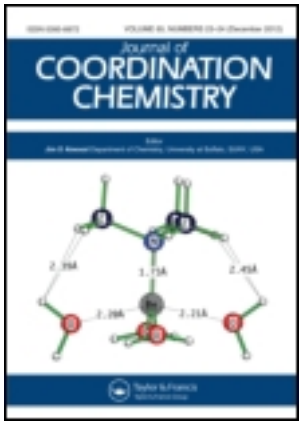

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Syntheses, spectroscopy, and X-ray structures of 3-{(R)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (Ar=Ph, $MeOC_6H_4$, BrC_6H_4, 1-naphthyl) and [Rh(η^4-cod){3-((R)-(Ar)-ethylimino)-3H-indol-2-olato}]

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Syntheses, spectroscopy, and X-ray structures of 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (Ar = Ph, $MeOC_6H_4$, BrC_6H_4, 1-naphthyl) and [Rh(η^4-cod){3-((*R*)-(Ar)-ethylimino)-3*H*-indol-2-olato}]

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Condensation of 1*H*-indole-2,3-dione (isatin) with (*R*)-(Ar)-ethylamines gives enantiopure Schiff bases, 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (**HL**) {Ar = Ph (**HL1**), 2-$MeOC_6H_4$ (**HL2**), 4-$MeOC_6H_4$ (**HL3**), 4-BrC_6H_4 (**HL4**), and 1-naphthyl (**HL5**)}. The Schiff bases readily coordinate to [Rh(μ-O_2CMe)(η^4-cod)]$_2$ (cod = 1,5-cyclooctadiene) to give mononuclear [Rh(η^4-cod){3-((*R*)-(Ar)-ethylimino)-3*H*-indol-2-olato}] {Ar = Ph (**1**), 4-$MeOC_6H_4$ (**2**), and 4-BrC_6H_4 (**3**)}, respectively. The Schiff bases and complexes have been fully characterized by IR, UV-Vis, ^{1}H-NMR, mass, and circular dichroism (CD) spectrometry. Polarimetry and CD measurements show the enantiopurity of the Schiff bases as well as the complexes. ^{1}H NMR measurements reveal slow conversion of the lactam to the enol form of the Schiff bases in solution. In the solid state the lactam form dominates as shown by crystal structures of **HL1** and **HL4**. While gross structural features of both are similar, the molecules differ significantly in the relative orientations of the aryl and lactam rings. The difference is mostly rotation about the N2–C9 bond with different C8–N2–C9–C11 torsion angle of +89.77(12)° for **HL1** and C2–N2–C9–C11 of +106.8(3)° for **HL4**.

Keywords: Chiral isatin Schiff bases; Rh(η^4-cod)(chiral isatin Schiff bases); Lactam–enol isomerization; Hydrogen-bond; X-ray structure

1. Introduction

1*H*-Indole-2,3-dione (isatin) is a commercially available and cheap indole derivative and is an attractive starting material for drug syntheses. Schiff bases of isatin are particularly noteworthy as they display a wide range of pharmacological properties including acting as antibacterial, antifungal, antiviral, antileukemic, anticancer, and antiprotozoal agents [1–3]. Consequently, syntheses of many achiral isatin Schiff bases and their derivatives, derived by condensation of isatin with arylamine [4], hydrazine [5]

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semicarbazide [6], thiosemicarbazide [7–10], and dithiocarbazate [11], respectively, or with N-substituted derivatives of these compounds, and transition metal-isatin Schiff-base complexes, have been reported. Somewhat surprisingly given the importance of chirality in drug efficiency, there are no reports of chiral isatin Schiff bases and their complexes with transition metals.

We recently reported syntheses of chiral Schiff bases (*R*)-*N*-(Ar)-ethyl-salicylaldimine [12] or (*R*)-*N*-(Ar)-ethyl-2-oxo-1-naphthyldimine [13, 14] derived from condensation of (*R*)-(Ar)-ethylamine with salicylaldehyde or 2-hydroxy-1-naphthaldehyde. The Schiff bases readily react with $[Rh(\mu\text{-}O_2CMe)(\eta^4\text{-cod})]_2$ (cod = 1,5-cyclooctadiene) to give [Rh(SB)(η^4-cod)] {SB^- = deprotonated Schiff bases = (*R*)-*N*-(Ar)-ethyl-salicyldeiminate or (*R*)-*N*-(Ar)-ethyl-2-oxo-1-naphthyldiminate} [12–14]. The X-ray results show that SB^- coordinate to Rh(η^4-cod) as six-membered *N*,*O*-chelates with distorted square-planar geometry at rhodium. Syntheses, stereochemistry, and spectroscopic characterizations of [Rh(η^4-cod){(*R*)-2-(X-benzaldimine)-2-phenylethanol-κ^2*N*,*O*}] (acetate) [15], [Rh(η^4-cod){(*R* or *S*)-2-(salicylaldiminato)-2-phenylethanol-κ^2*N*,*O*}] [16] and [Rh(η^4-cod){(*rac*)-2-(salicylaldiminato)-1-phenylethanol-κ^2*N*,*O*}] [16] have been reported. Similar reactions with chiral amino acids (HXY) or amino alcohols (AA) give [Rh(η^4-cod)(XY)] or [Rh(η^4-cod)(AA)](acetate) [17–19], where deprotonated amino acids or amino alcohols coordinate to Rh(η^4-cod) as five-membered *N*,*O*-chelates as shown by X-ray measurements. However, phosphine ligands (*dppe* or *dppp* or *triphos*) react with the [Rh(η^4-cod)(XY)] to give the cationic [Rh(*dppe*)$_2$](XY) or neutral [Rh(*dppp* or *triphos*)(XY)] [20].

Herein, we report the syntheses, spectroscopic characterizations, and molecular structures of enantiopure isatin Schiff bases, 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (Ar = Ph, 2-/4-$MeOC_6H_4$, 4-BrC_6H_4, and 1-naphthyl) and their complexes, [Rh(η^4-cod){3-((*R*)-(Ar)-ethylimino)-3*H*-indol-2-olato}].

2. Experimental

2.1. *Materials and methods*

Methanol was distilled over CaO. UV-Vis spectra were obtained with a Shimadzu UV 3150 spectrophotometer in $CHCl_3$ at 20°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 Elementaranalysensysteme GmbH. NMR spectra were run on a Bruker Avance DPX-300 or GEOL-400 or GEOL-500 spectrometer, operating at 300 MHz (^{1}H), 75 MHz (^{13}C), or at 400 MHz (^{1}H) or at 500 MHz (^{1}H) at 20°C with calibration against the residual protonated solvent signal ($CDCl_3$: 7.25 ppm for ^{1}H, 77.0 ppm for ^{13}C; acetone-d_6: 2.05 ppm for ^{1}H; DMSO-d_6: 2.50 ppm for ^{1}H). ESI-MS experiments 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 out with JASCO DIP-181 and Rudolph Research Analytical AUTOPOL II Instruments in $CHCl_3$ at 25°C; values of $[\alpha]^{25}$ were determined according to the literature [12]. Circular dichroism (CD) spectra were obtained with a JASCO J-170 Spectropolarimeter in $CHCl_3$ at 20°C.

