

Supporting information for:

## **A CH<sub>2</sub>Cl<sub>2</sub> Complex of a [Rh(pincer)]<sup>+</sup> Cation**

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## Experimental

All manipulations, unless otherwise stated, were performed under an argon atmosphere using standard Schlenk line and glove-box techniques. Glassware was oven dried at 130°C overnight and flamed under vacuum prior to use. CH<sub>2</sub>Cl<sub>2</sub> and pentane were dried using a Grubbs-type solvent purification system (MBraun SPS-800) and degassed by three successive freeze-pump-thaw cycles.<sup>1</sup> CD<sub>2</sub>Cl<sub>2</sub> and 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (pre-treated with alumina) were dried over CaH<sub>2</sub>, vacuum distilled and stored over 3 Å molecular sieves. Na[BAR<sup>F</sup><sub>4</sub>],<sup>2</sup> Rh(<sup>t</sup>BuPNP)Cl,<sup>3</sup> and Rh(<sup>t</sup>BuPONOP)Cl (**1**),<sup>4</sup> were prepared by literature methods. NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer or a Bruker Avance III HD nanobay 400 MHz NMR spectrometer at room temperature. Residual protio solvent was used as reference for <sup>1</sup>H spectra in deuterated solvent samples. When in 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> solvent, <sup>1</sup>H NMR spectra were pre-locked to a sample of C<sub>6</sub>D<sub>6</sub> (25%) and 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (75%), and referenced to the centre of the downfield solvent multiplet ( $\delta = 7.07$ ). <sup>31</sup>P NMR spectra were externally referenced to 85% H<sub>3</sub>PO<sub>4</sub>. All chemical shifts ( $\delta$ ) are quoted in ppm and coupling constants (*J*) in Hz. ESI-MS were recorded on a Bruker micrOTOF instrument interfaced with a glove-box.<sup>5</sup> Elemental microanalyses were performed by Stephen Boyer at London Metropolitan University. Fourier Transform Infrared Spectroscopy samples were made using a custom-built cell and spectra were measured using a Thermo-Scientific Nicolet iS5 with an iD1 transmission attachment.

### Formation of [Rh(<sup>t</sup>BuPONOP)( $\kappa^1$ -ClCH<sub>2</sub>Cl)][BAR<sup>F</sup><sub>4</sub>] (**2**)

To a J. Young flask charged with **1** (30 mg, 0.055 mmol) and Na[BAR<sup>F</sup><sub>4</sub>] (49.5 mg, 0.055 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added. Immediately, the dark orange solution turned orange/yellow and a precipitate formed (assumed to be NaCl). The solution was filtered and the solvent removed *in vacuo* yielding a light orange powder (61.2 mg, 81% yield). A CH<sub>2</sub>Cl<sub>2</sub> solution of **2** layered with pentane at 298 K yields light orange crystals suitable for X-ray crystallography – however <sup>31</sup>P NMR spectroscopy of the bulk crystallised sample indicated the formation of the corresponding  $\kappa^1$ -N<sub>2</sub> complex (**3**), as well as **2**, in an

approximate 1:1 ratio. Complex **3** was confirmed *via* an independent synthetic route. Crystal picking allowed for single crystal diffraction data of the appropriate CH<sub>2</sub>Cl<sub>2</sub> complex to be obtained. **2** was found to be stable in powder form and in CH<sub>2</sub>Cl<sub>2</sub> solvent, enabling further reactivity.

**<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):** δ 7.76 – 7.72 (obscured t, 1H, C<sub>5</sub>H<sub>3</sub>N), 7.72 (br, 8H, BAr<sup>F</sup>), 7.56 (br, 4H, BAr<sup>F</sup>), 6.73 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, C<sub>5</sub>H<sub>3</sub>N), 1.44 (app t, J<sub>PH</sub> = 7.7 Hz, 36H, <sup>t</sup>Bu)

**<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz):** δ 204.5 (d, <sup>1</sup>J<sub>RhP</sub> = 136 Hz, P<sup>t</sup>Bu<sub>2</sub>)

**ESI-MS (1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, 60°C, 4.5 kV):** Only the corresponding κ<sup>1</sup>-N<sub>2</sub> complex (**3**) is found due to the presence of N<sub>2</sub> in the flow gas.<sup>6</sup>

**Elemental Microanalysis:** Calc. C<sub>54</sub>H<sub>53</sub>BCl<sub>2</sub>F<sub>24</sub>NO<sub>2</sub>P<sub>2</sub>Rh (1450.55 gmol<sup>-1</sup>): C, 44.71; H, 3.68; N, 0.97. Found: C, 44.85; H, 3.55; N, 1.09.

