

Electronic Supporting Information

Elucidation of the Resting State of a Rhodium *NNN*-Pincer Hydrogenation Catalyst that Features a Remarkably Upfield Hydride ^1H NMR Chemical Shift

Mikko M. Hänninen,^a Matthew T. Zamora,^a Connor S. MacNeil,^a Jackson P. Knott^a and Paul G. Hayes^{*,a}

Experimental details

Manipulations of air- and moisture-sensitive materials and reagents were carried out under an argon atmosphere using double manifold vacuum techniques or in a glove box. Solvents used for air-sensitive manipulations were purified using an MBraun solvent purification system (SPS), stored in PTFE-sealed glass vessels over sodium benzophenone ketyl (THF) or “titanocene” (pentane, heptane, benzene, toluene), and freshly distilled at the time of use. Deuterated solvent (benzene-*d*₆) was dried over sodium benzophenone ketyl, degassed *via* three freeze–pump–thaw cycles, distilled *in vacuo* and stored over 4 Å molecular sieves in a glass bomb under argon. All NMR spectra were recorded at ambient temperature with a Bruker Avance II (300.13 MHz for ^1H , 75.47 MHz for ^{13}C , 121.49 MHz for ^{31}P , 46.07 MHz for ^2H) or Avance III (700.40 MHz for ^1H , 176.12 MHz for ^{13}C , 283.53 MHz for ^{31}P) NMR spectrometer. Chemical shifts are reported in parts per million relative to the external standards SiMe_4 (^1H , ^{13}C) and 85% H_3PO_4 (^{31}P). Residual H- C- and D-containing species in benzene-*d*₆ (δ 7.16, 128.1) and benzene (δ 7.16) were used as internal references (^1H , ^{13}C and ^2H respectively). Assignments were aided by the use of ^1H - ^1H COSY, $^{13}\text{C}\{^1\text{H}\}$ APT, $^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$, ^1H - $^{13}\text{C}\{^1\text{H}\}$ HSQC/HMBC, and ^1H - ^{31}P HSQC/HMBC experiments (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad, ov = overlapping signals). Infrared spectra were recorded on a Bruker Tensor 37 FT Infrared spectrometer (vs = very sharp, s = sharp, w = wide, vw = very wide, ov = overlapping). Elemental analyses were performed using an Elementar Vario Microcube instrument. The compound *N,N'*-((1*H*-pyrrole-2,5-diyl)bis(diphenylphosphoranylylidene))bis(4-*isopropylaniline*) (HL) was prepared according to literature methods.¹ All other reagents were purchased from commercial sources and used as received.

NaL•THF A mixture of HL (398.3 mg, 0.5675 mmol) and NaH (15.6 mg, 0.650 mmol) was added to a 100 mL round-bottomed flask attached to a double manifold vacuum line and dissolved in THF (50 mL) to afford a cloudy, white, effervescent slurry. The reaction mixture was stirred at ambient temperature for 17 h to generate a clear, colourless solution. The solvent was removed *in vacuo* to afford a white powder which was washed with pentane (3 × 20 mL) and dried *in vacuo*, resulting in a white powder (366.4 mg, 81.12%). ^1H NMR (benzene-*d*₆, 300.13 MHz): 7.84 (dd, 8H, $^3J_{\text{HP}} = 11.5$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, Ph CH); 6.98 (dd, 4H, $^3J_{\text{HH}} = 7.3$ Hz, $^4J_{\text{HP}} = 1.5$ Hz, Pipp CH); 6.86 (ov m, 12H, Ph CH); 6.77 (dd, 2H, $^3J_{\text{HP}} = 2.0$ Hz, $^4J_{\text{HP}} = 2.0$ Hz, 3,4-pyrrole CH); 6.66 (d, 4H, $^3J_{\text{HH}} = 7.3$ Hz, Pipp CH); 3.44 (m, 4H, OCH_2CH_2); 2.66 (sept, 2H, $^3J_{\text{HH}} = 6.7$ Hz, ^1Pr CH); 1.34 (m, 4H, OCH_2CH_2); 1.14 (d, 12H, $^3J_{\text{HH}} = 6.7$ Hz, ^1Pr CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene-*d*₆, 75.47 MHz): 150.3 (d, $^2J_{\text{CP}} = 5.1$ Hz, Pipp C); 137.8 (s, Pipp C); 135.8 (d, $^1J_{\text{CP}} = 20.4$ Hz, 2,5-pyrrole C); 133.7 (d, $^1J_{\text{CP}} = 85.9$ Hz, Ph C); 133.7 (d, $^2J_{\text{CP}} = 9.2$ Hz, Ph CH); 131.3 (s, Pipp CH); 128.7 (d, $^3J_{\text{CP}} = 11.6$ Hz, Ph CH); 127.6 (s, Pipp CH); 123.9 (d, $^4J_{\text{CP}} = 17.2$ Hz, Ph CH); 121.5 (dd, $^2J_{\text{CP}} = 32.0$ Hz, $^3J_{\text{CP}} = 12.9$ Hz, 3,4-pyrrole CH); 68.1 (s, OCH_2CH_2); 34.0 (s,

ⁱPr CH); 26.1 (s, OCH₂CH₂); 25.0 (s, ⁱPr CH₃). ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): 8.8 (s, 2P, *P*=N). Anal. Calcd. (%) for C₅₀H₅₂N₃NaOP₂: C: 75.45; H: 6.59; N: 5.28. Found C: 75.75; H: 6.94; N: 5.33.

LRh(COE) (1) In an argon filled glove box [RhCl(COE)₂]₂ (178.7 mg, 0.2491 mmol) and NaL (416.7 mg, 0.5236 mmol) were added to a 50 mL round-bottomed flask and dissolved in toluene (15 mL). The reaction vessel was attached to a double manifold vacuum line and the mixture heated at 50 °C for 1.5 h under an argon atmosphere. Volatiles were removed under reduced pressure, resulting in a brown solid. The flask was taken into a glove box and the solid redissolved in toluene (5 mL). The solution was filtered to remove sodium chloride and the remaining solid was washed with benzene (5 × 2 mL) and toluene (1 × 2 mL). All volatiles were removed *in vacuo* to afford pure **1** as an orange-red powder. Yield: 415.7 mg (91.30%). X-ray diffraction quality single crystals were grown from a concentrated toluene solution at -35 °C. ¹H NMR (benzene-*d*₆, 300.13 MHz): δ 7.76 (dd, 8H, ³J_{HP} = 12.0 Hz, ³J_{HH} = 8.1 Hz, Ph CH); 7.12 (dd, 4H, ³J_{HH} = 8.2 Hz, ⁴J_{HP} = 2.4 Hz, Pipp CH); 6.97–6.88 (ov m, 12H, Ph CH); 6.74 (d, 4H, ³J_{HH} = 8.2 Hz, Pipp CH); 6.72 (d, 2H, ³J_{HP} = 2.1 Hz, 3,4-pyrrole CH); 3.52 (d, 2H, ²J_{HRh} = 7.8 Hz, COE CH); 2.59 (br s, 2H, COE CH₂); 2.54 (sept, 2H, ³J_{HH} = 6.8 Hz, ⁱPr CH); 1.73–1.51 (ov m, 8H, COE CH₂); 1.28 (br s, 2H, COE CH₂); 1.02 (d, 12H, ³J_{HH} = 6.8 Hz, ⁱPr CH₃). ¹³C{¹H} NMR (benzene-*d*₆, 75.47 MHz): δ 147.3 (s, Ar C); 143.1 (d, ²J_{CP} = 3.8 Hz, Ar C); 133.5 (d, ²J_{CP} = 10.4 Hz, Ar CH); 132.4 (s, Ar C); 131.9 (ov d, ³J_{CP} = 7.2 Hz, Ar CH); 131.9 (s, Ar CH); 131.1 (s, 2,5-pyrrole C); 128.6 (d, ²J_{CP} = 12.7 Hz, Ar CH); 126.1 (s, Ar CH); 116.7 (dd, ²J_{CP} = 26.9 Hz, ³J_{CP} = 8.8 Hz, 3,4-pyrrole CH); 66.4 (d, ¹J_{CRh} = 14.9 Hz, COE CH); 34.1 (s, ⁱPr CH); 31.5 (s, COE CH₂); 30.3 (s, COE CH₂); 27.6 (s, COE CH₂); 24.6 (s, ⁱPr CH₃). ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): δ 33.8 (d, 2P, ³J_{PRh} = 6.0, *P*=N). IR (KBr): ν_{max} (cm⁻¹) 3448 (vw), 3076 (w), 3058 (w), 3018 (s), 2958 (s), 2918 (s), 2899 (w), 2866 (w), 2835 (s), 1734 (s), 1717 (s), 1684 (s), 1654 (s), 1617 (s), 1603 (s), 1589 (s), 1559 (s), 1541 (s), 1506 (vs), 1437 (s), 1330 (s), 1250 (s), 1181 (s), 1159 (s), 1112 (s), 1003 (s), 985 (s), 955 (s), 846 (s), 796 (s), 744 (s), 714 (s), 692 (s), 660 (s), 600 (w). Anal. Calcd. (%) for C₅₄H₅₈N₃P₂Rh: C, 70.97; H, 6.40; N, 4.60. Found: C, 70.73; H, 6.59; N, 4.81.

