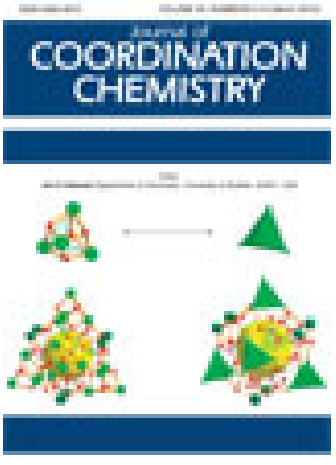

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Syntheses, spectroscopy, and catalysis of (η^4-cod)Rh(I)-complexes with (R or S)-2-(salicylaldimine)-2-phenylethanol or (rac)-2-(salicylaldimine)-1-phenylethanol

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Syntheses, spectroscopy, and catalysis of (η^4-cod)Rh(I)-complexes with (*R* or *S*)-2-(salicylaldimine)-2-phenylethanol or (*rac*)-2-(salicylaldimine)-1-phenylethanol

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Condensation of salicyldehyde with (*R* or *S*)-2-amino-2-phenylethanol or *rac*-2-amino-1-phenylethanol gives enantiopure (*R* or *S*)-2-(salicylaldimine)-2-phenylethanol (*R*- or *S*-H_2L1) or (*rac*)-2-(salicylaldimine)-1-phenylethanol (*rac*-H_2L2). The Schiff bases coordinate to [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ to afford mononuclear [Rh(η^4-cod){(*R* or *S*)-2-(salicylaldiminato)-2-phenylethanol-κ^2*N*,*O*}], [Rh(η^4-cod)(*R*- or *S*-HL1)] (**1** or **2**), or [Rh(η^4-cod){(*rac*)-2-(salicylaldiminato)-1-phenylethanol-κ^2*N*,*O*}], [Rh(η^4-cod)(*rac*-HL2)] (**3**). The Schiff base and complexes are characterized by IR-, UV/Vis-, ^{1}H/^{13}C-NMR-, mass-spectroscopy, circular dichroism (CD), and polarimetry. The synthetic and spectroscopic results suggest that deprotonated Schiff base coordinates to [Rh(η^4-cod)] as a six-membered *N*,*O*-chelate with distorted square planar geometry at rhodium. CD and polarimetry measurements show the enantiopurity of the Schiff bases as well as the complexes in solution. The *in situ* system composed of [Rh(η^4-cod)Cl]$_2$ and *S*-H_2L1 has been used as a catalyst for the reduction of acetophenone into *rac*-1-phenylethanol with 85% conversion in diphenylsilane at 0–5°C.

Keywords: Chiral *N*,*O*-chelate Schiff bases; Rh(η^4-cod)(chiral *N*,*O*-chelate) complexes; Enantiopurity; Catalysis

1. Introduction

Syntheses, stereochemistry, and crystal structures of transition metal complexes with chiral *N*,*O*-chelate ligands are of continued interest [1]. Chiral *N*,*O*-chelate Schiff bases react with dinuclear [Rh(O_2CCH_3)(η^4-cod)]$_2$ (cod = 1,5-cyclooctadiene) to give mononuclear [Rh(η^4-cod)(SB)] (SB = deprotonated Schiff base) and dinuclear [{Rh(η^4-cod)}$_2$(SB)] complexes, respectively [2]. Using chiral *N*,*N*-chelate Schiff bases give the analogous Rh(η^4-cod)(imine)-complexes [3]. The *in situ* systems composed of [Rh(η^4-cod)Cl]$_2$ and enantiopure Schiff bases have been used for asymmetric hydrogenation in diphenylsilane/1-naphthylphenylsilane with 3–57% ee [3] or in iso-propanol with 23–65% ee [4].

We have given attention to analogous [Rh(η^4-cod)(*N*,*O*-chelate)] (*N*,*O*-chelate = chiral amino-acids/-alcohols) complexes starting from [Rh(η^4-cod)(μ-O_2CMe)]$_2$ [5, 6]. The spectroscopic and X-ray results suggest five-membered *N*,*O*-chelation of the

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amino-carboxylate or amino-alcohol to [Rh(η^4-cod)] in a distorted tetrahedral geometry around the metal center. Some of these complexes readily react with the di-/triphosphine ligands (i.e., dppe or dppp or triphos) to give mononuclear [Rh(dppp/triphos)(*N*,*O*-chelate)] or [Rh(dppe)$_2$](*N*,*O*-chelate) complexes [7]. Similar reactions of [Rh(η^4-cod)(μ-O_2CMe)]$_2$ with chiral *N*,*O*-chelate Schiff bases give the analogous [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-salicylaldiminato-κ^2*N*,*O*}] (Ar = C_6H_5, *o*/*m*/*p*-$OCH_3C_6H_4$, *p*-BrC_6H_4, and 2-naphthyl} [8], [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] [9–11], and with achiral *N*,*O*,*N*,*O*-chelate Schiff bases giving [{Rh(η^4-cod)}$_2${*N*,*N*′-R-*bis*(salicylaldiminato-κ^2*N*,*O*)}] (R = ethylene or 1,2-phenylene) [9]. X-ray and spectroscopic results suggest six-membered *N*,*O*-chelation of the chiral Schiff bases to [Rh(η^4-cod)] in a distorted square planar geometry. We recently reported the syntheses, stereochemistry, spectroscopy, and optical properties of enantiopure *N*,*O*-chelate Schiff bases, (*R*)-2-(X-benzaldimine)-2-phenylethanol (X = H or 2,4-dimethoxy), and their complexes, [Rh(η^4-cod){(R)-2-(X-benzaldimine)-2-phenylethanol}] (acetate) [12].

