DOI: 10.1002/ejic.200501033

# Syntheses, Spectroscopic Studies, and Crystal Structures of Chiral [Rh(aminocarboxylato)($\eta^4$-cod)] and Chiral [Rh(amino alcohol)($\eta^4$-cod)]-(acetate) Complexes with an Example of a Spontaneous Resolution of a Racemic Mixture into Homochiral Helix-Enantiomers

**Mohammed Enamullah,*[a] Aisha Sharmin,[a] Miki Hasegawa,[b] Toshihiko Hoshi,[b] Anne-Christine Chamayou,[c] and Christoph Janiak*[c]**

**Keywords:** Rhodium(I) / Amino acids / Chirality / Spontaneous resolution / Helix

The dimeric complex acetato($\eta^4$-cycloocta-1,5-diene)rhodium(I), [Rh($O_2$CMe)($\eta^4$-cod)]$_2$ (cod = cycloocta-1,5-diene), reacts with amino acids [HAA = L-alanine, (*S*)-2-amino-2-phenylacetic acid (L-phenylglycine), *N*-methylglycine, and *N*-phenylglycine] and with the amino alcohol (*S*)-2-amino-2-phenylethanol to afford the aminocarboxylato($\eta^4$-cycloocta-1,5-diene)rhodium(I) complexes [Rh(AA)($\eta^4$-cod)] (AA = deprotonated amino acid = aminocarboxylato ligand) and [(*S*)-2-amino-2-phenylethanol]($\eta^4$-cycloocta-1,5-diene)-rhodium(I) acetate, [Rh{(*S*)-HOCH$_2$–CH(Ph)-NH$_2$}($\eta^4$-cod)]-($O_2$CMe) (**V**). The complexes are characterized by IR, UV/Vis, $^1$H/$^{13}$C NMR and mass spectroscopy. The achiral *N*-phenylglycine ligand gives a chiral *N*-phenylglycinato complex [Rh($O_2$C–CH$_2$–NHPh)($\eta^4$-cod)] (**IV**) with the amine nitrogen atom becoming the stereogenic center upon metal coordination. Complex **IV** crystallizes in the tetragonal, chiral space group $P4_3$ and the crystal structure reveals twofold spontaneous resolution of a racemic mixture into homochiral helix-enantiomers. The investigated crystal contained only one type of helix, namely (left-handed or *M*-) $4_3$-helical chains. This is traced first to an intermolecular N–H···O hydrogen bonding from the stereogenic amino group to a neighboring unligated carboxyl oxygen atom that connects only molecules of the same (*R*)-configuration into (left-handed or *M*-) $4_3$-helical chains. This intrachain homochirality is supplemented, secondly, by the interlocking of adjacent chains with their corrugated van der Waals surface to allow for an interchain transmission of the sense of helicity, building the single crystal from the same homochiral helix-enantiomer. The enantiomeric amino alcohol complex **V** crystallizes in the monoclinic, noncentrosymmetric (Sohncke) space group $P2_1$.


## Introduction

Syntheses and reactivities of metal complexes with amino acids or peptides are of considerable interest and some of them show potential applications as chiral catalysts.[1] Singh first reported the syntheses of [Rh(AA)($CO)_2$][2a,2b] and [Rh(AA)(CO)($L)_2$] (AA = deprotonated amino acid = aminocarboxylato ligand; L = $PPh_3$ or $AsPh_3$) complexes.[2c,2d] Later, Marko synthesized the [Rh(AA)($CO)_2$] complexes starting from the dimeric [Rh($O_2$CR)($\eta^4$-cod)]$_2$ by synthesis of the intermediate [Rh(AA)($\eta^4$-cod)] complexes (cod = cycloocta-1,5-diene).[3] Accordingly, Beck has reported the syntheses and crystal structures of the [Rh(AA)(CO)(L)] (L = $PPh_3$, $AsPh_3$)[4a] and [Rh(L-aziridin-2-carboxylato)($CO)_2$][4b] complexes and efforts to synthesize the analogous Ru$^{II}$-aminocarboxylato complexes containing the bidentate 2,7-dimethylocta-2,6-dien-1,8-diyl ligand.[4c] Molybdocene and titanocene compounds of the formulae [$Cp_2$Mo$^{IV}$($\kappa N$,$\kappa O$-AA)]$^+$Cl$^-$,[5] [$Cp_2$Mo$^{IV}$($\kappa N$,$\kappa O$-AA)]$^+$-$PF_6^-$,[6] [$Cp_2$Ti$^{IV}$($\kappa O$-AA)$_2$]$^{2+}$,[7,8] and the isoelectronic half-sandwich molybdenum compounds [CpMo$^{II}$($CO)_2$($\kappa N$,$\kappa O$-AA)][9] and [CpMo$^{II}$(NO)(*I*){$\kappa N$,$\kappa O$-L-$H_2$NCH(*t*Bu)-COO}][10] have been prepared and structurally elucidated (Cp = $\eta^5$-$C_5H_5$, $\eta^5$-cyclopentadienyl). However, no detailed studies on the syntheses, spectroscopy, and crystal structures of Rh($\eta^4$-cod) complexes containing chiral amino acid/amino alcohol or *N*-amino acids have been reported so far. It is envisioned that these coligands will exercise strong influences on the stereochemistry as well as the stability and reactivity of the Rh complexes and their uses as catalysts for the enantioselective hydrogenation of olefins, unsaturated carboxylates, amidocinnamic acids, and their ester derivatives.

[a] Department of Chemistry, Jahangirnagar University, Dhaka 1342, Bangladesh
E-mail: menam@juniv.edu
[b] Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Sagamihara-shi, Kanagawa 229-8558, Japan
[c] Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany
E-mail: janiak@uni-freiburg.de
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Recently, we attempted to synthesize and characterize the Rh($\eta^4$-cod/diphos/triphos) complexes containing chiral amino acids and amino alcohols as coligands[11] and to study their catalytic behaviors in an asymmetric hydrogenation reaction. Here, we report the syntheses and spectroscopic studies of the complexes [Rh(AA)($\eta^4$-cod)] {AA = L-alaninato (**I**), (*S*)-2-amino-2-phenylacetato (**II**), *N*-methylglycinato (**III**), *N*-phenylglycinato (**IV**)} and [Rh{(*S*)-$HOCH_2$–CH(Ph)-$NH_2$}($\eta^4$-cod)]($O_2CMe$) (**V**) as well as the crystal structures of **IV** and **V**.

## Results and Discussion

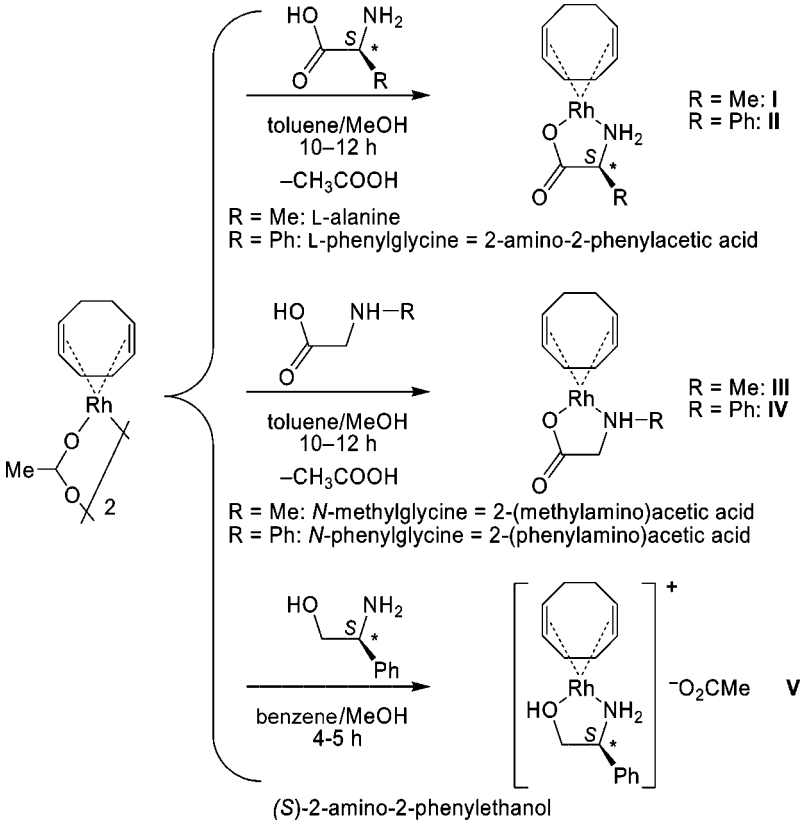
Reaction of dimeric [Rh($O_2CMe$)($\eta^4$-cod)]$_2$ (cod = 1,5-cyclooctadiene) with amino acids in toluene/MeOH yields the monomeric complexes [Rh(AA)($\eta^4$-cod)] (AA = deprotonated amino acid = aminocarboxylato) (**I**–**IV** in Scheme 1). Reaction of [Rh($O_2CMe$)($\eta^4$-cod)]$_2$ with the amino alcohol (*S*)-2-amino-2-phenylethanol gives the complex [Rh{(*S*)-$HOCH_2$–CH(Ph)-$NH_2$}($\eta^4$-cod)]($O_2CMe$) (**V** in Scheme 1).

