Monatshefte für Chemie Chemical Monthly © Springer-Verlag 1999 Printed in Austria

## Optically Active Transition Metal Complexes CXX [1]. New Ruthenium(II) Complexes Containing Two Different Types of Optically Active Ligands

## Henri Brunner<sup>\*</sup> and Josef Spitzer

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

**Summary.** The synthesis of novel ruthenium(II) complexes containing two different chiral ligands is described. These ligands are on the one-hand (-)-*diop* and on the other hand optically active imines derived from the condensation of (*S*)-1-phenylethylamine with 2-pyrrolealdehyde or 2-salicylaldehyde. The synthesis includes the preparation of the precursors containing 1,5-cyclooctadiene (*cod*) and the corresponding imine ligands. Although for the octahedral (-)-*diop*-imine-ruthenium(II) complexes six diastereomers are possible, in highly stereoselective reactions only one diastereomer is formed.

**Keywords.** Ruthenium(II) complexes; (–)-*diop*; Optically active co-ligands; Diastereomers; Stereoselectivity.

# Optisch aktive Übergangsmetallkomplexe, 120. Mitt. [1]. Neue Ruthenium(II)-Komplexe mit zwei verschiedenen Typen optisch aktiver Liganden

**Zusammenfassung.** Die Synthese von neuen Ruthenium(II)-Komplexen, die zwei verschiedene chirale Liganden enthalten, wird beschrieben. Diese Liganden sind zum einen (-)-diop und zum anderen optisch aktive Imine, die aus der Kondensation von (S)-1-Phenylethylamin mit 2-Pyrrolaldehyd oder 2-Salicyladehyd stammen. Die Synthese beinhaltet die Darstellung der Vorstufen, die aus 1,5-Cyclooctadien (cod) und den entsprechenden Iminliganden bestehen. Obwohl für die oktaedrischen (-)-diop-Imin-Ruthenium(II)-Komplexe sechs Diastereomere möglich sind, wird in einer hoch stereoselektiven Reaktion jeweils nur ein Diastereomer gebildet.

### Introduction

Ruthenium(II) complexes containing optically active chelate phosphanes. *e.g. diop* and *binap*, are well known catalysts [2–4] in the enantioselective hydrogenation of a wide range of substrates such as enamides [5],  $\alpha$ -acylamido acrylic acids [6], alkyl and aryl substituted acrylic acids [7],  $\alpha$ , $\beta$ -unsaturated carboxylic acids [7], allylic and homoallylic alcohols [8], and  $\beta$ -keto esters [9]. All ruthenium

<sup>\*</sup> Corresponding author

phosphane complexes have in common that their co-ligands are achiral. Thus, the chiral information in the catalytic reaction comes solely from the chiral chelate phosphane. In principle, it should be possible to modulate the enantioselectivity of the catalysts by chiral co-ligands in matched and mis-matched systems [10].

We here report the synthesis of the new ruthenium(II) complexes **3** and **4** containing the chelate phosphane (-)-*diop* and, in addition, the bidentate chiral ligands 2-N-((*S*)-1-phenylethyl)pyrrolylaldimine and N-((*S*)-1-phenylethyl)salicylal-dimine, respectively, prepared from the corresponding *cod* complexes **1** and **2** [11].

