# **Electronic Supplementary Information for**

# Ring Expansion of a 2-Rhodaoxetane: Insertion Chemistry with Unsaturated Molecules

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**I. General Considerations**: All reactions were carried out under nitrogen using standard Schlenk techniques. All reagents were used as received from commercial suppliers with no further purification. Tris(2-pyridylmethyl)amine was prepared by a slight modification of the literature procedure<sup>1</sup> and recrystallized from boiling petroleum ether (bp 35-60 °C) to give bright yellow flakes. Rhodaoxetane [**1**]**PF**<sub>6</sub>,<sup>2</sup> NaBAr<sup>F</sup><sub>4</sub><sup>3</sup> and ethyl 3-phenylpropiolate<sup>4</sup> were prepared according to the literature procedures. NMR yields are averaged over at least two separate reactions and were determined by referencing well-resolved product signals versus the aryl protons of 1,3,5-trimethoxybenzene (for complexes [**3**]**PF**<sub>6</sub> and [**4a-f**]**PF**<sub>6</sub>) or the methyl protons of acetophenone (for complexes [**2a-b**]**PF**<sub>6</sub>) as an internal standard. The relaxation delay for quantitative <sup>1</sup>H NMR spectroscopic experiments was set to at least 5 times the longest T<sub>1</sub> present. Room temperature corresponds to ~23 °C.

NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers and are referenced to residual protio solvent (5.32 ppm for  $CD_2Cl_2$ , 2.05 ppm for acetone-d<sub>6</sub>, and 3.31 ppm for MeOD) for <sup>1</sup>H NMR, solvent peaks (53.84 ppm for  $CD_2Cl_2$ , 29.84 ppm for acetone-d<sub>6</sub> and 49.00 ppm for MeOD) for <sup>13</sup>C NMR and 1-fluoro-3-nitrobenzene (-112.0 ppm)<sup>5</sup> for <sup>19</sup>F NMR. Mass spectrometry data were recorded on a Waters LC/MS for low resolution and a Waters/Micromass LCT for high resolution.

#### **II.** Organometallic Syntheses

Synthesis of [2a]PF<sub>6</sub>



To a suspension of  $[1]PF_6$  (19.7 mg, 0.034 mmol, 1.0 equiv) in dichloromethane (5 mL) was added dimethylacetylene dicarboxylate (4.2  $\mu$ L, 1.0 equiv). The resulting pale yellow slurry was stirred at RT for 1 hour, during which time the solution became homogeneous and darker yellow. To this solution was added Et<sub>2</sub>O (15 mL), which caused the precipitation of a fine, white solid. The supernatant was decanted, the residue was washed with hexanes and dried in vacuo to give 14.6 mg (60 % yield) of [2a]PF<sub>6</sub>.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ . 8.73 (d, J = 5.5 Hz, 1H), 8.30 (d, J = 5.6 Hz, 2H), 7.76-7.69 (m, 3H), 7.40-7.32 (m, 4H), 7.21 (t, J = 6.5 Hz, 2H), 5.90 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 16.3 Hz, 2H), 4.76 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 16.3 Hz, 2H) 4.69 (s, 2H), 4.02 (t, J = 7.4 Hz, 2H), 3.55 (s, 3H), 3.14 (dt, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, <sup>2</sup>J<sub>Rh,H</sub> = 2.8 Hz, 2H), 3.12 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  177.52, 165.09, 161.65, 160.51, 151.53, 149.14, 147.79, 141.92 (d, <sup>1</sup>J<sub>Rh,C</sub> = 34.4 Hz), 139.45, 138.96, 125.38, 124.81, 123.81, 122.76, 72.67, 68.88, 65.97, 51.89, 29.44 (d, <sup>1</sup>J<sub>Rh,C</sub> = 27.1 HZ). An HSQC experiment showed that the resonance for one of the Me groups was overlapping with the solvent signal.

HRMS (ESI) Calcd: 579.1115 (C<sub>26</sub>H<sub>28</sub>N<sub>4</sub>O<sub>5</sub>Rh<sup>+</sup>). Found 579.1110.