1*H*-Indole-2,3-dione (isatin) was used as received from Merck. The enantiopure amines, (*R*)-(Ar)-ethylamine, were used as received from the BASF, Germany.

2.2. *General procedure for syntheses of the Schiff bases 3-{(R)-(Ar)-ethylimino}-1, 3-dihydro-indol-2-one (HL1–HL5)*

To 1*H*-Indole-2,3-dione (isatin) (1.50 g, 10.20 mmol) in methanol (10 mL) was added 2–3 drops of conc. H_2SO_4 and stirred for 10 min. To this was added an equimolar amount of enantiopure (*R*)-(phenyl)-ethylamine (1.23 g, 10.20 mmol), resulting in a color change to orange-yellow, and the mixture was refluxed for 4–5 h. Then, the solvent was evaporated to 50% (v/v) and left standing at room temperature for crystallization. Orange-yellow crystals were formed after 3–4 days by slow evaporation of the solvent. The crystals were filtered off and washed three times with methanol (5 mL each). Drying the crystals in air gave enantiopure 3-{(*R*)-(phenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL1**). The same procedure was followed to synthesize 3-{(*R*)-(2-methoxyphenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL2**), 3-{(*R*)-(4-methoxyphenyl)-ethylimino}-1, 3-dihydro-indol-2-one (**HL3**), 3-{(*R*)-(4-bromophenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL4**), and 3-{(*R*)-(1-naphthyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL5**) using (*R*)-(2-methoxyphenyl)-ethylamine, (*R*)-(4-methoxyphenyl)-ethylamine, (*R*)-(4-bromophenyl)-ethylamine and (*R*)-(1-naphthayl)-ethylamine, respectively.

2.2.1. 3-{(*R*)-(phenyl)-ethylimino}-1,3-dihydro-indol-2-one (HL1). Yield: 2.15 g (84%) (from isatin). $[\alpha]^{25}$ ($c = 0.28$, $CHCl_3$): + 50.17° (598 nm). UV-Vis (4.88×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 381 (1454) and 290 (4080). CD (4.88×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm ($\Delta\epsilon_{max}$/dm mol^{-1} cm^{-1}) = 308 (−0.89) and 377 (−1.42). IR (KBr): 3300sb (νN–H), 3097, 3027, 2967, 2926m (νC–H), 1747, 1720vs (νC=Oasy), 1640, 1612, 1591vs (νC=N), and 1464vs (νC=Osy) cm^{-1}. MS (ESI): *m*/*z* (%) 539 (50) $[M_2 + K]^+$, 523 (25) $[M_2 + Na]^+$, 501 (10) $[M_2 + H]^+$, 289 (100) $[M + K]^+$, 273 (20) $[M + Na]^+$, and 251 (15) $[M + H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (d, $J_{HH} = 6.7$ Hz, 3H, C*H*$_3$–E), 1.74 (d, $J_{HH} = 7.2$ Hz, 3H, C*H*$_3$–L), 5.53 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–L), 6.58 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–E), 6.81 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–E), 6.97 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–L), 7.04 (ddd, $J_{HH} = 7.6$ Hz, 2.4 Hz, 2H, H_{Ar}–E, L), 7.22–7.29 (m, 2H, H_{Ar}–E, L), 7.30–7.37 (m, 6H, H_{Ar}–E, L), 7.49 (d, $J_{HH} = 7.4$ Hz, 2H, H_{Ar}–E), 7.56 (d, 2H, $J_{HH} = 7.4$ Hz, H_{Ar}–L), 7.67 (d, $J_{HH} = 7.5$ Hz, 1H, H_{Ar}–E), 7.71 (d, $J_{HH} = 7.7$ Hz, 1H, H_{Ar}–L), 8.70 (b, 1H, N*H*–L), and 9.88 (b, 1H, O*H*–E) ppm (L and E stand for lactam and enol forms, respectively, and lactam : enol *ca* 1 : 1). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 24.4, (*C*H$_3$–L), 24.7 (*C*H$_3$–E), 58.3 (*C*H–L), 61.6 (*C*H–E), 110.4 (*C*–Ar), 112.0 (*C*–Ar), 116.7 (*C*–Ar), 122.6 (*C*–Ar), 123.0 (*C*–Ar), 126.6 (2*C*–Ar), 126.9 (*C*–Ar), 127.0 (3*C*–Ar), 127.2 (2*C*–Ar), 128.4 (3*C*–Ar), 128.7 (3*C*–Ar), 132.7 (*C*–Ar), 133.5 (*C*–Ar), 142.8 (*C*–Ar), 144.0 (*C*–Ar), 145.3 (*C*–Ar), 151.3 (*C*=N–L), 153.4 (*C*=N–E), 160.2 (*C*=O–L), and 165.9 (*C*–OH–E) ppm. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.52 (d, $J_{HH} = 6.4$ Hz, 3H, C*H*$_3$–E), 1.62 (d, $J_{HH} = 6.4$ Hz, 3H, C*H*$_3$–L), 5.64 (q, $J_{HH} = 6.4$ Hz, 1H, C*H*–L), 6.61 (q, $J_{HH} = 6.4$ Hz, 1H, C*H*–E), 6.91 (d, $J_{HH} = 8.0$ Hz, 1H, H_{Ar}–E), 6.99 (dd, $J_{HH} = 6.8$ Hz, 0.8 Hz, 1H, H_{Ar}–L), 7.05 (ddd, $J_{HH} = 6.8$ Hz, 0.8 Hz, 2H, H_{Ar}–E, L), 7.21–7.24 (m, 2H, H_{Ar}–E, L), 7.30–7.37 (m, 4H, H_{Ar}–E, L), 7.38–7.43 (m, 2H, H_{Ar}–E & 1H, H_{Ar}–L), 7.50–7.55 (m, 2H, H_{Ar}–E), 7.55–7.60 (m, 2H, H_{Ar}–L), 7.91

(d, $J_{HH} = 7.2$ Hz, 1H, H_{Ar}–L), 9.73 (b, 1H, N*H*–L), and 9.84 (b, 1H, O*H*–E) ppm (lactam : enol *ca* 4.5 : 1, after 15 min of solution preparation). ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.48 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3–E), 1.54 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3–L), 5.55 (q, $J_{HH} = 6.4$ Hz, 1H, C*H*–L), 6.54 (q, $J_{HH} = 6.9$ Hz, 1H, C*H*–E), 6.84 (d, $J_{HH} = 7.5$ Hz, 1H, H_{Ar}–E), 6.90 (d, $J_{HH} = 7.5$ Hz, 1H, H_{Ar}–L), 7.01–7.05 (m, 2H, H_{Ar}–E, L), 7.21–7.26 (m, 2H, H_{Ar}–E, L), 7.32–7.36 (m, 6H, H_{Ar}–E, L), 7.37–7.39 (m, 1H, H_{Ar}–E), 7.39–7.42 (m, 2H, H_{Ar}–E), 7.47–7.52 (m, 2H, H_{Ar}–L), 7.87 (d, $J_{HH} = 7.5$ Hz, 1H, H_{Ar}–L), 10.84 (s, 1H, N*H*–L), and 10.94 (s, 1H, O*H*–E) ppm (lactam : enol *ca* 1.4 : 1). Anal. Calcd for $C_{16}H_{14}N_2O$ (250.30): C, 76.78; H, 5.64; N, 11.19. Found: C, 76.18; H, 5.42; N, 10.89.

