

**Reactivity of Rhodium and Iridium Peroxido Complexes  
towards Hydrogen in the Presence of  $B(C_6F_5)_3$  or  
 $[H(OEt_2)_2][B\{3,5-(CF_3)_2C_6H_3\}_4]$**

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## **Supporting Information**

## Experimental section

**General Methods and Instrumentation.** All experiments were carried out in an argon atmosphere using standard Schlenk techniques. All solvents were purified and dried using conventional methods and distilled under argon.  $B(C_6F_5)_3$  (sublimed before use) and  $BCl_2$  (1 M in hexane) were purchased from ABCR. *trans*-[Rh(4- $C_5F_4N$ )( $O_2$ )(CNtBu)( $PEt_3$ )<sub>2</sub>] and *trans*-[Ir(4- $C_5F_4N$ )( $O_2$ )(CNtBu)( $PiPr_3$ )<sub>2</sub>] were prepared according to literature procedures.<sup>1</sup> NMR analyses were carried out with a Bruker DPX 300 and Bruker Avance III 300 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced to the residual proton signals of the deuterated solvents (toluene- $d_8$  at  $\delta = 2.08$  or THF- $d_8$  at  $\delta = 1.80$  ppm). The external reference for the <sup>31</sup>P{<sup>1</sup>H} NMR spectra was  $H_3PO_4$  at  $\delta = 0.0$  ppm. <sup>19</sup>F NMR spectra were referenced externally to  $C_6F_6$  at  $\delta = -162.9$  ppm. The external reference for the <sup>11</sup>B and <sup>11</sup>B{<sup>1</sup>H} NMR was  $BF_3 \cdot OEt_2$  at  $\delta = 0.0$  ppm. IR spectra were recorded using a Bruker Vertex 70 spectrometer, which was equipped with an ATR unit (diamond). HR-ESI-MS analyses were carried out with an Agilent 6210 ToF spectrometer with electro spray ionization (ESI). Gastight syringes were used to directly introduce the sample into the nebulizer. The source was cooled down to 50°C and a fragmentation voltage of 100mV was used.

### Hydrogenation of *trans*-[Rh(4- $C_5F_4N$ )( $O_2$ )(CNtBu)( $PEt_3$ )<sub>2</sub>] (**1**) with $H_2$ in the presence of $B(C_6F_5)_3$

a) Toluene- $d_8$  was condensed into a Young®-NMR tube filled with *trans*-[Rh(4- $C_5F_4N$ )( $O_2$ )(CNtBu)( $PEt_3$ )<sub>2</sub>] (**1**, 24 mg, 0.04 mmol) and  $B(C_6F_5)_3$  (21 mg, 0.04 mmol) at -196°C. An  $H_2$  atmosphere (1.013 bar) was added. The solution was kept at -70°C for 15 min and shaken regularly, whereupon the colour changed from red-orange to pale yellow and very small amounts of a red-brown solid precipitated. The reaction mixture was examined by NMR spectroscopy after reaching room temperature. <sup>31</sup>P{<sup>1</sup>H} NMR measurements revealed the presence of  $OPe_3$ , *trans*-[Rh(4- $C_5F_4N$ )(CNtBu)( $PEt_3$ )<sub>2</sub>] (**3**) and a resonance for another rhodium complex. Integration of the resonance signals of the rhodium complex **3** and the unknown compound showed a ratio of 7:1.  $(H_2O) \cdot B(C_6F_5)_3$  was identified by comparison of NMR data with an authentic sample. The red-brown precipitate could not be identified and IR spectroscopic measurements showed no absorption bands characteristic for CNtBu ligands.

b) Into a Young®-NMR tube containing *trans*-[Rh(4- $C_5F_4N$ )( $O_2$ )(CNtBu)( $PEt_3$ )<sub>2</sub>] (**1**, 24 mg, 0.04 mmol) and  $B(C_6F_5)_3$  (21 mg, 0.04 mmol), a solution of  $PEt_3$  (6  $\mu$ L, 5 mg, 0.04 mmol) in toluene- $d_8$  (0.7 mL) was transferred. Afterwards, dihydrogen (1.013 bar) was added. The reaction mixture was allowed to warm up to -70°C and after 15 min to room temperature.  $(H_2O) \cdot B(C_6F_5)_3$  was identified by comparison

of NMR data with an authentic sample. NMR spectroscopic analysis showed the presence of  $\text{OPEt}_3$ , *trans*- $[\text{Rh}(4\text{-C}_5\text{F}_4\text{N})(\text{CNtBu})(\text{PEt}_3)_2]$  (**3**) and the unknown rhodium complex, in a ratio of 11:1 for the two rhodium compounds (determined by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy). The volatiles were removed in vacuo and collected in an external cooling trap. There was no evidence for the formation of  $\text{H}_2\text{O}_2$ , tested with Quantofix<sup>®</sup> peroxide test sticks and a reaction with titanysulfate solution.

