Syntheses, Spectroscopy and Crystal Structures of (*R*)-*N*-(1-Aryl-ethyl)salicylaldimines and [Rh{(*R*)-*N*-(1-aryl-ethyl)salicylaldiminato}(η^4-cod)] Complexes

Mohammed Enamullah[a], A. K. M. Royhan Uddin[a], Anne-Christine Chamayou[b], and Christoph Janiak[b]

[a] Department of Chemistry, Jahangirnagar University, Dhaka-1342, Bangladesh
[b] Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany

Reprint requests to Prof. M. Enamullah. Fax: +8802-7708069.
E-mail: menam@juniv.edu/enamullahju@yahoo.com or to
Prof. C. Janiak. Fax: +49-7612036147. E-mail: janiak@uni-freiburg.de

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Condensation of salicylaldehyde with enantiopure (*R*)-(1-aryl-ethyl)amines yields the enantiopure Schiff bases (*R*)-*N*-(1-aryl-ethyl)salicylaldimine (HSB*; aryl = phenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl (**4**), 4-bromophenyl (**5**), 2-naphthyl). These Schiff bases readily react with dinuclear (acetato)(η^4-cycloocta-1,5-diene)rhodium(I), [Rh(μ-O_2CMe)(η^4-cod)]$_2$, to afford the mononuclear complexes, cyclooctadiene-((*R*)-*N*-(1-aryl-ethyl)salicylaldiminato-$\kappa^2 N,O$)-rhodium(I), [Rh(SB*)(η^4-cod)] (SB* = deprotonated chiral Schiff base = salicylaldiminate; aryl = phenyl (**7**), 2-methoxyphenyl, 4-methoxyphenyl, 4-bromophenyl, 2-naphthyl). The complexes have been characterized by IR, UV/vis, ^{1}H/^{13}C NMR and mass spectrometry, optical rotation as well as by single-crystal X-ray structure determination for **4**, **5** and **7**. The structure of **5** shows C–Br$\cdots\pi$ contacts. Compound **7** is only the second example of a Rh(η^4-cod) complex with a six-membered Rh-*N,O*-chelate ring.

Key words: (*R*)-Schiff Bases, Rh(η^4-cod) Complexes, Chelate Complexes, π Interactions, Optical Activity, Chirality

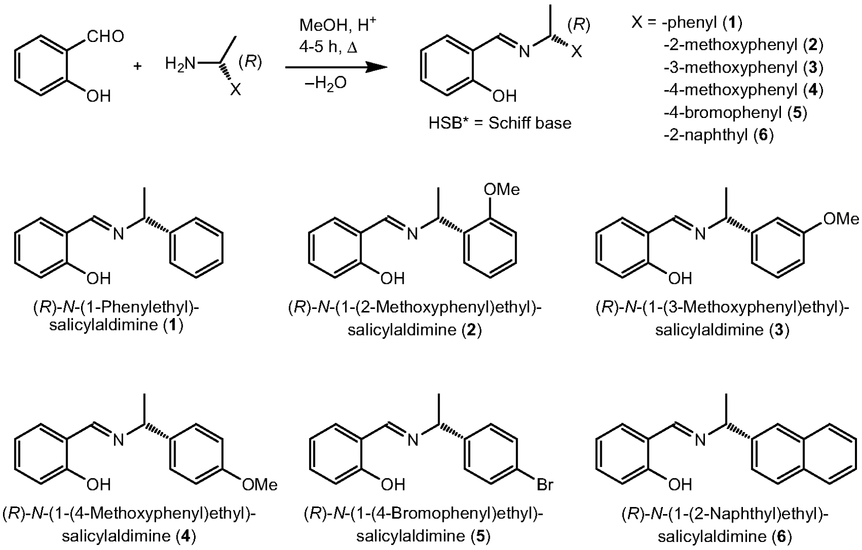
Introduction

The synthesis of chiral metal complexes is of constant interest [1]. There are continuous developments of optically active Schiff base ligands (HSB*) and their transition metal complexes for applications as chiral catalysts [2 – 9]. Examples of organometallic compounds with HSB* ligands are the half-sandwich complexes [Ru(SB*)*X*(η^6-benzene)] {SB* = (*S*)-*N*-1-phenylethylsalicylaldiminate; *X* = Cl, 4-/2-Me-py, PPh_3}, [M(SB*)*X*(η^6-arene)] (M = Ru(II), Os(II); *X* = Cl, I) [10, 11], [Ru(SB*)*X*(η^6-*p*-cymene)] (*X* = various monodentate ligands) [12, 13], and [Rh(SB*)-(η^4-cod)] {SB* = (*S*)-(α)-(2-pyridyl)-salicylaldiminate} [14].

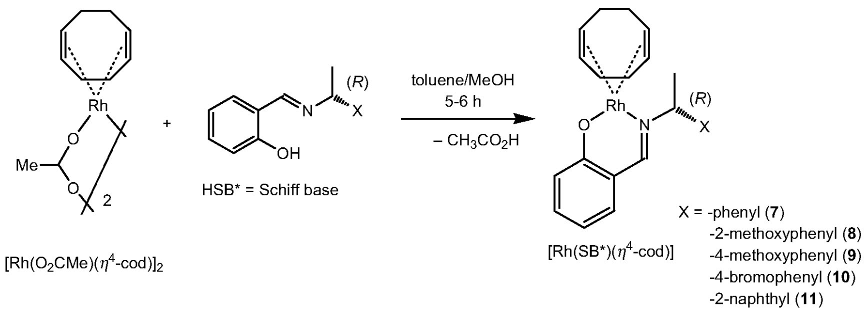
Bidentate (HSB) and tetradentate (H_2SB) Schiff bases react easily with dinuclear [Rh(μ-*X*)(η^4-cod)]$_2$ (*X* = Cl, OMe, O_2CMe; cod = 1,5-cyclooctadiene) to give mononuclear [Rh(SB)(η^4-cod)] (SB = salicylaldiminate) and dinuclear [{Rh(η^4-cod)}$_2$(SB)] (SB = *bis*-salicylaldiminate) complexes [14 – 20]. We recently synthesized Rh(η^4-cod) complexes containing chiral amino acids, chiral amino alcohols and tetradentate Schiff bases as co-ligands starting from dinuclear [Rh(μ-O_2CMe)(η^4-cod)]$_2$ [21 – 24]. In continuation, we report here the syntheses and characterizations of enantiopure Schiff base compounds HSB* and their [Rh(SB*)(η^4-cod)] complexes [SB* = (*R*)-*N*-(1-aryl-ethyl)salicylaldiminate, with *X* = phenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 4-bromophenyl, 2-naphthyl].

Results and Discussion

Condensation of the salicylaldehyde with enantiopure (*R*)-(1-aryl-ethyl)amines yields the optically active (*R*)-*N*-(1-aryl-ethyl)salicylaldimines [HSB*; aryl = phenyl (**1**), 2-methoxyphenyl (**2**), 3-methoxyphenyl (**3**), 4-methoxyphenyl (**4**), 4-bromophenyl (**5**), 2-naphthyl (**6**)] (Scheme 1). Reaction of dinuclear



Scheme 1. Synthetic route to (*R*)-*N*-(1-aryl-ethyl)salicylaldimines (HSB*; **1**–**6**).



Scheme 2. Synthetic route to Rh(SB*)(η^4-cod) (**7**–**11**).

[Rh(μ-O_2CMe)(η^4-cod)]$_2$ (cod = 1,5-cyclooctadiene) with (*R*)-*N*-(1-aryl-ethyl)salicylaldimine in toluene/MeOH affords the mononuclear complexes, cyclooctadiene-{(*R*)-*N*-(1-aryl-ethyl)salicylaldiminato-$\kappa^2 N,O$}-rhodium(I), [Rh(SB*)(η^4-cod)] (SB* = deprotonated chiral Schiff base = salicylaldiminate) (**7**–**11**), in Scheme 2.

