Supplementary Material (ESI) for Chemical Communications

A new NCN pincer ruthenium complex and its catalytic activity for enantioselective hydrogenation of ketones

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Electronic Supporting Information

The ligand **1a** was synthesised according to our previous report; see ref. 10 of the main text and S1.

Contents:

1. **Synthesis of 2a:** a flask was charged with $RuCl_3$•3(H_2O) (523 mg, 2.0 mmol), **1a**[S1] (329 mg, 1.0 mmol), and Zn (327 mg, 5.0 mmol). Under an argon atmosphere, ethanol (20 mL) and 1,5-cyclooctadiene (0.61 mL, 5.0 mmol) were added and the mixture was heated at refluxing temperature for 24 h. After removal of the solvent, the residue was extracted with toluene and the extract was concentrated. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate

(1:1) to give orange solids of dimeric compound (373 mg, 0.325 mmol, 65%); Anal. Calcd for $C_{42}H_{54}N_4O_6Cl_4Ru_2Zn$: C, 45.03; H, 4.86; N, 5.00. Found: C, 45.04; H, 4.99; N, 4.83. The compound (408 mg, 0.36 mmol) was treated with Na(acac) (264 mg, 2.16 mmol) in toluene (2.0 mL) at room temperature for 12 h under argon atmosphere. After removal of the solvent, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (5:1) to give **2a** as orange solids in 90% yield (365 mg, 0.66 mmol).

As a sequential procedure, acetylacetone (0.21 mL, 2.0 mmol) was added at room temperature to the reaction mixture prepared as above descried with $RuCl_3$•$3(H_2O)$ (523 mg, 2.0 mmol), **1a** (329 mg, 1.0 mmol), Zn (327 mg, 5.0 mmol), and 1,5-cyclooctadiene (0.61 mL, 5.0 mmol), and the complex **2a** was obtained in 47% yield (258 mg, 0.47 mmol).

2a: mp: 196–197 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): 0.61 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 1.66 (s, 3H), 1.86–1.95 (m, 1H), 2.03 (s, 3H), 2.06–2.12 (m, 1H), 2.51 (s, 6H), 3.73–3.79 (m, 1H), 4.00–4.05 (m, 1H), 4.34–4.65 (m, 4H), 5.13 (s, 1H), 6.56 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.3, 15.6, 19.0, 19.3, 19.35, 19.4, 28.3, 28.4, 29.5, 30.2, 67.7, 69.0, 70.1, 70.8, 97.9, 126.4, 129.6, 129.7, 138.6, 173.7, 174.2, 185.7, 187.7, 194.7, 201.7. IR (KBr):ν 1907, 1594, 1512 cm^{-1}. Anal. Calcd for $C_{26}H_{34}N_2O_5Ru$: C, 56.20; H, 6.17; N, 5.51. Found: C, 56.13; H, 6.18; N, 5.22.

2. **Synthesis of 1b**: To a suspension of 4,6-dimethylisophthalic acid[1] (1.94 mg, 10.0 mmol) in toluene (5 mL) was slowly added thionyl chloride (6.0 ml). The mixture was refluxed for 5 h and then excess thionyl chloride was removed under reduced pressure to give 4,6-dimethylisophthaloyl chloride, which was used in next step without further purification. A solution of 4,6-dimethylisophthaloyl chloride in THF (40 mL) was slowly added to a solution of (*S*)-(+)-2-phenylglycinol (2.74 g, 20.0 mmol) and triethylamine (40 mL) in THF (20 mL) at 0 °C. The mixture was stirred at room temperature for 3 h. Methanesulfonyl chloride (4.0 ml, 52 mmol) was added at 0 °C, and then the mixture was stirred at room temperature for 15 h. Formation of the product **1b** was monitored by TLC examination; Rf = 0.63 (ethyl acetate/hexane = 1:2). At 0 °C, aqueous potassium carbonate (1N) was added and the mixture was extracted with ethyl acetate. The organic layer was washed with saturated brine, was dried over magnesium sulfate, and was concentrated. The crude product was purified by column

chromatography on silica gel (ethyl acetate/hexane 1:5) to give **1b** in 54 % (2.14 g, 5.42 mmol) as colorless solid. Colorless solid; mp: 103-104 °C; [ ]$^{23}_{D}$ = -62.9 (c 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ = 2.69 (s, 6H), 4.20 (dd, *J* = 8.1, 8.3 Hz, 2H), 4.74 (dd, *J* = 8.1, 10.2 Hz, 2H), 5.44 (dd, *J* = 8.3, 10.2 Hz, 2H), 7.19 (s, 1H), 7.27-7.39 (m, 10H), 8.45 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ = 22.0, 70.3, 73.5, 76.5, 123.9, 126.1, 126.9, 128.1, 131.4, 134.0, 141.4, 142.0, 163.6 ppm; IR (KBr): ν 1635 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{24}N_2O_4$: C 78.76, H 6.10, N 7.07; found: C 78.39, H 6.11, N 6.77.

