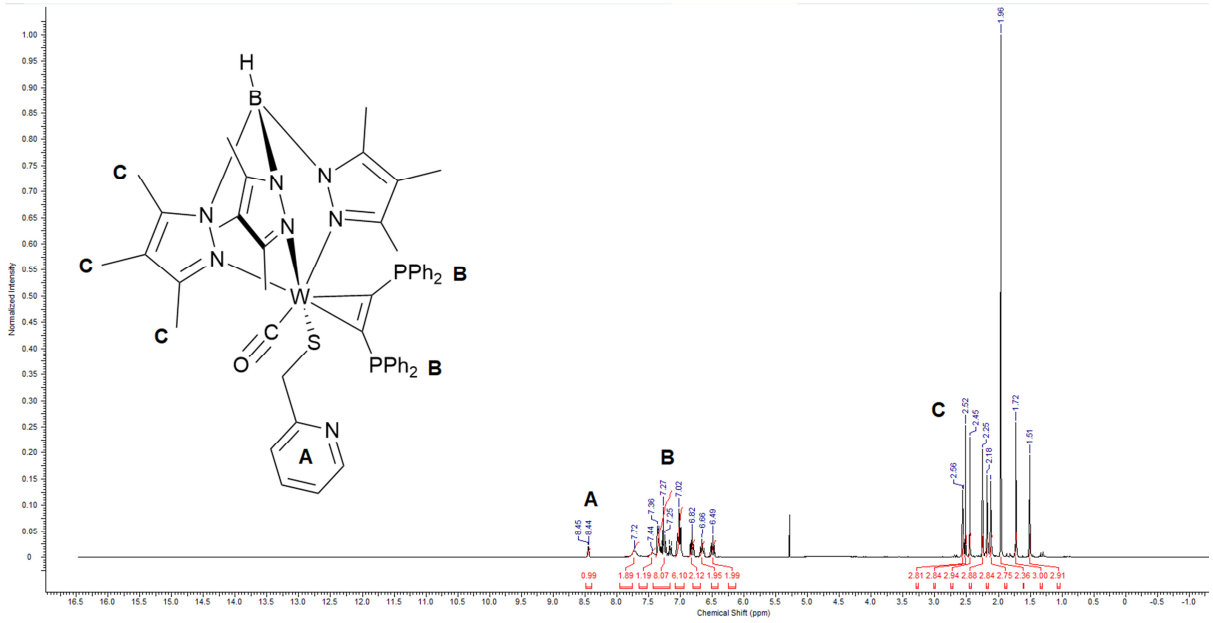



**Figure S38.** $^{1}H$ NMR of $\mathbf{5}^{\mathbf{SMePy}}$ ($CDCl_3$, 300 MHz, 298 K). Note very broad $CH_2$ protons at ca. 5 ppm.

