Supporting information:

Exploring the role of phosphorus substituents on the enantioselectivity of Ru-catalysed ketone hydrogenation using tridentate phosphine-diamine ligands

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Experimental

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and degassed prior to use. Unless otherwise stated reagents were purchased commercially and used as received. Solvents were removed by rotary evaporation on a Heidolph labrota 4000. Flash column chromatography was performed on Davisil silica gel Fluorochem 60 Å, particle size 35-70 µm, or on an automated Biotage Isolera™ system using pre-packed SNAP HP-SIL cartridges with silica gel, particle size 30 µm. Melting Points were determined with a Gallenkamp melting point apparatus No. 889339 or a Mettler FP82HT Hot Stage and are uncorrected. NMR spectra were recorded on Bruker Avance 300 and 400 instruments or on a Jeol Eclipse 400 instrument.. Proton chemical shifts are referenced to internal residual solvent protons. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of the above. Where appropriate, coupling constants (J) are quoted in Hz and are reported to the nearest 0.1 Hz. All spectra were recorded at room temperature and the solvent for a particular spectrum is given in parentheses. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 Spectrum GX FT-IR system or on a Perkin Elmer Spectrum One FT-IR Spectrometer.. Mass spectrometry was performed by the ESPSRC National Mass Spectrometry Service Centre, Swansea University, using Waters ZQ4000, Thermofisher LTQ Orbitrap XL and Finnigan MAT 900 XLT instruments, or by Mrs Caroline Horburgh at the University of St Andrews using a Waters Micromass GCT (Time of flight) fitted with lockspray for accurate mass (ESI) or GCT (CI), or in the case of P-chiral compounds, LRMS using a Perkin Elmer Sciex API 150 EX LC/MS or a Micromass GCT Mass Spectrometer for HRMS, at the Chemistry Centre of Lund University, Sweden. The masses are reported as the average of three runs. Optical rotations were measured on a Perkin Elmer 341 polarimeter using a 1 ml cell with a 1 dm path length at 20 ºC using the sodium D-line. Microanalysis for carbon, hydrogen and nitrogen were performed either using an EA 1110 CHNS CE instruments elemental analyser by Mrs Sylvia Williamson at the University of St Andrews, or by Mr Stephen Boyer at the London Metropolitan University.

Synthesis of P-Chiral PAMP-derived PNN Ligands

Preparation of ligand precursor (*S*)-2

The α-carboxymethyl-substituted phosphine borane (*S*)-**2** used as the precursor for ligand **5**, was prepared via deprotonation of (*S*)-PAMP with ^{s}BuLi, followed by reaction with CO_2(g), as reported by Ohashi et al.[1] Alternative procedures for the preparation of (*S*)-**2**, as well as characterization data for this compound have been reported by Hii and co-workers,[2] and Vargas et al.[3] (*S*)-PAMP was prepared following a procedure reported by Colby and Jamison[4] for the synthesis of related diarylmethylphosphine ligands, but can also be prepared as reported by Jugé et al.[5]

Preparation of (*S*)-2,5-dioxopyrrolidin-1-yl 2-(boronato(2-methoxyphenyl)phenylphosphino)-acetate, (*S*)-**3**

(*S*)-(2-Carboxyethyl)(2-methoxyphenyl)phenylphosphine-borane ((*S*)-**2**) (531 mg, 1.85 mmol) and *N*-hydroxysuccinimide (426 mg, 3.70 mmol) were dissolved in 15 mL dichloromethane. Dicyclohexylcarbodiimide (763 mg, 3.70 mmol) dissolved in 5 mL dichloromethane was added dropwise, resulting in the formation of a white precipitate. After stirring for 3 hours at ambient temperature (reaction followed by TLC, heptane/ethyl acetate 1:1) the reaction mixture was filtered through a pad of celite, and the resulting solution was concentrated by rotary evaporation. Flash chromatography (silica, gradient of 30-80% ethyl acetate in heptane) afforded (*S*)-**3** as a white solid (209 mg, 71%); mp 58 ºC. $[\alpha]_D^{20}$ +30.2 (c 0.13, $CHCl_3$); ν_{max}/cm^{-1} (film) 2942 (w), 2391 (m), 1813 (m), 1783 (m), 1740 (s), 1478 (m), 1203 (s), 1064 (s); δ_H (400 MHz, $CDCl_3$) 7.79-7.67 (3H, m, $C_{Ar}H$), 7.58-7.38 (4H, m, $C_{Ar}H$), 7.03 (1H, app br t, *J* 8, $C_{Ar}H$), 6.94 (1H, dd, *J* 8, 4, $C_{Ar}H$), 3.80 (3H, s, OCH_3), 3.79 (1H, dd, AB system J_{AB} 15, J_{HP} 12, PCH_AH_B, partial overlap with OCH_3), 3.74 (1H, dd, AB system J_{AB} 15, J_{HP} 10, PCH_AH_B), 2.67 (4H, s, $(CH_2)_2$), 1.45-0.65 (3H, br m, BH_3); δ_C (101 MHz, $CDCl_3$) 168.4 (2C, *C*(O)); 162.8 (d, *J* 3.8, *C*(O)), 161.1 (OC_{ipso}), 135.9 (d, *J* 15, $C_{Ar}H$), 134.4 ($C_{Ar}H$), 131.9 (2C, d, *J* 11, $C_{Ar}H$), 131.3 ($C_{Ar}H$), 128.6 (2C, d, *J* 11, $C_{Ar}H$), 128.0 (d, *J* 58, C_{ipso}), 121.2 (d, *J* 13, $C_{Ar}H$), 113.6 (d, *J* 54, C_{ipso}), 111.0 (d, *J* 4.6, $C_{Ar}H$), 55.5 (CH_3), 29.8 (d, *J* 33, PCH_2), 25.4 (2C, $(CH_2)_2$); δ_P ($CDCl_3$, 162 MHz) 16.4; *m/z* (ES+) 384.4, 372.3, 257.6, 299.6, 215.6; HRMS (EI+) found 385.1257 $C_{19}H_{21}BNO_5P$ requires 385.1250.

General procedure for the preparation of PNN amides (*R*,*R*)(S_P)- and (*S*,*S*)(S_P)-4

Amides (*S*,*S*)(S_P)-**4** and (*S*,*S*)(S_P)-**4**, were prepared from (*S*)-**3** following a procedure reported by Correia,[6] exemplified by the preparation of (*S*,*S*)(S_P)-**4**. Ester (*S*)-**3** (209 mg, 0.54 mmol) was dissolved in 3 mL dichloromethane and added dropwise, over a period of 3 h, to a solution of (1*S*,2*S*)-diaminocyclohexane (155 mg, 1.36 mmol) in 6 mL dichloromethane. The reaction mixture was subsequently diluted with water (10 mL) and extracted with dichloromethane (2 x 15 mL). The combined organic phases were dried over magnesium sulfate and concentrated *in vacuo*. Flash chromatography (silica gel, 2-15% methanol in dichloromethane) afforded 141 mg of(*S*,*S*)(S_P)-**4** (68%) as a foamy white solid.

