Inorganica Chimica Acta 387 (2012) 173–180

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, spectroscopy, catalysis and crystal structure of [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] (Ar = C_6H_5, 3-/4-$MeOC_6H_4$, and 4-BrC_6H_4)

Mohammed Enamullah [a,*], A.K.M. Royhan Uddin [a], Graeme Hogarth [b], Christoph Janiak [c]

[a] Department of Chemistry, Jahangirnagar University, Dhaka 1342, Bangladesh
[b] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK
[c] Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany

ARTICLE INFO

Article history:
Received 4 November 2011
Received in revised form 2 January 2012
Accepted 5 January 2012
Available online 14 January 2012

Keywords:
Chiral Schiff bases (*R*)-*N*-(Ar)ethyl-2-hydroxy-1-naphthaldimine
(η^4-cod)Rh(I)-complexes
Crystal structure
Enantiopurity
Catalysis

ABSTRACT

Condensation of 2-hydroxy-1-naphthaldehyde with (*R*)-(Ar)ethylamine yields the enantiopure Schiff bases, (*R*)-*N*-(Ar)ethyl-2-hydroxy-1-naphthaldimine (Ar = C_6H_5, 3-/4-$MeOC_6H_4$, 4-BrC_6H_4). These Schiff bases readily react with the dinuclear complex [Rh(η^4-cod)(μ-O_2CMe)]$_2$ to afford the mononuclear complexes [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] (Ar = C_6H_5 (**I**); 3-$MeOC_6H_4$ (**II**); 4-BrC_6H_4 (**III**)), respectively in C_6H_6/MeOH (5:1, v/v). The Schiff bases and complexes are characterized by IR, UV–Vis, $^1H/^{13}C$ NMR and mass spectrometry, polarimetry and HPLC. The polarimetric measurements show the enantiopurity of the Schiff bases as well as the complexes. The X-ray structure determination for **III** demonstrates that the deprotonated Schiff bases, (*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminate, coordinate to the [Rh(η^4-cod)]-fragment as a six-membered *N*,*O*-chelate ligand with distorted square planar geometry at the rhodium metal atom. Reaction of **III** with O_2 leads to the formation of the oxidative aduct [Rh(η^4-cod)(μ-O)]$_2$ (**IIIa**). Compound **I** or [Rh(η^4-cod){(*S* or *R*)-*N*-(phenyl)ethyl-salicylaldiminato}] were used for reduction of acetophenone with diphenylsilane into (±)-1-phenyl-ethanol, and conversions up to 93–97% have been achieved.

1. Introduction

Reactions of bidentate *N*,*O*-chelate (HSB) and tetradentate *N*,*O*,*N*,*O*-chelate (H_2SB′) Schiff base ligands with dinuclear [Rh(η^4-cod)(μ-X)]$_2$ (X = Cl, OMe, O_2CMe; cod = 1,5-cyclooctadiene) give mononuclear [Rh(η^4-cod)(SB)] and dinuclear [{Rh(η^4-cod)}$_2$(SB′)], respectively [1–7]. Similar reactions with the chiral bidentate *N*,*N*-chelate Schiff bases afford the analogous Rh(η^4-cod)(imine)-complexes [8–14]. The *in situ* systems composed of dinuclear [Rh(η^4-cod)Cl]$_2$ and chiral *N*,*N*-chelates have successfully been used for asymmetric reduction of ketone derivatives into the corresponding chiral secondary alcohol up to 65% ee.

We have given attention to synthesise the analogous Rh(η^4-cod) (chiral amino acids or amino alcohols) complexes starting from the dinuclear [Rh(η^4-cod)(μ-O_2CMe)]$_2$. We have reported the syntheses, spectroscopy and crystal structures of mononuclear [Rh(η^4-cod)(AA)] (AA = amino acetate: L/D-alaninato, *S*/*R*-phenylglycinato, *N*-methyl-/-phenyl-glycinato, *o*-amino-benzoato/-phenolato) and [Rh(η^4-cod)(AOH)](O_2CMe) (AOH = amino alcohol: *S*-phenylglycinol) (Scheme 1) [15–17]. The X-ray studies show five-membered *N*,*O*-chelation of amino-carboxylate or amino-alcohol to the Rh(η^4-cod)-fragment in distorted square planar symmetry. The [Rh(η^4-cod)(AA)] complexes readily react with di-/tri-phosphine ligands (diphos/triphos) to synthesise the mononuclear [Rh(diphos/triphos)(AA)] complexes [18]. The chiral bidentate *N*,*O*-chelate Schiff base ligands (*R*)-*N*-(Ar)ethyl-salicylaldimine (Ar = phenyl, *o*/*m*/*p*-methoxphenyl, *p*-bromophenyl and 1-naphthyl) (HSB) (Scheme 1) [19], (*R*)-*N*-(Ar)ethyl-naphthaldimine (HSB1) [20], (*R*)-2-(X-benzaldimine)-2-phenylethanol (X = H or 2,4-dimethoxy) (HL) [21] react with the dinuclear [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ to give mononuclear [Rh(η^4-cod)(SB)] [19], [Rh(η^4-cod)(SB1)] [6,20], and [Rh(η^4-cod)(HL)](acetate) [21], respectively. Similar reaction with achiral bidentate *N*,*O*-chelate Schiff base ligands, *N*-(Ar)ethyl-naphthaldimine (Ar = phenyl, *o*-tolyl) (HSB′) or with tetradentate *N*,*O*,*N*,*O*-chelate, *N*,*N*′-R_1-bis(salicylaldimine) {R_1 = ethylene (H_2salen) or 1,2-phenylene (H_2salophen)} give mononuclear [Rh(η^4-cod)(SB′)] or dinuclear [{Rh(η^4-cod)}$_2$(salen)] or [{Rh(η^4-cod)}$_2$(salophen)] complexes, respectively (Scheme 1) [6,20]. The X-ray results show six-membered *N*,*O*-chelation of salicylaldiminate (SB or salen or salophen) or naphthaldiminate (SB1 or SB′) to the Rh(η^4-cod)-fragment in these complexes. The structure of chiral enantiopure [Rh(η^4-cod)((*R*)-*N*-(4-methoxphenyl)ethyl-2-oxo-1-naphthaldiminato)]

* Corresponding author.
E-mail addresses: enamullahju@yahoo.com (M. Enamullah), g.hogarth@ucl.ac.uk (G. Hogarth), janiak@uni-duesseldorf.de (C. Janiak).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2012.01.013

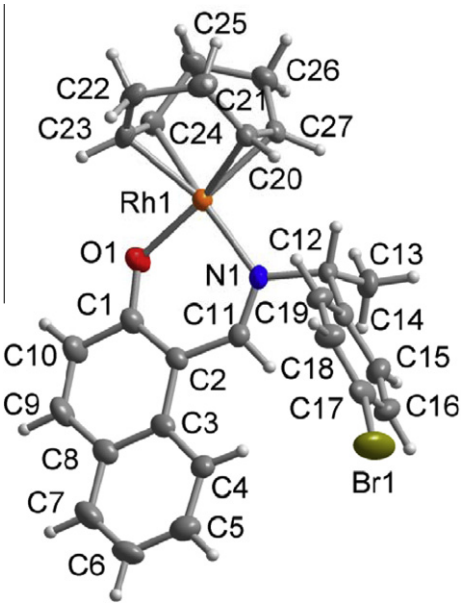


Fig. 1. Molecular structure of **III** (50% thermal ellipsoids, H atoms with arbitrary radii). Selected bond distances [Å] and angles [°]: Rh—O1 2.028(2), Rh—N 2.073(3), Rh—C_{cod} 2.111(3)–2.146(3), O1—C 1.302(4) and O1—Rh—N 88.87(10).

displays a herring-bone arrangement and achiral [Rh(η^4-cod)(*N*-(o-tolyl)-2-oxo-1-naphthaldiminato)] crystallizes in the non-centrosymmetric polar space group *Cc* where all molecules show the same orientation.

The present paper, in continuation, reports the synthesis, stereochemistry and enantiopurity of (*R*)-*N*-(Ar)ethyl-2-hydroxy-1-naphthaldimine (HSB1–HSB4), and [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] (**I**–**III**) (cf. Scheme 2). The single-crystal structure was determined for **III**. The *in situ* formed compound from [Rh(η^4-cod)Cl]$_2$ and (*R*)-*N*-(phenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB1) has been used as catalyst for reduction of acetophenone into (±)-1-phenyl-ethanol.