LRh(C₂H₄) (2) In an argon filled glove box, **1** (51.0 mg, 0.0558 mmol) was added to a two-neck 25 mL round-bottomed flask and dissolved in toluene (5 mL). The reaction vessel was attached to a double manifold vacuum line and C₂H₄ gas was bubbled into solution (3 × 3 min). Between each addition of C₂H₄, the contents of the round-bottomed flask were evaporated to remove volatiles, including extruded COE. The reaction mixture was stirred for a total of 90 min, and volatiles removed *in vacuo* to afford **2** as an orange powder. The product was recrystallized from a benzene/toluene/pentane (2:1:1) mixture at -35 °C as X-ray diffraction quality crystals. Yield: 42.8 mg (92.2%). ¹H NMR (benzene-*d*₆, 300.13 MHz): δ 7.75 (dd, 8H, ³J_{HH} = 7.2 Hz, ³J_{HP} = 11.7 Hz, Ph CH); 7.03–6.88 (ov m, 16H, Ph CH + Pipp CH); 6.73 (ov m, 4H, Ph CH + Pipp CH); 6.68 (d, 2H, ³J_{HP} = 1.8 Hz, 3,4-pyrrole CH); 3.14 (br s, 4H, CH₂=CH₂); 2.54 (sept, 2H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 0.97 (d, 12H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃). ¹³C{¹H} NMR (benzene-*d*₆, 75.47 MHz): δ 145.7 (s, Ar C); 142.6 (d, ²J_{CP} = 3.3 Hz, Ar C); 133.4 (d, ²J_{CP} = 9.9 Hz, Ar CH); 132.3 (s, Ar C); 132.0 (s, Ar CH); 131.1 (s, 2,5-pyrrole C); 130.6 (d, ³J_{CP} = 6.6 Hz, Ar CH); 128.8 (d, ³J_{CP} = 12.1 Hz, Ar CH); 126.5 (s, Ar CH); 116.8 (dd, ²J_{CP} = 28.6 Hz, ³J_{CP} = 8.8 Hz, 3,4-pyrrole CH); 51.8 (d, ¹J_{CRh} = 15.4 Hz, CH₂=CH₂); 34.0 (s, ⁱPr CH); 24.4 (s, ⁱPr CH₃). ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): δ 33.9 (d, 2P, ²J_{PRh} = 4.7 Hz, *P*=N). IR (KBr): ν_{max} (cm⁻¹) 3054 (w), 3018 (w), 2956 (s), 2926 (w), 2867 (w), 1951 (s), 1902 (s), 1820 (w), 1726 (w), 1671 (s), 1603 (w), 1589 (w), 1573 (w), 1504 (s), 1484 (s), 1458 (s), 1437 (vs), 1413 (s), 1382 (s), 1361 (s), 1342 (w), 1257 (w), 1184 (s), 1156 (s), 1108 (s), 1014-982 (ov), 849 (s), 795 (s), 719 (s), 693 (s), 603 (s), 567 (s). Anal. Calcd. (%) for C₄₈H₄₈N₃P₂Rh: C, 69.31; H, 5.82; N, 5.05. Found: C, 69.21; H, 5.81; N, 5.41.

LRh(PhCCPh) (3) In an argon filled glove box, **1** (91.3 mg, 0.0999 mmol) and diphenylacetylene (17.8 mg, 0.0999 mmol) were added to a 20 mL scintillation vial and dissolved in toluene (5 mL). The reaction mixture was stirred for 90 min at ambient temperature, after which all volatiles were removed *in vacuo* to afford pure **3** as an orange-red solid. Yield: 62.0 mg (63.2%). X-ray diffraction quality single crystals were recrystallized from a benzene/pentane mixture (2:1) at ambient temperature. ¹H NMR (benzene-*d*₆, 300.13 MHz): δ 8.34 (d, 4H, ³J_{HH} = 7.3 Hz, Ph_{PhCCPh} CH); 7.77–7.71 (ov m, 8H, Ph_L CH); 7.24 (t, 4H, ³J_{HH} = 7.3 Hz, Ph_{PhCCPh} CH); 7.12 (t, 2H, ³J_{HH} = 7.3 Hz, Ph_{PhCCPh} CH); 6.98–6.89 (ov m, 12H, Ar CH); 6.76 (d, 2H, ³J_{HP} = 2.1 Hz, 3,4-pyrrole CH); 6.64 (dd, 4H, ³J_{HH} = 8.1 Hz, ⁴J_{HP} = 1.8 Hz, Pipp CH); 6.45 (d, 4H, ³J_{HH} = 8.1 Hz, Pipp CH); 2.38 (sept, 2H, ³J_{HH} = 6.8 Hz, ⁱPr CH); 0.91 (d, 12H, ³J_{HH} = 6.8 Hz, ⁱPr CH₃). ¹³C{¹H} NMR (benzene-*d*₆, 75.47 MHz): δ 146.4 (s, Ar C); 141.9 (d, ²J_{CP} = 2.7 Hz, Ar C); 133.5 (d, ²J_{CP} = 10.4 Hz, Ar CH); 132.4 (s, Ar C); 132.1 (s, Ar CH); 131.2 (s, Ar C); 131.1 (s, Ar CH); 130.2 (d, ²J_{CRh} = 8.2 Hz, Ar CH); 128.8 (d, ²J_{CP} = 12.2 Hz, Ar CH); 127.8 (s, Ar CH); 125.9 (br s, Ar CH); 125.4 (s, Ar CH); 124.2 (s, Ar C); 117.0 (dd, ²J_{CP} = 27.5 Hz, ³J_{CP} = 8.8 Hz, 3,4-pyrrole CH); 95.7 (d, ¹J_{CRh} = 18.5 Hz, PhC≡CPh); 34.0 (s, ⁱPr CH); 24.6 (s, ⁱPr CH₃). ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): δ 32.1 (d, 2P, ²J_{PRh} = 4.6 Hz, P=N). IR (KBr): ν_{max} (cm⁻¹) 3453 (vw), 3073 (w), 3054 (w), 3021 (w), 2958 (w), 2927 (s), 2869 (w), 1932 (w), 1908 (w), 1890 (w), 1700 (s), 1653 (s), 1602 (s), 1590 (s), 1559 (s), 1541 (s), 1505 (s), 1489 (s), 1457 (s), 1437 (s), 1384 (s), 1337 (s), 1257 (w), 1159 (s), 1108 (w), 998 (s), 982 (w), 840 (s), 794 (s), 752 (s), 719 (s), 691 (s), 600 (s), 562 (s). Anal. Calcd. (%) for C₆₆H₆₀N₃P₂Rh ([LRh(PhCCPh)]·1C₆H₆): C, 74.78; H, 5.71; N, 3.96. Found: C, 74.86; H, 5.74; N, 4.28.