2.2.2. 3-{(*R*)-(2-methoxyphenyl)-ethylimino}-1,3-dihydro-indol-2-one (*HL2*). Isatin (1.50 g, 10.20 mmol) and (*R*)-(2-methoxyphenyl)ethylamine (1.54 g, 10.20 mmol). Yield: 2.41 g (84% from isatin). $[\alpha]^{25}$ ($c = 0.30$, $CHCl_3$): + 70.32° (589 nm). UV-Vis (4.22×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 381 (1456), and 291 (4070). IR (KBr): 3270sb (νN–H), 3094, 3028, 2968, 2923m (νC–H), 1749, 1724vs (νC=Oasy), 1640, 1619, 1593vs (νC=N), 1517vs (νC–Oasy), and 1464vs (νC=Osy) cm^{-1}. MS (ESI): *m*/*z* (%) 599 (70) $[M_2 + K]^+$, 583 (40) $[M_2 + Na]^+$, 561 (7) $[M_2 + H]^+$, 319 (100) $[M + K]^+$, 303 (15) $[M + Na]^+$, and 281 (30) $[M + H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.59 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3–E), 1.70 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3–L), 3.75 (s, OCH_3–E), 3.81 (s, OCH_3–L), 5.52 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–L), 6.56 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–E), 6.75 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–E), 6.88–6.91 (m, 4H, H_{Ar}–L, E), 6.92 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–L), 7.05 (t, $J_{HH} = 7.5$ Hz, 2H, H_{Ar}–L, E), 7.36 (ddd, $J_{HH} = 7.6$ Hz, 2H, H_{Ar}–L, E), 7.40 (d, $J_{HH} = 8.6$ Hz, 2H, H_{Ar}–E), 7.45 (d, 2H, $J_{HH} = 5.6$, H_{Ar}–L), 7.68 (d, $J_{HH} = 7.5$, 1H, H_{Ar}, E), 7.73 (d, $J_{HH} = 7.6$, 1H, H_{Ar}, L), 8.10 (b, 1H, N*H*–L), and 9.19 (b, 1H, O*H*–E) ppm (lactam : enol *ca* 1 : 1.2).

2.2.3. 3-{(*R*)-(4-methoxyphenyl)-ethylimino}-1,3-dihydro-indol-2-one (*HL3*). Isatin (1.50 g, 10.20 mmol) and (*R*)-(4-methoxyphenyl)ethylamine (1.54 g, 10.20 mmol). Yield: 2.35 g (82% from isatin). $[\alpha]^{25}$ (c = 0.24, $CHCl_3$): + 75.00° (589 nm). UV-Vis (4.20×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 382 (1400), and 291 (4130). IR (KBr): 3238sb (νN–H), 3090, 3008, 2981, 2920m (νC–H), 1751, 1722vs (νC=Oasy), 1639, 1612, 1590vs (νC=N), 1514vs (νC–Oasy), and 1466vs (νC=Osy) cm^{-1}. MS (ESI): *m*/*z* (%) 599 (90) $[M_2 + K]^+$, 583 (50) $[M_2 + Na]^+$, 561 (5) $[M_2 + H]^+$, 319 (100) $[M + K]^+$, 303 (12) $[M + Na]^+$, and 281 (30) $[M + H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3–E), 1.72 (d, $J_{HH} = 6.5$ Hz, 3H, CH_3–L), 3.78 (s, OCH_3–E), 3.79 (s, OCH_3–L), 5.50 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–L), 6.54 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–E), 6.79 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–E), 6.86–6.89 (m, 4H, H_{Ar}–L, E), 6.94 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–L), 7.04 (t, $J_{HH} = 7.5$ Hz, 2H, H_{Ar}–L, E), 7.34 (ddd, $J_{HH} = 7.6$ Hz, 2H, H_{Ar}–L, E), 7.41 (d, $J_{HH} = 8.6$ Hz, 2H, H_{Ar}–E), 7.47 (d, 2H, $J_{HH} = 5.6$, H_{Ar}–L), 7.66 (d, $J_{HH} = 7.5$, 1H, H_{Ar}, E), 7.72 (d, $J_{HH} = 7.6$, 1H, H_{Ar}, L), 8.14 (b, 1H, N*H*–L), and 9.17 (b, 1H, O*H*–E) ppm (lactam : enol *ca* 1 : 1.2). Anal. Calcd for $C_{17}H_{16}N_2O_2$ (280.32): C, 72.84; H, 5.75; N, 9.99. Found: C, 71.90; H, 5.50; N, 9.59.

2.2.4. 3-{(*R*)-(4-bromophenyl)-ethylimino}-1,3-dihydro-indol-2-one (*HL4*). Isatin (1.50 g, 10.20 mmol) and (*R*)-(4-bromophenyl)ethylamine (2.04 g, 10.20 mmol).

Yield: 2.85 (85% from isatin). $[\alpha]^{25}$ ($c = 0.19$, $CHCl_3$): + 42.00° (589 nm). UV-Vis (4.50×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 382 (1430), and 290 (4100). IR (KBr): 3278sb (νN–H), 3090, 3058, 2980, 2920m (νC–H), 1751, 1720vs (νC=Oasy), 1641, 1610, 1589vs (νC=N) and 1464vs (νC=Osy) cm^{-1}. MS (ESI): *m*/*z* (%) 351 (100) $[M + Na]^+$, and 329 (15) $[M + H]^+$ ($^{79/81}$Br isotopic pattern is clearly visible following these peaks). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, $J_{HH} = 6.4$ Hz, 3H, C*H*$_3$–E), 1.71 (d, $J_{HH} = 6.6$ Hz, 3H, C*H*$_3$–L), 5.49 (q, $J_{HH} = 6.6$ Hz, 1H, C*H*–L), 6.51 (q, $J_{HH} = 6.6$ Hz, 1H, C*H*–E), 6.81 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–E), 6.97 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–L), 7.06 (dt, $J_{HH} = 6.9$ Hz, 1.8 Hz, 2H, H_{Ar}–E, –L), 7.33–7.35 (m, 1H, H_{Ar}–E), 7.36–7.38 (m, 1H, H_{Ar}–L), 7.39–7.40 (m, 2H, H_{Ar}–E, –L), 7.41–7.44 (m, 3H, H_{Ar}–E + 2H, H_{Ar}–L), 7.46–7.48 (m, 1H, H_{Ar}–L), 7.66 (d, $J_{HH} = 7.4$ Hz, 1H, H_{Ar}–E), 7.68 (d, $J_{HH} = 7.6$ Hz, 1H, H_{Ar}–L), 8.45 (b, 1H, N*H*–L), and 9.54 (b, 1H, O*H*–E) ppm (lactam : enol *ca* 1 : 1.1). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 24.1, (*C*H$_3$–L), 24.7 (*C*H$_3$–E), 57.7 (*C*H–L), 60.9 (*C*H–E), 110.4 (*C*–Ar), 112.0 (*C*–Ar), 116.6 (*C*–Ar), 120.6 (Br*C*–Ar), 121.0 (Br*C*–Ar), 122.4 (*C*–Ar), 122.7 (*C*–Ar), 123.2 (*C*–Ar), 126.9 (*C*–Ar), 128.4 (2*C*–Ar), 128.7 (3*C*–Ar), 131.5 (3*C*–Ar), 131.7 (2*C*–Ar), 132.9 (*C*–Ar), 133.7 (*C*–Ar), 143.1 (*C*–Ar), 144.4 (*C*–Ar), 145.2 (*C*–Ar), 151.5 (*C*=N–L), 153.6 (*C*=N–E), 160.1 (*C*=O–L), and 165.5 (*C*–OH–E) ppm. Anal. Calcd for $C_{16}H_{13}BrN_2O$ (329.19): C, 58.38; H, 3.98; N, 8.51. Found: C, 58.12; H, 3.73; N, 8.33.