This article reports the results of syntheses, stereochemistry, and spectroscopy of enantiopure Schiff bases of (*R* or *S*)-2-(salicylaldimine)-2-phenylethanol (*R*- or *S*-H_2L1) and (*rac*)-2-(salicylaldimine)-1-phenylethanol (*rac*-H_2L2) and their complexes of [Rh(η^4-cod)(*R*-or *S*-HL1)] and [Rh(η^4-cod)(*rac*-HL2)], respectively. The *in situ* system composed of [Rh(η^4-cod)Cl]$_2$ and *S*-H_2L1 has been used as a catalyst for the reduction of acetophenone into (*rac*)-1-phenylethanol in diphenylsilane at 0–5°C.

2. Experimental

2.1. *Materials and methods*

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents 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 a Shimadzu UV 3150 spectrophotometer in $CHCl_3$ at 20°C. Circular dichroism (CD) spectra were obtained with an OLIS RSM spectropolarimeter, Rapid Scanning Monochromator (On-line Instrument System, Inc.) in $CHCl_3$ at 20°C. Infrared (IR) spectra were recorded on a Bruker Optik IFS 25 spectrometer as KBr discs at an ambient temperature. Elemental analyses were done on a VarioEL from Elementaranalysensysteme GmbH. NMR spectra were run on a Bruker Avance DPX 200 spectrometer operating at 300 MHz (^{1}H) or 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; DMSO-d_6: ^{1}H-NMR 2.50 ppm, ^{13}C-NMR 77.0 ppm). EI-MS spectra were taken on a Thermo-Finnigan TSQ 700. FAB-mass (positive) spectra were recorded on a Finnigan MAT 8400 with integrated Spectro-System (SS) 300, *m*-nitrobenzylalcohol (*m*-NBA) matrix, and 150°C ionization temperature. ESI-mass (positive) spectra were carried out on a QStar Elite quadrupole time-of-flight (Q-TOF) instrument (MDS Analytical Technologies, Concord, ON, Canada) equipped with a "turbo ion spray" ion source. Polarimetric measurements were carried with a Perkin-Elmer 241 instrument in $CHCl_3$ at 25°C and the values of $[\alpha]^{25}$ were determined according to the literature [8–10]. The starting compound,

$[Rh(\eta^4\text{-cod})(O_2CMe)]_2$, was synthesized from $[Rh(\eta^4\text{-cod})Cl]_2$ [5, 6]. Salicyldehyde, (*R*)-2-amino-2-phenylethanol, (*S*)-2-amino-2-phenylethanol, and (*rac*)-2-amino-1-phenylethanol were used as received from Merck.

2.2. *General procedure to synthesize R- or S-H_2L1 and rac-H_2L2*

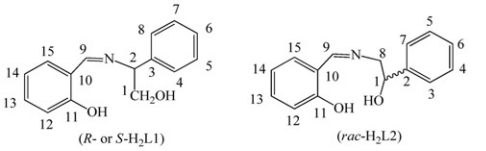
Salicyldehyde (1.73 g, 14.18 mmol) was dissolved into 10 mL of methanol, 2–3 drops of H_2SO_4 was added and the solution was stirred for 10 min. An equimolar amount of (*R*)-2-amino-2-phenylethanol (1.94 g, 14.16 mmol) was added into this solution and the reaction mixture was refluxed for 6–8 h, turning bright yellow. The solvent was evaporated to 50% *in vacuo* and left standing for crystallization at room temperature. The crystals were filtered off, washed thrice with methanol (5 mL in each), and dried in air for 2 days giving bright yellow crystals of (*R*)-2-(salicylaldimine)-2-phenylethanol (*R*-H_2L1). (*S*)-2-(salicylaldimine)-2-phenylethanol (*S*-H_2L1) and (*rac*)-2-(salicylaldimine)-1-phenylethanol (*rac*-H_2L2) were prepared following the same procedure using (*S*)-2-amino-2-phenylethanol and (*rac*)-2-amino-1-phenylethanol, respectively.

2.2.1. (*R*)-2-(salicylaldimine)-2-phenylethanol (*R*-H_2L1). Yield: 2.75 g (80%). $[\alpha]^{25}$ ($c = 0.40$, $CHCl_3$): +118° (598 nm). IR (KBr, cm^{-1}): 3230sb (νO–$H_{alc.}$), 3072w, 3055w, 2951s (νC–H), 1628vs (νC=N), and 1583s (νC=C). UV-Vis (6.630×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max} (nm) (ε_{max} ($mol^{-1}\,dm^3\,cm^{-1}$)) = 268.0 (20,533) and 320.0 (16,287). EI-MS (70 eV): *m*/*z* 241 (40) $[M]^+$, 210 (100) $[M–CH_2OH]^+$, 132 (15) $[C_6H_5C(NH)CHO–H]^+$, 121 (20) $[C_6H_5CH_2CH_2OH–H]^+$, and 103 (20) $[C_6H_5CHO–H_2–H]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 4.04$ (d, $J_{HH} = 6.8$ Hz, 2H, H_1), 4.93 (t, $J_{HH} = 6.7$ Hz, 1H, H_2), 6.87 (t, $J_{HH} = 7.5$ Hz, 1H, H_{12}), 7.08 (d, $J_{HH} = 8.2$ Hz, 1H, H_{14}), 7.32–7.46 (m, 7H, $H_{4–8,13,15}$), and 8.60 (s, 1H, H_9).