2. Experimental

The syntheses of Rh(I)(η^4-cod)-(*R*)-Schiff bases complexes were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents used were dried and distilled under nitrogen prior to use: benzene, diethyl ether, dichloromethane over Na metal and methanol over CaO. UV–Vis spectra were obtained with Shimadzu UV 3150 spectrophotometer in CH_2Cl_2 at 25 °C. IR-spectra were recorded on a Bruker Optik IFS 25 spectrometer as KBr disks at ambient temperature. Elemental analysis were done on a VarioEL from Elementaranalysensysteme GmbH. NMR-spectra were run on a Bruker Avance DPX 200 spectrometer operating at 200 MHz (^{1}H) or on a Bruker AC DPX 400 at 400 MHz (^{1}H) and 100 MHz (^{13}C) at 20 °C with calibration against the residual protonated solvent signal ($CDCl_3$: ^{1}H NMR 7.25 ppm, ^{13}C NMR 77.0 ppm). NMR grade solvent $CDCl_3$ was deoxygenated prior to use. EI-MS: Thermo-Finnigan TSQ 700. ESI-MS: QStar Elite quadrupole time-of-flight (Q-TOF) instrument (MDS Analytical Technologies, Concord, ON, Canada). Polarimetric measurements were carried with a Perkin–Elmer 241 instrument in $CHCl_3$ at 25 °C and values of $[\alpha]^{25}$ were determined according to the literature [19,22]. Analytical HPLC4: LaChrom Elite, equipped with OB-H chiral column was used for ee (%) value determination. The dinuclear [Rh(η^4-cod)(O_2CMe)]$_2$ was synthesized from [Rh(η^4-cod)Cl]$_2$ according to the literature [15]. (*S* or *R*)-*N*-(1-phenyl)ethylsalicylaldimine}] (*S*- or *R*-HSB) was synthesized according to literature [19]. Enantiopure (*R*)-(phenyl)ethylamine, (*R*)-(3-methoxyphenyl)

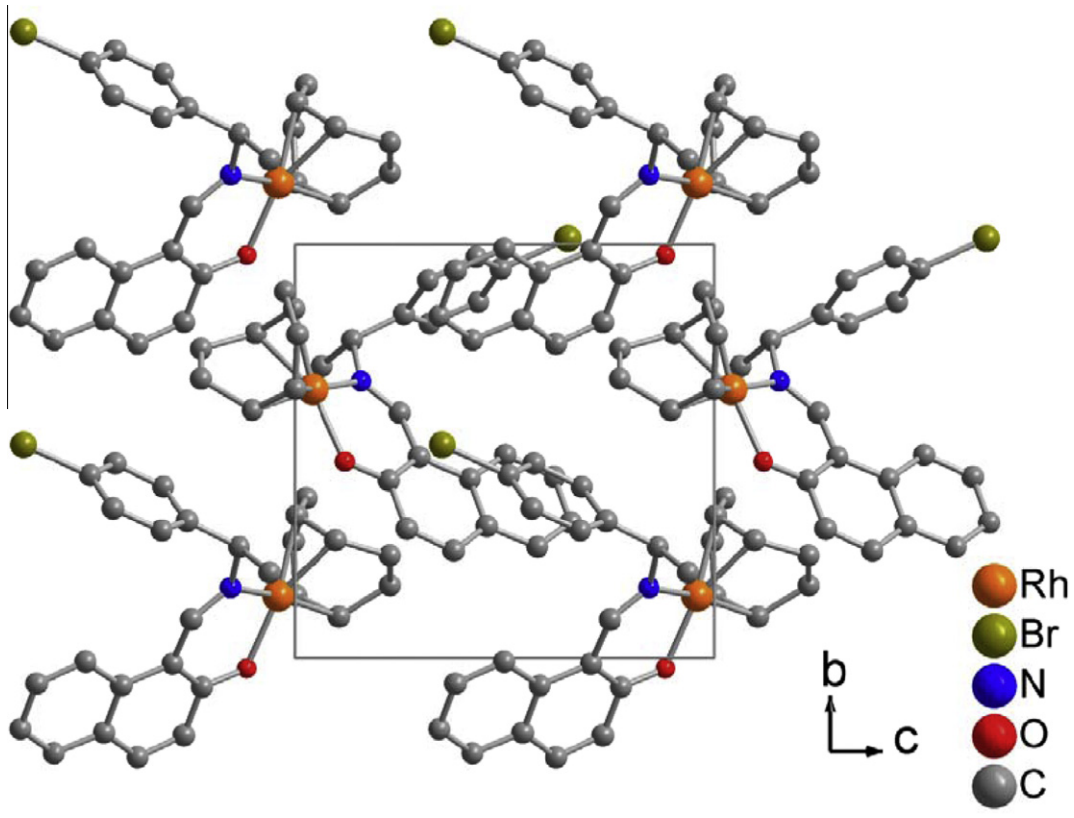
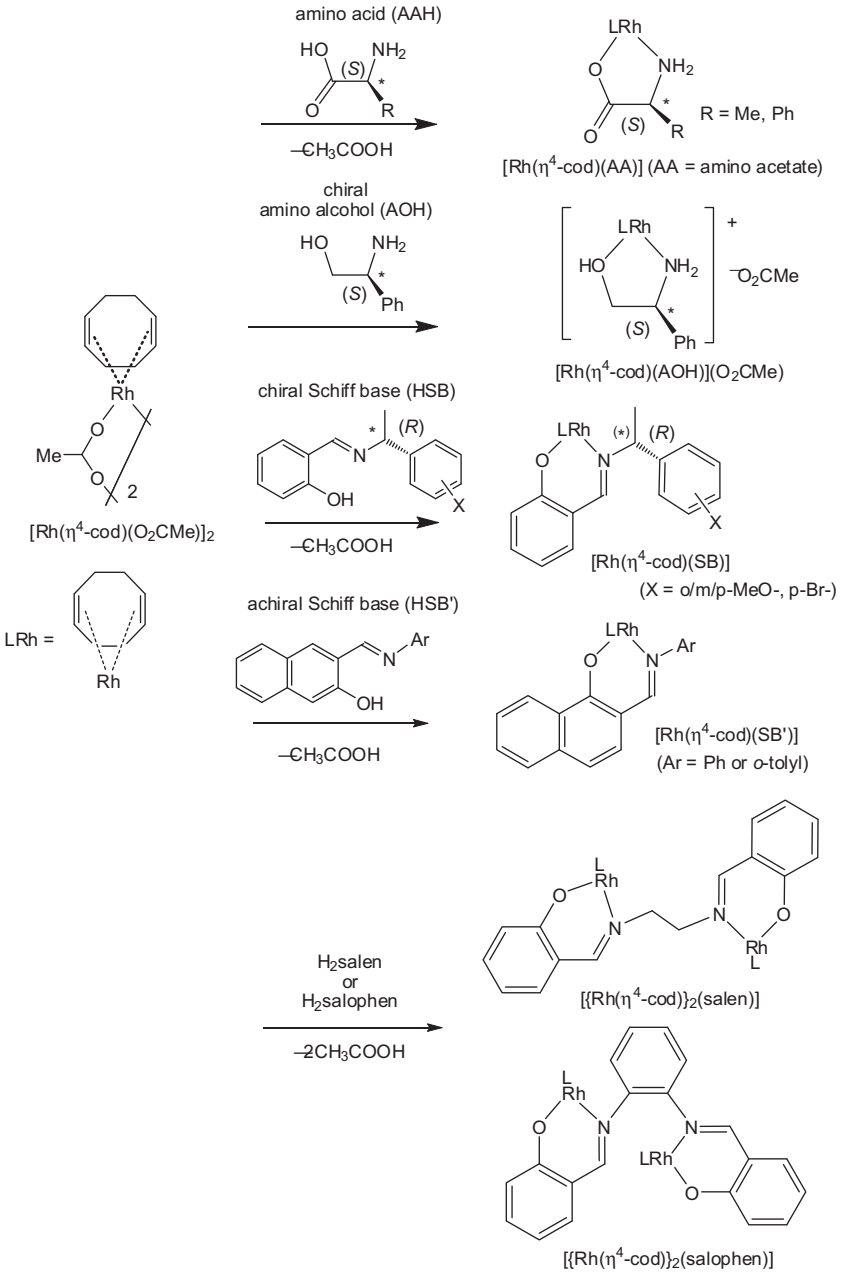


Fig. 2. Packing diagram of **III**, viewed along *a* (H atoms omitted for clarity).



