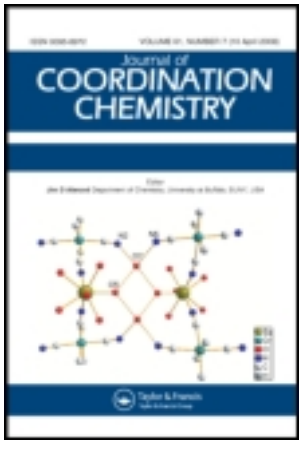


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, stereochemistry, and spectroscopic characterization of [Rh(η^4-cod){(R)-2-(X-benzaldimine)-2-phenylethanol-κ^2 N,O}](acetate) (X=H; 2,4-dimethoxy)

Mohammed Enamullah [a]
[a] Department of Chemistry , Jahangirnagar University , Dhaka-1342, Bangladesh
Published online: 04 May 2011.

To cite this article: Mohammed Enamullah (2011) Synthesis, stereochemistry, and spectroscopic characterization of [Rh(η^4-cod){(R)-2-(X-benzaldimine)-2-phenylethanol-κ^2 N,O}] (acetate) (X=H; 2,4-dimethoxy), Journal of Coordination Chemistry, 64:9, 1608-1616, DOI: 10.1080/00958972.2011.576757

To link to this article: http://dx.doi.org/10.1080/00958972.2011.576757

Journal of Coordination Chemistry
Vol. 64, No. 9, 10 May 2011, 1608–1616

Synthesis, stereochemistry, and spectroscopic characterization of [Rh(η^4-cod){(R)-2-(X-benzaldimine)-2-phenylethanol-κ^2N,O}](acetate) (X = H; 2,4-dimethoxy)

MOHAMMED ENAMULLAH*

Department of Chemistry, Jahangirnagar University, Dhaka–1342, Bangladesh

(*Received 11 November 2010; in final form 16 March 2011*)

Condensation of X-benzaldehyde with (R)-2-amino-2-phenylethanol gives the enantiopure Schiff bases (R)-2-(X-benzaldimine)-2-phenylethanol (X = H, HL1; 2,4-dimethoxy, HL2). The Schiff bases coordinate with dinuclear [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ to afford the cationic complexes [Rh(η^4-cod){(R)-2-(benzaldimine)-2-phenylethanol-κ^2N,O}](acetate), [Rh(η^4-cod)(HL1)](ac) (**1**) and [Rh(η^4-cod){(R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol-κ^2N,O}](acetate), [Rh(η^4-cod)(HL2)](ac) (**2**), respectively. The Schiff bases and complexes are isolated as solids in good yields and characterized by elemental analysis, IR, UV-Vis, ^{1}H/^{13}C-NMR, mass spectroscopy, and polarimetry.

Keywords: chiral Schiff bases; (R)-2-(X-benzaldimine)-2-phenylethanol; [Rh(η^4-cod){(R)-2-(X-benzaldimine)-2-phenylethanol-κ^2N,O}]$^+$; optical properties

1. Introduction

The bidentate (HSB) and tetradentate (H_2SB') *N*,*O*-chelate Schiff bases react with [Rh(μ-X)(η^4-cod)]$_2$ (X = Cl, OCH_3; cod = 1,5-cyclooctadiene) to give mononuclear [Rh(η^4-cod)(SB)] (SB = salicylaldiminato) and dinuclear [{Rh(η^4-cod)}$_2$(SB′)] {SB′ = *bis*-(salicylaldiminato)} complexes, respectively, [1–5]. Similar reactions with enantiopure *N*,*N*-chelate Schiff bases afford the Rh(η^4-cod)(imine)-complexes [6–9]. These complexes as well as *in situ* systems composed of [Rh(η^4-cod)Cl]$_2$ and Schiff bases have been used for asymmetric reduction of acetophenone/substituted ketones with diphenylsilane/1-naphthylphenylsilane into the corresponding chiral secondary alcohol with 3–57% ee. The same system with isopropanol shows 23–65% ee [10].

We are interested in the synthesis, stereochemistry, spectroscopy, and crystal structures of (η^4-cod)Rh(I)-complexes containing *N*,*O*-chelates such as achiral/chiral-amino acids or -amino alcohols as co-ligands [11–13]. Mononuclear [Rh(XY)(η^4-cod)] (XY = amino carboxylato = l/d-alaninato, l/d-phenylglycinato, *N*-methylglycinato,

*Email: enamullahju@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.576757

N-phenylglycinato, *o*-amino-benzoato, *o*-amino-phenolato) has been synthesized from the reaction of dinuclear $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ with chiral amino acids. Similar reaction with chiral amino alcohols gives $[Rh(AA)(\eta^4\text{-cod})](acetate)$ (AA = amino alcohol = (*R*/*S*)-2-amino-2-R_1-ethanol, (*R*/*S*)-2-amino-1-R_1-ethanol; $R_1 = CH_3$, Ph). The X-ray results suggest five-membered *N*,*O*-chelation of the amino carboxylate or amino alcohol to $Rh(\eta^4\text{-cod})$ in distorted square planar geometry. The $[Rh(\eta^4\text{-cod})(XY)]$ reacts with bidentate or tridentate phosphine ligands (i.e., dppe/dppp or triphos) to give the cationic $[Rh(dppe)_2](XY)$ or neutral [Rh(dppp/triphos)(XY)] complexes [14].