### **Results and Discussion**

## The isomer situation of the octahedral complexes $[M(LL)(NN^*)_2]$ and $[M(LL)(ON^*)_2]$

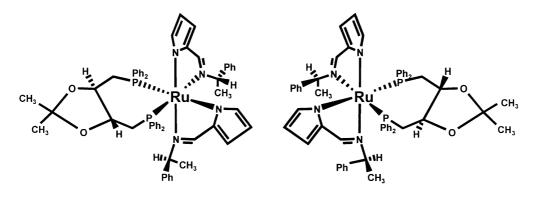
Ruthenium(II) complexes with an octahedral geometery consisting of a C<sub>2</sub>-symmetrical bidentate ligand, such as LL = (-)-diop or cod, and two optically active unsymmetrical co-ligands NN\* or ON\* form a total of six diastereomeric isomers. This is illustrated for complex **3** containing (-)-diop and two 2-N-((S)-1-phenyl-ethyl)pyrrolyladimine units as co-ligands in Scheme 1. Stereogenic elements in complexes of this type are on the one hand the Ru center which may have  $\Delta$ - and  $\Lambda$ -configuration [12] and on the other hand the *cis/trans*-arrangement of like and unlike halves of the unsymmetrical co-ligand NN\*. Three isomers have  $\Delta$ -configuration ( $\Delta$ -N,N-*cis*,N\*,N\*-*cis*,  $\Delta$ -N,N-*trans*,N\*,N\*-*cis*,  $\Delta$ -N,N-*cis*, N\*,N\*-*trans*), the other three are  $\Lambda$ -configurated ( $\Lambda$ -N,N-*cis*,N\*,N\*-*cis*,  $\Lambda$ -N, N-*trans*, N\*,N\*-*cis*,  $\Lambda$ -N, N-*trans*). The stereochemistry of (*R*,*R*)-(-)-diop and the optically active NN\*- and ON\*-ligands derived from (S)-1-phenylethylamine remain unchanged throughout this study.

Since the six isomers are diastereomers, they should differ in their <sup>1</sup>H NMR spectra. The four complexes  $\Delta$ - and  $\Lambda$ -N,N-*trans*,N\*,N\*-*cis* and  $\Delta$ - and  $\Lambda$ -N, N-*cis*, N\*,N\*-*trans* are C<sub>2</sub>-symmetric. Consequently, the protons of both ligands in each complex are equivalent. The two  $\Delta$ - and  $\Lambda$ -N,N-*cis*, N\*,N\*-*cis* configurated complexes, however, are asymmetric. Hence, the protons of the two co-ligands in each complex are inequivalent and should give different <sup>1</sup>H NMR signals.

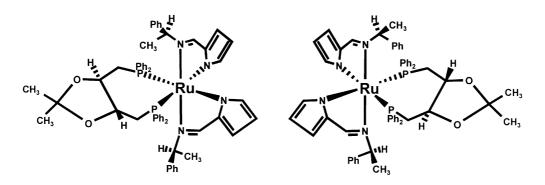
### Synthesis and NMR spectroscopy

The synthesis of the desired (-)-diop complexes **3** and **4** starts from the correponding *cod*-pyrrolylimine/salicylimine-ruthenium(II) complexes **1** and **2** which have to be prepared first. As a suitable precursor,  $[\operatorname{Ru}(cod)\operatorname{Cl}_2]_n$  was used [13]. The optically active bidentate imines for the synthesis of the complexes **1**–4 were prepared by *Schiff* base condensation of the primary amine (*S*)-1-phenylethylamine with 2-pyrrolealdehyde and 2-salicylaldehyde, respectively [14–16]. The pyrroleimine and salicylimine ligands were deprotonated with KO<sup>t</sup>Bu in toluene. To the suspension of the potassium salts of the imines,  $[\operatorname{Ru}(cod)\operatorname{Cl}_2]_n$  was added (Scheme 2).

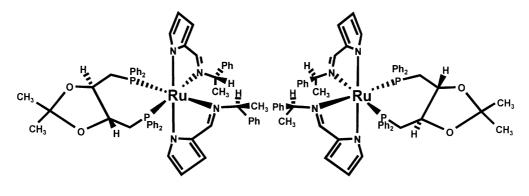
The complexes 1 and 2 were purified by chromatography on silica which had been heated in HV for 1 d. Cooling of the column to  $-20^{\circ}$ C prevents the



 $\Delta$  - N,N-*cis*,N<sup>\*</sup>,N<sup>\*</sup>-*cis*-  $\Lambda$  -



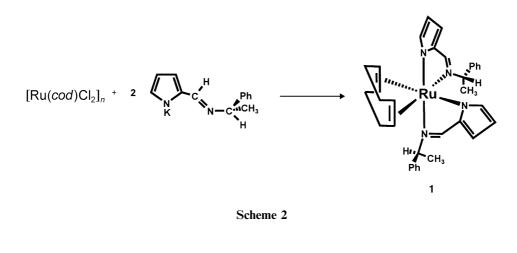
 $\Delta$  - N,N- trans, N<sup>\*</sup>, N<sup>\*</sup>-cis-  $\Lambda$  -