The ^{1}H/^{13}C NMR spectra of the Schiff bases **1**–**6** and their complexes **7**–**11** correspond well to those of related compounds [2, 3, 9–11, 25–35]. The presence of $o/m/p$-OCH_3, *p*-Br and 2-naphthyl groups in **2**–**6** shifts the proton signals downfield by 0.1–0.5 ppm in contrast to those in **1** due to their electron donating inductive effect.

In the ^{1}H NMR spectra the signals for the exo- and endo-methylene protons of the rhodium-coordinated 1,5-cyclooctadiene in [Rh(SB*)(η^4-cod)] (**7**–**11**) each appear as multiplets at about 1.90 and 2.40 ppm, respectively. The olefinic protons show two multiplets at 3.6–3.7 and 4.5–4.6 ppm (except for **8**, see below). The upfield resonance at 3.6–3.7 ppm is assigned to protons '*trans* to O', and the downfield resonance at 4.5–4.6 ppm to protons '*trans* to N' [20, 24–28, 30–35].

Complex [Rh(SB*)(η^4-cod)] (**8**) with SB* = (*R*)-*N*-(1-(2-methoxyphenyl-ethyl)salicylaldiminate shows four multiplets at 3.7, 4.3, 4.4 and 4.5 ppm. The *ortho*-OCH_3 substituent on the phenyl ligand leads to stronger steric interactions with the olefin protons in comparison to *meta*/*para*-OCH_3 and thereby creates sufficient differences in chemical shifts between 'left' and 'right' protons. Similar olefin proton resonances are observed in [M(sal=N-*o*/*p*-toluene)(η^4-cod)] (M = Rh, Ir) [20], showing three multiplets for *o*-toluene and two multiplets for *p*-toluene (see Table 1). Also, the dinuclear complexes [(Rh(η^4-cod))$_2$(salophen)] [24] and [Rh(μ-hp/μ-mhp)(η^4-cod)]$_2$ [27] show four multiplets.

In $CDCl_3$ the proton signal for C*H*=N of the Schiff bases at 8.2–8.4 ppm is shifted upon Rh complexa-

Table 1. ^{13}C NMR spectral data (δ in ppm) and $J(^{103}\text{Rh}–^{13}\text{C})$ (Hz) in the cod region in Rh(η^4-cod) complexes in $CDCl_3$ (unless noted otherwise).

complexes	methylene carbons	olefinic carbons ($J(^{103}\text{Rh}–^{13}\text{C})$ in parentheses) *trans* to N		*trans* to O	
		'left'	'right'[a]	'left'	'right'[a]
[Rh(SB*)(η^4-cod)] (**7**)	32.5, 32.0, 29.6, 29.2	85.7 (12.1)	85.3 (12.3)	73.5 (14.2)	71.4 (14.6)
[Rh(SB*)(η^4-cod)] (**8**)	33.1, 31.7, 30.1, 28.9	85.0 (12.6)	84.0 (12.0)	74.7 (13.4)	71.6 (14.5)
[Rh(SB*)(η^4-cod)] (**9**)	32.5, 32.0, 29.6, 29.1	85.7 (12.2)	85.3 (12.2)	73.6 (14.0)	71.2 (14.6)
[Rh(SB*)(η^4-cod)] (**10**)	31.1, 30.7, 28.2, 27.9	84.5 (11.8)	84.2 (12.2)	72.0 (14.6)	70.2 (14.1)
[Rh(SB*)(η^4-cod)] (**11**)	32.6, 32.1, 29.6, 29.2	85.8 (11.6)	85.4 (12.3)	73.7 (14.3)	71.4 (14.2)
[Rh(N,O)(η^4-cod)] [35][b]	32.1, 31.9, 29.6, 29.5	81.6	81.3	75.4	75.1
[Rh(sal=N-*o*-tol)(η^4-cod)] [20]	31.7, 31.3, 29.3, 28.8	85.1 (12.5)	84.6 (12.5)	74 (17.5)	72.5 (15.0)
[(Rh(η^4-cod))$_2$(salophen)] [24]	32.6, 30.3, 29.5, 27.9	85.8 (11.7)	84.3 (11.8)	74.3 (14.6)	69.7 (14.4)
[(Rh(η^4-cod))$_2$(salophen)] [20]	32.5, 30.3, 29.5, 27.9	85.8 (12.5)	84.3 (12.5)	74.3 (15.0)	69.7 (15.0)
[Rh(μ-hp/-mhp)(η^4-cod)]$_2$ [27][c]	35.0, 33.0, 30.1, 29.0/33.4, 32.1, 30.5, 29.2	89.1/87.7	772/76.6	74.4/72.8	70.9/72.2
[Rh(sal=N-CH_3/-Ph)(η^4-cod)] [20]	32.1, 28.9/31.3, 29.0	85.3 (12.5)/84.7 (12.5)		72.8 (12.5)/73.0 (12.5)	
[Rh(sal=N-*p*-tol)(η^4-cod)] [20]	31.4, 29.0	84.6 (12.5)		72.9 (15)	
[Rh(*o*-$O_2NC_6H_4NH$)(η^4-cod)] [28]	31.3, 29.4	84.4 (11)		71.8 (11)	
[{Rh(η^4-cod)}$_2$(dcbi)](NHEt$_3$) [29]	31.2, 30.0	82.7 (13)		71.7 (14)	
[{Rh(η^4-cod)}$_2$(salen)] [24]	31.7, 28.8	85.5 (11.9)		71.2 (14.2)	

[a] 'left' and 'right' is an arbitrary assignment for the olefinic carbons to either side of a plane bisecting the C=C bond; [b] in C_6D_6; [c] in [D$_8$]toluene.

tion to higher field (at 7.8 ppm) and splits into a symmetrical doublet by about 2.0 Hz (J) due to ^{103}Rh–^{1}H coupling [17, 19]. In [D$_6$]DMSO this signal remains a singlet at 8.0 – 8.1 ppm for the complexes.

In the ^{13}C NMR spectra the cod methylene carbon atoms in **7** – **11** give four singlets of equal intensity at δ = 29 – 31 ppm in contrast to only one singlet in [Rh(O_2CMe)(η^4-cod)]$_2$ [22] and [Rh(aminocarboxylato)(η^4-cod)] [22, 23]. Similarly, the four olefinic carbon atoms of cod give four doublets due to ^{103}Rh–^{13}C coupling, two at lower field (84 – 86 ppm) which are assigned to 'C *trans* to N', the other two at higher field (70 – 75 ppm) assigned to 'C *trans* to O' (see Table 1) [16, 20, 24, 26, 29, 30]. The observed ^{103}Rh–^{13}C(olefin) spin-spin coupling constants for 'C *trans* to N' (*ca*. J = 12 Hz) and 'C *trans* to O' (*ca*. J = 14 Hz) agree with data for related mononuclear Rh(η^4-cod) complexes [16, 20, 24, 27, 30, 35] (see Table 1). The occurrence of four singlets and four doublets is explained by steric and magnetic anisotropy effects in addition to the *trans* influence of the coordinated *N,O*-chelate on the carbon resonances [27]. The observed chemical shift difference between the 'left' and 'right' carbon atoms *trans* to the same donor atom are larger for '*trans* to O' than for '*trans* to N' in **7** – **11**.