In continuation, bidentate enantiopure *N*,*O*-chelate Schiff bases {(R)-*N*-(Ar)ethyl-salicylaldimine; Ar = phenyl, *o*/*m*/*p*-methoxphenyl, *p*-bromophenyl and 2-naphthyl} [15], {(R)-*N*-(Ar)ethyl-naphthaldimine} [16], and tetradentate *N*,*O*,*N*,*O*-chelate Schiff bases {*N*,*N*′-R_1-*bis*-(salicylaldimine), R_1 = ethylene or 1,2-phenylene} [13] have been synthesized. These Schiff bases readily react with $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ to give mononuclear $[Rh(\eta^4\text{-cod})\{(R)\text{-}N\text{-}(Ar)ethyl\text{-}salicylaldiminato/\text{-}naphthaldiminato\}]$ [15, 16] and dinuclear $[\{Rh(\eta^4\text{-cod})\}_2\{N,N'\text{-}R_1\text{-}bis\text{-}(salicylaldiminato)\}]$ [13]. X-ray results show *N*,*O*-chelation of the salicylaldiminate or naphthaldiminate to the $Rh(\eta^4\text{-cod})$-fragment.

This article reports the syntheses, stereochemistry, spectroscopy, and optical properties of the enantiopure *N*,*O*-chelate Schiff bases (R)-2-(X-benzaldimine)-2-phenylethanol (X = H, HL1; 2,4-dimethoxy, HL2) and their complexes $[Rh(\eta^4\text{-cod})(HL1)](ac)$ (**1**) and $[Rh(\eta^4\text{-cod})(HL2)](ac)$ (**2**), respectively.

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 and dichloromethane over Na metal and methanol over CaO. UV-Vis spectra were obtained with a Shimadzu UV 3150 spectrophotometer in dichloromethane at 25°C. IR spectra were recorded on a Bruker Optik IFS 25 spectrometer as KBr discs at ambient temperature. Elemental analyses were done on a VarioEL from Elementar analysensysteme GmbH. $^1H/^{13}C$-NMR spectra were run on a Bruker Avance DPX 200 spectrometer operating at frequencies 200 MHz (^1H) and 50 MHz (^{13}C) at 20°C with calibration against the residual protonated solvent signal ($CDCl_3$: ^1H-NMR 7.25 ppm, ^{13}C-NMR 77.0 ppm; DMSO-d_6: 2.50, 39.5 ppm). NMR grade solvents $CDCl_3$ and DMSO-d_6 were deoxygenated under nitrogen prior to use. EI- and CI-MS: Thermo-Finnigan TSQ 700, with NH_3 as ionization gas for CI. Polarimetric measurements were carried out with a Perkin Elmer 241 Instrument or Rudolph Research Analytical AUTOPOL II in CH_2Cl_2 or $CHCl_3$ at 25°C and the values of specific rotation ($[\alpha]^{25}$) were determined according to the literature [15, 16]. The dinuclear $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ was synthesized from $[Rh(\eta^4\text{-cod})Cl]_2$ [17] according to the literature [11a, 18]. $RhCl_3 \cdot 3H_2O$, 1,5-cyclooctadiene, silver acetate, benzaldehyde, 2,4-dimethoxy-benzaldehyde, and (R)-2-amino-2-phenylethanol were used as received from Merk and Lancaster.

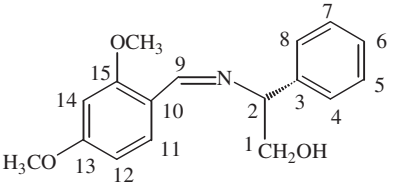
2.2. *General procedure to synthesize the Schiff bases*

Benzaldehyde (1.50 g, 14.15 mmol L^{-1}) was dissolved into 10 mL of methanol and 2–3 drops of concentrated H_2SO_4 was added into this solution, which was then stirred for 10 min at room temperature. An equimolar amount of (R)-2-amino-2-phenylethanol (1.94 g, 14.16 mmol L^{-1}) was added into this solution, yellow precipitate was formed and then the mixture was refluxed for 6 h. The solvent was evaporated to 50% *in vacuo* and yellow precipitate was left to stand for crystallization at room temperature. The precipitate was collected and washed thrice with MeOH (5 mL each), dried *in vacuo* at 40–50°C for 5–6 h to give bright yellow (R)-2-(benzaldimine)-2-phenylethanol (HL1). Compound (R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol (HL2) was prepared following the same procedure using 2,4-dimethoxy-benzaldehyde.