$^{31}\text{P}\{^1\text{H}\}$  NMR data for the unknown rhodium compound:

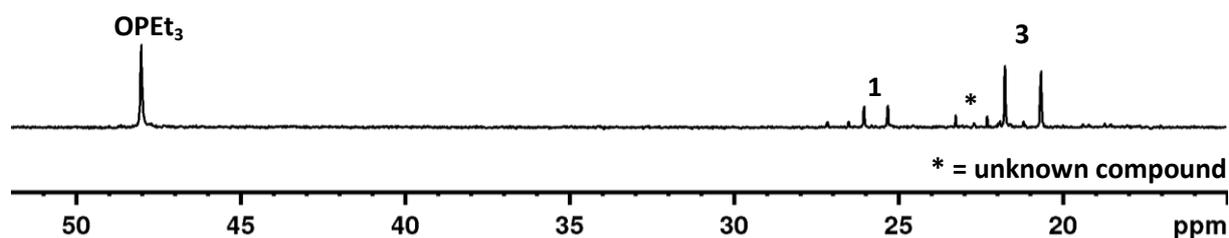
$^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz, toluene- $d_8$ , 25 °C):  $\delta = 20.2$  ppm (d,  $^1J_{\text{Rh,P}} = 134.0$  Hz).

Analytical data for  $(\text{H}_2\text{O})\cdot\text{B}(\text{C}_6\text{F}_5)_3$ :<sup>3</sup>

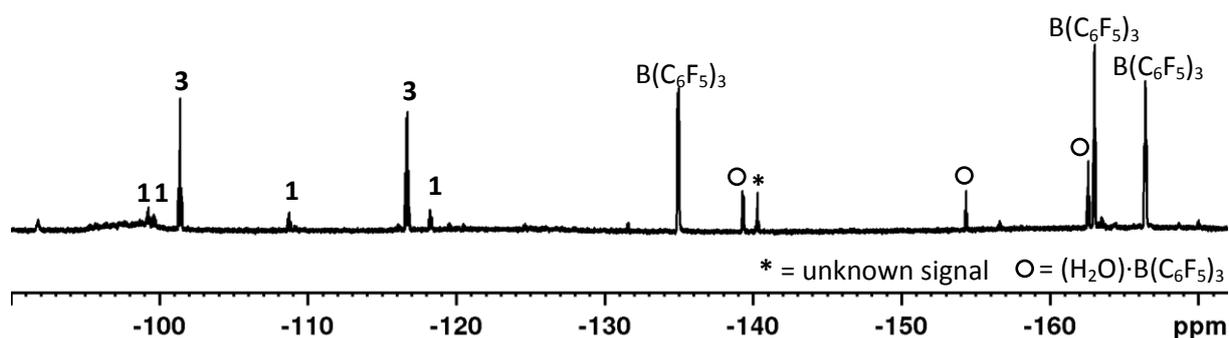
$^1\text{H}$  NMR (300.1 MHz, toluene- $d_8$ ):  $\delta = 4.66$  ppm (s, br, 2 H;  $(\text{H}_2\text{O})\cdot\text{B}(\text{C}_6\text{F}_5)_3$ ).

$^{19}\text{F}$  NMR (282.4 MHz, toluene- $d_8$ ):  $\delta = -135.2$  (dd,  $^3J_{\text{F,F}} = 23.4$ ,  $^4J_{\text{F,F}} = 8.3$  Hz, 6 F; *ortho*-CF),  $-154.8$  (t,  $^3J_{\text{F,F}} = 20.6$  Hz, 3 F; *para*-CF),  $-162.8$  ppm (m, 6 F; *meta*-CF).

$^{11}\text{B}\{^1\text{H}\}$  NMR (96.3 MHz, toluene- $d_8$ ):  $\delta = -2.0$  ppm (br).



$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of **1** with  $\text{H}_2$  in the presence of  $\text{B}(\text{C}_6\text{F}_5)_3$  after 2 days, when no additional phosphine is present.



