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PAPER

2-Diphenylphosphino-2′-hydroxy-1,1′-binaphthyl as a chiral auxiliary for asymmetric coordination chemistry

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In this study, the bidentate ligand (*R*)-2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (**HO-MOP**) was investigated as a chiral auxiliary for the asymmetric synthesis of ruthenium polypyridyl complexes. It was found that (*R*)-**HO-MOP** serves as an effective chiral auxiliary starting from different precursor complexes, most notably using the commercially available half-sandwich complex $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$.

Introduction

General methods for the stereocontrolled synthesis of octahedral metal complexes are needed in order to fully exploit the structural opportunities offered by octahedral coordination spheres in the areas of materials sciences and life sciences.[1] For example, octahedral metal complexes play an increasingly important role as structural scaffolds for the design of nucleic acid probes[2] and enzyme inhibitors[3] and for such applications of molecular recognition usually single enantiomers are desired (Fig. 1). However, since practical and general methods for the asymmetric synthesis of optically pure octahedral metal complexes are scarce, racemic mixtures are typically resolved by uneconomical chiral separation techniques. Clearly, the further development of the fields of inorganic medicinal chemistry and inorganic chemical biology would greatly benefit from an access to methods for the enantioselective synthesis of such metal complexes.

Chiral organic groups within coordinating ligands are capable of effectively controlling the absolute configuration of metal complexes during their formation, thereby transferring carbon-centered chirality to octahedral metal centers.[1] For example, von Zelewsky *et al.* utilized chiral tetradentate bis-2,2′-bipyridines for the highly diastereoselective synthesis of optically pure octahedral ruthenium polypyridyl complexes without the need for the separation of stereoisomers,[4] whereas Scott and coworkers recently demonstrated that simple chiral 2-iminopyridines afford optically pure single isomers of *fac*-tris(diimine) iron(II) complexes.[5]

If chiral metal complexes are desired which ultimately do not retain carefully designed chiral organic ligands in their coordination spheres, the strategy of using chiral coordinating ligands only temporarily, means as chiral auxiliaries, is probably the strategy of choice.[6] Such auxiliaries have the task to control the generation of the absolute configuration at the metal center during ligand exchange reactions, followed by a traceless removal of the chiral ligand. Reported examples using tartrate,[7] monodentate chiral sulfoxides,[8,9] chiral cleavable linkers,[10] and chiral counterions[11] mostly provided only unsatisfactory asymmetric inductions or were too specialized for a general use. A few years ago we therefore started a research program with the aim to design tailored powerful chiral auxiliaries for asymmetric coordination chemistry that give high asymmetric control, can afterwards be removed in a traceless fashion from the metal center without any loss of

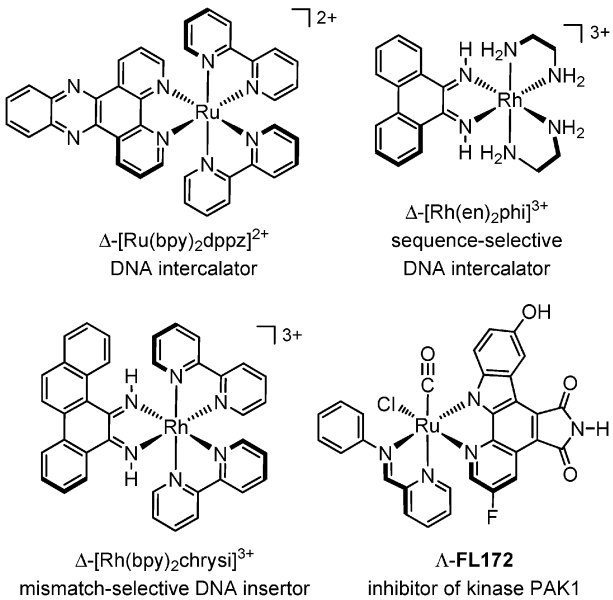

Fig. 1 Examples of substitutionally inert chiral octahedral metal complexes with biological activities. See ref. 2 and 3 for more details.