2.2.1. (R)-2-(benzaldimine)-2-phenylethanol (HL1). Yield: 2.61 g (82% from benzaldehyde). $[\alpha]^{25}$ (c = 0.48, CH_2Cl_2): −115° (578 nm). Calcd. for $C_{15}H_{15}NO$ (225.29) (%): C, 79.97; H, 6.71; N, 6.22. Found (%): C, 79.58; H, 6.60; N, 5.95. IR (KBr, cm^{-1}): 3212sb (νOH), 3022w (νCH_{Ar}), 2935s (νCH_{ali}), 1609vs (νCN), 1465s (δCH_2), 1383s (δCH_3), 1273s (νCO + νCN), 1034s (νCO), and 827, 759, 693s (δOH). MS (EI, 70 eV): *m*/*z* 224 (5) $[M-H]^+$, 194 (100) $[M-CH_2OH]^+$, 122 (10) $[C_6H_5CH_2CH_2OH]^+$, 106 (55) $[C_6H_5CHO]^+$, 91 (8) $[C_6H_5CH_2]^+$, 77 (15) $[C_6H_5]^+$. MS (CI, NH_3): *m*/*z* 226 (100) $[M+H]^+$, 194 (25) $[M-CH_2OH]^+$, 106 (5) $[C_6H_5CHO]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 3.03 (br, 1H, OH), 3.95 (m, 2H, CH_2), 4.50 (dd, J_{HH} = 7.8 Hz, J_{HH} = 5.0 Hz, 1H, CH), 7.23–7.45 (m, 10H, H-Ar), and 8.40 (s, 1H, CHN).

2.2.2. (R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol (HL2). 2,4-Dimethoxy-benzaldehyde (2.35 g, 14.16 mmol L^{-1}) and (R)-2-amino-2-phenylethanol (1.94 g, 14.16 mmol L^{-1}). Yield: 3.26 g (81% from 2,4-dimethoxy-benzaldehyde). $[\alpha]^{25}$ (*c* = 0.53, CH_2Cl_2): −104° (578 nm). Calcd. for $C_{17}H_{19}NO_3$ (285.34) (%): C, 71.56; H, 6.71; N, 4.91. Found (%): C, 70.90; H, 6.60; N, 4.59. IR (KBr, cm^{-1}): 3207sb (νOH), 3026m (νCH_{Ar}), 2934s (νCH_{ali}), 1611vs (νCN), 1467s (δCH_2), 1385s (δCH_3), 1271s (νCO + νCN), 1039s (νCO), and 833, 754, 697s (δOH). MS (EI, 70 eV): *m*/*z* 284 (5) $[M-H]^+$, 254 (100) $[M-CH_2OH]^+$, 135 (10) $[C_6H_5C(NH)CH_2OH]^+$, 121 (5) $[C_6H_5CH_2CH_2OH–H]^+$, 106 (5) $[C_6H_5CHO]^+$, 77 (3) $[C_6H_5]^+$. MS (CI, NH_3): *m*/*z* 286 (100) $[M+H]^+$, 254 (45) $[M-CH_2OH]^+$, 106 (3) $[C_6H_5CHO]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.70 (br, 1H, OH), 3.73 (d, J_{HH} = 9.4 Hz, 6H, OCH_3), 3.81 (dd, J_{HH} = 9.0, 7.3 Hz, J_{HH} = 4.9, 3.2 Hz, 2H, CH_2), 4.38 (dd, J_{HH} = 8.1, 7.9 Hz, J_{HH} = 4.8, 4.6 Hz, 1H, CH), 6.31 (d, J_{HH} = 2.1 Hz, 1H, H_{14}), 6.45 (dd, J_{HH} = 8.6 Hz, J_{HH} = 2.0 Hz, 1H, H_{12}), 7.15–7.36 (m, 5H, $H_{4–8}$), 7.91 (d, J_{HH} = 8.6 Hz, 1H, H_{11}), and 8.63 (s, 1H, CHN). ^{1}H-NMR (200 MHz, DMSO-d_6): δ = 3.65 (dd, J_{HH} = 11.9, 10 Hz, J_{HH} = 6.9, 5.0 Hz, 2H, CH_2), 3.86 (d, J_{HH} = 6.5 Hz, 6H, OCH_3), 4.34 (dd, J_{HH} = 7.9 Hz, J_{HH} = 4.8 Hz, 1H, CH), 4.81 (t, J_{HH} = 5.7 Hz, 1H, OH), 6.60 (d, J_{HH} = 2.3 Hz, 1H, H_{14}), 6.64 (s, 1H, H_{12}), 7.26–7.39 (m, 3H, $H_{4,6,8}$), 7.45–7.49 (m, 2H, $H_{5,7}$), 7.93 (d, J_{HH} = 8.7 Hz, 1H, H_{11}), and 8.64 (s, 1H, CHN). ^{13}C-NMR (50 MHz, DMSO-d_6): δ = 55.27, 55.60 (OCH_3), 66.52 (CH), 76.71 (CH_2), 97.92 (C_{14}), 106.03 (C_{12}), 117.15 (C_{10}), 126.58 (C_6), 127.24 ($C_{4,8}$), 128.02 ($C_{5,7,11}$), 142.14 (C_3), 155.21 (C_{15}), 159.82 (C_9),

