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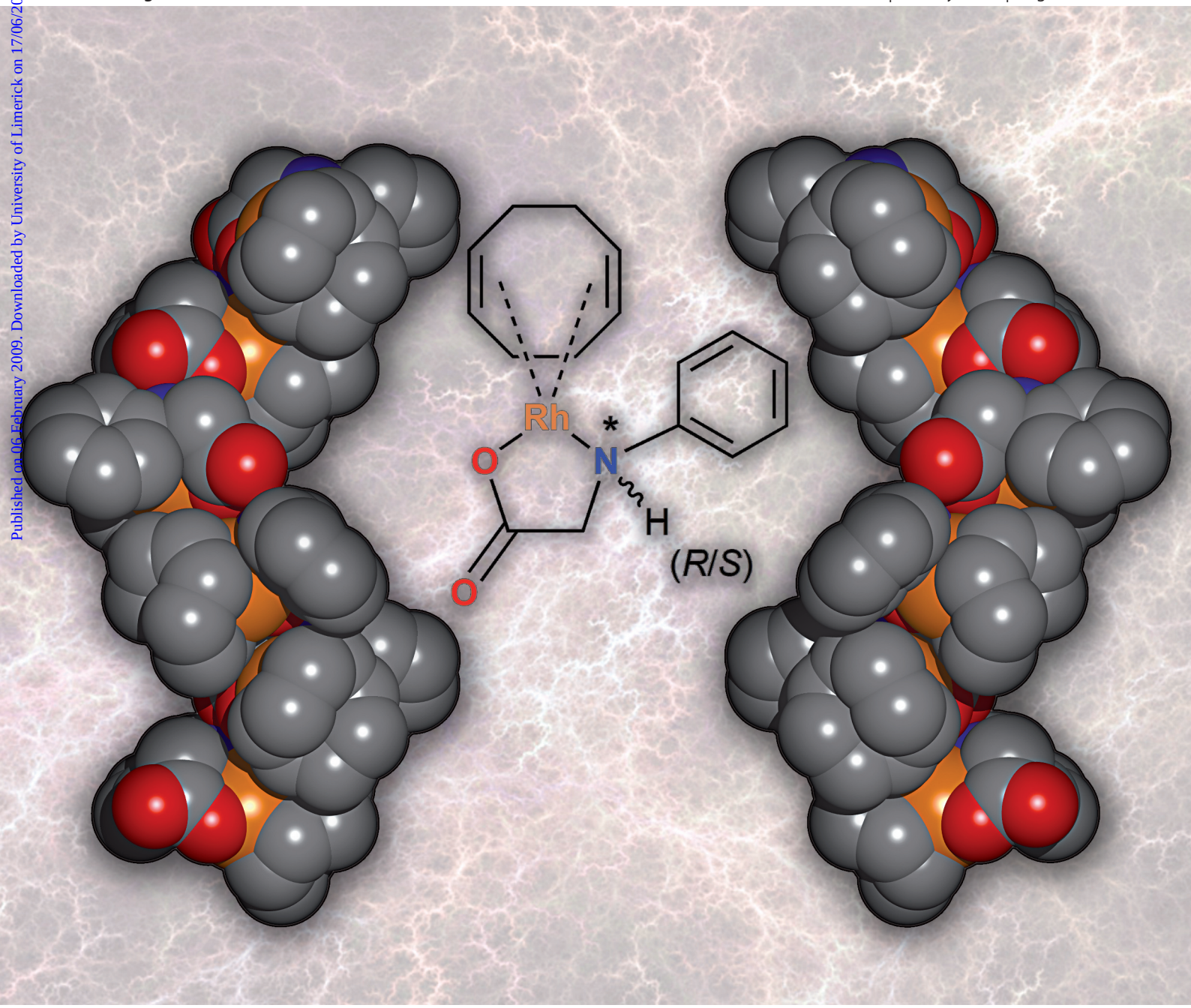

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Polymorphs, enantiomorphs, chirality and helicity in [Rh{*N,O*}(η⁴-cod)] complexes with {*N,O*} = salicylaldiminato Schiff base or aminocarboxylato ligands†‡

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The dimeric complex acetato(η⁴-cycloocta-1,5-diene)rhodium(I), $[Rh(O_2CMe)(\eta^4\text{-cod})]_2$ (cod = cycloocta-1,5-diene) reacts with *N*,*O*-chelating Schiff-base ligands or with *N*-phenylglycine to afford the diminato- or aminocarboxylato(η⁴-cycloocta-1,5-diene)rhodium(I) complexes [{Rh(η⁴-cod)}₂-(salen)] (**1**), [{Rh(η⁴-cod)}₂(salophen)] (**2**), [Rh((*S*)-*N*-phenylglycinato)(η⁴-cod)] (**3S**), [Rh(*rac*-*N*-phenylglycinato)(η⁴-cod)] (**3rac**), [Rh((*R*)-*N*-(4-methoxphenyl)ethyl-2-oxo-1-naphthaldiminato)(η⁴-cod)] (**4**) and [Rh(*N*-(*o*-tolyl)-2-oxo-1-naphthaldiminato)(η⁴-cod)] (**5**) [$salen^{2-}$ = *N,N′*-ethylene-bis(salicylaldiminato), $salophen^{2-}$ = *N,N′*-(1,2-phenylene)-bis(salicylaldiminato)]. The complexes are characterized by IR-, UV/Vis-, $^1H/^{13}C$-NMR- and mass-spectroscopy. Complexes **1**, **2**, **4** and **5** contain six-membered metallaaromatic Rh–(N–CCC–O)-chelate rings which accept C–H···π contacts. The crystal structure of **2** presents a polymorph (dimorph) (**2a**) to a previously reported structure (**2b**, CSD refcode SCLIRB10). Polymorphic forms **2a** and **2b** are traced to a different interlocking of adjacent dinuclear molecules with their corrugated van der Waals surface. The achiral *N*-phenylglycine ligand gives a chiral *N*-phenylglycinato complex [$Rh(O_2C\text{–}CH_2\text{–}NHPh)(\eta^4\text{-cod})$] (**3**) with the nitrogen atom becoming the stereogenic center upon metal coordination. Complex **3** can crystallize as the enantiomorph **3S** in the tetragonal, chiral space group $P4_1$ in a spontaneous resolution of the racemic mixture into homo-chiral helix-enantiomers due to inter-molecular N–H···O hydrogen bonding which connects only molecules of the same (*S*-) configuration into (right-handed or *P*-) 4_1-helical chains. Variation of the crystallization conditions gives **3** as a racemic polymorphic **3rac**. *R*- and *S*-complexes **3** assemble in the polymorph **3rac** in parallel chains along the 2_1-axes through N–H···O hydrogen bonding. Again, only molecules of the same configuration are combined into a chain, albeit neighboring chains have complexes of opposite configuration. The chiral enantiomeric naphthaldiminato complex **4** displays a herring-bone arrangement. Achiral compound **5** crystallizes in the non-centrosymmetric polar space group *Cc* where all molecules show the same orientation.

Introduction

Polymorphism, the occurence of different crystal structures for the same chemical entity,[1] is of timely interest[2–6] and of particular practical importance in industrial processes. Different physical properties of polymorphic forms can substantially alter the viability and quality of a product.[7] It is very complex to rationalize how and why compounds are packed in different forms. Polymorphism is associated with differences in molecular conformation, molecular orientation, crystal packing, solubility, color *etc.*[8,9] Polymorphs provide information on conformational flexibility and are the basis for *ab initio* crystal structure predictions.[10] The aggregation of flexible molecules depends on the compromise between intra- and inter-molecular weak bonding interactions in the crystal (external or extra-molecular interactions).[11,12] The transformation of different polymorphs may be triggered by the external stresses[8,13] and governed by the intra- and inter-molecular forces in the solid state.[14] Hence, there is a need for an understanding of intermolecular interactions in the context of crystal packing in view of the ongoing difficulty involved in investigating and quantifying structural differences between polymorphs.[8,9]

Polymorphism of transition metal complexes is of increasing interest.[2,3] Polymorphs of η⁴-cod and related Rh(I)-complexes include $[Rh(\eta^4\text{-cod})\{N,N\}]O_3SCF_3$,[15] $[Rh(\eta^4\text{-cod})\{P,P\}]O_3SCF_3$,[16] $[Rh(\eta^4\text{-nor})\{P,P\}]ClO_4$ (cod = 1,5-cyclooctadiene, nor = norbornadiene)[17] and a temperature-induced phase transition in

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† Dedicated to Prof. Ingo-Peter Lorenz on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: Crystal pictures of **3R**/**3S** and **3rac**, UV/Vis, IR, olefinic cod ^1H NMR data, Rh–cod distances, C–H···π contacts (Table and Figures). CCDC reference numbers 708787–708792. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820072f

$[Rh(\eta^4\text{-cod})(H_2O)_2)]O_3SCF_3$.[18] Polymorphs of Rh–Schiff base complexes are $[Rh^{I}Cl\{N,N,N\}]$[19] and $[Rh^{III}(ad)\{N,O,N,O\}$-(py)].[20]

At the same time molecular chiral metal complexes are of permanent interest.[21] There are continuous developments of optically active Schiff base (HSB*) ligands and their transition metal complexes for applications as chiral catalysts.[22–26] Organometallic compounds with anionic Schiff base (SB^{*-}) ligands are the half-sandwich complexes $[Ru(SB^*)X(\eta^6\text{-benzene})]$ {SB* = (*S*)-*N*-1-phenylethylsalicylaldiminato; *X* = Cl, 4-/2-Me-py, PPh_3}, $[M(SB^*)X(\eta^6\text{-arene})]$ (M = Ru(II), Os(II); *X* = Cl, I),[27,28] $[Ru(SB^*)X(\eta^6\text{-}p\text{-cymene})]$ (*X* = various monodentate ligands),[29,30] and $[Rh(SB^*)(\eta^4\text{-cod})]$ {SB* = (*S*)-(α)-(2-pyridyl)-salicylaldiminato,[31] (*R*)-*N*-(1-aryl-ethyl)-salicylaldiminato[32,33]}. Chiral $[Rh(SB^*)(\eta^4\text{-cod})]$ complexes with chiral Schiff bases, derived from (*S*)-α-(2-pyridyl)ethylamine and benzaldehyde derivatives, have been used successfully as enantioselective catalysts in the hydrosilylation of acetophenone with diphenylsilane.[31]