L₂Rh₂ (4): In an argon filled glove box, **1** (47.4 mg, 0.0519 mmol) was added to a 25 mL round-bottomed flask and dissolved in toluene (5 mL). The reaction vessel was attached to a double manifold vacuum line and the solution was degassed by three freeze–pump–thaw cycles. A hydrogen atmosphere was applied to the flask and the solution was stirred at ambient temperature for 24 h. All volatiles were removed *in vacuo* to afford **4** as a dark brown powder. The product was recrystallized from a benzene/pentane (10:1) mixture at ambient temperature as X-ray diffraction quality single crystals. Yield: 22.0 mg (55.0%). ¹H NMR (benzene-*d*₆, 700.39 MHz): δ 11.40 (d, 1H, ²J_{HP} = 2.5 Hz, NH); 9.21 (dd, 2H, ³J_{HP} = 11.3 Hz, ³J_{HH} = 7.5 Hz, Ph CH); 8.07 (ddd, 2H, ³J_{HP} = 11.6 Hz, ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.2 Hz, Ph CH); 8.01 (m, 2H, Ph CH); 7.97 (ddd, 2H, ³J_{HP} = 11.7 Hz, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 1.3 Hz, Ph CH); 7.95 (dd, 2H, ³J_{HH} = 8.3 Hz, ⁴J_{HP} = 1.9 Hz, Pipp CH); 7.82 (m, 2H, Pipp CH); 7.59 (m, 2H, Ph CH); 7.33 (ddd, 2H, ³J_{HP} = 10.2 Hz, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.2 Hz, Ph CH); 7.29 (dd, 2H, ³J_{HH} = 7.8 Hz, ³J_{HP} = 3.3 Hz, Ph CH); 7.25–7.11 (ov m, 9H, Ar CH); 7.07 (t, 2H, ³J_{HH} = 8.4 Hz, Ph CH); 7.06 (dd, 2H, ³J_{HH} = 7.5 Hz, ³J_{HP} = 2.0 Hz, Ph CH); 7.04 (dd, 2H, ³J_{HH} = 7.5 Hz, ³J_{HP} = 1.2 Hz, Ph CH); 7.01 (d, 2H, ³J_{HH} = 8.4 Hz, Ph CH); 6.98 (m, 2H, Pipp CH); 6.97 (m, 3H, Ph CH); 6.91 (m, 5H, Ph CH); 6.86 (td, 2H, ³J_{HH} = 7.8 Hz, ³J_{HP} = 2.7 Hz, Ph CH); 6.81 (d, 2H, ³J_{HH} = 8.1 Hz, Pipp CH); 6.68 (dd, 1H, ³J_{HP} = 3.15 Hz, ³J_{HH} = 3.15 Hz, 3,4-pyrrole CH); 6.50 (dd, 1H, ³J_{HP} = 2.3 Hz, ³J_{HH} = 1.6 Hz, 3,4-pyrrole CH); 6.49 (dd, 1H, ³J_{HP} = 3.3 Hz, ³J_{HH} = 3.3 Hz, 3,4-pyrrole CH); 6.34 (d, 2H, ³J_{HH} = 8.0 Hz, Pipp CH); 6.30 (dd, 1H, ³J_{HP} = 3.8 Hz, ³J_{HH} = 3.8 Hz, 3,4-pyrrole CH); 6.23 (dd, 1H, ³J_{HH} = 8.8 Hz, ³J_{HH} = 5.9 Hz, Pipp CH); 5.65 (ddd, 1H, ³J_{HH} = 9.2 Hz, ⁴J_{HH} = 5.2 Hz, ⁴J_{HP} = 5.2 Hz, Pipp CH); 4.85 (dd, 1H, ³J_{HP} = 10.1 Hz, ³J_{HH} = 7.0 Hz, Pipp CH); 3.28 (ddd, 1H, ³J_{HH} = 6.4 Hz, ³J_{HH} = 6.2 Hz, ³J_{HH} = 4.1 Hz, Pipp CH); 2.78 (sept, 2H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 2.53 (sept, 1H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 2.47 (sept, 1H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 2.34 (dd, 1H, ³J_{HP} = 12.6 Hz, ³J_{HH} = 5.9 Hz, Ph CH); 1.25 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.24 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.19 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.18 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.03 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.01 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 0.97 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 0.95 (d, 3H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); –35.84 (dd, 1H, ¹J_{HRh} = 19.8 Hz, ¹J_{HRh} = 19.8 Hz, Rh–H–Rh). ¹³C{¹H} NMR (benzene-*d*₆, 176.12 MHz): δ 151.6 (d, ²J_{CP} = 1.8 Hz, Pipp *ipso*-C); 149.2 (d, ²J_{CP} = 4.2 Hz, Pipp *ipso*-C); 144.0 (d, ²J_{CP} = 2.0 Hz, Pipp *ipso*-C); 143.4 (d, ²J_{CP} = 3.6 Hz, Pipp *ipso*-C); 141.7 (s, Pipp C); 141.4 (d, ¹J_{CP} = 14.0 Hz, 2,5-pyrrole C); 141.1 (s, Pipp C); 141.1 (s, Pipp C); 141.1 (d, ¹J_{CP} = 18.5 Hz, 2,5-pyrrole C); 140.7 (d,

$^1J_{CP} = 14.2$ Hz, 2,5-pyrrole C); 140.6 (s, Pipp C); 140.1 (d, 2,5-pyrrole); 135.9 (d, $^1J_{CP} = 90.2$ Hz, Ph *ipso*-C); 135.7 (d, $J_{CP} = 9.6$ Hz, Ph CH); 134.5 (d, $J_{CP} = 8.2$ Hz, Ph CH); 133.9 (d, $J_{CP} = 10.4$ Hz; Ph CH); 133.8 (dd, $J_{CP} = 10.2$ Hz, $J_{CRh} = 4.6$ Hz, Ph CH); 133.8 (d, $^1J_{CP} = 80.6$ Hz, Ph *ipso*-C); 133.5 (d, $J_{CP} = 9.0$ Hz, Ph CH); 132.7 (d, $^3J_{CP} = 2.2$ Hz, Pipp CH); 132.6 (d, $J_{CP} = 10.5$ Hz, Ph CH); 132.2 (d, $^3J_{CP} = 1.9$ Hz, Pipp CH); 132.2 (d, $^1J_{CP} = 91.3$ Hz, Pipp CH); 132.1 (s, Pipp CH); 131.8 (d, $^3J_{CP} = 2.4$ Hz, Pipp CH); 131.6 (s, Pipp CH); 131.1 (d, $J_{CP} = 12.4$ Hz, Ph CH); 131.0 (dd, $J_{CRh} = 10.3$ Hz, $J_{CP} = 1.8$ Hz, Ph CH); 130.6 (d, $J_{CP} = 7.6$ Hz, Ph CH); 129.5 (d, $J_{CP} = 11.7$ Hz, Ph CH); 129.0 (d, $J_{CP} = 11.9$ Hz, Ph CH); 128.9 (s, Pipp CH); 128.9 (d, $J_{CP} = 11.6$ Hz, Ph CH); 127.8 (d, $J_{CP} = 10.9$ Hz, Ph CH); 126.8 (s, Pipp CH); 125.9 (d, $^3J_{CP} = 1.7$ Hz, Pipp CH); 125.2 (d, $^1J_{CP} = 83.8$ Hz, Ph *ipso*-C); 125.2 (dd, $^2J_{CP} = 21.3$ Hz, $^3J_{CP} = 11.4$ Hz, 3,4-pyrrole CH); 124.5 (dd, $^2J_{CP} = 31.1$ Hz, $^3J_{CP} = 12.1$ Hz, 3,4-pyrrole CH); 119.7 (dd, $^2J_{CP} = 28.2$ Hz, $^3J_{CP} = 12.0$ Hz, 3,4-pyrrole CH); 119.3 (d, $J_{CP} = 8.4$ Hz, Ph CH); 115.9 (dd, $^2J_{CP} = 28.5$ Hz, $^3J_{CP} = 10.0$ Hz, 3,4-pyrrole); 57.6 (br m, Ph CH); 54.6 (br m, Ph CH); 48.3 (br m, Ph CH); 47.6 (br ddd, $^1J_{CP} = 113.28$ Hz, $^1J_{CRh} = 8.8$ Hz, $^1J_{CRh} = 1.8$ Hz, Ph CH); 34.2 (s, iPr CH); 34.1 (s, iPr CH); 34.1 (s, iPr CH); 34.0 (s, iPr CH); 25.3 (s, iPr CH₃); 25.0 (s, iPr CH₃); 24.9 (s, iPr CH₃); 24.7 (s, iPr CH₃); 24.7 (s, iPr CH₃); 24.6 (s, iPr CH₃); 24.1 (s, iPr CH₃). $^{31}P\{^1H\}$ NMR (benzene-*d*₆, 176.1 MHz): δ 31.1 (s, 1P, Ph₂P=NPipp); 23.5 (s, 1P, Ph₂P=NPipp); 11.8 (d, 1P, $^2J_{PRh} = 6.2$ Hz, Ph₂P=NHPipp); -1.9 (s, 1P, Ph₂P=NPipp). IR (KBr): ν_{max} (cm⁻¹) 3422 (vw), 3054 (w), 3019 (w), 2956 (s), 2925 (w), 2869 (w), 1967 (s), 1890 (s), 1828 (s), 1773 (s), 1700 (s), 1685 (s), 1647 (s), 1603 (s), 1576 (s), 1559 (s), 1541 (w), 1504 (s), 1457 (s), 1437 (s), 1382 (s), 1361 (s), 1277 (w), 1260 (w), 1182 (w), 1151 (s), 1108 (s), 1054 (w), 1014 (w), 998 (w), 946 (s), 846 (s), 798 (s), 743 (s), 719 (s), 692 (s), 669 (s), 604 (s), 569 (s). Anal. Calcd. (%) for C₉₂H₉₀N₆P₄Rh₂: C, 68.66; H, 5.64; N, 5.22. Found: C, 68.71; H, 5.08; N, 5.93.