$^{19}\text{F}$  NMR spectrum of the reaction mixture of **1** with  $\text{H}_2$  in the presence of  $\text{B}(\text{C}_6\text{F}_5)_3$  after 2 days, when no additional phosphine is present.

### Reduction of *trans*- $[\text{Rh}(4\text{-C}_5\text{F}_4\text{N})(\text{O}_2)(\text{CNtBu})(\text{PEt}_3)_2]$ (**1**) with $\text{D}_2$ in presence of $\text{B}(\text{C}_6\text{F}_5)_3$

$\text{PEt}_3$  (6  $\mu\text{L}$ , 5 mg, 0.04 mmol) was dissolved in toluene- $d_8$  (0.7 ml) and the solution was transferred into a Young<sup>®</sup>-NMR tube containing *trans*- $[\text{Rh}(4\text{-C}_5\text{F}_4\text{N})(\text{O}_2)(\text{CNtBu})(\text{PEt}_3)_2]$  (**1**, 24 mg, 0.04 mmol) and

$B(C_6F_5)_3$  (21 mg, 0.04 mmol) at  $-196^\circ C$ .  $D_2$  was added (1.013 bar) and the reaction mixture was kept at  $-70^\circ C$  for 15 min and shaken regularly. The colour changed from red-orange to pale yellow. At room temperature, NMR spectroscopy revealed the formation of *trans*-[Rh(4- $C_5F_4N$ )(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**3**), OPet<sub>3</sub><sup>2</sup> and  $(D_2O) \cdot B(C_6F_5)_3$ .

Analytical data for  $(D_2O) \cdot B(C_6F_5)_3$ :

<sup>19</sup>F NMR (282.4 MHz, toluene-*d*<sub>8</sub>):  $\delta = -135.2$  (dd, <sup>3</sup>*J*<sub>F,F</sub> = 23.4, <sup>4</sup>*J*<sub>F,F</sub> = 8.3 Hz, 6 F; *ortho*-CF),  $-154.8$  (t, <sup>3</sup>*J*<sub>F,F</sub> = 20.6 Hz, 3 F; *para*-CF),  $-162.8$  ppm (m, 6 F; *meta*-CF).

<sup>11</sup>B{<sup>1</sup>H} NMR (96.3 MHz, toluene-*d*<sub>8</sub>):  $\delta = -2.0$  ppm (br).

### Reaction of PEt<sub>3</sub> with $B(C_6F_5)_3$

$B(C_6F_5)_3$  (13 mg, 0.03 mmol) was dissolved in a solution of PEt<sub>3</sub> (5.5  $\mu$ L, 0.04 mmol) and toluene-*d*<sub>8</sub> (0.4 ml). <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F NMR spectroscopy revealed the formation of Et<sub>3</sub>P· $B(C_6F_5)_3$  which was compared to literature<sup>4</sup>.

### Reaction of *trans*-[Rh(4- $C_5F_4N$ )(O<sub>2</sub>)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**1**) with $B(C_6F_5)_3$

Compound **1** (10 mg 0.02 mmol) was dissolved in toluene-*d*<sub>8</sub> (0.4 ml) and  $B(C_6F_5)_3$  (8.5 mg, 0.02 mmol) was added at room temperature. The formation of Et<sub>3</sub>PO· $B(C_6F_5)_3$  was observed after 1 h in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum along with resonances in the <sup>19</sup>F NMR spectrum. The <sup>31</sup>P{<sup>1</sup>H} NMR was compared to literature.<sup>5</sup>

### Reaction of *trans*-[Ir(4- $C_5F_4N$ )(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**) with $B(C_6F_5)_3$

Compound **2a** (9 mg 0.01 mmol) was dissolved in THF-*d*<sub>8</sub> (0.5 ml) and  $B(C_6F_5)_3$  (6 mg, 0.01 mmol) was added at room temperature. The formation of an unknown iridium complex was observed after 1 h along with some resonances with low intensity. The reaction mixture was then cooled down to  $-50^\circ C$  and pyridine was added (1.2  $\mu$ L, 0.01 mmol). The iridium complex *trans*-[Ir(4- $C_5F_4N$ )(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**) was identified as the main product by NMR spectroscopy.<sup>1b</sup> An analogous reaction was observed when **2a** (8 mg, 0.01 mmol),  $B(C_6F_5)_3$  (5 mg, 0.01 mmol) and lutidine (1  $\mu$ L, 0.01 mmol) were used.

Analytical data for the unknown iridium compound:

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz, THF- $d_8$ ):  $\delta = 83.0$  (br) ppm.