2.2.5. 3-{(*R*)-(1-naphthyl)-ethylimino}-1,3-dihydro-indol-2-one (HL5). Isatin (1.50 g, 10.20 mmol) and (*R*)-(1-naphthyl)ethylamine (1.75 g, 10.22 mmol). Yield: 2.50 g (82% from isatin). $[\alpha]^{25}$ ($c = 0.23$, $CHCl_3$): + 21.74° (589 nm). UV-Vis (4.70×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 381 (1397), and 291 (4023). IR (KBr): 3253sb (νN–H), 3088, 3052, 2975, 2929m (νC–H), 1755, 1720vs (νC=O), 1645, 1612, 1578vs (νC=N) and 1464vs (νC=Osy) cm^{-1}. MS (ESI): *m*/*z* (%) 639 (10) $[M_2 + K]^+$, 623 (25) $[M_2 + Na]^+$, 601 (12) $[M_2 + H]^+$, 339 (15) $[M + K]^+$, 323 (20) $[M + Na]^+$, and 301 (100) $[M + H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.68 (d, $J_{HH} = 6.5$ Hz, 3H, C*H*$_3$–E), 1.82 (d, $J_{HH} = 6.6$ Hz, 3H, C*H*$_3$–L), 5.68 (q, $J_{HH} = 6.6$ Hz, 1H, C*H*–L), 6.73 (q, $J_{HH} = 6.5$ Hz, 1H, C*H*–E), 6.80 (d, $J_{HH} = 7.7$ Hz, 1H, H_{Ar}–E), 6.95 (d, $J_{HH} = 7.8$ Hz, 1H, H_{Ar}–L), 7.00–7.11 (m, 2H, H_{Ar}–E, L), 7.37–7.40 (m, 2H, H_{Ar}–E, L), 7.41–7.46 (m, 4H, H_{Ar}–E, L), 7.65 (dd, $J_{HH} = 6.7$ Hz, 1.7 Hz, 1H, H_{Ar}–L), 7.71–7.75 (m, 2H, H_{Ar}–E & 1H, H_{Ar}–L), 7.80–7.86 (m, 6H, H_{Ar}–E, L), 7.92 (s, 1H, H_{Ar}–E), 7.97 (s, 1H, H_{Ar}–L), 8.12 (b, 1H, N*H*–L), and 9.22 (b, 1H, O*H*-E) ppm (lactam : enol *ca* 1 : 1.3). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 24.5, (*C*H$_3$–L), 24.7 (*C*H$_3$–E), 58.5 (*C*H–L), 61.7 (*C*H–E), 110.3 (*C*–Ar), 111.8 (*C*–Ar), 122.6 (*C*–Ar), 122.7 (*C*–Ar), 123.1 (2*C*–Ar), 124.9 (*C*–Ar), 125.0 (*C*–Ar), 125.3 (2*C*–Ar), 125.5 (2*C*–Ar), 125.7 (2*C*–Ar), 125.9 (*C*–Ar), 126.1 (*C*–Ar), 127.1 (2*C*–Ar), 127.6 (2*C*–Ar), 127.9 (*C*–Ar), 128.1 (2*C*–Ar), 128.5 (*C*–Ar), 132.7 (2*C*–Ar), 133.5 (2*C*–Ar), 141.5 (*C*–Ar), 142.6 (*C*–Ar), 142.8 (*C*–Ar), 145.1 (*C*–Ar), 151.8 (*C*=N–L), 153.2 (*C*=N–E), 160.8 (*C*=O–L), and 166.1 (*C*–OH–E) ppm. Anal. Calcd for $C_{20}H_{16}N_2O$ (300.35): C, 79.98; H, 5.37; N, 9.33. Found: C, 79.29; H, 5.13; N, 9.03.

2.3. *General procedure to synthesize the [Rh(η^4-cod){3-((R)-(Ar)-ethylimino)-3H-indol-2-olato}] (1–3)*

Two equivalents of 3-{(*R*)-(phenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL1**) and one equivalent of $[Rh(\eta^4\text{-cod})(\mu\text{-}O_2CCH_3)]_2$ (cod = 1,5-cyclooctadiene) were dissolved

in 10 mL of C_6H_6/MeOH (4 : 1, v/v) and stirred at room temperature. The color changed from red-orange to red-brown after 10 min stirring. The solvent was evaporated *in vacuo* at 40°C after 5–6 h stirring. The products were dissolved in 10 mL of C_6H_6/MeOH (4 : 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 red-brown [Rh(η^4-cod){3-((*R*)-(phenyl)-ethylimino)-3*H*-indol-2-olato}] (**1**). The same procedure was followed for syntheses of **2** and **3** by using 3-{(*R*)-(4-methoxyphenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL3**) and 3-{(*R*)-(4-bromophenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL4**), respectively.

2.3.1. [Rh(η^4-cod){3-((*R*)-(phenyl)-ethylimino)-3*H*-indol-2-olato}] (1). HL1 (65 mg, 0.26 mmol) and [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ (70 mg, 0.13 mmol). Yield: 85 mg (71%). UV-Vis (1.66×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 344 (2675) and 506sh (308). CD (5.80×10^{-4} dm^{-3} mol, $CHCl_3$): λ_{max}/nm ($\Delta\epsilon_{max}$/dm mol^{-1} cm^{-1}) = 322 (+ 0.53), 412 (+ 0.22), and 584 (−0.19). IR (KBr): 3064, 3050, 2925w (νC–H), and 1734, 1618, 1577vs (νC=N) cm^{-1}. MS (ESI): *m*/*z* (%) 460 (100) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.74 (d, J_{HH} = 7.5 Hz, 3H, CH_3), 1.90 (m, 4H, CH_2cod$_{exo}$), 2.20, 2.37 (m, 4H, CH_2cod$_{endo}$), 4.10, 4.20 (m, 4H, C*H*cod), 4.58 (m, 1H, C*H*), 6.55 (d, J_{HH} = 6.5 Hz, 1H, H_{Ar}), 6.80 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}), 7.07 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}), 7.26–7.40 (m, 5H, H_{Ar}), and 7.55 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}).