#### **Formation of [Rh(<sup>t</sup>BuPONOP)(κ<sup>1</sup>-N<sub>2</sub>)] [BAr<sup>F</sup><sub>4</sub>] (**3**)**

A J. Young NMR tube containing a solution of **2** (30 mg, 0.022 mmol) in 0.5 mL CH<sub>2</sub>Cl<sub>2</sub> was freeze-pump-thaw degassed three times before 1 atm N<sub>2</sub> was added to the system. After 30 minutes, the solvent was removed *in vacuo* and an isolated yield of 15 mg of **3** was obtained (52%). Layering a CH<sub>2</sub>Cl<sub>2</sub> solution of **3** with pentane at 298 K under an argon atmosphere produced orange/brown crystals suitable for single crystal X-ray diffraction.

**<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):** δ 7.81 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1H, C<sub>5</sub>H<sub>3</sub>N), 7.72 (br, 8H, BAr<sup>F</sup>), 7.55 (br, 4H, BAr<sup>F</sup>), 6.82 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2H, C<sub>5</sub>H<sub>3</sub>N), 1.44 (app t, J<sub>PH</sub> = 8 Hz, 36H, <sup>t</sup>Bu)

**<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz):** δ 211.0 (d, <sup>1</sup>J<sub>RhP</sub> = 132 Hz, P<sup>t</sup>Bu<sub>2</sub>)

**IR ν(ATR; cm<sup>-1</sup>):** 2201.9 (s, N<sub>2</sub>)

**ESI-MS (1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, 60°C, 4.5 kV):** *m/z* = 530.16 [M]<sup>+</sup> (calc. 530.16)

**Elemental Microanalysis:** Calc. C<sub>53</sub>H<sub>51</sub>BF<sub>24</sub>N<sub>3</sub>O<sub>2</sub>P<sub>2</sub>Rh (1393.63 gmol<sup>-1</sup>): C, 45.68; H, 3.69; N, 3.02. Found: C, 45.61; H, 3.74; N, 2.97.

#### Formation of [Rh(<sup>t</sup>BuPONOP)(CO)][BAr<sup>F</sup><sub>4</sub>] (**4**)

**4** was formed using a method similar to that employed for **3**, with the substitution of CO for N<sub>2</sub> gas. The light orange solution turned bright yellow immediately after addition of 1 atm CO, indicating the reaction occurring instantly. An isolated yield of 17 mg of **4** was obtained (59%). Layering a CH<sub>2</sub>Cl<sub>2</sub> solution of **4** with pentane at 298 K under an argon atmosphere formed yellow needles suitable for single crystal X-ray diffraction.

**<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):** δ 7.91 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 1H, C<sub>5</sub>H<sub>3</sub>N), 7.73 (br, 8H, BAr<sup>F</sup>), 7.56 (br, 4H, BAr<sup>F</sup>), 6.92 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 2H, C<sub>5</sub>H<sub>3</sub>N), 1.41 (app t, J<sub>PH</sub> = 8.3 Hz, 36H, <sup>t</sup>Bu)

**<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz):** δ 219.8 (d, <sup>1</sup>J<sub>RhP</sub> = 127 Hz, P<sup>t</sup>Bu<sub>2</sub>)

**IR ν(ATR; cm<sup>-1</sup>):** 2019.8 (s, CO)

**ESI-MS (C<sub>6</sub>H<sub>5</sub>F, 60°C, 4.5 kV):** *m/z* = 530.14 [M]<sup>+</sup> (calc. 530.15)

**Elemental Microanalysis:** Calc. C<sub>54</sub>H<sub>51</sub>BF<sub>24</sub>NO<sub>3</sub>P<sub>2</sub>Rh (1393.63 gmol<sup>-1</sup>): C, 46.54; H, 3.69; N, 1.01. Found: C, 46.68; H, 3.58; N, 1.08.