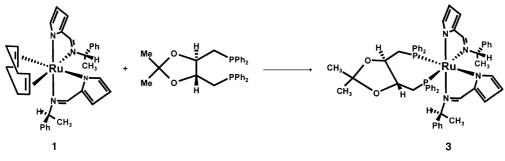


- $\Delta$  N,N-cis,N<sup>\*</sup>,N<sup>\*</sup>-trans  $\Lambda$  -
- Scheme 1. The six diastereomers of 3

decomposition of **1** and **2.1** and **2** were obtained from pentane solutions as yellow powders upon cooling. In solution, the *cod*-imine-ruthenium(II) complexes **1** and **2** are relatively unstable. On air they decompose within minutes (colour change).

The <sup>1</sup>H NMR spectrum of **1** in  $C_6D_6$  exhibits the signals of three diastereomers in a ratio of 54:39:7. Since for each of the isomers with 39 and 7% intensity two





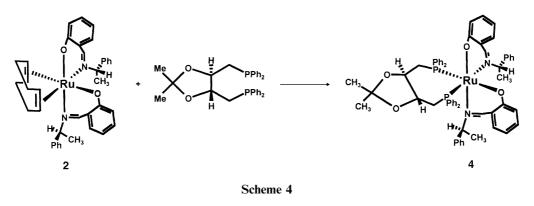
Scheme 3

sets of signals are observed, they have to be assigned to the two unsymmetric N, N-*cis*, N<sup>\*</sup>, N<sup>\*</sup>-*cis* forms. The 54% isomer is one of the four C<sub>2</sub>-symmetric diastereomers.

In the <sup>1</sup>H NMR spectrum of **2** in C<sub>6</sub>D<sub>6</sub>, the signals of three diastereomers occur in a ratio of 74:25: $\approx$ 1. Here, two of the four C<sub>2</sub>-symmetric diastereomers (74 and 25%) and one of the two possible *cis,cis*-isomers (1%) are present. By fractional crystallization from pentane, the 74% isomer could be obtained in pure form. A <sup>1</sup>H NMR measurement of a C<sub>6</sub>D<sub>6</sub> solution of this diastereomer after 24 h does not show any isomerization.

For the synthesis of the (-)-*diop* complex **3** the diastereomeric mixture of the corresponding *cod* complex **1** (54:39:7) and for the synthesis of **4** the pure 74% isomer of **2** were used. **1** or **2** and (-)-*diop* were heated in toluene for 8 h (Schemes 3, 4). **3** and **4** were purified by chromatography on silica. **3** could be obtained as a yellow powder and **4** as an orange powder from pentane solutions upon cooling. The (-)-*diop* complexes **3** and **4** are much more stable than the corresponding *cod* complexes **1** and **2**. The powders can be handled in air.

Surprisingly, the <sup>1</sup>H NMR spectra of **3** and **4** exhibit only the signals of one  $C_2$ -symmetric isomer, respectively, although a mixture of three isomers of **1** was used as the starting material for the synthesis of **3**. Thus, **3** and **4** are formed in highly stereoslective reactions as single diastereomers. In accordance with the <sup>1</sup>H



NMR spectra, the (-)-*diop* complexes **3** and **4** show just one singlet in the <sup>31</sup>P NMR spectrum and reveal signals for only one isomer in the <sup>13</sup>C NMR spectrum.