UV/Vis absorption spectra of complexes **I**–**IV**, measured in toluene at 25 °C, are identical with each other and different from those of the dimeric [Rh($O_2CMe$)($\eta^4$-cod)]$_2$ and [RhCl($\eta^4$-cod)]$_2$ complexes and different from those of the amino alcohol compound **V** (see Figure S1, Table S1 in the Supporting Information).[12]

In the infrared spectrum the aminocarboxylato complexes **I**–**IV** show a strong carbonyl band ($\nu CO_2$, asymmetric) around 1620 cm$^{-1}$, which is typical for the *N*,*O*-coordination of the aminocarboxylato ligand to $Rh^I$, as is the shifting and splitting of the $\nu NH_{asy}/\nu NH_{sy}$ stretching vibrations.[2–4,11] Absence of the νO–H stretching band (which is usually observed as a strong broad band at about 3450 cm$^{-1}$ for the free carboxylic group of the amino acid) in **I**–**IV** indicates acid deprotonation and bond formation between $Rh^I$ and $^-$O–C(O). The vibrational results strongly suggest that the amino acidato ligand is bound to Rh by its nitrogen and oxygen atoms as a *N*,*O*-chelate, as depicted in Scheme 1.[2–4,11] In contrast to these findings, van Koten synthesized the [Rh(L-alaninato)($\eta^4$-cod)]$_2$ complex starting from [Rh{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′-C,N}($\eta^4$-cod)] and described it as an *O*,*O*-coordinated carboxylato-bridged dimer.[14]

FAB-MS spectra are dominated by ions containing the species $M_2$, $M_2$ – AA = M + Rh(cod), M + $AAH_2$, M + H, M – $CO_2$, and Rh(cod) (M = molecule, AA = aminocarboxylato) for the aminocarboxylato complexes [Rh(AA)($\eta^4$-cod)] (**I**–**IV**). The appearance of dinuclear species may be due to intermolecular hydrogen bonding as evidenced by the crystal structure of **IV** (see below).

The rhodium-coordinated 1,5-cyclooctadiene ligand shows three proton NMR signals corresponding to the *exo*- and *endo*-methylene proton and to the methine proton.[11,15,16] The $CH_2cod_{exo}$ signal appears as doublet–doublet, while $CH_2cod_{endo}$ and CHcod exhibit a multiplet. In **V** the methylene protons of the chiral amino alcohol ligand are diastereotopic and couple differently to the vicinal




Scheme 1. Synthetic route to and formula of the complexes **I**–**V**.

$$[Rh(AA)(\eta^4\text{-cod})] + DCl \xrightarrow{D_2O/CD_3CN} 1/2\,[RhCl(\eta^4\text{-cod})]_2 + DAA$$

**I–IV** AA = deprotonated amino acid = aminocarboxylate

$$[Rh(S\text{-}HOCH_2\text{-}CHPh\text{-}NH_2)(\eta^4\text{-cod})](O_2CMe) + DCl \xrightarrow{D_2O/CD_3CN}$$

**V**

$$1/2\,[RhCl(\eta^4\text{-cod})]_2 + S\text{-}HOCH_2\text{-}CHPh\text{-}NH_2D^+ + {}^-O_2CMe$$

Scheme 2. Hydrolysis of complexes **I**–**V** from NMR studies.

methine proton, thereby showing two sets of doublet of doublets at 3.63 ppm and 3.71 ppm.[13] Similarly in **I** and **II** the amino protons of the chiral amino carboxylate ligands are diastereotopic and appear as two multiplets that are more than 0.7 ppm apart. $^{13}C$ NMR spectra of complexes **I**–**IV** show a singlet at about 30 ppm for *C*$H_2$cod and broad peaks at 72–80 ppm for *C*Hcod in [$D_6$]DMSO.[11,15,16] Complex **V** *shows two peaks* of equal intensity around 30 ppm for *C*$H_2$cod, indicating the nonequivalency of the carbon atoms at either side of the chiral amino alcohol ligand. In contrast to the related chiral complexes **I** and **II**, the nonequivalency of the *C*$H_2$cod carbon atoms may be enhanced in **V** by the acetate anion coordination through N–H···O hydrogen bonding (see structural analysis below).

Upon addition of acid (as 5% DCl/$D_2O$ in $CD_3CN$) the $^1H$ and $^{13}C$ NMR spectra indicate that complexes **I**–**V** are readily hydrolyzed with dissociation of the amino carboxylate or amino alcohol ligand to form the dimeric chloro complex [RhCl($\eta^4$-cod)]$_2$ and the free amino acid or amino alcohol (Scheme 2).[11]

Complexes **IV** and **V** could be crystallized and subjected to single-crystal X-ray diffraction studies. The single-crystal X-ray analysis proved the suggested *N*,*O*-chelate formation of the aminocarboxylato or amino alcohol ligand to the rhodium atom of the Rh($\eta^4$-cod) fragment (Figure 1 and Figure 2). Related Rh($\eta^4$-cod) complexes with a five-membered Rh-*N*,*O*-chelate ligand are structurally elucidated with 8-hydroxyquinolinato,[17] tryptophan benzyl ester,[18] 4-methylpyridinium 2-pyridylcarbonylmethylide,[19] 1-(2′-pyridyl)-3-(dimethylamino)-2-propenone,[20] imidazole-4,5-carboxylato,[21] orotato,[22] and 3-oxo-1-(pyridin-2-yl)-prop-1-en-1-olato.[16a] The five-membered *N*,*O*-chelate ring with rhodium is planar within (largest deviation) ±0.16 Å in **IV** and ±0.28 Å in **V**. Selected distances and angles are compared in Table 1. Both complexes are highly similar in their relevant bonding parameters. The Rh–O distance to the carboxylate oxygen in **IV** and to the alcohol oxygen in **V** is identical.

The achiral (prochiral) *N*-phenylglycine ligand acquires a stereogenic center at the nitrogen atom upon metal coordination. Initially this metal–ligand coordination will give a racemic mixture of (*R*)- and (*S*)-configured complexes. The chiral *N*-phenylglycinato complex [Rh($O_2C$–$CH_2$–NHPh)($\eta^4$-cod)] (**IV**) crystallizes in the tetragonal, chiral space group $P4_3$[23,24] with spontaneous resolution within the single crystal. The homochirality results from the solid-state packing in that N–H···O hydrogen bonding from the stereogenic amino group to a neighboring unligated car-

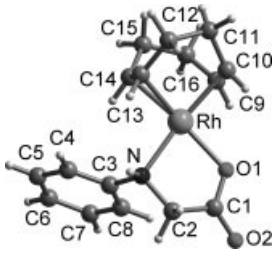



Figure 1. Molecular structure of **IV**.