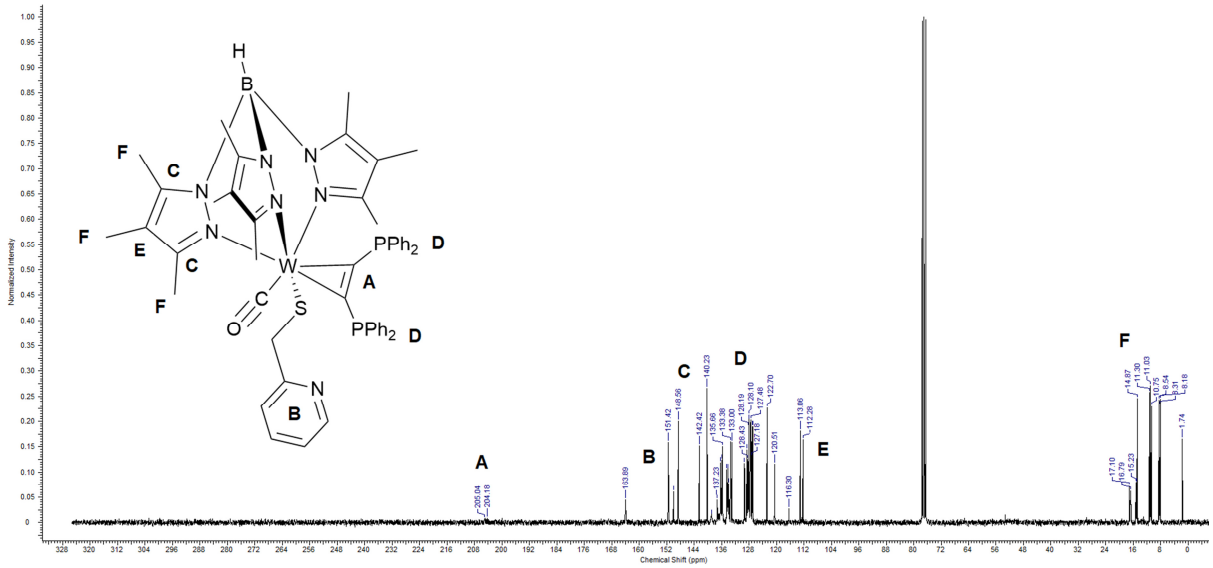



**Figure S39.** $^{13}$C NMR of **5**$^{\mathbf{SMePy}}$ ($CDCl_3$, 63 MHz, 300 K).$^{13}CH_2$ not resolved.

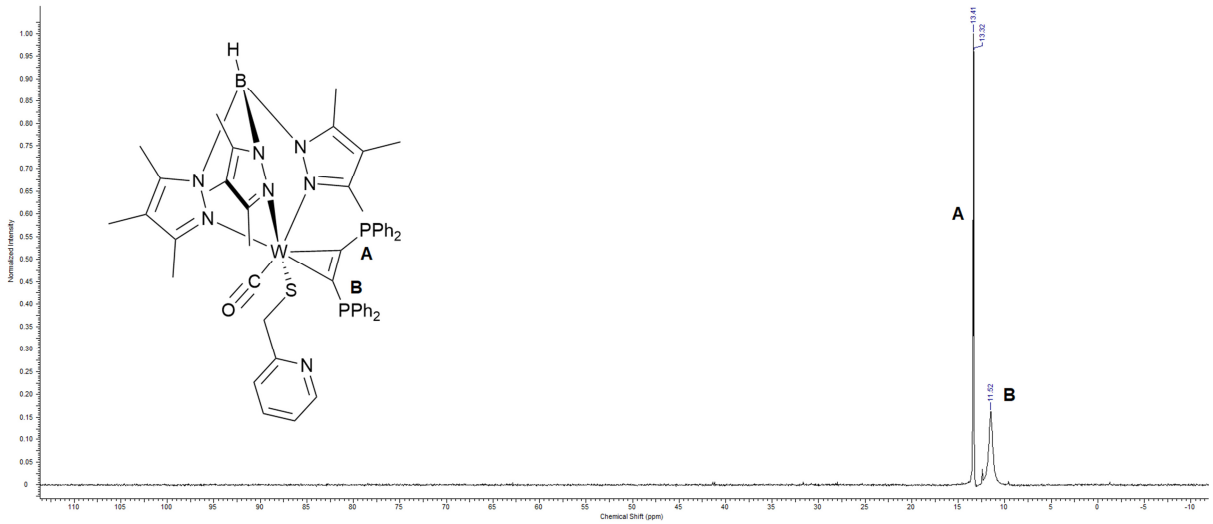



**Figure S40.** $^{31}$P NMR of **5**$^{\mathbf{SMePy}}$ ($CDCl_3$, 121 MHz, 298 K).