and 162.74 (C_{13}).



(Atoms numbering for NMR assignments in HL1 and HL2).

2.3. *General procedure to synthesize the complexes*

Two equivalents of (R)-2-(benzaldimine)-2-phenylethanol (HL1) (0.072 g, 0.32 mmol L^{-1}) and one equivalent of [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ (0.085 g, 0.16 mmol L^{-1}) were dissolved in 10 mL of C_6H_6:MeOH (4 : 1, v/v) and the solution was stirred for 5–6 h at room temperature. The color changed from red-orange to bright-yellow. The solvent was evaporated *in vacuo* at 40°C and the products were dissolved in 10 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 yield a yellow complex of [Rh(η^4-cod){(R)-2-(benzaldimine)-2-phenylethanol-κ^2N,O}](acetate) (**1**). The same procedure was followed for the synthesis of [Rh(η^4-cod){(R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol-κ^2N,O}](acetate) (**2**) using the (R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol (HL2).

2.3.1. [Rh(η^4-cod){(R)-2-(benzaldimine)-2-phenylethanol-κ^2N,O}](acetate) (1). Yield: 0.125 g (79% from [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$). Calcd. for [$C_{23}H_{27}NORh$](CH_3CO_2) (495.44) (%): C, 60.61; H, 6.10; N, 2.83. Found (%): C, 59.86; H, 6.23; N, 2.68. UV-Vis (2.06×10^{-4} mol dm^{-3}, CH_2Cl_2 at 25°C): λ_{max} ($\varepsilon_{410\,nm}$) = 410 nm (2230 dm^3 mol^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3246sb (νOH), 3023w (νCH_{Ar}), 2934s (νCH_{ali}), 1610vs (νCN), 1583vs (νCO_2 asy), 1459s (δCH_2), 1272s (νCO + νCN), 1034s (νCO), and 825, 757, 705s (δOH). MS (EI, 70 eV): *m*/*z* 435 (3) $[M-H]^+$, 419 (20) $[M-OH]^+$, 391 (100) $[M-CH_2CH_2OH]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.80 (m, 4H + 3H, CH_2cod_{exo} + CH_3), 2.63 (m, 4H, CH_2cod_{endo}), 3.10 (br, 1H, OH), 3.93 (m, 1H, CH_2), 4.15 (m, 4H, CHcod), 4.21 (dd, J_{HH} = 6.0, 5.8 Hz, J_{HH} = 1.8, 1.6 Hz 1H, CH_2), 4.50 (m, 1H, CH), 7.26–7.41 (m, 10H, H-Ar), and 8.41 (s, 1H, CHN).

2.3.2. [Rh(η^4-cod){(R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol-κ^2N,O}] (acetate) (2). (R)-2-(2,4-dimethoxy-benzaldeneamine)-2-phenylethanol (HL2) (0.091 g, 0.32 mmol L^{-1}) and [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ (0.085 g, 0.16 mmol L^{-1}). Yield: 0.145 g (82% from [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$). $[\alpha]^{22}$ (c = 0.25, $CHCl_3$): +32° (589 nm). Calcd for [$C_{25}H_{31}NO_3Rh$](CH_3CO_2) (555.48) (%): C, 58.36; H, 6.17; N, 2.52. Found: C, 57.75%; H, 5.79%; N, 2.20%. UV–Vis (1.88×10^{-4} mol dm^{-3}, CH_2Cl_2 at 25°C): λ_{max} ($\varepsilon_{410\,nm}$) = 414 nm (2304 dm^3 mol^{-1} cm^{-1}). IR (KBr, cm^{-1}): 3240sb (νOH),

