

## Supporting Information

### Unbridged Rh(II)-Rh(II) Complexes of *N*-Heterocyclic Carbene and Reactions with O<sub>2</sub> to Dirhodium( $\mu$ - $\eta^1$ : $\eta^1$ )-Peroxide Complexes

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#### Experimental Section

All the chemicals were obtained from commercial suppliers and used without further purification. 2-(Imidazolyl)pyridine and [H<sub>2</sub>L](PF<sub>6</sub>)<sub>2</sub> were prepared according to known procedures.<sup>1</sup> Elemental analyses were performed on a Flash EA1112 instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from TMS at  $\delta = 0$  ppm, and coupling constants (*J*) are expressed in Hz.

**Synthesis of [Rh(L)(MeCN)]<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>, 1.** A solution of [H<sub>2</sub>L](PF<sub>6</sub>)<sub>2</sub> (446 mg, 0.75 mmol) in 50 mL of CH<sub>3</sub>CN was treated with Ag<sub>2</sub>O (180 mg, 0.75 mmol). The mixture was allowed to react in the dark at 50 °C for 12 h, and the reaction solution was treated with [Rh(cod)Cl]<sub>2</sub> (370 mg, 0.75 mmol). After it was stirred for 12 hours at 50 °C, the solution was filtered. The filtrate was concentrated to *ca.* 10 mL. Addition of 40 mL of diethyl ether gave a yellow solid. Yield: 83%. Anal. Calcd for C<sub>38</sub>H<sub>34</sub>F<sub>24</sub>N<sub>14</sub>P<sub>4</sub>Rh<sub>2</sub>: C, 31.00; H, 2.33; N, 13.32. Found: C, 31.23; H, 2.65; N, 13.64. <sup>1</sup>H NMR (400 MHz, dms<sub>o</sub>-*d*<sub>6</sub>)  $\delta$ : 9.08 (d, *J* = 4.8 Hz, *o*-C<sub>5</sub>H<sub>4</sub>N, 4H), 8.47 (dt, *J* = 7.6 and 1.6 Hz, *p*-C<sub>5</sub>H<sub>4</sub>N, 4H), 8.34 (d, *J* = 2.4 Hz, NCHCHN, 4H), 8.15 (d, *J* = 8.4 Hz, *m*-C<sub>5</sub>H<sub>4</sub>N, 4H), 8.01 (d, *J* = 2.4 Hz, NCHCHN, 4H), 7.70 (dt, *J* = 7.6 and 1.6 Hz, *m*-C<sub>5</sub>H<sub>4</sub>N, 4H), 7.12 (d, *J* = 13.6 Hz, NCH<sub>2</sub>N, 2H), 6.95 (d, *J* = 13.6 Hz, NCH<sub>2</sub>N, 2H), 2.08 (s, CH<sub>3</sub>CN, 6H). <sup>13</sup>C NMR (100 MHz, dms<sub>o</sub>-*d*<sub>6</sub>)  $\delta$ : 169.4 (d, *J*<sub>RhC</sub> = 45 Hz), 151.1, 147.7, 141.8, 124.0, 123.5, 118.4, 117.0, 112.8, 64.2. Single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into its acetonitrile solution.

**Synthesis of [Rh(L)(NMI)]<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>, 2.** A solution of [Rh(L)(MeCN)]<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub> (466 mg, 0.3mmol) and 0.5 mL of *N*-methylimidazole in 20 mL of CH<sub>3</sub>CN was stirred for 12 hours at room temperature. The solution was filtered, and the filtrate was concentrated to *ca.* 5 mL. Orange crystalline solid was

collected after addition of diethyl ether. Yield: 85%. Anal. Calcd for  $C_{42}H_{40}F_{24}N_{16}P_4Rh_2$ : C, 32.45; H, 2.59; N, 14.42. Found: C, 32.58; H, 2.71; N, 14.54.  $^1H$  NMR (dms $o$ - $d_6$ ): 9.08 (d,  $J = 4.8$  Hz,  $o$ - $C_5H_4N$ , 4H), 8.31 (t,  $J = 7.6$  Hz,  $p$ - $C_5H_4N$ , 4H), 8.26 (d,  $J = 1.6$  Hz, NCHCHN, 4H), 7.98 (br,  $m$ - $C_5H_4N$ , 4H), 7.97 (br, NCHCHN, 4H), 7.63 (t,  $J = 7.6$  Hz,  $m$ - $C_5H_4N$ , 4H), 7.14 (d,  $J = 14.0$  Hz, NCH $_2$ N, 2H), 6.71 (s, NCHN, 2H), 6.59 (d,  $J_{HH} = 14.0$  Hz, NCH $_2$ N, 2H), 6.49 (br, NCHCHN, 2H), 5.70 (br, NCHCHN, 2H), 3.14 (s, NCH $_3$ , 6H).  $^{13}C$  NMR (dms $o$ - $d_6$ ): 176.2 (d,  $J_{RhC} = 45$  Hz), 151.3, 148.6, 142.0, 136.4, 124.8, 124.5, 124.2, 122.4, 118.5, 113.0, 65.1, 33.8.