Scheme 1. Rh(η^4-cod) (chiral/achiral ligand) complexes with chiral ligand = AA, chiral amino acetate or =AOH, chiral amino alcohol or =HSB, chiral Schiff base; and with achiral ligand = HSB′ or H_2salen or H_2salophen, achiral Schiff base.

ethylamine, (*R*)-(4-methoxyphenyl)ethylamine and (*R*)-(4-bromophenyl)ethylamine were used as received from the BASF AG, Ludwigshafen, Germany.

2.1. General procedure to synthesise the (R)-N-(Ar)ethyl-2-hydroxy-1-naphthaldimine (HSB1–HSB4)

2-Hydroxy-1-naphthaldehyde (5.0 g, 29 mmol) was dissolved in 10 ml of methanol, 2–3 drops of conc. H_2SO_4 added into this solution and the solution stirred for 10 min at room temperature. An equimolar amount of (*R*)-phenylethylamine (3.7 ml, 29 mmol) was added into this solution, the color changed to bright yellow and the solution was refluxed for 5–6 h. Afterward the solvent was evaporated in *vacuo* to about 50% and the yellow solution was then left standing for crystallization through slow solvent evaporation at room temperature. After 2–3 days bright-yellow needle-shaped crystals were obtained. The crystals were washed three times with MeOH (5 ml each) and dried in *vacuo* at 40 °C for 5–6 h to give (*R*)-*N*-(phenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB1) as a bright-yellow compound. The other (*R*)-*N*-(Ar)ethyl-2-hydroxy-1-naphthaldimine derivatives were obtained by using (*R*)-(3-methoxyphenyl)ethylamine (for HSB2), (*R*)-(4-methoxyphenyl)ethylamine (for HSB3), and (*R*)-(4-bromophenyl)ethylamine (for HSB4).

2.1.1. (R)-N-(phenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB1)

Yield: 6.5 g (81%). $[\alpha]^{25}$ (*c* = 0.54, $CHCl_3$): −176° (598 nm). *Anal.* Calc. for $C_{19}H_{17}NO$ (275.36): C 82.88; H 6.22; N 5.09. Found: C 82.26; H 6.30; N 5.03%. IR (KBr, cm^{-1}): 3050w, 2993m, 2934w (νH—Ar), 1628vs, 1611sh (νC=N), and 1597s (νC=C). MS (EI, 70 eV): *m/z* 275 (100) $[M]^+$, 260 (5) $[M-CH_3]^+$, 170 (60) $[M-CH(CH_3)(C_6H_5)]^+$, 105 (50) $[CH(CH_3)(C_6H_5)]^+$, and 77 (10)

Table 1
Crystal data and structure refinement for [Rh(η⁴-cod)(SB4)] (**III**).

Chemical formula	$C_{27}H_{27}BrNORh$
Formula weight	564.32
T (K)	150(2)
Crystal system, space group	monoclinic, $P2_1$
Unit cell parameters	
a (Å)	10.2218(14)
b (Å)	10.4813(15)
c (Å)	11.1563(16)
β (°)	107.771(2)
V (Å^3)	1138.2(3)
Z	2
$D_{calc.}$ (g/cm^3)	1.647
Absorption coefficient μ (mm^{-1})	2.525
F(000)	568
Crystal color and size (mm)	yellow, 0.28 × 0.24 × 0.18
θ range for data collection (°)	2.73–28.27
Index ranges, h, k, l	±13, ±13, ±14
Completeness to θ = 26.00°	99.3%
Reflections collected	9391
Independent reflections	4990 (R_{int} = 0.0308)
Reflections with $F^2 > 2\sigma$	4600
Minimum and maximum transmission	0.5383 and 0.6593
Weighting parameters a, b	0.0000, 0.0000
Data/restraints/parameters	4990/1/280
Final R indices [$F^2 > 2\sigma$]	R_1 = 0.0300, wR_2 = 0.0609
R indices (all data)	R_1 = 0.0337, wR_2 = 0.0619
Goodness-of-fit (GOF) on F^2	0.948
Absolute structure parameter, Flack value [30–32]	0.012(8)
Largest difference in peak and hole (e Å^{-3})	0.893 and −0.763

Table 2
Results for reduction of acetophenone with diphenylsilane (DPS) into (±)-1-phenylethanol using [Rh(η⁴-cod)(μ-Cl)]$_2$ (0.02 mmol) with chiral Schiff bases (L) at (0–5 °C).

Entry	Schiff bases (L)	Rh/acetophenone (molar ratio)	Rh/L (molar ratio)	Rh/DPS (molar ratio)	Time (h)	Conversion (%)
1	–	1:210	1:0	1:200	48	58
2	(*S*)-HSB	1:176	1:4.5	1:167	48	93
3	(*R*)-HSB	1:211	1:5.0	1:201	48	97
4	(*R*)-HSB1	1:196	1:5.4	1:186	1	85
					6	91
					24	95

HSB = (*S* or *R*)-*N*-(phenyl)ethyl-salicylaldimine; HSB1 = (*R*)-*N*-(phenyl)ethyl-1-naphthaldimine.

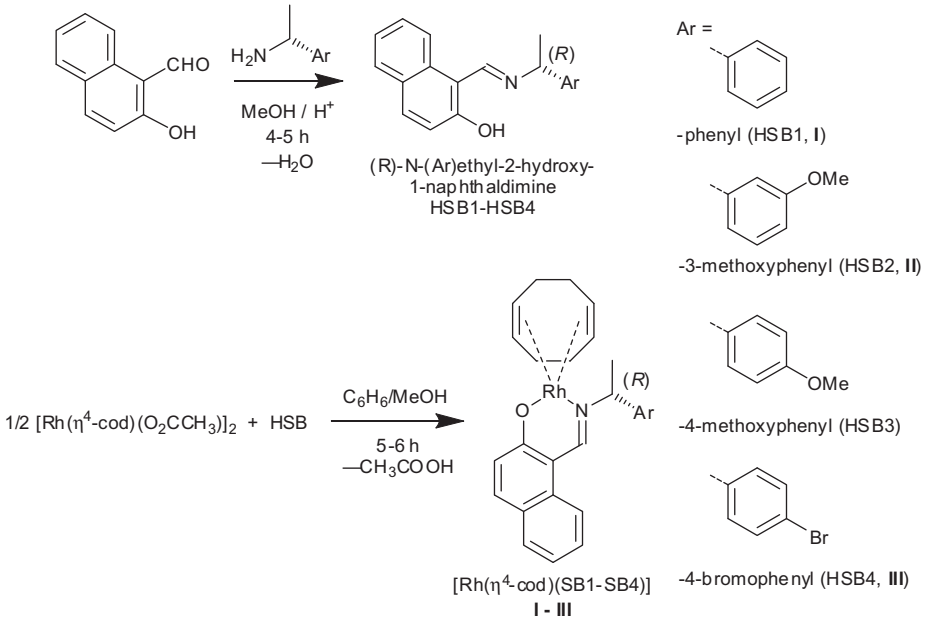
[C_6H_5]$^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (d, J_{HH} = 6.8 Hz, 3H, H13), 4.80 (q, J_{HH} = 6.8 Hz, 1H, H12), 7.05 (d, J_{HH} = 9.2 Hz, 1H, H17), 7.35 (m, 7H, H3, 6–7, 15–16, 18–19), 7.63 (dd, J_{HH} = 7.8 Hz, J_{HH} = 0.8 Hz, 1H, H8), 7.71 (d, J_{HH} = 9.2 Hz, 1H, H5), 7.82 (d, J_{HH} = 8.4 Hz, 1H, H4), 8.87 (s, 1H, H11), and 14.80 (br, 1H, OH).

2.1.2. (R)-N-(3-methoxyphenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB2)

Yield: 7.4 g (83%). [α]^{25} (*c* = 0.76, $CHCl_3$): −132° (598 nm). *Anal.* Calc. for $C_{20}H_{19}NO_2$ (305.39): C 78.66; H 6.27; N 4.59. Found: C 77.25; H 6.27; N 4.47%. IR (KBr, cm^{-1}): 3052m (νH—Ar), 1620vs (νC=N), and 1589vs (νC=C). MS (EI, 70 eV): *m/z* 305 (100) [M]$^+$, 290 (5) [M−CH_3]$^+$, 170 (40) [M−CH(CH_3)(C_6H_4OMe)]$^+$, 135 (50) [CH(CH_3)(C_6H_4OMe)]$^+$, 105 (10) [CH(CH_3)(C_6H_5)]$^+$, and 77 (8) [C_6H_5]$^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.73 (d, J_{HH} = 6.8 Hz, 3H, H13), 3.81 (s, 3H, H20), 4.75 (q, J_{HH} = 6.8 Hz, 1H, H12), 6.95 (m, 4H, H15, 17, 18–19), 7.35 (m, 3H, H3, 6–7), 7.62 (dd, J_{HH} = 7.2 Hz, J_{HH} = 0.8 Hz, 1H, H8), 7.71 (d, J_{HH} = 9.0 Hz, 1H, H5), 7.82 (d, J_{HH} = 8.4 Hz, 1H, H4), 8.85 (s, 1H, H11), and 14.85 (br, 1H, OH).