### Synthesis of [2b]PF<sub>6</sub>



To a suspension of [1]PF<sub>6</sub> (19.8 mg, 0.034 mmol) in dichloromethane (5 mL) was added diethylacetylene dicarboxylate (5.5  $\mu$ L, 1.0 equiv). The resulting slurry was stirred at RT for 1 hour, during which time the solution became homogeneous and darker yellow. To this solution was added Et<sub>2</sub>O (15 mL), which caused the precipitation of a fine, white solid. The supernatant was decanted, the residue was washed with hexanes and

dried in vacuo to give 11.8 mg (46 % yield) of [2b]PF<sub>6</sub>.

 $\mathsf{PF}_6^{\Theta}$ 

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.73 (d, J = 5.7 Hz, 1H), 8.32 (d, J = 5.8 Hz, 2H), 7.75-7.68 (m, 3H), 7.40-7.31 (m, 4H), 7.21 (t, J = 6.7 Hz, 2H), 5.96 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 16.3 Hz, 2H), 4.74 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 16.3 Hz, 2H), 4.68 (s, 2H), 4.03 (t, J = 7.4 Hz, 2H), 3.99 (q, J = 7.3 Hz, 2H), 3.59 (q, J = 7.4 Hz, 2H), 3.99 (q,

7.3 Hz, 2H), 3.13 (dt,  ${}^{3}J_{H,H} = 7.3$  Hz,  ${}^{2}J_{Rh,H} = 2.9$  Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H), 0.76 (t, J = 7.2 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ. 177.35, 165.13, 161.20, 160.53, 151.56, 149.27, 147.76, 141.52 ppm (d,  ${}^{1}J_{Rh,C} = 34.5$  Hz), 139.39, 138.94, 125.34, 124.79, 123.87, 122.74, 72.54, 68.78, 65.87, 61.00, 60.90, 29.41 (d,  ${}^{1}J_{Rh,C} = 26.7$  Hz), 14.39, 13.79.

HRMS (ESI) Calcd: 607.1428 (C<sub>28</sub>H<sub>32</sub>N<sub>4</sub>O<sub>5</sub>Rh<sup>+</sup>). Found 607.1436.

# Synthesis of [2b]BAr<sup>F</sup><sub>4</sub>



Cramer's dimer,  $[Rh(Cl)(C_2H_4)_2]_2$  (34.8 mg, 0.090 mmol, 0.5 equiv) and TPA (52.8 mg, 0.18 mmol, 1.0 equiv) were placed in a round bottom flask and the mixture was then cooled in a -78 °C bath. The flask was evacuated and backfilled with nitrogen gas three times. Sparged dichloromethane (2 mL) was added, and the suspension was stirred at -78 °C for 1 hour. The acetone/dry ice

bath was then replaced with an ice/brine bath, and subsequently 30 % aqeuous  $H_2O_2$  (40 uL, 0.35 mmol, 2.0 equiv) was added to the reaction mixture, which quickly developed a red-brown residue. After stirring for 1 hour, the pale yellow supernatant was decanted and the residue was dried *in vacuo* before NaBAr<sup>F</sup><sub>4</sub> (164.9 mg, 0.19 mmol, 1.0 equiv) and dichloromethane (2 mL) was added. After stirring this orange-yellow solution for 20 minutes, diethylacetylene dicarboxylate (40 µL, 0.25 mmol, 1.4 equiv) was added, causing a colour change to dark brown after a few minutes. The reaction was stirred for an additional hour, then was filtered through celite, which stranded a dark residue on the pad and gave an amber filtrate which was evaporated to dryness. Recrystallization of the solid residue from slow evaporation of a 2:1 DCM/hexanes solution gave 41.3 mg of [**2b]BAr**<sup>F</sup><sub>4</sub> (15 % yield) as X-ray quality crystals. Despite washing the