Mass spectra of the Schiff bases **1** – **6** and the [Rh(SB*)(η^4-cod)] complexes **7** – **11** show the parent ion peaks. UV/vis Electronic spectra of the rhodium complexes feature two broad bands with absorption maxima at λ_{max} = 234 – 244 nm (ε_{max} = 23750 – 59700 L·mol^{-1}·cm^{-1}), associated with the intra-ligand $\pi \rightarrow \pi^*$ transition, and at λ_{max} = 388 – 394 nm (ε_{max} = 5000 – 14700 L·mol^{-1}·cm^{-1}), associated with the metal-to-ligand charge transfer (MLCT) transitions of Rh→(η^4-cod) and Rh→SB* [21 – 23]. The polarimetric measurements in CH_2Cl_2 or CH_3Cl exhibit rotations to the left between −95° and −170° at 578 nm and 20 °C for enantiopure *R*-Schiff bases, and rotations to the right between +200° and +333° at 578 nm and 20 °C for the Rh(*R*-SB*)-complexes.

The single-crystal structures of the enantiopure Schiff bases **4** and **5** confirm the molecular composition and absolute configuration. The molecular structures are depicted in Figs. 1 and 2, respectively. Bond

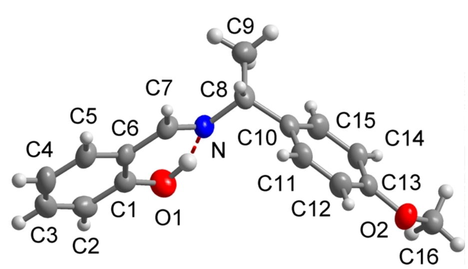
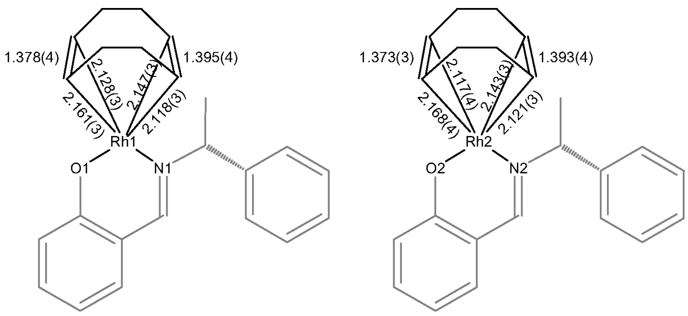


Fig. 1. Molecular structure of **4** with intramolecular hydrogen bond. Thermal ellipsoids with 50 % probability. Selected bond lengths (Å) and angles (deg): C13–O2 1.381(3), C7–N 1.275(3), N–C8 1.481(3); C7–N–C8 119.1(2). Hydrogen bonding interaction (dashed line) as O–H, H···N, O···N, O–H···N (Å, °): 1.00(3), 1.68(5), 2.580(2), 148(3).



Scheme 3. Bond lengths (Å) for Rh–C_{cod} and C=C_{cod} in the two symmetry-independent molecules in **7**.

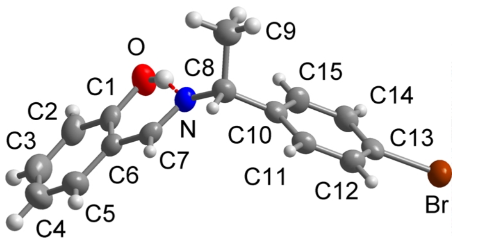


Fig. 2. Molecular structure of **5** with intramolecular hydrogen bond. Thermal ellipsoids with 50 % probability. Selected bond lengths (Å) and angles (deg): C13–Br 1.908(3), C7–N 1.275(3), N–C8 1.473(3); C7–N–C8 118.5(2). Hydrogen bonding interaction (dashed line) as O–H, H···N, O···N, O–H···N (Å, deg): 0.92(4), 1.72(4), 2.590(3), 156(4).

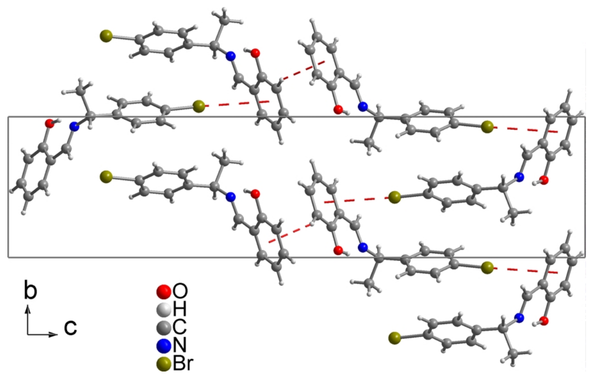


Fig. 3. Packing diagram of **5** to illustrate the C–H···π and C–Br···π contacts as dashed lines to the salicyl ring centroid.

lengths are within the expected range. The expected intramolecular hydrogen bond is observed between the salicyl-OH group and the imine nitrogen atom [36].

The molecular packing of **4** does not show π-π interactions [37–39] but only a C–H···π interaction C16–H···(C10–C15) with H···centroid 2.95 Å and C–H···π plane 60° [39–42]. The molecular packing in the structure of **5** is influenced by a C–H···π interaction C12–H···(C1–C6) with H···centroid 2.71 Å, C–H···centroid 138° and C–H···π plane 52°, and also by C–Br···π contacts to the salicyl ring (C1–C6) with Br···centroid 3.816(1) Å, C–Br···centroid 166.0° and C–Br···π plane 73.4° as illustrated in Fig. 3 [43].

The molecular structure of the rhodium complex **7** proves the suggested *N,O*-chelation of the deprotonated Schiff base salicylaldiminato ligand (Fig. 4). Again bond lengths and their variations are as expected [12, 16, 23, 24, 26, 27]. Compound **7** is only the second example of a Rh(η^4-cod) complex with a six-membered Rh-*N,O*-chelate ring. The other example is the dinuclear compound [{Rh(η^4-cod)}$_2$(*N,N*'-(1,2-phenylene)bis-(salicylaldiminato))] with an achiral tetradentate Schiff base ligand [15, 16, 44]. The cod-ligand in **7** is bound slightly asymmetrically (Scheme 3) which reflects the different *trans* nitrogen

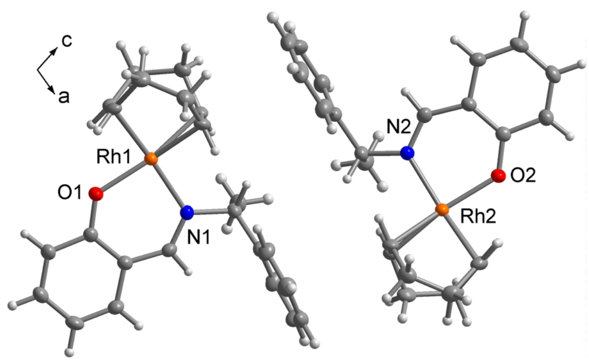


Fig. 4. Molecular structure of the two symmetry-related molecules of **7**. Selected bond lengths (Å) and angles (deg): Rh1–O1 2.0268(13), Rh1–N1 2.085(2), Rh1–C_{cod} 2.118(3)–2.161(3), Rh2–O2 2.0388(13), Rh2–N2 2.0840(19), Rh2–C_{cod} 2.117(4)–2.168(4); O1–Rh1–N1 90.93(7), O2–Rh2–N2 90.28(6).

or oxygen donor atoms and the 'left' and 'right' differentiation as mirrored in the four olefinic ^{13}C NMR resonances.

The unit cell in the crystal structure of **7** contains two symmetry-independent molecules which superficially appear related by a *pseudo* two-fold axis. No classical hydrogen bonds, π-π interactions or C–H···π

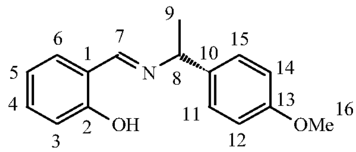
contacts are discernible in **7**. Van der Waals interactions between the molecules of **7** with their hydrophobic surface seem to control the packing.