#### Reaction of *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**) with H<sub>2</sub> in presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (10 mg, 0.02 mmol) was added to a solution of *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**), 15 mg, 0.02 mmol) in toluene- $d_8$  at -80°C. The solution was degassed three times using the freeze-pump-thaw method. H<sub>2</sub> was added to the frozen solution and the reaction mixture was allowed to warm up to room temperature. After 18 h, (H<sub>2</sub>O)·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was identified through comparison with an authentic sample. No iridium species could be identified, although **2a** was fully converted.

#### Reaction of *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**) with BClCy<sub>2</sub>

a) BClCy<sub>2</sub> (82  $\mu\text{l}$ , 0.08 mmol, 1 M in hexane) was added to a solution of *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**, 32 mg, 0.04 mmol) in benzene (5 ml) at room temperature and the reaction mixture was stirred for 2.5 h. The volatiles were removed in vacuo. The resulting solid was washed with hexane (4 x 0.5 ml) and lyophilized in toluene- $d_8$ . The complex *cis,trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(Cl)<sub>2</sub>(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**5**) was identified by NMR, IR and ESI-MS spectroscopy. <sup>1b</sup> Cy<sub>2</sub>BOBCy<sub>2</sub> and (CyBO)<sub>3</sub> were identified as borane species by NMR.

b) BClCy<sub>2</sub> (13  $\mu\text{l}$ , 0.01 mmol, 1 M in hexane) and PiPr<sub>3</sub> (2.5  $\mu\text{l}$ , 0.01 mmol) were dissolved in C<sub>6</sub>D<sub>6</sub> and the solution was transferred to *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**2a**, 10 mg, 0.01 mmol) using a PTFE cannula. Based on the obtained IR and HR-FT-ESI-MS data, *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(Cl)(OBCy<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] is proposed as the intermediate.

Analytical data for *trans*-[Ir(4-C<sub>5</sub>F<sub>4</sub>N)(Cl)(OBCy<sub>2</sub>)(CNtBu)(PiPr<sub>3</sub>)<sub>2</sub>] (**4a**):

<sup>1</sup>H NMR (300.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 2.85$  (m, CH), 1.19 (m, CH(CH<sub>3</sub>)<sub>2</sub>), 1.05 (s, C(CH<sub>3</sub>)<sub>3</sub>) ppm, integration of the resonances is not possible due to overlap with signals of the starting material and product as well as with cyclohexyl- and hexane-resonances.

<sup>11</sup>B NMR (96.3 MHz, toluene- $d_8$ ):  $\delta = 4$  (s, br), 0 (s, br) ppm.

<sup>19</sup>F NMR (282.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -99.3$  (m, 1 F, Ar<sub>F</sub>), -100.1 (m, 1 F, Ar<sub>F</sub>), -112.8 (m, 1 F, Ar<sub>F</sub>), -122.0 (m, 1 F, Ar<sub>F</sub>) ppm.

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -5.9$  (s) ppm.

IR (ATR):  $\tilde{\nu} = 2160$  (s, CN),  $821$  (m,  $^{16}\text{O}^{16}\text{O}$ )  $\text{cm}^{-1}$ .

FT-ESI-MS: calcd. for  $[\text{M}+\text{H}]^+$  with  $[\text{M}] = \text{C}_{40}\text{H}_{73}\text{BClF}_4\text{IrN}_2\text{O}_2\text{P}_2$ :  $m/z = 991.457$ ; found  $m/z = 991.405$ .

Analytical data for  $\text{Cy}_2\text{BOBCy}_2$ :

$^{11}\text{B}$  NMR (96.3 MHz, toluene- $d_8$ ):  $\delta = 52$  (br) ppm.

Analytical data for  $(\text{CyBO})_3$ :

$^{11}\text{B}$  NMR (96.3 MHz, toluene- $d_8$ ):  $\delta = 30$  (br) ppm.