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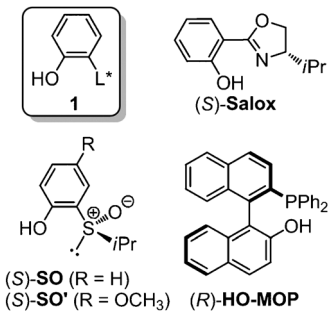


Fig. 2 Chelating chiral auxiliaries designed for asymmetric coordination chemistry.

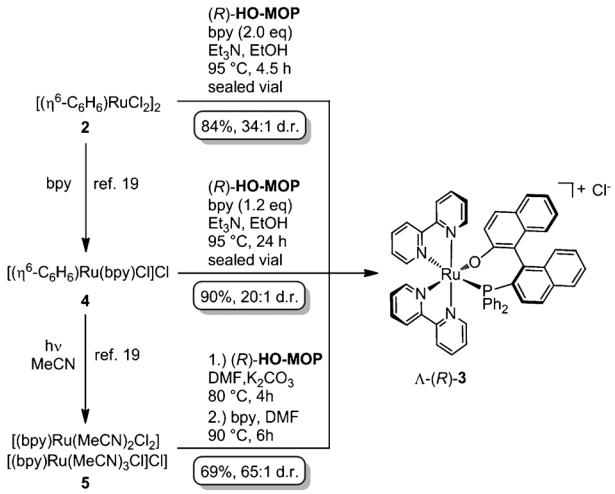
chiral information, and are of broad applicability. We made some progress towards this goal with chiral bidentate ligands of the general structures shown in Fig. 2.[12–14] In our design, the chelate effect ensures that the carbon- or sulfur-based chiral center is placed in a well defined position close to the metal center, as opposed to monodentate ligands which typically allow a rotation around the metal–ligand coordinative bond. In a key aspect, a phenol moiety serves as a coordination site that can be tuned in its coordination strength by deprotonation/reprotonation so that the coordination of the chiral bidentate phenolate ligand can be made reversible, even with inert metals such as ruthenium.

Here we now report the application of this design strategy to the well-known axially chiral binaphthyl system, namely 2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (**HO-MOP**,[15] Fig. 2). We describe the scope and limitation of this chiral ligand and compare it with previously developed auxiliaries.

Results and discussion

While exploring the reactivity of the **HO-MOP** ligand in different reaction schemes, we discovered that the reaction of the commercially available ruthenium complex $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ with 1.25 equivalents of (*R*)-**HO-MOP** and 2.0 equivalents of 2,2′-bipyridine (bpy) in dry ethanol and in the presence of Et_3N (12.5 equivalents) at 95 °C in a sealed vial afforded in one step and after workup and purification the complex *Λ*-[Ru(bpy)$_2${(*R*)-**HO-MOP**}]Cl (*Λ*-(*R*)-**3**) in a yield of 84% and with a satisfactory diastereoselectivity of 34 : 1 dr (Scheme 1).[16,17] The metal-centered configuration of complex *Λ*-(*R*)-**3** was assigned by CD-spectroscopy and later indirectly verified by the analysis of follow-up products (see below). In a variation of this synthesis, complex **2** was first reacted with bpy to afford the well known complex $[Ru(bpy)(\eta^6\text{-}C_6H_6)Cl]Cl$ (**4**),[18,19] followed by (*R*)-**HO-MOP** (1.2 equivalents) together with bpy (1.0 equivalents) and Et_3N (12 equivalents) in dry EtOH at 95 °C (sealed vial) to yield *Λ*-(*R*)-**3** in 90% with 20 : 1 dr.

However, if higher diastereoselectivities are desired, the precursor complex $[Ru(bpy)(MeCN)_2Cl_2]$/$[Ru(bpy)(MeCN)_3Cl]Cl$ (**5**) is the starting material of choice for asymmetric coordination chemistry with (*R*)-**HO-MOP**.[19] Accordingly, acetonitrile complex **5** can be obtained in one step from half-sandwich complex **4** by UV-photolysis with a medium pressure mercury lamp in acetonitrile.[19] Upon reaction of **5** first with



Scheme 1 Diastereoselective coordination chemistry with (*R*)-**HO-MOP** utilizing the complexes **2**, **4**, and **5** as the starting materials.