Experimental Section

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: toluene, diethyl ether over Na metal; methanol over CaO; chloroform over $CaCl_2$. IR spectra were recorded on a Bruker Optik IFS 25 spectrometer from KBr disks at ambient temperature. UV/vis Spectra were obtained with a Shimadzu UV 3150 spectrophotometer in CH_2Cl_2 at 20 °C. Elemental analyses were carried out on a Vario EL instrument from Elementaranalysensysteme GmbH. NMR Spectra were run on a Bruker Avance DPX 200 spectrometer operating at 200 MHz (^{1}H) and 50 MHz (^{13}C) at 25 °C with calibration against the residual protonated solvent signal ($CDCl_3$: 7.26 (^{1}H) and 77.0 (^{13}C); [D$_6$]DMSO: 2.52 (^{1}H) and 39.5 (^{13}C) ppm). The NMR grade solvents $CDCl_3$ and [D$_6$]DMSO were deoxygenated prior to use. EI- and CI-MS: Thermo-Finnigan TSQ 700, with NH_3 as ionization gas for CI. Polarimetric measurements were carried with a Perkin-Elmer 241 instrument in $CHCl_3$and CH_2Cl_2 at 20 °C, and the values of $[\alpha]^{20}$ were determined according to the literature [10]. The starting dinuclear [Rh(O_2CMe)(η^4-cod)]$_2$ complex was synthesized from [RhCl(η^4-cod)]$_2$ [45] according to the literature [22, 46]. The enantiopure amines (*R*)-1-phenyl-ethylamine, (*R*)-(2-methoxyphenyl)ethylamine, (*R*)-(3-methoxyphenyl)ethylamine, (*R*)-(4-methoxyphenyl)ethylamine, (*R*)-(4-bromophenyl)ethylamine and (*R*)-(2-naphthyl)ethylamine were used as received from BASF, Ludwigshafen, Germany.

*(R)-N-(1-Phenylethyl)salicylaldimine (**1**)*

Salicylaldehyde (8.35 mL, 78.36 mmol) was dissolved into 20 mL of methanol with 2 – 3 drops of conc. H_2SO_4 added into the solution which was then stirred for 10 min at r. t. An equimolar amount of (*R*)-1-phenyl-ethylamine (10 mL, 78.39 mmol) was added to the solution. The colour soon changed to bright yellow, and the mixture was refluxed for 5 – 6 h. Then, the solvent was evaporated to a volume of to 50 % *in vacuo* and the yellow solution was left standing at r. t. for crystallization through slow solvent evaporation. After 2 – 3 d, bright-yellow crystals suitable for X-ray measurements were obtained. The crystals were washed three times with MeOH (5 mL each) and dried *in vacuo* at 40 – 50 °C for 5 – 6 h to give a bright-yellow product. Yield: 16.60 g (94 %) (based on salicylaldehyde). – $[\alpha]^{20}$ (c = 0.84, $CHCl_3$): −95° (578 nm). – IR (KBr): ν = 3063 m, 3034 m (H-Ar), 1627 vs (C=N), 1578 (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.59 (d, J_{HH} = 6.7/6.8^a Hz, 3H, H9), 4.70 (q, J_{HH} = 6.6 Hz, 1H, H8), 6.93 (dd, J_{HH} = 7.7, 7.2 Hz, J_{HH} = 1.1 Hz, 2H, H4,6-sal), 7.31 – 7.51 (m, 7H, sal+Ph), 8.70 (s, 1H, H7), 13.55 (br, 1H, OH). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46 (d, J_{HH} = 6.7 Hz, 3H, H9), 4.37 (q, J_{HH} = 6.7 Hz, 1H, H8), 6.69 (ddd, J_{HH} = 7.7, 7.4 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.79 (d, J_{HH} = 7.9 Hz, 1H, H6), 7.03 – 7.22 (m, 7H, sal+Ph), 8.22 (s, 1H, H7), 13.43 (br, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.9 (C9), 68.5 (C8), 117.0 (C3), 118.6 (C5), 118.9 (C1), 126.4 (C11,15), 127.3 (C13), 128.7 (C12,14), 131.4 (C6), 132.3 (C4), 143.9 (C10), 161.1 (C2), 163.5 (C7). – MS (EI, 70 eV): m/z (%) = 225 (100) [M]$^+$, 121 (65) [M – $CH_3CC_6H_5$]$^+$, 105 (100) [$CH_3CHC_6H_5$]$^+$, 77 (10) [C_6H_5]$^+$. – $C_{15}H_{15}NO$ (225.29): calcd. C 79.97, H 6.71, N 6.22; found C 79.15, H 6.91, N 6.44.



Atom numbering for NMR assignemts in **1** – **5** and **7** – **10**.

Compounds **2** – **6** were prepared following the same procedure as described for **1** using (*R*)-1-(2-methoxyphenyl) ethylamine, (*R*)-1-(3-methoxyphenyl)ethylamine, (*R*)-1-(4-methoxyphenyl)ethylamine, (*R*)-1-(4-bromophenyl)ethylamine, and (*R*)-1-(2-naphthyl)ethylamine, respectively.

*(R)-N-(1-(2-Methoxyphenyl)ethyl)salicylaldimine (**2**)*

Yield: 18.0 g (90 %). – $[\alpha]^{20}$ (c = 0.49, CH_2Cl_2): −163° (578 nm), −255° (546 nm). – IR (KBr): ν = 3054 m (H-Ar), 1626 vs (C=N), 1578 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.65 (d, J_{HH} = 6.6 Hz, 3H, H9), 3.91 (s, 3H, H16), 5.05 (q, J_{HH} = 6.6 Hz, 1H, H8), 6.92 (ddd, J_{HH} = 8.4, 7.6 Hz, J_{HH} = 1.0 Hz, 2H, H4,13), 6.98 (d, J_{HH} = 6.4 Hz, 1H, H6), 7.05 (dd, J_{HH} = 6.5 Hz, J_{HH} = 1.4 Hz, 1H, H3), 7.29 (d, J_{HH}= 7.6 Hz, 2H, H12,14), 7.37 (ddd, J_{HH}= 8.0, 7.5 Hz, J_{HH}= 1.6 Hz, 1H, H5), 7.49 (dd, J_{HH}= 7.6 Hz, J_{HH} = 1.6 Hz, 1H, H11), 8.46 (s, 1H, H_7), 13.88 (br, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.7 (C9), 55.8 (C16), 62.1 (C8), 111.0 (C12), 117.5 (C3), 118.8 (C14), 119.4 (C5), 121.3 (C1), 127.4 (C10), 128.6 (C13), 131.8 (C15), 132.3 (C6), 132.6 (C4), 156.7 (C2), 161.9 (C11), 163.9 (C7). – MS (EI, 70 eV): m/z (%) = 255 (35) [M]$^+$, 135 (100) [$CH_3CHC_6H_4OMe$]$^+$, 105 (5) [$CH_3CHC_6H_5$]$^+$. – $C_{16}H_{17}NO_2$ (255.32): calcd. C 75.27, H 6.71, N 5.49; found C 75.44, H 6.53, N 5.38.