### 4.3.2 $5^{Br}$

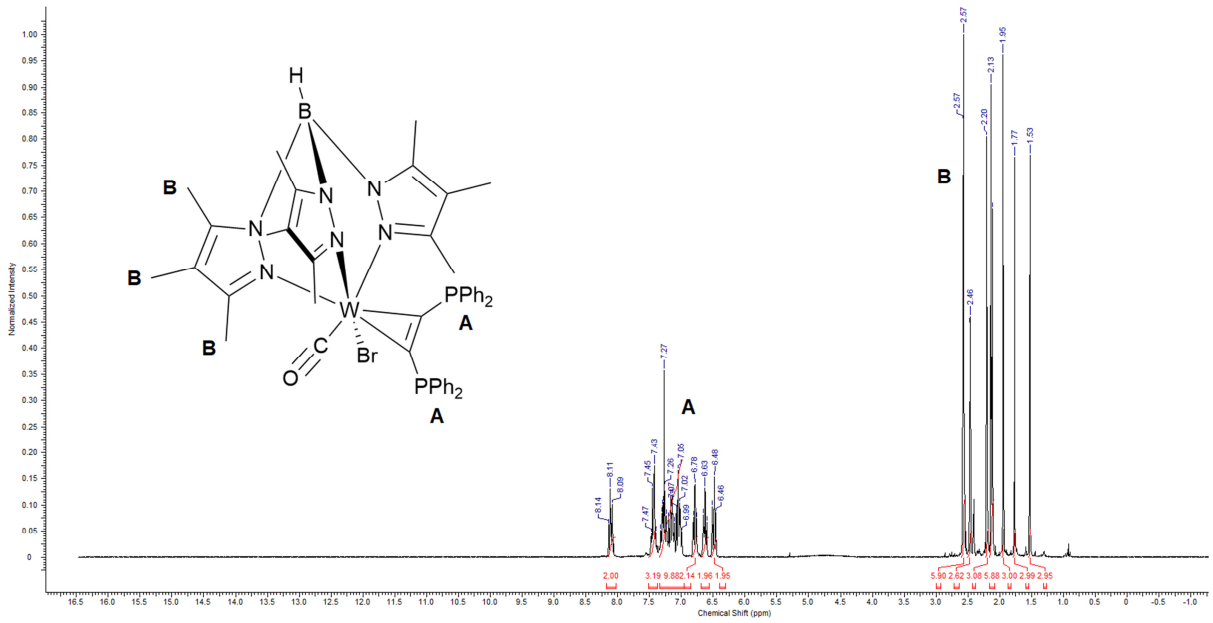



**Figure S41.** $^{1}$H NMR of $\mathbf{5^{Br}}$ ($CDCl_3$, 300 MHz, 298 K).

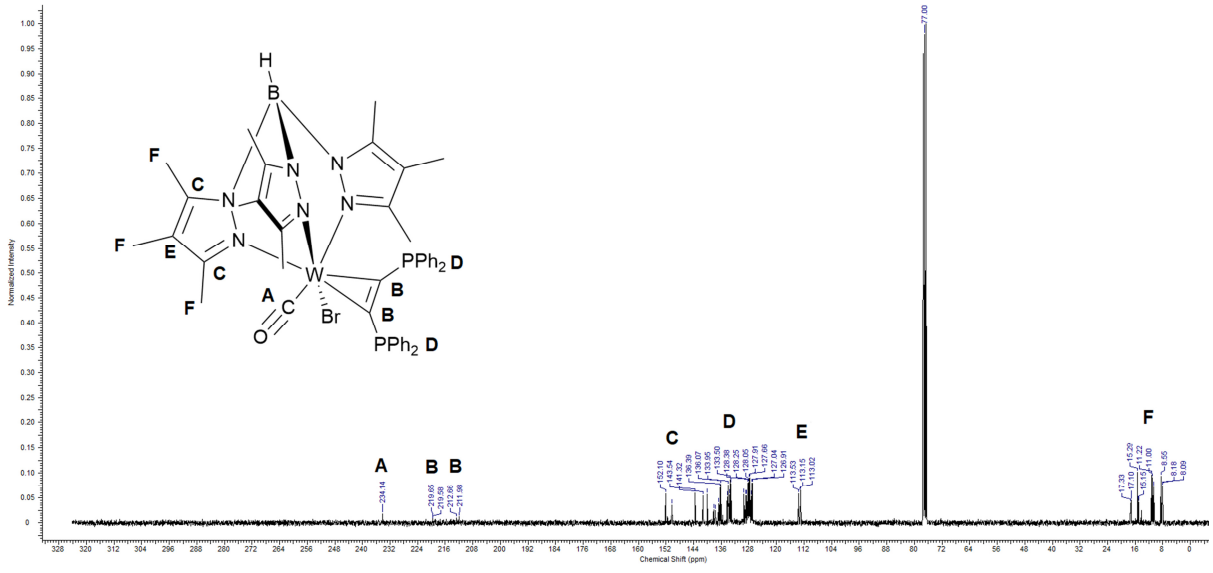



**Figure S42.** $^{13}$C NMR of $\mathbf{5^{Br}}$ ($CDCl_3$, 75 MHz, 298 K).

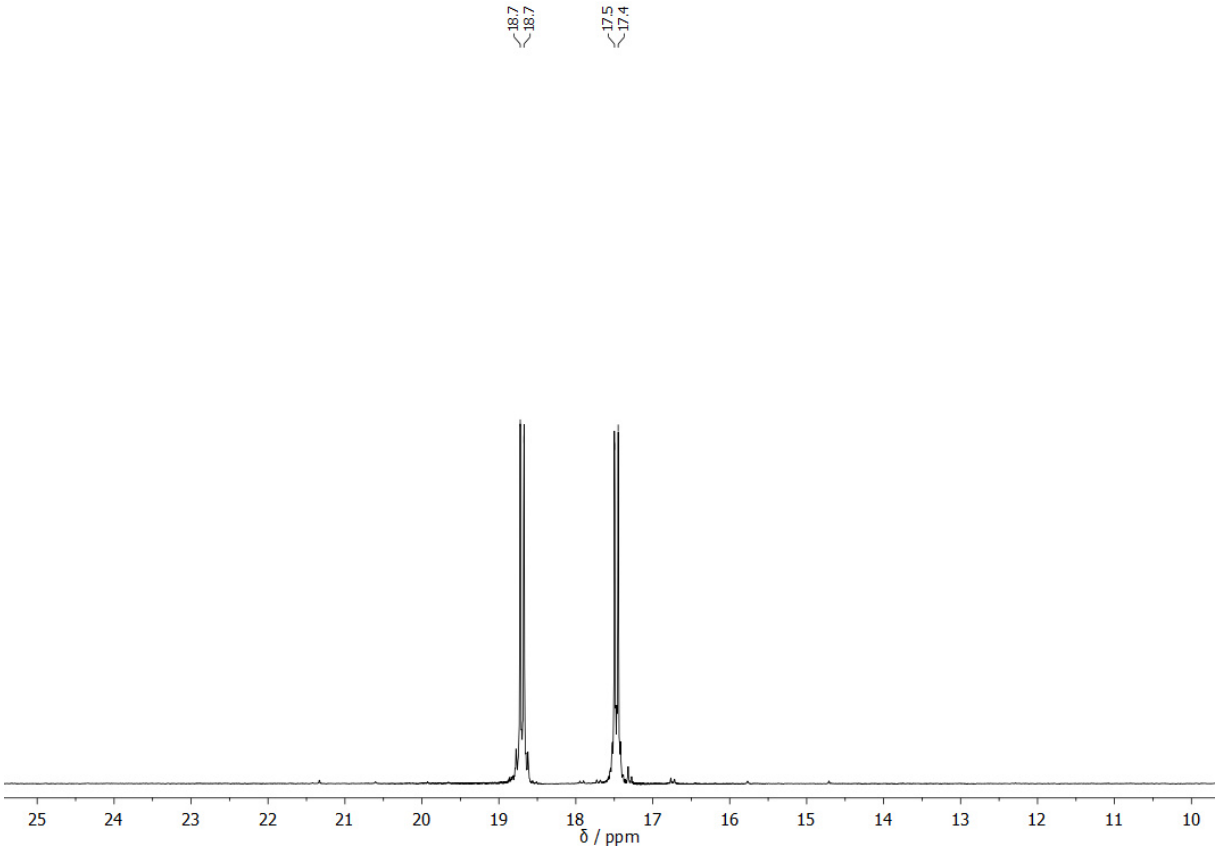