(*R*)-**HO-MOP** and K_2CO_3 followed by bpy, *Λ*-(*R*)-**3** was obtained in a modest yield of 69% but with a high dr of 65 : 1. Thus, all three starting materials, complexes **2**, **4**, and **5**, can be converted diastereoselectively to the complex *Λ*-(*R*)-**3** by the reaction with (*R*)-**HO-MOP** and bpy.

In order to better understand the preference for the formation of the *Λ*-(*R*) over the *Δ*-(*R*) diastereomer, we calculated the geometries and Gibbs free energies of *Λ*-(*R*)-**3** and *Δ*-(*R*)-**3** including solvent effects using the density functional theory at the M05/def2-SVP/CPCM level. As a result, *Δ*-(*R*)-**3** is destabilized by 1.1 kcal mol^{-1} compared to the favored diastereomer *Λ*-(*R*)-**3** and the displayed geometries in Fig. 3 indicate that this is mainly due to a direct steric interference between one of the naphthalene moieties and a bpy ligand. In contrast, in the more stable diastereomer *Λ*-(*R*)-**3**, one naphthalene moiety is

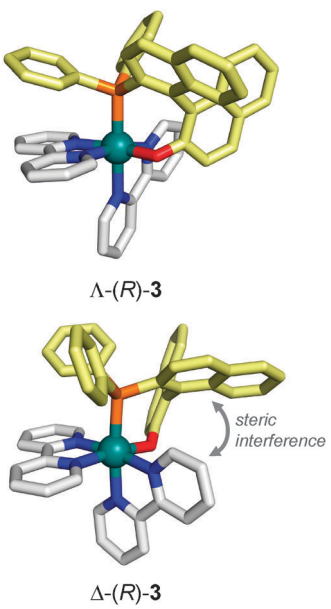
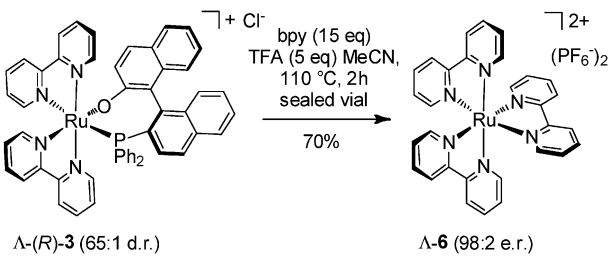


Fig. 3 The optimized geometries of the two diastereomers *Λ*-(*R*)-**3** and *Δ*-(*R*)-**3** at M05/def2-SVP/CPCM. The Gibbs free energies of the two diastereomers differ by 1.1 kcal mol^{-1} in favor of *Λ*-(*R*)-**3**.

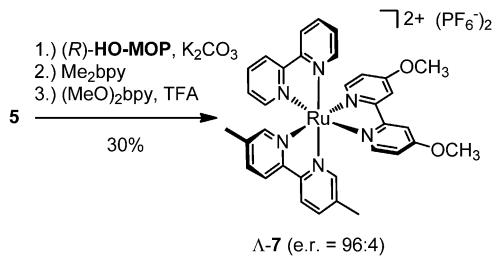
instead favorably stacked face-to-face with a bpy ligand. Thus, the thermodynamically preferred diastereomer is formed preferentially in analogy to the recently reported diastereoselective coordination chemistry with the **Salox** chiral auxiliary (Fig. 2) which occurred under thermodynamic control.[13] It can therefore be assumed that starting from complex **5**, for example, the reaction with (*R*)-**HO-MOP** will afford an intermediate in which bpy, deprotonated (*R*)-**HO-MOP**, in addition to two labile monodentate ligands (two MeCN ligands or MeCN plus chloride) are coordinated to the ruthenium center. The different possible diastereomers should then be in an equilibrium with each other, possibly through configurationally labile pentacoordinated complexes, in which the most stable of these intermediate diastereomers will predominate and react with bpy to afford *Λ*-(*R*)-**3**. Altered reaction conditions of the synthesis of *Λ*-(*R*)-**3** from **4** at lower reaction temperatures (80 °C, 65 °C) or shorter reaction time (3.0 h) lead to a decline in the dr to around 10 : 1, also indicating thermodynamic control. However, additional kinetic effects may also play a role.

