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Synthesis of Rh(I) diamine complexes and their exploitation for asymmetric hydrogen transfer processes

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ABSTRACT

In this paper, we report the synthesis and characterisation of two novel chiral diamine ligands and three new Rh(I) complexes. The diamine ligands were prepared by reducing the Schiff base precursors using $NaBH_4$. Unusually, when ligand **2** was recrystallised in a methanol:acetone solution (10:1) a five membered imidazolidine ring was formed, as confirmed by X-ray crystallography, multinuclear NMR spectroscopy and mass spectrometry. The Rh(I) cationic complexes were prepared in high yields and purities and these have been exploited for the asymmetric reduction of acetophenone to 1-phenylethanol. Modest conversions (up to 88%) and enantioselectivities (up to 50%) have been achieved.

1. Introduction

There is continued interested in the development of new chiral ligands and complexes for asymmetric catalysis. In recent years, significant advances have been achieved in this field [1–5]. One of the main driving forces for this interest is the need for stable and straightforward preparation protocols. One such class of ligands are chiral diamines, which have recently proved very attractive targets [6–10]. For example, complexes based on chiral diamines with Rh(I) and Ru(II) have been employed for chiral hydrogenations and transfer hydrogenations [6–10]. Both homogeneous and heterogeneous diamine complexes have proved highly effective in enantioselective catalysis [11,12]. Diamines offer several advantages over traditional phosphine systems, namely (i) they are much more robust to oxidation/hydrolysis and (ii) many chiral diamines are available in enantiomerically pure forms from the 'chiral pool'. As part of our continuing studies into chiral diamine systems in this paper the crystal structures of two new Rh(I) complexes are reported and this represents the first crystallographically characterised complex of the ferrocene ligand described. The preparation and characterisation of a new chiral diamine ligand and crystal structure of the product obtained when ligand **2** was recrystallised in a methanol/acetone mixture are also reported. The Rh(I) complexes show modest selectivity and activity for the asymmetric reduction of acetophenone.

2. Results and discussion

2.1. Synthesis

The ligands (**1**–**3**) were prepared by the condensation of an aldehyde with a chiral diamine to form the imine (Schiff base) intermediate. These intermediates were facilely reduced with $NaBH_4$ to afford the desired chiral ligand precursors, Scheme 1 [13,14].

Ligand **1** was prepared using (1*R*,2*R*)-1,2-diaminocyclohexane and ferrocene carboxaldehyde, **2** from (1*R*,2*R*)-1,2-diaminocyclohexane and benzaldehyde and **3** from (*R*)-2-amino-3-methylbutane with 2-pyridinecarboxaldehyde [13,14]. The intermediate Schiff bases (**1SB**, **2SB** and **3SB**, Scheme 1) were isolated and fully characterised before being reduced to the corresponding amine. All reactions are high yielding and the ligands have been characterised *via* ^1H and ^{13}C NMR spectroscopic methods and high resolution mass spectrometry. Ligand **2** was recrystallised from a methanol/acetone mix (10:1), interestingly a new compound **2A** formed, see Fig. 1.

During the recrystallisation **2** reacts with acetone to produce a new amine (water was produced as the by-product), which contains a five membered imidazolidine ring, Fig. 1. There is literature precedent for the reaction of acetone with diamines to produce imidazolidine rings [15]; however; this is the first reported example with (1*R*,2*R*)-1,2-diaminocyclohexane as the diamine. The cyclohexane ring adopts a chair configuration and the heterocycle an envelope configuration in the solid-state. **2A** has been further characterised *via* $^1H/^{13}C$ NMR and high resolution mass spectrometry, which are in agreement with the solid-state structure. Attempts to isolate similar products with ligand **1** *via* this method have