*(R)-N-(1-(3-Methoxyphenyl)ethyl)salicylaldimine (**3**)*

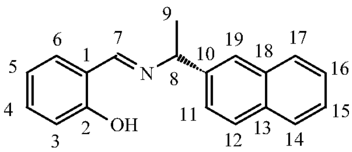
Yield: 18.2 g (91 %). – $[\alpha]^{20}$ (c = 0.42, CH_2Cl_2): −169° (578 nm). – IR (KBr): ν = 3053 m (H-Ar), 1624 vs (C=N), 1576 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.69 (d, J_{HH} = 6.6 Hz, 3H, H9), 3.87 (s, 3H, H16), 4.58 (q, J_{HH}= 6.6 Hz, 1H, H8), 6.89 (ddd, J_{HH} = 7.2, 6.8 Hz, J_{HH} = 1.6 Hz, 2H, H4,12), 6.95 (d, J_{HH} = 6.8 Hz, 2H, H6,13), 7.03 (dd, J_{HH} = 6.2 Hz, J_{HH} = 2.2 Hz, 1H, H3), 7.31 (dd, J_{HH} = 7.8 Hz, J_{HH} = 1.4 Hz, 1H, H11), 7.39 (ddd, J_{HH} = 6.8, 6.5 Hz, J_{HH} = 1.4 Hz, 1H, H5), 8.45 (s, 1H, H7), 13.55 (br, 1H, OH). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.3 (C9), 55.6 (C16), 68.8 (C8), 112.7 (C13), 112.9 (C11), 117.4 (C3), 119.0 (C15), 119.2 (C5), 119.3 (C1), 130.1 (C14), 131.8 (C6), 132.7 (C4), 145.9 (C10), 160.3 (C2), 161.5 (C12), 163.9 (C7). – $C_{16}H_{17}NO_2$ (255.32): calcd. C 75.27, H 6.71, N 5.49; found C 74.89, H 6.47, N 5.36.

*(R)-N-(1-(4-Methoxyphenyl)ethyl)salicylaldimine (**4**)*

Yield: 18.6 g (93 %). – $[\alpha]^{20}$ (c = 0.53, $CHCl_3$): −170° (578 nm). – IR (KBr): ν = 3054 m (H-Ar), 1626 vs (C=N), 1609, 1578 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.66 (d, J_{HH}= 6.7 Hz, 3H, H9), 3.85 (s, 3H, H16), 4.57 (q, J_{HH} = 6.7 Hz, 1H, H8), 6.87 – 7.01 (m, 4H, H3-6), 7.26 – 7.39 (m, 4H, H11,12,14,15), 8.43 (s, 1H, H7), 13.58 (br, 1H, OH). – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.56 (d, J_{HH} = 6.8 Hz, 3H, H9), 3.77 (s, 3H, H16), 4.65 (q, J_{HH} = 6.8 Hz, 1H, H8), 6.88 – 6.99 (m, 4H, H3-6), 7.33 – 7.47 (m, 4H, H11,12,14,15), 8.66 (s, 1H, H7), 13.53 (br, 1H, OH). – ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 24.5 (C9), 55.5 (C16), 66.6 (C8), 114.4 (C12,14), 116.8 (C3), 118.9 (C5), 119.1 (C1), 127.8 (C11,15), 132.0 (C6), 132.6 (C4), 136.3 (C10), 158.8 (C2), 160.9 (C13), 164.3 (C7). – MS (EI, 70 eV): *m*/*z* (%) = 255 (85) [M]$^+$, 135 (100) [$CH_3CHC_6H_4OMe$]$^+$, 121 (20) [M – $CH_3CC_6H_4OMe$]$^+$, 105 (10) [$CH_3CHC_6H_5$]$^+$. – $C_{16}H_{17}NO_2$ (255.32): calcd. C 75.27, H 6.71, N 5.49; found C 75.01, H 6.71, N 5.31.

*(R)-N-(1-(4-Bromophenyl)ethyl)salicylaldimine (**5**)*

Yield: 22.0 g (92 %). – $[\alpha]^{20}$ (c = 0.61, $CHCl_3$): −148° (578 nm). – IR (KBr): ν = 3049 m (H-Ar), 1616 vs (C=N), 1575 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.52 (d, J_{HH} = 6.8 Hz, 3H, H9), 4.43 (q, J_{HH} = 6.8 Hz, 1H, H8), 6.80 (ddd, J_{HH} = 7.4, 6.4 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.89 (d, J_{HH} = 8.2 Hz, 1H, H6), 7.16 (dd, J_{HH} = 6.2 Hz, J_{HH} = 1.8 Hz, 3H, H3,11,15), 7.24 (ddd, J_{HH} = 6.8, 7.0 Hz, J_{HH} = 1.8 Hz, 1H, H5), 7.40 (dd, J_{HH} = 4.8 Hz, J_{HH} = 1.8 Hz, 2H, H12,14), 8.32 (s, 1H, H7), 13.22 (br, 1H, OH). – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.56 (d, J_{HH} = 6.7 Hz, 3H, H9), 4.69 (q, J_{HH} = 6.6 Hz, 1H, H8), 6.93 (ddd, J_{HH} = 7.8, 6.6 Hz, J_{HH} = 1.0 Hz, 2H, H4,6), 7.38 (ddd, J_{HH} = 7.7, 6.4 Hz, J_{HH} = 1.7 Hz, 3H, H3,11,15), 7.48 (dd, J_{HH} = 6.4 Hz, J_{HH} = 1.7 Hz, 1H, H5), 7.57 (dd, J_{HH} = 6.7 Hz, J_{HH} = 1.7 Hz, 2H, H12,14), 8.69 (s, 1H, H7), 13.28 (br, 1H, OH). – ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 24.5 (C9), 66.6 (C8), 116.8 (C3), 119.1 (C13), 120.5 (C5), 128.9 (C11,15), 129.4 (C1), 131.8 (C12,14), 132.1 (C6), 132.8 (C4), 143.8 (C10), 160.7 (C2), 165.0 (C7). – MS (EI, 70 eV): *m*/*z* (%) = 304 (84) [M]$^+$, 183 (5) [$CH_3CHC_6H_4Br$]$^+$ ($^{79/81}$Br isotopic pattern clearly visible for patterns following the 304 and 183 peaks, with masses given for the slightly more abundant ^{79}Br-containing fragment), 121 (100) [M – $CH_3CC_6H_4Br$]$^+$, 104 (55) [$CH_3CHC_6H_4$]$^+$, 77 (10) [C_6H_5]$^+$. – $C_{15}H_{14}NOBr$ (304.19): calcd. C 59.23, H 4.64, N 4.60; found C 59.36, H 4.61, N 4.55.



Atom numbering for NMR assignemts in **6** and **11**.

*(R)-N-(1-(2-Naphthyl)ethyl)salicylaldimine (**6**)*

Yield: 20.0 g (93 %). – $[\alpha]^{20}$ (c = 0.52, CH_2Cl_2): −154° (578 nm), −173° (546 nm). – IR (KBr): ν = 3048 s (H-Ar), 1628 vs (C=N), 1602 s, 1573 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.69 (d, J_{HH} = 6.7 Hz, 3H, H9), 4.88 (q, J_{HH} = 6.6 Hz, 1H, H8), 6.94 (ddd, J_{HH} = 7.7, 8.2 Hz, J_{HH} = 1.0 Hz, 2H, H4,6), 7.36 (ddd, J_{HH} = 7.6, 8.4 Hz, J_{HH} = 1.7 Hz, 1H, H5), 7.52 (m, 3H, H3+nap), 7.60 (dd, J_{HH} = 8.5 Hz, J_{HH} = 1.7 Hz, 1H, nap), 7.91 – 7.97 (m, 4H, nap), 8.76 (s, 1H, H7), 13.55 (br, 1H, OH). – ^{13}C NMR (50 MHz, [D$_6$]DMSO): δ = 24.5 (C9), 67.3 (C8), 116.8 (C3), 119.1 (C5), 119.2 (C1), 125.0 (C15), 125.3 (C16), 126.2 (C19), 126.6 (C12), 127.9 (C17), 128.2 (C14), 128.7 (C11), 132.2 (C6), 132.7 (C13), 132.8 (C4), 133.4 (C18), 141.9 (C10), 160.9 (C2), 164.9 (C7). – MS (EI, 70 eV): *m*/*z* (%) = 275 (80) [M]$^+$, 155 (100) [$CH_3CHC_{10}H_7$]$^+$, 121 (20) [M – $CH_3CC_{10}H_7$]$^+$. – $C_{19}H_{17}NO$ (275.35): calcd. C 82.88, H 6.22, N 5.09; found C 82.54, H 6.10, N 4.96.

