

Iron(II) and zinc(II) monohelical binaphthyl salen complexes†

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A new chiral binaphthyl salen ligand with rigid polyaromatic sidearms gives monohelical complexes (Fe^{II} and Zn^{II}) of predetermined handedness.

The helix is one of the most important chiral motifs in natural systems and there is an increasing interest in the development of helical transition metal complexes and related supramolecular structures.¹ The majority of investigations concern helicates, which have two or more metal centers.² By contrast, few studies focus on simpler mononuclear helices (monohelices), particularly those with a single multidentate chiral ligand.³ The high asymmetry of these complexes makes them attractive candidates as asymmetric catalysts, and this has been explored in several studies.⁴

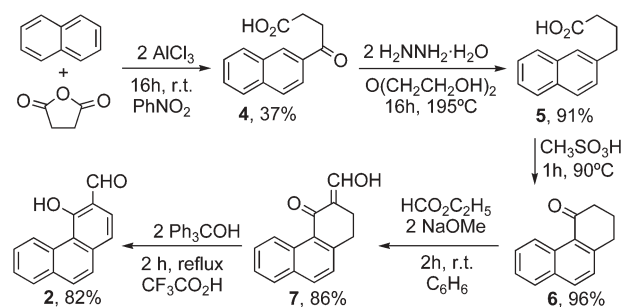
Single-stranded monohelices are synthetically challenging targets since multidentate ligands often prefer to bridge metal centers and produce helicates. The preference is the result of the specific geometric relationship between the donor atoms and the flexibility of the spacers between them.⁵ If the donors can orient themselves to form strong binding interactions with a single metal and if the ligand is pliable enough to allow for wrapping without strong steric repulsions, then a monohelical complex is likely. To date there have been no examples of monohelical metallosalen complexes, although 'stepped' complexes such as those synthesized by Katsuki *et al.*,⁶ Jacobsen *et al.*,⁷ and DiMauro and Kozlowski⁸ strongly suggest the possibility. Also, Katz *et al.*⁹ and Takata *et al.*¹⁰ have reported single-stranded polymeric salen helices.

Our approach to producing monohelices is to link two rigid planar fragments (sidearms) to a chiral directing unit (the backbone). The chirality of the backbone determines the handedness of the helix (*P* or *M*). An excellent candidate for the backbone precursor is the chiral 1,1'-binaphthyl-2,2'-diamine (**1**), which has been shown to be effective at producing significantly twisted tetradentate Schiff base ligands and complexes.¹¹ The dihedral angle between the naphthyl planes of the binaphthyl fragment is correlated to the strength of the steric repulsions between them: there is a flat-bottomed potential at 90° but a steep potential outside of the *ca.* 60° to 130° range.¹² Thus, donors attached to binaphthyl units have a great degree of flexibility in binding metals with different sizes and coordination geometries, but the limitations on the twisting and the steric bulk of the binaphthyl group tend to disfavor the formation of dihelicates.¹³

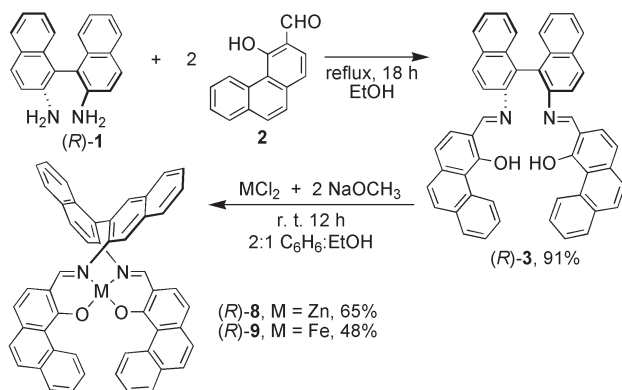
In order to form monohelices, the rigid sidearms attached to the binaphthyl backbone need low steric bulk so that they can approach one another and overlap upon complex formation.