The *N*,*O*-chelate type bidentate (HSB) and tetradentate (H_2SB) Schiff bases readily react with dinuclear $[Rh(\mu\text{-X})(\eta^4\text{-cod})]_2$ (X = Cl, OMe, O_2CMe) to give mononuclear $[Rh(SB)(\eta^4\text{-cod})]$ (SB = salicylaldiminato) and dinuclear $[\{Rh(\eta^4\text{-cod})\}_2(SB)]$ {SB = bis(salicylaldiminato)} complexes, respectively.[34–37] The similar reactions with *N*,*N*-chelate type enantiopure Schiff bases afford the mononuclear $[Rh(diminato)(\eta^4\text{-cod})]$ complexes.[31,38,39] Prior to our work only one $Rh(\eta^4\text{-cod})$ structure with an *N*,*O*-chelate ligand giving a six-membered Rh{*N*,*O*} chelate ring had been known.[35,40] We recently synthesised $Rh(\eta^4\text{-cod})$ complexes containing chiral Schiff bases, chiral aminocarboxylato or chiral amino alcohols as *N*,*O*-chelating ligands starting from dinuclear $[Rh(\mu\text{-}O_2CMe)(\eta^4\text{-cod})]_2$.[32,41–43]

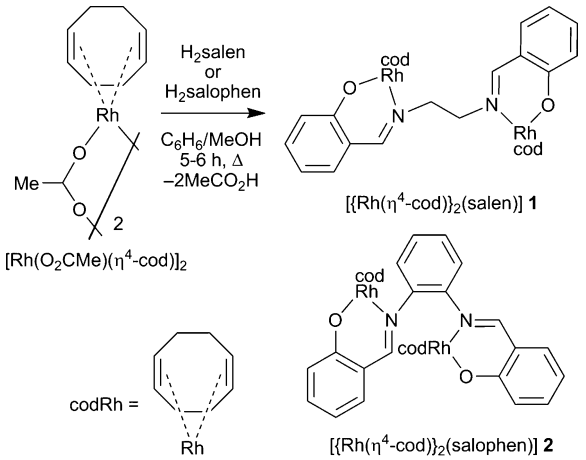
In continuation, we describe here the syntheses and structures of $Rh(\eta^4\text{-cod})$ complexes with the *N*,*O*-chelating ligands *N*,*N*′-ethylene-bis(salicylaldiminato) ($salen^{2-}$), *N*,*N*′-(1,2-phenylene)-bis(salicylaldiminato) ($salophen^{2-}$), *N*-phenylglycinato, (*R*)-*N*-(4-methoxyphenyl)ethyl-2-oxo-1-naphthaldiminato or *N*-(*o*-tolyl)-2-oxo-1-naphthaldiminato which present polymorphs, enantiomorphs with helical chains, chiral and acentric $[Rh\{N,O\}(\eta^4\text{-cod})]$ complexes.

Results and discussion

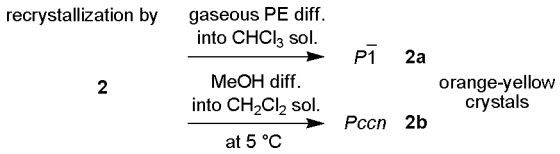
Dinuclear (acetato)(η^4-cycloocta-1,5-diene)rhodium(I), $[Rh(\mu\text{-}O_2CMe)(\eta^4\text{-cod})]_2$ reacts with the tetradentate Schiff bases *N*,*N*′-ethylene-bis(salicylaldimine) (H_2salen) and *N*,*N*′-(1,2-phenylene)-bis(salicylaldimine) (H_2salophen) in C_6H_6–MeOH (5 : 1, v/v) at 25 °C to afford the dinuclear complexes $[\{Rh(\eta^4\text{-cod})\}_2(salen)]$ (**1**) and $[\{Rh(\eta^4\text{-cod})\}_2(salophen)]$ (**2**), respectively (Scheme 1).

The structure of **2** revealed a case of polymorphism.[35] Crystallization of **2** by gas phase diffusion of petroleum ether (bp 40–60 °C) into a concentrated chloroform solution gave crystals of the same orange-yellow color but of a different space group (**2a**) as previously described[35] and obtained from slow diffusion at 5 °C of methanol into a concentrated dichloromethane solution (**2b**) (Scheme 2).

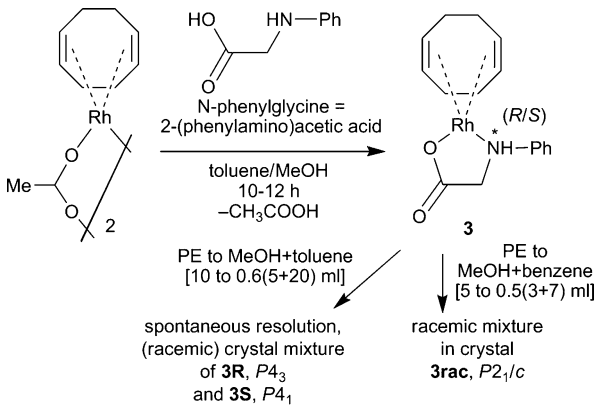
$[Rh(\mu\text{-}O_2CMe)(\eta^4\text{-cod})]_2$ reacts with the amino acid *N*-phenylglycine, (HO_2C–CH_2–NHPh) to mononuclear $[Rh(O_2C$–CH_2–$NHPh)(\eta^4\text{-cod})]$ (**3**) (Scheme 3). The structure of enantiomorph **3R** from a spontaneous resolution has recently been



Scheme 1 Synthesis of $[\{Rh(\eta^4\text{-cod})\}_2$(salen/salophen)] **1** and **2**, respectively.



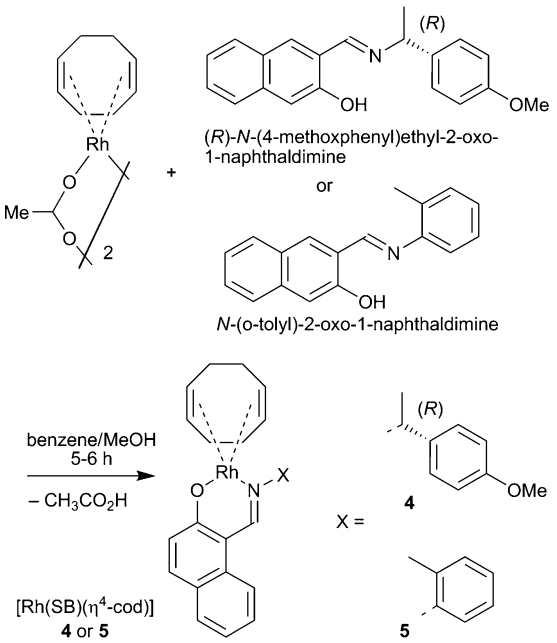
Scheme 2 Crystallization routes to the polymorphs of $[\{Rh(\eta^4\text{-cod})\}_2$-(salophen)] **2** (PE = petroleum ether, bp 40–60 °C).



Scheme 3 Synthesis and crystallization routes to the enantiomorphs and the racemic mixture of **3** (PE = petroleum ether, bp 40–60 °C).

reported by us.[41] The orange needle crystal mixture (Fig. S1a in ESI‡) of **3R** and **3S** was obtained by slowly adding 10 ml of PE (bp 40–60 °C) on the top of a warm (40 °C) concentrated (to 60%) mixture of initially 5 ml of MeOH and 20 ml of toluene (Scheme 3). When the crystallization conditions were changed to adding 5 ml of PE (bp 40–60 °C) on top of a concentrated (to 50%) mixture of initially 3 ml of MeOH and 7 ml of benzene red-brown intergrown crystals of **3rac** were obtained (Scheme 3, Fig. S1b‡). These polymorphic crystals analyzed as the racemic mixture of **3** in a centrosymmetric space group.

Furthermore, $[Rh(\mu\text{-}O_2CMe)(\eta^4\text{-cod})]_2$ reacts with the bidentate Schiff bases (*R*)-*N*-(4-methoxphenyl)ethyl-2-oxo-1-naphthaldimine or *N*-(*o*-tolyl)-2-oxo-1-naphthaldimine to mononuclear $[Rh(X\text{-}2\text{-oxo-}1\text{-naphthaldiminato})(\eta^4\text{-cod})]$ **4**, {*X* = (*R*)-*N*-(4-methoxphenyl)ethyl} and **5** {*X* = *N*-(*o*-tolyl)} (Scheme 4).



Scheme 4 Synthesis of [Rh(*X*-2-oxo-1-naphthaldiminato)(η⁴-cod)] **4** and **5**.