2.3.2. [Rh(η^4-cod){3-((*R*)-(4-methoxyphenyl)-ethylimino)-3*H*-indol-2-olato}] (2). HL3 (68 mg, 0.24 mmol) and [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ (65 mg, 0.12 mmol). Yield: 80 mg (68%). UV-Vis (1.79×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 346 (2755) and 506 (358). IR (KBr): 3060, 3055, 2930w (νC–H), and 1735, 1620, 1570vs (νC = N) cm^{-1}. MS (ESI): *m*/*z* (%) 490 (100) $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.73 (d, J_{HH} = 7.0 Hz, 3H, CH_3), 1.91 (m, 4H, CH_2cod$_{exo}$), 2.27, 2.42 (m, 4H, CH_2cod$_{endo}$), 3.71 (s, 3H, OCH_3), 4.08, 4.17 (m, 4H, C*H*cod), 4.55 (m, 1H, C*H*), 6.53 (d, J_{HH} = 6.5 Hz, 1H, H_{Ar}), 6.80 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}), 7.03 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}), 7.20–7.41 (m, 4H, H_{Ar}), and 7.62 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}).

2.3.3. [Rh(η^4-cod){3-((*R*)-(4-bromophenyl)-ethylimino)-3*H*-indol-2-olato}] (3). HL4 (79 mg, 0.24 mmol) and [Rh(η^4-cod)(μ-O_2CCH_3)]$_2$ (65 mg, 0.12 mmol). Yield: 85 mg (66%). UV-Vis (1.53×10^{-4} mol dm^{-3}, $CHCl_3$): λ_{max}/nm (ϵ_{max}/dm mol^{-1} cm^{-1}) = 348 (2695) and 506sh (348). IR (KBr): 3065, 3052, 2928w (νC–H), and 1738, 1622, 1572vs (νC = N) cm^{-1}. MS (ESI): *m*/*z* (%) 539 (20) $[M+H]^+$, 329 (15) $[\mathbf{HL4}+H]^+$, and 211 (30) $[Rh(\eta^4\text{-cod})]^+$ ($^{79/81}$Br isotopic pattern is clearly visible following the peaks at 539 and 329). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.71 (d, J_{HH} = 7.0 Hz, 3H, CH_3), 1.95 (m, 4H, CH_2cod$_{exo}$), 2.25, 2.40 (m, 4H, CH_2cod$_{endo}$), 4.05, 4.20 (m, 4H, C*H*cod), 4.52 (m, 1H, C*H*), 6.58 (d, J_{HH} = 6.5 Hz, 1H, H_{Ar}), 6.83 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}), 7.02 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}), 7.20–7.48 (m, 4H, H_{Ar}), and 7.71 (d, J_{HH} = 7.5 Hz, 1H, H_{Ar}).

2.4. *X-ray data collection and solution*

Single crystals were mounted on glass fibers and all geometric and intensity data were taken from these samples using Bruker Apex-II CCD (for **HL1**) or Bruker SMART APEX CCD (for **HL4**) diffractometers using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 172 ± 2 K (**HL1**) or 150 ± 2 K (**HL4**). Data reductions were carried out with SAINT PLUS and absorption corrections applied using SADABS. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference Fourier synthesis. All atoms were located by difference-Fourier synthesis and non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Structure solution used SHELXTL PLUS V6.10 program package.

2.4.1. Crystallographic data for HL1. Yellow needle, $C_{16}H_{14}N_2O$, $0.50 \times 0.28 \times 0.20\,mm^3$, orthorhombic, $P2_12_12_1$, $a = 9.898(2)$ Å, $b = 11.024(2)$ Å, $c = 12.001(2)$ Å, $V = 1309.5(3)$ Å^3, $Z = 4$, $d_{calc} = 1.270\,g\,cm^{-3}$, $\mu = 0.081\,mm^{-1}$, $F(000) = 528$, final R indices [$F^2 > 2\sigma$] $R_1 = 0.0389$, $wR_2 = 0.0999$; R indices (all data): $R_1 = 0.0432$, $wR_2 = 0.1040$, and Flack parameter = 0.3(11).

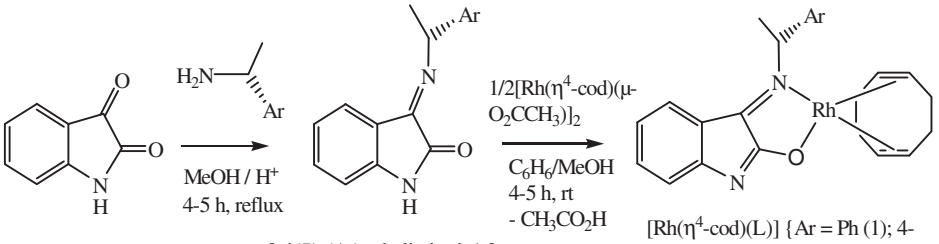
2.4.2. Crystallographic data for HL4. Yellow block, $C_{16}H_{13}BrN_2O$, $0.28 \times 0.20 \times 0.12\,mm^3$, monoclinic, $P2_1$, $a = 5.019(1)$ Å, $b = 9.515(2)$ Å, $c = 14.281(3)$ Å, $\beta = 91.057(4)^\circ$, $V = 681.9(3)$ Å^3, $Z = 2$, $d_{calc} = 1.603\,g\,cm^{-3}$, $\mu = 3.011\,mm^{-1}$, $F(000) = 332$, final R indices [$F^2 > 2\sigma$] $R_1 = 0.0339$, $wR_2 = 0.0704$; R indices (all data): $R_1 = 0.0409$, $wR_2 = 0.0721$, and Flack parameter = 0.003(10).

3. Results and discussion

Condensation of isatin with primary amines, (*R*)-(Ar)-ethylamine gives enantiopure isatin Schiff bases, 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (**HL**) {Ar = Ph (**HL1**), 2-MeOC$_6$H$_4$ (**HL2**), 4-MeOC$_6$H$_4$ (**HL3**) 4-BrC$_6$H$_4$ (**HL4**), and 1-naphthyl (**HL5**)} in high yields (82–85%) (scheme 1). The Schiff bases, upon conversion to the enol form, coordinate to [Rh(μ-O$_2$CMe)(η^4-cod)]$_2$ (cod = 1,5-cyclooctadiene) to give [Rh(η^4-cod){3-((*R*)-(Ar)-ethylimino)-3*H*-indol-2-olato}], [Rh(η^4-cod)(**L**)] {Ar = Ph (**1**), 4-MeOC$_6$H$_4$ (**2**) and 4-BrC$_6$H$_4$ (**3**)} in C$_6$H$_6$/MeOH (4 : 1, v/v) (scheme 1).