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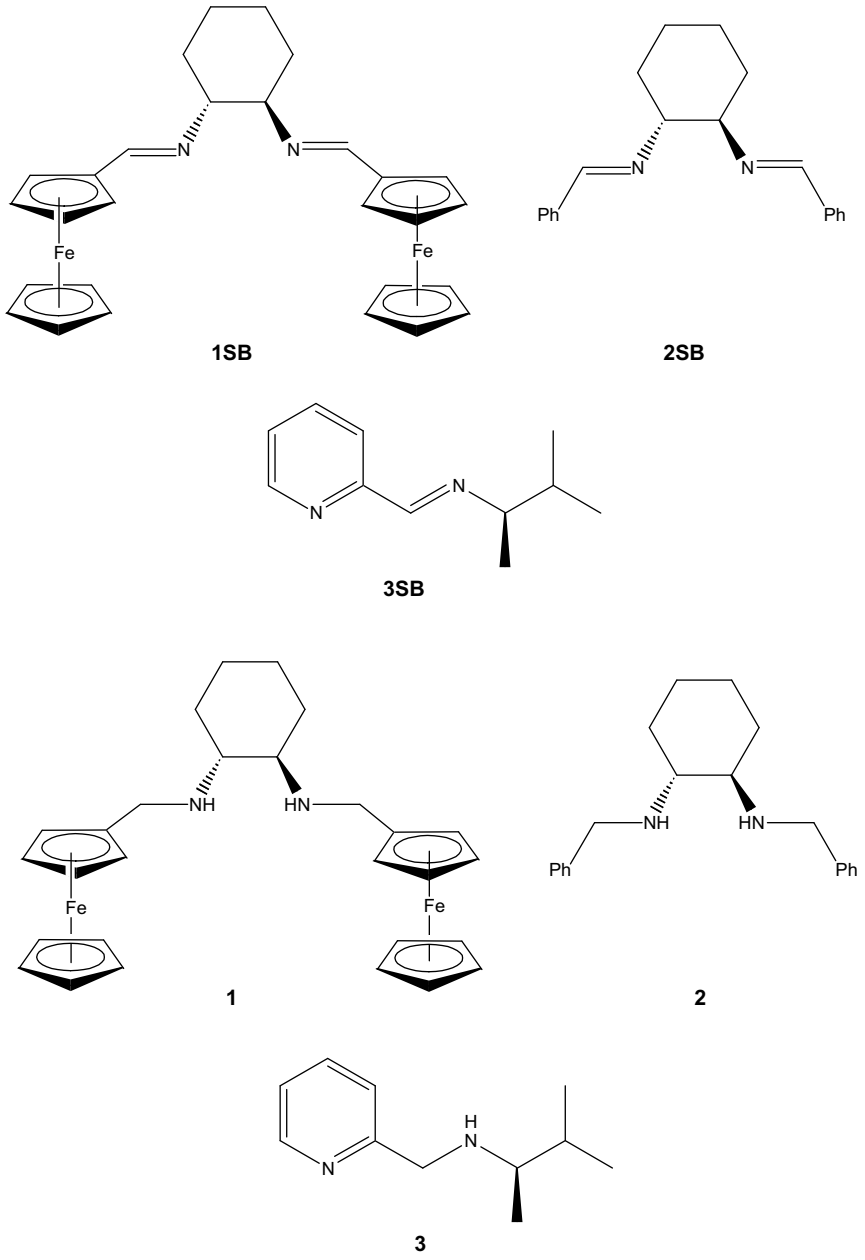

Scheme 1. Schiff base precursors and ligands utilised in this study.

proved unsuccessful. Bryce et al. have prepared imidazolidine rings of this type with ligand **1** *via* condensation with aldehydes [14].

The Rh(I) complexes were prepared by reacting $[RhCl(cod)]_2$ (where cod = 1,5-cyclooctadiene) with 2 equiv. of $AgCF_3SO_3$ in THF (tetrahydrofuran). The solution was filtered and to the $Rh(cod)(THF)_2$ solution 1 equiv. of the chiral diamine (**1**, **2** or **3**) was added. The solution was stirred for 1 h and the addition of hexane caused the precipitation of the desired complexes Rh(**1**)(cod)CF_3SO_3, Rh(**2**)(cod)CF_3SO_3 and Rh(**3**)(cod)CF_3SO_3. The products were confirmed by ^1H and ^{13}C NMR spectroscopic methods, high resolution mass spectrometry and elemental analysis. The identity of Rh(**1**)(cod)CF_3SO_3 and Rh(**2**)(cod)CF_3SO_3 was further confirmed by X-ray crystallography.

2.2. X-ray structure of Rh(1)(cod)CF_3SO_3 and Rh(2)(cod)CF_3SO_3

Rh(**1**)(cod)CF_3SO_3 crystallised in the orthorhombic space group $P2_12_12_1$ with one molecular entity in the asymmetric unit, Fig. 2. Upon complexation further chiral centres emerge at the nitrogen atoms N(1) and N(2), it is seen that N(1) has an *R* chirality whereas N(2) is *S*. If the extended structure is examined for Rh(**1**)(cod)CF_3SO_3 it is observed that there is relatively strong hydrogen bonding between the amine groups and the triflate anion, leading to the formation of zig-zag chains. The bond lengths and angles are in agreement with similar complexes in the literature,[16–20] with the typical Rh–C distance of 2.14 Å and Rh–N of 2.14 Å. To the best of our knowledge this is the first example of a crystallographically characterised example of ligand **1**, although there are reports in the literature of the preparation of the pure ligand [14].

An analogous complex was formed in the case of ligand **2** and Rh(**2**)(cod)CF_3SO_3 crystallises in the orthorhombic space group $P2_12_12_1$, Fig. 3. There are two Rh(I) complexes present in the asymmetric unit. Hydrogen bonding is again observed between the NH group and the triflate counter-ion in an analogous manner to Rh(**1**)(cod)CF_3SO_3. Bond lengths and bond angles are in agreement to those determined for Rh(**1**)(cod)CF_3SO_3.