Curved polyaromatics such as phenanthrenes meet this requirement and 4-hydroxy-3-phenanthrenecarboxaldehyde, **2**, is well suited for constructing the sidearms. This aldehyde is the key precursor to the ligand (*R*)-**3**, and was synthesized in five steps from naphthalene (Scheme 1). Friedel–Crafts acylation of naphthalene to give **4** followed the general method of Haworth¹⁴ but with significant improvement in the workup procedure, allowing for facile separation of the desired compound from its regioisomer.¹⁵ Wolff–Kishner reduction of **4** to give **5** and subsequent cyclization with methanesulfonic acid to give **6** followed established procedures.¹⁶ Condensation of **6** with ethyl formate to give **7** followed the procedure outlined by Cagniant and Kirsch.¹⁷ Oxidation of **7** with triphenylmethanol in trifluoroacetic acid¹⁸ gave **2** in good yield.¹⁹

Condensation of (*R*)-**1** with **2** in ethanol produced the neutral ligand (*R*)-**3** (Scheme 2).²⁰ Single crystals (orange prisms) suitable for X-ray analysis were grown by solvent diffusion of hexanes into a methylene chloride solution of (*R*)-**3**.²¹ The dihedral angle between the naphthyl planes is 103.4° and all four donor atoms are on one side of the molecule (Fig. 1). One half of the ligand has



Scheme 1 Synthesis of **2**.



Scheme 2 Synthesis of (*R*)-**3** and its Zn^{II} and Fe^{II} complexes.

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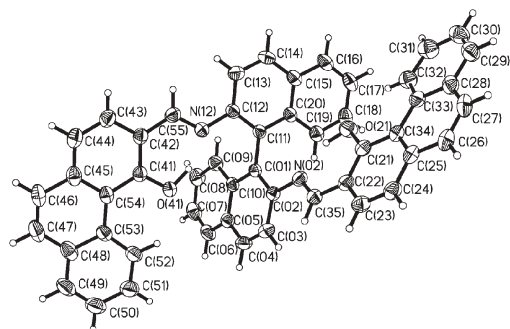


Fig. 1 Thermal ellipsoid plot (50% probability) of (*R*)-**3**. Selected bond lengths (Å): C(01)–C(11) 1.488(3), C(02)–N(02) 1.411(3), N(02)–C(35) 1.285(3), C(22)–C(35) 1.429(3), C(21)–O(21) 1.325(3).

nearly coplanar naphthyl and phenanthrene units (dihedral of 7.6°), indicating that the π system is largely delocalized, as has been seen for other binaphthyl salen ligands.²² The other half of the molecule shows a dihedral angle of 27.4°, suggesting that packing forces are enough to significantly disrupt the delocalization.

Both Zn^{II} and Fe^{II} complexes of (*R*)-**3** can be produced using the same general synthetic method.²³ The ligand is allowed to react with anhydrous MCl₂ in the presence of excess NaOCH₃, which deprotonates the phenolic hydrogens and prevents the build up of hydrogen chloride. The zinc complex, (*R*)-**8**, is bright yellow and the elemental analysis and NMR data indicate that the isolated material has no coordinated water or solvent, which is very unusual for a zinc salen complex.²⁴ Single crystals were grown from diffusion of methanol into a methylene chloride solution of (*R*)-**8**. The X-ray crystal structure²⁵ shows that only *M* helices are present and that methanol is coordinated to the zinc ion giving a five coordinate metal center (Fig. 2). The dihedral angle between the sidearms is 43.7° and the space-filling diagram indicates some degree of overlap. The dihedral angle between the naphthyl fragments is 66.9°, significantly smaller than in the free ligand, but still within the region where binaphthyl-based steric repulsions are relatively low.