*Cyclooctadiene-{(R)-N-(1-phenylethyl)salicylaldiminato-κ^2N,O}-rhodium(I) (**7**)*

Two equivalents of (*R*)-*N*-(1-phenylethyl)salicylaldimine (80.4 mg, 0.36 mmol) and one equivalent of [Rh(O_2CMe)(η^4-cod)]$_2$ (96.3 mg, 0.18 mmol) were dissolved in 10 mL of toluene/MeOH (5 : 1, v/v) and the solution stirred for 5 – 6 h at r. t. The colour soon changed from red-orange to bright-yellow. Then the solvent was evaporated *in vacuo* at 50 °C. The product was again dissolved in 10 mL of toluene/MeOH (5 : 1, v/v), the solution stirred for 30 min and the solvent evaporated *in vacuo*. This procedure was repeated three times, and finally the yellow the product was dried *in vacuo* (0.1 – 0.2 mbar) at 60 °C. Single crystals suitable for X-ray measurements were grown by slow diffusion of diethyl ether into a chloroform solution of complex **7** after one week at r. t. Yield: 0.130 g (81 %), based on [Rh(O_2CMe)(η^4-cod)]$_2$. – UV/vis ($7.109 \cdot 10^{-5}$ mol mL^{-1}, CH_2Cl_2): $\lambda_{max}(\lg \varepsilon_{max})$ = 392 nm (3.84), 234 nm (4.57). – $[\alpha]^{20}$ (c = 0.26, CH_2Cl_2): +250° (578 nm), +308° (546 nm). – $[\alpha]^{20}$ (c = 0.44, $CHCl_3$): +182° (578 nm). – IR (KBr): ν = 3060, 3030 w (H-Ar), 1626 sh (C=N), 1579 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.63 (d, J_{HH}= 6.9 Hz, 3H, H9), 1.87 (m, 4H, CH$_2$cod$_{exo}$), 2.40 (m, 4H, CH$_2$cod$_{endo}$), 3.77 (m, 2H, CHcod), 4.41 (m, 3H, H$_8$+CHcod), 6.48 (t, J_{HH} = 7.4/6.3 Hz, 1H, H4), 6.64 (d, J_{HH} = 8.8 Hz, 1H, H6), 7.23 (d, J_{HH} = 7.8 Hz, 2H, H3,5), 7.28 – 7.39 (m, 5H, H11-15), 8.13 (s, 1H, H7). – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.58 (d, J_{HH}= 6.9 Hz, 3H, H9), 1.85 (m, 4H, CH$_2$cod$_{exo}$), 2.43 (m, 4H, CH$_2$cod$_{endo}$), 3.72 (m, 2H, CHcod), 4.37 (q, J_{HH} = 6.8 Hz, 1H, H8), 4.54 (m, 2H, CHcod), 6.41 (ddd, J_{HH} = 6.8 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.77 (d, J_{HH} = 8.5 Hz, 1H, H6), 6.89 (dd, J_{HH} = 6.0 Hz, J_{HH} = 1.8 Hz, 1H, H3), 7.15 – 7.29 (m, 6H, H5,11,12,13,14,15), 7.82 (d, J_{HH} = 2.0 Hz, 1H, H7). – ^{13}C NMR (50 MHz, CDCl$_3$): δ = 22.5 (C9), 29.2, 29.6, 32.0, 32.5 (CH$_2$cod), 60.2 (C8), 71.4 (d, J_{CRh} = 14.6 Hz, CHcod), 73.5 (d, J_{CRh} = 14.2 Hz, CHcod), 85.3 (d, J_{CRh} = 12.3 Hz, CHcod), 85.7 (d, J_{CRh} = 12.1 Hz, CHcod), 114.6 (C3), 119.7 (C5), 121.8 (C1), 127.7 (C13), 128.0 (C11,15), 129.0 (C12,14), 135.0 (C6), 135.5 (C4), 143.2 (C10), 165.4 (C2), 166.1 (C7). – MS (EI, 70 eV): *m*/*z* (%) = 435 (86) [M]$^+$, 327 (100) [M – cod]$^+$, 225 (16) [HSB*]$^+$, 224 (12) [SB]$^+$, 208 (49) [HSB* – OH]$^+$, 206 (35) [SB* – H$_2$O]$^+$, 105 (30) [CH$_3$CHC$_6$H$_5$]$^+$, 103 (15) [Rh]$^+$, 77 (7) [C$_6$H$_5$]$^+$. – MS (CI, NH$_3$): *m*/*z* (%) = 436 (100) [M + H]$^+$, 327 (10) [M – cod]$^+$, 226 (85) [HSB* + H]$^+$, 225 (10) [HSB*]$^+$. – C$_{23}$H$_{26}$NORh (435.37): calcd. C 63.45, H 6.02, N 3.22; found C 63.53, H 6.13, N 3.24.

The same procedure was followed for the synthesis of the complexes **8** – **11** using the Schiff bases **2** – **6**, respectively.

*Cyclooctadiene-{(R)-N-(1-(2-methoxyphenyl)ethyl)salicylaldiminato-κ^{2}N,O}-rhodium(I) (**8**)*

Yield: 0.135 g (78 %). – UV/vis (8.526 · 10^{-5} mol mL^{-1}, CH$_2$Cl$_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 388 nm (3.80), 236 nm (4.53). – $[\alpha]^{20}$ (*c* = 0.25, CH$_2$Cl$_2$): +200° (578 nm), +220° (546 nm). – IR (KBr): ν = 3044 w (H-Ar), 1626 s (C=N), 1573 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.54 (d, J_{HH} = 6.9 Hz, 3H, H9), 1.84 (m, 4H, CH$_2$cod$_{exo}$), 2.43 (m, 4H, CH$_2$cod$_{endo}$), 3.73 (m, 1H, CHcod), 3.78 (s, 3H, H$_{16}$), 4.29 (m, 1H, CHcod), 4.42 (m, 1H, CHcod), 4.50 (m, 1H, CHcod), 4.63 (q, J_{HH} = 6.8 Hz, 1H, H8), 6.38 (ddd, J_{HH} = 6.8 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.76 (t, J_{HH} = 9.5 Hz, 2H, H3,6), 6.85 (dd, J_{HH} = 6.2 Hz, J_{HH} = 1.7 Hz, 1H, H5), 6.93 (d, J_{HH} = 7.4 Hz, 1H, H11), 7.15 (ddd, J_{HH} = 6.8 Hz, J_{HH} = 1.6 Hz, 1H, H13), 7.17 – 7.27 (m, 2H, H12,14), 7.73 (d, J_{HH} = 2.0 Hz, 1H, H7). – ^{13}C NMR (50 MHz, CDCl$_3$): δ = 22.8 (C9), 28.9, 30.1, 31.7, 33.1 (CH$_2$cod), 55.9 (C$_{16}$), 56.9 (C$_8$), 71.6 (d, J_{CRh} = 14.5 Hz, CHcod), 74.7 (d, J_{CRh} = 13.4 Hz, CHcod), 84.0 (d, J_{CRh} = 12.0 Hz, CHcod), 85.0 (d, J_{CRh} = 12.6 Hz, CHcod), 111.4 (C12), 114.3 (C3), 119.8 (C14), 120.6 (C5), 121.7 (C1), 128.4 (C10), 129.6 (C13), 130.2 (C15), 134.6 (C6), 135.5 (C4), 157.1 (C2), 162.5 (C11), 165.9 (C7). – MS (EI, 70 eV): *m*/*z* (%) = 465 (100) [M]$^+$, 357 (95) [M – cod]$^+$, 327 (12) [M – cod – HCHO]$^+$, 255 (5) [HSB*]$^+$, 234 (12) [SB – H$_2$O – H$_2$]$^+$, 135 (12) [CH$_3$CHC$_6$H$_4$OMe]$^+$, 103 (5) [Rh]$^+$. – C$_{24}$H$_{28}$NO$_2$Rh (465.40): calcd. C 61.94, H 6.06, N 3.01; found C 62.85, H 6.12, N 2.45.