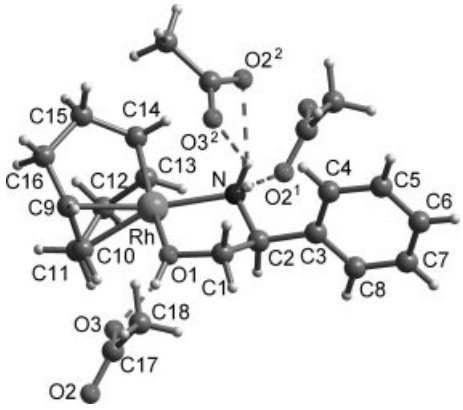



Figure 2. Molecular structure of **V** showing the hydrogen bonding to the surrounding symmetry-related acetate anions. Hydrogen-bonding interactions (dashed lines) as D–H, H···A, D···A, D–H···A [Å (°)]: O1–H1···O3 0.89(5), 1.58(4), 2.429(4), 159(4); N–H2···O2$^2$ 0.99(5), 2.14(5), 3.001(7), 145(4); N–H2···O3$^2$ 0.99(5), 2.51(5), 3.278(7), 134(4); N–H3···O2$^1$ 0.89(4), 2.00(4), 2.885(5), 173(3); symmetry transformations 1 = 1 + *x*, *y*, *z*; 2 = 1 – *x*, *y* + 1/2, 2 – *z*.

Table 1. Selected bond lengths [Å] and angles [°] in **IV** and **V**.

| | **IV** | **V** |
|---|---|---|
| Rh–O1 | 2.059(3) | 2.058(2) |
| Rh–N | 2.145(3) | 2.110(2) |
| Rh–C9 | 2.112(5) | 2.144(6) |
| Rh–C10 | 2.131(4) | 2.113(6) |
| Rh–C13 | 2.108(4) | 2.093(6) |
| Rh–C14 | 2.125(4) | 2.105(6) |
| O1–Rh–N | 80.82(12) | 79.94(8) |
| O1–Rh–C9 | 90.82(16) | 95.8(2) |
| O1–Rh–C10 | 95.39(16) | 93.9(2) |
| O1–Rh–C13 | 160.63(15) | 162.5(2) |
| O1–Rh–C14 | 161.03(17) | 159.0(2) |
| N–Rh–C9 | 158.73(18) | 164.3(2) |
| N–Rh–C10 | 161.51(17) | 156.7(2) |
| N–Rh–C13 | 95.59(16) | 95.97(18) |
| N–Rh–C14 | 99.11(18) | 96.32(17) |

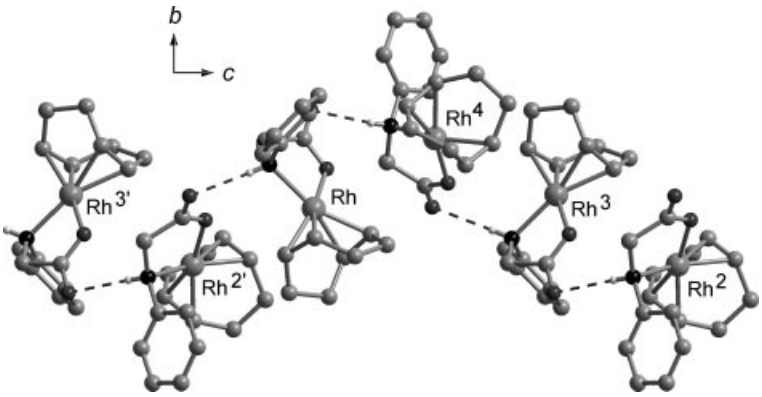



Figure 3. $4_3$-Helical chain in **IV** along *c*. Hydrogen-bonding interaction (dashed line) as D–H, H···A, D···A, D–H···A [Å (°)]: N–H···O2$^{2'}$ 0.73(4), 2.19(4), 2.925(5), 176(5); symmetry transformations: 2 = 2 – *y*, *x*, 0.75 + *z*; 2′ = 2 – *y*, *x*, –0.25 + *z*; 3 = 2 – *x*, 2 – *y*, 0.5 + *z*; 3′ = 2 – *x*, 2 – *y*, –0.5 + *z*; 4 = *y*, 2 – *x*, 0.25 + *z*.

boxyl oxygen atom (Figure 3 and Figure 4) connects and assembles only molecules of the same configuration [here (*R*), see Figure 1 and Figure 3] into a (left-handed or *M*-) $4_3$-helical chain (in the crystal investigated) along *c* (Figure 3 and Figure 4).

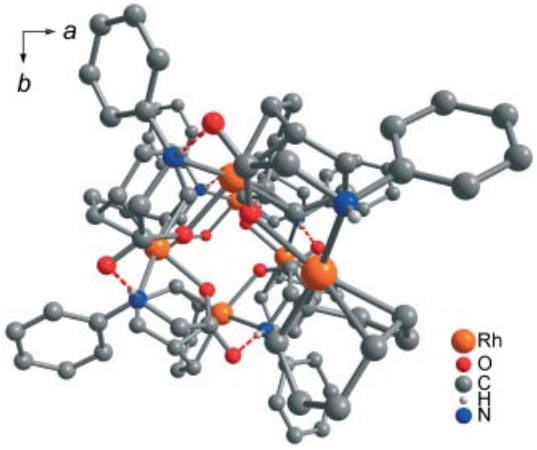



Figure 4. Left-handed $4_3$-helical chain in **IV** viewed along the chain direction.

Yet, most homochiral helices that are formed from achiral ligands and even from racemic mixtures of chiral building blocks almost always lead to racemic mixtures of *P*- and *M*- (right- and left-handed) helices.[25–30] Of interest are structures that spontaneously resolve to contain only one type of helix (within a crystal), that is a single, homochiral helix-enantiomer that requires a sufficient homochiral helicating element in the molecular building block, for example, the ligand. This is typically a stereogenic center of an enantiomerically pure ligand in combination with strong interhelix supramolecular interactions. However, in the structure of **IV** there are no classical hydrogen-bonding interactions between neighboring chains. The exterior of the chains is covered by CH bonds (Figure 4). Also, there are no noteworthy reasonable π–π stacking or C–H···π interactions seen in **IV** (or **V**) [that is, for π–π with centroid–centroid distances <6.0 Å, a dihedral angle between the ring planes <10° and an angle between the centroid vector Cg(I)···Cg(J) and the normal to the plane *I* <60°; for C–H···π, H···Cg < 3.0 Å and an angle between the vector H···Cg(J) and the normal to the plane *J* <30°].[31,32] In **IV** the shortest perpendicular distance of H on a phenyl ring plane is 3.3 Å, about 0.4–0.5 Å longer than seen in typical C–H···π interactions.[33]

The investigated crystal of **IV** contained only one type of helix, namely (left-handed or *M*-) $4_3$-helical chains, thereby representing a case of spontaneous resolution of a racemic mixture into homochiral helix-enantiomers. To account for this fact we invoke an interlocking of adjacent chains with their corrugated van der Waals surface in order to transmit the sense of helicity upon crystallization (Figure 5). The overall ensemble of the crystals in a batch of **IV** can be expected to be racemic, that is, to contain crystals of space groups $P4_3$ and $P4_1$ with left- and right-handed helices based on (*R*)- and (*S*)-configured metal–ligand complexes, respectively, in equal amounts.

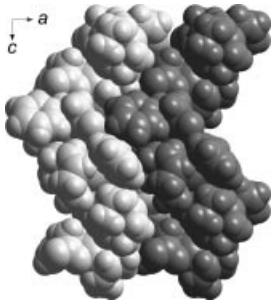



Figure 5. The interlocking of two neighboring left-handed (*M*-) $4_3$-helical chains in **IV** based on the corrugated van der Waals surface without any strong supramolecular interactions; space-filling representation of the chains, which are differentiated by light and dark gray shading.