### **Experimental**

The complexes were prepared under an atmosphere of dried nitrogen. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra: Bruker AC 250 and ARX 400 spectrometers (250 or 400 MHz (<sup>1</sup>H), 63 or 100 MHz (<sup>13</sup>C), and 162 MHz (<sup>31</sup>P)), chemical shifts in ppm downfield from *TMS* or 85% H<sub>3</sub>PO<sub>4</sub>, respectively. NMR assignments were made on the basis of 2D techniques. FD mass spectra: Finnigan MAT 95 instrument. Optical rotations: Perkin-Elmer 241 polarimeter.  $[Ru(cod)Cl_2]_n$ , [9], 2-N-((*S*)-1phenylethyl)pyrrolealdimine [14], and N-((*S*)-1-phenylethyl)salicyladimine [15, 16] were prepared according to the published procedures.

#### $(\eta^4 - 1, 5 - Cyclooctadiene) bis(2 - N - ((S) - 1 - phenylethyl) pyrrolatoaldimine) ruthenium(II)$ (1)

1.0 g (5.05 mmol) of 2-N-((S)-1-phenylethyl)pyrrolealdimine was dissolved in 100 ml of absolute toluene, and 561 mg (5.0 mmol) of potassium *tert*-butylate were added. The suspension was stirred at room temperature until a fine white precipitate of the potassium salt of the pyrroleimine was formed. After the conversion to the potassium salt was complete, 700 mg (2.5 mmol) of  $\eta^4$ -1, 5-cyclooctadiene(dichloro)ruthenium(II) were added and the reaction mixture was stirred for 12 h. To separate insoluble residues it was passed through a SiO<sub>2</sub> column (5×2 cm) with toluene. The yellow solution was chromatographed on a column (SiO<sub>2</sub>/toluene, 2×90 cm) cooled to -20°C. The first violet band – byproduct *tris*(2-N((S)-1-phenylethyl)pyrrolatoaldimine)ruthenium(III) – and the third yellow band – byproduct ( $\eta^4$ -1,5-cyclooctadiene)(2-N-((S)-1-phenylethyl)pyrrolatoaldimine)-(2-pyrrolatoaldehyde)-ruthenium(II) – were discarded. The desired product could be eluted as a broad yellow zone. After removal of the solvent the residue was dissolved in pentane. Upon cooling to -78°C, **1** could be obtained as a yellow powder.

Yield: 996 mg (66%); m.p.: 115–120°C (decomp.); diastereomer ratio (21°C, C<sub>6</sub>D<sub>6</sub>): 54:39:7; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 54% *isomer*:  $\delta = 0.66$  (d, <sup>3</sup>J = 7 Hz, 6H, CH<sub>3</sub>), 1.48–1.85, 2.01–2.54 (2m, 8H, *cod* –CH<sub>2</sub>), 3.45, 4.06 (2m, 4H, *cod*–CH), 5.35 (q, <sup>3</sup>J = 7 Hz, 2H, CH), 6.06–7.51 (m, 16H, H<sup>3</sup>–H<sup>5</sup> of the pyrrole ring+arom. H), 7.82 (s, 2H, N=CH) ppm; 39% *isomer*:  $\delta = 0.54$  (d, <sup>3</sup>J = 7 Hz, 3H, CH<sub>3</sub>), 1.48–1.85, 2.01–2.54 (2m, 8H, *cod*–CH<sub>2</sub>), 3.25, 4.30 (2m, 4H, *cod*–CH), 4.79 (q, <sup>3</sup>J = 7 Hz, 1H, CH), 5.22 (q, <sup>3</sup>J = 7 Hz, 1H, CH), 6.06–7.51 (m, 16H, H<sup>3</sup>–H<sup>5</sup> of the pyrrole ring+arom. H), 7.60 (s, 1H, N=CH), 8.25 (s, 1H, N=CH) ppm; 7% *isomer*:  $\delta = 0.93$  (d, <sup>3</sup>J = 7 Hz, 3H, CH<sub>3</sub>), 1.11 (d, <sup>3</sup>J = 7 Hz, 3H, CH<sub>3</sub>), 1.48–1.85, 2.01–2.54 (2m, 8H, *cod*–CH<sub>2</sub>), 3.29, 4.38 (2m, 4H, *cod*–CH), 4.87 (q, <sup>3</sup>J = 7 Hz, 1H, CH), 5.08 (q, <sup>3</sup>J = 7 Hz, 1H, CH), 6.06–7.51 (m, 16H, H<sup>3</sup>–H<sup>5</sup>