UV/Vis

The Rh(η⁴-cod)–Schiff base complexes show very similar electronic spectra, which mainly feature: (i) a very strong band at higher energy (<360 nm), associated with the intra-ligand π→π* transitions of the Schiff base imino group and the η⁴-cod moiety and (ii) a strong broad band at 400–500 nm ($\lambda_{max}/\varepsilon_{max}$ = 403 nm/8655 l mol^{-1} cm^{-1} for **1**, 413 nm/8077 l mol^{-1} cm^{-1} for **2**, 411 nm/13150 l mol^{-1} cm^{-1} for **4** and 416 nm/3828 l mol^{-1} cm^{-1} for **5**), assigned to the metal-to-ligand charge transfer (MLCT) transitions between Rh(I) and the diminato ligand (Schiff base anion). The CT transitions for the [Rh(η⁴-cod)] moiety, which are observed at λ_{max} = 356 nm in the starting material, [Rh(O$_2$CMe)(η⁴-cod)]$_2$, likely shift to the higher energy and overlap with the very strong intra-ligand π→π* transitions, and are not detectable in Rh(η⁴-cod)–Schiff base/–amino acid complexes (further details in Fig. S2 and Table S1 in ESI‡).[27,32,41–45]

Infrared spectroscopy

The complexes show two new bands (which are absent in the free ligands) around 675–680 cm^{-1} and 459–465 cm^{-1} which are assigned to *ν*Rh–N and *ν*Rh–O, respectively. Further, the *ν*O–H stretching band of the free Schiff bases, usually observed at 3250–3254 cm^{-1}, disappears in the complexes, which indicates dissociation of the protic hydrogen and formation of a bond between Rh and the hydroxyl oxygen atom (for further details see Table S2 in ESI‡).[28,32,41–46]

Mass spectroscopy

EI, CI or FAB mass spectra show the parent ion peaks [M]$^+$ corresponding to the formation of dinuclear **1** and **2** and mononuclear **3**, **4** and **5**. Further peaks present the species [M + H]$^+$, [M – cod]$^+$, [Rh(cod)]$^+$, Schiff base/deprotonated Schiff base or *N*-phenylglycine. The FAB-MS of **3** includes ions such as [M$_4$ – AA]$^+$, [M$_3$ – AA]$^+$, [M$_2$]$^+$ and [M$_2$ – AA]$^+$ (AA = *N*-phenylglycinato) possibly due to inter-molecular hydrogen bonding as shown in the structure of **3** (see below).

Polarimetry

The polarimetric measurement of **4** in $CHCl_3$ shows a rotation to the right ($[\alpha]^{25}$ = +91°, *c* = 0.92, at 598 nm), while the free Schiff base turns left ($[\alpha]^{25}$ = –222°, *c* = 0.52, at 598 nm).[47]

NMR spectroscopy

In ^{1}H NMR the 1,5-cyclooctadiene in [Rh{*N,O*}(η⁴-cod)] complexes shows the signals as expected for the exo- and endo-methylene protons as well as the olefin protons.[32,33,41–44,48–50] The exo-methylene protons show two multiplets at 1.6–1.8 ppm in dinuclear [{Rh(η⁴-cod)}$_2${*N,O*}] (**1**, **2**) and one multiplet at 1.7–2.0 ppm for the mononuclear [Rh{*N,O*}(η⁴-cod)] (**3**–**5**). The endo-methylene protons appear at 2.1–2.55 as two (**1**) or one multiplet in **2**–**5**. The multiplets for the olefinic protons are listed in Table S3 in ESI‡ together with other related Rh{*N,O*}(η⁴-cod) complexes.

The different signals for exo- and endo-methylene protons and the olefin protons are explained by the *trans effects* of the co-ordinated *N,O*-chelate on proton resonances.[32–35,41–44,46,48,49] In Rh(I)(η⁴-cod)–Schiff base complexes two kinds of olefin proton resonances (two multiplets) arise from the two sets of two equivalent protons *trans* to N and *trans* to O, respectively. The occurrence of more than two multiplets for the olefin proton resonances is explained due to the steric and magnetic anisotropy effects in addition to this *trans effect*,[32,48c] as will be seen later in the ^{13}C NMR studies. Complex **2** shows the C*H*=N signal relatively downfield (8.58 ppm) due to interactions with the neighboring phenyl ring (*cf*. 7.57 ppm for **1**).

In ^{13}C NMR of [Rh{*N,O*}(η⁴-cod)] complexes the cod methylene carbon atoms can give *two* singlets and the olefin carbon give *two* doublets. The observations of two signal groups each are explained by the *trans effect* of the coordinated *N,O*-chelate on the carbons resonances.[32,33,41–44,46,48,49] The doublets are due to the coupling of the olefinic carbon with the rhodium atom. The ^{103}Rh–^{13}C(olefin) spin–spin coupling constants for *trans* to N (*J* = 12–13 Hz) and *trans* to O (*J* = 14–15 Hz) are in good agreement with those found for the related mono- and dinuclear (η⁴-cod)Rh–Schiff bases complexes (see Table S4 in ESI‡). Similarly, two broad signals for methylene and olefin carbons each are found in a [Rh(*o*-aminophenolato)(η⁴-cod)] complex (Table S4‡).[43] Yet, *four* singlets and *four* doublets can be observed for the methylene and olefinic carbon atoms in **2**, **4** and **5** and other related complexes (Table S4‡). The occurrence of four singlets and four doublets is explained by steric and magnetic anisotropy effects in addition to this *trans effect*.[32,48c] Two downfield doublets (84–86 ppm) are assigned to the olefinic carbon resonances *trans* to N, the other two upfield doublets (69–75 ppm) *trans* to O (see Table S4‡). Contrary to these findings, [Rh(*N*-phenylglycinato)(η⁴-cod)] (**3**) and Rh(amino acetato)(η⁴-cod) (see Tables S3, S4‡) show only one multiplet for the olefin protons and one broad signal for the olefin carbon atoms. This might be due to a ring opening of the five membered *N,O*-chelate resulting in a rapid exchange on the NMR time scale.

[{Rh(η⁴-cod)}₂(salen)] 1 and [{Rh(η⁴-cod)}₂(salophen)] 2 (with dimorphs 2a and 2b)

The molecular structures of the rhodium complexes **1** and **2** prove the *N,O*-chelation of the deprotonated *N,N′*-ethylene-bis(salicylaldiminato) (salen^{2-}) and *N,N′*-(1,2-phenylene)-bis(salicylaldiminato) (salophen^{2-}) Schiff base ligands, respectively, to two Rh(η⁴-cod) groups (Fig. 1 and Fig. 2). Bond lengths and angles are as expected.[29,32,35,41,48b,c] Compound **1** is only the third structurally authenticated example of Rh(η⁴-cod) complexes with six-membered Rh-*N,O*-chelate rings.[32,35,40] The ethylene bridge between the two salicylaldiminato moieties in **1** is in the *s-trans* conformation. The two N–C–C planes form an angle of 156.4(3)°. The metallacycle Rh–(N–CCC–O) planes are tilted 83.3(1)° with respect to each other in **1**. The intermolecular packing in **1** shows a π···π contact between the Rh2-metallacycles[51–53] and complementary C–H···π contacts[54] from salen-CH_2 groups onto the Rh2-metallacycle and the aromatic salicyl ring C3–8 (see Table S5 and Fig. S3–S5 in ESI†). The π-stacking between the parallel Rh2-metallacycle ring planes (symmetry relation $2 - x$, $1 - y$, $1 - z$) exhibits a short centroid–centroid distance (3.86 Å), a small slippage of 1.62 Å and a small slip angle of 25°. Masui had suggested an active electron delocalization within a metal–*N*-heterocyclic chelate ring in such a way that it could exhibit some degree of "metalloaromaticity".[55,56] The packing index[57] ("calc void" with PLATON[58]) of **1** is 74.5%.

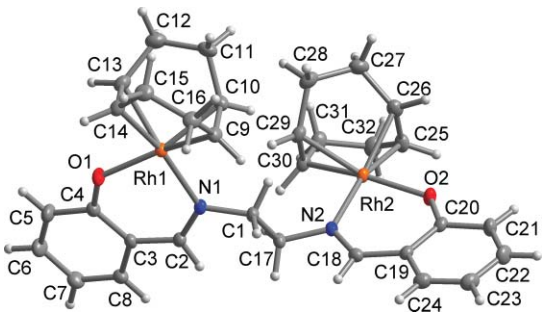


Fig. 1 Thermal ellipsoid plot for [{Rh(η⁴-cod)}₂(salen)] (**1**) at 50% probability level; bond lengths and angles in Table 1.

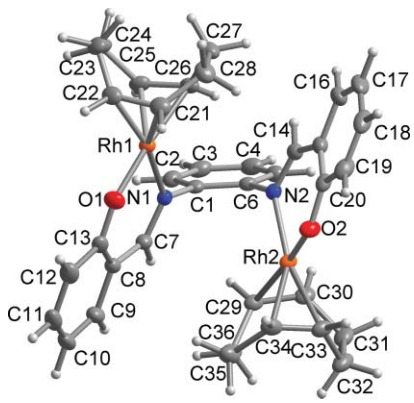


Fig. 2 Thermal ellipsoid plot for [{Rh(η⁴-cod)}₂(salophen)] (**2**) at 50% probability level; bond lengths and angles in Table 1.

Both cod-ligands in each complex are slightly asymmetrically bound (see Scheme S1 in ESI‡) which reflects the different *trans* nitrogen or oxygen donor atoms and the 'left' and 'right' differentiation as mirrored in the four olefinic ^{13}C NMR resonances.

Table 1 Selected bond lengths [Å] and angles [°] in **1** and **2**

1		**2**	
Rh1–O1	2.0299(18)	Rh1–O1	2.0316(15)
Rh1–N1	2.096(2)	Rh1–N1	2.0859(16)
Rh1–C9	2.109(3)	Rh1–C21	2.118(2)
Rh1–C10	2.117(3)	Rh1–C22	2.133(2)
Rh1–C13	2.135(3)	Rh1–C25	2.094(2)
Rh1–C14	2.146(2)	Rh1–C26	2.119(2)
Rh2–O2	2.0353(18)	Rh2–O2	2.0311(14)
Rh2–N2	2.093(2)	Rh2–N2	2.0805(17)
Rh2–C25	2.132(3)	Rh2–C29	2.118(2)
Rh2–C26	2.140(3)	Rh2–C30	2.097(2)
Rh2–C29	2.117(3)	Rh2–C33	2.143(2)
Rh2–C30	2.138(3)	Rh2–C34	2.121(2)
O1–Rh1–N1	90.34(8)	O1–Rh1–N1	90.03(6)
O2–Rh2–N2	89.49(8)	O2–Rh2–N2	89.83(6)

The crystal structure of **2** presents a polymorph (dimorph) (**2a**) to a previously reported X-ray structure of the same compound (**2b**, CSD refcode SCLIRB10, *cf*. Scheme 2).[35] From an overlay of the molecules of the dimorphs **2a** and **2b** in Fig. 3 there are slight conformational differences in the interplanar angles (Table 2) which goes together with a different packing arrangement.