2.2.2. (*S*)-2 -(salicylaldimine)-2-phenylethanol (*S*-H_2L1). Yield: 2.85 g (83%). $[\alpha]^{25}$ ($c = 0.46$, $CHCl_3$): –109° (598 nm). Calcd for $C_{15}H_{15}NO_2$ (241.29) (%): C 74.67; H 6.27; N 5.80. Found (%): C 74.09; H 6.33; N 5.73. IR (KBr, cm^{-1}): 3226sb (νO–$H_{alc.}$), 3070w, 3050w, 2953s (νC–H), 1626vs (νC=N), and 1581s (νC=C). UV-Vis (4.893×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max} (nm) (ε_{max} ($mol^{-1}\,dm^3\,cm^{-1}$)) = 266.0 (27,573) and 320.0 (19,694). EI-MS (70 eV): *m*/*z* 241 (70) $[M]^+$, 210 (100) $[M–CH_2OH]^+$, 132 (8) $[C_6H_5C(NH)CHO–H]^+$, 121 (10) $[C_6H_5CH_2CH_2OH–H]^+$, and 103 (10) $[C_6H_5CHO–H_2–H]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 4.00$ (d, $J_{HH} = 6.7$ Hz, 2H, H_1), 4.72 (t, $J_{HH} = 6.7$ Hz, 1H, H_2), 6.89 (t, $J_{HH} = 7.4$, 1H, H_{12}), 7.04 (d, $J_{HH} = 8.2$ Hz, 1H, H_{14}), 7.32–7.42 (m, 7H, $H_{4–8,13,15}$), and 8.54 (s, 1H, H_9).

2.2.3. (*rac*)-2 -(salicylaldimine)-1-phenylethanol (*rac*-H_2L2). Yield: 2.78 g (81%). Calcd for $C_{15}H_{15}NO_2$ (241.29) (%): C 74.67; H 6.27; N 5.80. Found (%): C 73.25; H 6.33; N 5.96. IR (KBr, cm^{-1}): 3341sb, 3230sh (νO–$H_{alc.}$), 3060w, 3024w (νC–H), 1647vs, 1636vs, 1610s (νC=N), and 1580s (νC=C). UV-Vis (6.030×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max} (nm) (ε_{max} ($mol^{-1}\,dm^3\,cm^{-1}$)) = 268.0 (22,413) and 320.0 (18,977). EI-MS (70 eV): *m*/*z* 241 (70) $[M]^+$, 135 (70) $[C_6H_5C(NH)CH_2OH]^+$, 134 (100) $[C_6H_5C(NH)CH_2OH–H]^+$, 121 (8) $[(OH)C_6H_4(CHNH)]^+$, and 107 (75) $[C_6H_5CHO + H]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 3.75$ (ddd, $J_{HH} = 8.0$, 7.2 Hz, $J_{HH} = 1.0$ Hz, 1H, H_8),

3.96 (ddd, $J_{HH} = 8.0$, 7.4 Hz, $J_{HH} = 1.0$ Hz, 1H, H_8), 5.06 (dd, $J_{HH} = 8.0$ Hz, $J_{HH} = 4.0$ Hz, 1H, H_1), 6.87 (t, $J_{HH} = 7.5$ Hz, 1H, H_{12}), 6.99 (d, $J_{HH} = 8.0$ Hz, 1H, H_{14}), 7.24–7.45 (m, 7H, $H_{4\text{-}8,13,15}$), and 8.36 (s, 1H, H_9).



(atom numbering for NMR assignments)

2.3. *General procedure to synthesize 1–3*

Two equivalents of (*R*)-2-(salicylaldimine)-2-phenylethanol (*R*-H_2L1) (78 mg, 0.32 mmol) and one equivalent of $[Rh(O_2CCH_3)(\eta^4\text{-cod})]_2$ (86 mg, 0.16 mmol) were dissolved in 10 mL of C_6H_6/MeOH (4 : 1, v/v) and the solution as stirred for 5–6 h at room temperature. The color changed from red-orange to orange-yellow and then the solvent was evaporated *in vacuo* at 40°C. The products were again dissolved in 5 mL of C_6H_6/MeOH (4 : 1, v/v), stirred for 30 min and the solvent was evaporated again *in vacuo*. This procedure was repeated thrice, and finally the products were dried *in vacuo* (0.1–0.2 mbar) at 40°C to give orange-yellow [Rh(η^4-cod){(*R*)-2 -(salicylaldimine)-2-phenylethanol-κ^2N,O}] (**1**). The same procedure was followed for the syntheses of **2**, and **3** by using the Schiff bases *S*-H_2L1, and *rac*-H_2L2, respectively.

2.3.1. [Rh(η^4-cod){(*R*)-2 -(salicylaldiminato)-2-phenylethanol-κ^2N,O}], [Rh(η^4-cod)(*R*-HL1)] (1). Yield: 108 mg (75% w.r.t. $[Rh(O_2CCH_3)(\eta^4\text{-cod})]_2$). UV-Vis ($1.989 \times 10^{-4}$ mol dm^{-3}, $CHCl_3$): λ_{max}(nm) (ε_{max} (mol^{-1} dm^3 cm^{-1})) = 246.0 (47,794) and 398.0 (5779). IR (KBr, cm^{-1}): 3240sh (νO–$H_{alc.}$), 3060w, 3025w, 2956w (νH–C), 1624vs, 1603vs (νC=N), 1565sh (νC=C). ESI-MS: *m*/*z* 452 (25) $[M + H]^+$ and 242 (100) $[H_2L1 + H]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.82$ (m, 4H, CH_2cod$_{exo}$), 2.38 (s, 1H, O*H*), 2.47 (m, 4H, CH_2cod$_{endo}$), 3.83 (m, 2H, C*H*cod), 3.91 (d, $J_{HH} = 8.0$ Hz, 2H, H_1), 4.46 (m, 1H, H_2), 4.58 (m, 2H, C*H*cod), 6.50 (t, $J_{HH} = 8.6$ Hz, 1H, H_{12}), 6.86 (dd, $J_{HH} = 9.8$ Hz, $J_{HH} = 1.5$ Hz, 1H, H_{14}), 6.98 (t, $J_{HH} = 10.4$ Hz, 1H, H_6), 7.28–7.37 (m, 2H, $H_{5,7}$), 7.37–7.39 (m, 4H, $H_{4,8,13,15}$), and 7.97 (s, 1H, H_9).