of the pyrrole rings+arom. H), 7.77 (s, 1H, N=CH), 8.02 (s, 1H, N=CH) ppm; MS (FD, toluene): m/z = 604 (M<sup>+</sup> relative to <sup>102</sup>Ru); IR (KBr): 1590 cm<sup>-1</sup> (C=N); C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>Ru (603.66); calcd.: C 67.65, H 6.34, N 9.28; found: C 67.15, H 6.31, N 8.80.

#### $(\eta^4-1,5-Cyclooctadiene)bis(N((S)-1-phenylethyl)salicylatoaldimine)ruthenium(II)$ (2)

1.14 g (5.05 mmol) of N-((*S*)-1-phenylethyl)salicylaldimine and 561 mg (5.0 mmol) of potassium *tert*-butylate were stirred at room temperature in 100 ml of absolute toluene. The potassium salt of the pyrrolimine was formed as a fine, white powder within 1 h. To the suspension, 700 mg (2.5 mmol) of  $\eta^4$ -1,5-cyclooctadiene(dichloro)ruthenium(II) were added, and the reaction mixture was heated to reflux for 5 h. To separate insoluble residues it was filtered through a SiO<sub>2</sub> column (5×2 cm). The yellow solution was chromatographed on a SiO<sub>2</sub> column (toluene, 2×90 cm) cooled to -20°C. The product was eluted as a broad, yellow zone. After removing the solvent, the residue was dissolved in 1 ml of toluene at room temperature, and 100 ml of pentane were added. Upon cooling to -78°C **2** was obtained as a yellow powder.

In the <sup>1</sup>H NMR spectrum three diastereomers could be identified unambigously. The 74% isomer could be separated in pure form by fractional crystallization. 1.0 g (1.5 mmol) of **2** was dissolved in 1 ml of toluene and 100 ml of pentane. After 12 h at  $-24^{\circ}$ C a yellow powder precipitated. The yellow solution was decanted, and diastereomerically pure 74% isomer could be isolated.

Yield: 1.18 g (72%); diastereomer ratio (21°C, C<sub>6</sub>D<sub>6</sub>): 74:25:≈1; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 74% *isomer*:  $\delta = 1.13$  (d, <sup>3</sup>*J* = 7 Hz, 6H, CH<sub>3</sub>), 1.74, 1.94 (2m, 4H, *cod*-CH<sub>2</sub>), 2.34 (m, 4h, *cod*-CH<sub>2</sub>), 4.44, 4.63 (2m, 4H, *cod*-CH), 6.14 (q, <sup>3</sup>*J* = 7 Hz, 2H, CH), 6.42 (m, 2H, H<sup>4</sup>), 6.67 (m, 2H, H<sup>6</sup>), 7.08-7.23 (m, 14H, H<sup>3</sup>, H<sup>5</sup> of the salicyl rings+arom. H), 7.94 (s, 2H, N=CH) ppm; 25% *isomer*:  $\delta = 1.29$  (d, <sup>3</sup>*J* = 7 Hz, 6H, CH<sub>3</sub>), 1.83, 2.06 (2m, 4H, *cod*-CH<sub>2</sub>), 2.46 (m, 4H, *cod*-CH<sub>2</sub>) 4.44, 4.72 (2m, 4H, *cod*-CH), 5.93 (q, <sup>3</sup>*J* = 7 Hz, 2H, CH), 6.46 (m, 2H, H<sup>4</sup>), 6.75–6.88, 7.06–7.23 (2m, 16H, H<sup>3</sup>, H<sup>5</sup>, H<sup>6</sup> of the salicyl rings+arom. H), 7.98 (s, 2H, N=CH) ppm; *1% isomer*:  $\delta = 0.88$  (d, <sup>3</sup>*J* = 7 Hz, 3H, CH<sub>3</sub>), 1.34 (d, <sup>3</sup>*J* = 7 Hz, 3H, CH<sub>3</sub>), 1.64–1.96, 2.22–2.54 (2m, 8H, *cod*-CH<sub>2</sub>), 4.43, 4.67 (2m, 4H, *cod*-CH), 6.11 (q, <sup>3</sup>*J* = 7 Hz, 1H, CH), 6.13 (q, <sup>3</sup>*J* = 7 Hz, 1H, CH), 6.39–7.26 (m, 18H, H<sup>3</sup>-H<sup>6</sup> of the salicyl rings+arom. H), 7.75 (s, 1H, N=CH), 8.19 (s, 1H, N=CH) ppm.