The Fe^{II} complex, (*R*)-**9**, was isolated as an air and moisture sensitive paramagnetic red-brown powder. Repeated attempts to

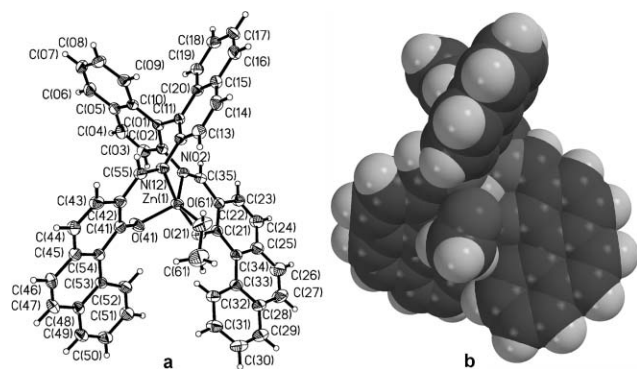


Fig. 2 (a) Thermal ellipsoid plot (50% probability) of (*R*)-**8**(CH₃OH). Selected bond lengths (Å) and angles (°): Zn(1)–O(21) 1.9828(15), Zn(1)–O(41) 1.9553(16), Zn(1)–O(61) 2.1542(18), Zn(1)–N(02) 2.0708(18), Zn(1)–N(12) 2.0861(18), C(21)–O(21) 1.281(3), C(22)–C(35) 1.432(3), C(35)–N(02) 1.301(3), N(02)–C(02) 1.427(3), C(41)–O(41) 1.297(3), C(42)–C(55) 1.433(3), C(55)–N(12) 1.284(3), N(02)–Zn(1)–N(12) 92.26(7), O(21)–Zn(1)–O(41) 100.52(7). (b) Space filling plot.

grow single crystals suitable for X-ray analysis were unsuccessful but the racemic compound, (*R/S*)-**9**, could be crystallized by solvent diffusion of methanol into a methylene chloride solution. The crystal structure²⁶ shows racemic helices, with the *R* enantiomer giving *M* helices and the *S* enantiomer producing *P* helices (Fig. 3). The structure of the *R* enantiomer is similar to that of the zinc complex, except that the iron has a distorted tetrahedral geometry, with no coordinated solvent molecule. As a result, the iron complex is more twisted and this is perhaps most evident from the dihedral angle between the sidearms (74.5°), which is significantly larger than in the zinc complex. The dihedral angle between the naphthyl fragments (68.6°) is similar to the zinc complex.

In both complexes there is significant rotation of the aromatic arms relative to the naphthyl units (the range is 63.9° to 83.8°) indicating that there is little delocalization of π electrons between these aromatic segments. A roughly perpendicular relationship between the naphthyl units and the aromatic sidearms has been observed in other binaphthyl Schiff base complexes.¹¹

We have demonstrated the first synthesis of monohelical salen complexes and have shown that the 1,1'-binaphthyl backbone is an effective helix-forming unit, producing only the helical form predicted based on its chirality. The aromatic phenanthrene-based sidearms are effective because they are rigid and planar and therefore can approach each other in the helix without strong steric repulsions. We are undertaking a series of theoretical calculations and CD spectral analyses in order to understand the solution chemistry of these complexes and are examining several metal centers to establish their catalytic activity for asymmetric transformations.