L₂Rh₂-d₂ (4-d₂): In an argon filled glove box, **1** (88.1 mg, 0.096 mmol) was added to a 25 mL round-bottomed flask equipped with a stir-bar, and dissolved in toluene (7 mL). The reaction vessel was attached to a double manifold vacuum line and the solution was degassed by three freeze-pump-thaw cycles. A deuterium atmosphere was applied to the flask and the solution was stirred at ambient temperature for 18 h. All volatiles were removed *in vacuo* to afford **4-d₂** as a dark brown powder. Yield: 46.1 mg (59.7%). 1H NMR (benzene-*d*₆, 300.13 MHz): δ 9.21 (dd, 2H, $^3J_{HP} = 11.9$ Hz, $^3J_{HH} = 7.9$ Hz, Ph CH); 8.46 (ddd, 2H, $^3J_{HP} = 10.9$ Hz, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.7$ Hz, Ph CH); 8.11 (m, 2H, Ph CH); 8.01 (m, 2H, Ph CH); 7.96 (dd, 2H, $^3J_{HH} = 7.3$ Hz, $^4J_{HP} = 1.8$ Hz, Pipp CH); 7.86 (m, 2H, Pipp CH); 7.69 (m, 2H, Ph CH); 7.35 (ddd, 2H, $^3J_{HP} = 11.3$ Hz, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.7$ Hz, Ph CH); 7.21 (dd, 2H, $J_{HH} = 7.8$ Hz, $J_{HP} = 3.3$ Hz, Ph CH); 7.19–7.11 (ov m, 9H, Ar CH); 7.06 (t, 2H, $J_{HH} = 8.4$ Hz, Ph CH); 7.01 (dd, 2H, $J_{HH} = 7.5$ Hz, $J_{HP} = 2.0$ Hz, Ph CH); 6.98 (dd, 2H, $J_{HH} = 7.5$ Hz, $J_{HP} = 1.2$ Hz, Ph CH); 6.96 (d, 2H, $J_{HH} = 8.4$ Hz, Ph CH); 6.94 (m, 10 H, Ph CH); 6.90 (td, 2H, $J_{HH} = 7.8$ Hz, $J_{HP} = 2.7$ Hz, Ph CH); 6.81 (d, 2H, $^3J_{HH} = 8.1$ Hz, Pipp CH); 6.68 (dd, 1H, $^3J_{HP} = 4.6$ Hz, $^3J_{HH} = 3.2$ Hz, 3,4-pyrrole CH); 6.50 (dd, 1H, $^3J_{HP} = 2.3$ Hz, $^3J_{HH} = 1.6$ Hz, 3,4-pyrrole CH); 6.45 (dd, 1H, $^3J_{HP} = 3.3$ Hz, $^3J_{HH} = 3.3$ Hz, 3,4-pyrrole CH); 6.35 (d, 2H, $^3J_{HH} = 8.0$ Hz, Pipp CH); 6.30 (dd, 1H, $^3J_{HP} = 3.5$ Hz, $^3J_{HH} = 3.5$ Hz, 3,4-pyrrole CH); 6.23 (dd, 1H, $J_{HH} = 8.4$ Hz, $^3J_{HH} = 5.9$ Hz, Pipp CH); 5.67 (ddd, 1H, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 5.4$ Hz, $^4J_{HP} = 5.0$ Hz, Pipp CH); 4.84 (dd, 1H, $J_{HP} = 10.4$ Hz, $J_{HH} = 6.1$ Hz, Pipp CH); 3.27 (ddd, 1H, $J_{HH} = 7.4$ Hz, $J_{HH} = 5.8$ Hz, $J_{HH} = 4.1$ Hz, Pipp CH); 2.83 (sept, 2H, $^3J_{HH} = 6.4$ Hz, iPr CH); 2.58 (sept, 1H, $^3J_{HH} = 7.0$ Hz, iPr CH); 2.47 (sept, 1H, $^3J_{HH} = 7.2$ Hz, iPr CH); 2.37 (dd, 1H, $J_{HP} = 12.6$ Hz, $J_{HH} = 5.9$ Hz, Ph CH); 1.26 (d, 3H, $^3J_{HH} = 7.4$ Hz, iPr CH₃); 1.20 (d, 3H, $^3J_{HH} = 6.4$ Hz, iPr CH₃); 1.19 (d, 3H, $^3J_{HH} = 6.4$ Hz, iPr CH₃); 1.18 (d, 3H, $^3J_{HH} = 6.4$ Hz, iPr CH₃); 1.03 (d, 3H, $^3J_{HH} = 6.4$ Hz, iPr CH₃); 1.01 (d, 3H, $^3J_{HH} = 7.0$ Hz, iPr CH₃); 0.97 (d, 3H, $^3J_{HH} = 6.4$ Hz, iPr CH₃); 0.95 (d, 3H, $^3J_{HH} = 6.4$ Hz, iPr CH₃). $^{31}P\{^1H\}$ NMR (benzene-*d*₆, 121.49 MHz): δ 31.2 (s, 1P, Ph₂P=NPipp); 23.5 (s, 1P, Ph₂P=NPipp); 11.8 (d, 1P, $^2J_{PRh} = 7.3$ Hz, Ph₂P=NHPipp); -1.8 (s, 1P, Ph₂P=NPipp). $^{13}C\{^1H\}$ NMR spectra were consistent with that of **4**. $^2H\{^1H\}$ NMR (benzene-*d*₆, 46.07MHz): δ 11.18 (br s, 1D, ND); -35.28 (br s, 1D,

Rh–D–Rh), coupling constants could not be ascertained due to the inherent broad nature of deuterium resonances.

LRh(*trans*-PhCH=CHPh) (5): Method 1: In an argon filled glove box, **3** (10.0 mg, 0.0102 mmol) was added to a J. Young NMR tube and dissolved in 0.5 mL of benzene-*d*₆. The J. Young NMR tube was attached to a double manifold vacuum line and the solution was degassed by three freeze–pump–thaw cycles. A hydrogen atmosphere (1 atm) was applied to the tube and hydrogenation progress was monitored by multinuclear NMR spectroscopy. After 72 h at ambient temperature, the tube was heated at 50 °C for 18 h, after which complete conversion of **3** to **5** was observed. The J. Young NMR tube was brought back into a glove box and the benzene-*d*₆ solution was layered with pentane. X-ray quality crystals formed overnight at ambient temperature. **Method 2:** In an argon filled glove box, **1** (75.7 mg, 0.0828 mmol) and *trans*-1,2-diphenylethylene (15.1 mg, 0.0838 mmol) were added to a 25 mL round-bottomed flask and dissolved in toluene (5 mL). The reaction vessel was attached to a double manifold vacuum line and the mixture heated at 50 °C for 18 h under an argon atmosphere. Volatiles were removed under reduced pressure, resulting in a red solid. The flask was taken into a glove box and the solid redissolved in toluene (1.5 mL) and precipitated with pentane (12.0 mL). The mixture was filtered, the isolated solid was washed with pentane (5 × 1.5 mL) and then dried *in vacuo* to afford pure **5** as a red powder. Yield: 60.5 mg (87.0%). **Method 3:** In an argon filled glove box, **2** (65.3 mg, 0.0785 mmol) and *trans*-1,2-diphenylethylene (14.5 mg, 0.0804 mmol) were added to a 20 mL scintillation vial and dissolved in toluene (1 mL). The mixture was stirred for 18 h under an argon atmosphere, followed by removal of volatiles under reduced pressure, resulting in a red solid. The solid was redissolved in toluene (1.5 mL) and precipitated with pentane (7.5 mL). The solution was decanted and the remaining solid was washed with pentane (5 × 1.5 mL). The residue was dried *in vacuo* to afford pure **5** as a red powder. Yield: 59.3 mg (89.9%). ¹H NMR (benzene-*d*₆, 300.13 MHz): δ 7.67 (m, 4H, Ph CH); 7.36 (m, 9H, Ph CH); 7.21 (m, 11H, Ph CH); 7.07 (ov m, 6H, Ph CH + Pipp CH); 7.77 (ov m, 5H, Ph CH + 3,4-pyrrole CH); 6.65 (ov m, 5H, Ph CH + Pipp CH); 5.18 (br s, 2H, PhCH=CHPh); 2.58 (sept, 2H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 1.05 (d, 6H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.04 (d, 6H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃). ¹³C{¹H} NMR (benzene-*d*₆, 75.47 MHz): 148.5 (d, ³J_{CRh} = 1.4 Hz, PhCH=CHPh *ipso*-C); 147.4 (br s, Pipp C); 143.0 (br s, Pipp C); 134.4 (d, ²J_{CP} = 10.1 Hz, Ph CH); 134.3 (d, ¹J_{CP} = 11.4 Hz, 2,5-pyrrole C); 133.2 (d, ¹J_{CP} = 101.6 Hz, Ph C); 132.9 (d, ³J_{CP} = 11.1 Hz, Ph CH); 129.2 (d, ⁴J_{CP} = 13.2 Hz, Ph CH); 128.9 (s, Pipp CH); 128.0 (s, PhCH=CHPh CH); 127.9 (s, Pipp CH); 125.8 (s, PhCH=CHPh CH); 124.0 (s, PhCH=CHPh CH); 61.3 (br s, PhCH=CHPh); 34.1 (s, ⁱPr CH); 24.6 (s, ⁱPr CH₃); 24.6 (s, ⁱPr CH₃). Signal (dd) for 3,4-pyrrole CH was not observed. ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): δ 34.0 (d, ²J_{PRh} = 4.9 Hz, P=N). IR (KBr): ν_{max} (cm⁻¹) 3448 (vw), 3075 (w), 3049 (s), 3016 (s) 2957 (s), 2930 (bs), 2869 (s), 1963 (s), 1893 (s), 1670 (s), 1653 (s), 1637 (s), 1599 (s), 1577 (s), 1560 (s), 1496 (s), 1457 (s), 1437 (s), 1407 (s), 1383 (s), 1362 (s), 1310 (s), 1250 (w), 1181 (s), 1161 (s), 1111 (s), 1071 (s), 1029 (s), 997 (s), 979 (w), 845 (s), 797 (s), 752 (s), 743 (s), 721 (s), 692 (s), 602 (s), 564 (s). Anal. Calcd. (%) for C₆₀H₅₆N₃P₂Rh: C, 73.24; H, 5.74; N, 4.27. Found: C, 73.36; H, 6.00; N, 4.54.