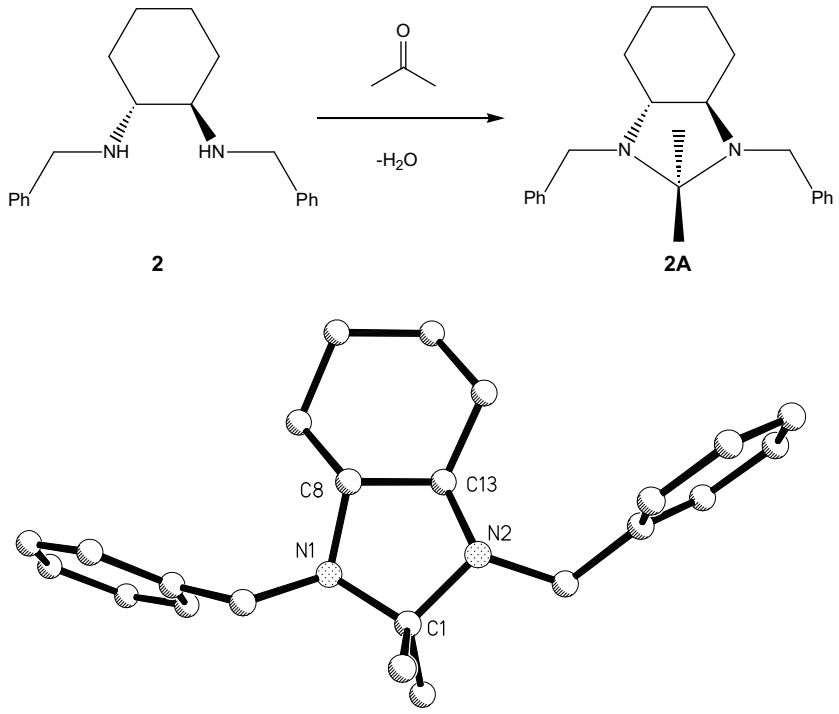

Fig. 1. Top: formation of **2A**. Bottom: the molecular structure of **2A**, selected bond lengths [Å] and angles [°] are N(1)–C(8) 1.4578(13), N(1)–C(1) 1.4964(13), N(2)–C(13) 1.4572(13), N(2)–C(1) 1.4919(13). N(1)–C(1)–N(2) 103.07(8).

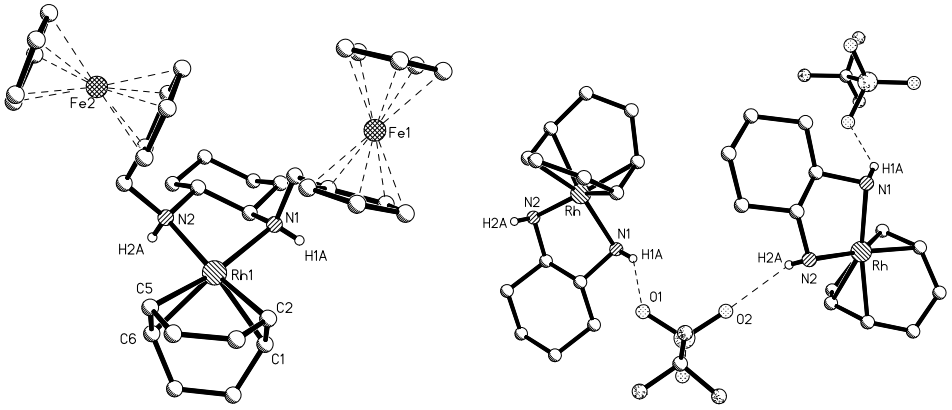

Fig. 2. Left: the molecular structure of Rh(**1**)(cod)CF_3SO_3, solvent and H-atoms not involved in hydrogen bonding have been removed for clarity selected bond lengths [Å] and angles [°] are: Rh(1)-N(1) 2.139(3), Rh(1)–N(2) 2.147(3), Rh(1)–C(1) 2.143(4), Rh(1)–C(2) 2.151(3), Rh(1)–C(5) 2.129(4), Rh(1)–C(6) 2.143(4). N(1)–Rh(1)–N(1) 80.80(11), C(1)–Rh(1)–C(2) 37.79(15), C(5)–Rh(1)–C(6) 37.80(16). Right: The hydrogen bonding motif observed in Rh(**1**)(cod)CF_3SO_3, the ferrocene moiety has been removed for clarity. H(1A)–N(1) 0.80(4), H(1A)–O(1) 2.28(4), N(1)–O(1) 2.968(5), N(1)–H(1A)–O(1) 145(3).[1] H(2A)–N(2) 0.75(4), H(2A)–O(2) 2.27(4), N(2)–O(2) 2.913(4), N(2)–H(2A)–O(2) 146(4).[2] ([1] −x, y − 1/2, −z + 3/2; [2] x, y, z).