Spontaneous resolution of achiral or of racemic chiral molecular materials within the single crystal, that is, crystallization in noncentrosymmetric (polar) space groups, can be dictated by supramolecular solid-state packing interactions. This phenomenon has been observed by us in the crystallization of *achiral* hydrotris(pyrazolyl)boratothallium(I) (in $P2_1$),[34,35] dihydrobis(1,2,4-triazolyl)boratothalli-

um(I)[35] and -potassium (in $P2_12_12_1$),[36] hydrotris(indazolyl)boratothallium(I) (in $C2$),[35,37] and hydrotris(1,2,4-triazolyl)boratosilver(I) (in polar $Pna2_1$).[38] The spontaneous resolution of a *racemic chiral* material within a noncentrosymmetric space group was seen in the crystallization of $[Ag^+(NH_3)_2](BINOLAT^-)(BINOL)(EtOH)$ (in $P1$).[39] The crystallization of a racemic chiral material within a noncentrosymmetric polar space group was encountered in the crystallization of $[\Lambda/\Delta\text{-}Fe^3(DABP)_3]^{2+}[\Delta/\Lambda\text{-}Fe^2(DABP)_3\subset \Lambda/\Delta\text{-}Fe^1(DABP)_3(nitrophenolate)_6]^{2-}$ (in $P3_1c$).[40] The spontaneous resolution of *rac*-2,3-dihydro-2,3-dipyridylbenzo[*e*]indole with $Cd(ClO_4)_2\cdot 6H_2O$ is a recent example of symmetry breaking through supramolecular interactions and solvent, where in the presence of either 2-butanol or ethanol crystals of the opposite enantiomers were favored (crystallizing in the enantiomorphous space groups $P6_122$ and $P6_522$).[41] Particularly intriguing is the formation of a homochiral (helical) polymer from achiral components through spontaneous enantiomer resolution. A homochiral helix winding together with homochiral crystallization was reported for the adduct of 5-(9-anthracenyl)pyrimidine with $Cd(NO_3)_2\cdot H_2O\cdot EtOH$. The chirality arises from a pyrimidine-$Cd^{2+}$ helical array and is preserved in each crystal by homochiral interstrand water–nitrate hydrogen bonding. All the crystals are of the same chirality as a result of single-colony homochiral crystal growth (homochiral crystallization).[42] The achiral building blocks in $^{\infty}_1\{[Ni(PhCOO)_2(4,4'\text{-bipy})]\cdot 2MeOH\}$ gave rise to a $4_1$- or $4_3$-helical polymer with homochirality in the crystal. Different crystals contain statistically either *P*- or *M*-helices.[43] Homochiral right-handed (*P*-) $6_1$ helices of $Cd\{B(OMe)_4\}$ are found in $^{\infty}_3\{[Cd(tcm)\{B(OMe)_4\}]\cdot x MeOH\}$ with neighboring helices connected by the tricyanomethanide (tcm) ion.[44] Compound $^{\infty}_1\{[Mn(hfac)_2\{ferrocenyl\ bis(nitronyl\ nitroxide)\}]\cdot CH_2Cl_2\}$ spontaneously resolves in enantiomorphous crystals with either Λ- or Δ-configuration at Mn and an additional six sources of chirality within the *P*- or *M*-helices, respectively (hfac = hexafluoroacetylacetonate).[45] Variation of the proton content with $KOH/HCl_{aq}$ allows for a reversible interconversion between the achiral molecular square of $[Cu(HL)(H_2O)_{0.5}]_4(ClO_4)_4$ (high pH) and a spontaneously resolved homochiral double-chain motif of $^{\infty}_1\{[H_3O]_2[Cu_3(L)_2Cl](ClO_4)_2(Cl)\}$ (low pH) {$H_2L$ = 1,5-diazacyclooctane-1,5-bis(3-propionic acid)}.[46]

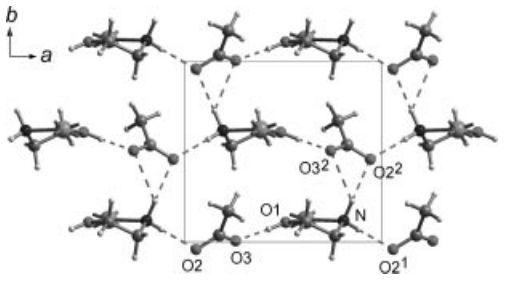



Figure 6. Two-dimensional hydrogen-bonded network in **V**. Phenyl groups and cod ligands are not shown for clarity but only indicated as broken-off bonds. For details of the hydrogen bonds see caption to Figure 2.

The enantiomeric amino alcohol complex **V** crystallizes in the monoclinic, noncentrosymmetric (Sohncke) space group $P2_1$.[23,24] Hydrogen-bonding interactions between the amino and hydroxy donor groups in the metal complex to the acetate anion acceptors link the building blocks into supramolecular two-dimensional nets co-planar to the *ab* plane (Figure 6). Along *c* the nets are separated by the phenyl groups and cod ligands without meaningful π–π-stacking or C–H···π interactions (see above).

## Conclusions

Aminocarboxylato($\eta^4$-cycloocta-1,5-diene)rhodium(I) complexes [Rh(AA)($\eta^4$-cod)] could be easily prepared from dimeric $[Rh(O_2CMe)(\eta^4\text{-cod})]_2$ with amino acids in toluene/MeOH. The compounds [Rh(AA)($\eta^4$-cod)] (AA = deprotonated amino acid = aminocarboxylato) were found to be monomeric. Solid-state structures of $[Rh(O_2C\text{–}CH_2\text{–}NHPh)(\eta^4\text{-cod})]$ (**IV**) and $[Rh\{(S)\text{-}HOCH_2\text{–}CH(Ph)\text{–}NH_2\}(\eta^4\text{-cod})](O_2CMe)$ (**V**) reveal strong intermolecular N–H···O hydrogen-bonding interactions to assemble the molecular units into 1D chains (**IV**) or 2D nets (**V**). In **IV** the achiral (prochiral) *N*-phenylglycine ligand acquires a stereogenic center at nitrogen upon complexation and the racemic compound undergoes spontaneous resolution upon crystallization. Supramolecular N–H···O and van der Waals interactions are responsible for collecting only one enantiomer along fourfold screw axes of the same handedness within a single crystal. This could be called a twofold spontaneous resolution in two homochiral building units, namely the molecular complex and the fourfold helix.

## Experimental Section

All reactions were carried out under dry nitrogen using Schlenk techniques. Solvents used were highly purified and distilled: toluene and benzene over Na metal; petroleum ether (PE) (boiling range 40–60 °C) over $CaH_2$; methanol and ethanol over CaO under nitrogen. The starting complex $[Rh(O_2CMe)(\eta^4\text{-cod})]_2$ was synthesized from $[RhCl(\eta^4\text{-cod})]_2$[47] according to the literature.[3a] UV/Vis spectra were obtained with a Shimadzu UV 3150 spectrophotometer in toluene at 25 °C. IR spectra were recorded as KBr disks with a Bruker IFS 66 FTIR Spectrometer at ambient temperature. NMR spectra were run on a Bruker AC DPX 200 spectrometer operating at 200 MHz ($^1$H) and a JEOL AC 500 at 500 MHz ($^1$H), 125 MHz ($^{13}$C) at 25 °C. NMR grade solvents [$D_6$]DMSO, $CD_3OD$, $CD_3CN$, and $DCl/D_2O$ solution (20% v/v) were used as internal standard and deoxygenated prior to use. $^1$H and $^{13}$C NMR chemical shifts are expressed in ppm relative to $SiMe_4$ ($\delta$ = 0 ppm). FAB-MS (positive mode): Finnigan MAT 8230 with data system SS 300, matrix: *m*-nitrobenzyl alcohol (NBA). EI- and CI-MS: Thermo-Finnigan TSQ 700, with $NH_3$ as ionization gas for CI.

**(L-Alaninato)($\eta^4$-cycloocta-1,5-diene)rhodium(I), {Rh[(*S*)-$O_2C$–CHMe–$NH_2$]($\eta^4$-cod)} (I):** L-Alanine (166 mg, 1.86 mmol) was dissolved in methanol (5 mL) and this solution was poured into a solution of $[Rh(O_2CMe)(\eta^4\text{-cod})]_2$ (503 mg, 0.93 mmol) in toluene (20 mL). Stirring the solution for 10–12 h at room temperature led to the formation of a yellow precipitate. After the solvent was evap-