2.3.2. [Rh(η^4-cod){(*S*)-2 -(salicylaldiminato)-2-phenylethanol-κ^2N,O}], [Rh(η^4-cod)(*S*-HL1)] (2). Yield: 105 mg (73%). $[\alpha]^{25}$ ($c = 1.00$, $CHCl_3$): –105° (578 nm). Calcd for $[C_{23}H_{26}NO_2Rh]$ (451.37) (%): C 61.20; H 5.81; N 3.01. Found (%): C 60.85; H 6.04; N 2.43. UV-Vis (3.716×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max} (nm) (ε_{max} (mol^{-1} dm^3 cm^{-1})) = 246.0 (28,926) and 398.0 (3836). IR (KBr, cm^{-1}): 3228sh (νO–$H_{alc.}$), 3060w, 3025w, 2956w (νH–C), 1624vs, 1603vs (νC=N), 1565sh (νC=C). EI-MS (70 eV): *m*/*z* 451 (60) $[M]^+$, 421 (15) $[M–HCHO]^+$, 343 (100) [M–cod = Rh(HL1)]$^+$, 330 (10) $[M–C_6H_5CHCH_2OH]^+$, 241 (40) $[H_2L1]^+$, 211 (20) $[Rh(cod)]^+$, 210 (75) $[H_2L1–CH_2OH]^+$, 149 (55) $[H_2L1–C_6H_5CH_3]^+$, 121 (15) $[C_6H_5CH_2CH_2OH–H]^+$, 106 (20) $[C_6H_5CHO]^+$, and 91 (20) $[C_6H_5CH_2]^+$. APCI-MS (pos.): *m*/*z* 794 (20) $[M_2 - cod]^+$, 793 (45) $[M_2–cod–H]^+$, 662 (15) $[M_2–HL1]^+$, 601 (55) $[M + (Rh–OCH_2NH_2) + H)]^+$,

452 (100) $[M+H]^+$, and 242 (10) $[H_2L1+H]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.82$ (dd, $J_{HH} = 8.0$ Hz, 4H, CH_2cod$_{exo}$), 2.37 (s, 1H, OH), 2.48 (m, 4H, CH_2cod$_{endo}$), 3.80 (m, 2H, CHcod), 3.94 (d, $J_{HH} = 7.7$ Hz, 2H, H_1), 4.45 (m, 1H, H_2), 4.62 (m, 2H, CHcod), 6.45 (dd, $J_{HH} = 6.8$ Hz, $J_{HH} = 1$ Hz, 1H, H_{12}), 6.85 (dd, $J_{HH} = 7.0$ Hz, $J_{HH} = 1.2$ Hz, 1H, H_{14}), 6.97 (dd, $J_{HH} = 6.2$ Hz, $J_{HH} = 1.8$ Hz, 1H, H_6), 7.23–7.33 (m, 2H, $H_{5,7}$), 7.34–7.38 (m, 4H, $H_{4,8,13,15}$), and 7.98 (s, 1H, H_9).

2.3.3. [Rh(η^4-cod){(*rac*)-2 -(salicylaldiminato)-1-phenylethanol-κ^2N,O}], [Rh(η^4-cod)(*rac*-HL2)] (3). Yield: 110 mg (76%). Calcd for $[C_{23}H_{26}NO_2Rh]$ (451.37) (%): C 61.20; H 5.81; N 3.01. Found (%): C 60.65; H 6.00; N 2.63. IR (KBr, cm^{-1}): 3224sh (νO–H$_{alc.}$), 3055sh, 3026w (νH–Ar), 1629vs (νC=N), and 1583sh (νC=C). UV-Vis (8.575×10^{-5} mol dm^{-3}, $CHCl_3$): λ_{max} (nm) (ε_{max} (mol^{-1} dm^3 cm^{-1})) = 242.0 (61,248) and 398.0 (6808). FAB-MS (pos.): m/z 452 (50) $[M+H]^+$, 451 (40) $[M]^+$, 343 (100) [M–cod = Rh(HL2)]$^+$, 241 (10) $[H_2L2]^+$, and 211 (15) $[Rh(cod)]^+$. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.83$, 1.93 (m, 4H, CH_2cod$_{exo}$), 2.36 (s, 1H, OH), 2.49 (m, 4H, CH_2cod$_{endo}$), 3.30 (dd, $J_{HH} = 8.0$ Hz, $J_{HH} = 1.5$ Hz, 1H, H_8), 3.37 (dd, $J_{HH} = 8.5$ Hz, $J_{HH} = 1.5$ Hz, 1H, H_8), 3.70, 3.75 (m, 2H, CHcod), 4.54, 4.60 (m, 2H, CHcod), 4.94 (dd, $J_{HH} = 7.7$ Hz, $J_{HH} = 1.0$ Hz, 1H, H_1), 6.55 (dt, $J_{HH} = 6.8$ Hz, $J_{HH} = 1.0$ Hz, 1H, H_{12}), 6.83 (d, $J_{HH} = 8.6$ Hz, 1H, H_{14}), 7.14 (d, $J_{HH} = 7.9$ Hz, 1H, H_6), 7.26–7.34 (m, 3H, $H_{4-5,7}$), 7.35–7.37 (m, 3H, $H_{8,13,15}$), and 7.96 (s, 1H, H_9). ^{1}H-NMR (400 MHz, DMSO-d_6): $\delta = 1.80$, 1.92 (m, 4H, CH_2cod$_{exo}$), 2,30 2.42 (m, 4 H, CH_2cod$_{endo}$), 3.20 (dd, $J_{HH} = 8.6$ Hz, $J_{HH} = 1.0$ Hz, 1H, H_8), 3.25 (d, $J_{HH} = 8.7$ Hz, 1H, H_8), 3.72 (m, 2H, CHcod), 4.33, 4.44 (m, 2H, CHcod), 4.74 (m, 1H, H_1), 5.64 (d, $J_{HH} = 4.8$ Hz, 1H, OH), 6.53 (dt, $J_{HH} = 6.9$ Hz, $J_{HH} = 1.0$ Hz, 1H, H_{12}), 6.65 (d, $J_{HH} = 8.3$ Hz, 1H, H_{14}), 7.24–7.36 (m, 3H, H_{4-6}), 7.35–7.37 (m, 4H, $H_{7-8,13,15}$), and 8.11 (s, 1H, H_9). ^{13}C-NMR (100 MHz, $CDCl_3$) 28.5, 29.3, 31.2, 32.2 (CH_2cod), 66.6 (C8), 69.7 (d, $J_{CRh} = 16.6$ Hz, CHcod), 72.7 (d, $J_{CRh} = 15.0$ Hz, CHcod), 74.9 (C1), 84.9 (d, $J_{CRh} = 16.4$ Hz, CHcod), 85.6 (d, $J_{CRh} = 15.9$ Hz, CHcod), 114.6 (C12), 119.1 (C14), 121.4 (C10), 125.9 (C3,7), 127.5 (C5), 128.6 (C4,6), 134.8 (C15), 135.4 (C13), 141.1 (C2), 166.2 (C9), and 167.4 (C11).