To the best of our knowledge Rh(**1**)(cod)CF_3SO_3 and Rh(**2**)(cod)CF_3SO_3 represent the first crystallographic characterisation of a Rh(I) 1,5-cyclooctadiene diamine complex based on (1*R*,2*R*)-1,2-diaminocyclohexane [21]. Complex Rh(**3**)(cod)CF_3SO_3 was prepared in an analogous manner, in this case crystals suitable for X-ray diffraction could not be obtained. However, high resolution ESI mass spectrometry, elemental analysis and $^1H/^{13}C$ NMR confirm the complex to be Rh(**3**)(cod)CF_3SO_3.

2.3. Catalytic results

The results for the hydrogen transfer of acetophenone to 1-phenylethanol are summarised in Table 1. Conversions were determined by ^1H NMR spectroscopy and the enantiomeric excess *via* chiral HPLC. The catalysis was performed at 60 °C and 40 °C for 24 and 48 h, respectively. In refluxing isopropanol no selectivity was observed, but as the temperature was lowered moderate enantioselectivities and conversions could be obtained. As expected the 40 °C runs afforded slightly higher ee's than the 60 °C runs.

3. Conclusions

In conclusion, a series of diamine ligands have been prepared and fully characterised, as have their Rh(I) complexes. The complexes show modest activity and selectivity for the reduction of acetophenone with the highest ee of 50%. Work is currently being undertaken to prepare heterogeneous systems based on these ligands, *via* ionic and covalent methods, for asymmetric catalysis.

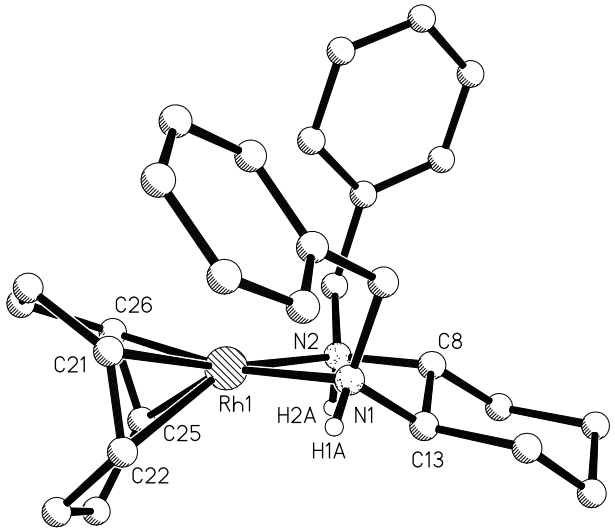

Fig. 3. The molecular structure of Rh(**2**)(cod)CF_3SO_3, selected bond lengths [Å] and angles [°] are: Rh(1)–N(1) 2.137(3), Rh(1)–N(2) 2.156(3), Rh(1)–C(21) 2.163(3), Rh(1)–C(22) 2.156(3), Rh(1)–C(25) 2.126(3), Rh(1)–C(26) 2.169(3). N(2)–Rh(1)–N(1) 80.75(1), C(21)–Rh(1)–C(26) 81.24(14), C(21)–Rh(1)–C(22) 37.01(13).

Table 1
Results for the hydrogen transfer of acetophenone to 1-phenylethanol

Catalyst	Temperature	Conversion	ee
Rh(**1**)(cod)CF_3SO_3	60	71	22 (*S*)
Rh(**1**)(cod)CF_3SO_3	40	75	50 (*S*)
Rh(**2**)(cod)CF_3SO_3	60	69	2 (*S*)
Rh(**2**)(cod)CF_3SO_3	40	40	11 (*S*)
Rh(**3**)(cod)CF_3SO_3	60	88	14 (*S*)
Rh(**3**)(cod)CF_3SO_3	40	74	20 (*S*)

The molar ratio of acetophenone:KOH:catalyst was 100:1:1. For the 60 °C runs the reaction time was 24 h and for the 40 °C run 48 h.

4. Experimental

4.1. General

(1*R*,2*R*)-1,2-diaminocyclohexane was resolved from the commercially available *cis*/*trans*-1,2-diaminocyclohexane by the method of Jacobson [22]. (*R*)-2-amino-3-methylbutane and $[RhCl(cod)]_2$ were purchased from Aldrich, ferrocenecarboxaldehyde was purchased from Alfa Aesar and used without further purification. THF/hexane/Et_2O were degassed and dried over activated alumina columns before use. Water free isopropanol was used for the catalytic runs and purchased from Aldrich and used without further purification.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 300 MHz or 500 MHz Avance spectrometer and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A.K. Carver at the Department of Chemistry, University of Bath. Mass spectra were recorded by ESI or EI.