***N*-((1*R*,2*R*)-2-Aminocyclohexyl)-2-((*S*)-(boronato(2-methoxyphenyl)phenylphosphino)acetamide,** (*R*,*R*)(*S*$_P$)-**4**
White foamy solid (64 mg, 64%). $[\alpha]_D^{20}$ -73.5 (c 0.16, $CDCl_3$); ν_{max}/cm^{-1} (IR) (film) 3280 (m), 2933 (s), 2381 (s), 1651 (s), 1537 (s), 1249 (s) 1020 (m), 806 (m); δ_H (400 MHz, $CDCl_3$) 7.75 (1H, ddd, *J* 14, 8, 1, $C_{Ar}H$), 7.69 (2H, dd, *J* 11, 7, $C_{Ar}H$), 7.47 (1H, t, *J* 8, $C_{Ar}H$), 7.45-7.34 (3H, m, $C_{Ar}H$), 7.01 (1H, app t, *J* 8, $C_{Ar}H$), 6.87 (1H, dd, *J* 8, 4, $C_{Ar}H$), 6.52 (1H, d, *J* 9, N*H*C(O)), 3.71 (3H, s, OCH_3), 3.46 (2H, app br d, *J* 12, C*H*N), 3.00 (2H, br s, NH_2), 2.46-2.37 (2H, m, PCH_2C(O)), 1.87 (1H, app br d, *J* 12, cyclohexyl C*H*), 1.69 (1H, app br d, *J* 13, cyclohexyl C*H*), 1.64-1.52 (2H, m, cyclohexyl CH_2) 1.30-0.70 (7H, m, cyclohexyl CH_2 and BH_3); δ_C (101 MHz, $CDCl_3$) 165.7 (*C*(O)), 161.3 (OC_{ipso}), 135.6 (d, *J* 15, C_{Ar}H), 134.2 (C_{Ar}H), 131.7 (2C, d, *J* 10, C_{Ar}H), 131.0 (s, C_{Ar}H), 128.6 (d, *J* 60, C_{ipso}), 128.4 (2C, d, *J* 11, C_{Ar}H), 121.0 (d, *J* 13, C_{Ar}H), 114.9 (d, *J* 56, C_{ipso}), 111.3 (d, *J* 4.6, C_{Ar}H), 55.9 (*C*H), 55.5 (OCH_3), 54.5 (*C*H), 33.9 (cyclohexyl *C*H_2), 33.5 (d, *J* 31, P*C*H_2), 31.9 (cyclohexyl *C*H_2), 24.7 (cyclohexyl *C*H_2), 24.6 (cyclohexyl *C*H_2); δ_P ($CDCl_3$, 162 MHz) 12.6; *m/z* (ES+) 385.6 ($[M+H]^+$), 371.4 ($[M-BH_3+H]^+$), 357.6; HRMS (FAB+) found 769.4343, $C_{42}H_{61}B_2N_4O_4P_2$ (dimer of $[C_{21}H_{30}BN_2O_2P]+H^+$) requires 769.4354.

***N*-((1*S*,2*S*)-2-Aminocyclohexyl)-2-((*S*)-(boronato(2-methoxyphenyl)phenylphosphino)acetamide,** (*S*,*S*)(*S*$_P$)-**4**
White foamy solid (141 mg, 68%). $[\alpha]_D^{20}$ -67.4 (c 0.14, $CDCl_3$); ν_{max}/cm^{-1} (IR) (film) 3286 (m), 2930 (s), 2856 (m), 2382 (s), 1643 (s), 1537 (s), 1248 (s) 757 (s), 699 (s); δ_H (400 MHz, $CDCl_3$) 7.85 (1H, dd, *J* 14, 8, $C_{Ar}H$), 7.70-7.60 (2H, m, $C_{Ar}H$), 7.54-7.46 (1H, m, $C_{Ar}H$), 7.45-7.31 (3H, m, $C_{Ar}H$), 7.07 (1H, app br t, *J* 8, $C_{Ar}H$), 6.90 (1H, br d, *J* 6, $C_{Ar}H$), 6.35 (1H, br d, *J* 9, N*H*C(O)), 3.75 (3H, s, OCH_3), 3.61 (1H, app br t, *J* 14, C*H*N), 3.38 (1H, dd, *J* 14, 11, C*H*N), 2.35 (2H, app dt, *J* 11, 4, PCH_2), 1.95-1.55 (6H, m, NH_2 and cyclohexyl CH_2), 1.45-0.65 (7H, m, BH_3 and cyclohexyl CH_2); δ_C (101 MHz, $CDCl_3$) 165.9 (*C*(O)), 161.6 (OC_{ipso}), 136.0 (d, *J* 15, C_{Ar}H), 134.6 (C_{Ar}H), 131.6 (d, *J* 10, C_{Ar}H), 131.1 (C_{Ar}H), 129.0 (d, *J* 63, C_{ipso}), 128.6 (d, *J* 11, C_{Ar}H), 121.4 (d, *J* 12, C_{Ar}H), 114.7 (d, *J* 56, C_{ipso}), 111.6 (d, *J* 4, C_{Ar}H), 56.2 (*C*H), 55.7 (OCH_3), 55.0 (*C*H), 34.2 (cyclohexyl *C*H_2), 34.0 (d, *J* 36, P*C*H_2, partial overlap with signal at 34.2 ppm), 32.1 (cyclohexyl *C*H_2), 25.0 (cyclohexyl *C*H_2), 24.9 (cyclohexyl *C*H_2); δ_P ($CDCl_3$, 162 MHz) 12.4; *m/z* (ES+) 385.6 ($[M+H]^+$), 371.5 ($[M-BH_3+H]^+$), 257.6; HRMS (FAB+) found 769.4340, $C_{42}H_{61}B_2N_4O_4P_2$ (dimer of $[C_{21}H_{30}BN_2O_2P]+H^+$) requires 769.4354.

General procedure for the reduction of PNN amides 4 to form PNN amines 5
PNN amide (*S*,*S*)(*S*$_P$)-**4** (98 mg, 0.25 mmol) was dissolved in 2 mL of THF and cooled to 0 ˚C. While stirring, borane (1M in THF, 2.5 mL) was added dropwise and the resulting solution was warmed to room temperature and left to stir for 16 h. The reaction was quenched by the slow addition of water at 0 ˚C and subsequently diluted with Et_2O. The phases were separated and the water phase extracted with Et_2O three times. The combined organics were washed three times with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave a pale milky oil. Due to problems with the formation of mixed P- and N-boronated compounds during the reduction, borane-protected ligands **5** were deprotected fully for characterization purposes: The milky

residue was dissolved in 3 mL neat $HNEt_2$ and stirred at 50 ˚C for 3h. The solution was then concentrated and filtered through a short plug of neutral Al_2O_3, eluting with 1% MeOH in CH_2Cl_2. After a final evaporation under reduced pressure, aminophosphine deprotected-(*S*,*S*)(*S*$_P$)-**5** was obtained as a pale milky oil (23 mg, 26%). The product can also be purified by flash chromatography on neutral Al_2O_3 using a gradient of 0-30% MeOH in CH_2Cl_2.