3.1. *Mass spectra*

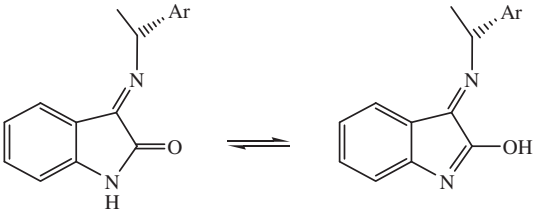
ESI-MS spectral data of the Schiff bases show the parent ion peak $[M + H]^+$ at $m/z = 251$ (**HL1**), 281 (**HL2** or **HL3**), 329 (**HL4**), and 301 (**HL5**), respectively. The spectra are further dominated by several ion peaks for $[M + Na/K]^+$, $[M_2 + H/Na/K]^+$, and $[CH(CH_3)(Ar)]^+$ species, respectively. Mass spectra of the complexes show the parent ion peak $[M + H]^+$ at $m/z = 460$ (**1**), 490 (**2**), and 539 (**3**), respectively. Further, $^{79/81}$Br isotopic pattern is clearly visible from the mass spectra at $m/z = 351$, 329 in **HL4** and at $m/z = 539$, 329 in **3**.



3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (HL) {Ar = Ph (HL1); 2-$MeOC_6H_4$ (HL2); 4-$MeOC_6H_4$ (HL3); 4-BrC_6H_4 (HL4); 1-naphthyl (HL5)}

[Rh(η^4-cod)(L)] {Ar = Ph (1); 4-$MeOC_6H_4$ (2); 4-BrC_6H_4 (3)}

Scheme 1. Synthetic route to the formulation of 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (**HL**) and [Rh(η^4-cod)(**L**)].



3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one

(Lactam, L)

3-{(*R*)-(Ar)-ethylimino}-3 *H*-indol-2-ol

(Enol, E)

Scheme 2. Lactam (L) ⇌ enol (E) isomerization in solution.

3.2. *IR spectra*

IR spectral data (Supplementary material) are mainly characteristic of the Schiff bases [9–15]. Thus each shows a strong broad band at 3300–3238 cm^{-1} assigned to ν(N–H). Two very strong bands at 1755–1720 cm^{-1} and 1466–1464 cm^{-1} are assigned to the ν(C=O) asymmetric stretch and symmetric stretch, respectively, in the Schiff bases. Several strong bands at 1645–1640, 1620–1612, and 1598–1590 cm^{-1} are assigned to ν(C=N) in the Schiff bases and complexes. The Schiff bases undergo lactam (L) ⇌ enol (E) isomerization (scheme 2) in solution, and subsequently, the enol form coordinates to Rh(η^4-cod) to form the complexes. The O–H bond (enol form) is deprotonated while forming the ionic bond between the Rh^+ and O^- in the complexes (scheme 1). As a result, any bands associated with ν(N–H) and/or ν(O–H) are absent in the complexes. Similarly, two very strong ν(C=O) bands of the Schiff bases are absent in the complexes. Several weaker bands at 3097–3008 and 2980–2925 cm^{-1} are assigned to ν(H–C) for aromatic and aliphatic hydrogen atoms, respectively.

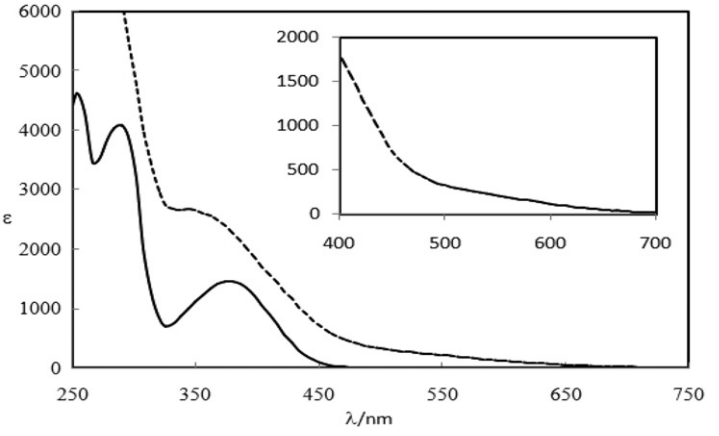


Figure 1. Electronic spectra of 3-((*R*)-(1-phenyl)-ethylimino)-1,3-dihydro-indol-2-one (**HL1**) (—: 4.88×10^{-4} mol dm^{-3}) and [Rh(η^4-cod){3-((*R*)-(phenyl)-ethylimino)-3*H*-indol-2-olato}] (**1**) (- - -: 1.66×10^{-4} mol dm^{-3}) in $CHCl_3$ at 20°C.

3.3. *Polarimetry*

Polarimetric measurements in $CHCl_3$ exhibit rotations to the right at +50.17° (**HL1**), +70.32° (**HL2**), +75.00° (**HL3**), +42.00° (**HL4**), and +21.74° (**HL5**) at 589 nm and 25°C for the enantiopure Schiff bases of 3-{(*R*)-(*Ar*)-ethylimino}-1,3-dihydro-indol-2-one.

3.4. *Electronic spectra*

Electronic spectra (figure 1) show (i) a strong broad band at 325–450 nm with absorption maxima at $\lambda_{max} = 381$–382 nm ($\epsilon_{max} = 1397$–1456 dm^3 mol^{-1} cm^{-1}), associated with intraligand $n \rightarrow \pi^*$ transitions of imine, and (ii) a very strong band at higher energy (<325 nm) with absorption maxima at $\lambda_{max} = 290$–291 nm ($\epsilon_{max} = 4070$–4130 dm^3 mol^{-1} cm^{-1}), associated with intraligand $\pi \rightarrow \pi^*$ transitions in the Schiff bases [12–20]. The same bands are also found in the complexes (figure 1). The complexes further show a weak broad band at lower energy (450–700 nm) due to charge-transfer (CT) transitions based on the formation of [Rh(η^4-cod)]$^+$ and [Rh(**L1**)] (**L1** = deprotonated Schiff base) species [12–20].

3.5. *CD spectra*

CD spectrum of **HL1** (figure 2) shows the presence of two strong bands (below 320 nm and 320–450 nm) with two negative ellipticity maxima at 308 nm ($\Delta\epsilon = -0.89$ dm^3 mol^{-1} cm^{-1}) and 377 nm ($\Delta\epsilon = -1.42$ dm^3 mol^{-1} cm^{-1}) for intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, confirming the enantiopurity of the Schiff base. Complex **1** shows the same bands (figure 2) with positive ellipticity maxima at 322 nm ($\Delta\epsilon = +0.53$ dm^3 mol^{-1} cm^{-1}) and 412 nm ($\Delta\epsilon = +0.22$ dm^3 mol^{-1} cm^{-1}), respectively, confirming its enantiopurity. A weak broad band at 450–700 nm with negative ellipticity maximum at 584 nm ($\Delta\epsilon = -0.19$ dm^3 mol^{-1} cm^{-1}) is due to CT transitions of [Rh(η^4-cod)]$^+$ and [Rh(**L1**)] (**L1** = deprotonated Schiff base) species [12–20].