2.4. *Catalytic reduction of acetophenone into (rac)-1-phenylethanol*

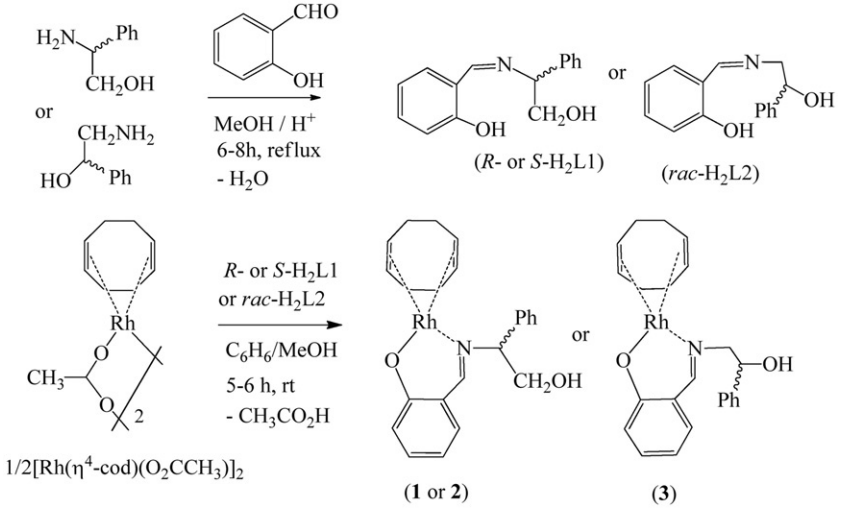
Acetophenone (482 mg, 4.02 mmol), [Rh(η^4-cod)Cl]$_2$ (10 mg, 0.02 mmol, [Rh]/[acetophenone] = 1 : 201), and (*S*)-2 -(salicylaldimine)-2-phenylethanol (*S*-H$_2$L1) (23.1 mg, 0.096 mmol, [Rh]/[*S*-H$_2$L1] = 1 : 4.8) were combined into a 50 mL Schlenk tube containing 5 mL CH_2Cl_2. The mixture was then degassed thrice times by evacuation and refilling with N_2, and the Schlenk tube was left standing in an ice bath (0–5°C). After 10–15 min, diphenylsilane (DPS) (780 mg, 4.24 mmol, [Rh]/[DPS] = 1 : 212) was very slowly added into the reaction mixture with a syringe and continued stirring 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 h, 6 h, and 28 h in $CDCl_3$. In course of reaction, the singlet for CH_3 of acetophenone disappeared, and simultaneously, a doublet for (*rac*)-1-phenylethanol appeared. Comparison of integration values for these two peaks gave the conversion (%) of acetophenone into (*rac*)-1-phenylethanol. The same procedure was followed using (*S*)-2-amino-2-phenylethanol with $[Rh(cod)Cl]_2$.

3. Results and discussion

Condensation of salicyldehyde with (*R* or *S*)-2-amino-2-phenylethanol or (*rac*)-2-amino-1-phenylethanol gives enantiopure (*R* or *S*)-2-(salicylaldimine)-2-phenylethanol (*R*- or *S*-H_2L1) or (*rac*)-2-(salicylaldimine)-1-phenylethanol (*rac*-H_2L2). The Schiff bases coordinate to $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ to give $[Rh(\eta^4\text{-cod})\{(R \text{ or } S)\text{-2-(salicylaldiminato)-2-phenylethanol-}\kappa^2N,O\}]$, $[Rh(\eta^4\text{-cod})(R\text{- or } S\text{-HL1})]$ (**1** or **2**) or $[Rh(\eta^4\text{-cod})\{(rac)\text{-2-(salicylaldiminato)-1-phenylethanol-}\kappa^2N,O\}]$, $[Rh(\eta^4\text{-cod})(rac\text{-HL2})]$ (**3**) in C_6H_6/MeOH (4 : 1, v/v), respectively (scheme 1).

3.1. *Mass spectra*

EI-mass spectra of the Schiff bases show the parent ion peaks ($[M]^+$) at *m*/*z* 241 and base peaks at *m*/*z* 210 for $[M-CH_2OH]^+$. ESI-mass spectrum of **1** shows the parent ion peak as $[M+H]^+$ at *m*/*z* 452 and the base peak at *m*/*z* 242 for $[H_2L1+H]^+$. EI-mass spectrum of **2** shows the parent ion peak ($[M]^+$) at *m*/*z* 451 and base peak at *m*/*z* 343 for $[M-cod]^+$. FAB-mass spectrum of **3** shows the parent ion peak as $[M+H]^+$ at *m*/*z* 452 and the base peak at *m*/*z* 343 for $[M-cod]^+$. In addition, the complexes show several peaks for $[Rh(\eta^4\text{-cod})]^+$, Schiff bases, and fragmented Schiff bases, respectively. APCI-mass spectrum of **2** shows ion peaks for dinuclear species at *m*/*z* 794 ($[M_2-cod)]^+$), 662 ($[M_2-HL1]^+$), and 601 ($[M+(Rh{-}OCH_2NH_2)+H]^+$) in addition to the peaks for mononuclear species at *m*/*z* 452 ($[M+H]^+$) and 242 ($[H_2L1+H]^+$), respectively. The dinuclear species are formed due to strong inter-molecular hydrogen bonding, as reported in the related $Rh(\eta^4\text{-cod})$-amino acid/amino alcohol/Schiff base complexes [5, 6, 9]. Thus the mass spectral results correspond well to the formulation of the Schiff bases as well as the complexes proposed in reaction scheme 1.