**Figure S43.** $^{31}$P NMR of **5$^{Br}$** ($CDCl_3$, 121 MHz, 298 K).

### 4.3.3 5$^{OTf}$

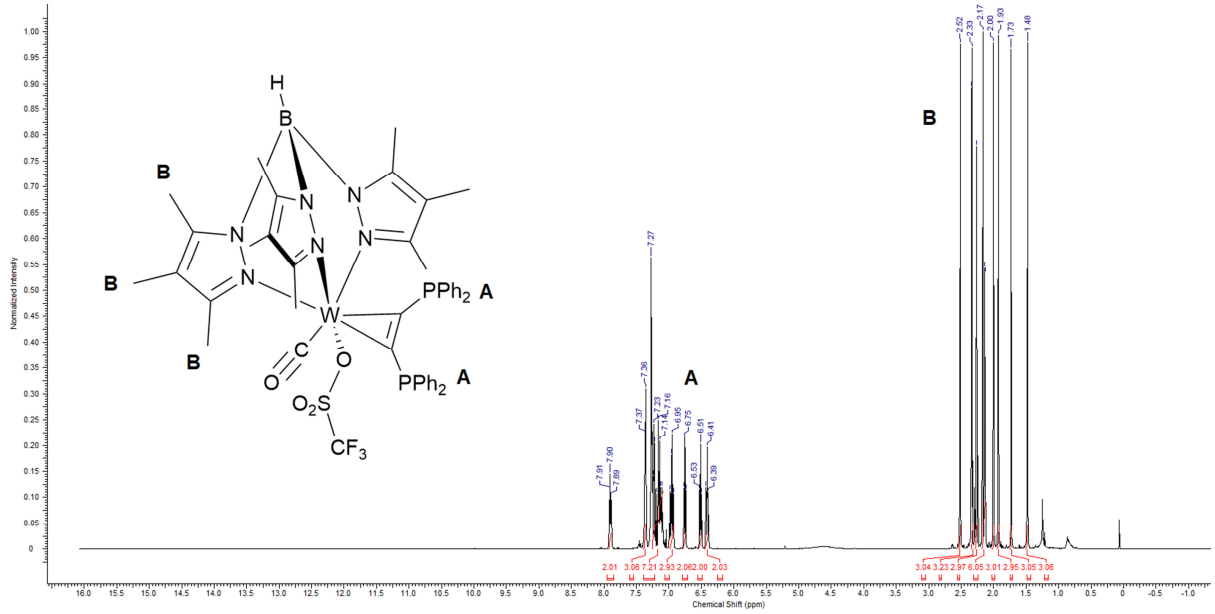



**Figure S44.** $^{1}$H NMR of **5$^{OTf}$** ($CDCl_3$, 500 MHz, 298 K).

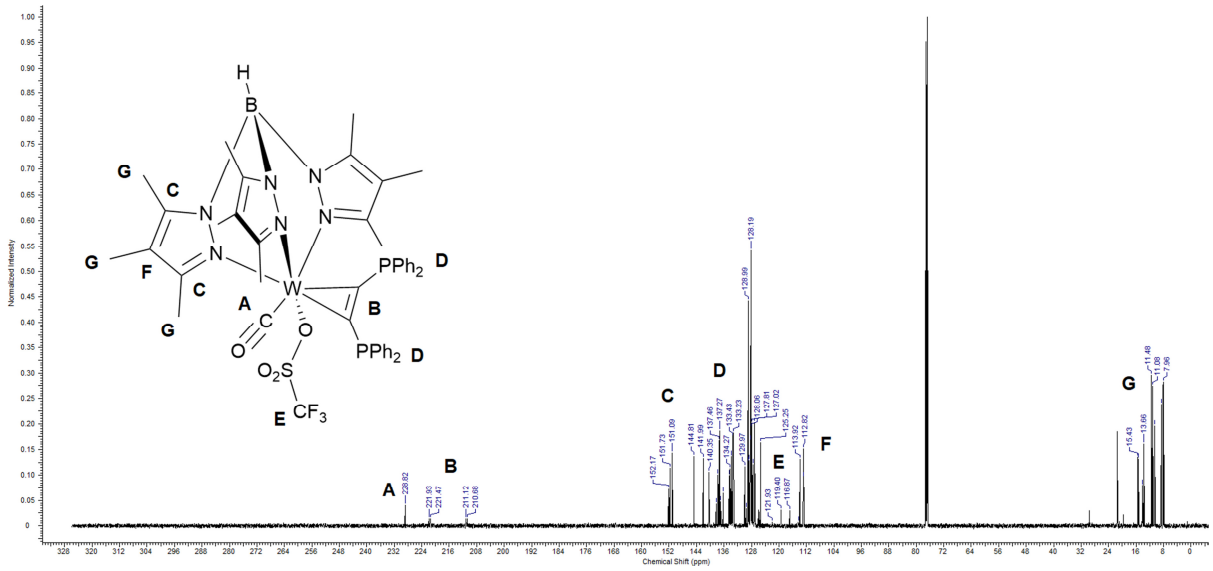