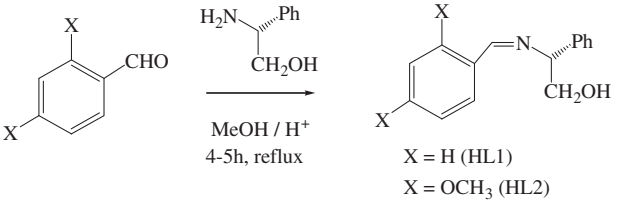
3031w (νCH_{Ar}), 2930s (νCH_{ali}), 1603vs (νCN), 1581vs (νCO_2 asy), 1456s (δCH_2), 1275s ($\nu CO + \nu CN$), 1031s (νCO), and 828, 760, 701s (δOH). MS (EI, 70 eV): m/z 494 (5) $[M - H_2]^+$, 492 (8) $[M - 2H_2]^+$, 416 (5) $[M - C_6H_5 - H_2 - H]^+$, 279 (20) $[HL2 - 3H_2]^+$, 254 (100) $[HL2 - CH_2OH]^+$, 167 (22) $[C_6H_3(OCH_3)_2CH_2NH_2]^+$, 149 (55) $[HL2 - C_6H_3(OCH_3)_2 + H]^+$, 106 (10) $[C_6H_5CHO]^+$. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.70$ (m, 4H+3H, $CH_2cod_{exo} + CH_3$), 2.60 (m, 4H + 1H, $CH_2cod_{endo} + OH$), 3.74 (d, $J_{HH} = 10.1$ Hz, 6H, OCH_3), 3.86 (m, 1H, CH_2), 4.02 (m, 4H, CHcod), 4.14 (dd, $J_{HH} = 6.0$, 5.7 Hz, $J_{HH} = 1.7$, 1.4 Hz, 1H, CH_2), 4.41 (m, 1H, CH), 6.32 (d, $J_{HH} = 2.2$ Hz, 1H, H_{14}), 6.51 (d, $J_{HH} = 7.9$ Hz, 1H, H_{12}), 7.18–7.33 (m, 4H, $H_{4,6,8,11}$), 7.39–7.46 (m, 2H, $H_{5,7}$), and 8.61 (s, 1H, CHN). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 24.08$ (CH_3), 30.83 (CH_2cod), 55.48, 55.59 (OCH_3), 68.13 (CH), 77.12 (CH_2), 77.55, (CHcod), 97.85 (C_{14}), 105.77 (C_{12}), 119.07 (C_{10}), 127.53 (C_6), 128.48 ($C_{4,8}$), 128.65 (C_7), 128.77 (C_5), 130.71 (C_{11}), 130.85 (C_3), 163.61 (C_{15}), 166.17 (C_9), 167.71 (C_{13}), and 188.27 (CO_2^-).

3. Results and discussion

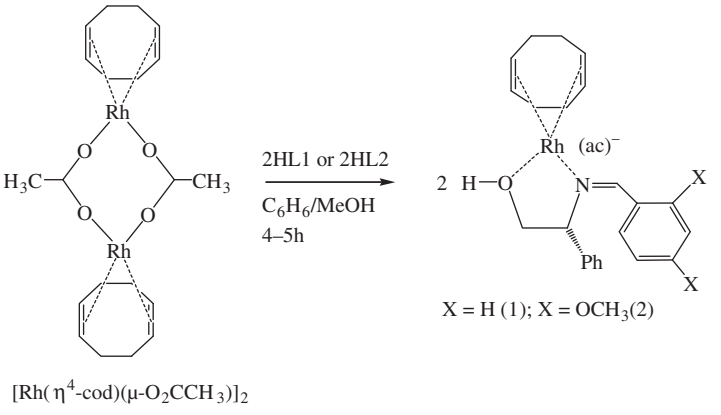
Condensation of (R)-2-amino-2-phenylethanol with benzaldehyde or 2,4-dimethoxy-benzaldehyde gives enantiopure Schiff bases (R)-2-(benzaldimine)-2-phenylethanol (HL1) or (R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol (HL2) (scheme 1). The Schiff bases react with $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ to give $[Rh(\eta^4\text{-cod})\{$(R)-2-(benzaldimine)-2-phenylethanol-$\kappa^2 N,O\}$](acetate), $[Rh(\eta^4\text{-cod})(HL1)]$(ac) (**1**) or $[Rh(\eta^4\text{-cod})\{$(R)-2-(2,4-dimethoxy-benzaldimine)-2-phenylethanol-$\kappa^2 N,O\}$](acetate), $[Rh(\eta^4\text{-cod})(HL2)]$(ac) (**2**) in C_6H_6 : MeOH (4 : 1, v/v) (scheme 2).

3.1. *Mass spectra*

EI-/CI-mass spectra of the Schiff bases and complexes are listed in the experimental section. EI-mass spectra show the parent ion peak ($[M - H]^+$) at m/e 224 (HL1), 284 (HL2) and base peak at m/e 194 (HL1), 254 (HL2) for $[M–CH_2OH]^+$. The parent ion peak ($[M - H]^+$) is found at m/e 435 and base peak at m/e 391 ($[M - CH_2CH_2OH]^+$) in **1**; the parent ion peak is at m/e 494 ($[M - H_2]^+$) and base peak at m/e 254 ($[HL2 - CH_2OH]^+$) in **2**. CI-mass spectra show the parent ion peak ($[M + H]^+$) as the base peaks at m/e 226 in HL1 and 286 in HL2. The mass spectra are dominated by several ion



Scheme 1. Synthetic route to HL1–HL2.