2.1.3. (R)-N-(4-methoxyphenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB3)

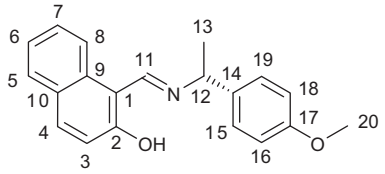
Yield: 7.5 g (85%). [α]^{25} (*c* = 0.52, $CHCl_3$): −222° (598 nm). *Anal.* Calc. for $C_{20}H_{19}NO_2$ (305.39): C 78.66; H 6.27; N 4.59. Found: C 77.02; H 6.30; N 4.56%. IR (KBr, cm^{-1}): 3051w, 2970m (νH—Ar), 1624vs, 1600sh (νC=N), 1590sh (νC=C), and 1251s (νC—O). MS (EI, 70 eV): *m/z* 305 (50) [M]$^+$, 170 (5) [M−CH(CH_3)(C_6H_4OMe)]$^+$, 135 (100) [CH(CH_3)(C_6H_4OMe)]$^+$, and 105 (7) [CH(CH_3)(C_6H_5)]$^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71 (d, J_{HH} = 6.4 Hz, 3H, H13), 3.80 (s, 3H, H20), 4.73 (q, J_{HH} = 6.4 Hz, 1H, H12), 6.95 (m, 3H, H15–16,18), 7.35 (m, 4H, H3, 6–7, 19), 7.60 (d, J_{HH} = 7.7 Hz, 1H, H8), 7.68 (d, J_{HH} = 9.3 Hz, 1H, H5), 7.78 (d, J_{HH} = 8.0 Hz, 1H, H4), 8.78 (s, 1H, H11), and 14.72 (br, 1H, OH).



Scheme 2. Synthetic route to the formation of (*R*)-*N*-(*Ar*)ethyl-1-naphthaldimine (HSB1–HSB4) and [Rh(η⁴-cod){(*R*)-*N*-(*Ar*)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] (**I**–**III**).

2.1.4. (R)-N-(4-bromophenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB4)

Yield: 8.7 g (85%). $[\alpha]^{25}$ (c = 0.48, $CHCl_3$): −104° (598 nm). *Anal.* Calc. for $C_{19}H_{16}NOBr$ (354.26): C 64.42; H 4.55; N 3.95. Found: C 63.58; H 4.55; N 3.86%. IR (KBr, cm^{-1}): 3049m, 2984m (νH—Ar), 1628vs, 1600sh (νC=N), and 1590s (νC=C). MS (EI, 70 eV): m/z 353 (100) $[M]^+$, 338 (10) $[M-CH_3]^+$, 183 (40) $[CH(CH_3)(C_6H_4Br)]^+$, 170 (80) $[M-CH(CH_3)(C_6H_4Br)]^+$, 104 (55) $[CH(CH_3)(C_6H_5)-H]^+$, and 77 (10) $[C_6H_5]^+$ (the $^{79/81}$Br isotopic pattern is clearly visible for patterns following the 353, 338, and 183 peaks, with masses given for the slightly more abundant ^{79}Br-containing fragment). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71 (d, J_{HH} = 6.6 Hz, 3H, H13), 4.74 (q, J_{HH} = 6.6 Hz, 1H, H12), 7.05 (d, J_{HH} = 9.2 Hz, 1H, H15), 7.28 (m, 3H, H3, 6, 19), 7.45 (m, 3H, H7, 16, 18), 7.65 (d, J_{HH} = 7.8 Hz, 1H, H8), 7.73 (d, J_{HH} = 9.0 Hz, 1H, H5), 7.87 (d, J_{HH} = 8.4 Hz, 1H, H4), 8.93 (s, 1H, H11), and 14.80 (br, 1H, OH).



*2.2. General procedure to synthesise [Rh(η⁴-cod){(R)-N-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ²N,O}] (**I**–**III**)*

(*R*)-*N*-(phenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB1) (0.38 mmol) and $[Rh(\eta^4\text{-cod})(O_2CMe)]_2$ (102 mg, 0.19 mmol) were dissolved in 10 ml of C_6H_6/MeOH (5:1, v/v) and the solution stirred for 5–6 h at room temperature. The color changed from red-orange to bright-yellow. Then the solvent was evaporated in *vacuo* at 40 °C. The products were again dissolved in 10 ml of C_6H_6/MeOH (5:1, v/v), stirred for 30 min and the solvent evaporated in *vacuo*. This procedure was repeated three times, and finally the products were dried in *vacuo* (0.1–0.2 mbar) at 40 °C to give the yellow complex of [Rh(η⁴-cod){(*R*)-*N*-(phenyl)ethyl-2-oxo-1-naphthaldiminato-κ²*N*,*O*}] (**I**). The same procedure was followed for syntheses of **II** and **III** by using the Schiff bases of HSB2, and HSB4, respectively.

*2.2.1. [Rh(η⁴-cod){(R)-N-(phenyl)ethyl-2-oxo-1-naphthaldiminato-κ² N,O}] [Rh(η⁴-cod)(SB1)] (**I**)*

(*R*)-*N*-(phenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB1) (104 mg, 0.38 mmol). Yield: 150 mg (82%) (based on $[Rh(\eta^4\text{-cod})(O_2CMe)]_2$). $[\alpha]^{25}$ (c = 0.85, $CHCl_3$): +88° (578 nm). *Anal.* Calc. for $C_{27}H_{28}NORh$ (485.43): C 66.81; H 5.81; N 2.89. Found: C 67.91; H 6.35; N 2.46%. UV–Vis (6.339×10^{-4} mol dm^{-3}, $CHCl_3$, 25 °C): λ_{max} = 394 nm; ε_{max} = 4985 dm^3 mol^{-1} cm^{-1}. IR (KBr, cm^{-1}): 3056w (νH—Ar), 1618vs (νC=N), and 1577vs (νC=C). MS (EI, 70 eV): m/z 485 (100) $[M]^+$, 377 (78) $[M-cod]^+$, 275 (5) $[HSB1]^+$, 218 (15) $[Rh(C_6H_5CH_3CN)]^+$, 211 (5) $[Rh(cod)]^+$, 208 (12) $[Rh(cod)-H_2-H]^+$, and 105 (12) $[CH(CH_3)(C_6H_5)]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74 (d, J_{HH} = 6.8 Hz, 3H, H13), 1.96 (m, 4H, CH_2cod_{exo}), 2.49 (m, 4H, CH_2cod_{endo}), 3.94 (m, 2H, CHcod), 4.45 (q, J_{HH} = 6.8 Hz, 1H, H12), 4.58 (m, 2H, CHcod), 6.98–7.03 (m, 2H, H_{Ar}), 7.24–7.42 (m, 6H, H_{Ar}), 7.51–7.69 (m, 3H, H_{Ar}), and 8.85 (d, J_{HH} = 2.0 Hz, 1H, H11).