**Figure S45.** $^{13}C$ NMR of **5**$^{OTf}$ ($CDCl_3$, 126 MHz, 298 K).

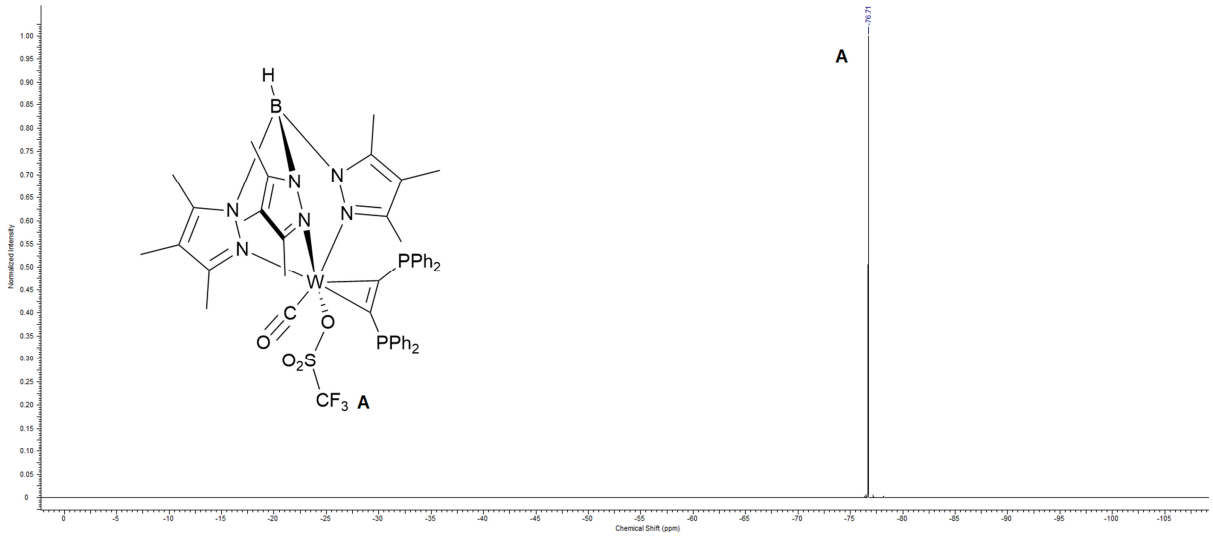



**Figure S46.** $^{19}F$ NMR of **5**$^{OTf}$ ($CDCl_3$, 471 MHz, 298 K).

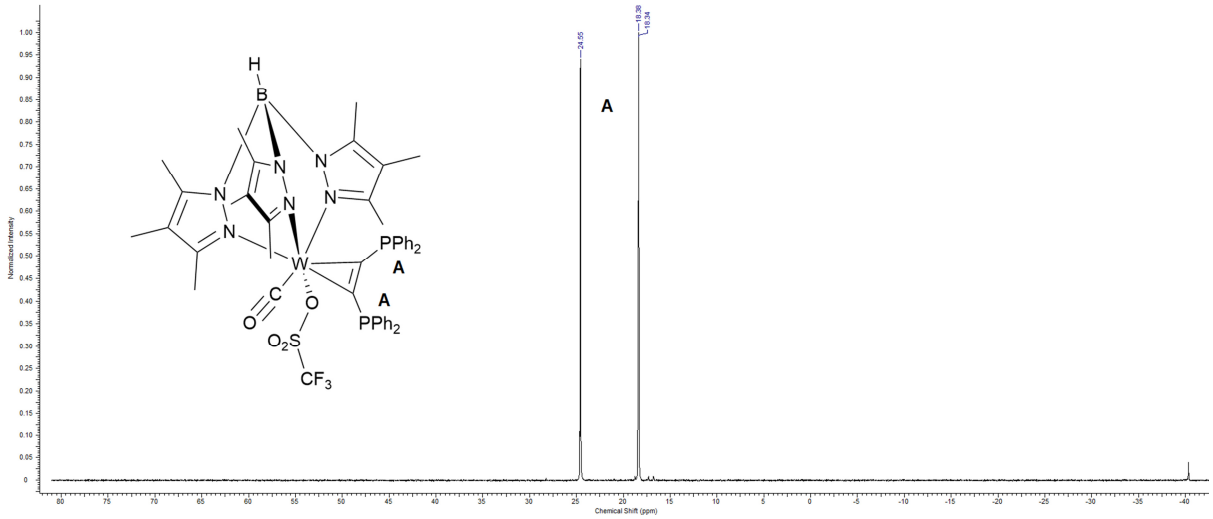