4.2. Synthesis of imine (Schiff-base) precursors

1SB: Ferrocenecarboxaldehyde (640 mg, 3.0 mmol) was dissolved in MeOH (20 ml) to this solution (1*R*,2*R*)-1,2-diaminocyclohexane (170 mg, 1.5 mmol) was added. A red precipitate was immediately produced, which was filtered, washed with cold methanol and dried. ^1H NMR (300 MHz, $CDCl_3$) 1.45 (m, 2H), 1.71 (m, 4H), 1.83 (m, 2H), 3.27 (m, 2H, NCH), 4.02 (s, 10H), 4.24 (m, 4H), 4.50 (m, 4H), 8.12 (s, 2H, CH=N). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 24.6 (CH_2), 33.5 (CH_2), 68.1 (CH), 68.6 (CH), 69.0 (CH), 70.0 (CH), 70.2 (CH), 74.7(CH), 80.6 (C), 160.2 (C=N). Mass spec: HR-EI Calc for $[M^+]$ 506.1102. Found 506.1099.

2SB: An analogous procedure was followed with benzaldehyde. ^1H NMR (300 MHz, $CDCl_3$) 1.47 (m, 2H, CH_2), 1.84 (m, 6H, CH_2), 3.40 (m, 2H, NCH), 7.21–7.30 (m, 6H, Ph), 7.52–7.56 (m, 4H, Ph), 8.19 (s, 2H, CH=N). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 24.4 (CH_2), 32.9 (CH_2), 73.7 (NCH), 127.9 (CH), 128.3 (CH), 130.1(CH), 136.3(C), 160.9 (CH=N). Mass spec: HR-ESI Calc for $[M+H^+]$ 291.1861. Found 291.1875.

3SB: An analogous procedure was followed with 2-pyridinecarboxaldehyde and (*R*)-2-amino-3-methylbutane. ^1H NMR (300 MHz, CD_3OD) 0.81 (d J = 6 Hz, 3 H, CH_3), 0.88 (d J = 6 Hz, 3H, CH_3), 1.16 (d J = 6 Hz, 3H, CH_3), 1.71, (m, 1H, CH), 3.05 (sept J = 6 Hz, 1H, CH), 7.34 (m, 1H, Ar–H), 7.79 (m, 1H, Ar–H), 7.99 (m, 1H, Ar–H), 8.27 (s, 1H, HC=N), 8.54 (m, 1H, Ar–H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD) 19.8 (CH_3), 20.3 (CH_3), 35.1 (CH), 73.5 (CH), 122.5 (CH), 126.2 (CH), 138.4 (CH), 150.1 (CH), 155.5 (C), 160.9 (CH=N). HR-ESI Calc for $[M+H^+]$ 177.1383. Found 177.1392.

4.3. Synthesis of diamine ligands

Ligand 1: 1SB (620 mg, 1.2 mmol) was dissolved in hot methanol (100 ml) to this $NaBH_4$ (110 mg, 2.9 mmol) was added the red solution immediately turned orange. This was stirred for a further 1 h at room temperature. After which time the MeOH was removed *in vacuo* to afford an orange oil. The oil was dissolved in EtOAc and the solution was washed with water (3 × 100 ml). The EtOAc was dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to afford analytically pure ligand as an orange powder. ^1H NMR (300 MHz, $CDCl_3$) 1.04 (m, 2H), 1.26 (m, 2H), 1.74 (m, 2H), 1.89 (br s, 2H, NH), 2.12 (m, 2H), 2.24 (m, 2H), 3.36 (d J = 12.5 Hz, 2H, NCH_2), 3.63 (d J = 12.5 Hz, 2H, NCH_2), 4.08 (m, 4H), 4.12 (s, 10H), 4.18 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 25.2 (CH_2), 31.7 (CH_2), 46.1 (NCH_2), 61.1 (CH), 67.4 (CH), 67.8 (CH), 67.9 (CH), 68.2 (CH), 87.7 (C). Mass spec: HR-EI Calc for $[M^+]$ 510.1415. Found 510.1408.

Ligand 2: An analogous procedure was followed: ^1H NMR (300 MHz, $CDCl_3$) 1.03 (m, 2H), 1.20 (m, 2H), 1.69 (m, 2H), 1.95 (br s, 2H, NH), 2.12 (m, 2H), 2.23 (m, 2H), 3.62 (d J = 13.0 Hz, 2H, NCH_2), 3.86 (d J = 13.0 Hz, 2H, NCH_2), 7.15–7.33 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 24.8 (CH_2), 31.3 (CH_2), 50.6 (NCH_2), 60.7 (NCH), 126.5 (CH), 127.8 (CH), 128.1 (CH), 140.9 (C). Mass spec: HR-ESI Calc for $[M+H^+]$ 295.2174. Found 295.2164.