(1*R*,2*R*)-*N*^{1}-(2-((*S*)-(2-Methoxyphenyl)(phenyl)phosphino)ethyl)cyclohexane-1,2-diamine, deprotected (*R*,*R*)(*S*$_P$)-5

Pale milky oil (11 mg, 12%). $[\alpha]_D^{20}$ -21.1 (c 1.53, $CDCl_3$); ν_{max}/cm^{-1} (IR) 3285 (m), 2929 (s), 2855 (m), 1585 (m), 1462 (s) 1241 (s) 754 (s); δ_H (400 MHz, $CDCl_3$) 7.55-7.42 and 7.36-7.26 (6H, m $C_{Ar}H$), 7.10 (1H, app ddd, *J* 8,6,2, $C_{Ar}H$), 6.91 (1H, app br t, *J* 7, $C_{Ar}H$), 6.84 (1H, dd, *J* 8,5, $C_{Ar}H$), 3.76 (3H, s, OCH_3), 2.95-2.25 (4H, m) and 2.21-0.85 (13H, m, PCH_2CH_2N, NH, NH_2, CH and cyclohexyl CH_2); δ_C (101 MHz, $CDCl_3$) 161.1 (d, *J* 13, OC_{ipso}), 137.3 (d, *J* 12, C_{ipso}), 133.1 (d, *J* 20, $C_{Ar}H$), 132.3 (d, *J* 5, $C_{Ar}H$), 130.0 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.3 (d, *J* 7, $C_{Ar}H$), 126.7 (d, *J* 15, C_{ipso}), 120.9 (d, *J* 3, $C_{Ar}H$), 110.3 (d, *J* 2, $C_{Ar}H$), 63.8 (*C*H), 55.5 and 55.3 (OCH_3 and *C*H), 44.0 (d, *J* 22, PCH_2CH_2N), 36. 0 (cyclohexyl CH_2), 31.4 (cyclohexyl CH_2), 27.8 (d, *J* 13, PCH_2CH_2N), 25.2 (2 cyclohexyl CH_2); δ_P ($CDCl_3$, 162 MHz) -30.0; *m/z* (ES+) 357.4 $[M+H]^+$, 215.6; HRMS (FAB+) found 713.4114, $C_{42}H_{59}N_4O_2P_2$ (dimer of $[C_{21}H_{29}N_2OP]+H^+$) requires 713.4113.

(1*S*,2*S*)-*N*^{1}-(2-((*S*)-(2-Methoxyphenyl)(phenyl)phosphino)ethyl)cyclohexane-1,2-diamine, deprotected (*S*,*S*)(*S*$_P$)-5

Pale milky oil (23 mg, 26%). $[\alpha]_D^{20}$ +35.4 (0.73, $CDCl_3$); ν_{max}/cm^{-1} (IR) 3281 (w), 2927 (s), 2855 (s), 1573 (m), 1462 (s), 1242 (s), 1216 (s), 750 (s); δ_H (400 MHz, $CDCl_3$) 7.58-7.23 (6H, m, $C_{Ar}H$), 7.14-7.06 (1H, m, $C_{Ar}H$), 6.96-6.78 (2H, m, $C_{Ar}H$), 3.75 (3H, s, OCH_3), 3.00-2.15 (5H, m) and 2.01-0.75 (12H, m, PCH_2CH_2N, NH, NH_2, CH and cyclohexyl CH_2); δ_C (101 MHz, $CDCl_3$) 161.0 (d, *J* 13, OC_{ipso}), 137.6 (d, *J* 13, C_{ipso}), 133.2 (d, *J* 20, $C_{Ar}H$), 132.1 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.3 (d, *J* 7, $C_{Ar}H$), 126.7 (d, *J* 15, C_{ipso}), 120.8 ($C_{Ar}H$), 110.3 ($C_{Ar}H$), 63.8 (*C*H), 55.5 and 55.3 (OCH_3 and *C*H), 44.0 (d, *J* 22, PCH_2CH_2N), 36.0 (cyclohexyl CH_2), 31.4 (cyclohexyl CH_2), 27.7 (d, *J* 11, PCH_2CH_2N), 25.2 (2 cyclohexyl CH_2); δ_P ($CDCl_3$, 162 MHz) -30.0; *m/z* (ES+) 357.4 $[M+H]^+$, 215.5; HRMS (FAB+) found 713.4117, $C_{42}H_{59}N_4O_2P_2$ (dimer of $[C_{21}H_{29}N_2OP]+H^+$) requires 713.4113.

Synthesis of 2-(diarylphosphino)benzaldehydes

(2-(1,3-Dioxolan-2-yl)phenyl)*bis*(3,5-di-tert-butylphenyl)phosphine, 10

To a solution of 2-bromobenzaldehyde ethylene acetal (0.277 mL, 1.9 mmol) in dry THF (5 mL) at -78 °C, *n*-butyllithium (1.25 mL, 1.6 M solution in THF, 2.0 mmol) was added slowly and the resulting mixture stirred at

this temperature for 2h. The creamy/white suspension was then transferred portionwise *via* cannula to a solution of phosphorus trichloride (1.66 mL, 19 mmol) in THF (10 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min then warmed to rt. The solvent and excess phosphorus trichloride were removed *in vacuo* at 60 °C, before the residue was redissolved in THF (5 mL) immediately. To this was added a solution prepared by adding *n*-butyllithium (2.5 mL, 1.6 M solution in THF, 40 mmol) to a solution of 3,5-di-*tert*-butylbenzene (1.00 g, 37 mmol) in dry THF (10 mL), and stirring for 2 h at -78 °C. This addition was achieved *via* cannula keeping all reactants at -78 °C and the resultant mixture was stirred for a further 30 min at -78 °C. The reaction mixture was then warmed to rt. The reaction mixture was concentrated and applied directly to a silica column. Flash chromatography (dichloromethane:hexane 1:1) afforded the title compound as a sticky white solid (0.435 g, 41 %), mp 102-103.5°C . ν_{max}/cm^{-1} (film) 3420 (m), 3059 (w), 2963 (s), 1589 (s), 1477 (s), 1420 (m), 1394 (m), 1363 (m), 1249 (m), 1129 (m), 1091 (s) 945 (m), 875 (m), 738 m) and 710 (m); δ_H ($CDCl_3$, 300 MHz) 7.66-7.56 (1H, m, $C_{Ar}H$), 7.34-7.13 (4H, m, $C_{Ar}H$), 7.06-6.97 (4H, m, $C_{Ar}H$), 6.90-6.81 (1H, m, $C_{Ar}H$), 6.40 (1H, d, *J* 5, C, C*H*), 4.07-3.86 (4H, m, CH_2) and 1.15 (36H, s, $C(CH_3)_3$); δ_C ($CDCl_3$, 101 MHz) 150.4 (d, *J* 6, C_q), 141.8 (C_q), 137.4 (C_q), 135.9 (d, *J* 8, C_q), 133.8 ($C_{Ar}H$), 128.9 (d, *J* 25, $C_{Ar}H$), 128.1 (d, *J* 20, $C_{Ar}H$), 126.1 (d, *J* 7, $C_{Ar}H$), 122.5 ($C_{Ar}H$), 122.3 ($C_{Ar}H$), 101.7 (d, *J* 25, *C*H), 65.4 (CH_2), 34.9 ($C(CH_3)_3$) and 31.4 ($C(CH_3)_3$); δ_P ($CDCl_3$, 162 MHz) -13.7; *m/z* (ES+) 581.03 ($[M+Na]^+$, 100%) and 597.03 ($[M=O+Na]^+$, 40); HRMS (ES+) found 581.3520, $C_{37}H_{51}O_2NaP$ requires 581.3524.