*2.2.2. [Rh(η⁴-cod){(R)-N-(3-methoxphenyl)ethyl-2-oxo-1-naphthaldiminato-κ²N,O}] [Rh(η⁴-cod)(SB2)] (**II**)*

(*R*)-*N*-(3-methoxyphenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB2) (116 mg, 0.38 mmol). Yield: 165 mg (85%). $[\alpha]^{25}$ (c = 0.75, $CHCl_3$): +65° (578 nm). *Anal.* Calc. for $C_{28}H_{30}NO_2Rh$ (515.46): C 65.24; H 5.87; N 2.72. Found: C 64.91; H 5.96; N 2.50%. UV–Vis (5.149×10^{-4} mol dm^{-3}, $CHCl_3$, 25 °C): λ_{max} = 396 nm; ε_{max} = 4835 dm^3 mol^{-1} cm^{-1}. IR (KBr, cm^{-1}): 3060 (νH—Ar), 1615vs (νC=N), and 1578vs (νC=C). MS (EI, 70 eV): m/z 515 (100) $[M]^+$, 407 (55) $[M-cod]^+$, 305 (5) $[HSB3]^+$, and 218 (10) $[Rh(C_6H_5CH_3CN)]^+$. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.76 (d, J_{HH} = 6.8 Hz, 3H, H13), 2.02 (m, 4H, CH_2cod_{exo}), 2.51 (m, 4H, CH_2cod_{endo}), 3.85 (m, 3H, H20), 3.95 (m, 2H, CHcod), 4.45 (q, J_{HH} = 6.8 Hz, 1H, H12), 4.64 (m, 2H, CHcod), 7.02 (m, 2H, H_{Ar}), 7.21 (m, 6H, H_{Ar}), 7.62 (m, 2H, H_{Ar}), and 8.83 (d, J_{HH} = 1.8 Hz, 1H, H11). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5 (C13), 28.2, 28.8, 31.1, 31.7 (CH_2cod), 54.8 (C12), 60.2 (C20), 71.0 (d, J_{CRh} = 14.3 Hz, CHcod), 73.2 (d, J_{CRh} = 14.2 Hz, CHcod), 84.2 (d, J_{CRh} = 11.65 Hz, CHcod), 84.6 (d, J_{CRh} = 11.75 Hz, CHcod), 113.5 (C3, 17, 18), 118.1 (C1), 121.4 (C6), 124.5 (5), 126.1 (C7), 126.8 (C8), 128.5 (C15, 19), 128.5 (C10), 134.6 (C4), 134.7 (C14), 134.8 (C9), 157.6 (C2), 158.5 (C16), and 165.4 (C11).

*2.2.3. [Rh(η⁴-cod){(R)-N-(4-bromophenyl)ethyl-2-oxo-1-naphthaldiminato-κ²N,O}], [Rh(η⁴-cod)(SB4)] (**III**)*

(*R*)-*N*-(4-bromophenyl)ethyl-2-hydroxy-1-naphthaldimine (HSB4) (135 mg, 0.38 mmol). Yield: 160 mg (75%). $[\alpha]^{25}$ (c = 0.27, $CHCl_3$): +52° (589 nm). *Anal.* Calc. for $C_{27}H_{27}BrNORh$ (564.33): C 57.47; H 4.82; N 2.48. Found: C 57.21; H 5.07; N 2.55%. UV–Vis (5.316×10^{-4} mol dm^{-3}, $CHCl_3$, 25 °C): λ_{max} = 392 nm; ε_{max} = 5 175 dm^3 mol^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3057w (νH—Ar), 1610vs, 1601vs (νC=N), and 1584vs (νC=C). MS (ESI): m/z 602 (8) $[M+K]^+$, 586 (20) $[M+Na]^+$, 376 (5) $[HSB4+Na]^+$, and 183 (40) $[CH_3CHC_6H_4Br]^+$ (the $^{79/81}$Br isotopic pattern is clearly visible for patterns following the 602, 586, 376 and 183 peaks, with masses given for the slightly more abundant ^{79}Br-containing fragment). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (d, J_{HH} = 6.8 Hz, 3H, H13), 1.95, 2.01 (m, 4H, CH_2cod_{exo}), 2.48, 2.62 (m, 4H, CH_2cod_{endo}), 3.86 (m, 2H, CHcod), 4.47 (q, J_{HH} = 6.6 Hz, 1H, H12), 4.66 (m, 2H, CHcod), 7.04 (d, J_{HH} = 9.1 Hz, 1H, H3), 7.18 (t, J_{HH} = 7.3 Hz, 1H, H6), 7.32 (m, 3H, H7,15,19), 7.46 (d, J_{HH} = 8.4 Hz, 1H, H5), 7.54 (d, J_{HH} = 7.8 Hz, 2H, H16, 18), 7.62 (d, J_{HH} = 7.8 Hz, 1H, H8), 7.67 (d, J_{HH} = 9.2 Hz, 1H, H4), and 8.86 (s, 1H, H11). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6 (C13), 28.7, 29.1, 31.5, 31.9 (CH_2cod), 60.2 (C12), 71.7 (d, J_{CRh} = 14.3 Hz, CHcod), 73.4 (d, J_{CRh} = 14.2 Hz, CHcod), 84.6 (d, J_{CRh} = 11.6 Hz, CHcod), 85.1 (d, J_{CRh} = 11.5 Hz, CHcod), 109.1 (C1), 118.4 (C3), 121.3 (C8), 121.8 (C17), 124.9 (C6), 126.6 (C7), 127.1 (C5), 128.8 (C10), 129.2 (C15,19), 131.7 (C16,18), 134.9 (C4), 135.1 (C9), 142.5 (C14), 158.1 (C2), and 166.0 (C11).

*2.2.4. Reaction of [Rh(η⁴-cod)(SB4)] (**III**) with O_2*

The orange-yellow solution of [Rh(η⁴-cod)(SB4)] (**III**) in $CHCl_3$ was left standing for 2 weeks in air, and the color changed to red-orange. The products were dried, and a products mixture of [Rh(η⁴-cod)(SB4)] (**III**), $[Rh(\eta^4\text{-cod})(\mu\text{-O})]_2$ (**IIIa**), and (HSB4) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (d, J_{HH} = 6.7 Hz, 3H, H13 HSB4), 1.73 (d, J_{HH} = 6.9 Hz, 3H, H13 **III**), 1.75, 1.92 (m, 4H, CH_2cod_{exo} **IIIa**), 1.95, 2.03 (m, 4H, CH_2cod_{exo} **III**), 2.57 (m, 4H, CH_2cod_{endo} **III**), 2.49 (m, 4H, CH_2cod_{endo} **IIIa**), 3.83 (m, 2H, CHcod **III**), 4.24 (m, 4H, CHcod **IIIa**), 4.46 (q, J_{HH} = 6.6 Hz, 1H, H12 **III**), 4.64 (m, 2H, CHcod **III**), 4.74 (q, J = 6.8 Hz, 1H, H12 HSB4), 8.84 (d, J_{HH} = 1.8 Hz, 1H, H11 **III**), 8.91 (s, 1H, H11 HSB4), and 14.95 (br, 1H, OH HSB4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6 (C13 **III**), 24.2 (C13 HSB4), 28.7, 29.1, 31.5, 31.9 (CH_2cod **III**), 30.8 (CH_2cod **IIIa**), 60.2 (C12 **III**), 63.4 (C12 HSB4), 71.7 (d, J_{CRh} = 14.3 Hz, CHcod **III**), 73.4 (d, J_{CRh} = 14.2 Hz, CHcod **III**), 78.6 (d, J_{CRh} = 13.9 Hz, CHcod **IIIa**), 84.6 (d, J_{CRh} = 11.6 Hz, CHcod **III**), 85.1 (d, J_{CRh} = 11.5 Hz, CHcod **III**), 157.3 (C11 HSB4), 158.1 (C2 **III**), and 166.0 (C11 **III**) (aromatic protons and carbons are not given).

The above product mixture was dissolved again in $CHCl_3$, and left standing for a further 2 weeks in air. The products were dried,

and a mixture of (**IIIa**), and (HSB4) was obtained (that is, **III** completely disappeared and was no longer seen by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (d, J_{HH} = 6.7 Hz, 3H, H13 HSB4), 1.77, 1.92 (m, 4H, CH_2cod_{exo} **IIIa**), 2.50 (m, 4H, CH_2cod_{endo} **IIIa**), and 4.25 (m, 4H, CHcod **IIIa**), and 9.02 (s, 1H, H11 HSB4). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9 (C13 HSB4), 30.8 (CH_2cod **IIIa**), and 78.6 (d, J_{CRh} = 13.9 Hz, CHcod **IIIa**). MS (ESI): *m/z* 455 (35) [{Rh(cod)(μ-O)}$_2$+H]$^+$, 354 (10) [HSB4+H]$^+$, 252 (100) [{Rh(cod)(μ-O)}+H_2+Na]$^+$, and 239 (35) [Rh(cod)(CO)]$^+$ ($^{79/81}$Br isotopic pattern is clearly visible following *m/z* 354).

Isolation of [Rh(η^4-cod)(μ-O)]$_2$ (**IIIa**): the product mixture of (**IIIa**) and (HSB4) was partly dissolved in C_6H_6:diethyl ether (50:50 vol.%) to yield a yellow suspension. The insoluble part was filtered off, the red-orange filtrate was collected and dried to give only **IIIa** according to ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75, 1.94 (m, 4H, CH_2cod_{exo}), 2.48 (m, 4H, CH_2cod_{endo}), and 4.25 (m, 4H, CHcod). MS (ESI): *m/z* 455 (25) [{Rh(cod)(μ-O)}$_2$+H]$^+$.