Ligand 2A: 2 (1.0 g, 3.4 mmol) was recrystallised in a MeOH/acetone mix (20 ml 10:1). After standing at room temperature for 2 days a near quantitative yield of crystals of **2A** were produced. ^1H NMR (300 MHz, $CDCl_3$) 0.82 (m, 2H, CH_2), 0.98 (m, 2H, CH_2), 1.03 (s, 6H, CH_3), 1.38 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 2.28 (m, 2H, NCH), 3.49 (d J = 14.5 Hz, 2H, NCH_2), 3.83 (d J = 14.5 Hz, 2H, NCH_2), 7.05–7.36 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 24.5 (CH_2), 24.8 (CH_3), 31.0 (CH_2), 52.0 (NCH_2), 67.1 (NCH), 79.4 (C) 126.3 (CH), 127.8 (CH), 128.1 (CH), 142.9 (C). Mass spec: HR-ESI Calc for $[M+H^+]$ 335.2482. Found 335.2467.

Ligand 3: An analogous procedure was followed, except that an oil was produced which was purified *via* vacuum distillation at 90 °C. ^1H NMR (300 MHz, $CDCl_3$) 0.80 (m, 6H, CH_3), 0.91 (d J = 6.5 Hz, 3H, CH_3), 1.64, (m, 1H, CH), 1.76 (br s, 1H, NH), 2.42 (m, 1H, CH), 3.70 (d J = 14.5 Hz, 1H, NCH_2), 3.81 (d J = 14.5 Hz, 1H, NCH_2), 7.18 (m, 1H Ar–H), 7.35 (m, 1H Ar–H), 7.68 (m, 1H Ar–H), 8.39 (m, 1H Ar–H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) 15.2 (CH_3), 16.6 (CH_3), 18.7 (CH_3), 31.6 (CH), 52.3 (CH_2), 57.3 (CH), 121.1 (CH), 121.6 (CH), 135.6 (CH), 148.5 (CH), 159.6 (C). Mass spec: HR-ESI Calc for $[M+H^+]$ 179.1541. Found 179.1548.

4.4. Synthesis of metal complexes

Rh(**1**)(cod)CF_3SO_3: $[RhCl(cod)]_2$ (100 mg, 0.2 mmol) was dissolved in THF to which $AgCF_3SO_3$ (104 mg, 0.4 mmol) was added and the solution stirred for 1 h. The yellow solution was filtered (to remove AgCl) and to the solution **1** (204 mg, 0.4 mmol) was added and stirred for 1 h. After which time hexane was added to precipitate the desired product and filtered. The yellow/orange residue was washed with Et_2O (3 × 20 ml) and recrystallised from a MeOH/Et_2O/hexane mix. ^1H NMR (500 MHz, CD_3OD) 1.28–1.45 (br m, 4 H, CH_2), 1.67–2.04 (br m, 8H, CH_2), 2.41 (m, 4H, CH_2), 2.42–2.50 (m, 1H), 2.54–2.60 (m, 1H), 2.69–2.79 (m, 1H), 2.90–3.00 (m, 1H), 3.02–3.11 (m, 1H), 3.80 (m, 1H) 4.17–4.37 (m, 18H, Fc), 4.51 (d J = 19 Hz, 2H, CH cod), 4.71 (d J = 19 Hz, 2H, CH cod). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) 25.8, 25.9, 30.2, 30.7, 30.9, 31.1, 31.4, 34.8 (CH_2), 44.7, 48.2 (N–CH_2), 58.2, 66.4 (NCH), 69.4, 69.6, 70.1, 70.1, 70.2, 71.0, 71.1, 71.7, 72.9, 73.2 (CH), 77.5 (CH cod d J = 13 Hz), 82.5 (C), 82.6 (CH cod d J = 13 Hz), 83.3 (CH cod d J = 13 Hz), 83.5 (CH cod d J = 13 Hz), 83.7 (C). Anal. Calc. for $C_{37}H_{46}N_2Rh_1Fe_2F_3O_3S_1$: C, 51.05; H, 5.33; N, 3.22. Found: C, 51.1; H, 5.46; N, 3.12%. HR-ESI Calc. for (M^+) 721.1415. Found 721.1411.

Rh(**2**)(cod)CF_3SO_3: an analogous procedure was followed: ^1H NMR (300 MHz, CD_3OD) 0.93–1.50 (m, 4H, CH_2), 1.54–2.03 (m, 6H, CH_2) 2.05–2.84 (m, 6H, CH_2), 3.13 (m, 2H, NCH), 3.6–4.6 (m, 8H, CH cod, CH_2 lig), 7.58 (m, 8H, Ar–H), 8.05 (d J = 7 Hz, 1H, Ar–H), 8.30 (d J = 7 Hz, 1H, Ar–H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD) 25.3, 25.7, 25.8, 27.8, 29.9, 30.3, 31.2, 34.6 (CH_2), 52.5, 58.9, 61.4, 68.9 (C–N) 83.0 (CH cod d J = 13 Hz), 85.5 (CH cod d J = 13 Hz), 129.2, 129.7, 129.8, 129.9, 130.0, 130.1, 130.3, 130.8, 131.7, 134.5, 136.6, 138.2 (Ar). Anal. Calc. for $C_{29}H_{38}N_2Rh_1F_3O_3S_1$: C, 53.21; H, 5.85; N, 4.28. Found: C, 53.1; H, 5.99; N, 4.10%. HR-ESI Calc. for (M^+) 505.2090. Found 505.2083.