crystals with hexanes, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy show residual diethylacetylene dicarboxylate.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.75 (d, J = 5.4 Hz, 1H), 8.33 (d, J = 5.6 Hz, 2H), 7.78 (broad s, 8H), 7.72 (dt, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.4 Hz, 2H), 7.66 (dt, <sup>3</sup>J = 7.9 Hz, <sup>4</sup>J = 1.5 Hz, 1H), 7.55 (broad s, 4H), 7.34 (t, J = 6.4 Hz, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.26-7.18 (m, 3H), 6.11 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 16.2 Hz, 2H), 4.55 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 16.2 Hz, 2H), 4.51 (s, 2H), 4.03 (t, J = 7.2 Hz, 2H), 4.00 (q, J = 7.2 Hz, 2H), 3.55 (q, J = 7.2 Hz, 2H), 3.17 (dt, <sup>3</sup>J<sub>H,H</sub> = 7.2, <sup>2</sup>J<sub>Rh,H</sub> = 2.9 Hz, 2H), 1.16 (t, J = 7.1 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 177.61, 164.37, 162.13 (q, <sup>1</sup>J<sub>B,C</sub> = 49.9 Hz), 161.18, 159.40, 151.96, 149.77, 148.29, 139.53, 139.10, 135.21 (broad s), 129.20 (q, <sup>2</sup>J<sub>C,F</sub> = 32.3 Hz), 125.75, 125.12, 124.98 (q, <sup>1</sup>J<sub>C,F</sub> = 270.0 Hz), 123.54, 122.18, 117.91(m), 72.50, 69.18, 66.14, 61.13, 61.01, 29.76 (d, <sup>1</sup>J<sub>Rh,C</sub> = 27.6 Hz), 14.36, 13.74. The resonance due to C4 could not be observed, probably due to coupling to <sup>103</sup>Rh and the low intensity of quaternary carbon signals. The resonance may also be overlapping with signals from the BAr<sup>F</sup><sub>4</sub> anion.

### Synthesis of [3]PF<sub>6</sub>



In a Wilmad screw-cap NMR tube, a solution of [1]PF<sub>6</sub> (5.0 mg, 0.0086 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL) was chilled to -78 °C. An excess of CS<sub>2</sub> (1.0  $\mu$ L, 1.8 equiv) was added via microsyringe, the tube was inverted three times to thoroughly mix and the solution was left to slowly warm to RT over the course of 12 hours, giving compound [3]PF<sub>6</sub> in 76% yield by <sup>1</sup>H NMR spectroscopy, as well

as other minor TPA-containing impurities. Compound [3]PF<sub>6</sub> was found to decompose in solution at RT over ~5 days but was stable for 3 weeks when stored at -20  $^{\circ}$ C.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.67 (d, J = 5.7 Hz, 1H), 8.33 (d, J = 5.6 Hz, 2H), 7.82 (dt, <sup>3</sup>J = 5.6Hz, <sup>4</sup>J = 1.4 Hz, 2H), 7.72 (dt, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.4 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 7.38-7.28 (m, 4H), 5.36 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 15.8 Hz, 2H), 5.05 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 15.8 Hz, 2H), 4.95 (s, 2H), 4.60 (m, 2H), 3.30 (m, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 223.67, 163.97, 162.20, 149.98, 147.79, 139.95, 139.81, 126.39, 125.89, 125.03, 123.01, 78.82, 67.70, 66.80, 33.34 (d, <sup>1</sup>J<sub>Rh,C</sub> = 26.3 Hz).

HRMS (ESI) Calcd: 513.0290 (C<sub>21</sub>H<sub>22</sub>N<sub>4</sub>OS<sub>2</sub>Rh<sup>+</sup>). Found 513.0302.

### Synthesis of [4a]PF<sub>6</sub>



To a solution of  $[1]PF_6$  (25.5 mg, 0.044 mmol) in dichloromethane (5 mL) was added an excess of paraformaldehyde (8.0 mg, 6.1 equiv). The resulting slurry was stirred at RT for 1 hour before being filtered through celite. To this yellow filtrate was added Et<sub>2</sub>O (15 mL), which caused the precipitation of a fine, white solid. The very pale yellow supernatant was decanted, and the residue was dried *in vacuo* to give 15.9 mg (59 % yield)

of [4a]PF6.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.54 (d, J = 5.8 Hz, 1H), 8.47 (d, J = 5.4 Hz, 2H), 7.79 (dt, <sup>3</sup>J = 7.8, <sup>4</sup>J = 1.5 Hz, 2H), 7.61 (dt, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.3 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 6.4 Hz, 2H), 7.25-7.22 (m, 2H), 5.52 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 14.9 Hz, 2H), 4.91 (s, 2H), 4.87 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 14.9 Hz, 2H), 4.10 (d, <sup>3</sup>J<sub>Rh,H</sub> = 1.1 Hz, 2H), 3.93 (t, J = 5.9 Hz, 2H), 3.07 (dt, <sup>3</sup>J<sub>H,H</sub> = 5.9, <sup>2</sup>J<sub>Rh,H</sub> = 2.7 Hz, 2H).