Next, starting with *Λ*-(*R*)-**3** (65 : 1 dr) we investigated the removal of the (*R*)-**HO-MOP** auxiliary from the ruthenium coordination sphere. Indeed, using our standard reaction conditions[13] of trifluoroacetic acid (TFA) (5 equivalents) and an excess of bpy in MeCN led to a smooth substitution of (*R*)-**HO-MOP** against bpy under retention of configuration to afford *Λ*-$[Ru(bpy)_3](PF_6)_2$ after workup and chromatography with 70% yield and 98 : 2 er (Scheme 2).[20]

Finally, we evaluated whether (*R*)-**HO-MOP** is suitable for synthesizing tris-heteroleptic ruthenium polypyridyl complexes in an asymmetric fashion and we therefore reacted starting complex **5** first with (*R*)-**HO-MOP**, followed by 5,5′-dimethyl-2,2′-bipyridine (Me_2bpy), and subsequently, after a brief workup, with 4,4′-dimethoxy-2,2′-bipyridine {$(MeO)_2$bpy} in the presence of TFA to afford *Λ*-[Ru(bpy)(Me_2bpy){$(MeO)_2$bpy}]-$(PF_6)_2$ (*Λ*-**7**) with 30% yield and an er of 96 : 4 (Scheme 3).



Scheme 2 TFA-induced replacement of the (*R*)-**HO-MOP** chiral auxiliary under retention of configuration.



Scheme 3 Asymmetric synthesis of a tris-heteroleptic ruthenium polypyridyl complex using (*R*)-**HO-MOP** as a chiral auxiliary.

This study demonstrates that (*R*)-**HO-MOP** serves as a valuable chiral auxiliary for converting the achiral complexes **2**, **4** and **5** into ruthenium polypyridyl complexes in an asymmetric fashion. Compared to our previously developed chiral auxiliaries, **Salox** and **SO** (**SO′**) (Fig. 2), (*R*)-**HO-MOP** has the advantage that the complex *Λ*-(*R*)-**3** can be accessed from a commercially available starting material in one step and this reaction is most likely applicable to other substituted 2,2′-bipyridines and 1,10-phenanthroline ligands (pp). Consequently, complexes of the type $[Ru(pp)_2(pp')]^{2+}$, such as for example Barton's "DNA molecular light switch" *Δ*-$[Ru(bpy)_2(dppz)]^{2+}$ (Fig. 1),[2] should be accessible asymmetrically in a very straightforward fashion. On the other hand, some drawbacks may limit the general applicability of **HO-MOP** as a chiral auxiliary for asymmetric coordination chemistry. Firstly, the observed diastereoselectivities are only modest compared to our previous work with **Salox** and **SO**/**SO′**, and secondly all investigated complexes containing the deprotonated **HO-MOP** ligand are quite labile and therefore need to be handled with great care by avoiding proton sources and Lewis acids. This instability is most likely due to the unfavorable 7-membered chelate in combination with a large steric crowding within the coordination sphere.

In conclusion, we demonstrated for the first time that (*R*)-**HO-MOP** is an effective chiral auxiliary for the asymmetric synthesis of ruthenium polypyridyl complexes. This chiral auxiliary will be an attractive tool for the straightforward synthesis of bis-heteroleptic complexes of the type $[Ru(pp)_2(pp')]^{2+}$ starting directly from the commercially available half-sandwich complex $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$.

