### **Electronic Supplementary Information**

# N-H Cleavage as a Route to New Pincer Complexes

## of High-Valent Rhenium

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Figure S01.  ${}^{31}P{}^{1}H$  NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of PN<sup>H</sup>N<sup>H,Mes</sup> (1)



**Figure S02.** <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ) spectrum of  $PN^HN^{H,Mes}$  (1). Sample contains residual silicone grease and toluene.



Figure S03. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>, 23 °C) spectrum of (PNP)ReOCl<sub>2</sub> (2).



Figure S04. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, toluene-d<sub>8</sub>, 80 °C) spectrum of (PNP)ReOCl<sub>2</sub> (2).



**Figure S05.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 23 °C) spectrum of (PNP)ReOCl<sub>2</sub> (**2**). Sample contains residual toluene.



**Figure S06.** <sup>1</sup>H NMR (500 MHz, toluene-d<sub>8</sub>, 80 °C) spectrum of (PNP)ReOCl<sub>2</sub> (**2**). Sample contains residual pentane.

<sup>1</sup>H NMR (500 MHz, toluene-d<sub>8</sub>, 80 °C):  $\delta$  0.93 (dvt, *J* = 14.6, 7.2 Hz, 6H), 1.47 (m, 12H), 1.60 (dvt, *J* = 8.0 Hz, 6H), 2.27 (s, 6H), 2.44 (m, 2H), 3.10 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 7.16 (br s, 2H), 7.22 (d, *J* = 8.4 Hz, 2H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, toluene-d<sub>8</sub>, 80 C):  $\delta$  33.4 (br s).



Figure S07.<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>) spectrum of (PNN<sup>H</sup>)ReOCl<sub>2</sub> (3-Cl)



**Figure S08.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of (PNN<sup>H</sup>)ReOCl<sub>2</sub> (**3-Cl**). Sample contains residual silicone grease, pentane, and toluene.



Figure S09.<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>) spectrum of (PNN<sup>H</sup>)ReOBr<sub>2</sub> (3-Br)



**Figure S10.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of (PNN<sup>H</sup>)ReOBr<sub>2</sub> (**3-Br**). Sample contains residual silicone grease and pentane.

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Figure S11. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>) spectrum of (PNN)ReOCl (4-Cl)

**Reaction of (PNN)ReOCI (4-CI) with HCl\_{(aq)}:** No precautions against introduction of air were taken. To a J. Young tube was added a CDCl<sub>3</sub> solution of (**4-CI**) (26.1 mg, 0.04 mmol) and 12M aqueous hydrochloric acid (5  $\mu$ L, 0.06 mmol). The solution was then monitored by <sup>31</sup>P{<sup>1</sup>H} and <sup>1</sup>H NMR spectroscopy. After 10 min it was observed that a clean ca. 15% conversion had occurred to (PNN<sup>H</sup>)ReOCl<sub>2</sub> (**3-CI**) by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, with an N-H resonance observed in the <sup>1</sup>H NMR spectrum. The green solution was then placed on a rotator for 2 h after which time full, clean conversion was observed to (PNN<sup>H</sup>)ReOCl<sub>2</sub> (**3-CI**) by both <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.



**Figure S12.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of (PNN)ReOCl (**4-Cl**) with major isomer integrated. Sample contains residual pentane.



Figure S13. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>) spectrum of (PNN)ReOBr(4-Br)

**Reaction of (PNN)ReOBr (4-Br) with Me<sub>3</sub>SiCI:** To a J.Young tube was added (PNN)ReOBr (**4-Br**) (17.6 mg, 0.023 mmol) which was dissolved in C<sub>6</sub>D<sub>6</sub>. To the resultant green solution was added 10 eq. Me<sub>3</sub>SiCI ( 30  $\mu$ L, 0.23 mmol) and the tube was rotated for 24 h prior to NMR analysis. A clean ca. 14% conversion to (PNN)ReOCI (**4-CI**) was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy which was corroborated by <sup>1</sup>H NMR evidence showing the presence of only (PNN)ReOBr (**4-Br**), (PNN)ReOCI (**4-CI**), excess Me<sub>3</sub>SiCI, and Me<sub>3</sub>SiBr which had formed from the reaction. Attempts with excess equivalents of Me<sub>3</sub>SiCI revealed that the metathesis reaction, though clean in formation of **4-CI**, remains sluggish under these conditions.