Scheme 1. Synthetic route to the formation of chiral Schiff bases, (*R*- or *S*-H_2L1, *rac*-H_2L2), and complexes, $[Rh(\eta^4\text{-cod})(R\text{- or } S\text{-HL1})]$ (**1** or **2**) and $[Rh(\eta^4\text{-cod})(rac\text{-HL2})]$ (**3**).

3.2. *Polarimetry*

Polarimetric measurements show rotation to the right at +118° for *R*-H_2L1, and to the left at −109° for *S*-H_2L1, confirming the enantiopurity of the Schiff bases in $CHCl_3$ at 25°C [8, 9].

3.3. *IR spectra*

The main IR bands of the Schiff bases and complexes are very similar, showing a strong broad band at 3340–3200 cm^{-1} due to νO–H (alcohol) [12, 13, 14]. The most characteristic band of the Schiff bases due to νC=N is at 1630–1610 cm^{-1} [6–13, 14]. The νC–H and νC=C bands are observed at 3060–2950 and 1590–1578 cm^{-1}, respectively. However, the absence of any νN–H band in the Schiff bases, usually observed as a strong band at 3300–3100 cm^{-1} in the amino alcohol [13], suggests the formation of imine bond.

3.4. *Electronic spectra*

Electronic spectra of the Schiff bases (Supplementary material; table 1) in $CHCl_3$ mainly feature: (i) a very strong band at higher energy (<270 nm) with an absorption maximum $\lambda 1_{max} = 268$ nm ($\varepsilon_{max} = 20{,}533$–$27{,}573$ $mol^{-1}\,dm^3\,cm^{-1}$), associated with the intraligand $\pi \rightarrow \pi^*$ transitions, (ii) a strong broad band at 280–360 nm with an absorption maximum at $\lambda 2_{max} = 320$ nm ($\varepsilon_{max} = 16{,}287$–$19{,}694$ $mol^{-1}\,dm^3\,cm^{-1}$), associated with intraligand $n \rightarrow \pi^*$ transitions for C=N group [8–12]. The same bands are found below 360 nm in **1**–**3** (table 1). However, a moderate broad band is found at lower energy (360–460 nm) with an absorption maximum at $\lambda 3_{max} = 398$ nm ($\varepsilon_{max} = 3836$–6808 $mol^{-1}\,dm^3\,cm^{-1}$), assigned to the metal-to-ligand charge transfer (ct) band based on the formation of $[Rh(\eta^4\text{-cod})]^+$ and [Rh(salicylaldiminato)] [6–12, 15] (table 1). In fact, the ct bands for $[Rh(\eta^4\text{-cod})]^+$ and $[Rh(\mu\text{-}O_2CCH_3)]$ are observed separately at 330–370 nm (λ_{max}/356 nm; ε_{max}/1783 $mol^{-1}\,dm^3\,cm^{-1}$) and at 380–480 nm (λ_{max}/421 nm; ε_{max}/3540 $mol^{-1}\,dm^3\,cm^{-1}$), respectively, in $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]$ [5]. However, the ct band for [Rh(salicylaldiminato)] shifts to higher energy and overlaps

Table 1. Electronic spectral data of the Schiff bases and complexes in $CHCl_3$ at 20°C.

	Assignments[a]		
Entity*	$\pi \rightarrow \pi^*$ ($\lambda 1_{max}$ (nm))	$n \rightarrow \pi^*$ ($\lambda 2_{max}$ (nm))	ct ($\lambda 3_{max}$ (nm))
(*R*-H_2L1) (6.630×10^{-4})	268 (20,533)	320 (16,287)	–
(*S*-H_2L1) (4.893×10^{-4})	266 (27,573)	320 (19,694)	–
(*rac*)-H_2L2 (6.030×10^{-4})	268 (22,413)	320 (18,977)	–
1 (1.989×10^{-4})	246 (47,794)	300 (sh)	398 (5779)
2 (3.716×10^{-4})	246 (28,926)	300 (sh)	398 (3836)
3 (8.575×10^{-5})	242 (61,248)	300 (sh)	398 (6808)

*Concentration in mol dm^{-3}.
[a]Values in parentheses are molar absorptivity (ε ($mol^{-1}\,dm^3\,cm^{-1}$)).

with the nearby same band for [Rh(η^4-cod)]$^+$, appearing as a moderate broad band at 360–460 nm in the complexes [6–12].

3.5. *CD spectra*

The CD spectra of (*R*-H_2L1) and (*S*-H_2L1) (figure 1a, table 2) show absorption bands with a positive ellipticity maximum at 341 nm ($\Delta\varepsilon = +1.63\,mol^{-1}\,dm^3\,cm^{-1}$) and a negative ellipticity maximum at 341 nm ($\Delta\varepsilon = -1.14\,mol^{-1}\,dm^3\,cm^{-1}$), respectively, for intraligand $\pi\rightarrow\pi^*/n\rightarrow\pi^*$ transitions, confirming the enantiopurity of the Schiff bases; the racemic *rac*-H_2L2 shows no such absorption. The same band is found below 350 nm with a positive ellipticity maximum at 328 nm ($\Delta\varepsilon = +2.04\,mol^{-1}\,dm^3\,cm^{-1}$) for **1** and a negative ellipticity maximum at 327 nm ($\Delta\varepsilon = -0.2\,mol^{-1}\,dm^3\,cm^{-1}$) for **2** (figure 1b, table 2). Complex **1** further shows a broad absorption with two negative ellipticity maxima at 365 nm ($\Delta\varepsilon = -0.24\,mol^{-1}\,dm^3\,cm^{-1}$), 425 nm ($\Delta\varepsilon = -0.24\,mol^{-1}\,dm^3\,cm^{-1}$),