orated in vacuo, toluene/MeOH (4:1, v/v) (10 mL) was added to the dried precipitate and evaporated again. This procedure was repeated three times. Finally, the precipitate was dried in vacuo (0.1–0.2 mbar) at 40 °C to give a yellow powder (yield 417 mg, 75%). $^1$H NMR (200 MHz, $CD_3OD$): $\delta$ = 1.45 (d, $J$ = 7.0 Hz, 3 H, C$H_3$), 1.88 (dd, $J$ = 8.2 Hz, 4 H, C$H_2$cod$_{exo}$), 2.46 (m, 4 H, C$H_2$cod$_{endo}$), 3.43 (q, $J$ = 7.0 Hz, 1 H, C$H$), 4.13 (m, 4 H, C$H$cod) ppm. $^1$H NMR (500 MHz, [D$_6$]DMSO): $\delta$ = 1.20 (d, $J$ = 7.0 Hz, 3 H, C$H_3$), 1.72 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.32 (m, 4 H, C$H_2$cod$_{endo}$), 3.09 (q, $J$ = 7.0 Hz, H, C$H$), 3.68 (m, 1 H, N$H$), 3.92 (m, 4 H, C$H$cod), 4.31 (m, 1 H, N$H$) ppm. $^1$H NMR (500 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 1.50 (d, $J$ = 8 Hz, 3 H, C$H_3$), 1.77 (dd, $J$ = 8.5 Hz, 4 H, C$H_2$cod$_{exo}$), 2.36 (m, 4 H, C$H_2$cod$_{endo}$), 4.02 (q, $J$ = 8.5 Hz, 1 H, C$H$), 4.22 (m, 4 H, C$H$cod) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO): $\delta$ = 20.4 (s, $C$H$_3$), 30.1 (s, $C$H$_2$cod), 52.5 (s, $C$H), 72.1, 79.6 (br., $C$Hcod), 183.2 (s, $CO_2$) ppm. $^{13}$C NMR (125 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 15.1 (s, $C$H$_3$), 30.2 (s, $C$H$_2$cod), 48.5 (s, $C$H), 80.3 (d, $J_{C,Rh}$ = 13 Hz, $C$Hcod), 171.1 (s, $CO_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3258 s, 3190 sh ($\nu$NH$_{asy}$), 3134 s, 3109 s ($\nu$NH$_{sy}$), 2940 s ($\nu$CH), 1620 vs ($\nu$CO$_{2\ asy}$), 1585 sh ($\delta$NH), 1383 s ($\delta$CH$_3$), 1363 s ($\nu$CO$_{2\ sy}$) cm$^{-1}$. MS (FAB): $m/z$ (%) = 601 (20) [M$_2$ + H$^+$ + 2H]$^+$, 510 (58) [M$_2$ – AA$^-$ = M + Rh(cod)$^+$]$^+$, 392 (40) [M + AAH$_2^+$ + 2H]$^+$, 300 (100) [M + H]$^+$, 255 (25) [M$^{+\cdot}$ – CO$_2$]$^+$, 211 (68) [Rh(cod)]$^+$ (AA = aminocarboxylato). MS (EI = 70 eV): 299 (7) [M]$^+$, 297 (13) [M – 2H]$^+$, 255 (40) [M – CO$_2$]$^+$, 210 (50) [Rh(cod) – H]$^+$, 208 (55) [Rh(cod) – 3H]$^+$, 44 (100) [CO$_2$]$^+$. $C_{11}H_{18}NO_2Rh$ (299.18): calcd. C 44.16, H 6.06, N 4.68; found C 44.26, H 6.38, N 4.69.

**[(*S*)-2-Amino-2-phenylacetato](η$^4$-cycloocta-1,5-diene)rhodium(I), (η$^4$-Cycloocta-1,5-diene)(L-phenylglycinato)rhodium(I), {Rh[(*S*)-O$_2$C–CHPh–NH$_2$](η$^4$-cod)} (II):** The compound was prepared following the same procedure as for **I**, using (*S*)-2-amino-2-phenylacetic acid (L-phenylglycine). The complex was obtained as a yellow powder (yield 470 mg, 70%). $^1$H NMR (200 MHz, $CD_3CN$): $\delta$ = 1.84 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.44 (m, 4 H, C$H_2$cod$_{endo}$), 2.81 (m, 1 H, N$H$), 3.57 (m, 1 H, N$H$), 4.05 (m, 4 H, C$H$cod), 4.36 (m, 1 H, C$H$), 7.42 (m, 3 H, $H_{p/m}$-Ar), 7.76 (d, $J$ = 6.6, 2 H, $H_o$-Ar) ppm. $^1$H NMR (200 MHz, $CD_3OD$): $\delta$ = 1.92 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.48 (m, 4 H, C$H_2$cod$_{endo}$), 4.16 (m, 4 H, C$H$cod), 4.49 (m, 1 H, C$H$), 7.47 (m, 3 H, $H_{p/m}$-Ar), 7.76 (m, 2 H, $H_o$-Ar) ppm. $^1$H NMR (500 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 1.76 (dd, $J$ = 8.5 Hz, 4 H, C$H_2$cod$_{exo}$), 2.36 (m, 4 H, C$H_2$cod$_{endo}$), 4.13 (m, 1 H, N$H$), 4.21 (m, 4 H, C$H$cod), 5.07 (m, 1 H, C$H$), 7.46–7.75 (m, 5 H, $H$-Ar) ppm. $^{13}$C NMR (125 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 30.4 (s, $C$H$_2$cod), 56.1 (s, $C$H), 80.5 (d, $J_{C,Rh}$ = 13 Hz, $C$Hcod), 128.2 (s, $C_m$-Ar), 128.7 (s, $C_p$-Ar), 129.3 (s, $C_o$-Ar), 130.0 (s, $C$-Ar), 170.0 (s, $CO_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3259 m, 3213 m ($\nu$NH$_{asy}$), 3136 sh, 3102 m ($\nu$NH$_{sy}$), 3056 s ($\nu$H-Ar), 2935 s ($\nu$CH), 1621 vs ($\nu$CO$_{2\ asy}$), 1591 s ($\delta$NH), 1363 s ($\nu$CO$_{2\ sy}$) cm$^{-1}$. MS (FAB): $m/z$ (%) = 1017 (20) [(RhAA)$_4$ + 4H + H$^+$]$^+$, 722 (8) [M$_2$]$^+$, 572 (30) [M$_2$ – AA$^-$ = M + Rh(cod)$^+$]$^+$, 362 (100) [M + H]$^+$, 317 (45) [M$^{+\cdot}$ – CO$_2$]$^+$, 211 (60) [Rh(cod)]$^+$ (AA = aminocarboxylato). $C_{16}H_{20}NO_2Rh$ (361.25): calcd. C 53.20, H 5.58, N 3.88; found C 54.04, H 6.57, N 3.98.

**(η$^4$-Cycloocta-1,5-diene)(*N*-methylglycinato)rhodium(I), [Rh(O$_2$C–CH$_2$–NHMe)(η$^4$-cod)] (III):** Two equiv. of *N*-methylglycine [2-(methylamino)acetic acid] (50 mg, 0.56 mmol) were dissolved in MeOH (5 mL) and this solution was poured into a solution of [Rh(O$_2$CMe)(η$^4$-cod)]$_2$ (150.4 mg, 0.28 mmol) in toluene (20 mL). A yellow precipitate was formed after stirring the solution for 10–12 h at room temperature. After the solvent was evaporated in vacuo at 40 °C, the dried precipitate was dissolved in toluene/MeOH (4:1, v/v) (10 mL) and evaporated again. This procedure was repeated three times. Then the dried precipitate was again dissolved in toluene/MeOH (4:1) (10 mL) and the volume reduced to 50% in vacuo at 40 °C. PE (40/60) (10 mL) was added very slowly to this hot solution. The precipitate formed was filtered off, washed with PE (40/60) and dried in vacuo (0.1–0.2 mbar) at 40 °C to give a yellow powder (yield 125 mg, 75%). $^1$H NMR (200 MHz, [D$_6$]-DMSO): $\delta$ = 1.71 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.14 (s, 2 H, C$H_2$), 2.30 (m, 4 H, C$H_2$cod$_{endo}$), 2.74 (s, 3 H, C$H_3$), 3.51 (m, 4 H, C$H$cod), 3.64 (m, 1 H, N$H$) ppm. $^1$H NMR (500 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 1.75 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.35 (m, 4 H, C$H_2$cod$_{endo}$), 2.70 (s, 3 H, C$H_3$), 3.86 (s, 2 H, C$H_2$), 4.19 (m, 4 H, C$H$cod) ppm. $^{13}$C NMR (125 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 30.6 (s, $C$H$_2$cod), 33.0 (s, $C$H$_3$), 48.7 (s, $C$H$_2$), 80.3 (d, $J_{C,Rh}$ = 13 Hz, $C$Hcod), 167.5 (s, $CO_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3197 m ($\nu$NH$_{asy}$), 3100 sh ($\nu$NH$_{sy}$), 2931 s ($\nu$CH), 1623 vs ($\nu$CO$_{2\ asy}$), 1590 sh ($\delta$NH), 1484 s ($\delta$CH$_2$), 1381 s ($\delta$CH$_3$), 1365 s ($\nu$CO$_{2\ sy}$) cm$^{-1}$. MS (FAB) $m/z$ (%) = 600 (30) [M$_2$ + H$^+$ + H]$^+$, 510 (50) [M$_2$ – AA$^-$ = M + Rh(cod)$^+$]$^+$, 391 (35) [M + AAH$_2^+$ + H]$^+$, 300 (100) [M + H]$^+$, 255 (35) [M – CO$_2$]$^+$, 211 (55) [Rh(cod)]$^+$ (AA = aminocarboxylato). $C_{11}H_{18}NO_2Rh$ (299.18): calcd. C 44.16, H 6.06, N 4.68; found C 43.85, H 5.89, N 4.53.