**Figure S47.** $^{31}$P NMR of **5$^{OTf}$** ($CDCl_3$, 202 MHz, 298 K).

## 4.4 (5$^{Br}$)$PdCl_2$

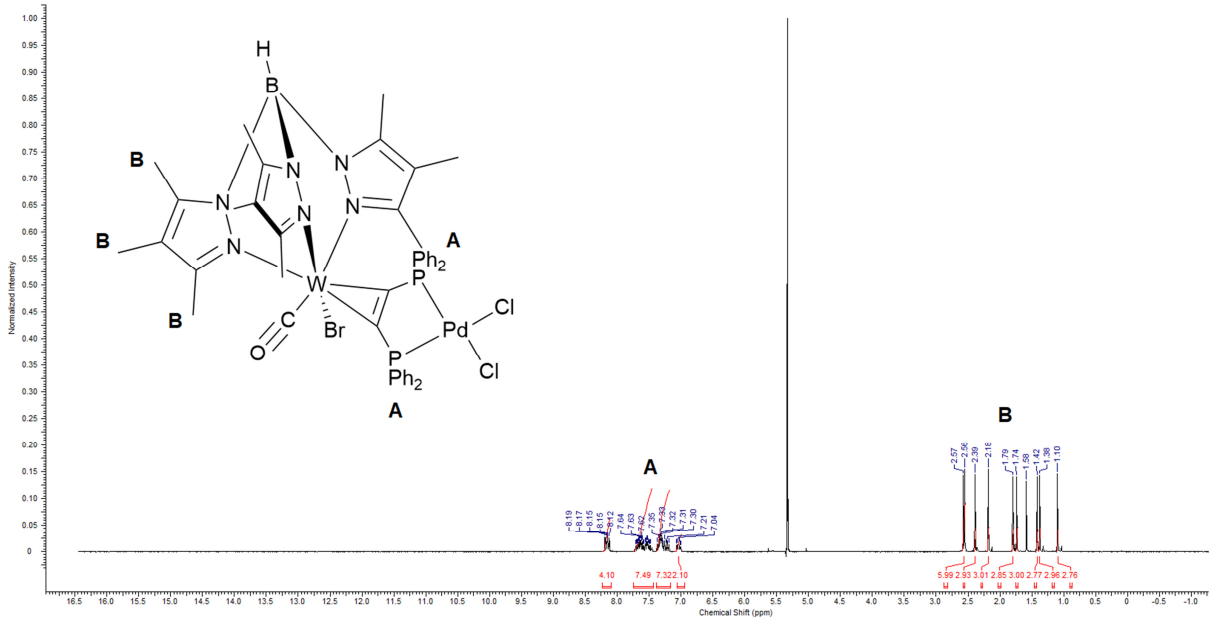



**Figure S48.** $^{1}$H NMR of (**5$^{Br}$**)**$PdCl_2$** ($CD_2Cl_2$, 300 MHz, 298 K).

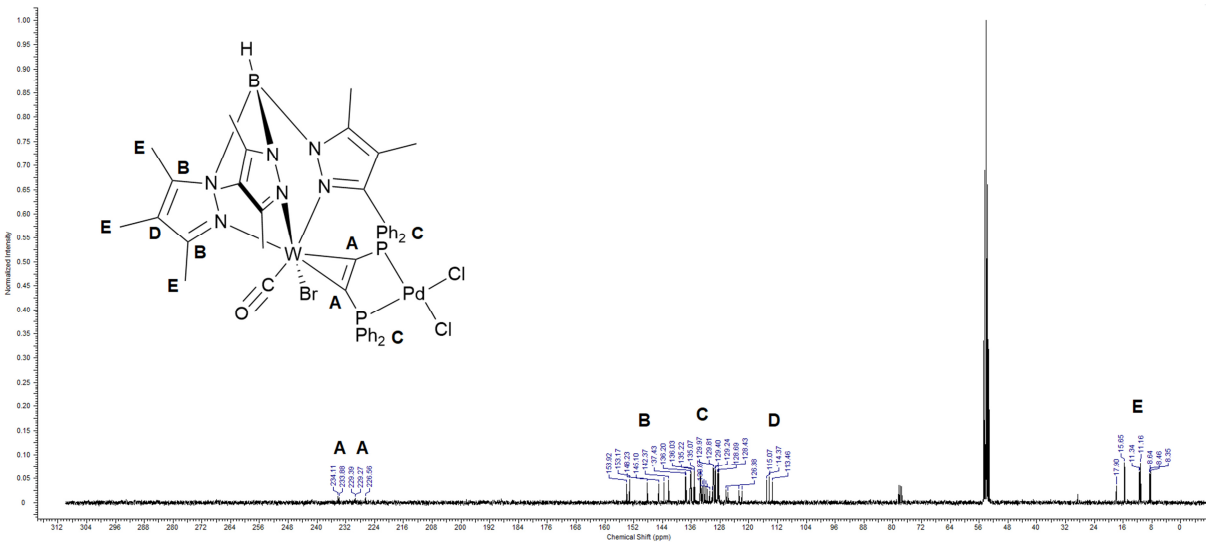