2.3. Reduction of acetophenone

Acetophenone (0.470 g, 3.92 mmol), [Rh(cod)Cl]$_2$ (10.8 mg, 0.02 mmol, for [Rh]/[acetophenone] = 1:196) and (*R*)-*N*-(phenyl)-ethyl-2-hydroxy-1-naphthaldimine (HSB1) (29.7 mg, 0.11 mmol, for [Rh]/[HSB1] = 1:5.4) were combined into a 50 mL Schlenk tube. The mixture was degassed three times by evacuation and refilling with N_2, and the Schlenk tube was placed in an ice bath (0–5 °C). After 10 min diphenylsilane (DPS) (0.685 g, 3.72 mmol, for [Rh]/[DPS] = 1:186) was very slowly added into the mixture with a syringe, and stirring was continued until the reaction was completed. The progress of the catalytic reaction was monitored by taking ^{1}H NMR spectra of the reaction mixture after 1, 6 and 24 h in $CDCl_3$. In the course of the reaction, the singlet for CH_3 of acetophenone disappeared, and simultaneously, a doublet for the same group of (±)-1-phenyl-ethanol appeared. Comparison of integration values for these two peaks give the conversion (%) of acetophenone into (±)-1-phenyl-ethanol. Eventually the mixture was diluted in acetone (5 ml) and hydrochloric acid solution (2.5 ml 37% HCl + 5 ml H_2O) and vigorous stirring continued for 2 h more in the ice bath. The mixture was extracted with diethylether, and the organic layer dried over K_2CO_3. The ether was then removed and the crude product was purified by bulb-to-bulb distillation. The fraction from 100 to 110 °C (at 0.8–1.0 mbar) was collected as pure product and used for chiral HPLC measurement to determine a potential enantiomeric excess. The same procedure was followed using the Schiff bases (*S* or *R*)-*N*-(phenyl)ethyl-salicylaldimine [19] with [Rh(cod)Cl]$_2$.

2.4. X-ray crystallography

Single crystals suitable for X-ray diffraction were grown from slow diffusion of diethyl ether into a concentrated chloroform solution of **III** over 3–4 days at room temperature. A single-crystal was mounted on a glass fiber and all geometric and intensity data were taken from this sample using a Bruker SMART APEX CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction was carried out with SAINT PLUS absorption correction with SADABS [23]. The structure was solved by direct methods (SHELXS), refinement was done by full-matrix least squares on F^2 using the SHELXL program suite [24]; all non-hydrogen positions refined with anisotropic displacement parameters. Hydrogen atoms for aromatic CH, aliphatic or olefinic CH, CH_2 and methyl groups were positioned geometrically (C—H=0.95 Å for aromatic CH, C—H = 1.00 Å for aliphatic and olefinic CH, C—H = 0.99 Å for CH_2, C—H = 0.98 Å for CH_3) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 13 for aliphatic CH, AFIX 23 for CH_2, AFIX 33 or 137 for CH_3), with U_{iso}(H) = 1.2U_{eq}(CH, CH_2) and U_{iso}(H) = 1.5U_{eq}(CH_3). Details of the X-ray structure determinations and refinements are provided in Table 1. Graphics were drawn with DIAMOND (Version 3.2) [25]. Computations on the supramolecular interactions were carried out with PLATON for Windows [26].

3. Results and discussion

Condensation of 2-hydroxy-1-naphthaldehyde with enantiopure (*R*)-(Ar)ethylamines yields the enantiopure Schiff bases, (*R*)-*N*-(Ar)ethyl-2-hydroxy-1-naphthaldimine (HSB; Ar = phenyl (HSB1); 3-methoxphenyl (HSB2); 4-methoxphenyl (HSB3); 4-bromophenyl (HSB4)) (Scheme 2). These Schiff bases readily react with the dinuclear [Rh(η^4-cod)(μ-O_2CMe)]$_2$ to afford the mononuclear [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] (Ar = phenyl (**I**); 3-methoxphenyl (**II**); 4-bromophenyl (**III**)) complexes, respectively in C_6H_6/MeOH (5:1, v/v) (Scheme 2).

3.1. Spectroscopy and analyzes

IR spectra show a very strong band at 1600–1628 cm^{-1} for νC=N and characteristic for the imine group in a Schiff base as well as in its complexes [1–3,6,7,19–22]. EI mass spectra show the parent ion peaks ([M]$^+$) at *m/z* 275 (HSB1), 305 (HSB2 or HSB3), 353 (HSB4), 485 (**I**), and 515 (**II**), respectively (Section 2). ESI mass shows the parent ion peaks as ([M+Na/K]$^+$) at *m/z* 586/602 for **III**. The spectra are further dominated by several ion peaks for [M−CH_3]$^+$, [M−CH(CH_3)(C_6H_4-H/OMe/Br)]$^+$, [CH(CH_3)(C_6H_4-H/OMe/Br)]$^+$, [CH(CH_3)(C_6H_5)]$^+$ in Schiff bases, and for [M−cod]$^+$, [Rh(η^4-cod)]$^+$ in the complexes (Section 2). The polarimetric measurements show the rotations to the left at −176° (HSB1), −132° (HSB2), −222° (HSB3), and −176° (HSB4) for the enantiopure *R*-Schiff bases, and to the right at +88° (**I**), +65° (**II**), and +52° (**III**) for the Rh(η^4-cod)-(*R*)-Schiff base complexes in $CHCl_3$ [6,7,19–22].

^{1}H-/^{13}C NMR spectral data of the Schiff bases (HSB1–HSB4) and complexes **I**–**III** are summarized in the Section 2, and their assignments are made based on the related literature [1–6,19–22,33–45]. The methyl protons appear as a doublet at δ = 1.70–1.75 ppm (J = 6.8 Hz) both in the Schiff bases and complexes. The methine proton appears as a quartet at δ = 4.73–4.80 ppm (J = 6.8 Hz) in Schiff bases which shifts upfield by δ = 0.30 ppm in the complexes (δ = 4.43–4.47 ppm). The imine proton appears as a singlet at δ = 8.85–8.93 ppm in Schiff bases, and as a doublet (J = 2.0 Hz) in the complexes due to ^{103}Rh–^{1}H coupling [1,4–8,19–22]. The phenolic proton appears as a broad signal at δ = 14.72–14.85 ppm in Schiff bases due to strong intermolecular hydrogen bonding [6,19,20], which is obviously absent in the complexes. Further, the methoxy protons appear as singlet at δ = 3.81–3.82 ppm in HSB2, HSB3, and **II**. The exo- and endo-methylene protons of the co-ordinated cod to the Rh(I) appear as multiplets at δ = 1.95–2.00 and 2.49–2.55 ppm in complexes **I**–**III**, respectively (Fig. S1 and Table S1). The olefin protons show two multiplets, the downfield one (δ = 4.58–4.66 ppm) is assigned to 'H *trans* to N', and the upfield one (δ = 3.85–3.95 ppm) to 'H *trans* to O' [1,3,6–8,19–22,40] (Fig. S1 and Table S1). The difference in chemical shifts (0.7 ppm) between these two multiplets reflects a different *trans* effect of *N*,*O*-chelation on the olefinic protons resonances.

In ^{13}C NMR spectra of **I**–**III**, the four methylene carbon atoms of co-ordinated cod give four singlets of equal intensity at δ = 28.3–31.9 ppm (Fig. S2 and Table S2) in contrast to only one singlet in the dinuclear [Rh(η^4-cod)(Cl)]$_2$ [15], mononuclear [Rh(η^4-cod)(amino-carboxylato)], and [Rh(η^4-cod)(amino-alcohol)](acetate) [15,16]. The four olefin carbon atoms give four doublets, two of them downfield (δ = 84.0–85.1 ppm), assigned to 'C *trans* to N', and two upfield (δ = 71.0–73.3 ppm), assigned to 'C *trans* to O'

[1,3,6,19,20,40,43] (Fig. S2 and Table S2). However, the doublets are due to coupling of olefinic carbon atoms with the Rh(I), giving different ^{103}Rh–^{13}C(olefin) spin–spin coupling constants values (Table S2), and thus reflecting fully asymmetric nature of each olefin carbon atom. The observed *J*-values for 'C *trans* to N' (11.6–11.8 Hz) and 'C *trans* to O' (14.2–14.3 Hz) agree well with those found for the related Rh(η^4-cod)–imine complexes [1,3,6–8,19–22,40]. However, the observation of four singlets and four doublets for methylene and olefin carbons, respectively, has been explained by steric and magnetic anisotropy effects in addition to the *trans* influences of the *N*,*O*-chelate ligand on carbon resonances [19,20,40]. The observed chemical shift differences between the 'left' and 'right' carbon atoms *trans* to the same donor atom are larger for '*trans* to O' ($\Delta\delta$ = 2.0 ppm) than for '*trans* to N' ($\Delta\delta$ = 0.5 ppm) ('left' and 'right' is an arbitrary assignment for the olefinic carbons to either side of a plane bisecting the C=C bond).