#### Reaction of *trans*- $[\text{Ir}(4\text{-C}_5\text{F}_4\text{N})(^{18}\text{O}_2)(\text{CNtBu})(\text{PiPr}_3)_2]$ (**2b**) with $\text{BClCy}_2$

The complex *trans*- $[\text{Ir}(4\text{-C}_5\text{F}_4\text{N})(^{18}\text{O}_2)(\text{CNtBu})(\text{PiPr}_3)_2]$  (**2b**, 12 mg, 0.02 mmol) was dissolved in benzene (0.9 ml) and the solution was treated at room temperature with  $\text{PiPr}_3$  (5  $\mu\text{l}$ , 0.03 mmol) and subsequently with  $\text{BClCy}_2$  (19  $\mu\text{l}$ , 0.02 mmol, 1 M in hexane). After 30 min, the formation of an intermediate was observed by IR and mass spectroscopy, that was assigned to be *trans*- $[\text{Ir}(4\text{-C}_5\text{F}_4\text{N})(\text{Cl})(^{18}\text{O}^{18}\text{OBCy}_2)(\text{CNtBu})(\text{PiPr}_3)_2]$  (**4b**). The final product is *cis,trans*- $[\text{Ir}(4\text{-C}_5\text{F}_4\text{N})(\text{Cl})_2(\text{CNtBu})(\text{PiPr}_3)_2]$  (**5**).<sup>1b</sup>

Analytical data for *trans*- $[\text{Ir}(4\text{-C}_5\text{F}_4\text{N})(\text{Cl})(^{18}\text{O}^{18}\text{OBCy}_2)(\text{CNtBu})(\text{PiPr}_3)_2]$  (**4b**):

IR (ATR):  $\tilde{\nu} = 787$  (m,  $^{18}\text{O}^{18}\text{O}$ )  $\text{cm}^{-1}$ .

FT-ESI-MS: calcd. for  $[\text{M}+\text{H}]^+$  with  $[\text{M}] = \text{C}_{40}\text{H}_{73}\text{BClF}_4\text{IrN}_2^{18}\text{O}_2\text{P}_2$ :  $m/z = 995.466$ ; found  $m/z = 995.400$ .

#### Hydrogenation of *trans*- $[\text{Rh}(4\text{-C}_5\text{F}_4\text{N})(\text{O}_2)(\text{CNtBu})(\text{PEt}_3)_2]$ (**1**) with $\text{H}_2$ in presence of $[\text{H}(\text{OEt}_2)_2][\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$

a) THF- $d_8$  (0.8 ml) was condensed at  $-196^\circ\text{C}$  into a Young<sup>®</sup>-NMR tube containing a mixture of  $[\text{H}(\text{OEt}_2)_2][\text{B}\{3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}_4]$  (43 mg, 0.04 mmol) and *trans*- $[\text{Rh}(4\text{-C}_5\text{F}_4\text{N})(\text{O}_2)(\text{CNtBu})(\text{PEt}_3)_2]$  (**1**, 29 mg, 0.05 mmol). Dihydrogen was added (1.013 bar). The reaction mixture was kept at  $-70^\circ\text{C}$  for 15 min and shaken regularly, whereupon the colour changed from red-orange to pale yellow. The solution was allowed to warm up to room temperature and studied by NMR and IR spectroscopy.

After two days, *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**3**) and *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>] were identified (ratio 3:2, determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy). The volatiles were then removed in vacuo and collected in a separate cooling trap. Decolouration of Quantofix<sup>®</sup> peroxide test sticks and a test with an aqueous titanylsulfate solution provided evidence for the presence of hydrogen peroxide, along with a broad resonance in the <sup>1</sup>H NMR spectrum at  $\delta = 2.89$  ppm.

b) To a *Young*<sup>®</sup>-NMR tube containing [H(OEt<sub>2</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>] (5.4 mg, 0.005 mmol) and *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**1**, 32 mg, 0.05 mmol) was added THF-d<sub>8</sub> (0.8 ml) via condensation at -196°C. An H<sub>2</sub> atmosphere (1.013 bar) was added. Primarily, the solution was allowed to warm up to -70°C (and shaken regularly) and after 15 min to room temperature. The colour changed from red-orange to pale yellow. The reaction mixture was analysed by NMR and IR spectroscopy. After two days, *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**3**) and *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>] were again identified as the only compounds present (ratio 8:1, determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy). The formation of H<sub>2</sub>O<sub>2</sub> was confirmed Quantofix<sup>®</sup> peroxide test sticks and reaction with titanylsulfate solution.

Analytical data for *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>]:<sup>6</sup>

IR (ATR, evaporation of a THF-d<sub>8</sub> reaction mixture):  $\tilde{\nu} = 2212$  cm<sup>-1</sup> (w, br; CNtBu).