3. **Synthesis of 2b:** The complex was prepared by the sequential method with $RuCl_3$•3(H_2O) (208 mg, 0.795 mmol), Zn (163 mg), **1b** (184 mg, 0.50 mmol), EtOH (10 mL), COD (0.3 mL), H(acac) (0.60 mL) in 45 % yield (147 mg, 0.236 mmol). The complex was purified by column chromatography with hexane/ethyl acetate (1:1). Orange solid; mp: 201-202 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ = 1.40 (s, 3H), 1.61 (s, 3H), 2.61 (s, 6H), 4.46-4.53 (m, 2H), 4.66 (s, 1H), 4.74 (t, *J* = 9.9 Hz, 1H), 4.98-5.11 (m, 3H), 6.64 (s, 1H), 7.09-7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$, rt): δ = 19.4, 19.5, 27.5, 28.3, 67.5, 68.1, 77.8, 98.0, 126.4, 127.1, 127.3, 127.4, 127.8, 127.9, 128.2, 129.6, 129.8, 139.25, 139.29, 139.4, 139.5, 174.8, 175.3, 184.3, 187.3, 194.0, 203.9 ppm; IR (KBr): ν = 1913, 1594, 1518 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{30}N_2O_5Ru$: C 61.63, H 4.85, N 4.49; found: C 61.67, H 4.84, N 4.77.

4. **X-ray analysis of 2a:** A single crystal was obtained was obtained from solution of hexane/ethyl acetate. The diffraction data were collected on a Brucker SMART APEX CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). An empirical absorption correction was applied by using SADABS. The structure was solved by direct method and refined by full-matrix lease-square on F^2 using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located on calculated positions and refined as rigid groups. The crystallographic and refined data were summarized as follows:

Formula	$C_{26}H_{36}N_2O_5Ru•0.5(H_2O)$
Fw	564.63
Cryst syst	Hexagonal
Space group	$P6_5$
a, Å	21.191(5)
b, Å	21.191(5)
c, Å	10.778(5)
α, deg	90
β, deg	90
γ, deg	120
V, Å^3	4192(2)
Z value	6
D_{calc}, g cm^{-3}	1.342
temp, ºC	-100
μ(MoKα), mm^{-1}	0.598
radiation, λ, Å	0.71073
no. of rflns collected	29361
no. of indep rflns	6074 [R(int) = 0.0681]
R1 ($I > 2\sigma(I)$)	0.0324
wR2 ($I > 2\sigma(I)$)	0.0683
R1 (all data)	0.0396
wR2 (all data)	0.06705
parameters	319
Flack parameter	-0.03(3) [Friedel pairs = 2706]

CCDC-673251 contains the supplementary crystallographic data for **2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

5. Determination of enantioselectivity for 4:

(*S*)-(-)-1-(4'-Methoxyphenyl)ethanol (4a): $[\alpha]^{25}_{D}$ -27.3 (c 5.11, $CHCl_3$), [lit.[2] gives $[\alpha]^{22}_{D}$ -51.9 (c 0.718, $CHCl_3$, 64% ee (*S*))]. Chiral HPLC (Daicel Chiralpak AS-H, hexane/IPA 95:5, 0.8 mL/min) showed 64% ee (t_R = 26.4 min, t_S = 36.1 min).

(*S*)-(-)-1-(2'-Methoxyphenyl)ethanol (4b): $[\alpha]^{25}_{D}$ -19.6 (c 2.33, $CHCl_3$), [lit.[2] gives $[\alpha]^{23}_{D}$ -63.0 (c 1.10, $CHCl_3$, 99% ee (*S*))]. Chiral HPLC (Daicel Chiralcel OB-H, hexane/IPA 95:5, 0.8 mL/min) showed 81% ee (t_S = 11.6 min, t_R = 20.1 min).

(*S*)-(-)-1-(2' Naphthyl))ethanol (4c): $[\alpha]^{25}_{D}$ -30.3 (c 0.996, $CHCl_3$), [lit.[3] gives $[\alpha]^{25}_{D}$ -31.0 (c 1.0, $CHCl_3$, 95% ee (*S*))]. Chiral HPLC (Daicel Chiralcel OJ-H, hexane/IPA 95:5, 0.8 mL/min) showed 90% ee (t_S = 33.4 min, t_R =44.7 min).

(*S*)-(-)-2-methyl-1-phenyl-1-propanol (4d): $[\alpha]^{25}_{D}$ -27.5 (c 1.08, $CHCl_3$), [lit.[2] gives $[\alpha]^{26}_{D}$ -49.1 (c 0.828, ether, 99% ee (*S*))]. Chiral HPLC (Daicel Chiralpak AD-H, hexane/IPA 99:1, 0.8 mL/min) showed 83% ee (t_R = 20.4 min, t_S = 21.5 min).

(*S*)-(-)-1-phenyl-1-hexanol (4e): $[\alpha]^{24}_{D}$ -15.5 (c 0.435, $CHCl_3$), [lit.[4] gives $[\alpha]^{24}_{D}$ -35.0 (c 0.88, $CHCl_3$, 92% ee (*S*))]. Chiral HPLC (Daicel Chiralcel OB-H, hexane/IPA 95:5, 0.8 mL/min) showed 85% ee (t_{minor} = 23.1 min, t_{major} = 29.0 min).

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