Diastereomerically pure 74% isomer: m.p.: 204°C (decomp.);  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 21.5$  (s, CH<sub>3</sub>), 29.1 (s, cod –CH<sub>2</sub>), 98.8 (s, cod –CH), 114.3 (s, Sal-C<sup>4</sup>), 121.5 (s, Sal-C<sup>2</sup>), 123.9 (s, Sal-C<sup>3</sup>), 127.3 (s, Ph-C<sup>para</sup>), 128.4 (s, Ph-C<sup>ortho</sup>), 128.7 (s, Ph-C<sup>meta</sup>), 133.8 (s, Sal-C<sup>5</sup>), 135.6 (s, Sal-C<sup>6</sup>), 143.9 (s, Sal-C<sup>1</sup>), 164.0 (s, N=CH), 166.2 (s, Ph-C<sup>ipso</sup>) ppm;  $[\alpha]_{\lambda}$  (c = 2.0 mg/100 ml, pentane):  $-450^{\circ}$  (578 nm),  $-650^{\circ}$  (546 nm),  $+750^{\circ}$  (436 nm),  $+2600^{\circ}$  (365 nm); CD (pentane):  $\lambda_{max}$  ( $\Delta \varepsilon$  (1·mol<sup>-1</sup>·cm<sup>-1</sup>)): 325 (+13.1), 436 (–16.2) nm;  $\lambda_0$ : 279, 398, 482 nm; MS (FD, toluene): m/z = 658.1 (M<sup>+</sup> relative to  ${}^{102}$ Ru); IR (KBr): 1615 cm<sup>-1</sup> (CN); C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>Ru (656.3); calcd.: C 69.40, H 6.14, N 4.27; found: C 69.76, H 6.45, N 4.03.

#### ((4R,5R)-trans-4,5-Bis(diphenylosphanylmethyl)-2,2-dimethyl-1,3-dioxolane)bis(2-N-((S)-1-phenylethyl)pyrrolatoaldimine)ruthenium(II) (**3**)

603 mg (1.0 mmol) of **1** (isomer mixture) and 504 mg (0.01 mmol) of (-)-*diop* were dissolved in 50 ml of absolute toluene. The yellow solution was refluxed for 8 h. The solvent was removed. The residue was dissolved in toluene/ether (50:1) and chromatographed on a SiO<sub>2</sub> column (toluene/ether 50:1,  $2 \times 90$  cm). **3** was eluted as a yellow band. After removal of the solvent, the residue was dissolved in pentane and **3** was obtained as a yellow powder upon cooling to  $-24^{\circ}$ C.

Yield: 736 mg (74%); m.p.: 195°C (decomp.); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.46$  (d, <sup>3</sup>J = 6.9 Hz, 6H, CH<sub>3</sub>), 1.38 (s, 6H, *diop*-CH<sub>3</sub>), 2.50, 2.89 (2m, 4H, *diop*-CH<sub>2</sub>), 4.06 (q, <sup>3</sup>J = 6.9 Hz, 2H, CH), 4.27 (m, 2H, *diop*-CH), 6.42 (m, 2H, H<sup>4</sup>), 6.62 (m, 2H, H<sup>3</sup>), 6.77 (m, 2H, H<sup>5</sup>), 6.90–7.06 (m, 24H, arom. H), 7.50 (s, 2H, N=CH), 7.64, 7.80 (2s, 6H, *ortho*-phenyl-H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 25.5$ 