2-(*bis*(4-Chlorophenyl)phosphino)benzaldehyde, 11

To a solution of 2-bromobenzaldehyde ethylene acetal (2.24 mL, 15 mmol) in dry THF (30 mL) at -78 °C, *n*-butyllithium (6mL, 2.5M solution in THF, 16 mmol) was added dropwise and the resulting mixture stirred at this temperature for 2h. The creamy/white suspension was then transferred portionwise *via* cannula to a solution of phosphorus trichloride (13 mL, 0.15 mol) in THF (100 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min then warmed to rt. The solvent and excess phosphorus trichloride were removed *in vacuo* at 60 °C before the residue was redissolved in THF (100 mL). The solution was cooled to -78 °C and to this was added *p*-chlorophenylmagnesium bromide (30 mL, 1M solution in THF, 30 mmol) dropwise, and the mixture was stirred at -78 °C for 2h. The reaction mixture was then warmed to rt and quenched with degassed water (10 mL). The phases were separated, the water layer extracted with diethyl ether (2 x 30 mL), then the combined organic phases dried with magnesium sulfate, filtered, and concentrated in vacuum to give **8** (δ_P = ~ -18.1 ($CDCl_3$). The resultant yellow viscous liquid was dissolved in degassed acetone (100 mL), *p*-toluenesulfonic acid monohydrate (0.285g, 1.5 mmol) added, and the reaction was heated to reflux for 4h. The solvent was then evaporated, and the residue purified by column chromatography on silica (dichloromethane:petroleum ether 3:1) to furnish the pure compound as a yellow viscous liquid which solidified upon standing (2.83g, 53%), mp 78-80°C. Found: C, 63.24; H, 2.94%; $C_{19}H_{13}Cl_2OP$ requires C, 63.71; H, 3.38; ν_{max}/cm^{-1} (KBr) 3450 (m), 3055 (w), 2963 (w), 2824 (w), 2745

(m), 1702 (s), 1682 (m), 1561 (m), 1476 (s), 1382 (s), 1294 (m), 1261 (m), 1201 (s), 1082 (s), 1010 (s) 817 (s) and 737 (m); δ_H ($CDCl_3$, 300 MHz) 10.25 (d, $^4J_{HP}$ 5, 1H, C*H*O), 7.93-7.87 (m, 1H, $C_{Ar}H$), 7.52-7.38 (m, 2H, $C_{Ar}H$), 7.30-7.21 (m, 4H, $C_{Ar}H$), 7.16-7.06 (m, 4H, $C_{Ar}H$) and 6.90-6.83 (m, 1H, $C_{Ar}H$); δ_C ($CDCl_3$, 75 MHz) 192.0 (d, $^3J_{CP}$=13.4 Hz, *C*HO), 140.3 (d, J_{CP}=27.2 Hz, C_q), 138.7 (d, J_{CP}=14.5 Hz, C_q), 136.1 (s, C_q), 135.6 (d, J_{CP}=21.4 Hz), 135.0 (d, J_{CP}=11.0 Hz, C_q), 134.2 (s), 134.1 (s), 132.9 (d, J_{CP}=3.9 Hz), 129.6 (s or d) and 129.5 (d, J_{CP}=7.7 Hz); δ_P ($CDCl_3$, 121 MHz) -11.1; *m/z* (ES+): 380.88 ($[M+Na]^+$).

2-(*bis*(4-Methoxyphenyl)phosphino)benzaldehyde, 12

To a solution of 2-bromobenzaldehyde ethylene acetal (2.24 mL, 15 mmol) in dry THF (30 mL) at -78 °C, *n*-butyllithium (6mL, 2.5M solution in THF, 16 mmol) was added dropwise and the resulting mixture stirred at this temperature for 2h. The creamy/white suspension was then transferred portionwise *via* cannula to a solution of phosphorus trichloride (13 mL, 0.150 mol) in THF (100 mL) at -78 °C. The mixture was stirred at -78 °C for 30 min then warmed to rt. The solvent and excess phosphorus trichloride were removed *in vacuo* at 60 °C before the residue was redissolved in THF (100 mL). The solution was cooled to -78 °C and to this was added *p*-methoxyphenylmagnesium bromide (60 mL, 0.5M solution in THF, 30 mmol) dropwise, and the mixture stirred at -78 °C for 2h. The reaction mixture was then warmed to rt and quenched with degassed water (10 mL). The phases were separated, the water layer extracted with diethyl ether (2 x 30 mL), then the combined organic phases dried with magnesium sulfate, filtered, and concentrated in vacuum to give **9** (δ_P = ~ -19.1 ($CDCl_3$). The resultant yellow viscous liquid was dissolved in degassed acetone (100 mL), *p*-touenesulfonic acid monohydrate (0.285g, 1.5 mmol) added, and reaction was heated to reflux for 8h. The solvent was then evaporated, and the residue purified by column chromatography on silica (dichloromethane:petroleum ether 3:1) to furnish the pure compound as a yellow viscous liquid which solidified upon standing (1.57 g, 30%), mp 71-73 °C. Found: C, 71.66; H 5.33%; $C_{21}H_{19}O_3P$ requires C, 71.99; H, 5.47%; ν_{max}/cm^{-1} (KBr) 2925 (w), 2833 (w), 1696 (m), 1673 (s), 1593 (s), 1562 (m), 1496 (s), 1456 (m), 1401 (w), 1284 (s), 1250 (s), 1177 (s), 1093 (m), 1027 (s), 828 (w) and 764 (m); δ_H ($CDCl_3$, 300 MHz) 10.40 (d, $^4J_{HP}$=5.4Hz, 1H, C*H*O), 7.89-7.81 (m, 1H, $C_{Ar}H$), 7.38-7.33 (m, 2H, $C_{Ar}H$), 7.17-7.09 (m, 4H, $C_{Ar}H$), 6.92-7.84 (m, 1H, $C_{Ar}H$), 6.83-6.76 (m, 4H, $C_{Ar}H$), 3.70 (s, 6H, 2 x OCH_3); δ_C ($CDCl_3$, 75 MHz) 190.6 (d, $^3J_{CP}$=19.8 Hz, *C*HO), 159.4 (s, C_q), 141.5 (d, J_{CP}=26.0 Hz, C_q), 137.0 (d, J_{CP}=14.1 Hz, C_q), 134.5 (d, J_{CP}=21.9 Hz), 132.5 (s), 132.3 (s), 129.2 (d, J_{CP}=3.4 Hz), 127.5 (s), 126.1 (d, J_{CP}=6.7 Hz, C_q), 113.4 (d, J_{CP}=8.3 Hz), 54.1 (O*C*H_3); δ_P ($CDCl_3$, 121.5 MHz) -14.9; *m/z* (ES+) 372.99 ($[M+Na]^+$, 100%), 389.00 ($[M+K]^+$, 50).