Scheme 2. Synthetic route to [Rh(η^4-cod)(HL1/HL2)](ac) (**1** and **2**).

peaks for $[HL2–C_6H_3(OCH_3)_2+H]^+$, $[C_6H_5C(NH)CH_2OH]^+$, $[C_6H_5CH_2CH_2OH]^+$, and $[C_6H_5CHO]^+$ as found for the Schiff bases as well as the complexes (section 2).

3.2. *Polarimetry*

Polarimetric measurements show the rotation to the left for the enantiopure Schiff bases HL1 ($[\alpha]^{25} = -115^\circ$, $c = 0.48$), HL2 ($[\alpha]^{25} = -104^\circ$, $c = 0.53$) in CH_2Cl_2 at 578 nm, and rotation to the right for **2** ($[\alpha]^{22} = +32^\circ$, $c = 0.25$) in $CHCl_3$ at 589 nm [15, 19].

3.3. *IR spectra*

The main IR bands of the Schiff bases and complexes are listed in section 2 and their assignments are made based on the related literature [11–20]. Spectra show a strong broad band at 3207–3245 cm^{-1} due to (νOH) in the free Schiff bases and complexes. The (νHC_{Ar}) and (νCH_{ali}) are at 2930–3031 cm^{-1}. A very strong band at 1603–1611 cm^{-1} is assigned to (νCN), the most characteristic band for the imine group in the Schiff base. However, the absence of a (νNH) band in HL1 and HL2 (usually observed as strong bands at 3300 3100 cm^{-1} in the amino alcohol [20]) suggests the formation of the imine bond. In fact, very strong (νCO_2) asymmetric vibrations found at 1581–1583 cm^{-1} confirm the presence of acetate as counter anion.

3.4. *Electronic spectra*

Electronic spectra of the complexes in CH_2Cl_2 at 25°C are identical with each other and different from [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$. The main features of the spectra are: (1) a very strong band at higher energy (<350 nm), assigned to intra-ligand $\pi \rightarrow \pi^*$ transitions of the imine group and (η^4-cod) and (2) a strong broad band at 350–500 nm with an absorption maxima (λ_{max}) at 410–414 nm ($\varepsilon_{410\,nm} = 2230$ and 2304 $dm^3\,mol^{-1}\,cm^{-1}$ for **1** and **2**, respectively), assigned to the charge transfer (ct) transitions based on the formation of $[Rh(\eta^4\text{-cod})]^+$ and $[Rh(HL1/HL2)]^+$ [11–15].

The reactant $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ shows two separate ct bands at 330–370 nm (λ_{max}/355 nm, $\varepsilon_{355\,nm}$/1866 $dm^3\,mol^{-1}\,cm^{-1}$) due to $[Rh(\eta^4\text{-cod})]^+$ and at 380–480 nm (λ_{max}/421 nm, $\varepsilon_{421\,nm}$/3564 $dm^3\,mol^{-1}\,cm^{-1}$) due to $[Rh(\mu\text{-}O_2CCH_3)]$ in addition to intra-ligand $\pi\rightarrow\pi^*$ transitions of η^4-cod [11a, 12]. However, the ct band due to $[Rh(HL1/HL2)]^+$ shifts to higher energy and overlaps with the nearby ct band for $[Rh(\eta^4\text{-cod})]^+$, not separately detectable in Rh(η^4-cod)-Schiff base/-amino acid complexes [11–15].