Electronic spectra (Fig. S3) of **I**–**III** mainly feature: (a) a very strong band below 350 nm (<300 nm for **IIIa**), associated with the intra-ligand $\pi \rightarrow \pi^*$ transition of the azomethine group and η^4-cod, (b) a strong broad band at 350–450 nm with absorption maxima at λ_{max} = 392–394 nm (ε_{max} = 4800–5200 dm^3 mol^{-1} cm^{-1}), attributed to a charge transfer (ct) transition based on the formation of [Rh(η^4-cod)]$^+$ and [Rh(SB)] [6,15,19,21,46]. However, the ct transition shows two separate bands at 300–380 nm (λ_{max}/326 nm) and 380–470 nm for [Rh(η^4-cod)]$^+$ and [Rh(μ-O)], respectively in **IIIa** (Fig. S3). The spectrum of **IIIa** is very similar to the analogous dinuclear bridged [Rh(η^4-cod)(μ-Cl)]$_2$ and [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ [6,15] (Fig. S3). The ct bands are found at 320–370 nm (λ_{max}/350 nm) and 370–430 nm for [Rh(η^4-cod)]$^+$ and [Rh(μ-Cl)], respectively in [Rh(η^4-cod)(μ-Cl)]$_2$. Similarly, the same bands are found at 330–370 nm (λ_{max}/355 nm) and 380–480 nm (λ_{max}/421 nm) for [Rh(η^4-cod)]$^+$ and [Rh(μ-O_2CCH_3)], respectively in [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$.

3.2. Reaction of [Rh(η^4-cod)(SB4)] (**III**) with O_2 to [Rh(η^4-cod)(μ-O)]$_2$ (**IIIa**)

The solution of [Rh(η^4-cod)(SB4)] (**III**) in $CHCl_3$ was left standing in air for 2 and 4 weeks, and color changed from orange-yellow to red-orange. The UV–Vis/^{1}H/^{13}C NMR- and mass-spectral results suggest that the complex reacts with molecular oxygen (from air) and leads to the formation of dinuclear oxidative aduct of [Rh(η^4-cod)(μ-O)]$_2$ (**IIIa**), resulting from oxidation of Rh(I) to Rh(II) [47–52]. A products mixture of (**III**), (**IIIa**), and (HSB4) was obtained after 2 weeks, whereas, a mixture of (**IIIa**), and (HSB4) was obtained after 4 weeks. The proton integration values show that about 50% of reaction occurs after 2 weeks (i.e., solution contains **III**, **IIIa** and HSB4), and 100% occurs after 4 weeks (i.e., solution contains **IIIa**, and HSB4). In ^{1}H NMR spectrum of products mixture of **IIIa** and HSB4, the exo- and endo-methylene protons show multiplets at δ = 1.77, 1.92 and 2.50 ppm (Fig. S1 and Table S1), respectively. The olefin protons show one multiplet at δ = 4.25 ppm instead of two multiplets separated by 0.80 ppm in **III** or in **II**, as mentioned in the above section. The methylene and olefin carbon atoms of co-ordinated cod to Rh(I) give a singlet at δ = 30.8 ppm, and a doublet at δ = 78.6 ppm (J_{CRh} = 13.9 Hz), respectively (Fig. S2 and Table S2). In contrary, the methylene and olefin carbon atoms give four singlets and four doublets, respectively in **III** or in **II** (Fig. S2 and Table S2). The spectrum, further, shows different peaks for proton and carbon atoms associated to the HSB4 (Fig. S1 and Tables S1, S2). In fact, the proton and carbon peaks assignment for **IIIa** corresponds well to the analoguos dinuclear bridged [Rh(η^4-cod)(μ-Cl)]$_2$ and [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ [15] (Tables S1, S2). ESI mass spectrum of products mixture of **IIIa** and HSB4 shows the parent ion peaks ([**IIIa** or HSB4+H]$^+$) at *m*/*z* 455 (**IIIa**) and 354 (HSB4), respectively. The red-orange (**IIIa**) was isolated in C_6H_6:diethyl ether (50%). The exo- and endo-methylene protons show multiplets at δ = 1.75, 1.94 and 2.48 ppm (Table S1), respectively. The olefinic protons exhibit a multiplet at δ = 4.25 ppm. ESI mass shows the parent ion peaks ([**IIIa**+H]$^+$) at *m*/*z* 455. However, ^{1}H/^{13}C NMR spectra of products mixture after 2 weeks show the proton and carbon peaks correspond well to the (**III**), (**IIIa**), and (HSB4) in solution, respectively (Figs. S1, S2 and Tables S1, S2). The spectrum shows a broad peak at δ = 14.95 ppm for phenolic proton (OH) for HSB4.

3.3. Catalytic reduction of acetophenone into (±)-1-phenyl-ethanol

The *in situ* formed compounds from [Rh(η^4-cod)(μ-Cl)]$_2$ and (*R*)-*N*-(phenyl)ethyl-1-naphthaldimine (*R*-HSB1) or (*S* or *R*)-*N*-(1-phenyl)ethylsalicylaldimine}] (*S*- or *R*-HSB) have been used for the reduction of acetophenone with diphenylsilane into (±)-1-phenyl-ethanol [7–10]. The conversion of acetophenone into (±)-1-phenyl-ethanol is found to be 95% (*R*-HSB1), 93% (*S*-HSB), and 97% (*R*-HSB), respectively (Table 2) at 0–5 °C. The progress of catalytic reaction using *R*-HSB1 has been monitored by taking ^{1}H NMR spectra of the reaction mixture after 1, 6, 24 h, and conversion is 85%, 91%, and 95%, respectively (Table 2). To our knowledge, this is the first catalytic system composed of [Rh(η^4-cod)(μ-Cl)]$_2$ and chiral *N*,*O*-chelate ligands (*S*- or *R*-HSB, *R*-HSB1) showing the highest conversions in comparison to related systems in literature [7–10]. In fact, in the absence of the chiral *N*,*O*-chelate ligand, the conversion is 58% (Table 2). However, the ee (%) measurement shows the formation of the racemic (±)-1-phenyl-ethanol in equal amounts.

3.4. Crystal structure

The molecular structure of complex **III** ascertains the six-membered Rh-*N*,*O*-chelate ring formation of the 2-oxo-1-naphthaldiminato ligand and rhodium-bound η^4-cod fragment (Fig. 1). The intermolecular packing in **III** shows no significant π···π or C—H···π contacts (see Table S3) despite the presence of an extended aromatic system in the naphthyl ring [53–58]. Only one C—H···Br contact [27–29] can be noted (see Table S3 in Supporting information). The crystal packing in **III** is a herring-bone pattern (Fig. 2), akin to the packing in [Rh(η^4-cod)((*R*)-*N*-(4-methoxphenyl)ethyl-2-oxo-1-naphthaldiminato)] [6,20].

4. Conclusions

Enantiopure [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] complexes with Ar = C_6H_5 (**I**); 3-$MeOC_6H_4$ (**II**); 4-BrC_6H_4 (**III**) are easily obtained from the reaction of dinuclear [Rh(η^4-cod)(μ-O_2CMe)]$_2$ and the enantiopure Schiff base naphthaldimine ligand. The deprotonated Schiff bases co-ordinate as expected to the [Rh(η^4-cod)]-fragment as a six-membered *N*,*O*-chelate ligand. The Schiff base ligand is more labile than the cod-ligand. Reaction of **III** with O_2 replaces the Schiff base with the formation of the oxidation product [Rh(η^4-cod)(μ-O)]$_2$ (**IIIa**). Enantiopure compounds **I** and [Rh(η^4-cod){(*S* or *R*)-*N*-(phenyl)-ethyl-salicylaldiminato}] were used for the attempted enantioselective reduction of acetophenone with diphenylsilane into (±)-1-phenyl-ethanol. Yet, with no enantiomeric excess found it can be concluded that the labile chiral Schiff base ligand was replaced upon catalyst activation. Thus, introduction of chirality in a rhodium(I) complex through a labile Schiff base ligand in the presence of an inert cod-ligand does not allow to retain the chirality for subsequent stoichiometric or catalytic reactions.