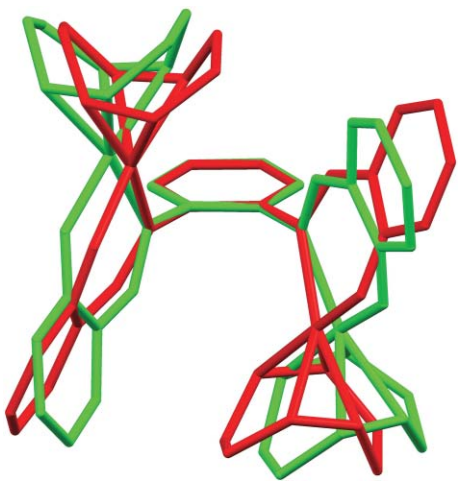


Fig. 3 Overlay of the molecular structures of the dimorphs **2a** (in red) and **2b** (CSD refcode SCLIRB10, in green) by specifying the carbon atoms of the central phenylene ring as pairs in the two structures (RMS = 0.0405).

The crystal packing of **2a** does not have π···π[51] but one C–H···π interaction[54] (see Table S5 and Fig. S6 in ESI‡). In the packing of **2b** there are still no π···π but some weak C–H···π contacts from cod-CH_2 groups onto the $RhNC_3O$ metallacycle and the anellated salicyl ring of an adjacent molecule (see Table S5 and Fig. S7 in ESI‡). In the packing of both **2a** and **2b** we invoke a different interlocking of adjacent dinuclear molecules with their corrugated van der Waals surface.[41] The Rh-metallacycles form an opening or a cleft with the anellated salicyl rings in the dinuclear molecule (Fig. 2). A motif found in the packing of **2a** is a "cupping" arrangement where the openings created by the anellated ring planes of two inversion-symmetry related Rh_2 molecules fit into each other (Fig. 4).[2] In the dimorph **2b** each phenylene ring interdigitates into the cleft formed by the salicyl–metallacycle ring

Table 2 Intramolecular distances and angles in the [{Rh(η⁴-cod)}₂-(salophen)] complexes of the two polymorphs **2a** and **2b**

	2a (red)	**2b** (green) [a,b]
Rh···Rh/Å	4.905(1)	5.737(1)
Acute interplanar angle between central phenylene ring···$RhNC_3O$ metallacycle/°		
Rh1	73.25(9)	86.5(4)
Rh2	74.19(9)	86.5(4) [c]
Acute interplanar angle between central phenylene ring···C_6-salicyl ring/°		
Rh1	69.2(1)	84.2(5)
Rh2	67.1(1)	84.2(5) [c]

[a] Calculated from the deposited cif-file SCLIRB10[35] with PLATON.[58] [b] Corresponding colors in Fig 4. [c] The asymmetric unit in **2b** consists of half of [{Rh(η⁴-cod)}₂(salophen)]. The two halves of the dinuclear molecule in **2b** are related by a two-fold rotation axis, located at the midpoints of two C–C bonds of the central phenylene ring.

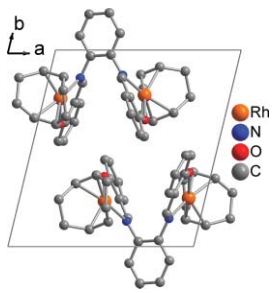


Fig. 4 Cupping motif in the packing of the dimorph structure of **2a** (hydrogen atoms omitted for clarity).

planes of the next molecule along the 2_1-screw axis parallel to *c* in *Pccn* (Fig. 5). The packing index[57,58] of polymorph **2a** and **2b** is virtually identical with 72.5% and 72.2%, respectively.

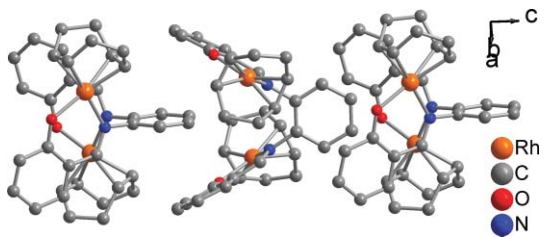


Fig. 5 Interdigitating motif in the packing of the dimorph structure of **2b** (hydrogen atoms omitted for clarity).

[Rh(O₂C–CH₂–NHPh)(η⁴-cod)] 3 (with polymorphs 3R, 3S and 3rac)

Complex **3** in the crystal structures of **3S** and **3rac** has the prochiral phenylglycinato ligand coordinated with *N,O*-chelate formation to the rhodium atom of the Rh(η⁴-cod) fragment (Fig. 6). Related Rh(η⁴-cod) complexes with a five-membered Rh-*N,O*-chelate ligand are structurally elucidated with 8-hydroxyquinolinato,[48a] tryptophan benzyl ester,[15] 4-methylpyridinium 2-pyridylcarbonylmethylide,[59] 1-(2′-pyridyl)-3-dimethylamino-2-propenone,[60] imidazole-4,5-carboxylato,[49a] orotato[46a] and 3-oxo-1-(pyridin-2-yl)prop-1-en-1-olato.[48b]

Table 3 Selected bond lengths [Å] and angles [°] in **3S**, **3rac**, **3R**

	3S	**3rac**	**3R**[41]
Rh–O1	2.053(8)	2.075(1)	2.059(3)
Rh–N	2.151(9)	2.145(2)	2.145(3)
Rh–C9	2.11(1)	2.124(2)	2.112(5)
Rh–C10	2.12(1)	2.099(2)	2.131(4)
Rh–C13	2.07(1)	2.113(2)	2.108(4)
Rh–C14	2.09(1)	2.104(2)	2.125(4)
O1–Rh–N	81.0(3)	80.84(5)	80.8(1)
O1–Rh–C9	90.8(4)	95.53(7)	90.8(2)
O1–Rh–C10	95.8(4)	89.35(7)	95.4(2)
O1–Rh–C13	160.2(4)	157.81(7)	160.6(2)
O1–Rh–C14	160.9(4)	163.65(7)	161.0(2)
N–Rh–C9	157.9(3)	161.85(9)	158.7(2)
N–Rh–C10	162.1(3)	157.93(9)	161.5(2)
N–Rh–C13	94.5(4)	99.58(7)	95.6(2)
N–Rh–C14	99.4(5)	96.09(7)	99.1(2)

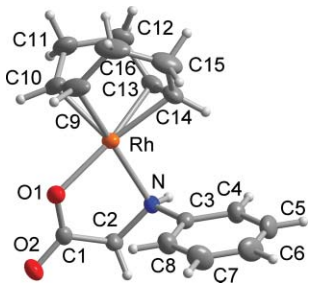


Fig. 6 Thermal ellipsoid plot for [Rh(O₂C–CH₂–NHPh)(η⁴-cod)] (**3**) from the structure of **3rac** (showing the *R* enantiomer in this racemic structure). The numbering scheme in **3S** is identical (except that this polymorph contains only the *S* enantiomer); bond lengths and angles in Table 3.

The nitrogen atom of the prochiral *N*-phenylglycinato ligand becomes a stereogenic center upon metal coordination, yielding a racemic mixture of *R*- and *S*-configured complexes. From the racemic mixture the complex with the *R*-configuration at nitrogen [Rh((*R*)-O₂C–CH₂–NHPh)(η⁴-cod)] (**3R**) crystallizes in the tetragonal, chiral space group $P4_3$ under the appropriate conditions (see Scheme 3). The crystal structure revealed a case of a two-fold spontaneous resolution of a racemic complex mixture into homo-chiral helix-enantiomers.[41] The overall crystal ensemble (Fig. S1a in ESI‡) is racemic which we prove here with the structure of the *S*-configured enantiomorphic complex **3S** in the tetragonal space group $P4_1$. The chiral space groups $P4_3$ and $P4_1$ form an enantiomorphous pair.[61,62] It was not possible to visibly distinguish the crystals with the *R*-and *S*-configuration (*cf*. Fig. S1a‡) so we had to carry out full data set collections on various crystals to determine the space group. By investigating six of the needle-shaped crystals in Fig. S1a‡ four of them were found to contain the *R*-configured complex in $P4_3$ and two of them contained the *S*-configured complex in $P4_1$. The *S*-configured complexes in the enantiomorph **3S** assemble in a right-handed (or *P*) 4_1-helical chain through N–H···O hydrogen bonding from the stereogenic amino group to a neighboring unligated carboxyl oxygen atom (Fig. 7 and Fig. 8). Only molecules of the same *S*-configuration are combined into a chain and neighboring chains are of the same 4_1 handedness.

An attempt was made to collect circular dichroism (CD) spectra on a toluene solution of a single crystal with X-ray

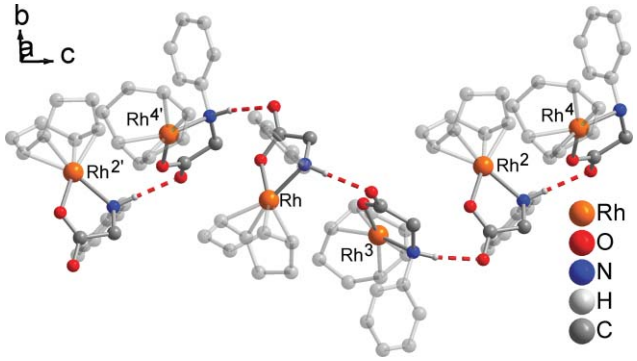


Fig. 7 Right-handed (*P*) 4_1-helical chain in **3S**. Hydrogen bonding interaction (dashed red line) [Å, °]: N–H 0.9(1), H···O^3 2.0(1), N···O^3 2.90(1), N–H···O^3 170(10); symmetry transformations: 2 = 2 − *x*, 2 − *y*, 0.5 + *z*; 2′ = 2 − *x*, 2 − *y*, −0.5 + *z*; 3 = 2 − *y*, *x*, 0.25 + *z*; 4 = y, 2 − *x*, 0.75 + *z*; 4′ = *y*, 2 − *x*, −0.25 + *z*. Carbon atoms of the phenyl and cod rings are depicted semi-transparent and C–H hydrogen atoms are omitted for clarity.