#### Formation of [Rh(<sup>t</sup>BuPNP)(CH<sub>2</sub>Cl)Cl][BAr<sup>F</sup><sub>4</sub>] (**5**)

To a J. Young flask charged with Rh(<sup>t</sup>BuPNP)Cl (30 mg, 0.056 mmol) and Na[BAr<sup>F</sup><sub>4</sub>] (49.8 mg, 0.056 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added. After 12 h stirring, the red solution had turned green and a precipitate formed (assumed to be NaCl). The solution was filtered and layered with pentane at 298 K yielding green crystals suitable for X-ray crystallography. <sup>31</sup>P NMR spectroscopy data of the crystals indicated several phosphorus environments, all showing coupling to rhodium (<sup>1</sup>J<sub>RhP</sub> = 97 – 122 Hz), and repeating the experiment shows varying proportions of these species. <sup>1</sup>H NMR spectroscopy data indicated that some ligand reactivity may occur (hence the lower than expected integral value for the <sup>t</sup>Bu<sub>2</sub> groups in the <sup>1</sup>H NMR spectrum). In accordance with the X-ray diffraction data obtained it is proposed that two of these species are **5** and another Rh<sup>III</sup> species, [Rh(<sup>t</sup>BuPNP)(H)Cl][BAr<sup>F</sup><sub>4</sub>] (**6**), both of which are postulated to be products from C–Cl activation of the CH<sub>2</sub>Cl<sub>2</sub> solvent. The X-ray

crystallography data additionally shows that there is an approximate 50:50 ratio of **5:6** in the crystalline lattice.

**<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):** *Mixture of products.* δ 8.11 – 6.42 (br, 3H, C<sub>5</sub>H<sub>3</sub>N), 7.70 (br, 8H, BAr<sup>F</sup>), 7.51 (br, 4H, BAr<sup>F</sup>), 4.21 – 3.19 (br, 4H, PCH<sub>2</sub>), 2.12 – 0.93 (br, 31H, <sup>t</sup>Bu), –15.48 (br, 0.5H, RhH)

**<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz):** *Major signals given.* δ 47.0 (d, <sup>1</sup>J<sub>RhP</sub> = 100 Hz, P<sup>t</sup>Bu<sub>2</sub>), 40.2 (d, <sup>1</sup>J<sub>RhP</sub> = 97 Hz, P<sup>t</sup>Bu<sub>2</sub>)

### Formation of [Rh(<sup>t</sup>BuPONOP)(η<sup>2</sup>-H<sub>2</sub>)] [BAr<sup>F</sup><sub>4</sub>]

Rh(<sup>t</sup>BuPONOP)(η<sup>2</sup>-H<sub>2</sub>)] [BAr<sup>F</sup><sub>4</sub>] was formed using an analogous method to that employed for **3** and **4**, with H<sub>2</sub> gas used as the reactant gas. The light orange solution turned yellow after 30 minutes stirring under 1 atm H<sub>2</sub>. NMR spectroscopy data were consistent with the literature,<sup>7</sup> obtaining 21 mg of [Rh(<sup>t</sup>BuPONOP)(η<sup>2</sup>-H<sub>2</sub>)] [BAr<sup>F</sup><sub>4</sub>] (76% yield).

### Crystallography

Single crystal X-ray diffraction data for complex **2** was collected on an Enraf-Nonius Kappa CCD diffractometer using Mo K<sub>α</sub> radiation (λ = 0.71073 Å) and data for complexes **3**, **4** and **5** were collected on an Agilent SuperNova diffractometer using graphite monochromated Cu K<sub>α</sub> radiation (λ = 1.54180 Å). Raw frame data were reduced using the DENZO-SMN package.<sup>8</sup> Intensity data were corrected using multi-scan method with SCALEPACK (within DENZO-SMN). The structures were solved using direct methods with SIR92<sup>9</sup> or SuperFlip<sup>10</sup> and refined using full-matrix least squares refinement on all F<sup>2</sup> data using the CRYSTALS program suite.<sup>11, 12</sup> Rotational disorder of some of the CF<sub>3</sub> groups of the [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup> anion was treated by modelling the fluorine atoms over two sites and restraining their geometry.