κ²-N,N'-LRh(CO)₂: Method 1: In an argon filled glove box, **1** (10.0 mg, 0.0109 mmol) was added to a J. Young NMR tube and dissolved in 0.5 mL of benzene-*d*₆. The J. Young NMR tube was attached to a double manifold vacuum line and the solution was degassed by three freeze–pump–thaw cycles. A carbon monoxide atmosphere (1 atm) was applied to the tube and the reaction was monitored by multinuclear NMR spectroscopy. After 24 h at ambient temperature, complete conversion was observed. **Method 2:** In an argon filled glove box, **1** (48.1 mg, 0.055 mmol) was added to a 25 mL round-bottomed flask equipped with a stir bar and dissolved in benzene. The entire apparatus was attached to a double manifold vacuum line and the solution was degassed by three freeze–pump–thaw cycles. An excess of carbon monoxide was condensed into the vessel, and the mixture was allowed

to stir at ambient temperature for 18 h. Volatiles were removed *in vacuo* and the residue was washed with pentane (3 × 5 mL). The complex was isolated as a bright yellow powder. Yield: 30.1 mg (63.9%). ¹H NMR (benzene-*d*₆, 300.13 MHz): δ 8.17 (dd, 4H, ³J_{HP} = 11.9 Hz, ³J_{HH} = 7.2 Hz, Ph CH); 7.70 (dd, 4H, ³J_{HP} = 11.8 Hz, ³J_{HH} = 7.5 Hz, Ph CH); 7.56 (d, 2H, ³J_{HH} = 8.1 Hz, Pipp CH); 7.31 (d, 2H, ³J_{HH} = 7.8 Hz, Pipp CH); 7.13–7.01 (ov m, 14H, Ph CH + Pipp CH); 6.88 (d, 2H, ³J_{HH} = 8.1 Hz, Pipp CH); 6.75 (s, 1H, 3,4-pyrrole CH); 6.57 (s, 1H, 3,4-pyrrole CH); 3.00 (sept, 1H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 2.64 (sept, 1H, ³J_{HH} = 6.9 Hz, ⁱPr CH); 1.41 (d, 6H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); 1.08 (d, 6H, ³J_{HH} = 6.9 Hz, ⁱPr CH₃); ¹³C{¹H} NMR (benzene-*d*₆, 75.47 MHz): 185.8 (d, ¹J_{CRh} = 67.9 Hz, CO); 183.1 (d, ¹J_{CRh} = 70.2 Hz, CO); 150.7 (s, Ar C); 147.9 (d, ¹J_{CP} = 3.4 Hz, Ph C); 143.3 (s, Ar C); 136.6 (s, Ar C); 135.5 (s, Ar C); 134.1 (s, Ar C); 134.0 (s, Ar C); 133.2 (d, ¹J_{CP} = 10.4 Hz, 2,5-pyrrole C); 132.7 (d, ¹J_{CP} = 9.9 Hz, 2,5-pyrrole C); 132.4 (s, Ar C); 130.8 (s, Ar C); 129.0 (d, ²J_{CP} = 6.8 Hz, Ph C); 128.6 (d, ²J_{CP} = 12.4 Hz, Ph C); 126.8 (s, Ph C); 126.7 (d, ²J_{CP} = 8.9 Hz, Ph C); 126.3 (s, Ar C); 123.9 (d, ¹J_{CP} = 10.4 Hz, Ph C); 117.0 (dd, ²J_{CP} = 27.2 Hz, ³J_{CP} = 9.6 Hz, 3,4-pyrrole CH); 33.7 (s, ⁱPr CH); 33.3 (s, ⁱPr CH); 24.6 (s, ⁱPr CH₃); 23.8 (s, ⁱPr CH₃). ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): δ 32.3 (s, 1P, P=N–Rh); –2.9 (s, 1P, P=N); IR (KBr): ν_{max} (cm⁻¹) 2955 (ov), 2922 (ov), 2853 (ov), 2065 (vs, C–O), 1994 (vs, C–O), 1942 (s), 1602 (s), 1503 (vs), 1436 (vs), 1326 (w), 1258 (w), 1154 (s), 1107 (ov).

LRh(PPh₃): In an argon filled glove box, **1** (47.3 mg (0.0518 mmol) and PPh₃ (14.3 mg, 0.0545 mmol) were added to a 20 mL scintillation vial equipped with a stir bar. Addition of 7 mL of benzene resulted in a deep red solution, which was allowed to stir for 18 h at 55 °C. Volatiles were removed *in vacuo* and the resulting red-orange solid was washed with pentane (3 × 5 mL). Yield: 48.8 mg (86.4%). ¹H NMR (benzene-*d*₆, 300.13 MHz): δ 7.80 (m, 8H, Ph CH); 7.59 (m, 8H, Ph CH); 7.19 (m, 4H, Ph CH); 7.13–6.87 (ov m, 21H, Ph CH + PPh₃ CH); 6.79 (dd, 2H, ³J_{HP} = 1.6 Hz, ⁴J_{HP} = 1.6 Hz, 3,4-pyrrole CH); 6.45 (m, 2H, Ph, CH); 2.48 (sept, 2H, ³J_{HH} = 7.1 Hz, ⁱPr CH); 0.98 (d, 12H, ³J_{HH} = 7.1 Hz, ⁱPr CH₃). ¹³C{¹H} NMR (benzene-*d*₆, 75.47 MHz): δ 150.4 (s, Pipp C); 140.6 (d, ²J_{CP} = 2.3 Hz, Pipp C); 138.8 (d, ¹J_{CP} = 32.4 Hz, 2,5-pyrrole C); 134.8 (d, ¹J_{CP} = 11.6 Hz, Ph CH); 133.1 (d, ¹J_{CP} = 11.6 Hz, Ph CH); 131.5 (d, ¹J_{CP} = 90.2 Hz, Ph C); 131.1 (s, Pipp CH); 129.5 (d, ¹J_{CP} = 8.9 Hz, Ph CH); 127.9 (s, Ph CH); 127.6 (s, Ph CH); 127.2 (s, Ph CH); 126.8 (d, ¹J_{CP} = 8.7 Hz, Ph CH); 124.6 (s, Pipp CH); 116.5 (dd, ²J_{CP} = 27.9 Hz, ³J_{CP} = 8.8 Hz, 3,4-pyrrole CH); 33.3 (s, ⁱPr CH); 24.1 (s, ⁱPr CH₃). ³¹P{¹H} NMR (benzene-*d*₆, 121.49 MHz): δ 50.1 (dt, 1P, ¹J_{PRh} = 204.6 Hz, ³J_{PP} = 4.5 Hz, PPh₃); 31.8 (dd, 2P, ²J_{PRh} = 4.5 Hz, ³J_{PP} = 4.5 Hz, P=N).