<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  8.74 (d, J = 5.4 Hz, 1H), 8.68 (d, J = 5.5 Hz, 2H), 7.93 (dt, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.3 Hz, 2H), 7.74 (dt, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.3 Hz, 1H), 7.64 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 6.5 Hz, 2H), 7.40 (t, J = 6.6 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 5.56 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 14.9 Hz, 2H), 5.16 (s, 2H), 5.06 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 14.9 Hz, 2H), 4.13 (d, <sup>3</sup>J<sub>Rh,H</sub> = 1.1 Hz, 2H), 3.89 (t, J = 5.9 Hz, 2H), 3.15 (dt, <sup>3</sup>J<sub>H,H</sub> = 5.9, <sup>2</sup>J<sub>Rh,H</sub> = 2.7 Hz, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.79, 163.56, 151.07, 148.93, 139.46, 138.74, 125.53, 125.20, 124.46, 122.53, 95.94, 69.71, 66.10, 65.06, 28.43 (d,  ${}^{1}J_{Rh,C} = 27.7$  Hz).

HRMS (ESI) Calcd: 467.0954 (C<sub>21</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>Rh<sup>+</sup>). Found 467.0956.

### General preparation of substituted rhodaacetals

To a solution of  $[1]PF_6$  in 0.6 mL of  $CD_2Cl_2$  in a Wilmad screw-cap NMR tube was added 3 equiv of the appropriate aldehyde. The tube was inverted three times to thoroughly mix the contents before being stored at the appropriate temperature (reactions at -20 °C were stored in a freezer at that temperature). The reaction was monitored periodically by <sup>1</sup>H NMR until complete consumption of  $[1]PF_6$  was observed. Excess aldehyde from complexes  $[4a-d]PF_6$  could be removed by pumping the solution to dryness *in vacuo* and redissolving the residue in dichloromethane or acetone.

### Synthesis of [4b]PF<sub>6</sub>



 $\mathsf{PF}_6^{\odot}$  The title compound was prepared using the general method above with 1.0 µL of acetaldehyde and a reaction time of 17 hours at -20 °C. NMR yield: 81 %.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ . 8.55-8.50 (m, 2H), 8.45 (d, J = 5.5

Hz, 1H), 7.80 (dt,  ${}^{3}J = 7.9$  Hz,  ${}^{4}J = 1.6$  Hz, 1H), 7.76 (dt,  ${}^{3}J = 7.7$  Hz,  ${}^{4}J = 1.5$  Hz, 1H), 7.59 (dt,  ${}^{3}J = 7.8$  Hz,  ${}^{4}J = 1.4$  Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.31-7.25 (m, 2H), 7.25-7.16 (m, 2H), 5.54 (d[AB],  ${}^{2}J_{H,H} = 14.9$  Hz, 1H), 5.49 (d[AB],  ${}^{2}J_{H,H} = 14.7$  Hz, 1H), 4.89 (s, 2H), 4.86 (d[AB],  ${}^{2}J_{H,H} = 14.9$  Hz, 1H), 4.82 (d[AB],  ${}^{2}J_{H,H} = 14.8$  Hz, 1H), 4.11 (q, J = 4.9 Hz, 1H), 4.07 (apparent dt, J = 12.8 Hz, J = 4.5 Hz, 1H), 3.65 (ddd, J = 12.9 Hz, J = 10.4 Hz, J = 3.8 Hz, 1H), 3.15-3.08 (m, 1H), 3.03-2.98 (m, 1H), 0.84 (d, J = 4.9 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.77, 164.74, 163.52, 151.52, 150.49, 149.16, 139.30, 139.19, 138.54, 125.57, 125.27, 125.09, 124.40, 124.17, 122.43, 99.98, 68.43, 66.18, 65.85, 64.85, 30.99, 30.20 (d,  ${}^{1}J_{Rh,C} = 27.7$  Hz).

HRMS (ESI) Calcd. 488.1111 (C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>Rh<sup>+</sup>). Found 488.1107.