3.5. *NMR spectra*

^1H-/^{13}C-NMR spectra of the Schiff bases and complexes in $CDCl_3$ or DMSO-d_6 are summarized in section 2. The spectral assignments are made based on the related literature [11–16, 19, 21–23]. The OH appears as a broad peak at $\delta = 3.03$ (HL1), 2.70 (HL2), 3.10 (**1**), and 2.60 ppm (**2**) in $CDCl_3$, due to intermolecular hydrogen bonding [12, 19, 24]. This peak shifts downfield and appears as a triplet at $\delta = 4.81$ (HL2) in DMSO-d_6 due to further hydrogen bonding with the solvent [24, 25]. The methine proton appears as a doublet of doublet at $\delta = 4.50$ ppm (HL1), 4.38 ppm (HL2), and a multiplet at $\delta = 4.50$ (**1**) and 4.41 ppm (**2**). The methylene protons appear as a multiplet at $\delta = 3.95$ ppm in HL1 and a doublet of doublet at $\delta = 3.81$ ppm in HL2. However, the same protons show two signals separated by *ca* 0.30 ppm in each complex, one of which is multiplet at $\delta = 3.93$ (**1**) and 3.86 ppm (**2**), and other one is doublet of doublet at $\delta = 4.21$ (**1**) and 4.14 ppm (**2**). The methylene protons adjacent to the chiral center are diastereotopic and couple differently to the vicinal methine proton, thereby showing two signals [12, 13, 19]. The imine proton appears most downfield as a singlet at $\delta = 8.40$ (HL1), 8.63 (HL2), 8.41 (**1**), and 8.61 ppm (**2**). The methyl protons of OCH_3 show a doublet at $\delta = 3.73$ and 3.74 ppm in HL2 and **2**, respectively. The exo- and endo-methylene protons of Rh(I)-coordinated 1,5-cyclooctadiene show multiplets at $\delta = 1.80$ (**1**), 1.70 ppm (**2**) and at 2.63 (**1**), 2.60 ppm (**2**), respectively [12, 13, 15, 22]. The olefinic protons show a multiplet at $\delta = 4.14$ (**1**) and 4.02 ppm (**2**). The acetate anion shows the methyl protons at $\delta = 1.70$–1.80 ppm which overlap with the exo-methylene protons in **1** and **2**.

In ^{13}C-NMR spectra of HL2 and **2**, the methyl carbons of two OCH_3 groups give two singlets at $\delta = 55.3$, 55.6 ppm (HL2) and 55.5, 55.6 ppm (**2**). The methylene and methine carbons show singlets at $\delta = 76.7$ (HL2), 77.1 ppm (**2**) and at 66.5 (HL2), 68.1 ppm (**2**), respectively. The imine carbon shows a singlet relatively downfield at $\delta = 159.8$ (HL2) and 166.2 ppm (**2**). The remaining aromatic carbons show several singlets in the range of $\delta = 98.0$–167.7 ppm (section 2). The methylene and olefinic carbons of Rh(I)-coordinated 1,5-cyclooctadiene show a singlet at $\delta = 30.8$ ppm and a broad peak at 77.5 ppm, respectively, in **2**. Similar studies show that the methylene and olefinic carbons are a singlet and a broad peak at 29.7 and 77.9 ppm in [Rh(*N*-phenylglycinato)(η^4-cod)] [12, 13], and at 30.0, 75.8 ppm in [Rh((*S*)-2-amino-2-phenylethanol)(η^4-cod)](ac) [12]. The X-ray structure determination of these complexes reveals that the *N*-phenylglycinate or (*S*)-2-amino-2-phenylethanol coordinates to $[Rh(\eta^4\text{-cod})]^+$ as a five-membered *N*,*O*-chelate in a distorted square planar geometry. Olefinic carbons are bound to Rh(I) slightly asymmetrically, reflecting different *trans* nitrogen or oxygen donors. The acetate has methyl carbon at $\delta = 24.1$ ppm and carboxylate carbon downfield at $\delta = 188.3$ ppm in **2** [12].

In conclusion, condensation of X-benzaldehyde with (R)-2-amino-2-phenylethanol gives the enantiopure (R)-2-(X-benzaldimine)-2-phenylethanol (HL1–HL2), which in turn reacts with dinuclear $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ to afford the cationic $[Rh(\eta^4\text{-cod})\{(R)\text{-}2\text{-}(X\text{-benzaldimine})\text{-}2\text{-phenylethanol-}\kappa^2N,O\}](acetate)$ (**1** and **2**). Synthetic and spectroscopic results as well as comparison with the literature strongly suggest that the enantiopure Schiff bases coordinate to the rhodium of $[Rh(\eta^4\text{-cod})]^+$ as a five-membered *N*,*O*-chelate in a distorted square planar geometry.

Acknowledgments

This study was carried out under the financial support of Jahangirnagar University Research Project-2008/09, Dhaka, Bangladesh. Department of Chemistry, Jahangirnagar University, is gratefully acknowledged for carrying out the experimental works. The author sincerely thanks Prof. Dr C. Janiak, Institute of Inorganic and Analytical Chemistry, University of Freiburg, Germany, for taking mass and elemental data.