**Table S-1** Selected crystallographic data for [Rh(<sup>t</sup>BuPONOP)]<sup>+</sup> complexes **2**, **3** and **4**

Complex	<b>2</b>	<b>3</b>	<b>4</b>
Formula	C <sub>54</sub> H <sub>53</sub> BF <sub>24</sub> Cl <sub>2</sub> NO <sub>2</sub> P <sub>2</sub> Rh	C <sub>53</sub> H <sub>51</sub> BF <sub>24</sub> N <sub>3</sub> O <sub>2</sub> P <sub>2</sub> Rh	C <sub>54</sub> H <sub>51</sub> BF <sub>24</sub> NO <sub>3</sub> P <sub>2</sub> Rh
<i>M</i>	1450.54	1393.62	1393.62
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C 1 2/c 1	C 1 2/c 1	C 1 2/c 1
<i>T</i> [K]	150 (2)	150 (2)	150 (2)
<i>a</i> [Å]	16.9996 (5)	16.8578 (4)	16.8459 (2)
<i>b</i> [Å]	18.1716 (4)	18.1533 (3)	18.1341 (2)
<i>c</i> [Å]	39.8254 (10)	39.7792 (7)	39.7346 (7)
$\alpha$ [deg]	90	90	90
$\beta$ [deg]	96.458 (2)	95.9972 (17)	96.1653 (13)
$\gamma$ [deg]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	12224.4 (5)	12106.8 (4)	12068.1 (3)
<i>Z</i>	8	8	8
Density [g cm <sup>-3</sup> ]	1.576	1.529	1.534
$\mu$ [mm <sup>-1</sup> ]	0.533	3.831	3.847
Reflns collected	38940	42721	43229
<i>R</i> <sub>int</sub>	0.029	0.031	0.024
No. of data/restr/param	15991/912/892	12162/912/887	12280/1140/910
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0814	0.0483	0.0511
<i>wR</i> <sub>2</sub> [all data]	0.1692	0.1183	0.1211
<i>GoF</i>	0.9484	1.0139	1.0051
CCDC number	1044744	1044745	1044743

**Table S-2** Selected crystallographic data for [Rh(<sup>t</sup>BuPNP)]<sup>+</sup> complex **5**

Complex	5*
Formula	C <sub>56</sub> H <sub>57</sub> BF <sub>24</sub> Cl <sub>2</sub> NP <sub>2</sub> Rh:C <sub>55</sub> H <sub>56</sub> BF <sub>24</sub> CINP <sub>2</sub> Rh
<i>M</i>	1422.36
Crystal system	Monoclinic
Space group	P 1 2 <sub>1</sub> /c 1
<i>T</i> [K]	150 (2)
<i>a</i> [Å]	13.8327 (2)
<i>b</i> [Å]	23.4907 (3)
<i>c</i> [Å]	20.1051 (2)
<i>α</i> [deg]	90
<i>β</i> [deg]	97.5982 (11)
<i>γ</i> [deg]	90
<i>V</i> [Å <sup>3</sup> ]	6475.59 (14)
<i>Z</i>	2
Density [g cm <sup>-3</sup> ]	1.459
<i>μ</i> [mm <sup>-1</sup> ]	4.115
Reflns collected	26785
<i>R</i> <sub>int</sub>	0.029
No. of data/restr/param	12823/912/928
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.1064
<i>wR</i> <sub>2</sub> [all data]	0.2958
<i>GoF</i>	1.0109
CCDC number	1044741

\* Formed as a mixture of **5** and [Rh(<sup>t</sup>BuPNP)(H)Cl][BAr<sup>F</sup><sub>4</sub>], **6**.

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