Experimental part

Materials and general methods

All reactions were carried out under a nitrogen atmosphere. Reactions involving the formation of chiral ruthenium complexes were carried out in the dark as a precaution against light-induced decomposition and isomerization. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, DMF) or sodium/benzophenone (Et_2O, THF). Ethanol was either used as HPLC grade or dry, distilled from an activated 4 Å molecular sieve under nitrogen. $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (**2**),[21] $[Ru(bpy)(\eta^6\text{-}C_6H_6)Cl]Cl$ (**4**),[19] $[Ru(bpy)(MeCN)_2Cl_2]$/$[Ru(bpy)(MeCN)_3Cl]Cl$ (**5**),[19] and (*R*)-2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl[22] were prepared according to published procedures. All other reagents were purchased from Acros, Aldrich or Alfa and used without further purification. Column chromatography was performed with silica gel (230–400 mesh) or basic alumina. NMR spectra were recorded on a Bruker Avance 300 or Bruker DRX400 spectrometer at room temperature. Chemical shifts are reported in parts per million (ppm) with the residual solvent peak as internal standard. IR spectra were obtained on a Bruker Alpha-P series FT-IR spectrometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter. Chiral HPLC chromatograms were obtained with an Agilent 1200 Series HPLC instrument. High-resolution mass spectra were recorded in ESI mode on a ThermoScientific LTQ-FT spectrometer.

Λ-(*R*)-3

Synthesis from 2. A solution of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (**2**) (7.0 mg, 14 μmol), 2,2′-bipyridine (8.7 mg, 56 μmol) and (*R*)-2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (15.9 mg, 35 μmol) in dry ethanol (11 mL) was purged with nitrogen for 20 min before dry triethylamine (49 μL, 0.35 mmol) was added. The mixture was heated at 95 °C in a sealed flask for 4.5 h. After cooling to room temperature, the solution was dried under reduced pressure and the crude product was subjected to basic aluminium oxide chromatography with CH_2Cl_2/methanol (50 : 1 to 15 : 1). Triethylamine (0.3 mL) was added to the combined deep red product fractions and the mixture was dried under reduced pressure without heating. The residue was dissolved in 2 mL CH_2Cl_2 into which 15 mL Et_2O was added. The red precipitate was centrifuged, washed twice with Et_2O and dried under high vacuum to afford *Λ*-(*R*)-**3** (21.2 mg, 84%) as a red solid. A dr of 34 : 1 was determined by ^{1}H NMR integration.

Synthesis from 4. A mixture of $[Ru(bpy)(\eta^6\text{-}C_6H_6)Cl]Cl$ (**4**) (6.0 mg, 15 μmol), 2,2′-bipyridine (2.3 mg, 15 μmol) and (*R*)-2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (8.4 mg, 18 μmol) in dry ethanol (6 mL) was purged with nitrogen for 20 min before triethylamine (25.9 μL, 185 μmol) was added. The solution was stirred at 95 °C in a sealed flask for 24 h. After drying under reduced pressure the crude product was subjected to basic aluminium oxide chromatography with CH_2Cl_2/methanol (50 : 1 to 15 : 1). Triethylamine (0.3 mL) was added to the combined deep red product fractions and the mixture was dried under reduced pressure without heating. The red precipitate was centrifuged, washed twice with Et_2O and dried under high vacuum to afford *Λ*-(*R*)-**3** (12.0 mg, 90%) as a red solid. A dr of 20 : 1 was determined by ^{1}H-NMR integration.