**Synthesis of  $[RhO(L)(PPh_3)]_2(PF_6)_4$ , **3** and  $[RhO(L)(CH_3CN)]_2(PF_6)_4$ , **4**.** Method 1: A solution of  $[H_2L](PF_6)_2$  (446 mg, 0.75 mmol) in 50 mL of  $CH_3CN$  was treated with  $Ag_2O$  (180 mg, 0.75 mmol). The mixture was allowed to react in the dark at 50 °C for 12 hours, and the reaction solution was added  $RhCl(PPh_3)_3$  (370 mg, 0.75 mmol). After the mixture was stirred for another 12 hours at 50 °C, the solution was filtered. The filtrate was concentrated to *ca.* 10 mL. Addition of 40 mL of diethyl ether gave a brown solid. Yield: 51%. Method 2: A solution of  $[Rh(L)(MeCN)]_2(PF_6)_4$  **1** (466 mg, 0.3 mmol) and  $PPh_3$  (157 mg, 0.6 mmol) in 20 mL of  $CH_3CN$  was stirred for 12 hours at 50 °C. The filtrate was concentrated to *ca.* 5 mL. Addition of 20 mL of diethyl ether gave a brown solid. Yield: 72%. Single crystals of **3** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into its acetonitrile solution. Simultaneously, a few yellow needlelike crystals assigned to  $[RhO(L)(CH_3CN)]_2(PF_6)_4$  **4** were obtained.

$[RhO(L)(PPh_3)]_2(PF_6)_4$ , **3**, Anal. Calcd for  $C_{70}H_{58}F_{24}N_{12}O_2P_6Rh_2$ : C, 43.18; H, 3.00; N, 8.63. Found: C, 43.73; H, 3.32; N, 8.78.  $^1H$  NMR (400 MHz, dms $o$ - $d_6$ ): 8.83 (d,  $J = 5.6$  Hz,  $o$ - $C_5H_4N$ , 4H), 8.18 (m,  $p$ - $C_5H_4N$  and  $C_6H_5$ , 8H), 7.74 (m, NCHCHN,  $C_6H_5$ , 8H), 7.41 (m,  $m$ - $C_5H_4N$  and  $C_6H_5$ , 10H), 7.21 (m, NCHCHN and  $C_6H_5$ , 12H), 6.53 (m,  $p$ - $C_5H_4N$  and  $C_6H_5$ , 12H), 6.25 (d,  $J = 13.6$  Hz, NCH $_2$ N, 2H), 5.44 (d,  $J = 13.6$  Hz, NCH $_2$ N, 2H).  $^{13}C$  NMR (100 MHz, dms $o$ - $d_6$ ): 170.0 (dd,  $J_{CRh} = 43.0$  Hz,  $J_{CP} = 11.2$  Hz), 151.0, 148.6, 142.2, 131.7 (d,  $^2J_{CP} = 10.4$  Hz), 131.5, 129.2 (d,  $^2J_{CP} = 9.9$  Hz), 126.8 (d,  $^1J_{CP} = 47$  Hz), 124.0, 123.6, 118.3, 113.0, 63.8.  $^{31}P$  NMR (162 MHz, dms $o$ - $d_6$ ): 19.9 (d,  $J_{RhP} = 92$  Hz), -144.1 (sep,  $J_{PF} = 712$  Hz).

**Synthesis of  $[RhO(L)(PCy_3)]_2(PF_6)_4$ , **5**.** A solution of  $[Rh(L)(MeCN)]_2(PF_6)_4$  (466 mg, 0.3 mmol) and  $PCy_3$  (168 mg, 0.6 mmol) in 20 mL of  $CH_3CN$  was stirred for 12 hours at 50 °C. The solution was filtered, and the filtrate was concentrated to *ca.* 5 mL. Addition of 20 mL of diethyl ether gave a brown solid. Yield: 65%. Anal. Calcd for  $C_{70}H_{94}F_{24}N_{12}O_2P_6Rh_2$ : C, 42.39; H, 4.78; N, 8.48. Found: C, 42.56; H, 4.92; N, 8.79.  $^1H$  NMR (dms $o$ - $d_6$ ): 8.72 (d,  $J = 4.8$  Hz,  $o$ - $C_5H_4N$ , 4H), 8.45 (dt,  $J = 7.6$  Hz and 1.6 Hz,  $p$ - $C_5H_4N$ , 4H), 8.29 (d,  $J = 2.4$  Hz, NCHCHN, 4H), 8.10 (d,  $J = 8.4$  Hz,  $m$ - $C_5H_4N$ , 4H), 7.86 (d,  $J =$