(s, Pyrr-CH<sub>3</sub>), 77.9 (d, <sup>2</sup>*J*(P,C) 5.4 Hz, CH), 78.0 (d, <sup>2</sup>*J*(P,C) 5.4 Hz, CH), 107.9 (s, *diop*-C<sup>quart</sup>), 112.4 (s, Pyrr-C<sup>3</sup>), 117.4 (s, Pyrr-C<sup>5</sup>), 126.2, 127.6–128.4 (s, arom. C, arom. C<sup>benzene</sup>, Pyrr-C<sup>4</sup>), 129.8, 132.7–133.4 (s, arom. C), 134.9 (s, phenyl *diop*-C<sup>ortho</sup>), 139.0 (d, <sup>1</sup>*J*(P, C) = 14.7 Hz, phenyl diop-C<sup>ipso</sup>), 139.5 (d, <sup>1</sup>*J*(P, C) = 14.3 Hz, phenyl *diop*-C<sup>ipso</sup>), 140.0 (s, phenyl *diop*-C<sup>ortho</sup>), 143.9 (s, phenyl Pyrr-C<sup>ipso</sup> or Pyrr-C<sup>2,quart</sup>), 144.5 (s, phenyl Pyrr-C<sup>ipso</sup> or Pyrr-C<sup>2,quart</sup>), 158.1 (s, N=CH) ppm; <sup>31</sup>P {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 32.08 (s, *diop*-P) ppm; [ $\alpha$ ]<sub> $\lambda$ </sub> (*c* = 1.0 mg/100 ml, pentane): -153° (578 nm), -211° (546 nm), -1538° (436 nm), +19106° (365 nm); [ $\alpha$ ]<sub> $\lambda$ </sub> (*c* = 1.2 mg/100, toluene): -83° (578 nm), -166° (546 nm), -1333° (436 nm), +19667° (365 nm); CD (pentane):  $\lambda_{max}$  ( $\Delta \varepsilon$  (1·mol<sup>-1</sup>·cm<sup>-1</sup>)); 322 (+35.2), 377 (-36.5) nm;  $\lambda_0$ : 299, 350, 409 nm; MS (FD, toluene): m/z = 994 (M<sup>+</sup>relative to <sup>102</sup>Ru); IR (KBr): 1575 cm<sup>-1</sup> (C=N); C<sub>57</sub>H<sub>58</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ru (994.14); calcd.: C 68.81, H 5.88, N 5.64; found: C 69.23, H 6.17, N 5.35.

## ((4R,5R)-trans-4,5-Bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane)bis(N-((S)-1-phenylethyl)salicylatoaldimine)ruthenium(II) (**4**)

657 mg (1.0 mmol) of the 74% *isomer* of **2** (diastereomerically pure) and 504 mg (1.01 mmol) of (–)*diop* were dissolved in 50 ml of absolute toluene. The yellow solution was heated to reflux for 6 h. After removing the solvent, the residue was dissolved in toluene and purified by chromatography (SiO<sub>2</sub>/toluene,  $2 \times 90$  cm). **4** was eluted as an orange zone. After removing the solvent, the residue was dissolved in pentane. Upon cooling to  $-24^{\circ}$ C, **4** could be obtained as a microcrystalline, orange powder.