Synthesis from 5. A solution of precursor $[Ru(bpy)(MeCN)_2Cl_2]$/$[Ru(bpy)(MeCN)_3Cl]Cl$ (**5**) (45.2 mg, 0.10 mmol), (*R*)-2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (54.5 mg, 0.12 mmol) and K_2CO_3 (33.1 mg, 0.24 mmol) in freshly distilled DMF (20 mL) was purged with argon for 20 min and then heated at 80 °C for 4 h. The resulting brown solution was cooled to room temperature, to which 2,2′-bipyridine (124.8 mg, 0.80 mmol) was added. The mixture was heated at 90 °C for 6 h. After cooling to room temperature, it was dried under high vacuum, washed with Et_2O (3 × 10 mL), and then subjected to basic aluminium oxide chromatography with CH_2Cl_2/methanol (50 : 1 to 10 : 1) containing 0.1% of triethylamine. The brownish fraction was collected and concentrated to 2 mL under reduced pressure without heating. After addition of 15 mL of Et_2O, the brown precipitate was centrifuged, washed twice with Et_2O, dried under high vacuum to afford *Λ*-(*R*)-**3** (62.1 mg, 69%). A dr of 65 : 1 was determined by ^{1}H NMR integration.

The *Λ*-configuration of *Λ*-(*R*)-**3** was assigned based on the CD spectrum and is consistent with the absolute configuration determined for the follow-up product *Λ*-**6**.

^{1}H-NMR (300.1 MHz, $CDCl_3$): δ (ppm) 9.49 (dd, J = 5.6, 1.0 Hz, 1H), 8.66 (d, J = 8.1, 2H), 8.45 (d, J = 8.1, 1H), 8.09 (m, 2H), 7.91 (m, 3H), 7.80 (d, J = 8.7, 1H), 7.02–7.59 (m, 18H), 6.96 (m, 1H), 6.85 (m, 2H),6.71 (td, J = 8.2, 2.3 Hz, 2H), 6.29 (m, 4H), 5.69 (d, 8.8 Hz, 1H).

^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 44.02 (s).

IR (neat): ν (cm^{-1}) 3048, 1600, 1584, 1455, 1442, 1417, 1351, 1324, 1303, 1274, 1239, 1155, 1087, 1021, 976, 936, 824, 745, 730, 696, 672, 627, 585, 562, 550, 423.

CD (MeCN): λ, nm ($\Delta\varepsilon$, M^{-1} cm^{-1}) 237 (+236), 253 (−252), 301 (+75).

HRMS calcd for $RuN_4OC_{52}H_{38}P$ $(M - Cl)^+$ 867.1821, found: 867.1819.

Λ-6

In a sealed brown glass vial, a solution of *Λ*-(*R*)-**3** (4.5 mg, 0.0050 mmol, dr = 65 : 1), 2,2′-bipyridine (11.7 mg, 0.075 mmol) and trifluoroacetic acid (1.9 μL, 0.025 mmol) in CH_3CN (0.1 mL) was heated at 110 °C (oil bath temperature) for 2 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and dried *in vacuo*. The crude material was subjected to silica gel chromatography with acetonitrile and later acetonitrile/water/saturated aqueous KNO_3 (50 : 6 : 2). The product eluents were concentrated to dryness, and the resulting material was dissolved in minimal amounts of ethanol/water. The product was precipitated by the addition of excess solid NH_4PF_6. The orange precipitate was centrifuged, washed twice with water, and dried under high vacuum to afford $[Ru(bpy)_3](PF_6)_2$ (*Λ*-**6**, 3.0 mg, 70%). The *Λ*-configuration was assigned by CD spectroscopy. An er = 98 : 2 was determined by chiral HPLC analysis under the following conditions: Daicel Chiralcel OD-R, 250 × 4 mm, flow rate 0.5 ml min^{-1}, column temperature 40 °C, UV-detection at 254 nm, solvent A = 0.087% H_3PO_4, solvent B = MeCN, with a linear gradient of 8% to 14% B in 20 min.