**(η$^4$-Cycloocta-1,5-diene)(*N*-phenylglycinato)rhodium(I), [Rh(O$_2$C–CH$_2$–NHPh)(η$^4$-cod)] (IV):** Two equiv. of *N*-phenylglycine [2-(phenylamino)acetic acid] (85.9 mg, 0.57 mmol) were dissolved in MeOH (5 mL). This solution was poured into a solution of [Rh(O$_2$CMe)(η$^4$-cod)]$_2$ (150.4 mg, 0.28 mmol) in toluene (20 mL) and stirred for 10–12 h at room temperature. The volume was reduced to 60% in vacuo at 40 °C, PE (40/60) (10 mL) was very slowly added to the hot solution, and the combined solution was left for crystallization. Red-orange needle crystals, suitable for X-ray measurement, were obtained after 3 days. The crystals were filtered off and washed three times with PE (5 mL each). Finally, the red-orange crystals were dried in vacuo (0.1–0.2 mbar) at 40 °C (yield 150 mg, 75%). $^1$H NMR (500 MHz, [D$_6$]DMSO): $\delta$ = 1.64 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.09 (s, 2 H, C$H_2$), 2.25 (m, 4 H, C$H_2$cod$_{endo}$), 3.60 (m, 4 H, C$H$cod), 3.67 (m, 1 H, N$H$), 7.01 (t, $J$ = 7.0 Hz, 2 H, $H_o$-Ar), 7.27 (t, $J$ = 6.5 Hz, 1 H, $H_p$-Ar), 7.33 (t, $J$ = 7.5 Hz, 2 H, $H_m$-Ar) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO): $\delta$ = 29.7 (s, $C$H$_2$cod), 55.9 (s, $C$H$_2$), 77.9 (br., $C$Hcod), 119.5 (s, $C_o$-Ar), 124.3 (s, $C_p$-Ar), 129.2 (s, $C_m$-Ar), 146.1 (s, N$C$-Ar), 179.2 (s, $CO_2$) ppm. $^1$H NMR (500 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 1.76 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 2.33 (m, 4 H, C$H_2$cod$_{endo}$), 4.19 (m, 3 H, C$H_2$ + N$H$), 4.22 (m, 4 H, C$H$cod), 7.45–7.52 (m, 5 H, $H$-Ar) ppm. $^{13}$C NMR (125 MHz, $CD_3CN$ + 5% DCl/$D_2O$): $\delta$ = 29.9 (s, $C$H$_2$cod), 50.7 (s, $C$H$_2$), 80.5 (d, $J_{CRh}$ = 13 Hz, $C$Hcod), 122.5 (s, $C_o$-Ar), 129.6 (s, $C_p$-Ar), 130.0 (s, $C_m$-Ar), 134.4 (s, N$C$-Ar), 167.3 (s, $CO_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3142 m ($\nu$NH$_{asy}$), 3097 m ($\nu$NH$_{sy}$), 3053 s ($\nu$HAr), 2943 s ($\nu$CH), 1616 vs ($\nu$CO$_{2\ asy}$), 1600 s ($\delta$NH), 1491 s ($\delta$CH$_2$), 1366 s ($\nu$CO$_{2\ sy}$) cm$^{-1}$. MS (FAB) $m/z$ (%) = 723 (5) [M$_2$ + H]$^+$, 573 (100) [M$_2$ + H$^+$ – AA = M + H$^+$ + Rh(cod)]$^+$, 363 (100) [M + H$^+$ + H]$^+$, 315 (100) [M$^{+\cdot}$ – H$_2$ – CO$_2$]$^+$, 211 (100) [Rh(cod)]$^+$ (AA = aminocarboxylato). $C_{16}H_{20}NO_2Rh$ (361.25): calcd. C 53.20, H 5.58, N 3.88; found C 52.90, H 5.46, N 4.00.

**[(*S*)-2-Amino-2-phenylethanol](η$^4$-cycloocta-1,5-diene)rhodium(I) Acetate, [Rh{(*S*)-HOCH$_2$–CH(Ph)-NH$_2$}(η$^4$-cod)](O$_2$CMe) (V):** Two equiv. of (*S*)-2-amino-2-phenylethanol (71 mg, 0.52 mmol) were dissolved in MeOH (5 mL). This solution was poured into a solution of [Rh(O$_2$CMe)(η$^4$-cod)]$_2$ (133.4 mg, 0.25 mmol) in benzene (20 mL) and stirred for 4–5 h at room temperature. The volume was reduced to 60% in vacuo at 40 °C, PE (40/60) (10 mL) was very slowly added to the hot solution, and the combined solution was left for crystallization. Bright-yellow crystals, suitable for

X-ray measurement, were obtained after 3 days at room temperature. The crystals were filtered off and washed three times with PE (5 mL each). Finally, the bright-yellow crystals were dried in vacuo (0.1–0.2 mbar) at 40 °C (yield 141 mg, 70%). $^1$H NMR (500 MHz, [D$_6$]DMSO): $\delta$ = 1.65 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 1.73 (s, 3 H, C$H_3$), 2.25 (m, 4 H, C$H_2$cod$_{endo}$), 3.55 (t, $J$ = 9.0 Hz, 1 H, C$H$), 3.63 (dd, $^3J$ = 10.5 Hz, $^4J$ = 5.5 Hz, 1 H, C$H_2$), 3.71 (dd, $^3J$ = 8.5 Hz, $^4J$ = 5.5 Hz, 1 H, C$H_2$), 3.87 (m, 4 H, C$H$cod), 7.27 (t, $J$ = 7.5 Hz, 1 H, $H_p$-Ar), 7.34 (t, $J$ = 7.5 Hz, 2 H, $H_o$-Ar), 7.45 (d, $J$ = 7.5 Hz, 2 H, $H_m$-Ar) ppm. $^{13}$C NMR (125 MHz, [D$_6$]DMSO): $\delta$ = 23.6 (s, $C$H$_3$), 30.0, 30.1 (d, $C$H$_2$cod), 60.8 (s, $C$H), 69.1 (s, $C$H$_2$), 75.8 (br., $C$Hcod), 127.2 (s, $C_o$-Ar), 127.3 (s, $C_p$-Ar), 128.1 (s, $C_m$-Ar), 140.3 (s, $C$-Ar), 174.6 (s, $C$O$_2$) ppm. $^1$H NMR (500 MHz, CD$_3$CN + 5% DCl/D$_2$O): $\delta$ = 1.77 (dd, $J$ = 8.0 Hz, 4 H, C$H_2$cod$_{exo}$), 1.93 (s, 3 H, C$H_3$), 2.36 (m, 4 H, C$H_2$cod$_{endo}$), 3.87 (dd, $J$ = 7.0 Hz, 2 H, C$H_2$), 4.21 (m, 4 H, C$H$cod), 4.45 (t, $J$ = 6.0 Hz, 1 H, C$H$), 7.27 (m, 3 H, $H_{p/o}$-Ar), 7.48 (d, $J$ = 2.0 Hz, 2 H, $H_m$-Ar) ppm. $^{13}$C NMR (125 MHz, CD$_3$CN + 5% DCl/D$_2$O): $\delta$ = 20.1 (s, $C$H$_3$), 30.6 (s, $C$H$_2$cod), 57.1 (s, $C$H), 62.7 (s, $C$H$_2$), 80.1 (d, $J_{C,Rh}$ = 13.0 Hz, $C$Hcod), 127.7 (s, $C_o$-Ar), 129.0 (s, $C_m$-Ar), 129.2 (s, $C_p$-Ar), 134.1 (s, $C$-Ar), 173.0 (s, $C$O$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3410 m ($\nu$OH), 3193 m ($\nu$NH$_{asy}$), 3083 s ($\nu$NH$_{sy}$), 3055 s ($\nu$HAr), 2937 s ($\nu$CH), 1575 s ($\delta$NH), 1558 sh ($\nu$CO$_{2\ asy}$), 1486 s ($\delta$CH$_2$), 1442 s ($\nu$CO$_{2\ sy}$), 1385 s ($\delta$CH$_3$) cm$^{-1}$. MS (EI = 70 eV): 210 (2) [Rh(cod) – H]$^+$, 106 (100) [AA – CH$_2$OH = Ph–CH–NH$_2$]$^+$. MS (CI, NH$_3$): 348 (0.4) [M – acetate = Rh(AA)(cod)]$^+$, 228 (1.5) [Rh(NH$_3$)-(cod)]$^+$, 138 (100) [AA + H]$^+$, 106 (45) [AA – CH$_2$OH = Ph–CH–NH$_2$]$^+$ (AA = amino alcohol). C$_{18}$H$_{26}$NO$_3$Rh (407.31): calcd. C 53.08, H 6.43, N 3.44; found C 53.06, H 6.33, N 3.44.