Acknowledgements

We acknowledge the financial support from MSICT Project 2005 under the Ministry of Science and Information & Communication Technology, Dhaka, Bangladesh. Our sincere thank to Professor A.B.P. Lever, Department of Chemistry, York University, Toronto, Canada for taking mass spectra. We thank the Alexander-von-Humboldt Foundation (AvH), Bonn, for a fellowship to M. Enamullah and Dr. Klaus Ditrich (ChiPros) at BASF, Ludwigshafen for providing the enantiopure (*R*)-(Ar)ethylamines.

Appendix A. Supplementary material

Supplementary material CCDC 851336 contains the supplementary crystallographic data for the complex for **III**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2012.01.013.

References

[1] N. Platzer, N. Goasdoue, R. Bonnaire, J. Organomet. Chem. 160 (1978) 455.
[2] R. Bonnaire, C. Potvin, J.M. Manoli, Inorg. Chim. Acta 45 (1980) L255.
[3] R. Bonnaire, J.M. Manoli, C. Potvin, N. Platzer, N. Goasdoue, D. Davoust, Inorg. Chem. 21 (1982) 2032.
[4] R.J. Cozens, K.S. Murray, B.O. West, J. Organomet. Chem. 27 (1971) 399.
[5] C.A. Rogers, B.O. West, J. Organomet. Chem. 70 (1974) 445.
[6] C. Janiak, A.-C. Chamayou, A.K.M. Royhan Uddin, M. Uddin, Karl S. Hagen, M. Enamullah, Dalton Trans. (2009) 3698.
[7] A.K.M. Royhan Uddin, M. Enamullah, J. Bangladesh Chem. Soc. 23 (2009) 145.
[8] H. Brunner, H. Fisch, J. Organomet. Chem. 335 (1987) 1.
[9] H. Brunner, G. Riepl, Angew. Chem. 94 (1982) 369.
[10] H. Brunner, B. Reiter, G. Riepl, Chem. Ber. 117 (1984) 1330.
[11] M.E. Wright, S.A. Svejda, A.M. Arif, Inorg. Chim. Acta 175 (1990) 13.
[12] M.D. Jones, M.F. Mahon, J. Organomet. Chem. 693 (2008) 2377.
[13] G. Zassinovich, F. Grisoni, J. Organomet. Chem. 247 (1983) C24.
[14] V.A. Pavlov, M.G. Vinogradov, E.V. Starodubtseva, G.V. Cheltsova, V.A. Ferapontov, O.R. Malyshev, G.L. Heise, Russ. Chem. Bull. Intl. Ed. 50 (2001) 734.
[15] M. Enamullah, M. Hasegawa, J. Okubo, T. Hoshi, J. Bangladesh Chem. Soc. 18 (2005) 154.
[16] M. Enamullah, A. Sharmin, M. Hasegawa, T. Hoshi, A.-C. Chamayou, C. Janiak, Eur. J. Inorg. Chem. (2006) 2146.
[17] M. Enamullah, A.K.M. Royhan Uddin, M. Uddin, J. Bangladesh Chem. Soc. 21 (2008) 28.
[18] M. Enamullah, M. Uddin, W. Linert, J. Coord. Chem. 60 (2007) 2309.
[19] M. Enamullah, A.-C. Chamayou, C. Janiak, Z. Naturforsch. b62 (2007) 807.
[20] A.K.M. Royhan Uddin, Dissertation, Department of Chemistry, Jahangirnagar University, Dhaka-1342, Bangladesh, 2009.
[21] M. Enamullah, J. Coord. Chem. 64 (2011) 1608.
[22] H. Brunner, R. Oeschey, B. Nuber, J. Chem. Soc., Dalton Trans. (1996) 1499.
[23] G. Sheldrick, Program SADABS: area-detector absorption correction, University of Göttingen, Germany, 1996.
[24] G.M. Sheldrick, Acta Cryst. A64 (2008) 112.
[25] DIAMOND 3.2 for Windows. Crystal Impact Gbr, Bonn, Germany; <http://www.crystalimpact.com/diamond>.
[26] A.L. Spek, Acta Crystallogr., A 46 (1990) C34. PLATON – A multipurpose crystallographic tool, Utrecht University, Utrecht, The Netherlands, A.L. Spek 2005.
[27] H.D. Flack, G. Bernardinelli, Chirality 20 (2008) 681.
[28] H.D. Flack, G. Bernardinelli, Acta Crystallogr., Sect. A 55 (1999) 908.
[29] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.
[30] C. Zhang, G. Rheinwald, V. Lozan, B. Wu, P.G. Lassahn, H. Lang, C. Janiak, Z. Anorg, Allg. Chem. 628 (2002) 1259.
[31] S.P. Rath, T. Ghosh, S. Mondal, Polyhedron 16 (1997) 4179.
[32] H. Brunner, T. Zwack, M. Zabel, W. Beck, A. Boehm, Organometallics 22 (2003) 1741.
[33] S.K. Mandal, A.R. Chakravarty, J. Organomet. Chem. 417 (1991) C59.
[34] S.K. Mandal, A.R. Chakravarty, J. Chem. Soc., Dalton Trans. (1992) 1627.
[35] J.G. Leipoldt, E.C. Grobler, Inorg. Chim. Acta 72 (1983) 17.
[36] A.P. Martinez, M.P. Garcia, F.J. Lahoz, L.A. Oro, Inorg. Chem. Commun. 5 (2002) 245.
[37] G.S. Rodman, K.R. Mann, Inorg. Chem. 27 (1988) 3338.
[38] C. Tejel, M.A. Ciriano, M. Bordonaba, J.A. Lopez, F.J. Lahoz, L.A. Oro, Inorg. Chem. 41 (2002) 2348.
[39] J.C. Bayon, G. Net, P.G. Rasmussen, J.B. Kolowich, J. Chem. Soc., Dalton Trans. (1987) 3003.
[40] R. Bonnaire, J.M. Manoli, N. Potvin, N. Platzer, N. Goasdoue, Inorg. Chem. 20 (1981) 2691.
[41] S.L. James, D.M.P. Mingos, X. Xu, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (1998) 1335.
[42] R. Aumann, I.G. Schnetmann, R. Froehlich, P. Saarenketo, C. Holst, Chem. Eur. J. 7 (2001) 711.
[43] G.N. Massubayashi, S. Akazawa, Polyhedron 4 (1985) 419.
[44] R.L. Harlow, D.L. Thorn, R.T. Baker, N.L. Jones, Inorg. Chem. 31 (1992) 993.
[45] F.A. Cotton, T.R. Felthouse, Inorg. Chem. 19 (1980) 2347.
[46] F.A. Cotton, T.R. Felthouse, Inorg. Chem. 21 (1982).
[47] T. Yoshimura, K. Umakoshi, Y. Sasaki, Inorg. Chem. 42 (2003) 7106.
[48] E.V. Dikarev, K.W. Andreini, M.A. Petrukhina, Inorg. Chem. 43 (2004) 3219.
[49] Y.B. Koh, G.G. Christoph, Inorg. Chem. 17 (1978) 2590.
[50] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.
[51] X.J. Yang, F. Drepper, B. Wu, W.H. Sun, W. Haehnel, C. Janiak, Dalton Trans. (2005) 256, and supplementary material therein.
[52] M. Nishio, CrystEngComm 6 (2004) 130.
[53] M. Nishio, M. Hirota, Y. Umezawa, The CH/π interaction (Evidence, Nature and consequences), Wiley-VCH, New York, 1998.
[54] Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa, M. Nishio, Bull. Chem. Soc. Jpn. 71 (1998) 1207.
[55] C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M.J. Kolm, T.G. Scharmann, O.M. Zipffel, Eur. J. Inorg. Chem. (2000) 1229.
[56] H.A. Habib, A. Hoffmann, H.A. Höppe, G. Steinfeld, C. Janiak, Inorg. Chem. 48 (2009) 2166.
[57] W. Zhang, X. Tang, H. Ma, W.H. Sun, C. Janiak, Eur. J. Inorg. Chem. (2008) 2830–2836.
[58] F. Neve, A. Crispini, Cryst. Growth Des. 1 (2001) 287.