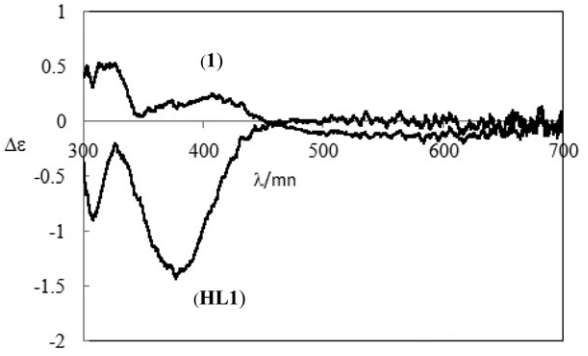


Figure 2. CD spectra of 3-((*R*)-(1-phenyl)-ethylimino)-1,3-dihydro-indol-2-one (**HL1**) (4.88×10^{-4} mol dm^{-3}) and [Rh(η^4-cod){3-((*R*)-(phenyl)-ethylimino)-3*H*-indol-2-olato}] (**1**) (5.80×10^{-4} mol dm^{-3}) in $CHCl_3$ at 20°C.

3.6. *NMR spectra*

3.6.1. ^{1}H NMR spectra and lactam–enol interconversion. ^{1}H NMR spectra of **HL1–HL5** in $CDCl_3$ are shown in "Supplementary material," and spectral data are summarized in section 2. The spectra correspond well with those of related compounds [8–15]. The Schiff bases undergo slow isomerization from one tautomer to another, lactam (L) ⇌ enol (E) (scheme 2), and both forms appear simultaneously in solution as shown from the ^{1}H NMR spectrum of **HL1** (Supplementary material). The methyls are two doublets of equal intensities at δ 1.6–1.7 and 1.7–1.8 ppm ($J = 6.5$ Hz) for the enol and lactam forms, respectively. The methine protons are quartets at δ 5.6 and 6.6 ppm ($J = 6.5$ Hz), the enol form being shifted to lower field by *ca* 1.0 ppm. The N–*H* (lactam) and O–*H* (enol) protons show broad signals between δ 8.1–8.7 and 9.2–9.8 ppm, respectively. Methoxy protons are singlets at δ 3.75–3.77 and δ 3.79–3.81 ppm for the enol and lactam forms, respectively, in **HL2** and **HL3**. Several doublets and multiplets are observed at the range of δ 6.6–7.8 ppm for the aromatic protons (section 2).

In order to further probe the lactam and enol forms, time-dependent ^{1}H NMR spectra of **HL1** were taken in acetone-d_6 (figure 3). The spectra show that immediately upon dissolution (*ca* 15 min) the major tautomer is the lactam form with only a small amount of the enol form present (lactam : enol *ca* 4.5 : 1). This ratio becomes 1 : 1 after approximately 2 h, and after 1 day the enol form is the major tautomer (lactam:enol *ca* 1 : 4.5). No further significant changes were noted upon further standing, suggesting that equilibrium has been established. The peak assignments for the lactam and enol forms are made based on the time-dependent ^{1}H NMR spectra of **HL1** in acetone-d_6 (figure 3).

3.6.2. Solvent effects. To study solvent effects the ^{1}H NMR spectrum of **HL1** was run in acetone-d_6 and DMSO-d_6. The chemical shifts of C*H*$_3$, C*H*, and aromatic protons for both the enol and lactam forms remain almost unchanged in $CDCl_3$, acetone-d_6, and DMSO-d_6 solution (see section 2). The N–*H* (lactam) signal shifts to lower field in acetone-d_6 (δ 9.73 ppm) in contrast to that in $CDCl_3$ (δ 8.70 ppm), whereas the O–*H* (enol) signal remains unchanged (δ 9.88 ppm in $CDCl_3$ and 9.84 ppm in acetone-d_6).

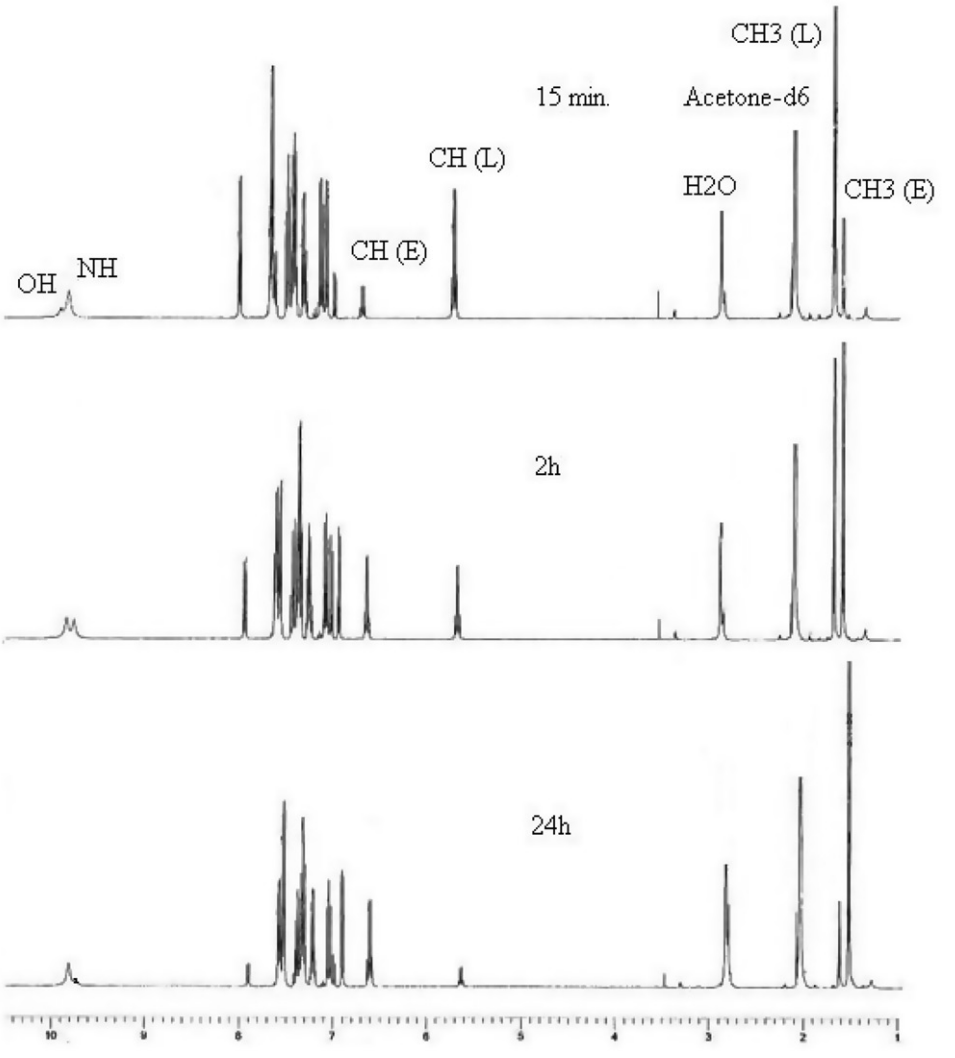


Figure 3. Time-dependent ^{1}H NMR spectrum of 3-{(*R*)-(phenyl)-ethylimino}-1,3-dihydro-indol-2-one (**HL1**) in acetone-d_6 at 20°C.