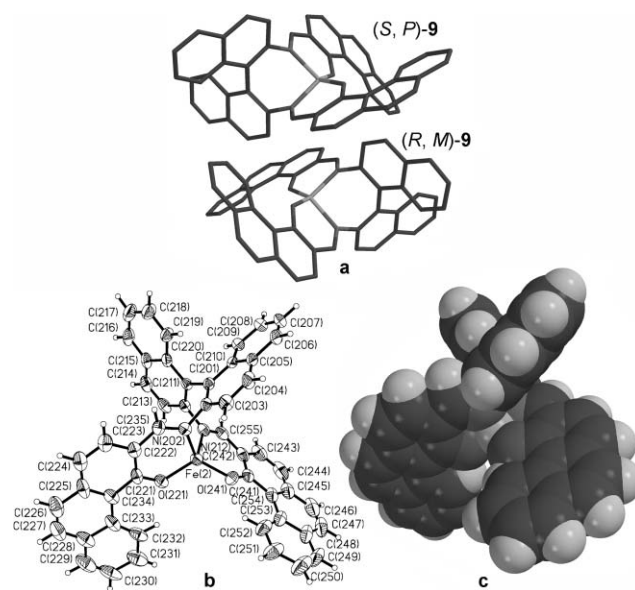


Fig. 3 (a) *P* and *M* helices in the structure of (*R/S*)-**9**(CH₂Cl₂). (b) Thermal ellipsoid plot (50% probability) for the *R,M* molecule. Selected bond lengths (Å) and angles (°): Fe(2)–O(221) 1.907(2), Fe(2)–O(241) 1.879(3), Fe(2)–N(202) 2.010(3), Fe(2)–N(212) 2.022(3), C(221)–O(221) 1.311(4), C(222)–C(235) 1.424(5), C(235)–N(202) 1.285(4), C(202)–N(202) 1.422(4), C(241)–O(241) 1.306(4), C(242)–C(255) 1.412(6), C(255)–N(212) 1.290(5), C(212)–N(212) 1.426(5), N(202)–Fe(2)–N(212) 94.80(12), O(221)–Fe(2)–O(241) 121.06(11). (c) and (d) Space filling plots of the *R,M* molecule.

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- 20 A mixture of **2** (2.077 g, 9.3 mmol) and (*R*)-**1** (1.329 g, 4.7 mmol) in ethanol (100 mL) was refluxed for 18 h and the resultant suspension was filtered while hot. The precipitate was washed with hot ethanol (40 mL) and dried *in vacuo* to give (*R*)-**3** (2.958 g, 91% yield) as a bright red solid. Anal. calc. for C₅₀H₃₂N₂O₂: C 86.68, H 4.66, N 4.04. Found: C 86.93, H 4.85, N 4.25. (*S*)-**3** was synthesized using the same procedure, with (*S*)-**1** in place of the (*R*)-**1**. Anal. calc. for C₅₀H₃₂N₂O₂: C 86.68, H 4.66, N 4.04. Found: C 86.66, H 4.88, N 4.12.
- 21 Crystal data for (*R*)-**3**. Bruker SMART 1000, C₅₀H₃₂N₂O₂, *M* = 692.78, orthorhombic, *a* = 11.0977(6) Å, *b* = 16.4934(10) Å, *c* = 18.7071(11) Å, *V* = 3424.1(3) Å³, *T* = 203(2) K, space group *P*2₁2₁ (no. 19), *Z* = 4, 2θ collection range 2.13 to 28.28°, μ(Mo-Kα) = 0.08 mm⁻¹, 24779 reflections collected, 4512 unique (*R*_{int} = 0.0886) which were used in all calculations. *R*₁ = 0.0646 (all data) and *wR*(*F*²) = 0.1182 (all data). CCDC 276257. See <http://dx.doi.org/10.1039/b508538a> for crystallographic data in CIF or other electronic format.
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- 26 Crystal data for (*R*)-**9**·CH₂Cl₂. Bruker SMART 1000, C₅₁H₃₂Cl₂FeN₂O₂, *M* = 831.54, triclinic, *a* = 13.1443(12) Å, *b* = 16.4557(15) Å, *c* = 18.9601(17) Å, α = 99.736(6)°, β = 104.006(6)°, γ = 94.156(4)°, *V* = 3894.1(6) Å³, *T* = 173(2) K, space group *P*1, *Z* = 4, 2θ collection range 1.26 to 28.39°, μ(Mo-Kα) = 0.57 mm⁻¹, 49344 reflections collected, 17792 unique (*R*_{int} = 0.1024) which were used in all calculations. *R*₁ = 0.1632 (all data) and *wR*(*F*²) = 0.1642 (all data). CCDC 276259. See <http://dx.doi.org/10.1039/b508538a> for crystallographic data in CIF or other electronic format.