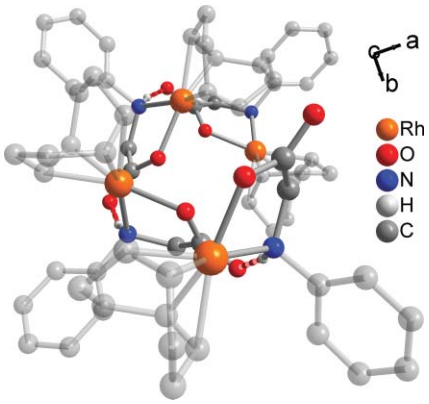


Fig. 8 Right-handed 4_1-helical chain in **3S** viewed along the chain direction. Carbon atoms of the phenyl and cod rings are depicted semi-transparent and C–H hydrogen atoms are omitted for clarity.

determined absolute *R*- or *S*-configuration at the nitrogen atom. However, no useful CD spectra could be obtained either due to the low absolute amount of a single crystal with its subsequent low concentration or because of a rapid racemization in solution.

The homochirality, that is, the same handedness of the helices and, thereby, the packing in a chiral space group can only be due to the corrugated van der Waals surface of the helix (Fig. 9). No noteworthy π–π-stacking or C–H···π interactions are found between the helices in **3S** or **3R**,[41] despite the presence of phenyl rings.

When the crystallization conditions for **3** were changed slightly (*cf.* Scheme 3) a racemic mixture of *R*- and *S*-configured complexes crystallizes in the monoclinic, centrosymmetric space group $P2_1/c$ as **3rac**. Crystals of **3rac** can be considered a polymorph to the two enantiomorphs **3R** and **3S**. Bond lengths of **3** in the different forms are identical within experimental error (3σ) (Table 3) and an overlay of *R*-complexes from **3R** and **3rac** in Fig. 10 reveals only slight conformational differences.

As before molecules in the polymorph **3rac** assemble in chains through N–H···O hydrogen bonding (Fig. 11). Again,

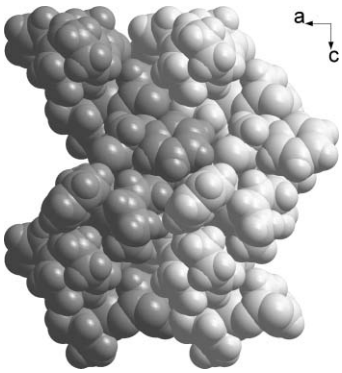


Fig. 9 The interlocking of two neighboring right-handed (*P*) 4_1-helical chains in **3S** with their corrugated van der Waals surface; space-filling representation of the chains, which are differentiated by light and dark gray shading.

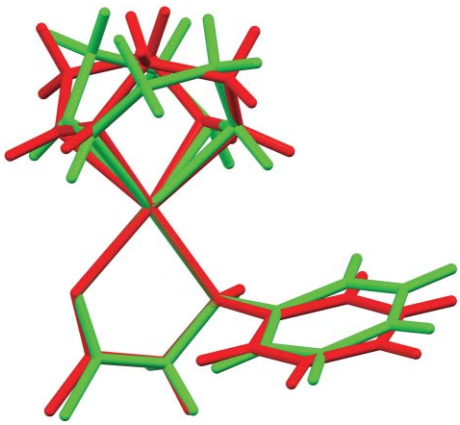


Fig. 10 Overlay of the molecular structures of the polymorphs **3rac** (in red) and **3R** (CSD refcode DEGQUC,[41] in green) by specifying the Rh, N and (Rh–)O atom as pairs in the two structures (RMS = 0.00727).

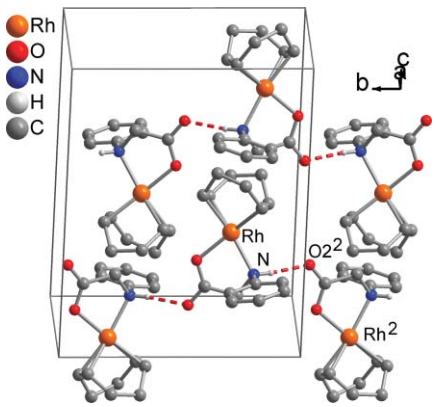


Fig. 11 Hydrogen-bonded complexes in two parallel chains along the 2_1-axes, parallel to the *b*-axis in **3rac**. Here, the lower chain contains only *R*-configured, the upper chain only *S*-configured complexes. Hydrogen bonding interaction (dashed red line) [Å, °]: N–H 0.82(2), H···O^2 2.01(2), N···O^2 2.820(2), N–H···O^2 171(2); symmetry transformations: 2 = −*x*, −1/2 + *y*, 1/2 − *z*. C–H hydrogen atoms are omitted for clarity.

only molecules of the same configuration are combined into a chain, albeit now neighboring chains have complexes of opposite configuration. As in **3R** or **3S** no noteworthy π–π-stacking or

C–H $\cdots\pi$ interactions are found between the chains. The packing index[57,58] of 71.3% in **3rac** is slightly higher than in **3R** or **3S** with 68.7–69.8%.

[Rh(*X*-2-oxo-1-naphthaldiminato)(η⁴-cod)] 4, {*X* = (*R*)-*N*-(4-methoxphenyl)ethyl} and 5 {*X* = *N*-(*o*-tolyl)}

Complexes **4** and **5** have the 2-oxo-1-naphthaldiminato ligand coordinated with a six-membered Rh–*N,O*-chelate ring formation and the rhodium-bound η⁴-cod fragment (Fig. 12 and Fig. 13). The intermolecular packing in **4** and **5** shows no $\pi\cdots\pi$ contacts despite the presence of an extended aromatic system in the naphthyl ring.[51–53] Only two or one C–H $\cdots\pi$ contacts onto the $RhNC_3O$ metallacycle can be noted[54] in **4** or **5**, respectively (see Table S5 and Fig. S8 and S9 in ESI‡). The crystal packing in **4** is a herring-bone pattern (Fig. 14). Compound **5** crystallizes in the non-centrosymmetric polar space group *Cc*. Accordingly, all molecules show the same orientation, *e.g.* the naphthyl–Rh–cod axes or the *o*-tolyl planes, respectively, are oriented parallel to each other, with the naphthyl ring or the methyl group of the *o*-tolyl, respectively, all pointing in the same direction (Fig. 15). The packing index[57,58] is 68.7% for **4** and 69.8% for **5**.

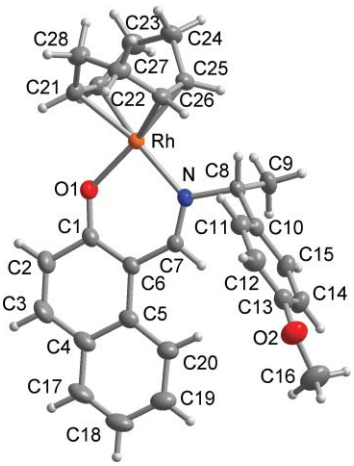


Fig. 12 Thermal ellipsoid plot (50% level) for **4**; bond lengths and angles in Table 4.

Table 4 Selected bond lengths [Å] and angles [°] in **4** and **5**

	4	5
Rh–O(1)[a]	2.0273(10)	2.033(5)
Rh–N	2.0684(12)	2.053(5)
Rh–C21	2.1460(16)	2.138(7)
Rh–C22	2.1288(14)	2.106(7)
Rh–C25	2.1311(15)	2.131(6)
Rh–C26	2.1058(14)	2.107(6)
O(1)–Rh–N	89.16(5)	88.52(19)
O(1)–Rh–C21	86.28(6)	87.0(2)
O(1)–Rh–C22	86.92(6)	89.0(2)
O(1)–Rh–C25	165.75(5)	168.1(2)
O(1)–Rh–C26	153.14(6)	151.8(2)
N–Rh–C21	164.02(6)	168.1(2)
N–Rh–C22	156.97(5)	153.2(3)
N–Rh–C25	97.91(5)	96.8(2)
N–Rh–C26	95.38(6)	96.9(2)

[a] O1 in **4**, O in **5**.

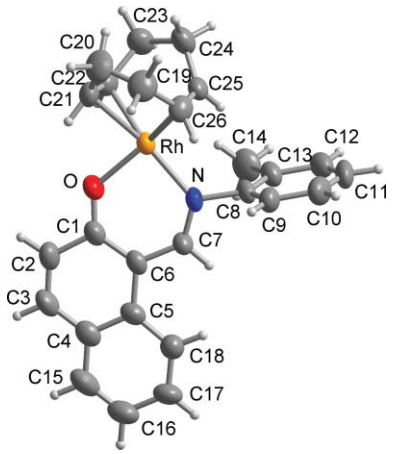


Fig. 13 Thermal ellipsoid plot (50% level) for **5**; bond lengths and angles in Table 4.

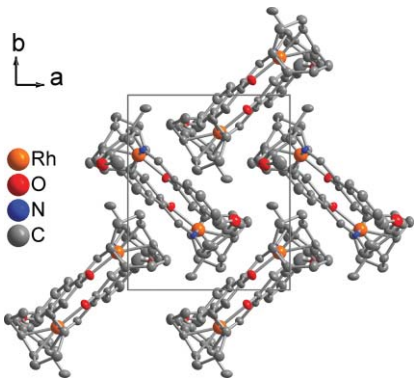


Fig. 14 Herring-bone motif in the packing of the chiral complex **4** (hydrogen atoms omitted for clarity).