2-(*bis*(3,5-di-*tert*-Butylphenyl)phosphino)benzaldehyde, 13

To a solution of **10** (0.106 g, 1.90 mmol) in degassed acetone (10 mL) was added *p*-touenesulfonic acid monohydrate (0.036 g, 0.19 mmol), and the reaction stirred at rt for 4h. The solvent was then evaporated, and the residue purified by column chromatography on silica (dichloromethane:hexane 1:1) to furnish the pure compound as a yellow viscous liquid which solidified upon standing (0.090 g, 92 %), mp 135-136°C. ν_{max}/cm^{-1} (film) 3441 (w), 2962 (s), 1698 (m), 1586 (m), 1477 (w), 1419 (w), 1393 (w), 1363 (m), 1249 (m), 1198 (m), 1131 (w), 875 (w), 758 (w) and 710 (m); δ_H ($CDCl_3$, 300 MHz) 10.63 (1H, d, *J* 6, C*H*O), *7*.95-7.88 (1H, m, $C_{Ar}H$), 7.43-7.36 (2H, m, $C_{Ar}H$), 7.34-7.30 (2H, m, $C_{Ar}H$), 7.03 (2H, d, *J* 2, $C_{Ar}H$), 7.00 (2H, d, *J* 2, $C_{Ar}H$), 6.94-6.88 (1H, m, $C_{Ar}H$) and 1.15 (36H, s, C(CH_3)$_3$); δ_C ($CDCl_3$, 101 MHz) 191.9 (*C*HO), 150.9 (d, *J* 7, C_q), 134.9 (d, *J* 9, C_q), 133.6 (d, *J* 17, $C_{Ar}H$), 128.8 ($C_{Ar}H$), 128.8 ($C_{Ar}H$), 128.7 ($C_{Ar}H$), 128.3 (d, *J* 21, $C_{Ar}H$), 123.6 (C_q), 122.9 ($C_{Ar}H$), 34.9 (*C*(CH_3)$_3$) and 31.4 (C(*C*H_3)$_3$); δ_P ($CDCl_3$, 121 MHz) -11.8; *m/z* (ES+) 536.90 ($[M+Na]^+$, 100%); HRMS (ES+) found 537.3256, $C_{35}H_{47}ONaP$ requires 537.3262.

General Procedure for Preparation of Diaryl phosphino PNN Ligands

A solution of the requisite 2-(diarylphosphino)benzaldehyde (1 equivalent) in absolute ethanol at 45 °C was added dropwise over a period of 5 h to a solution of diamine (3 equivalents) in absolute ethanol at rt. The reaction was monitored by ^1H and ^{31}P NMR and upon completion, sodium borohydride (4 equivalents) was added portionwise and the reaction was stirred for 12 h at rt. Once ^1H NMR had shown complete reduction of the imine, the reaction was quenched by addition of acetone and the solvent was then removed under reduced pressure. The residue was dissolved by stirring with saturated ammonium chloride solution and dichloromethane. The organic phase was separated, washed with water, dried over magnesium sulfate, filtered and concentrated to yield the crude product. In most cases this yielded ligand which was deemed sufficiently pure for full characterisation and subsequent complexation. In some cases, as noted below, a significant amount of phosphine oxide was also present and purification techniques were unsuccessful in removing this due to the surprising sensitivity of the ligand to oxygen (this air sensitivity and difficulties to handle varies wildly between different diamines starting materials, and is in spite of the starting aldehydes being fairly insensitive to air). In any case, direct complexation resulted in a mixture of desired complex and ligand oxide, and the components were easily separated by column chromatography, and thus pure complex was obtained.

(1*R*,2*R*)- N^1-(2-(bis(4-chlorophenyl)phosphino)benzyl)cyclohexane-1,2-diamine, (*R*,*R*)-**15**

Prepared by the general procedure giving ligand (*R*,*R*)-**15** as a solid residue (0.86 g, 86 %). ν_{max}/cm^{-1} (KBr) 3423 (s), 2933 (w), 1578 (m), 1478 (s), 1387 (m), 1262 (m), 1180 (w), 1088 (m), 1013 (m), 818 (m) and 741 (m); δ_H

($CDCl_3$, 400 MHz) 7.50-7.35 (2H, m, $C_{Ar}H$), 7.30-7.21 (5H, m, $C_{Ar}H$), 7.17-7.04 (4H, m, $C_{Ar}H$), 6.80-6.74 (1H, m, $C_{Ar}H$), 6.14 (2H, br s, NH_2), 3.99 (1H, d, AB system J_{AB} 13, $ArCH_AH_BNH$), 3.75 (1H, d, AB system J_{BA} 13, $ArCH_AH_BNH$), 2.66-2.51 (m, 1H, CHN), 2.49-2.38 (m, 1H, CHN), 2.24-2.13 (m, 1H, cyclohexyl CH), 2.08-2.00 (m, 1H, cyclohexyl CH), 1.65-1.55 (m, 3H, 2 cyclohexyl CH, 1 NH), 1.26-1.10 (m, 2H, cyclohexyl) and 0.93-0.76 (m, 2H, cyclohexyl CH); δ_C (101 MHz, $CDCl_3$) 143.2 (d, J 24, C_{ipso}), 135.5 (C_{ipso}), 135.2 (d, J 20, $C_{Ar}H$), 134.9 (d, J 20, $C_{Ar}H$), 134.3 (m, 4 x C_{ipso}), 133.8 ($C_{Ar}H$), 130.2 (d, J 7, $C_{Ar}H$), 129.8 ($C_{Ar}H$), 129.2 (d, J 8, $C_{Ar}H$), 129.0 (d, J 8, $C_{Ar}H$), 128.1 ($C_{Ar}H$), 59.3 (CH), 55.6 (CH), 49.7 (d, J 17, CH_2Ar), 31.1 (cyclohexyl CH_2), 29.8 (cyclohexyl CH_2), 24.7 (cyclohexyl CH_2) and 24.1 (cyclohexyl CH_2); δ_P (162 MHz, $CDCl_3$) -18.0; MS (ES+) m/z: 456.95 ($[M+H]^+$); HRMS (ES+) found 457.1360, $C_{25}H_{27}Cl_2N_2P$ requires 456.1289.

(1*R*,2*R*)- N^1-(2-(bis(4-methoxyphenyl)phosphino)benzyl)cyclohexane-1,2-diamine, (*R*,*R*)-**16**

Prepared by the general procedure giving ligand (*R*,*R*)-**16** as gummy solid. Due to the sensitivity of the phosphine, this material could only be obtained in ~80% purity (~20% ligand oxide) and was thus complexed immediately without any further purification. δ_H ($CDCl_3$, 300 MHz) 7.52-7.33 (2H, m, $C_{Ar}H$), 7.30-7.21 (1H, m, $C_{Ar}H$), 7.16-7.01 (4H, m, $C_{Ar}H$), 6.96-6.87 (1H, m, $C_{Ar}H$), 6.83-6.71 (4H, m, $C_{Ar}H$), 4.09-3.84 (1H, m, benzylic CH), 3.72 (6H, s, $-OCH_3$ x 2), 3.50 (1H, dd, J 14, 7, benzylic CH), 2.48-2.35 (1H, m, CHN), 2.30-1.47 (5H, m, CHN, cyclohexyl CH) and 1.25-.072 (4H, m, cyclohexyl CHN); δ_C (101 MHz, $CDCl_3$) 162.0 (C_{ipso}), 160.4 (C_{ipso}), 143.9 (C_{ipso}), 135.2 ($C_{Ar}H$), 133.5 ($C_{Ar}H$), 131.4 ($C_{Ar}H$), 129.0 ($C_{Ar}H$), 127.7 (C_{ipso}), 127.3 ($C_{Ar}H$), 114.5 (C_{ipso}), 63.4 (CH), 61.1 (CH), 55.2 (OCH_3), 49.3 (d, J 21, CH_2Ar), 31.5 (cyclohexyl CH_2), 29.7 (cyclohexyl CH_2), 25.2 (cyclohexyl CH_2) and 24.5 (cyclohexyl CH_2); δ_P ($CDCl_3$, 121 MHz) -18.8; *m/z* (CI+) 449.24 ($[M+H]^+$, 90%), 337.14 (66), 261.11 (45), 203.15 (79) and 95.05 (100); HRMS (CI+) found 449.2374, $C_{35}H_{47}ONaP$ requires 449.2358.