Λ-7

A solution of precursor $[Ru(bpy)(MeCN)_2Cl_2]$/$[Ru(bpy)(MeCN)_3Cl]Cl$ (**5**) (36.2 mg, 0.080 mmol), (*R*)-2-diphenylphosphino-2′-hydroxy-1,1′-binaphthyl (43.6 mg, 0.096 mmol), and K_2CO_3 (26.5 mg, 0.19 mmol) in freshly distilled DMF (16 mL) was purged with argon for 20 min and then heated at 80 °C for 4 h. The resulting brown solution was cooled down to room temperature, to which 5,5′-dimethyl-2,2′-bipyridine (117.8 mg, 0.64 mmol) was added. The mixture was heated at 90 °C for 6 h. After cooling down to room temperature, it was dried under high vacuum, washed with Et_2O (3 × 10 mL), and then subjected to basic aluminium oxide chromatography with CH_2Cl_2/methanol (50 : 1 to 10 : 1) containing 0.1% triethylamine. The brownish fraction was collected and concentrated to 2 mL. After addition of 15 mL of Et_2O, the brown precipitate was centrifuged, washed twice with Et_2O, and dried under high vacuum to yield a very labile **HO-MOP** ruthenium complex intermediate (32.0 mg). In a sealed brown glass vial, a part of this intermediate (4.6 mg), together with 4,4′-dimethoxy-2,2′-bipyridine (16.2 mg, 0.075 mmol), and trifluoroacetic acid (1.9 μL, 0.025 mmol) in CH_3CN (0.1 mL) was heated at 110 °C (oil bath temperature) for 2 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and dried under reduced pressure. The crude material was subjected to silica gel chromatography

with acetonitrile and later acetonitrile/water/saturated aqueous KNO_3 (50 : 3 : 1). The product eluents were concentrated to dryness, and the resulting material was dissolved in minimal amounts of ethanol/water. The product was precipitated by the addition of excess solid NH_4PF_6. The orange precipitate was centrifuged, washed twice with water, and then dried under high vacuum to afford *Λ*-**7** (3.3 mg, 30% from **5**). The *Λ*-configuration was assigned by CD spectroscopy. An er of 96 : 4 was determined by chiral HPLC analysis under the following conditions: Daicel Chiralcel OD-R, 250 × 4 mm, flow rate 0.5 ml min^{-1}, column temperature 40 °C, UV-detection at 254 nm, solvent A = 0.087% H_3PO_4, solvent B = MeCN, with a linear gradient of 15% to 30% B in 20 min.

^{1}H-NMR (300.1 MHz, CD_3CN): δ (ppm) 8.49 (d, J = 8.1 Hz, 2H), 8.32 (dd, J = 8.4, 3.0 Hz, 2H), 8.03 (m, 4H), 7.82 (m, 3H), 7.73 (d, J = 5.1 Hz, 1H), 7.59 (s, 1H), 7.35–7.49 (m, 5H), 6.95 (m, 2H), 4.01 (s, 3H), 4.00 (s, 3H), 2.16 (s, 6H).

^{13}C-NMR (75.5 MHz, CD_3CN): δ (ppm) 151.9, 151.8, 151.5, 151.23, 151.19, 151.0, 137.7, 136.9, 127.0, 126.9, 123.83, 123.78, 122.8, 113.4, 113.3, 110.8, 56.39, 56.35, 17.3, 17.2.

IR (film): ν (cm^{-1}) 2969, 2927, 1616, 1558, 1494, 1475, 1445, 1420, 1338, 1313, 1279, 1248, 1225, 1046, 1034, 1019, 838, 765, 731, 558, 521, 500, 431, 413.

CD (MeCN): λ, nm ($\Delta\varepsilon$, M^{-1} cm^{-1}) 274 (−48), 294 (+112).

HRMS calcd for $RuN_6O_2C_{34}H_{32}PF_6$ $(M - PF_6)^+$ 803.1267, found: 803.1264.

Computational details

The geometry optimizations and frequency calculations of Λ-(*R*)-**3** and *Λ*-(*R*)-**3** were carried out using the M05[23] functional in conjunction with a def2-SVP[24] basis set as implemented in Gaussian09.[25] CPCM-SCRF[26] calculations were performed using a dielectric constant of 37.219 for *N*,*N*-dimethylformamide to estimate the solvation effect. In CPCM, the choice of cavities is important because the computed energies and properties depend on the cavity size. In this study, the UFF was used, which uses radii from the UFF force field.[27]

Acknowledgements

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