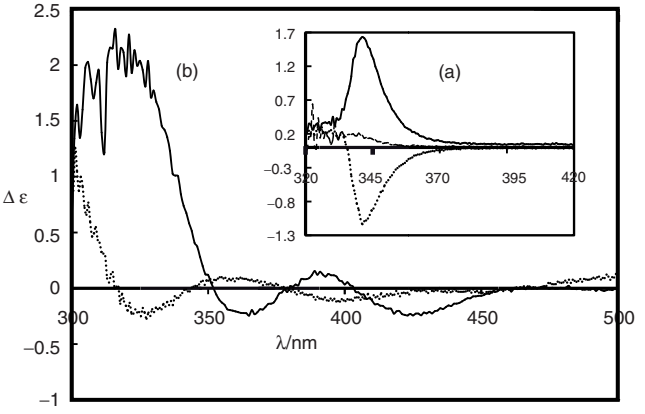


Figure 1. CD spectra of the Schiff bases (a): *R*-H_2L1 (solid line, $1.326 \times 10^{-2}\,mol\,dm^{-3}$); *S*-$H_2$L1 (dot, $1.450 \times 10^{-2}\,mol\,dm^{-3}$); (*rac*)-$H_2$L2 (dash, $1.492 \times 10^{-2}\,mol\,dm^{-3}$); and complexes (b): [Rh(η^4-cod)(*R*-HL1)] (**1**) (solid,$1.193 \times 10^{-2}\,mol\,dm^{-3}$); [Rh($\eta^4$-cod)(*S*-HL1)] (**2**) (dot, $1.152 \times 10^{-2}\,mol\,dm^{-3}$) in $CHCl_3$ at 20°C.

Table 2. CD spectral data of the Schiff bases and complexes in $CHCl_3$ at 20°C.

	Assignments[a]			
Entity*	$\pi\rightarrow\pi^*/n\rightarrow\pi^*$ (λ_{max} (nm))	ct (λ_{max} (nm))		
(*R*-H_2L) (1.326×10^{-2})	341 (+1.63)			
(*S*-H_2L) (1.450×10^{-2})	341 (–1.14)			
(*rac*)-H_2L2 (1.492×10^{-2})	–			
1 (1.193×10^{-2})	328 (+2.04)	365 (–0.24)	391 (+0.15)	425 (–0.24)
2 (1.152×10^{-2})	327 (–0.27)	362 (+0.10)	394 (–0.11)	–

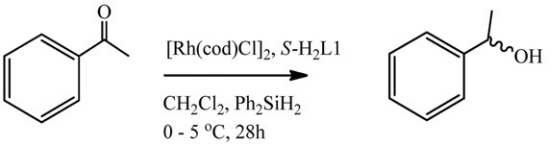
*Concentration in $mol\,dm^{-3}$.
[a]Values in parentheses are molar CD ($\Delta\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$)).

and one positive ellipticity maximum at 391 nm ($\Delta\varepsilon = +0.15\,mol^{-1}\,dm^3\,cm^{-1}$) for ct transitions of [Rh(η^4-cod)]$^+$ and [Rh(salicylaldiminato)] species. The opposite situation is observed in **2** (figure 1b, table 2), confirming the enantiopurity of **1** and **2**.

3.6. *NMR spectra*

^{1}H-NMR spectral data of the Schiff bases and complexes are summarized in section 2, and their assignments are based on the related literature [5–12, 14, 16, 17]. The imine proton is a singlet in the Schiff bases at 8.36–8.60 ppm and shifts to higher field at 7.95–7.98 ppm in **1**–**3**. The alcohol and phenol (from salicylaldimine) protons of the Schiff bases are not observed in $CDCl_3$ due to strong and rapid interactions with solvent on the NMR time scale. However, the alcohol proton is found as a singlet at 2.37 ppm in the complexes. The absence of phenolic proton in the complexes indicates dissociation forming the ionic bond between Rh^+ and O^-. Two methylene protons show a doublet at 4.04 (*R*-H_2L1), 4.00 (*S*-H_2L1), 3.91 (**1**), and 3.94 ppm (**2**), respectively. The methine proton appears as a triplet at 4.97 (*R*-H_2L1), 4.72 ppm (*S*-H_2L1), and as a multiplet at 4.46 (**1**) and 4.45 ppm (**2**). Two methylene protons show two sets of doublets of doublets of doublets (ddd, six lines) at 3.75 and 3.96 ppm, respectively, in *rac*-H_2L2. While, the same protons show two sets of doublets of doublets (dd, four lines) at 3.30 and 3.37 ppm, respectively, in **3**. The methine proton shows a doublet of doublets at 5.06 ppm (*rac*-H_2L2) and 4.94 ppm (**3**), respectively. The alcohol proton shows a singlet at 2.36 ppm in $CDCl_3$, which shifts to low field at 5.64 ppm in DMSO-d_6, due to strong intermolecular hydrogen bonding with the solvent in **3**. However, all other peaks remain unchanged in DMSO-d_6 (section 2). The four exo- and endo-methylene protons of Rh(I)-coordinated 1,5-cyclooctadiene (cod) appear as multiplets at 1.82–1.95 and 2.40–2.50 ppm, respectively, in the complexes. The four olefin protons show two multiplets, the upfield one (*ca* 3.80 ppm) is assigned to "H *trans* to O," while the downfield one (*ca* 4.60 ppm) to "H *trans* to N" [8–12, 16, 17] in **1** and **2**. These protons show four multiplets, two upfield (3.70 and 3.75 ppm), and two downfield (4.54 and 4.60 ppm) in **3**. The difference in chemical shifts between these two multiplets (or four multiplets in **3**) is explained by the *trans* effect of the coordinated *N*,*O*-chelate on the olefin proton resonances [8–12, 16, 17].