(1*R*,2*R*)-N^1-(2-(bis(3,5-dimethylphenyl)phosphino)benzyl)cyclohexane-1,2-diamine, (*R*,*R*)-**17**

Prepared by the general procedure giving ligand (*R*,*R*)-**17** as a pale yellow solid (0.181 g, 67 %), mp 125-127°C. ν_{max}/cm^{-1} (IR card) 3383 (s), 3028 (w), 2859 (m), 1622 (m), 1599 (m), 1446 (s), 1379 (m), 1272 (s), 1159 (m), 1128 (s), 1038 (m), 872 (w), 851 (s), 800 (m), 760 (m), 694 (s), 579 (s), 534 (w) and 486.8 (m) ; δ_H ($CDCl_3$, 300 MHz) 7.47-7.36 (1H, m $C_{Ar}H$), 7.27-7.19 (1H, m $C_{Ar}H$), 7.12-7.03 (2H, m $C_{Ar}H$), 6.87 (2H, s $C_{Ar}H$), 6.83-6.71 (4H, m, $C_{Ar}H$), 4.70 (2H, br s, NH_2), 4.05 (1H, d (AB system, J 12, $ArCH_AH_BNH$), 3.77 (1H, d (AB system, J 12, $ArCH_AH_BNH$), 2.54-2.34 (1H, m, CHN), 2.19 (12H, s, Ar-CH_3), 2.11-1.93 (1H, m, CHN), 1.73-0.67 (9H, m, cyclohexyl CH and NH); δ_C (75 MHz, $CDCl_3$) 143.8 (C_{ipso}), 138.6 (C_{ipso}), 138.2 (C_{ipso}), 136.2 (C_{ipso}), 134.0 ($C_{Ar}H$), 131.8 (d, J 14, $C_{Ar}H$), 131.5 (d, J 14, $C_{Ar}H$), 130.7 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 127.4 ($C_{Ar}H$), 60.9 (CHN), 55.8 (CHN), 49.5 (d, J 22, CH_2Ar), 32.3 (cyclohexyl CH_2), 31.1 (cyclohexyl CH_2), 25.0 (cyclohexyl CH_2), 24.7

(cyclohexyl CH_2) and 21.4 (Ar-CH_3); δ_P ($CDCl_3$, 121 MHz) -16.1; m/z (ES+) 445.24 ($[M+H]^+$, 100%); HRMS (ES+) found 445.2758, $[C_{29}H_{38}N_2P]^+$ requires 445.2773.

(1*R*,2*R*)- N^1-(2-(bis(3,5-di-tert-butylphenyl)phosphino)benzyl)cyclohexane-1,2-diamine, (*R*,*R*)**-18**

Prepared by the general procedure giving ligand (*R*,*R*)-**18** as gummy solid. Due to the sensitivity of the phosphine, this material could only be obtained in ~60% purity and was thus complexed immediately without any futher purification. The corresponding Ru complex was fully purified and characterised. δ_P ($CDCl_3$, 121 MHz) -13.5; m/z (ES+) 613.46 ($[M+H]^+$, 100%); HRMS (ES+) found 613.4651, $C_{41}H_{62}N_2P$ requires 613.4651.

Synthesis of PNN-Ru(II) Catalysts

General Procedure for Preparation of PNN -Ruthenium(II) Complexes

To dichlorotetrakis(dimethylsulfoxide) ruthenium(II) (1 eq.) in a sealed microwave tube under nitrogen was added a solution of the requisite ligand (1 eq.) in tetrahydrofuran (3 mL). The reaction was heated in the microwave for 20 min at 120 °C. The mixture was filtered to removed excess ruthenium(II) precursor and the solvent was removed *in vacuo*.

Complex (*R*,*R*)**-19 (from Ligand** (*R*,*R*)**-15)**

Prepared by the general procedure giving complex (*R*,*R*)-**19,** after column chromatography (silica, DCM:acetone 95:5 →90:10), as a brown/red solid (0.106 g, 63 %), m.p. 191 °C (decomp.). Found: C, 44.25; H, 4.40; N, 3.70%; $C_{27}H_{33}Cl_2N_2OPRuS$ requires C, 45.84; H, 4.70; N, 3.96%; $[\alpha]_D^{20}$ +60.0 (*c* 0.2, $CDCl_3$); ν_{max}/cm^{-1} (KBr) 3287 (w), 3227 (w), 3132 (w), 2926 (m), 2852 (w), 2361 (m), 2230 (w), 1578 (w), 1483 (m), 1081 (m), 1014 (m), 910 (m), 819 (m) and 738 (m); δ_H (300 MHz, $CDCl_3$) 7.62-7.18 (11H, m, $C_{Ar}H$), 7.04-6.95 (1H, m, $C_{Ar}H$), 4.32 (1H, t, *J* 11, C*H*), 4.06-3.97 (1H, m, C*H*), 3.79-3.70 (1H, m, C*H* or N*H*), 3.69-3.58 (1H, m, C*H* or N*H*), 3.21 (1H, t, *J* 11, C*H*) 3.15-2.97 (1H, m, C*H*), 2.98 (3H, s, $C(H_A)_3SOC(H_B)_3$), 2.67-2.58 (1H, m, N*H*), 2.54 (3H, s, $C(H_A)_3SOC(H_B)_3$), 1.78-1.62 (4H, m, N*H* + cyclohexyl C*H*), 1.38 (1H, m, cyclohexyl C*H*), 1.24-1.08 (3H, m, cyclohexyl C*H*) and 0.99 (1H, m, cyclohexyl C*H*); δ_C (300 MHz, $CDCl_3$) 141.0 (d, *J* 20, C_{ipso}), 136.5 (d, *J* 12, $C_{Ar}H$), 136.4 (C_{ipso}), 135.4 (d, *J* 10, $C_{Ar}H$), 134.0 (d, *J* 42, C_{ipso}), 132.6 ($C_{Ar}H$), 132.3 (d, *J* 42, C_{ipso}), 131.3 ($C_{Ar}H$), 131.1 ($C_{Ar}H$), 129.2 (d, *J* 8, $C_{Ar}H$), 128.6 (d, *J* 12, C_{ipso}), 128.4 ($C_{Ar}H$), 128.3 (d, *J* 10, C_{ipso}), 128.0 ($C_{Ar}H$), 63.4 (*C*HN), 57.5 (*C*HN), 52.5 (d, *J* 8, CH_2Ar), 47.0 ($C(H_A)_3SOC(H_B)_3$), 45.8 ($C(H_A)_3SOC(H_B)_3$), 36.1 (cyclohexyl CH_2), 30.6 (cyclohexyl CH_2), 24.8 (cyclohexyl CH_2) and 24.3 (cyclohexyl CH_2); δ_P (121 MHz, $CDCl_3$) + 43.9; HRMS (ES+) found 705.9922 (M^+), $C_{27}H_{33}Cl_4N_2OPRuS$ requires 705.9849.