**X-ray Crystallography:** *Data Collection:* Bruker AXS with CCD area-detector, temperature 203(2) K, Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å), graphite monochromator, $\omega$-scans, data collection and cell refinement with SMART,[48] data reduction with SAINT,[48] experimental absorption correction with SADABS.[49] *Structure Analysis and Refinement:* The structure was solved by direct methods (SHELXS-97);[50] refinement was done by full-matrix least-squares on $F^2$ using the SHELXL-97 program suite.[50] For **IV** structure refinement has also been attempted in the enantiomorphic space group $P4_1$ but this gave a Flack parameter of 1 with the message "absolute structure probably wrong – invert and repeat refinement". All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms on oxygen (–OH) and nitrogen (–NH–Ph, –NH$_2$) were found and refined with $U_{eq}$(H) = 1.2$U_{eq}$(N) in **IV** and freely in **V**. 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$U_{eq}$(C) (CH, CH$_2$) or $U_{eq}$(H) = 1.5$U_{eq}$(C) (CH$_3$). Details of the X-ray structure determinations and refinements are provided in Table 2. Graphics were drawn with DIAMOND (Version 3.0e).[51] Computations on the supramolecular interactions were carried out with PLATON for Windows.[52]

CCDC-297844 (for **IV**) and -297845 (for **V**) 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.

**Supporting Information** (for details see the footnote on the first page of this article): UV/Vis spectra and data.

Table 2. Crystal data and structure refinement for **IV** and **V**.

| Compound | **IV** | **V** |
|---|---|---|
| Empirical formula | $C_{16}H_{20}NO_2Rh$ | $C_{18}H_{26}NO_3Rh$ |
| $M$ [g mol$^{-1}$] | 361.24 | 407.31 |
| Crystal size [mm] | 0.42 × 0.10 × 0.09 | 0.40 × 0.27 × 0.16 |
| $\theta$ range [°] | 4.26–58.00 | 3.42–57.56 |
| $h$; $k$; $l$ range | –12, 12; –12, 12; –21, 21 | –12, 12; –10, 10; –16, 17 |
| Crystal system | tetragonal | monoclinic |
| Space group | $P4_3$ | $P2_1$ |
| $a$ [Å] | 9.556(3) | 9.5506(15) |
| $b$ [Å] | 9.556(3) | 7.9810(13) |
| $c$ [Å] | 16.281(6) | 12.773(2) |
| $\alpha$ [°] | 90 | 90 |
| $\beta$ [°] | 90 | 111.524(2) |
| $\gamma$ [°] | 90 | 90 |
| $V$ [Å$^3$] | 1486.8(8) | 905.7(2) |
| $Z$ | 4 | 2 |
| $D_{calcd}$ [g cm$^{-3}$] | 1.614 | 1.493 |
| $F$(000) | 736 | 420 |
| $\mu$ [mm$^{-1}$] | 1.149 | 0.956 |
| Max./min. transmission | 0.9076/0.6440 | 0.8620/0.7010 |
| Reflections collected | 13666 | 8286 |
| Independent reflections | 3671 ($R_{int}$ = 0.0719) | 4189 ($R_{int}$ = 0.0187) |
| Observed reflections [$I > 2\sigma(I)$] | 2700 | 3800 |
| Parameters refined | 184 | 200 |
| Max./min. $\Delta\rho$[a] [e Å$^{-3}$] | 0.566/–0.452 | 0.891/–0.502 |
| $R_1/wR_2$ [$I > 2\sigma(I)$][b] | 0.0372/0.0594 | 0.0265/0.0636 |
| $R_1/wR_2$ (all reflect.) [b] | 0.0581/0.0646 | 0.0295/0.0647 |
| Goodness-of-fit on $F^2$ [c] | 0.897 | 0.976 |
| Weight scheme $w$; $a/b$[d] | 0.0217/0.0000 | 0.0370/0.0000 |
| Absolute structure parameter (Flack value[53]) | 0.01(4) | 0.01(3) |

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

## Acknowledgments

We thank the Alexander von Humboldt Foundation (AvH), Bonn, and the Matsumae International Foundation (MIF), Tokyo, for offering a post-doctoral fellowship to M.E. Our sincere thanks go to Dr. Inayoshi for collecting the mass spectra at the Department of Chemistry, College of Science and Engineering, Aoyama Gekuin University, Tokyo. We acknowledge the financial support under the JU projects, Department of Chemistry, Jahangirnagar University, Bangladesh, by the Deutsche Forschungsgemeinschaft through grant JA-466/14-1, and the Fonds der Chemischen Industrie.

[1] a) H. Brunner, B. Reiter, G. Riepl, *Chem. Ber.* **1984**, *117*, 1330–1354; b) L. Marko, Z. Nagy-Magos, P. Kvintovics, *Abstract*, *IX Intl. Conf. Organomet. Chem.*, Dijon, **1979**; c) P. Kvintovics, B. R. James, B. Heil, *J. Chem. Soc., Chem. Commun.* **1986**, 1810–1811; d) K. Severin, K. Sünkel, W. Beck, *Chem. Ber.* **1994**, *127*, 615–620; e) K. Severin, W. Beck, *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 275–279; f) J. Cai, X. Hu, X. Feng, W. Shao, L. Ji, I. Bernal, *Eur. J. Inorg. Chem.* **2000**, 2199–2205; g) R. Dreos, G. Nardin, L. Randaccio, P. Siega, G. Tauzher, *Inorg. Chem.* **2004**, *43*, 3433–3440.

[2] a) D. Dowerah, M. M. Singh, *J. Indian Chem. Soc.* **1980**, *LVII*, 368–371; b) D. Dowerah, M. M. Singh, *Transition Met. Chem.* **1976**, *1*, 294–295; c) D. Dowerah, M. M. Singh, *J. Chem. Res., Synop.* **1979**, 38; d) D. Dowerah, M. M. Singh, *J. Chem. Res. (M)* **1979**, 255–263; e) T. Giraldi, G. Zassinovich, G. Mestroni, *Chem. Biol. Interact.* **1974**, *9*, 389–394; f) T. Giraldi, G. Eava, G. Bertoli, G. Mestroni, G. Zassinovich, *Cancer Res.* **1977**, *37*, 2662–2666.

[3] a) Z. Nagy-Magos, S. Vastag, B. Heil, L. Marko, *J. Organomet. Chem.* **1979**, *171*, 97–102; b) Z. Nagy-Magos, P. Kvintovics, L. Marko, *Transition Met. Chem.* **1980**, *5*, 186–188.

[4] a) K. Severin, S. Mihan, W. Beck, *Chem. Ber.* **1995**, *128*, 1127–1130; b) T. Hauck, K. Sünkel, W. Beck, *Inorg. Chim. Acta* **1995**, *235*, 391–396; c) K. Severin, S. Mihan, W. Beck, *Chem. Ber.* **1995**, *128*, 1117–1125.

[5] G. Vujevic, C. Janiak, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2585–2590.

[6] K. Prout, S. R. Critchley, E. Cannillo, V. Tazzoli, *Acta Crystallogr., Sect. B: Struct. Sci.* **1977**, *33*, 456–462.