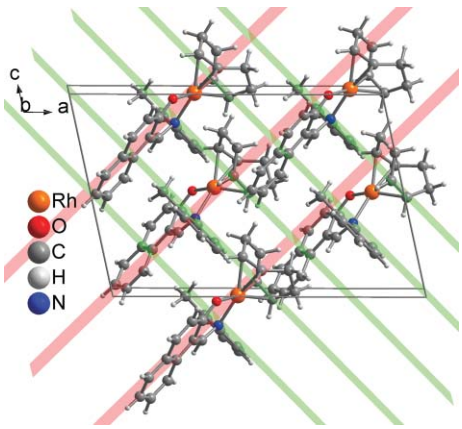


Fig. 15 Polar packing in the structure of complex **5**. The naphthyl–Rh–cod axes lie approximately parallel to the (–5 0 4) lattice planes (in red) and the naphthyl or cod groups, respectively point in the same direction. Also, the *o*-tolyl planes lie parallel to the (4 0 2) lattice planes (in green) and the methyl groups are oriented in the same direction.

Conclusions

The [Rh{*N,O*}(η⁴-cod)] complexes with the salicylaldiminato Schiff base ligands described here have an unpolar molecule surface, such that their crystal packing can only be controlled

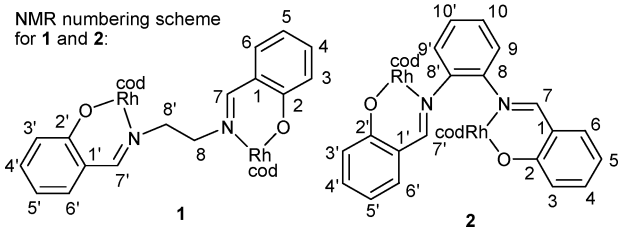
by weak C–H $\cdots$ π and van der Waals contacts. The salophen complex **2** is then found in a second polymorph. The weak interactions in the *N*-(*o*-tolyl)-2-oxo-1-naphthaldiminato complex **5** enable the molecules arranged in the same orientation to give polar packing. Only the *N*-phenylglycinato complex [Rh(O_2C–CH_2–NHPh)(η^4-cod)], **3** has a hydrogen-bonding functionality which leads to chain formation of homochiral molecules. In between the chains only van der Waals interactions persist. Subsequently, polymorphic forms of **3** crystallize with either helical chains around a fourfold screw axis (4_1 or 4_3) or chains along a twofold screw axis (2_1). The corrugated van der Waals surface of the fourfold helical chains allows only for a homochiral assembly so that spontaneous resolution occurs. *R*-Complexes of **3** crystallize in the chiral space group $P4_3$ and *S* complexes in $P4_1$ with the crystal ensemble being racemic. The 2_1 chains alternate in *R*- and *S*-composition so that the structure **3rac** contains the racemic mixture within each crystal.

Experimental section

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents used were dried and distilled under nitrogen prior to use: benzene and petroleum ether (bp 40–60 °C) over Na metal; methanol over CaO. IR spectra were recorded on a Bruker Optik IFS 25 spectrometer as KBr disks at ambient temperature. UV/Vis spectra were obtained with a Shimadzu UV 3150 spectrophotometer in C_6H_6 or CH_2Cl_2 at 25 °C. Elemental analyses were done on a VarioEL from Elementaranalysensysteme GmbH. NMR spectra were run on Bruker AC DPX 400 operating at 400 MHz (^{1}H) and 100 MHz (^{13}C) at 25 °C with calibration against the residual protonated solvent signal ($CDCl_3$ ^{1}H NMR 7.26 ppm, ^{13}C NMR 77.0 ppm; DMSO-d_6 ^{1}H NMR 2.52 ppm). The NMR grade solvents $CDCl_3$ and DMSO-d_6 were deoxygenated prior to use. FAB-MS (positive mode): Finnigan MAT 8230 with data system SS 300, matrix: *m*-nitrobenzyl alcohol. 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 $CHCl_3$ at 25 °C and the values of $[\alpha]^{25}$ were determined according to the literature.[27,32] The starting dinuclear [Rh(O_2CMe)(η^4-cod)]$_2$ complex was synthesized from [RhCl(η^4-cod)]$_2$ according to the literature.[42,50,63] The crystallization of **3R** and **3S** has been described before.[41] $RhCl_3 \cdot 3H_2O$ (Wako), Na_2CO_3 (Lancaster), 1,5-cyclooctadiene (Wako) were used as received. The Schiff bases (*R*)-*N*-(4-methoxyphenyl)ethyl-2-hydroxy-1-naphthaldimine, *N*-(*o*-tolyl)-2-oxo-1-naphthaldimine, *N,N′*-ethylene-bis(salicylaldimine) (H_2salen) and *N,N′*-(1,2-phenylene)-bis(salicylaldimine) (H_2salophen) were synthesized according to the literature.[47] The enantiopure amine (*R*)-*N*-(4-methoxyphenyl)ethylamine was used as received from BASF, Ludwigshafen, Germany.

Bis(η^4-cycloocta-1,5-diene)(μ-*N,N′*-1,2-diaminoethane-bis(salicylaldiminato)-κ^4*N,O:N′,O′*)dirhodium(I), [{Rh(η^4-cod)}$_2$(salen)] (1)

Equimolar amounts of *N,N′*-ethylene-bis(salicylaldimine) (H_2salen) (67.4 mg, 0.25 mmol) and [Rh(O_2CMe)(η^4-cod)]$_2$ (135.3 mg, 0.25 mmol) were dissolved in 10 ml of C_6H_6–MeOH (5 : 1, v/v) and the solution stirred for 5–6 h at room temperature. The color soon changed from red-orange to bright-yellow. The solvent was evaporated *in vacuo*, the residue dissolved in 10 ml of C_6H_6–MeOH (5 : 1, v/v), the solution stirred for 30 min and the solvent evaporated again. This procedure was repeated three more times in order to remove the acetic acid. Finally, the residue was dried *in vacuo* (0.1–0.2 mbar) at 60 °C to give bright-yellow **1** (yield 145 mg, 84%). Single crystals suitable for X-ray measurement were grown by gas phase diffusion of petroleum ether (bp 40–60 °C) into a concentrated chloroform solution of **1** within one week at 25 °C. IR (see ESI‡). UV/Vis (see ESI‡). MS (FAB, +) [*m*/*z* (%)]: 689 (15) [M + H]$^+$, 580 (100) [M – cod]$^+$, 578 (25) [M – cod – H_2]$^+$, 461 (15) [M – cod – C_6H_4(OH)(CN)]$^+$, 391 (52) [(RhOC_6H_5)$_2$ – H]$^+$, 327 (45) [Rh(cod)OC_6H_4(CN) – H_2]$^+$, 289 (35) [(RhOC_6H_5)$_2$ – Rh]$^+$, 267 (30) [H_2Salen – H]$^+$ and 207 (55) [Rh_2 + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (m, 4H, CH_2cod$_{exo}$), 1.81 (m, 4H, CH_2cod$_{exo}$), 2.14 (m, 4H, CH_2cod$_{endo}$), 2.36 (m, 4H, CH_2cod$_{endo}$), 3.29 (s, 4H, $H_{8,9}$), 3.58 (m, 4H, C*H*cod), 4.40 (m, 4H, C*H*cod), 6.32 (t, J = 7.0 Hz, 2H, $H_{4,4'}$), 6.70 (d, J = 8.5 Hz, 2H, $H_{6,6'}$), 6.81 (d, J = 7.6 Hz, 2H, $H_{3,3'}$), 7.15 (t, J = 7.0 Hz, 2H, $H_{5,5'}$) and 7.57 (s, 2H, $H_{7,7'}$). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.71 (m, 4H, CH_2cod$_{exo}$), 1.84 (m, 4H, CH_2cod$_{exo}$), 2.09 (m, 4H, CH_2cod$_{endo}$), 2.32 (m, 4H, CH_2cod$_{endo}$), 3.41 (s, 4H, $H_{8,9}$), 3.78 (m, 4H, C*H*cod), 4.28 (m, 4H, C*H*cod), 6.50 (t, J = 7.0 Hz, 2H, $H_{4,4'}$), 6.68 (d, J = 8.4 Hz, 2H, $H_{6,6'}$), 7.15 (d, J = 7.8 Hz, 2H, $H_{3,3'}$), 7.27 (t, J = 7.0 Hz, 2H, $H_{5,5'}$) and 8.00 (s, 2H, $H_{7,7'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.8, 31.7 (s, CH_2cod), 60.9 (s, $C_{8,8'}$), 71.2 (d, $J_{C\text{-}Rh}$ = 14.2 Hz, *C*Hcod), 85.50 (d, $J_{C\text{-}Rh}$ = 11.9 Hz, *C*Hcod), 114.5 (s, $C_{3,3'}$), 118.8 (s, $C_{5,5'}$), 121.3 (s, $C_{1,1'}$), 135.0 (s, $C_{6,6'}$), 135.4 (s, $C_{4,4'}$), 166.5 (s, $C_{2,2'}$) and 166.9 (s, $C_{7,7'}$). $C_{32}H_{38}N_2O_2Rh_2$ (688.46) calcd C 55.83, H 5.56, N 4.07; found C 55.85, H 5.55, N 3.73%.