Complex (*R*,*R*)-20 (from Ligand (*R*,*R*)-16)

Prepared by the general procedure giving complex (*R*,*R*)-**20**, after column chromatography (silica, DCM:acetone 100:0 → 50:50), as a brown/red solid (0.092 g, 85 %), m.p. 177-180 °C (decomp.). Found: C, 49.75; H, 5.52; N, 3.98%; $C_{29}H_{39}Cl_2N_2O3PRuS$ requires C, 49.86; H, 5.63; N, 4.01%; $[\alpha]_D^{20}$ +37.9 (*c* 0.4, $CHCl_3$); ν_{max}/cm^{-1} (PTFE Card) 3906 (w), 3403 (m), 2928 (m), 2855 (w), 1567 (s), 1593 (m), 1500 (m), 1440 (m), 1401 (w), 1287 (m), 1251 (m), 1183 (s), 1144 (m), 1094 (s), 1056 (w), 1024 (m), 827.8 (m), 798.0 (m), 758.5 (w), 718.9 (w), 680.8 (m), 539.8 (m), 431.3 (w) and 435.2 (w); δ_H (300 MHz, $CDCl_3$) 7.43-7.22 (7H, m, $C_{Ar}H$), 7.12 (1H, app ddd, *J* 9,8,1, $C_{Ar}H$), 6.78 (4H, app ddd, *J* 13,9,2, $C_{Ar}H$), 4.35 (1H, t, *J* 11, C*H*), 4.00 (1H, dd, *J* 12,6, C*H*), 3.97-3.89 (1H, m, N*H*), 3.74 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 3.24 (1H, t, *J* 12, C*H*), 3.11 (1H, qd, *J* 14, 4, C*H*), 2.98 (3H, s, $C(H_A)_3SOC(H_B)_3$), 2.67-2.58 (1H, m, N*H*), 2.54 (3H, s, $C(H_A)_3SOC(H_B)_3$), 1.78-1.62 (4H, m, N*H* + cyclohexyl C*H*), 1.38 (1H, m, cyclohexyl C*H*), 1.24-1.08 (3H, m, cyclohexyl C*H*) and 0.99 (1H, m, cyclohexyl C*H*); δ_C (300 MHz, $CDCl_3$) 160.8 (d, *J* 7, C_{ipso}), 140.8 (d, *J* 19, C_{ipso}), 136.9 (d, *J* 13, $C_{Ar}H$), 135.6 (d, *J* 11, $C_{Ar}H$), 134.0 (d, *J* 38, C_{ipso}), 132.4 ($C_{Ar}H$), 131.0 (d, *J* 9, $C_{Ar}H$), 130.5 ($C_{Ar}H$), 128.8 (d, *J* 9, $C_{Ar}H$), 126.6 (d, *J* 46, C_{ipso}), 122.2 (d, *J* 46, C_{ipso}), 119.1 (C_{ipso}), 113.7 (d, *J* 14, $C_{Ar}H$), 113.2 (d, *J* 14, $C_{Ar}H$), 63.7 (*C*HN), 57.1 (*C*HN), 55.2 (OCH_3), 55.1 (OCH_3), 52.4 (d, *J* 8, CH_2Ar), 46.9 ($C(H_A)_3SOC(H_B)_3$), 45.5 ($C(H_A)_3SOC(H_B)_3$), 36.0 (cyclohexyl CH_2), 30.6 (cyclohexyl CH_2), 24.8 (cyclohexyl CH_2) and 24.4 (cyclohexyl CH_2); δ_P (121 MHz, $CDCl_3$) + 39.6 ; *m/z* (ES+) 584.63 ($[M\text{-}Cl\text{-}DMSO]^+$, 100%); HRMS (ES+) found 585.1008, $[C_{27}H_{33}ClN_2O_2PRu]^+$ requires 585.1012.

Complex (*R*,*R*)-21 (from Ligand (*R*,*R*)-17)

Prepared by the general procedure giving complex (*R*,*R*)-**21**, after column chromatography (silica, DCM:acetone 75:25), as a brown/red solid (0.141 g, 70 %), m.p. 175-176°C (decomp.). This complex showed a single peak in the ^{31}P NMR, and the expected spectroscopic data that confirm its structure and purity, but held onto some residual solvents even after drying. $[\alpha]_D^{20}$ +28.2 (*c* 0.2, $CDCl_3$); ν_{max}/cm^{-1} (IR card) 2921 (m), 2857 (w), 1583 (m), 1446 (m), 1268 (m), 1194 (m), 1131 (m), 1045 (s), 999 (s), 852 (m), 758 (m), 694 (s), 574 (m) and 467 (m); δ_H (400 MHz, C_6D_6) 7.40-7.05 (6H, m, $C_{Ar}H$), 7.02-6.87 (4H, m, $C_{Ar}H$), 4.32 (1H, app t, *J* 10, CH_AH_BAr), 4.10-3.95 (2H, m, N*H* + CH_AH_BAr), 3.82-3.65 (1H, br s, N*H*), 3.34-3.09 (2H, m, N*H* + C*H*), 3.05 (3H, s, $C(H_A)_3SOC(H_B)_3$), 2.66-2.58 (1H, m, C*H*), 2.43 (3H, s, $C(H_A)_3SOC(H_B)_3$, 2.17 (6H, 2 x Ar-CH_3), 2.14 (6H, 2 x Ar-CH_3), 1.80-1.58 (3H, m, cyclohexyl C*H*), and 1.42-0.90 (5H, m, cyclohexyl C*H*); δ_C (101 MHz, C_6D_6) 139.9 (d, *J* 15, C_{ipso}), 136.5 (d, *J* 10, C_{ipso}-CH_3), 135.7 (d, *J* 10, C_{ipso}-CH_3), 134.0 (d, *J* 40, C_{ipso}), 132.4 (d, *J* 40, C_{ipso}), 132.0 ($C_{Ar}H$), 131.9 ($C_{Ar}H$), 131.6 ($C_{Ar}H$), 130.7 ($C_{Ar}H$), 130.5 (d, *J* 11, $C_{Ar}H$), 129.8 (d, *J* 7, $C_{Ar}H$), 129.5 (d, *J* 44, $C_{Ar}H$), 129.4 ($C_{Ar}H$), 127.7 (d, *J* 6, $C_{Ar}H$), 62.9 (*C*HN), 55.9 (*C*HN), 51.5 (d, *J* 8, CH_2Ar), 45.7 ($C(H_A)_3SOC(H_B)_3$), 43.9 ($C(H_A)_3SOC(H_B)_3$), 34.9 (cyclohexyl CH_2), 29.6 (cyclohexyl CH_2), 23.8 (cyclohexyl CH_2), 23.4 (cyclohexyl CH_2), 20.5 (Ar-CH_3) and 20.4 (Ar-CH_3); δ_P (121 MHz, $CDCl_3$) + 40.6; *m/z* (ES+) 717.11 ($[M+Na]^+$, 100%); HRMS (ES+) found 717.1176, $[C_{31}H_{43}Cl2N_2PRuSNa]^+$ requires 711.1179.