Rh(**3**)(cod)CF_3SO_3: an analogous procedure was followed: ^1H NMR (300 MHz, CD_3OD) 1.00 (m, 6H, CH_3), 1.30 (br s, 3H, CH_3), 1.8–2.3 (br m, 5H, CH_2 cod and CH lig), 2.3–2.8 (br m, 5H, CH_2 cod and lig), 4.0–4.8 (br m, 6H, CH cod and CH_2 lig), 7.45 (t J = 7 Hz, 1H, Ar–H), 7.68 (d J = 8 Hz, 1H, Ar–H), 7.89 (br s, 1H, Ar–H), 8.01 (t J = 8 Hz, 1H, Ar–H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD) 17.5, 19.3, 20.6 (CH_3), 30.2 (CH_2 cod), 31.6 (CH), 32.2 (CH_2 cod), 53.1 (NCH_2), 63.3 (NCH), 83.3 (d J = 13 Hz, CH cod), 85.6 (CH cod) 122.0 (q J = 320 Hz, CF_3), 123.4, 125.4, 141.4, 149.0, 165.8 (Ar). Anal. Calc. for $C_{20}H_{30}N_2Rh_1F_3O_3S_1$: C, 44.61; H, 5.62; N, 5.20. Found: C, 44.8; H, 5.65; N, 5.22%. HR-ESI Calc. for (M^+) 389.1464. Found 389.1464.

4.5. X-ray crystallography

All data were collected on a Nonius Kappa CCD area detector diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 150 K, and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs [23]. Hydrogen atoms, were included in idealised positions and refined using the riding model. Except those involved in hydrogen bonding for Rh(**1**)(cod)CF_3SO_3, which were located in difference maps and refined freely. For Rh(**2**)(cod)CF_3SO_3 the hydrogen atoms bound to N(1) and N(2) were placed in calculated positions. One of the Cp rings in Rh(**1**)(cod)CF_3SO_3 contains a significant amount of disorder, this Cp ring (C32–C36) was modelled over two sites with an occupancy of 60:40.

Crystal data for **2A**: $C_{23}H_{30}N_2$, M = 334.49, 0.20 × 0.10 × 0.10 mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 6.050(1), b = 16.365(2), c = 19.591(3) Å, V = 1939.67(5) $Å^3$, Z = 4, D_c = 1.145 g/cm^3, F_{000} = 728, $2\theta_{max}$ = 55.0°, 37230 reflections collected, 4439 unique (R_{int} = 0.0437). Final GooF = 1.038, R_1 = 0.0333, wR_2 = 0.0775, R indices based on 4119 reflections with $I > 2\sigma(I)$ (refinement on F^2), 228 parameters, 0 restraints. μ = 0.066 mm^{-1}. Absolute structure parameter = −0.2(18) [24].

Crystal data Rh(**1**)(cod)CF_3SO_3: $C_{43}H_{60}F_3Fe_2N_2O_3RhS$, M = 956.60, yellow block, 0.20 × 0.15 × 0.10 mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.858(1), b = 14.875(2), c = 21.724(3) Å, V = 4154.99(9) $Å^3$, Z = 4, D_c = 1.529 g/cm^3, F_{000} = 1984, λ = 0.71073 Å, T = 150(2)K, $2\theta_{max}$ = 55.0°, 60356 reflections collected, 9497 unique (R_{int} = 0.0653). Final GooF = 1.044, R_1 = 0.0364, wR_2 = 0.0836, R indices based on 8207 reflections with $I > 2\sigma(I)$ (refinement on F^2), 552 parameters, 10 restraints. Lp and absorption corrections applied, μ = 1.187 mm^{-1}. Absolute structure parameter = −0.016(17) [24].

Crystal data Rh(**2**)(cod)CF_3SO_3: $C_{29}H_{38}F_3N_2O_3RhS$, M = 654.58, yellow block, 0.30 × 0.25 × 0.10 mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 11.682(1), b = 14.190(1), c = 35.699(4) Å, V = 5917.74(9) $Å^3$, Z = 8, D_c = 1.469 g/cm^3, F_{000} = 2704, $2\theta_{max}$ = 50.1°, 45120 reflections collected, 10302 unique (R_{int} = 0.0714). Final GooF = 0.990, R_1 = 0.0350, wR_2 = 0.0567, R indices based on 8500 reflections with $I > 2\sigma(I)$ (refinement on F^2), 703 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.699 mm^{-1}. Absolute structure parameter = −0.036(16) [24].