2.4 Hz, NCHCHN, 4H), 7.66 (dt,  $J = 7.6$  Hz and 1.6 Hz,  $m$ -C<sub>5</sub>H<sub>4</sub>N, 4H), 6.68 (d,  $J = 14.0$  Hz, NCH<sub>2</sub>N, 2H), 6.37 (d,  $J = 14.0$  Hz, NCH<sub>2</sub>N, 2H), 1.45 (m, CH<sub>2</sub>, 18H), 1.04 (m, CH<sub>2</sub>, 18H), 0.83 (m, CH<sub>2</sub>, 18H), 0.56 (m, CH, 12H). <sup>13</sup>C NMR (dms<sub>o</sub>-*d*<sub>6</sub>): 169.8 (dd,  $J_{CRh} = 43.0$  Hz,  $^2J_{CP} = 10.6$  Hz), 150.3, 148.1, 141.9, 123.3, 122.9, 117.2, 117.0, 112.1, 63.8, 63.1, 34.3 (d,  $^1J_{CP} = 17.6$  Hz), 27.0, 25.6 (d,  $^2J_{CP} = 9.3$  Hz), 24.1. <sup>31</sup>P NMR (162 MHz, dms<sub>o</sub>-*d*<sub>6</sub>): 29.7 (d,  $J_{PRh} = 90$  Hz), -144.2 (sep,  $J_{PF} = 712$  Hz).

**X-ray Structural Determination.** Single-crystal X-ray diffraction data were collected at 293(2) K for **1**, **2**, **4** and **5** and 150 K for **3** on a Siemens Smart/CCD area-detector diffractometer with a Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using the  $\omega$ - $2\theta$  scan mode. Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  using the SHELXTXL package. Hydrogen atom positions for all of the structures were calculated and allowed to ride on their respective C atoms with C-H distances of 0.93–0.97 Å and  $U_{iso}(H) = -1.2 - 1.5U_{eq}(C)$ .

**Table S1.** Summary of X-ray crystallographic data for complexes **1-5**.

compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
CCDC No.	1883809	1883810	1883811	1883813	1883812
formula	[Rh(L)(MeCN)] <sub>2</sub> (PF <sub>6</sub> ) <sub>4</sub> 2MeCN	[Rh(L)(NMI)] <sub>2</sub> (PF <sub>6</sub> ) <sub>4</sub> ·3MeCN·Et <sub>2</sub> O	[RhO(L)(PPh <sub>3</sub> ) <sub>2</sub> (PF <sub>6</sub> ) <sub>4</sub> MeCN	[RhO(L)(CH <sub>3</sub> CN)] <sub>2</sub> (PF <sub>6</sub> ) <sub>4</sub> 2MeCN	[RhO(L)(PCy <sub>3</sub> ) <sub>2</sub> (PF <sub>6</sub> ) <sub>4</sub> ·2MeCN·Et <sub>2</sub> O
<i>F</i> <sub>w</sub>	1554.60	1751.88	2111.14	1586.60	2139.44
crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	<i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	10.7295(8)	19.0638(6)	14.0615(4)	11.146(3)	13.1037(15)
<i>b</i> /Å	12.2235(6)	15.4706(5)	12.6084(3)	12.035(3)	14.8822(17)
<i>c</i> /Å	12.5730(7)	26.2772(9)	24.0897(7)	12.880(3)	15.3583(11)
$\alpha$ /deg	79.434(4)	90	90	79.125(18)	104.336(8)
$\beta$ /deg	73.363(5)	103.647(3)	95.831(3)	69.88(2)	111.184(9)

$\gamma/\text{deg}$	65.209(6)	90	90	65.98(2)	106.435(10)
$V/\text{\AA}^3$	1430.54(15)	7531.1(4)	4248.8(2)	1479.4(6)	2465.1(5)
$Z$	1	4	2	1	1
$D/\text{g cm}^{-3}$	1.805	1.545	1.650	1.781	1.441
reflns collected	5027	17813	7469	5190	8675
ind reflns, $R_{\text{int}}$	4298	12406	6170	3887	7158
goodness-of- fit on $F^2$	1.055	1.034	1.032	1.013	1.056
$R1, wR2 [I > 2\sigma(I)]$	0.0519, 0.1294	0.0710, 0.1860	0.0516, 0.1206	0.0630, 0.1426	0.0512, 0.1214
$R1, wR2$ (all data)	0.0635, 0.1424	0.1063, 0.2198	0.0659, 0.1327	0.0895, 0.1652	0.0659, 0.1456

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## Reference

1. Z. Xi, X. Zhang, W. Chen, S. Fu, D. Wang, *Organometallics*, 2007, **26**, 6636.