[7] I. C. Tornieporth-Oetting, P. S. White, *Organometallics* **1995**, *14*, 1632–1636.

[8] T. M. Klapötke, H. Köpf, I. C. Tornieporth-Oetting, P. S. White, *Organometallics* **1994**, *13*, 3628–3633.

[9] W. Petri, J. Meder, M. Girnth-Weller, K. Bartel, V. Bejenke, G. Huttner, W. Beck, *Chem. Ber.* **1982**, *115*, 846–859.

[10] M. Maurus, B. Aechter, W. Hoffmüller, K. Polborn, W. Beck, *Z. Anorg. Allg. Chem.* **1997**, *623*, 299–303.

[11] a) M. Enamullah, M. Hasegawa, T. Hoshi, *Abstract*, *Bangladesh Chem. Soc. Conf.,* Jahangirnagar University, Dhaka, **2003**; b) M. Enamullah, M. Hasegawa, J. Okubo, T. Hoshi, *Abstract*, *Bangladesh Chem. Soc. Conf.*, Dhaka University, Dhaka, **2004**; c) M. Enamullah, M. Hasegawa, J. Okubo, T. Hoshi, *J. Bangladesh Chem. Soc.*, to be submitted.

[12] See Supporting Information for UV/Vis spectra and data.

[13] E. Pretsch, J. T. Clerc, *Spectra Interpretation of Organic Compounds*, Weinheim, New York, Basel, Cambridge, Tokyo, **1997**, pp. 9, 23.

[14] A. A. H. van der Zeijden, G. van Koten, R. A. Nordemann, B. Kojic-Prodic, A. L. Spek, *Organometallics* **1988**, *7*, 1957–1966.

[15] a) J. Karas, G. Huttner, K. Heinze, P. Rutsh, L. Zsolnai, *Eur. J. Inorg. Chem.* **1999**, 405–420; b) J. Scherer, G. Huttner, M. Buchner, *Chem. Ber.* **1996**, *129*, 697–713.

[16] a) A. P. Martinez, M. P. Garcia, F. J. Lahoz, L. A. Oro, *Inorg. Chem. Commun.* **2002**, *5*, 245–248; b) G. S. Rodman, K. R. Mann, *Inorg. Chem.* **1988**, *27*, 3338–3346.

[17] J. G. Leipoldt, E. C. Grobler, *Inorg. Chim. Acta* **1983**, *72*, 17–20.

[18] J. Rouzaud, M. D. Jones, R. Raja, B. F. G. Johnson, J. M. Thomas, M. J. Duer, *Helv. Chim. Acta* **2003**, *86*, 1753–1759.

[19] G. Matsubayashi, S. Akazawa, *Polyhedron* **1985**, *4*, 419–424.

[20] A. P. Martinez, M. P. Garcia, F. J. Lahoz, L. A. Oro, *Inorg. Chim. Acta* **2003**, *347*, 86–98.

[21] J. C. Bayon, G. Net, P. G. Rasmussen, J. B. Kolowich, *J. Chem. Soc., Dalton Trans.* **1987**, 3003–3007.

[22] S. L. James, D. M. P. Mingos, X. Xu, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **1998**, 1335–1340.

[23] H. D. Flack, *Helv. Chim. Acta* **2003**, *86*, 905–921.

[24] A chiral space group needs to have an element from one of the following four pairs of enantiomorphous screw rotations: $\{3_1, 3_2\}$, $\{4_1, 4_3\}$, $\{6_1, 6_5\}$, $\{6_2, 6_4\}$. Only 22 out of the 230 space groups are chiral. A crystal structure in $P2_1$ is chiral but the space group itself is achiral as it does not form one member of an enantiomorphous pair.

[25] C. Janiak, *Dalton Trans.* **2003**, 2781–2804.

[26] H.-P. Wu, C. Janiak, G. Rheinwald, H. Lang, *J. Chem. Soc., Dalton Trans.* **1999**, 183–190.

[27] H.-P. Wu, C. Janiak, L. Uehlin, P. Klüfers, P. Mayer, *Chem. Commun.* **1998**, 2637–2638.

[28] a) M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2327–2329; b) A. J. Blake, N. R. Champness, A. N. Khlobystov, S. Parsons, M. Schröder, *Angew. Chem. Int. Ed.* **2000**, *39*, 2317–2320.

[29] F. Bodar-Houillon, T. Humbert, A. Marsura, J.-B. Regnouf de Vains, O. Dusausoy, N. Bouhmaida, N. E. Ghermani, Y. Dusausoy, *Inorg. Chem.* **1995**, *34*, 5205–5209.

[30] C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem. Int. Ed.* **1998**, *37*, 920–922.

[31] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.

[32] a) M. Nishio, *CrystEngComm* **2004**, *6*, 130–158; b) M. Nishio, M. Hirota, Y. Umezawa, *The CH/π Interaction: Evidence, Nature and Consequences*, Wiley-VCH, Weinheim, Germany, **1998**; c) Y. Umezawa, S. Tsuboyama, K. Honda, J. Uzawa, M. Nishio, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1207–1213; d) C. Janiak, S. Temizdemir, S. Dechert, W. Deck, F. Girgsdies, J. Heinze, M. J. Kolm, T. G. Scharmann, O. M. Zipffel, *Eur. J. Inorg. Chem.* **2000**, 1229–1241.

[33] T. Dorn, A.-C. Chamayou, C. Janiak, *New J. Chem.* **2006**, *30*, 156–167; and references cited therein.

[34] C. Janiak, S. Temizdemir, T. G. Scharmann, *Z. Anorg. Allg. Chem.* **1998**, *624*, 755–756.

[35] E. Craven, E. Mutlu, D. Lundberg, S. Temizdemir, S. Dechert, H. Brombacher, C. Janiak, *Polyhedron* **2002**, *21*, 553–561.

[36] C. Janiak, T. G. Scharmann, unpublished results.

[37] C. Janiak, S. Temizdemir, S. Dechert, *Inorg. Chem. Commun.* **2000**, *3*, 271–275.

[38] C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow, R. Macdonald, *J. Am. Chem. Soc.* **1996**, *118*, 6307–6308.

[39] B. Paul, C. Näther, K. M. Fromm, C. Janiak, *CrystEngComm* **2005**, *7*, 309–319.

[40] X.-J. Yang, B. Wu, C. Janiak, *CrystEngComm* **2004**, *6*, 126–129.

[41] Q. Ye, X.-S. Wang, H. Zhao, R.-G. Xiong, *Tetrahedron: Asymmetry* **2005**, *16*, 1596–1602.

[42] T. Ezuhara, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 3279–3283.

[43] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem. Int. Ed.* **1999**, *38*, 492–495.

[44] S. R. Batten, B. F. Hoskins, R. R. Robson, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 636–637.

[45] C. Sporer, K. Wurst, D. B. Amabilino, D. Ruiz-Molina, H. Kopacka, P. Jaitner, J. Veciana, *Chem. Commun.* **2002**, 2342–2343.

[46] M. Du, X.-H. Bu, Y.-M. Guo, J. Ribas, C. Diaz, *Chem. Commun.* **2002**, 2550–2551.

[47] a) G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1979**, *19*, 218; b) J. Chatt, L. M. Venanzi, *J. Chem. Soc.* **1957**, 4735–4741.

[48] *SMART*, Data Collection Program for the CCD Area-Detector System; *SAINT*, Data Reduction and Frame Integration Program for the CCD Area-Detector System. Bruker Analytical X-ray Systems, Madison, Wisconsin, USA, **1997**.
[49] G. Sheldrick, *Program SADABS: Area-detector absorption correction*, University of Göttingen, Germany, **1996**.
[50] G. M. Sheldrick, *SHELXS-97*, *SHELXL-97*, Programs for Crystal Structure Analysis, University of Göttingen, Germany, **1997**.
[51] *DIAMOND 3.0e for Windows*, Crystal Impact Gbr, Bonn, Germany, http://www.crystalimpact.com/diamond.
[52] a) A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, C34; b) A. L. Spek, *PLATON – A multipurpose crystallographic tool*, Utrecht University, Utrecht, The Netherlands, **2005**. Windows implementation: L. J. Farrugia, University of Glasgow, Scotland, **2005**, version 80205.
[53] H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 876–881.

Received: November 17, 2005
Published Online: March 30, 2006