*Cyclooctadiene-{(R)-N-(1-(4-methoxyphenyl)ethyl)salicylaldiminato-κ^{2}N,O}-rhodium(I) (**9**)*

Yield: 0.130 g (75 %). – UV/vis (1.398 · 10^{-4} mol mL^{-1}, CH$_2$Cl$_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 392 nm (3.70), 240 nm (4.38). – $[\alpha]^{20}$ (*c* = 0.41, CH$_2$Cl$_2$): +207° (578 nm), +280° (546 nm). – $[\alpha]^{20}$ (*c* = 0.56, CHCl$_3$): +241° (578 nm). – IR (KBr): ν = 3062, 3030 w (H-Ar), 1624 s (C=N), 1577 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.59 (d, J_{HH} = 6.5 Hz, 3H, H9), 1.88 (m, 4H, CH$_2$cod$_{exo}$), 2.42 (m, 4H, CH$_2$cod$_{endo}$), 3.74 (s, 3H, H16), 3.76 (m, 2H, CHcod), 4.34 (q, J_{HH} = 6.8 Hz, 1H, H8), 4.43 (m, 2H, CHcod), 6.47 (t, J_{HH} = 7.4/6.8 Hz, 1H, H4), 6.63 (d, J_{HH} = 8.4 Hz, 1H, H6), 6.94 (d, J_{HH} = 8.8 Hz, 2H, H3,5), 7.25 (m, 4H, H11,12,14,15), 8.04 (s, 1H, H7). – ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.55 (d, J_{HH} = 6.8 Hz, 3H, H9), 1.88 (m, 4H, CH$_2$cod$_{exo}$), 2.42 (m, 4H, CH$_2$cod$_{endo}$), 3.70 (m, 2H, CHcod), 3.73 (s, 3H, H16), 4.53 (m, 2H, CHcod), 4.32 (q, J_{HH} = 6.8 Hz, 1H, H8), 6.40 (ddd, J_{HH} = 6.8 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.81 (m, 2H, H3,6), 6.89 (ddd, J_{HH} = 6.1 Hz, J_{HH} = 1.8 Hz, 1H, H5), 7.15 – 7.22 (m, 4H, H11,12,14,15), 7.78 (d, J_{HH} = 2.0 Hz, 1H, H7). – ^{13}C NMR (50 MHz, CDCl$_3$): δ = 22.7 (C9), 29.1, 29.6, 32.0, 32.5 (CH$_2$cod), 55.7 (C16), 59.7 (C8), 71.2 (d, J_{CRh} = 14.3 Hz, CHcod), 73.6 (d, J_{CRh} = 14.0 Hz, CHcod), 85.3 (d, J_{CRh} = 12.2 Hz, CHcod), 85.7 (d, J_{CRh} = 12.2 Hz, CHcod), 114.4 (C12,14), 114.6 (C3), 119.7 (C5), 121.8 (C1), 129.2 (C11,15), 134.9 (C6), 135.2 (C4), 135.5 (C10), 159.2 (C2), 165.2 (C13), 166.0 (C7). – MS (EI, 70 eV): *m*/*z* (%) = 465 (70) [M]$^+$, 357 (100) [M – cod]$^+$, 327 (13) [M – cod – HCHO]$^+$, 255 (21) [HSB*]$^+$, 238 (41) [HSB* – OH]$^+$, 135 (100) [CH$_3$CHC$_6$H$_4$OMe]$^+$, 105 (23) [CH$_3$CHC$_6$H$_5$]$^+$, 103 (15) [Rh]$^+$, 77 (10) [C$_6$H$_5$]$^+$. – MS (CI, NH$_3$): *m*/*z* (%) = 466 (85) [*M* + H]$^+$, 256 (100) [HSB* + H]$^+$, 135 (20) [CH$_3$CHC$_6$H$_4$OMe]$^+$. – C$_{24}$H$_{28}$NO$_2$Rh (465.40): calcd. C 61.94, H 6.06, N 3.01; found C 61.51, H 6.07, N 2.89.

*Cyclooctadiene-{(R)-N-(1-(4-bromophenyl)ethyl)salicylaldiminato-κ^{2}N,O}-rhodium(I) (**10**)*

Yield: 0.150 g (79 %). – UV/vis (7.408 · 10^{-5} mol mL^{-1}, CH$_2$Cl$_2$): $\lambda_{max}(\lg\varepsilon_{max})$ = 394 nm (4.09), 244 nm (4.66). – $[\alpha]^{20}$ (*c* = 0.24, CH$_2$Cl$_2$): +333° (578 nm), 479° (546 nm). – $[\alpha]^{20}$ (*c* = 0.47, CHCl$_3$): +308° (578 nm). – IR (KBr): ν = 3045 w (H-Ar), 1620 sh (C=N), 1604 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.62 (d, J_{HH} = 6.3 Hz, 3H, H9), 1.88 (m, 4H, CH$_2$cod$_{exo}$), 2.40 (m, 4H, CH$_2$cod$_{endo}$), 3.72 (m, 2H, CHcod), 4.37 (q, J_{HH} = 6.8 Hz,

Table 2. Crystal structure data for **4**, **5** and **7**.

	4	**5**	**7**
Formula	$C_{16}H_{17}NO_2$	$C_{15}H_{14}BrNO$	$C_{23}H_{26}NORh$
M_r	255.31	304.18	435.36
Cryst. size [mm^3]	$0.42 \times 0.13 \times 0.12$	$0.45 \times 0.21 \times 0.03$	$0.39 \times 0.26 \times 0.12$
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a [Å]	5.724(2)	5.8401(7)	12.9992(16)
b [Å]	12.633(5)	7.6145(10)	10.2131(13)
c [Å]	19.237(7)	31.146(4)	14.6849(18)
β [deg]	90	90	102.961(2)
V [Å^3]	1391.1(9)	1385.0(3)	1899.9(4)
Z	4	4	4
D_{calcd} [g cm^{-3}]	1.219	1.459	1.522
μ(MoK_α) [cm^{-1}]	0.80	29.55	9.10
F(000) [e]	544	616	896
hkl range	±7; ±16; ±25	±7; -9, 10; -42, 41	±17; ±13; ±19
$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.675	0.677	0.680
Refl. measured	12144	12448	17341
Refl. unique	1979	3358	8750
R_{int}	0.0504	0.0449	0.0182
Param. refined	176	167	469
$R(F)/wR(F^2)$[a] (all reflexions)	0.0827/0.1116	0.0587/0.0607	0.0295/0.0465
x(Flack)	[b]	0.017(9)	$-0.006(16)$
GoF (F^2)[a]	1.037	0.844	0.936
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.164/-0.197	0.393/-0.352	0.388/-0.381

[a] $R(F) = [\Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|]$; $wR(F^2) = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2]]^{1/2}$. – Goodness-of-fit = $[\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(n-p)]^{1/2}$. – Weighting scheme w; a/b = 0.0601/0.0000 for **4**, 0.0273/0.0000 for **5** and 0.0201/0.0000 for **7** with $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ where $P = (\max(F_o{}^2$ or $0) + 2F_c{}^2)/3$. – [b] Anomalous scattering power is too small in combination with the data quality at hand to give a meaningful Flack parameter; Friedel opposites were therefore merged (MERG 4). The absolute configuration was established by the known absolute configuration of the starting amine.