In DMSO-d_6, both the N–*H* and O–*H* signals shift to lower field by *ca* 1–2 ppm (δ 10.84 and 10.94 ppm, respectively) in contrast to those in $CDCl_3$ (δ 8.73 and 9.85 ppm). These results suggest that both the N–*H* and O–*H* protons are involved in intermolecular hydrogen-bonding and/or hydrogen-bonding to the solvent molecules [8, 14].

3.6.3. ^{13}C NMR spectra. ^{13}C NMR spectra of the chiral Schiff bases in $CDCl_3$ (section 2) also show the existence of the enol and lactam forms simultaneously, as shown in Supplementary material for **HL4**. Thus each Schiff base shows two methyl singlets at δ 24.1–24.5 ppm and δ 24.5–24.7 ppm for the enol and lactam forms, respectively. The methine carbon appears as two singlets at δ 57.7–58.5 ppm and δ 60.9–61.7 ppm for the

lactam and enol forms, respectively. The imide carbon (H*C*=N) shows singlets at δ 151.3 (**HL1**), 151.5 (**HL4**), and 151.8 ppm (**HL5**) for lactam forms, and at δ 153.4 (**HL1**), 153.6 ppm (**HL4**), and 153.2 ppm (**HL5**) for enol forms. The ketonic carbon (*C*=O) shows singlets at δ 160.2 (**HL1**), 160.1 (**HL4**), and 160.8 ppm (**HL5**) and the enolic carbon (*C*–OH) at δ 165.9 (**HL1**), 165.5 (**HL4**), and 166.1 ppm (**HL5**). The aromatic carbons show several singlets for both the enol and lactam forms at δ 110.0–145.0 ppm (section 2).

3.6.4. ^{1}H NMR spectra of complexes. The exo-methylene protons of the coordinated 1,5-cyclooctadiene to Rh(I) show a multiplet at δ 1.90–1.95 ppm, whereas the endo-methylene protons show two multiplets at δ 2.20–2.27 ppm and 2.37–2.42 ppm in **1**–**3**. The olefin protons show two multiplets, the downfield one at δ 4.17–4.20 ppm isassigned to "H *trans* to N" and the upfield one at 4.05–4.10 ppm to "H *trans* to O" [12–17]. The methyl protons of coordinated Schiff base show doublets at δ 1.71–1.74 ppm ($J = 7.0$ Hz), while the methine proton is a multiplet at δ 4.52–4.58 ppm. The methoxy protons are a singlet at δ 3.71 ppm in **2**. However, the N–*H* (lactam) and/or O–*H* (enol) protons are absent in the complexes (broad peaks at δ 8.1–8.7 and 9.2–9.8 ppm, respectively, in the free Schiff bases), suggesting formation of an ionic bond between Rh^+ and O^- *via* deprotonation due to complexation. Several doublets and multiplets are observed at δ 6.5–7.7 ppm for aromatic protons (section 2) in the complexes.

3.7. *Solid-state structures of the Schiff bases*

In order to fully elucidate the structures of the chiral Schiff bases in the solid state, single-crystal X-ray studies were carried out on both **HL1** and **HL4**. The molecular structures are shown in figure 4 together with a summary of key bond lengths and angles. Both molecules crystallize in chiral space groups; **HL1** in orthorhombic $P2_12_12_1$ and **HL4** in the monoclinic $P2_1$ space group and the R-handed chirality is clear (absolute structure parameter 0.3(11) for **HL1**, 0.003(10) for **HL4**). Both compounds exist in the lactam form observed for the related achiral benzylamine-derived Schiff bases of isatin [4–6]. Further discussion of these structures is presented in "Supplementary material."

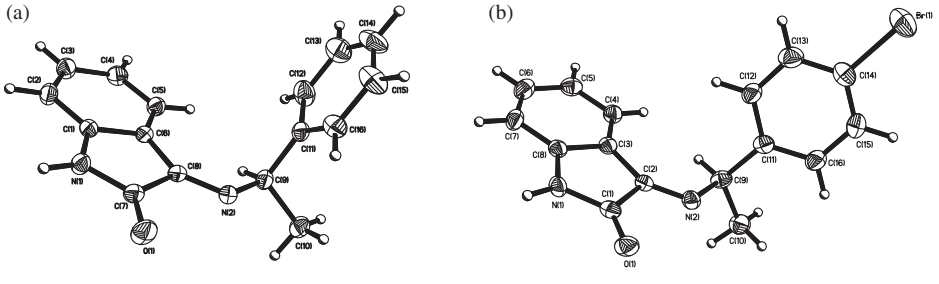


Figure 4. Molecular structures of (a) **HL1** and (b) **HL4** showing 50% probability displacement ellipsoids and the atom-numbering schemes. Selected bond lengths (Å) and angles (°); **HL1**: C(7)–O(1) 1.216(1), C(7)–C(8) 1.535(2), C(7)–N(1) 1.365(2), N(2)–C(8) 1.273(1), N(2)–C(9) 1.479(2), C(8)–N(2)–C(9) 119.8(1); **HL4**: C(1)–O(1) 1.203(3), C(1)–C(2) 1.545(4), C(1)–N(1) 1.373(4), N(2)–C(2) 1.270(4), N(2)–C(9) 1.481(4), C(14)–Br(1) 1.904(3), C(2)–N(2)–C(9) 120.8(3).

4. Conclusion

We have shown that the synthesis and purification of enantiopure Schiff bases of isatin, 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one is straightforward, suggesting that such species are readily available for biological testing. In solution the Schiff bases show similar behavior with slow conversion of the lactam to the enol form, both observed. In the solid state the lactam form dominates as shown by the crystal structures. The Schiff bases, upon conversion to the enol form, coordinate to [Rh(μ-O_2CMe)(η^4-cod)]$_2$ giving enantiopure [Rh(η^4-cod){3-((*R*)-(Ar)-ethylimino)-3*H*-indol-2-olato}]. Unlike previously reported Rh(η^4-cod)-chiral Schiff bases (where six-membered *N*,*O*-chelation occurs), the isatin Schiff bases coordinate to Rh(η^4-cod) as a five-membered *N*,*O*-chelate. Further investigations to elucidate the molecular structures of the complexes are in progress.

Supplementary material

Supplementary data contain figures S1–S6. CIF files provide details of the X-ray crystallographic structure determinations. This material is available free of charge *via* the Internet at http://pubs.acs.org. Crystal data files are also available at http://www.ccdc.cam.ac.uk/conts/retrieving.html as supplementary publications CCDC Nos 792 122 and 792123, CCDC, 12 Union Road, Cambridge, CB2 1FZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk

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