<sup>1</sup>H-NMR (300.1 MHz, THF-d<sub>8</sub>):  $\delta = 7.80$  (m, 8 H; *ortho*-CH<sub>Ar</sub>), 7.59 (m, 4H; *para*-CH<sub>Ar</sub>), 1.87 (m, 12 H; CH<sub>2</sub>CH<sub>3</sub>), 1.53 (s, 18 H; C(CH<sub>3</sub>)<sub>3</sub>), 1.07 ppm (dt, <sup>3</sup>J<sub>P,H</sub> = 15.6, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, 18 H; CH<sub>2</sub>CH<sub>3</sub>).

<sup>19</sup>F NMR (282.4 MHz, THF-d<sub>8</sub>):  $\delta = -63.4$  ppm (s).

<sup>11</sup>B{<sup>1</sup>H} NMR (96.3 MHz, THF-d<sub>8</sub>):  $\delta = -6.8$  ppm (s).

<sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, v):  $\delta = 23.3$  ppm (d, <sup>1</sup>J<sub>Rh,P</sub> = 116.0 Hz).

### Reduction of *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**1**) with D<sub>2</sub> in presence of [H(OEt<sub>2</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>]

To [H(OEt<sub>2</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>] (45 mg, 0.04 mmol) and *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(O<sub>2</sub>)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**1**, 30 mg, 0.05 mmol) in a *Young*<sup>®</sup>-NMR tube, THF-d<sub>8</sub> (0.8 ml) was added via condensation at -196°C. D<sub>2</sub> was then added (1.013 bar) and the reaction mixture was allowed to warm up. At -70°C, the solution was kept for 15 min and shaken regularly, whereupon the colour changed from red-orange to pale yellow. After two days, *trans*-[Rh(4-C<sub>5</sub>F<sub>4</sub>N)(CNtBu)(PEt<sub>3</sub>)<sub>2</sub>] (**3**) and *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>] were identified as the only complexes (ratio 3:2, determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy). The volatiles were removed in vacuo and the formation of H<sub>2</sub>O<sub>2</sub> was confirmed by the decolouration of Quantofix<sup>®</sup> peroxide test sticks and a test with an aqueous titanylsulfate solution.

The broad signal for H<sub>2</sub>O<sub>2</sub> in <sup>1</sup>H NMR spectrum at  $\delta = 2.89$  ppm could not be detected in the reaction with D<sub>2</sub>.

## Notes and References

- 1 (a) M. Ahijado, T. Braun, D. Noveski, N. Kocher, B. Neumann, D. Stalke, H.-G. Stammer, *Angew. Chem.*, 2005, **117**, 7107; *Angew. Chem. Int. Ed.*, 2005, **44**, 6947; (b) H. Baumgarth, G. Meier, T. Braun, B. Braun-Cula, *Eur. J. Inorg. Chem.*, 2016, **28**, 4565.
- 2 S. Hawkeswood, D. W. Stephan, *Dalton Trans.*, 2005, **12**, 2182.
- 3 (a) T. Beringhelli, D. Maggioni, G. D'Alfonso, *Organometallics*, 2001, **20**, 4927; (b) C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Firesner, G. Parkin, *J. Am. Chem. Soc.*, 2000, **122**, 10581; (c) A. A. Danopoulos, J. R. Galsworthy, M. L. H. Green, S. Cafferkey, L. H. Doerrer, M. B. Hursthouse, *Chem. Commun.*, 1998, **22**, 2529.
- 4 (a) K. Huynh, A. J. Lough, M. A. M. Forgeron, M. Bendle, A. Presa Soto, R. E. Wasylshen, I. Manners, *J. Am. Chem. Soc.*, 2009, **131**, 7905; (b) G. C. Welch, R. Prieto, M. A. Dureen, A. J. Louch, O. A. Labeodan, T. Höltrichter-Rössmann, D. W. Stephan, *Dalton Trans.*, 2009, 1559.
- 5 (a) M. Mewald, R. Fröhlich, M. Oestreich, *Chem. Eur. J.*, 2011, **17**, 9406; (b) M. A. Dureen, C. C. Brown, D. W. Stephan, *Organometallics*, 2010, **29**, 6422.
- 6 The <sup>31</sup>P{<sup>1</sup>H} NMR of the cation *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][B{3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>4</sub>] is comparable with the NMR data of the cationic rhodium compound *trans*-[Rh(CNtBu)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>][Rh{ $\kappa^2$ -(O,O)-OC(O)O}<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] from: H. Baumgarth, *Rhodiumkomplexe mit fluorierten Liganden zur Aktivierung von Disauerstoff*, diploma thesis, Humboldt-Universität zu Berlin, 2012.