1H, H8), 4.42 (m, 2H, CHcod), 6.49 (t, J_{HH} = 7.6/7.4 Hz, 1H, H4), 6.65 (d, J_{HH} = 8.6 Hz, 1H, H6), 7.28 (m, 4H, H3,5,11,15), 7.58 (d, J_{HH} = 8.2 Hz, 2H, H12,14), 8.12 (s, 1H, H7). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.56 (d, J_{HH} = 6.8 Hz, 3H, H9), 1.88 (m, 4H, CH_2cod_{exo}), 2.42 (m, 4H, CH_2cod_{endo}), 3.66 (m, 2H, CHcod), 4.29 (q, J_{HH} = 6.8 Hz, 1H, H8), 4.55 (m, 2H, CHcod), 6.42 (ddd, J_{HH} = 6.8 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.77 (d, J_{HH} = 8.5 Hz, 1H, H6), 6.90 (dd, J_{HH} = 6.2 Hz, J_{HH} = 1.8 Hz, 1H, H3), 7.14 (d, J_{HH} = 8.5 Hz, 2H, H11,15), 7.20 (ddd, J_{HH} = 6.8Hz, J_{HH} = 1.8 Hz, 1H, H5), 7.41 (dd, J_{HH} = 5.8 Hz, J_{HH} = 1.8 Hz, 2H, H12,14), 7.75 (d, J_{HH} = 2.0 Hz, 1H, H7). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.1 (C9), 27.9, 28.2, 30.7, 31.1 (CH_2cod), 58.3 (C8), 70.2 (d, J_{CRh} = 14.1 Hz, CHcod), 72.0 (d, J_{CRh} = 14.6 Hz, CHcod), 84.2 (d, J_{CRh} = 12.2 Hz, CHcod), 84.5 (d, J_{CRh} = 11.8 Hz, CHcod), 113.4 (C3), 118.2 (C13), 120.5 (C5), 128.1 (C1), 128.3 (C11,15), 130.8 (C12,14), 133.9 (C6), 134.2 (C4), 141.1 (C10), 164.1 (C2), 164.9 (C7). – MS (EI, 70 eV): m/z (%) = 513 (81) [M]$^+$, 405 (96) [M – cod]$^+$, 332 (40) [M – $CH_3CHC_6H_4Br$ + H_2]$^+$, 303 (6) [HSB*]$^+$, 223 (14) [SB*–Br], 211 (15) [Rhcod]$^+$, 184 (25) [$CH_3CHC_6H_4Br$ + H]$^+$, 104 (8) [$CH_3CHC_6H_4$]$^+$, 103 (5) [Rh]$^+$ ($^{79/81}$Br isotopic pattern clearly visible for patterns following the 513, 405, and 184 peaks, with masses given for the slightly more abundant ^{79}Br-containing fragment). – $C_{23}H_{25}BrNORh$ (514.27): calcd. C 53.72, H 4.90, N 2.72; found C 53.21, H 5.00, N 2.51.

*Cyclooctadiene-{(R)-N-(1-(2-naphthyl)ethyl)salicylaldiminato-κ^{2}N,O}-rhodium(I) (**11**)*

Yield: 0.145 g (81 %). – UV/vis ($5.722 \cdot 10^{-5}$ mol mL^{-1}, CH_2Cl_2): $\lambda_{max}(\lg\varepsilon_{max})$ = 392 nm (4.17), 244 nm (4.78). – $[\alpha]^{20}$ (c = 0.35, CH_2Cl_2): +329° (578 nm), +429° (546 nm). – IR (KBr): ν = 3053 w, 3040 w (H-Ar), 1622 vs (C=N), 1577 vs (C=C) cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.68 (d, J_{HH} = 6.8 Hz, 3H, H9), 1.89 (m, 4H, CH_2cod_{exo}), 2.44 (m, 4H, CH_2cod_{endo}), 3.77 (m, 2H, CHcod), 4.50 (q, J_{HH} = 6.8 Hz, 1H, H8), 4.57 (m, 2H, CHcod), 6.35 (ddd, J_{HH} = 6.5, 6.1 Hz, J_{HH} = 1.0 Hz, 1H, H4), 6.79 (ddd, J_{HH} = 7.8, 7.1 Hz, J_{HH} = 1.5 Hz, 2H, H3,6), 7.16 (ddd, J_{HH} = 6.9, 6.7 Hz, J_{HH} = 1.5 Hz, 1H, H5), 7.38 (ddd, J_{HH} = 8.9, 7.9 Hz, J_{HH} = 1.3 Hz, 2H, nap), 7.42 (d, J_{HH} = 6.8 Hz, 1H, nap), 7.72 (m, 4H, nap), 7.82 (d, J_{HH} = 2.0 Hz, 1H, H7). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.6 (C9), 29.2, 29.6, 32.1, 32.6 (CH_2cod), 60.4 (C8), 71.4 (d, J_{CRh} = 14.2 Hz, CHcod), 73.7 (d, J_{CRh} = 14.3 Hz, CHcod), 85.4 (d, J_{CRh} = 12.3 Hz, CHcod), 85.8 (d, J_{CRh} = 11.6 Hz, CHcod), 114.7 (C3), 119.7 (C5), 121.8 (C1), 126.1 (C15), 126.6 (C16), 126.7 (C19), 126.8 (C12), 128.0 (C17), 128.5 (C14), 129.0 (C11), 133.0 (C6), 133.5 (C13), 135.1 (C4), 135.6 (C18), 140.7 (C10), 165.6 (C2), 166.1 (C7). – MS (EI, 70 eV): *m/z* (%) = 485 (64) $[M]^+$, 377 (100) $[M-cod]^+$, 275 (5) $[HSB^*]^+$, 258 (13) $[HSB^* - OH]^+$, 155 (7) $[CH_3CHC_{10}H_7]^+$. – $C_{27}H_{28}NORh$ (485.43): calcd. C 66.81, H 5.81, N 2.89; found C 66.71, H 6.45, N 2.38.

X-Ray structure determinations

Data Collection: Bruker AXS with CCD area detector, temperature 203(2) K, MoK_α radiation (λ = 0.71073 Å), graphite monochromator, ω scans, data collection and cell refinement with SMART [47], data reduction with SAINT [47], experimental absorption correction with SADABS [48].

Structure Analysis and Refinement: The structure was solved by Direct Methods (SHELXS-97) [49], refinement was carried out by full-matrix least-squares on F^2 using the SHELXL-97 program suite [49]. All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on oxygen (–OH) were found and fully refined in **4** and **5**. Hydrogen atoms on C (phenyl, CH, CH_2 and CH_3) were calculated with appropriate riding models (AFIX 43, 13, 23 and 33, respectively) and U_{eq}(H) = 1.2 U_{eq}(CH) or U_{eq}(H) = 1.5 U_{eq}(CH_3). Details of the X-ray structure determinations and refinements are provided in Table 2. Graphics were drawn with DIAMOND (Version 3.1c) [50]. Computations on the supramolecular interactions were carried out with PLATON for Windows [15].

CCDC 636 583 for **4**, 636 584 for **5**, and 636 585 for **7** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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