4.6. Catalytic runs

In a typical run, the catalyst (0.04 mmol) was dissolved in isopropyl alcohol (20 ml) containing KOH (0.04 mmol) to which acetophenone (0.5 ml, 4 mmol) was added. The reaction vessel was then sealed and place in an oil bath at 40 or 60 °C for either 24 or 48 h. After which time the solvent was removed *in vacuo* (at this point a mass balance was performed to ensure no products or reactants had been lost during this process.) The enantiomeric excesses (ee) were determined by chiral HPLC using a CHIRALCEL OD-H column, with hexane:isopropanol (95:5) as the mobile phase at a flow rate of 1 ml per minute and compared to authenticated samples of the pure enantiomers. The *S* enantiomer eluted after 10 min and the *R* after 12 min, standard known mixtures were prepared for calibration purposes. The following formula was used to determine the ee: % ee = ([*S*] − [*R*])/([*S*] + [*R*]) × 100%. The conversion was determined *via* ^1H NMR spectroscopy ($CDCl_3$), by comparing the integrals of the singlet at 2.5 ppm (ArCOC**H**$_3$-substrate) to the doublet at 1.4 ppm (ArC(H)(OH)C**H**$_3$-product) and the conversion is given by the following formula: % Con. = (Integral of product)/(Integral of substrate + Integral of product) × 100%.

Supplementary material

CCDC 680122, 680123 and 680124 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] R. Noyori, Angew. Chem., Int. Ed. 41 (2002) 2008.
[2] A. Corma, H. Garcia, Adv. Synth. Catal. 348 (2006) 1391.
[3] C.E. Song, S.G. Lee, Chem. Rev. 102 (2002) 3495.
[4] M.D. Jones, R. Raja, J.M. Thomas, B.F.G. Johnson, Top. Catal. 25 (2003) 71.
[5] G. Desimoni, G. Faita, K.A. Jorgensen, Chem. Rev. 106 (2006) 3561.

[6] R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97.
[7] P. Gamez, F. Fache, M. Lemaire, Tetrahedron: Asymmetry 6 (1995) 705.
[8] M.L. Tommasino, C. Thomazeau, F. Touchard, M. Lemaire, Tetrahedron: Asymmetry 10 (1999) 1813.
[9] F. Fache, E. Schulz, M.L. Tommasino, M. Lemaire, Chem. Rev. 100 (2000) 2159.
[10] M. Yamakawa, H. Ito, R. Noyori, J. Am. Chem. Soc. 122 (2000) 1466.
[11] J.M. Thomas, R. Raja, J. Organomet. Chem. 689 (2004) 4110.
[12] M.D. Jones, R. Raja, J.M. Thomas, B.F.G. Johnson, D.W. Lewis, J. Rouzaud, K.D.M. Harris, Angew. Chem., Int. Ed. 42 (2003) 4326.
[13] D.-J. Cho, S.-J. Jeon, H.-S. Kim, C.-S. Cho, S.-C. Shim, T.-J. Kim, Tetrahedron: Asymmetry 10 (1999) 3833.
[14] O.B. Sutcliffe, M.R. Bryce, A.S. Batsanov, J. Organomet. Chem. 656 (2002) 211.
[15] S. Liu, E. Wong, S.J. Rettig, C. Orvig, Inorg. Chem. 32 (1993) 4268.
[16] M.D. Jones, F.A.A. Paz, J.E. Davies, B.F.G. Johnson, Acta Crystallogr., Sect. E 59 (2003) m6.
[17] M.D. Jones, F.A.A. Paz, J.E. Davies, B.F.G. Johnson, J. Klinowski, Acta Crystallogr., Sect. E 59 (2003) m1091.
[18] M. Beller, H. Trauthwein, M. Eichberger, C. Breindl, T.E. Müller, A. Zapf, J. Organomet. Chem. 566 (1998) 277.
[19] B. de Bruin, R.J.N.A.M. Kicken, N.F.A. Suos, M.P.J. Donners, C.J. den Reijer, A.J. Sandee, R. de Gelder, J.M.M. Smits, A.W. Gal, A.L. Spek, Eur. J. Inorg. Chem. 9 (1999) 1581.
[20] M.T. Reetz, E. Bohres, R. Goddard, Chem. Commun. (1998) 935.
[21] Search of the Cambridge Structural Database version 5.27: F.H. Allen, Acta Crystallogr., Sect. B 58 (2002) 380.
[22] J.F. Larrow, E.N. Jacobsen, Y. Gao, Y.P. Hong, X.Y. Nie, C.M. Zeep, J. Org. Chem. 59 (1994) 1939.
[23] G.M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
[24] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.