Regeneration of 2 from 4: In an argon filled glove box, **4** (8.4 mg, 0.0052 mmol) was added to a J. Young NMR tube and dissolved in 0.5 mL of benzene-*d*₆. The J. Young NMR tube was attached to a double manifold vacuum line and the solution was degassed by three freeze–pump–thaw cycles. An ethylene atmosphere (1 atm) was applied to the tube and the solution was left at ambient temperature for 96 h. The formation of **2** was monitored by multinuclear NMR spectroscopy.

General procedure for hydrogenation of COE: In an argon filled glove box, **1** (41.1 mg, 0.0450 mmol) was dissolved in 1.5 mL of benzene-*d*₆, giving a 0.03 M pre-catalyst stock solution. For a typical catalytic run, 0.15 mL of the stock solution was taken and mixed with 0.3 mL of benzene-*d*₆ and 30 equiv of substrate in a J. Young NMR tube. For COE hydrogenation, this equates to 0.01 M of **1** and 0.3 M of substrate. The J. Young NMR tube was attached to a double manifold vacuum line and the solution was degassed by three freeze–pump–thaw cycles. A hydrogen atmosphere (1 atm) was applied to the tube at ambient temperature, or at –196 °C (to provide approximately 4 atm of H₂ upon warming to ambient temperature). The J. Young NMR tube was continually inverted at 30 turns min⁻¹ to ensure adequate mass transfer. The tube was refilled to 4 atm of hydrogen every 2 hours to maintain the desired pressure. All catalytic runs were monitored periodically using multinuclear NMR

spectroscopy. All reactions resulted in quantitative conversion of product into substrate (>95 %) at ambient temperature. Between 30 and 60 equiv of substrate were used in catalytic experiments.

Further experimental and structural discussion

Unfortunately, single crystals of **2** succumb to rapid decomposition upon removal from the mother liquor, resulting in the crystals becoming covered with amorphous material. However, inner portions of the crystals remain intact, allowing for modest diffraction of X-ray radiation, despite interference from the polycrystalline material. The data is not ideal, however, and therefore discussions of the metrical parameters are not included in the body of the manuscript. The data set does, however, allow for qualitative discussions associated with the connectivity of atoms, and thus, the geometry of complex **2**. The structure of **2** is depicted in **Fig. S1**

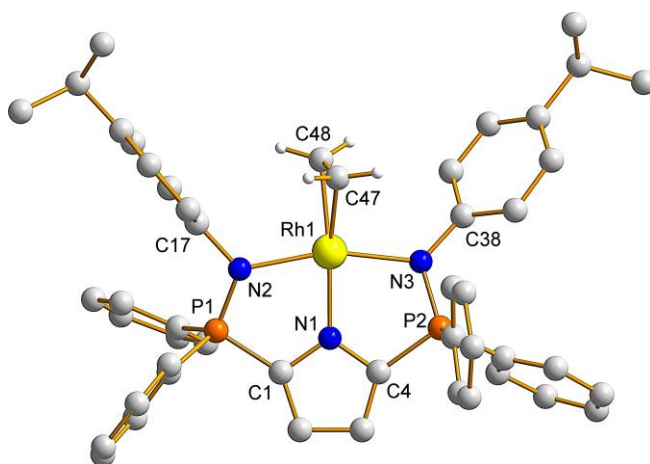


Fig. S1 The solid state structure of **2**. Atoms are presented by ball and stick model and all hydrogen atoms, except those on the ethylene moiety, are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh–N1 = 2.009(9), Rh–N2 = 2.105(9), Rh–N3 = 2.128(8), Rh–C47 = 2.087(12), Rh–C48 = 2.096(12), P1–N2 = 1.626(9), P2–N3 = 1.631(9), C47–C48 = 1.408(17); N1–Rh–C47 = 154.5(4), N1–Rh–C48 = 166.0(4), N2–Rh–N3 = 163.1(3), N2–P1–C1 = 103.4(5), N3–P2–C4 = 104.2(5).

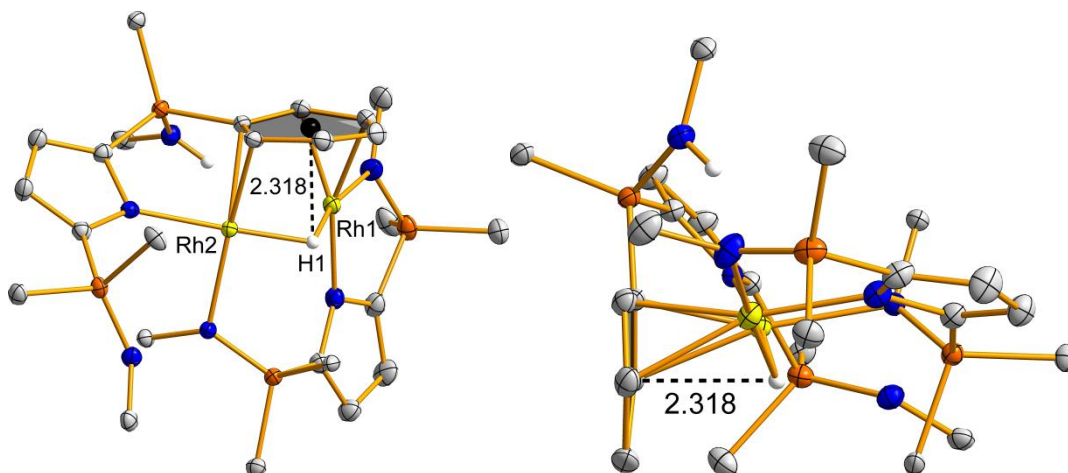
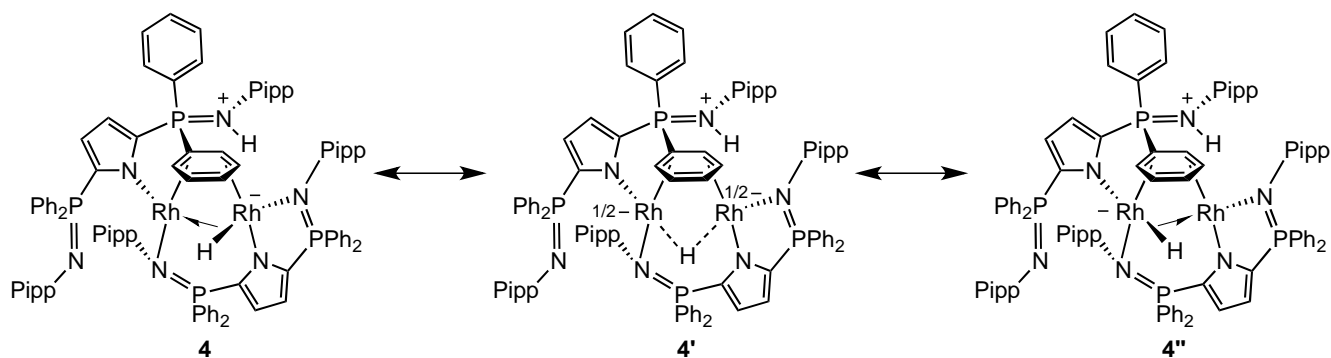


Fig. S2 Hydride arrangement with respect to the bridging phenyl ring. The bridging hydride (H1) is positioned directly below (2.318 Å) the centroid of the phenyl group with an average H1–Centroid–C(aryl) angle of = 90.01°. Notably, this distance is substantially less than the distance between the aromatic protons to the centroid, which have an average H–centroid distance of 3.373 Å.



Scheme S1 Resonance forms of **4** to correlate Lewis structure to geometry observed in the solid state by X-ray diffraction.

Formation of **5**

Hydrogenation of the coordinated diphenylacetylene ligand in complex **3** would be expected to proceed through 1,2-diphenylethylene, which could potentially form as either the *E* or *Z* isomer. Therefore determining the stereoselectivity of hydrogenation is important. Upon hydrogenation of **3**, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicated formation of only one product (**5**) which exhibited symmetric phosphorus environments as evidenced by the appearance of only one signal at δ 34.0. Analysis of X-ray quality crystals grown from this mixture indicated that only the (*E*)-isomer was present (**Fig. S3**). It is important to note that no disorder implying the presence of the (*Z*)-isomer was observed. The absence of the (*Z*)-isomer can possibly be rationalized on the basis of steric factors, as its formation would most likely require detachment of one of the phosphinimine groups from the rhodium centre, thus rendering this reaction energetically unfavourable. In addition, complete hydrogenation of diphenylacetylene was observed when 4 atm of H_2 was introduced, as indicated by the emergence of resonances attributed to 1,2-diphenylethane in the ^1H NMR spectrum.