Bis(η^4-cycloocta-1,5-diene)(μ-*N,N′*-*o*-phenylene-bis(salicylaldiminato)-κ^4*N,O:N′,O′*)dirhodium(I), [{Rh(η^4-cod)}$_2$(salophen)] (2)

The same procedure was followed as for the synthesis of **1** using *N,N′*-(1,2-phenylene)-bis(salicylaldimine) (H_2salophen) to give orange-yellow **2** (yield 152 mg, 82%). Single crystals suitable for X-ray measurement were obtained by gas phase diffusion of petroleum ether (bp 40–60 °C) into a concentrated chloroform solution of **2** within one week at 25 °C. IR (see ESI‡). UV/Vis (see ESI‡). MS (FAB, +) [*m*/*z* (%)]: 737 (5) [M + H]$^+$, 628 (25) [M – cod]$^+$, 486 (18) [M – cod$_2$ – 2OH]$^+$, 418 (25) [M – salophen – 2H_2]$^+$, 391 (100) [(RhOC_6H_5)$_2$ – H]$^+$, 307 (92) [Rh(cod)OC_6H_5 + H_2 + H]$^+$, 289 (80) [(RhOC_6H_5)$_2$ – Rh]$^+$, 219 (65) [RhOC_6H_4(CN) – H_2]$^+$ and 207 (25) [Rh_2 + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (m, 4H, CH_2cod$_{exo}$), 1.79 (m, 4H, CH_2cod$_{exo}$), 2.17 (m, 8H, CH_2cod$_{endo}$), 2.45 (m, 2H, C*H*cod), 3.53 (m, 2H, C*H*cod), 4.37 (m, 2H, C*H*cod), 4.54 (m, 2H, C*H*cod), 6.62 (t, J = 7.0 Hz, 2H,

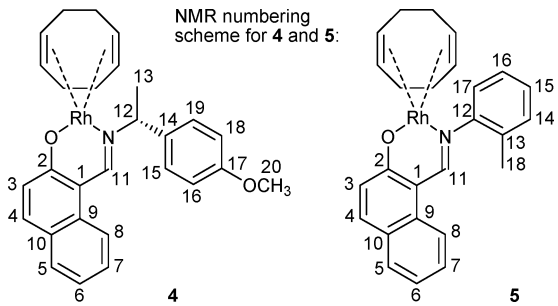
$H_{4,4'}$), 6.81 (d, J = 8.5 Hz, 2H, $H_{6,6'}$), 7.01 (m, 2H, $H_{3,3'}$), 7.18 (m, 2H, $H_{5,5'}$), 7.33 (m, 2H, $H_{10,10'}$), 7.43 (d, J = 7.8 Hz, 2H, $H_{9,9'}$) and 8.58 (s, 2H, $H_{7,7'}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.9, 29.5, 30.3, 32.6 (s, CH_2cod), 69.7 (d, $J_{C\text{-}Rh}$ = 14.4 Hz, CHcod), 74.3 (d, $J_{C\text{-}Rh}$ = 14.6 Hz, CHcod), 84.3 (d, $J_{C\text{-}Rh}$ = 11.8 Hz, CHcod), 85.8 (d, $J_{C\text{-}Rh}$ = 11.7 Hz, CHcod), 114.8 (s, $C_{3,3'}$), 119.1 (s, $C_{5,5'}$), 122.2 (s, $C_{1,1'}$), 124.2 (s, $C_{9,9'}$), 126.1 (s, $C_{10,10'}$), 135.5 (s, $C_{6,6'}$), 135.6 (s, $C_{4,4'}$), 143.7 (s, $C_{8,8'}$), 166.2 (s, $C_{2,2'}$) and 167.1 (s, $C_{7,7'}$). $C_{36}H_{38}N_2O_2Rh_2$ (736.52) calcd C 58.71, H 5.20, N 3.80; found C 57.26, H 5.27, N 3.54%.

(η⁴-Cycloocta-1,5-diene)(*rac*-*N*-phenylglycinato-κ²*N*,*O*)rhodium(I), [Rh(*N*-phenylglycinato)(η⁴-cod)] (3rac)

Two equivalents of *N*-phenylglycine (70 mg, 0.46 mmol) were dissolved in 3 ml of MeOH. This solution was poured into a solution of $[Rh(O_2CMe)(\eta^4\text{-cod})]_2$ (123 mg, 0.23 mmol) in 7 ml of benzene and stirred for 8–10 h at room temperature. The volume was reduced to 50% *in vacuo* at 30 °C, then 5 ml of PE (bp 40–60 °C) was very slowly added on the top of this solution and the combined solution was left standing for crystallization at room temperature. Crystal formation started after 2 d and block-shaped red-brown crystals, suitable for X-ray measurement, were obtained after 5 d. The crystals were filtered off and washed 3 times with PE (5 ml each). Finally, the crystals were dried *in vacuo* (0.1–0.2 mbar) at 40 °C (yield 120 mg, 73%). IR (see ESI‡). MS (EI, 70 eV) [*m*/*z* (%)]: 361 (4) $[M + H]^+$, 359 (10) $[M - H_2]^+$, 317 (16) $[M - CO_2]^+$, 315 (35) $[M - H_2 - CO_2]^+$, 285 (10) $[M - Ph + H]^+$, 211 (13) [M – AA – Rh(cod)]$^+$, 208 (25) $[Rh(cod) - H_2 - H]^+$, 151 (14) [HAA]$^+$, 106 (100) $[cod - H_2]^+$ and 77 (57) $[Ph]^+$ (AA = *N*-phenylglycinato). MS (FAB, +) [*m*/*z* (%)]: 1293 (2) $[M_4 - HAA]^+$, 1143 (4) $[M_4 - (AA)_2 - H]^+$, 933 (38) $[M_3 - AA]^+$, 722 (4) $[M_2]^+$, 572 (100) $[M_2 - AA]^+$, 362 (48) $[M + H]^+$, 360 (4) $[M - H]^+$, 211 (4) [M – AA – Rh(cod)]$^+$. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.70 (dd, J = 7.2 Hz, 4H, CH_2cod$_{exo}$), 2.33 (m, 4H, CH_2cod$_{endo}$), 3.83 (m, 4H, CHcod), 4.00 (m, 2H, CH_2), 4.24 (m, 1H, NH), 7.12 (m, 2H, H_o-Ar), 7.30 (m, 3H, $H_{m,p}$-Ar). ^{1}H NMR (DMSO-d_6, 200 MHz): δ = 1.63 (dd, J = 8.05 Hz, 4H, CH_2cod$_{exo}$), 2.23 (m, 4H, CH_2cod$_{endo}$), 3.34 (s, 2H, CH_2), 3.58 (m, 4H, CHcod), 3.61 (m, 1H, NH), 7.01 (d, J = 8.19 Hz, 2H, H_o-Ar), 7.32 (t, J = 7.9, 7.5 Hz, 3H, $H_{m,p}$-Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 29.8 (s, CH_2cod), 56.1 (s, CH_2), 78.5 (br, CHcod), 119.6 (s, C_o-Ar), 124.5 (s, C_p-Ar), 129.0 (s, C_m-Ar), 145.4 (s, NC-Ar), 179.3 (s, CO_2^-). ^{13}C NMR (DMSO-d_6, 50 MHz): δ = 30.1 (s, CH_2cod), 56.3 (s, CH_2), 78.2 (br, CHcod), 119.9 (s, C_o-Ar), 124.8 (s, C_p-Ar), 129.6 (s, C_m-Ar), 146.4 (s, NC-Ar), 179.6 (s, CO_2^-). $C_{16}H_{20}NO_2Rh$ (361.25) calcd C 53.20, H 5.58, N 3.88; found C 51.81, H 5.26, N 3.67%.

(η⁴-Cycloocta-1,5-diene){(*R*)-*N*-(4-methoxphenyl)ethyl-2-oxo-1-naphthaldiminato-κ²*N*,*O*}rhodium(I) (4)

Two equivalents of (*R*)-*N*-(4-methoxyphenyl)ethyl-2-hydroxy-1-naphthaldimine (116 mg, 0.38 mmol) and one equivalent of $[Rh(O_2CMe)(\eta^4\text{-cod})]_2$ (102 mg, 0.19 mmol) were dissolved in 10 ml of C_6H_6–MeOH (5 : 1, v/v). The color soon changed from red-orange to bright-yellow. The solution was stirred for 5–6 h at room temperature and the solvent evaporated *in vacuo* at 40 °C. The yellow product was then dissolved in 10 ml of C_6H_6–MeOH (5 : 1, v/v), the solution stirred for another 30 min and the solvent evaporated again *in vacuo*. This procedure was repeated three times, and finally the product was dried *in vacuo* (0.1–0.2 mbar) at 40 °C to give yellow **4** (yield 165 mg, 85%). Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a concentrated chloroform solution of **4** after 3–4 d at room temperature. $[\alpha]^{25}$ (c = 0.92, $CHCl_3$): +91° (578 nm). IR (see ESI‡). UV/Vis (see ESI‡). MS (EI, 70 eV) [*m*/*z* (%)]: 515 (100) $[M]^+$, 407 (60) $[M - cod]^+$, 379 (10) $[M - cod - CO]^+$, 305 (6) $[HSB]^+$, 238 (20) $[Rh(cod) + CO - H]^+$, 218 (10) $[Rh(C_6H_5CH_3CN)]^+$, 211 (5) $[Rh(cod)]^+$, 207 (10) $[Rh(cod) - 2H_2]^+$, 135 (10) $[CH_3CHC_6H_4OMe]^+$, 103 (8) $[Rh]^+$, 77 (5) $[C_6H_5]^+$ (HSB = free Schiff base = $C_{20}H_{19}NO_2$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.73 (d, J_{HH} = 6.8 Hz, 3H, H_{13}), 2.00 (m, 4H, CH_2cod$_{exo}$), 2.53 (m, 4H, CH_2cod$_{endo}$), 3.82 (m, 3H, H_{20}), 3.91 (m, 2H, CHcod), 4.43 (q, J_{HH} = 6.8 Hz, 1H, H_{12}), 4.61 (m, 2H, CHcod), 6.91–7.03 (m, 2H, H_{Ar}), 7.13–7.17 (m, 1H, H_{Ar}), 7.23–7.43 (m, 5H, H_{Ar}), 7.56–7.65 (m, 2H, H_{Ar}), 8.86 (d, J_{HH} = 2.0 Hz, 1H, H_{11}). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.7 (s, C_{13}), 28.3, 28.9, 31.1, 31.8 (s, CH_2cod), 54.9 (s, C_{12}), 60.1 (s, C_{20}), 71.1 (d, $J_{C\text{-}Rh}$ = 14.3 Hz, CHcod), 73.3 (d, $J_{C\text{-}Rh}$ = 14.2 Hz, CHcod), 84.1 (d, $J_{C\text{-}Rh}$ = 11.65 Hz, CHcod), 84.7 (d, $J_{C\text{-}Rh}$ = 11.75 Hz, CHcod), 113.7 (s, $C_{3,16,18}$), 118.3 (s, C_1), 121.3 (s, C_6), 124.6 (s, C_5), 126.3 (s, C_7), 126.7 (s, C_8), 128.4 (s, $C_{15,19}$), 128.5 (s, C_{10}), 134.5 (s, C_4), 134.8 (s, C_{14}), 134.9 (s, C_9), 157.6 (s, C_2), 158.4 (s, C_{17}), 165.4 (s, C_{11}). $C_{28}H_{30}NO_2Rh$ (515.46) calcd C 65.24, H 5.87, N 2.72; found: C 64.91, H 5.96, N 2.50%.