# Synthesis of [4c]PF<sub>6</sub>



 $\mathsf{PF}_6^{\odot}$  The title compound was prepared using the general method above with 1.2 µL of propionaldehyde and a reaction time of 19 hours at -20 °C. NMR yield: 82 %.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ . 8.55 (d, J = 5.6 Hz, 1H), 8.50 (d, J = 5.6 Hz, 1H), 8.45 (d, J = 5.7 Hz, 1H), 7.80 (dt, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J =

1.3 Hz, 1H), 7.76 (dt,  ${}^{3}J = 7.7$  Hz,  ${}^{4}J = 1.4$  Hz, 1H), 7.59 (dt,  ${}^{3}J = 7.8$  Hz,  ${}^{4}J = 1.4$  Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.32 -7.25 (m, 2H), 7.24-7.17 (m, 2H), 5.54 (d[AB],  ${}^{2}J_{H,H} = 15.0$  Hz, 1H), 5.48 (d[AB],  ${}^{2}J_{H,H} = 14.8$  Hz, 1H), 4.91 (s, 2H), 4.88 (d[AB],  ${}^{2}J_{H,H} = 15.0$  Hz, 1H), 4.83 (d[AB],  ${}^{2}J_{H,H} = 14.7$  Hz, 1H), 4.08 (apparent dt, J = 12.7 Hz, J = 4.6 Hz, 1H), 3.77 (dd, J = 5.7 Hz, J = 4.6 Hz, 1H), 3.67 (ddd, J = 13.2, J = 10.3, J = 3.9 Hz, 1H), 3.11 (m, 1H), 3.00 (m, 1H), 1.09 (m, 2H), 0.62 (t, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.70 (2 overlapping signals), 163.52, 151.53, 154.42, 149.16, 139.37, 139.22, 138.55, 126.63, 125.30, 125.10, 124.36, 124.21, 122.44, 104.64, 68.57, 66.22, 65.90, 64.89, 31.61, 30.05 (d, <sup>1</sup>J<sub>Rh,C</sub> = 27.7 Hz), 10.22.

HRMS (ESI) Calcd: 495.1267 (C<sub>23</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub>Rh<sup>+</sup>). Found 495.1250.

#### Synthesis of [4d]PF<sub>6</sub>



 $\mathsf{PF}_6^{\odot}$  The title compound was prepared using the general method above with 1.5 µL of isobutyraldehyde and a reaction time of 45 hours at -20 °C. NMR yield: 80%.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.88 (d, J = 5.7 Hz, 1H), 8.49 (d, J = 5.5 Hz, 1H), 8.46 (d, J = 5.5 Hz, 1H), 7.80 (dt, <sup>3</sup>J = 7.9, <sup>4</sup>J = 1.4

Hz, 1H), 7.76 (dt,  ${}^{3}J = 7.7$ ,  ${}^{4}J = 1.3$  Hz, 1H), 7.59 (dt,  ${}^{3}J = 7.8$  Hz,  ${}^{4}J = 1.4$  Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.32-7.27 (m, 2H), 7.24-7.18 (m, 2H), 5.51 (d[AB],  ${}^{2}J_{H,H} = 14.7$  Hz, 1H), 5.47 (d[AB],  ${}^{2}J_{H,H} = 14.9$  Hz, 1H), 4.90 (s, 2H), 4.88 (d[AB],  ${}^{2}J_{H,H} = 15.9$  Hz, 1H), 4.84 (d[AB],  ${}^{2}J_{H,H} = 15.2$  Hz, 1H), 4.10 (apparent dt, J = 12.8 Hz, J = 4.6 Hz, 1H), 3.67 (ddd, J = 13.3 Hz, J = 10.1 Hz, J = 3.8 Hz, 1H), 3.47 (d, J = 5.6 Hz, 1H), 3.15-3.08 (m, 1H), 3.02-2.96 (m, 1H), 1.25 (m, 1H), 0.62 (d, J = 6.8 Hz, 3H), 0.59 (d, J = 6.8 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.75, 164.67, 163.50, 151.47, 150.23, 149.16, 139.31, 139.14, 138.49, 125.56, 125.21, 125.07, 124.26, 124.12, 122.43, 108.09, 68.98, 66.31, 65.93, 64.98, 35.53, 30.26 (d,  ${}^{1}J_{Rh,C} = 27.9$  Hz), 18.86, 18.34.

HRMS (ESI) Calcd: 509.1424 (C<sub>24</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Rh<sup>+</sup>). Found 509.1429.

## Synthesis of [4e]PF<sub>6</sub>



The title compound was prepared using the general method above with 2.4 mg of *p*-nitrobenzaldehyde and a reaction time of 18 hours at RT. NMR yield: 85 %.

<sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ )  $\delta$  8.58-8.53 (m, 3H), 7.95 (d, J = 8.8 Hz, 2H), 7.83 (dt, <sup>3</sup>J = 7.9 Hz, <sup>4</sup>J = 1.5 Hz, 1H), 7.75 (dt, <sup>3</sup>J = 7.9 Hz, <sup>4</sup>J = 1.5 Hz, 1H), 7.62 (dt, <sup>3</sup>J = 7.9 Hz, <sup>4</sup>J = 1.5 Hz, 1H), 7.53

(d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.34 (t, J = 6.8 Hz, 1H), 7.32-7.26 (m, 3H), 7.26-7.20 (m, 2H), 5.54 (d[AB],  ${}^{2}J_{H,H} = 15.0$  Hz, 1H), 5.43 (d[AB],  ${}^{2}J_{H,H} = 15.0$  Hz, 1H), 5.02 (s, 1H), 4.97 (d[AB],  ${}^{2}J_{H,H} = 15.0$  Hz, 1H), 4.96 (s, 2H), 4.87 (d[AB],  ${}^{2}J_{H,H} = 14.9$  Hz, 1H), 4.24 (apparent dt, J =12.8 Hz, J = 4.3 Hz, 1H), 3.94 (ddd, J = 12.8 Hz, J = 10.3 Hz, J = 4.2 Hz, 1H), 3.29-3.20 (m, 1H), 3.18-3.11 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.80, 164.59, 163.57, 152.87, 151.57, 151.20, 150.42, 149.31, 147.11, 139.63, 139.41, 138.76, 127.13, 125.80, 125.38, 125.30, 124.16, 123.07, 122.51, 101.15, 69.05, 66.40, 66.07, 65.00, 30.44 (d, <sup>1</sup>J<sub>Rh,C</sub> = 27.3 Hz).

HRMS (ESI) Calcd. 588.1118 (C<sub>27</sub>H<sub>27</sub>N<sub>5</sub>O<sub>4</sub>Rh<sup>+</sup>). Found 588.1116.

# Synthesis of [4f]PF<sub>6</sub>



 $\mathsf{PF}_6^{\odot}$  The title compound was prepared using the general method above with 2.0 µL of pentafluorobenzaldehyde and a reaction time of 17 hours at -20 °C. NMR yield: 63 %. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.60-8.51 (m, 3H), 7.85 (dt, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.5 Hz, 1H), 7.80 (dt, <sup>3</sup>J = 7.7 Hz, <sup>4</sup>J = 1.5 Hz, 1H), 7.63 (dt, <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.4 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.38-7.29 (m 2H), 7.27-7.21 (m, 2H), 5.48 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 14.9 Hz, 1H), 5.36 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 15.1 Hz, 1H), 4.96 (s, 1H), 4.94 (s, 2H), 4.91 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 15.0 Hz, 1H), 4.84 (d[AB], <sup>2</sup>J<sub>H,H</sub> = 14.9 Hz, 1H), 4.32 (apparent dt, J = 12.8 Hz, J = 4.9 Hz, 1H), 3.81 (ddd, J = 13.4 Hz, J = 9.8 Hz, J = 4.2 Hz, 1H), 3.30-3.22 (m, 1H), 3.13-3.06 (m, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 165.08, 164.75, 163.73, 151.36, 150.09, 149.23, 139.69, 139.38, 138.78, 125.75, 125.26, 125.20, 124.50, 124.06, 122.59, 97.32, 69.74, 66.38, 66.00, 65.20, 30.11 (d,  ${}^{1}J_{Rh,C} = 27.6$  Hz). The aryl resonances of the C<sub>6</sub>F<sub>5</sub> ring could not be located, probably due broadening due to  ${}^{13}C{}^{-19}F$  coupling and the low intensity of quaternary carbon signals.

<sup>19</sup>F NMR (280 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -73.8 (d,  ${}^{1}J_{P,F}$  = 712 Hz), -140.7 (m), -151.9 (m), -163.6 (m).

HRMS (ESI) Calcd: 633.0796 (C<sub>27</sub>H<sub>23</sub>N<sub>4</sub>O<sub>2</sub>F<sub>5</sub>Rh<sup>+</sup>). Found 633.0792.

# III. Discussion of the <sup>1</sup>H NMR Spectrum of [3]PF<sub>6</sub>



The RhCH<sub>2</sub>CH<sub>2</sub>O moiety of [3]PF<sub>6</sub> display unusual multiplicities for this family of compounds. The splitting remains the same in both  $CD_2Cl_2$  and acetone-d<sub>6</sub>, and variable temperature NMR studies show only a slight broadening of the peaks down to -70 °C.