**Figure S14.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of (PNN)ReOBr(**4-Br**) with major isomer integrated. Sample contains residual silicone grease, pentane, and Et<sub>2</sub>O.



Figure S15.  ${}^{31}P{}^{1}H$  NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReOCI(PMe<sub>3</sub>) (4-PMe<sub>3</sub>).



**Figure S16.** <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ) spectrum of (PNN)ReOCl(PMe<sub>3</sub>) (**4-PMe<sub>3</sub>**) with major isomer integrated. Sample contains residual silicone grease, pentane,  $Et_2O$ , and  $CH_2Cl_2$  from solvent.



Figure S17.<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReO(OTf)(4-OTf)



**Figure S18.** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReO(OTf)(**4-OTf**) with major isomer integrated. Sample contains residual silicone grease, pentane, Et<sub>2</sub>O, and CH<sub>2</sub>Cl<sub>2</sub>.



Figure S19.  ${}^{31}P{}^{1}H$  NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReO(OAc) (4-OAc)



**Figure S20.** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReO(OAc) (**4-OAc**) with major isomer integrated. Sample contains residual silicone grease, pentane, Et<sub>2</sub>O, and CH<sub>2</sub>Cl<sub>2</sub>.



Figure S21. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReO(H) (4-H)



**Figure S22.** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) spectrum of (PNN)ReO(H) (**4-H**) with major isomer integrated. Sample contains residual silicone grease, pentane.

#### X-ray Diffractometry Details for (PNP)ReOCl<sub>2</sub> (2), CCDC 1504712

A dark green, multi-faceted block of suitable size (0.35 x 0.29 x 0.05 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (150 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube,  $K_{\alpha} = 0.71073$  Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.<sup>1</sup> An absorption correction was applied using SADABS.<sup>2</sup> The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . The structure was solved in the monoclinic P 2/n space group using XS<sup>3</sup> (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. Elongated/unusual thermal ellipsoid on Re1, Cl1, and O1 indicated that these atoms are disordered and was modeled successfully with half occupancies. The structure was refined (weighted least squares refinement on  $F^2$ ) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.<sup>4</sup>

#### X-ray Diffractometry Details for (PNN<sup>H</sup>)ReOCl<sub>2</sub> (3-Cl), CCDC 1504713

A dark green, multi-faceted block of suitable size (0.33 x 0.25 x 0.15 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (150 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube,  $K_{\alpha} = 0.71073$  Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.<sup>1</sup> An absorption correction was applied using SADABS.<sup>2</sup> The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . The structure was solved in the triclinic P-1 space group using XS<sup>3</sup> (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on  $F^2$ ) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.<sup>4</sup>

#### X-ray Diffractometry Details for (PNN)ReOCI (4-CI), CCDC 1504714

A green, multi-faceted block of suitable size (0.90 x 0.62 x 0.10 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube,  $K_{\alpha} = 0.71073$  Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.<sup>1</sup> An absorption correction was applied using SADABS.<sup>2</sup> The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . The structure was solved in the triclinic C 2/c space group using XS<sup>3</sup> (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on  $F^2$ ) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.<sup>4</sup>

#### X-ray Diffractometry Details for (PNN)ReO(OTf) (4-OTf), CCDC 1504715

A dark red, multi-faceted block of suitable size (0.15 x 0.12 x 0.08 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (150 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube,  $K_{\alpha} = 0.71073$  Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.<sup>1</sup> An absorption correction was applied using SADABS.<sup>2</sup> The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on  $F^2$ . The structure was solved in the triclinic P-1 space group using XS<sup>3</sup> (incorporated in SHELXLE). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on  $F^2$ ) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.<sup>4</sup>

#### **ESI References.**

- <sup>1</sup> APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.
- <sup>2</sup> G. M. Sheldrick, SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames., University of Göttingen, 2008.
- <sup>3</sup> G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122
- <sup>4</sup> A. L. Spek, PLATON, A Multipurpose Crystallographic Tool., Utrecht University, Utrecht, The Netherlands, 1998.