(η⁴-Cycloocta-1,5-diene){*N*-(*o*-tolyl)-2-oxo-1-naphthaldiminato-κ²*N*,*O*}rhodium(I) (5)

The procedure for the synthesis of **4** was followed using *N*-(*o*-tolyl)-2-oxo-1-naphthaldimine to give yellow **5** (yield 130 mg, 77%). Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a concentrated chloroform solution of **5** after 3–4 d at room temperature. IR (see ESI‡). UV/Vis (see ESI‡). MS (EI, 70 eV) [*m*/*z* (%)]: 471 (100) $[M]^+$, 363 (11) $[M - cod]^+$, 335 (55) $[M - C_6H_4(CH_3)(NHCHO) - H]^+$, 260 (10) $[HSB - H]^+$, 218 (35) $[HSB - CO_2 + H]^+$, 211 (10) $[Rh + cod]^+$, 208 (20) $[Rh + cod - H_2 - H]^+$, 103 (5) $[Rh]^+$ (HSB = free Schiff base = $C_{18}H_{15}NO$). MS (CI, NH_3) [*m*/*z* (%)]: 472 (100) $[M + H]^+$, 471 (12) $[M]^+$, 262 (50) $[HSB + H]^+$, 261 (10) $[HSB]^+$, 108 (8) ($C_6H_5CH_2OH$). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.76 (m, 4H, CH_2cod$_{exo}$), 2.31 (s, 3H, CH_3), 2.35 (m, 4H, CH_2cod$_{endo}$), 2.62 (m, 1H, CHcod), 3.32 (m, 1H, CHcod), 4.53 (m, 1H, CHcod), 4.59 (m, 1H, CHcod), 6.92 (d, J_{HH} = 7.6 Hz, 1H, H_3), 7.00 (d, J_{HH} = 9.2 Hz, 1H, H_6), 7.12 (m, 4H, H_{14-17}), 7.21 (dd, J_{HH} = 8.3 Hz, J_{HH} = 1.5 Hz, 1H, H_7), 7.56 (dd, J_{HH} = 8.0 Hz, J_{HH} = 1.2 Hz, 1H, H_8), 7.64 (d, J_{HH} = 9.2 Hz, 1H, H_5), 7.73 (d, J_{HH} = 8.4 Hz, 1H, H_4), 8.68 (d, J_{HH} = 2.0 Hz, 1H, H_{11}). ^{13}C NMR (50 MHz, $CDCl_3$):

Table 5 Crystal data for [{Rh(η⁴-cod)}₂(salen)] (**1**), [{Rh(η⁴-cod)}₂(salophen)] (**2**), [Rh(*S*-*N*-phenylglycinato)(η⁴-cod)] (**3S**), [Rh(*rac*-*N*-phenylglycinato)(η⁴-cod)] (**3rac**), **4** and **5**

Compound	**1**	**2**	**3S**	**3rac**	**4**	**5**
Empirical formula	$C_{32}H_{38}N_2O_2Rh_2$	$C_{36}H_{38}N_2O_2Rh_2$	$C_{16}H_{20}NO_2Rh$	$C_{16}H_{20}NO_2Rh$	$C_{28}H_{30}NO_2Rh$	$C_{26}H_{26}NORh$
M/g mol^{-1}	688.46	736.50	361.24	361.24	515.44	471.39
Crystal size/mm	0.16 × 0.12 × 0.10	0.17 × 0.15 × 0.07	0.28 × 0.12 × 0.09	0.20 × 0.16 × 0.08	0.49 × 0.21 ×0.14	0.35 × 0.26 × 0.11
2θ range/°	4.02–60.02	3.46–60.06	4.28–51.96	4.52–52.4	3.54–56.8	4.26–51.7
h; k; l range	±16; ±16; ±17	±14; ±16; –17, 16	±11; ±11; ±19	±10; ±13; ±22	±12; ±14; ±30	±19; ±14; ±13
Crystal system	Triclinic	Triclinic	Tetragonal	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P4_1$	$P2_1/c$	$P2_12_12_1$	Cc
a/Å	11.578(1)	10.6521(8)	9.5338(6)	8.1730(1)	9.1961(2)	16.254(3)
b/Å	11.676(1)	11.9883(8)	9.5338(6)	10.8373(2)	11.0473(3)	11.992(3)
c/Å	12.500(1)	12.0891(9)	16.209(2)	17.9416(3)	22.9704(5)	10.771(2)
α/°	112.549(2)	77.496(1)	90	90	90	90
β/°	115.690(2)	89.989(1)	90	114.589(1)	90	102.288(3)
γ/°	96.732(2)	76.808(1)	90	90	90	90
V/Å^3	1322.3(3)	1465.4(2)	1473.3(2)	1445.04(4)	2333.6(1)	2051.4(7)
Z	2	2	4	4	4	4
D_{calc}/g cm^{-3}	1.729	1.669	1.629	1.660	1.467	1.526
F(000)	700	748	736	736	1064	968
μ/mm^{-1}	1.282	1.163	1.160	1.182	0.757	0.850
Max/min transmission	0.8825/0.8212	0.9923/0.8268	0.9038/0.7335	0.9155/0.7945	0.8982/0.7076	0.9123/0.7553
Reflect. collected (R_{int})	20655 (0.0271)	22946 (0.0277)	4821 (0.0298)	25789 (0.0283)	61679 (0.0225)	7908 (0.0335)
Independent reflections	7677	8494	2352	2900	5854	3912
Obs. reflect. [$I > 2\sigma(I)$]	6836	7406	2258	2688	5778	3200
Parameters refined	343	379	184	184	289	263
Max./min. $\Delta\rho$ [a]/e Å^{-3}	1.445/–0.458	1.077/–0.394	0.940/–0.839	0.411/–0.338	0.310/–0.399	1.616/–0.572
R_1/wR_2 [$I > 2\sigma(I)$] [b]	0.0326/0.0809	0.0299/0.0735	0.0464/0.1304	0.0183/0.0474	0.0165/0.0442	0.0425/0.0959
R_1/wR_2 (all reflect.) [b]	0.0373/0.0831	0.0355/0.0765	0.0520/0.1377	0.0203/0.0485	0.0170/0.0449	0.0609/0.1045
Goodness-of-fit on F^2 [c]	1.070	1.045	1.385	1.061	1.088	1.004
Weighting scheme w; a/b [d]	0.0360/1.9483	0.0388/0.4090	0.0000/10.3862	0.0228/0.9439	0.0265/0.5149	0.0604/0.0000
Flack parameter [e]	—	—	–0.01(10)	—	–0.008(14)	0.13(5)

[a] Largest difference peak and hole. [b] $R_1 = [\sum(\|F_o| - |F_c\|)/\sum|F_o|]$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$. [e] Absolute structure parameter.[68]

$\delta = 17.6$ (s, C_{18}), 27.9, 28.2, 30.3, 30.7 (s, CH_2cod), 72.3 (d, $J_{C\text{-}Rh} = 14.1$ Hz, CHcod), 73.4 (d, $J_{C\text{-}Rh} = 14.1$ Hz, CHcod), 83.2 (d, $J_{C\text{-}Rh} = 11.8$ Hz, CHcod), 83.7 (d, $J_{C\text{-}Rh} = 12.2$ Hz, CHcod), 117.9 (s, C_1), 121.1 (s, C_3), 122.5 (s, C_{17}), 124.9 (s, C_6), 125.1 (s, C_7), 126.3 (s, C_8), 127.3 (s, $C_{5,15,16}$), 128.0 (s, C_{10}), 129.6 (s, C_{14}), 130.0 (s, C_{13}), 134.1 (s, C_4), 134.6 (s, C_9), 150.9 (s, C_{12}), 157.5 (s, C_2), 166.4 (s, C_{11}). $C_{26}H_{26}NORh$ (471.36) calcd C 66.25, H 5.56, N 2.97; found C 67.30, H 5.88, N 2.21%.

X-Ray crystallography

Data collection. Bruker AXS with CCD area-detector, temperature 173(2) K for **1** and **2**, 203(2) K for **3–5**[64], Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, ω-scans. Data collection and cell refinement with SMART,[65] data reduction with SAINT,[64] experimental absorption correction with SADABS.[66]

Structure analysis and refinement. The structures were solved by direct methods (SHELXS-97),[67] refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite.[66] All non-hydrogen positions were refined with anisotropic temperature factors. Hydrogen atoms on nitrogen (–NH) were found and refined in **3S** and **3rac** with $U_{iso}(H) = 1.2U_{eq}(N)$. Hydrogen atoms on carbon were positioned geometrically (C–H = 0.94 Å for aromatic CH, 0.99 Å for aliphatic CH, 0.98 Å for CH_2, 0.97 Å for CH_3) and refined using a riding model (AFIX 43 for aromatic CH, 13 for aliphatic CH, 23 for CH_2, AFIX 33 or 137 for CH_3) with $U_{iso}(H) = 1.2U_{eq}(CH, CH_2)$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$. Details of the X-ray structure determinations and refinements are provided in Table 5. Graphics were drawn with DIAMOND (Version 3.1f).[67] Computations on the supramolecular interactions were carried out with PLATON for Windows.[58] π-Stacking interactions can be viewed as medium to weak if they exhibit rather long centroid–centroid distances (Cg···Cg> 4.0 Å) together with large slip angles (β, γ > 30 °) and vertical displacements (d > 2.0 Å). In comparison, strong π-stackings show rather short centroid–centroid contacts (< 3.8 Å), small slip angles (β, γ < 25 °) and vertical displacements (d < 1.5 Å) which translate into a sizable overlap of the aromatic planes.[51–53] CCDC reference numbers 780787–780792 for **1–5**, respectively.

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