Figure S1 Resonances in the <sup>1</sup>H NMR for H1 and H2 of complex [3]PF<sub>6</sub>

COSY and  ${}^{1}H{}^{1}H{}$  experiments show that H2 is solely coupled to H1, and H1 is coupled to both H2 and Rh with a  ${}^{2}J_{Rh,H}$  of 2.6 Hz.



Figure S2 Resonances in the <sup>1</sup>H NMR for H1 and H2 of complex [3] $PF_6$  after each signal has been decoupled from the other.

The use of DAISY, a simulating feature of Bruker's Topspin (Version 3.2), shows that the resonances can be approximately modeled as having a  ${}^{3}J_{H,H}$  of 5.4 Hz. However, this assumes only first order coupling, and the fit is poor for the H2 resonance. An alternate possibility could be than this is an example of second order coupling between protons that are chemically equivalent but not magnetically equivalent, although why [3]PF<sub>6</sub> would display this feature and other related compounds do not is under investigation.



Figure S3- DAISY simulation (blue) and experimental spectrum (red) of the resonances of H1 and H2 of complex [3]PF<sub>6</sub>

# IV. Discussion of the <sup>13</sup>C NMR spectra of [2a]PF<sub>6</sub>, [2b]PF<sub>6</sub> and [3]PF<sub>6</sub>

The resonances in the <sup>13</sup>C NMR spectra of [2a]PF<sub>6</sub> and [2b]PF<sub>6</sub> attributed to the C4 carbons are quite weak, as is to be expected from quaternary carbons that do not benefit from the nuclear Overhauser effect. In addition, both carbon nuclei are coupled to <sup>103</sup>Rh, further weakening their signal intensity. However, they do have reasonable chemical shifts in line with those in the literature and, more tellingly, have <sup>1</sup>J<sub>Rh,C</sub> coupling constants (34.4 Hz for [2a]PF<sub>6</sub>, 34.5 Hz for [2b]PF<sub>6</sub>) that agree quite well with those of other rhodium alkenyl complexes (typically 33-40 Hz).<sup>6</sup>



Figure S4 Overlay of the <sup>13</sup>C NMR spectra of  $[2a]PF_6$  (bottom, blue) and  $[2b]PF_6$  (top, red) showing the weak signals assigned as the C4 resonances

The C3 carbon resonance of  $[3]PF_6$  also suffers from a lack of signal strength for similar reasons, although it is not coupled to <sup>103</sup>Rh. This resonance was assigned as C3 based on its similarities in chemical shift to other xanthate compounds in the literature, which typically have a chemical shift from 208-231 ppm.<sup>7</sup>



Figure S5 The weak resonance assigned as C3 in the  ${}^{13}$ C NMR spectrum of [3]PF<sub>6</sub>

V. NOESY analysis of [4c]PF<sub>6</sub>



Figure S6 2D NOESY spectrum of [4c]PF<sub>6</sub> showing NOE contacts of the metallacycle.



# V. <sup>1</sup>H and <sup>13</sup>C NMR Spectra

Figure S7<sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [2a]PF<sub>6</sub>.



Figure S9 <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [2b]PF<sub>6</sub>.



Figure S10 <sup>13</sup>C NMR spectrum (100 MHz,  $CD_2Cl_2$ , RT) of [2b]PF<sub>6</sub>. [2b]BAr<sup>F</sup><sub>4</sub>



Figure S11 <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [2b]BAr<sup>F</sup><sub>4</sub>. \* indicates excess DEAD.







Figure S13<sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [3]PF<sub>6</sub>.



Figure S14 <sup>13</sup>C NMR spectrum (100 MHz,  $CD_2Cl_2$ , RT) of [3]PF<sub>6</sub>. See Figure S5 for the C3 resonance. [4a]PF<sub>6</sub>  $\textcircled{\oplus}$  PF<sub>6</sub>  $\textcircled{\oplus}$ 



Figure S15 <sup>1</sup>H NMR spectrum (400 MHz, acetone-d<sub>6</sub>, RT) of [4a]PF<sub>6</sub>.





Figure S17 <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [4b]PF<sub>6</sub>.



Figure S18 <sup>13</sup>C NMR spectrum (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [4b]PF<sub>6</sub>. \* indicates excess MeCHO.