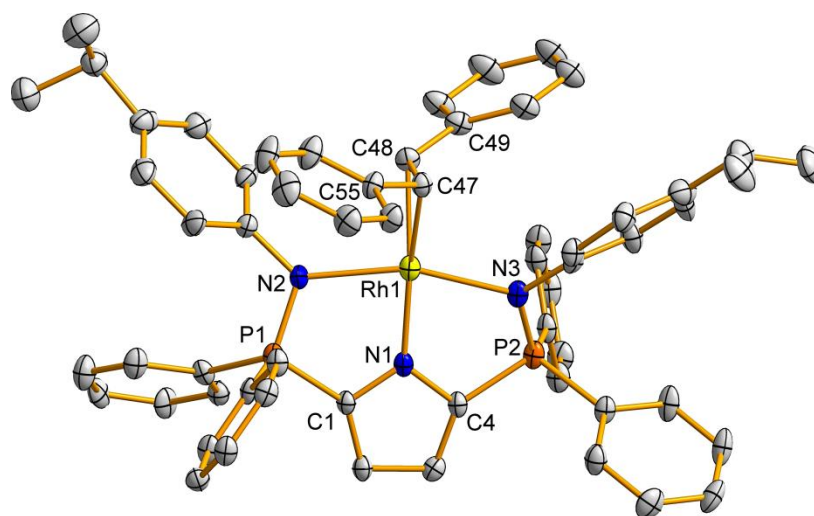


Fig. S3 The solid state structure of **5**. Thermal ellipsoids are drawn with 30% probability and all hydrogen atoms are omitted for clarity. Only the main component of the disordered Pipp-groups is shown. Selected bond distances (Å) and angles (deg): Rh1–N1 = 2.004(5), Rh1–N2 = 2.179(5), Rh1–N3 = 2.162(5), Rh1–C47 = 2.111(5), Rh1–C48 = 2.117(6), P1–N2 = 1.617(5), P2–N3 = 1.617(5), C47–C48 = 1.391(9); N1–Rh1–C47 = 160.7(2), N1–Rh1–C48 = 160.8(2), N2–Rh1–N3 = 160.5(2), C1–P1–N2 = 104.3(3), C4–P2–N3 = 103.5(3), C47–C48–C49 = 124.1(5), C48–C47–C55 = 125.4(5); C55–C47–C48–C49 = 144.1(6).

Computational details

All calculations were performed using the Gaussian 09 program package.² Complex **4** was truncated for the sake of computational resources by substituting all but the bridging phenyl group with methyl groups (**Fig. S4**). The geometry of **4'** was optimized at the DFT level using the PBE1PBE³⁻⁵ hybrid functional and Def2-TZVP⁶ basis set with an effective core potential (def-ECP)⁷ obtained from the EMSL Basis Set Exchange.⁸ Full vibrational analysis was performed to ensure that the geometry obtained by the optimization was a minimum on the potential energy surface. Proton chemical shifts were calculated using the Gauge-Independent Atomic Orbital (GIAO) method as implemented in the Gaussian 09 program package.

The calculated chemical shifts (**Table S1**) are generally in good agreement with the experimental data. The upfield shift for the hydride signal was predicted to appear at $\delta -27.85$ which is significantly downfield compared to that observed in the experimental spectrum ($\delta -35.84$), but nonetheless, still agrees reasonably well. The discrepancy most likely originates from the inability of the effective-core potential to properly take into account the relativistic effects of the Rh atoms and from the size of the basis set utilized. The large absolute difference in the calculated NH chemical shift may stem from the substitution of the nitrogen bound Pipp moiety for a methyl group.

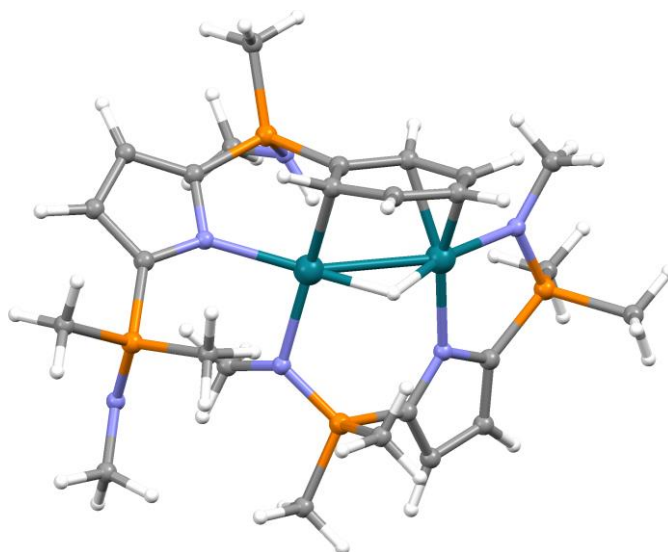


Fig. S4 Ball-and-stick presentation of the truncated model of compound **4'**.

Table S1. Calculated ¹H NMR chemical shifts of **4'**.

Type	X-ray #	Def2-TZVP/Opt δ (ppm)	“EXP” δ (ppm)	Absolute difference
Hydride	H1	-27.85	-35.84	7.99
NH	H6	6.48	11.4	4.92
Ph	H83	2.13	2.34	0.21
Ph	H84	6.60	7.07	0.47
Ph	H85	6.88	7.07	0.19
Ph	H86	3.07	3.28	0.21
Ph	H87	5.02	4.85	0.17
Pyrrole(1)	H2	6.50	6.30	0.20
Pyrrole(1)	H3	6.62	6.49	0.13
Pyrrole(2)	H52	6.89	6.50	0.39
Pyrrole(2)	H53	6.91	6.68	0.23

Table S2. XYZ coordinates of the optimized truncated model of compound **4'**.

C	0.156574147913	-0.010601485536	0.025086840799	H	5.246753871626	0.582458111977	6.632564471211
C	0.096621787707	0.193479567368	1.401072853713	H	1.943271094318	-0.137871199608	-1.279346836053
N	1.340538056748	0.329786784567	1.931276306595	H	2.292496820245	3.613535152367	6.111780525847
C	2.210934231070	0.214504968774	0.896628234923	H	8.540941902788	-2.855698164963	5.928394517821
C	1.515330134360	-0.000153416501	-0.297761425772	H	-0.671879559366	-0.153601814937	-0.653590488596
Rh	1.530739593595	0.630730650907	3.970466076345	H	4.631413795348	2.965653650295	6.427973890281
N	-0.585530845323	0.368675920681	3.980686850488	H	10.510123685821	-0.131287123569	3.838688999657
C	-1.454152550680	0.491444038565	5.131012028554	H	9.802686942975	-0.260057781563	5.466217779148
P	3.973963006255	0.345235462249	1.146263103089	H	10.189346761126	-1.727370128460	4.528469539620
C	4.360435414397	2.078820411509	1.425679404741	H	8.303447012284	1.622055910839	3.020778928805
P	-1.242776631568	0.339667527981	2.528733574778	H	6.659500249053	1.159393668482	3.538153459690
C	-2.222287246969	1.805741144710	2.101921442952	H	7.918602543908	1.481824393880	4.753102110731
Rh	4.235538850590	-0.063082618240	4.280220050034	H	8.549300445181	-1.531866145273	0.258799757870
C	3.268331603637	-0.183025363081	6.121163412070	H	8.540240648820	0.131528374336	0.832261700221
C	4.277827023889	0.829301777325	6.210859707512	H	9.898358728256	-0.933897156922	1.208797093888
C	3.870036127497	2.212205356537	6.257742952234	H	4.361245337898	0.712535309402	-1.203727728738
C	2.579341110941	2.567638441512	6.083838333519	H	5.768639586928	-0.012679895263	-0.383999813234
C	1.548092456842	1.575790833673	5.887591216366	H	4.369356981945	-1.020166896178	-0.810867247074
C	1.859069505730	0.195726684826	5.980364502769	H	3.932762713627	2.395291039745	2.376389766994
P	3.684314576868	-1.868216780430	6.446166250003	H	5.444106991095	2.203433901590	1.450819609655
C	3.454292076079	-2.449656484803	8.138267871490	H	3.932370142053	2.673716061281	0.616718696910
N	5.801484472629	-1.275650714037	5.007743650363	H	-2.388084134371	-0.078445220412	5.026297133738
C	5.375637674188	-2.050599270579	6.047395005164	H	-0.956339872071	0.094133159117	6.018832125585
C	6.425522059174	-2.810692588974	6.570998724268	H	-1.733094655143	1.530819410664	5.357251784762
C	7.539675380058	-2.469553837843	5.811551371217	H	-2.600426896502	1.735430356237	1.080037472701
C	7.122144372896	-1.521067020674	4.863299108619	H	-3.066102380079	1.906575910413	2.788551821968
P	8.177618227099	-0.694183405178	3.676164155858	H	-1.580614470772	2.683404572181	2.188428129037
C	7.724014092273	1.066437581942	3.7622622001877	H	-2.741481411892	-1.025356614490	1.216292037305
N	4.630816883389	-0.554919373241	2.296337207003	H	-1.883909870348	-1.965706489820	2.460159584118
N	2.570338220707	-2.723703077053	5.553045421562	H	-3.267124270726	-0.935687803356	2.907961637193
C	2.712667681469	-4.156027226595	5.359776453096	H	2.408544725875	-2.327405077224	8.421489006663
C	4.680962697566	-0.032117567702	-0.473882057142	H	3.730520255311	-3.502231626757	8.225669116288
C	-2.398547865032	-1.027334396980	2.252950206951	H	4.090215738942	-1.864685680127	8.802953237546
C	9.822886175029	-0.701713704497	4.468604503816	H	1.840884781934	-4.527640550505	4.819859445332
N	8.100511336236	-1.381371403118	2.280801266227	H	3.615221162794	-4.429626893003	4.801975765728
C	8.798606839592	-0.903206062453	1.121736785019	H	2.737991709690	-4.666422348999	6.324946035948
H	3.121525020655	1.119070243523	3.798625170980	C	4.850225983556	-1.965347607082	1.991698441170
H	0.530794531657	1.897964484482	6.081741948818	H	3.909409240549	-2.530369636870	1.920899814713
H	2.354740496072	-2.206423447801	4.702339258455	H	5.410524451820	-2.104421100644	1.061461654114
H	6.381483691061	-3.512619537971	7.390848368622	H	5.461954951759	-2.405417256488	2.775206835184
H	1.108379607451	-0.516466468134	6.311513568280				