**Figure S49.** $^{13}C$ NMR of (**5$^{Br}$**)**PdCl$_2$** ($CD_2Cl_2$, 75 MHz, 299 K).

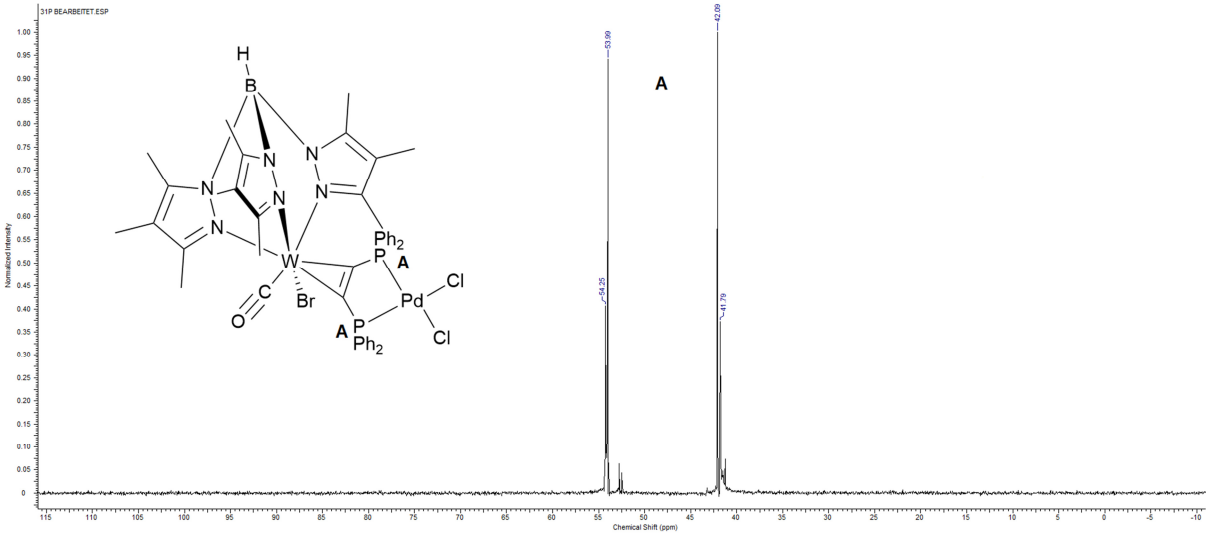



**Figure S50.** $^{31}P$ NMR of (**5$^{Br}$**)**PdCl$_2$** ($CD_2Cl_2$, 121 MHz, 299 K).

# 4 References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S2 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, **1996**, 96, 877–910.

S3 G. M. Sheldrick, *SHELXS-2013, Program for Solution of Crystal Structure*, Univ. Göttingen, **2013**.

S4 G. M. Sheldrick, *SHELXL-2013, Program for Refinement of Crystal Structure*, Univ. Göttingen, **2013**.