Complex (*R*,*R*)-22 (from Ligand (*R*,*R*)-18)

Prepared by the general procedure giving complex (*R*,*R*)-**22**, after column chromatography (silica, DCM:acetone 80:20), as a brown/red solid (0.030 g, 50 %), m.p. 180-181°C (decomp.). This complex showed a single peak in the ^{31}P NMR, and the expected spectroscopic data that confirm its structure and purity, but held onto some residual solvents even after drying. $[\alpha]_D^{20}$ +50.0 (*c* 0.2, $CDCl_3$); ν_{max}/cm^{-1} (IR card); 3287 (br s), 2960 (m), 2140 (w), 1634 (m), 1476 (w), 1362 (w), 1263 (w), 1201 (m), 1147 (w), 1093 (w), 1015 (m), 798 (w), 752 (w), 709 (w), 637 (w), 601 (w) and 489 (w); δ_H (400 MHz, C_6D_6) 7.87-7.78 (2H, m, $C_{Ar}H$), 7.68 (1H, app t, *J* 8, $C_{Ar}H$), 7.42-7.39 (1H, m, $C_{Ar}H$), 7.36-7.33 (1H, m, $C_{Ar}H$), 7.10-6.96 (4H, m, $C_{Ar}H$), 6.80 (1H, dd, *J* 7, 3, $C_{Ar}H$), 4.53 (1H, t, *J* 12, C*H*), 4.14 (1H, br s, N*H*), 3.87-3.76 (1H, m, C*H*), 3.44 (1H, dd, *J* 12, 4, C*H*), 3.21 (3H, s, $C(H_A)_3SOC(H_B)_3$), 2.94 (1H, dd, *J* 12, 4, C*H*), 2.26 (3H, s, $C(H_A)_3SOC(H_B)_3$, 1.76 (1H, d, *J* 12, cyclohexyl C*H*), 1.27-0.73 (9H, m, cyclohexyl C*H*, NH_2), 1.17 (18H, s, 2 x C(CH_3)$_2$) and 1.10 (18H, s, 2 x C(CH_3)$_2$); δ_C (300 MHz, C_6D_6) 150.4 (d, *J* 9, C_{ipso}), 150.1 (d, *J* 9, C_{ipso}), 141.8 (d, *J* 17, C_{ipso}), 135.9 (d, *J* 40, C_{ipso}), 134.9 (d, *J* 36, C_{ipso}), 132.6 (C_{Ar}H), 132.6 (C_{Ar}H), 132.1 (d, *J* 40, C_{ipso}), 131.1 (C_{Ar}H), 131.1 (C_{Ar}H), 130.9 (C_{Ar}H), 129.9 (C_{Ar}H), 123.4 (C_{Ar}H), 122.4 (C_{Ar}H), 63.8 (*C*HN), 56.6 (*C*HN), 52. 6 (d, *J* 8, *C*H_2Ar), 46.7 ($C(H_A)_3SOC(H_B)_3$), 44.3 ($C(H_A)_3SOC(H_B)_3$), 35.1 (cyclohexyl *C*H_2), 35.1 (cyclohexyl *C*H_2), 35.0 (cyclohexyl *C*H_2), 34.9 (cyclohexyl *C*H_2), 31.4 (C(*C*H_3)$_3$), 31.2 (C(*C*H_3)$_3$), 24.4 (*C*(CH$_3$)$_3$) and 24.1 (*C*(CH$_3$)$_3$); δ_P (162 MHz, $CDCl_3$) + 45.2; *m/z* (ES+) 748.71 ([M-Cl-DMSO]$^+$, 100%); HRMS (ES+) found 749.3304, $[C_{41}H_{61}ClN_2PRu]^+$ requires 749.3302.

Hydrogenation Using Preformed [RuCl$_2$(P^N^N)L] Catalysts

A solution of substrate (*ca* 1 mmol), catalyst and potassium *tert*-butoxide (1 M solution in pentane) in degassed isopropanol (3 mL) was prepared in a microwave vial under an atmosphere of nitrogen. The microwave vial was placed inside a steel autoclave with two syringe needles piercing the lid of the vial. The autoclave was then sealed and flushed three times with hydrogen before being charged with hydrogen to the required pressure. The reactions were stirred at the same speed for the desired times at the required temperature using a stainless steel heating jacket connected to a thermocouple and heater. After the desired time passed, the autoclave was opened and the reaction mixture concentrated *in vacuo*. The conversion of substrate to product was calculated by ^{1}H NMR spectroscopy (In these experiments only starting material and product were observed negating the use of an internal standard). The products were isolated by column chromatography or short-path distillation and characterised by comparison of NMR, IR, MS, optical rotation and where appropriate melting point data, with authentic samples. The enantiopurity of the product (where applicable) was determined using high performance liquid chromatography with the chiral stationary phase noted for each product.

In situ Hydrogenation

A solution of $[RuCl_2(DMSO)_4]$ (0.5 mol%), ligand (0.7 mol%), and potassium *tert*-butoxide (1 M solution in pentane) in degassed isopropanol (3 mL) was prepared in a capped microwave vial under an atmosphere of nitrogen. After stirring for 30 min at room temperature, the substrate (*ca* 1 mmol) was added. The microwave vial was placed inside a steel autoclave with two syringe needles piercing the lid of the vial. The autoclave was then sealed and flushed three times with hydrogen before being charged with hydrogen to the required pressure. The reactions were stirred at the same speed for the desired times at the required temperature using a stainless steel heating jacket connected to a thermocouple and heater. After the desired time passed, the autoclave was opened and the reaction mixture concentrated *in vacuo*. The conversion of substrate to product was calculated by ^{1}H NMR spectroscopy (In these experiments only starting material and product were observed negating the use of an internal standard). The products were isolated by column chromatography or short-path distillation and characterised by comparison of NMR, IR, MS, optical rotation and where appropriate melting point data, with authentic samples. The enantiopurity of the product was determined using high performance liquid chromatography with the chiral stationary phase noted for each product.

Ketone Hydrogenation Products

1-Phenylethanol

$[\alpha]_D^{20}$ -32.0 (60% e.e., *c* 2.5, $CHCl_3$) (lit.[7] (*S,* 100 % e.e.) $[\alpha]_D^{25}$ -53.5 (*c* 2.6, $CHCl_3$)); δ_H (400 MHz, $CDCl_3$) 7.18-7.33 (5H, m, $C_{Ar}H$), 4.84 (1H, q, *J* 6, C*H*OH), 1.63 (1H, br s, -O*H*) and 1.43 (3H, d, *J* 6, CH_3); δ_C (75 MHz, $CDCl_3$) 145.8 (C_{ipso}), 128.5 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 125.4 ($C_{Ar}H$), 70.5 (*C*HOH) and 25.2 (CH_3). Enantioselectivity determined by HPLC, ChiralPak OD-H, 0.5 mL/min, 95:5 hexane:2-propanol. Retention times: 17.4 min (*R*)-(+)-enantiomer and 21.2 min (*S*)-(–)-enantiomer.

2,2-Dimethyl-1-phenylpropan-1-ol[8]

m.p. 45 ºC (lit.[8] 45 ºC); $[\alpha]_D^{20}$ -19.3 (74 % e.e., *c* 0.3, acetone) (lit.[7] (*S,* 100 % e.e.) $[\alpha]_D^{25}$ -30.3 (*c* 3.64, acetone)); δ_H (300 MHz, $CDCl_3$) 7.25-7.19 (5H, m, $C_{Ar}H$), 4.31 (s, 1H, C*H*OH), 1.97 (1H, br s, CHO*H*) and 0.85 (9H, s, $C(CH_3)_3$); δ_C (75.5 MHz, $CDCl_3$) 142.2 (C_{ipso}), 127.6 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 127.3 ($C_{Ar}H$), 82.4 (*C*HOH), 35.6 ($C(CH_3)_3$) and 26.0 ($C(CH_3)_3$); m/z (ES+) 187.10 ($(M+Na)^+$, 100%). Enantioselectivity determined by chiral HPLC. Chiralpak OD-H, 1 mL/min, 98:2 hexane:2-propanol. Retention times: 10.5 min (*S*, major enantiomer) and 15.0 (*R*, minor enantiomer).

Notes and references

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