Crystallographic details

Single crystals of **1** were obtained from toluene at $-35\text{ }^{\circ}\text{C}$, crystals of **2** were acquired from a benzene/toluene/pentane mixture at $-35\text{ }^{\circ}\text{C}$, whereas crystals of **3**, **4**, and **5** were grown from benzene/pentane (or benzene-*d*₆/pentane) mixtures at ambient temperature (see experimental section for additional details). Crystals were coated in dry Paratone oil under an argon atmosphere and mounted onto a MiTeGen microloop. Data were collected at 173K using a Bruker SMART APEX II diffractometer (Mo K α radiation, $\lambda = 0.71073\text{ \AA}$) outfitted with a CCD area-detector and a KRYO-FLEX liquid nitrogen vapour cooling device. Data collection with 0.5° or 1.0° steps yielded complete data sets. Unit cell parameters were determined and refined on all observed reflections using APEX2 software.⁹ Data reduction and correction for Lorentz polarization were performed using SAINT-Plus software.¹⁰ Absorption corrections were applied using SADABS¹¹ as implemented in the APEX2 software. The structures were solved by direct methods and refined by the full-matrix least squares method on F^2 using the SHELX software suite¹² and Olex2 program.¹³ All non-hydrogen atoms were refined anisotropically. C–H hydrogen atom positions (excluding the ethylene hydrogens in **2** which were treated similarly to N–H) were calculated and isotropically refined as riding models to their parent atoms whereas hydride and N–H hydrogens

were located from the Fourier difference maps and isotropically refined (with a fixed N–H bond length). Summary of selected data collection and refinement parameters is presented below (**Table S3**).

Table S3. Crystal data and structure refinement for complexes **1-5**.

	1	2	3·2C₆H₆	4·1C₆H₆	5
Empirical formula	C ₅₄ H ₅₈ N ₃ P ₂ Rh	C ₄₈ H ₄₈ N ₃ P ₂ Rh	C ₇₂ H ₆₆ N ₃ P ₂ Rh	C ₉₈ H ₉₆ N ₆ P ₄ Rh ₂	C ₆₀ H ₅₆ N ₃ P ₂ Rh
Formula weight	913.88	831.74	1138.12	1687.50	983.92
Temperature/K	173	173	173	173	173
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n	C2/c	P2 ₁ /n
a/Å	13.580(3)	16.185(10)	13.567(4)	42.986(11)	13.907(7)
b/Å	21.768(6)	18.144(11)	28.198(8)	17.237(4)	27.103(13)
c/Å	17.290(4)	15.477(10)	16.293(5)	27.577(9)	16.593(9)
α/°	90	90	90	90	90
β/°	111.548(4)	118.406(8)	109.213(6)	119.527(5)	112.133(11)
γ/°	90	90	90	90	90
Volume/Å ³	4754(2)	3998(4)	5886(3)	17779(9)	5793(5)
Z	4	4	4	8	4
ρ _{calc} /cm ³	1.277	1.382	1.284	1.261	1.128
μ/mm ⁻¹	0.465	0.545	0.390	0.492	0.386
F(000)	1912.0	1728	2376.0	7008.0	2048.0
Crystal size/mm ³	0.32 × 0.32 × 0.05	0.10 × 0.10 × 0.10	0.2 × 0.12 × 0.1	0.2 × 0.16 × 0.1	0.34 × 0.2 × 0.04
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.148 to 52	3.636 to 50.190	2.888 to 49.996	2.996 to 50	3.006 to 49.998
Index ranges	-16 ≤ h ≤ 16, -26 ≤ k ≤ 26, -21 ≤ l ≤ 20	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -18 ≤ l ≤ 18	-16 ≤ h ≤ 16, -33 ≤ k ≤ 33, -19 ≤ l ≤ 19	-52 ≤ h ≤ 53, -21 ≤ k ≤ 21, -33 ≤ l ≤ 34	-16 ≤ h ≤ 17, -27 ≤ k ≤ 32, -20 ≤ l ≤ 16
Reflections collected	59111	31351	74858	105476	34510
Independent reflections	9342 [R _{int} = 0.0617, R _{sigma} = 0.0401]	7034 [R _{int} = 0.4529, R _{sigma} = 0.4385]	10367 [R _{int} = 0.0700, R _{sigma} = 0.0609]	15648 [R _{int} = 0.0767, R _{sigma} = 0.0551]	10077 [R _{int} = 0.1280, R _{sigma} = 0.2171]
Data/restraints/parameters	9342/180/639	7034/317/507	10367/282/725	15648/353/1139	10077/215/632
Goodness-of-fit on F ² (S) ^a	1.053	0.894	1.119	1.077	0.896
Final R indexes [I >= 2σ (I)] ^b	R ₁ = 0.0331, wR ₂ = 0.0757	R ₁ = 0.0832, wR ₂ = 0.1122	R ₁ = 0.0619, wR ₂ = 0.1491	R ₁ = 0.0412, wR ₂ = 0.1085	R ₁ = 0.0658, wR ₂ = 0.1357
Final R indexes [all data] ^b	R ₁ = 0.0457, wR ₂ = 0.0827	R ₁ = 0.2886, wR ₂ = 0.1692	R ₁ = 0.0828, wR ₂ = 0.1600	R ₁ = 0.0609, wR ₂ = 0.1168	R ₁ = 0.1645, wR ₂ = 0.1579
Largest diff. peak/hole / e Å ⁻³	0.46/-0.41	0.59/-0.84	0.93/-1.05	0.85/-0.63	0.52/-1.09

Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

^a $S = [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0540P)^2 + 22.8160P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$

References

1. K. R. D. Johnson, M. A. Hannon, J. S. Ritch and P. G. Hayes, *Dalton Trans.*, 2012, **41**, 7873.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 Revision D.01*, Gaussian Inc. , Wallingford CT, 2009.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
4. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
5. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
6. F. Weigend and R. Ahlrichs, *PCCP*, 2005, **7**, 3297.
7. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123.
8. K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li and T. L. Windus, *J. Chem. Inf. Model.*, 2007, **47**, 1045.
9. *APEX2*, (2010) Bruker AXS, Madison, WI.
10. *SAINT-Plus*, (2009) Bruker AXS, Madison, WI.
11. G. M. Sheldrick, *SADABS*, (2008) Bruker AXS, Madison, WI.
12. G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112.
13. O. V. Dolomanov, J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.