In ^{13}C-NMR spectra of **3**, the four methylene carbons of Rh(I)-coordinated 1,5-cyclooctadiene (cod) give four singlets of equal intensity at 28.5, 29.3, 31.2, and 32.2 ppm, indicating their non-symmetrical nature in the complex. Similarly, the four olefin carbons give four doublets, two of them relatively downfield (84.9 and 85.6 ppm), assigned to "C *trans* to N" ("left" and "right" carbons, while "left" and "right" is an arbitrary assignment for the olefinic carbons to either side of a plane bisecting the C=C bond) and the other two upfield (69.7 and 72.7 ppm) are assigned to "C *trans* to O" ("left" and "right" carbons) [8–12]. The doublets are due to the coupling of carbon with Rh(I) and giving different ^{103}Rh–^{13}C(olefin) coupling constants ($J = 16.6$, 15.0, 16.4, and 15.9 Hz), reflecting fully asymmetric nature of each olefin carbon. The observed *J*-values agree well to those found for related Rh(η^4-cod)-complexes [8–12, 16]. However, the observance of four singlets and four doublets for methylene and olefin carbons, respectively, is explained by steric and magnetic anisotropy effects in addition to the *trans* influences of the coordinated *N*,*O*-chelate on carbon resonances [8–12, 16, 17]. The chemical shift differences between the "left" and "right" carbons



Scheme 2. Catalytic reduction of acetophenone into (*rac*)-1-phenylethanol.

Table 3. Results for reduction of acetophenone into (*rac*)-1-phenylethanol using [Rh(η^4-cod)(μ-Cl)]$_2$ (0.02 mmol) and enantiopure *N*,*O*-chelate (L) in diphenylsilane (DPS) at (0–5°C).

Entity	L	[Rh]/[Acetophenone]*	[Rh]/[L]	[Rh]/[DPS]	Time (h)	Conversion (%)
1	–	1 : 210	1 : 0	1 : 200	48	58 [a]
2	*S*-H_2L1	1 : 201	1: 4.8	1 : 212	28	85
3	*S*-APE	1 : 230	1 : 6.2	1 : 218	48	60

*Molar ratio; [Rh] = [Rh(η^4-cod)(μ-Cl)]$_2$; *S*-APE = (*S*)-2-amino-2-phenylethanol.
[a]Ref. [11].

trans to the same donor are larger for *trans* to O ($\Delta\delta = 3.0$ ppm) than for *trans* to *N* ($\Delta\delta = 0.7$ ppm) [8–12]. The methylene (C8) and methine (C1) give singlets at 66.6 and 74.9 ppm, respectively. The imine (C9) and phenol (C11) show singlets at the most downfield, 166.2 and 167.4 ppm, respectively. The other aromatic carbons show singlets at 114.6–141.1 ppm. The NMR results are very similar to those found for the analogous [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-salicylaldiminato-κ^2*N*,*O*}] [8], [Rh(η^4-cod){(*R*)-*N*-(Ar)ethyl-2-oxo-1-naphthaldiminato-κ^2*N*,*O*}] [9–11], and [{Rh(η^4-cod)}$_2${*N*,*N*′-R-*bis*(salicylaldiminato-κ^2*N*,*O*)}] (R = ethylene or 1,2-phenylene) [9]. The X-ray results of these complexes suggest that the deprotonated Schiff base coordinates to [Rh(η^4-cod)] as a six-membered *N*,*O*-chelate with distorted square planar geometry.

3.7. *Catalytic reduction of acetophenone into (rac)-1-phenylethanol*

The *in situ* system composed of [Rh(η^4-cod)(μ-Cl)]$_2$ and (*S*)-2-(salicylaldimine)-2-phenylethanol (*S*-H_2L1) has been used for the reduction of acetophenone into (*rac*)-1-phenylethanol (scheme 2) in DPS at 0–5°C [3, 4]. The conversion of acetophenone into (*rac*)-1-phenylethanol is 85%, the highest value in comparison to related systems in the literature [3, 4]. In fact, 58% conversion (table 3) was reported for the same system using [Rh(η^4-cod)(μ-Cl)]$_2$ [11]. However, the *in situ* system composed of [Rh(η^4-cod)(μ-Cl)]$_2$ and (*S*)-2-amino-2-phenylethanol (*S*-APE) shows conversion up to 60% (table 3), indicating that the use of *S*-APE has no extra effect on catalysis due to its inability to form a complex with Rh(η^4-cod)-fragment.

4. Conclusion

Salicyldehyde reacts with (*R* or *S*)-2-amino-2-phenylethanol or *rac*-2-amino-1-phenylethanol to give (*R* or *S*)-2-(salicylaldimine)-2-phenylethanol or

(*rac*)-2-(salicylaldimine)-1-phenylethanol, which in turn coordinates to [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ to afford [Rh(η^4-cod){(*R* or *S*)-2-(salicylaldiminato)-2-phenylethanol-κ^2N,O}] or [Rh(η^4-cod){(*rac*)-2-(salicylaldiminato)-1-phenylethanol-κ^2N,O}]. Synthetic and spectroscopic results as well as comparison studies with the literature strongly suggest that deprotonated Schiff base coordinates to [Rh(η^4-cod)] as a six-membered *N*,*O*-chelate with distorted square planar geometry. The CD and polarimetry measurements show enantiopurity of the Schiff bases as well as the complexes in solution. Reduction of acetophenone into *rac*-1-phenylethanol with 85% conversion was achieved using the *in situ* system composed of [Rh(η^4-cod)Cl]$_2$ and (*S*)-2-(salicylaldimine)-2-phenylethanol in diphenylsilane at 0–5°C.

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