References

[1] N. Platzer, N. Goasdoue, R. Bonnaire. *J. Organomet. Chem.*, **160**, 455 (1978).
[2] R. Bonnaire, C. Potvin, J.M. Manoli. *Inorg. Chim. Acta*, **45**, L255 (1980).
[3] R. Bonnaire, J.M. Manoli, C. Potvin, N. Platzer, N. Goasdoue, D. Davoust. *Inorg. Chem.*, **21**, 2032 (1982).
[4] R.J. Cozens, K.S. Murray, B.O. West. *J. Organomet. Chem.*, **27**, 399 (1971).
[5] C.A. Rogers, B.O. West. *J. Organomet. Chem.*, **70**, 445 (1974).
[6] H. Brunner, H. Fischer. *J. Organomet. Chem.*, **335**, 1 (1987).
[7] H. Brunner, G. Riepl. *Angew. Chem.*, **94**, 369 (1982).
[8] H. Brunner, B. Reiter. *G. Riepl. Chem. Ber.*, **117**, 1330 (1984).
[9] M.E. Wright, S.A. Svejda, A.M. Arif. *Inorg. Chim. Acta*, **175**, 13 (1990).
[10] (a) G. Zassinovich, F. Grisoni. *J. Organomet. Chem.*, **247**, C24 (1983); (b) V.A. Pavlov, M.G. Vinogradov, E.V. Starodubtseva, G.V. Cheltsova, V.A. Ferapontov, O.R. Malyshev, G.L. Heise. *Russ. Chem. Bull., Int. Ed.*, **50**, 734 (2001).
[11] (a) M. Enamullah, M. Hasegawa, J. Okubo, T. Hoshi. *J. Bangladesh Chem. Soc.*, **18**, 165 (2005); (b) M. Enamullah, A.K.M. Royhan Uddin, M. Uddin. *J. Bangladesh Chem. Soc.*, **21**, 28 (2008).
[12] M. Enamullah, A. Sharmin, M. Hasegawa, T. Hoshi, A.-C. Chamayou, C. Janiak. *Eur. J. Inorg. Chem.*, 2146 (2006).
[13] C. Janiak, A.-C. Chamayou, A.K.M. Royhan Uddin, M. Uddin, K.S. Hagen, M. Enamullah. *Dalton Trans.*, 3698 (2009).
[14] M. Enamullah, M. Uddin, W. Linert. *J. Coord. Chem.*, **60**, 2309 (2007).
[15] M. Enamullah, A.K.M. Royhan Uddin, A.-C. Chamayou, C. Janiak. *Z. Naturforsch.*, **62b**, 807 (2007).
[16] A.K.M. Royhan Uddin. Syntheses, stereochemistry, catalyses and crystal structures of transition metal complexes with chiral N, O-chelate ligands, Thesis, Department of Chemistry, Jahangirnagar University, Dhaka-1342, Bangladesh (2009).
[17] G. Giordano, R.H. Crabtree. *Inorg. Synth.*, **28**, 8 (1990).
[18] (a) Z. Nagy-Magos, S. Vastag, B. Heil, L. Marko. *J. Organomet. Chem.*, **171**, 97 (1979); (b) Z. Nagy-Magos, P. Kvintovics, L. Marko. *Transition Met. Chem.*, **5**, 186 (1980).
[19] (a) H. Brunner, T. Zwack, M. Zabel, W. Beck, A. Boehm. *Organometallics*, **22**, 1741 (2003); (b) H. Brunner, R. Oeschey, B. Nuber. *J. Chem. Soc., Dalton Trans.*, 1499 (1996).
[20] E. Pretsch, J.T. Clerc. *Spectra Interpretation of Organic Compounds*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo (1997).
[21] (a) C. Zhang, G. Rheinwald, V. Lozan, B. Wu, P.-G. Lassahn, H. Lang, C. Janiak. *Z. Anorg. Allg. Chem.*, **628**, 1259 (2002); (b) S.P. Rath, T. Ghosh, S. Mondal. *Polyhedron*, **16**, 4179 (1997).

[22] (a) J.G. Leipoldt, E.C. Grobler. *Inorg. Chim. Acta*, **72**, 17 (1983); (b) A.P. Martinez, M.P. Garcia, F.J. Lahoz, L.A. Oro. *Inorg. Chem. Commun.*, **5**, 245 (2002); (c) G.S. Rodman, K.R. Mann. *Inorg. Chem.*, **27**, 3338 (1988); (d) C. Tejel, M.A. Ciriano, M. Bordonaba, J.A. Lopez, F.J. Lahoz, L.A. Oro. *Inorg. Chem.*, **41**, 2348 (2002).
[23] (a) J.C. Bayon, G. Net, P.G. Rasmussen, J.B. Kolowich. *J. Chem. Soc., Dalton Trans.*, 3003 (1987); (b) R. Bonnaire, J.M. Manoli, N. Potvin, N. Platzer, N. Goasdove. *Inorg. Chem.*, **20**, 2691 (1981); (c) R. Ugo, G. La Monica, S. Cenini, F. Bonati. *J. Organomet. Chem.*, **11**, 159 (1968).
[24] M. Enamullah, A.K.M. Royhan Uddin, G. Hogarth (submitted).
[25] G.A. Bain, D.X. West, J. Krejci, J. Valdes-Martinez, S. Hernandez-Ortega, R.A. Toscano. *Polyhedron*, **16**, 855 (1997).