Figure S19 <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [4c]PF<sub>6</sub>.



Figure S21 <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [4d]PF<sub>6</sub>. \* indicates excess iPrCHO.



Figure S22 <sup>13</sup>C NMR spectrum (100 MHz,  $CD_2Cl_2$ , RT) of [4d]PF<sub>6</sub>. [4e]PF<sub>6</sub>  $\textcircled{\begin{tabular}{ll} \end{tabular}} \mathbb{PF}_6^{\begin{tabular}{ll} \end{tabular}}} \mathbb{PF}_6^$ 



**Figure S23** <sup>1</sup>H NMR spectrum (400 MHz,  $CD_2Cl_2$ , RT) of **[4e]PF**<sub>6</sub>. \* indicates excess *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO.



Figure S24 <sup>13</sup>C NMR spectrum (100 MHz,  $CD_2Cl_2$ , RT) of [4e]PF<sub>6</sub>. \* indicates excess *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CHO. [4f]PF<sub>6</sub>



Figure S25 <sup>1</sup>H NMR spectrum (400 MHz,  $CD_2Cl_2$ , RT) of [4f]PF<sub>6</sub>. \* indicates excess  $C_6F_5CHO$ .



Figure S26<sup>13</sup>C NMR spectrum (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, RT) of [4f]PF<sub>6</sub>. \* indicates excess C<sub>6</sub>F<sub>5</sub>CHO.

### VI. X-ray Crystallography

A single crystal of [2b]BAr<sup>F</sup><sub>4</sub> was mounted on a glass fiber and measurements were made on a Bruker X8 APEX II diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The data was collected at a temperature of -173.0 ± 0.2 °C in a series of  $\phi$  and  $\omega$  scans in 0.50° oscillations. Data was collected and integrated using the Bruker SAINT software package<sup>8</sup> and were corrected for absorption effects using the multi-scan technique (SADABS).<sup>9</sup> The data was corrected for Lorentz and polarization effects and the structure was solved by direct methods.<sup>10</sup> Included in the lattice is one half-molecule of water, disordered in two orientations as well as about an inversion center. As a result of this disorder the water hydrogen atoms could not be located and were thus not included in the refinement model. The missing hydrogen atoms were, however, included in the final empirical formula. Additionally, four of the six CF<sub>3</sub> groups are disordered, with rotation of the fluorine atoms about the C-C bond. In each case the disorder was

modeled in two orientations most cases this was simply the three fluorine atoms rotating about the C-C bond however in the case of the  $CF_3$  group containing C43, the carbon atom is also disordered. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. RIGU, ISOR and SADI restraints were employed to establish reasonable geometries and displacement parameters. All refinements were performed using the SHELXTL crystallographic software package of Bruker-AXS.<sup>11</sup> The molecular drawings were generated by the use of ORTEP-3<sup>12</sup> and POV-Ray.

Compound Number	[2b]BAr <sup>F</sup> <sub>4</sub>
Formula	$C_{60}H_{45}BN_4O_{5.5}F_{24}Rh$
Formula Weight	1479.72
Crystal Color, Habit	yellow, needle
Crystal Dimensions, mm	0.11 x 0.27 x 0.57 mm
Crystal System	Triclinic
Space Group	P -1
<i>a</i> , Å	9.5642(13)
b, Å	18.249(4)
<i>c</i> , Å	19.551(3)
$\alpha$ , °	116.345(3)
$\beta$ , °	96.706(4)
γ, °	91.811(4)
$V, Å^3$	3023.8(7)
Z	2
D calc, $g/cm^3$	1.625
F <sub>000</sub>	1486.00
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	4.11
Data Images (no., $t/s$ )	1870, 15
$2\theta_{\text{max}}$	50.5
Reflections measrd	60329
Unique reflcn, R <sub>int</sub>	15109, 0.054
Absorption, $T_{min}$ , $T_{max}$	0.689, 0.956
Observed data (I> $2.00\sigma(I)$ )	12535
No. parameters	971
R1, wR2 ( $F^2$ , all data)	0.059, 0.122
R1, wR2 (F, I>2.00σ(I))	0.047, 0.115
Goodness of Fit	1.03

**Table S1.** X-ray crystallographic data for [2b]BAr<sup>F</sup><sub>4</sub>.

Max, Min peak,  $e^{-}/Å^{3}$  1.34, -1.52

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