Yield: 828 mg (79%); m.p.: 162°C (decomp.); <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta = 0.77$  (d, <sup>3</sup>J = 7 Hz, 6H, CH<sub>3</sub>), 1.40 (s, 6H, *diop*-CH<sub>3</sub>), 2.77, 3.01 (2m, 2H, *diop*-CH<sub>2</sub>), 4.58 (m, 2H, *diop*-CH), 5.38 (q,  ${}^{3}J = 7$  Hz, 2H, CH), 6.27 (m, 2H, H<sup>4</sup>), 6.37–7.25, 8.30 (2m, 36H, H<sup>3</sup>, H<sup>5</sup>, H<sup>6</sup> of the salicyl rings +arom. H), 7.72 (d,  ${}^{4}J$  (H, P) = 4 Hz, 2H, N=CH) ppm;  ${}^{1}H{}^{31}P$  NMR: 7.72 (s, 2H, N=CH) ppm;  ${}^{13}C{}^{1}H$  NMR  $(C_6D_6): \delta = 24.9$  (s, Sal-CH<sub>3</sub>), 27.4 (s, *diop*-CH<sub>3</sub>), 32.1 (d, <sup>1</sup>J(P,C) = 12.3 Hz, *diop*-CH<sub>2</sub>), 32.2  $(d, {}^{1}J(P,C) = 12.3 \text{ Hz}, diop-CH_{2}), 32.2 (d, {}^{1}J(P,C) = 12.3 \text{ Hz}, diop-CH_{2}), 64.0 (s, Sal-CH), 77.2$ (d,  ${}^{1}J(P,C) = 5.0$  Hz, diop-CH), 77.3 (d,  ${}^{2}J(P,C) = 5.0$  Hz, diop-CH), 107.4 (s, diop-C<sup>quart</sup>) 112.6 (s, Sal-C<sup>4</sup>), 122.4 (s, Sal-C<sup>2,quart</sup>), 123.3 (s, Sal-C<sup>6</sup>), 123.9 (s, phenyl Sal-C<sup>4</sup>), 126.4 (s, phenyl Sal-C<sup>2</sup>), 126.9 (s, phenyl Sal-C<sup>3</sup>), 127.3–133.2 (s, arom. C, arom. C<sup>benzene</sup>), 134.9 (s, phenyl *diop*-C<sup>ortho</sup>), 136.1 (s, Sal-C<sup>3</sup>), 136.5 (s, Sal-C<sup>5</sup>), 139.2 (d,  ${}^{1}J(P,C) = 16.7$  Hz, phenyl *diop*-C<sup>*ipso*</sup>), 139.3 (d, {}^{1}J(P C) = 16.0 Hz, phenyl diop-C<sup>ipso</sup>), 142.7 (s, phenyl Sal-C<sup>1,quart</sup>), 162.1 (s, phenyl diop-C<sup>ortho</sup>), 163.2 (s, N=CH), 167.4 (s, Sal-C<sup>1,quart</sup>) ppm;  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>): 28.15 (s, diop-P) ppm;  $[\alpha]_{\lambda}$  $(c = 10.0 \text{ mg/ml}, \text{hexane}): -360^{\circ} (589 \text{ nm}), -460^{\circ} (578 \text{ nm}), -1050^{\circ} (546 \text{ nm}); \text{CD (pentane): } \lambda_{\text{max}}$  $(\Delta \varepsilon (1 \cdot \text{mol}^{-1} \text{cm}^{-1})):$  252 (+20.4), 297 (-4.1), 329 (+5.1), 357 (-2.1), 395 (+1.5) nm;  $\lambda_0:$  232, 277, 312, 346, 374, 412 nm; MS (FD, toluene): m/z = 1048 (M<sup>+</sup> relative to <sup>102</sup>Ru); IR (KBr): 1610 cm<sup>-1</sup> (C=N); C<sub>61</sub>H<sub>60</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Ru (1048.49); calcd.: C 69.88, H 5.77, N 2.67; found: C 69.11, H 5.97, N 2.54.

#### References

- [1] 119. Mitt.: Brunner H, Tracht T (1998) Tetrahedron: Asymmetry 9: 3763
- [2] Ohta T, Takaya H, Noyori R (1988) Inorg Chem 27: 566
- [3] Genet JP, Mallart S, Pinel C, Jugé S, Lafitte JA (1991) Tetrahedron: Asymmetry 2: 43
- [4] Genet JP, Pinel C, Ratovelomanana-Vidal V, Mallart S, Pfister X, Cano de Andrade MC, Laffite JA (1994) Tetrahedron: Asymmetry 5: 665
- [5] Noyori R, Ohta M, Hsiao Y, Kitamura M, Ohta T, Takaya H (1986) J Am Chem Soc 108: 7117
- [6] Ikariya T, Ishii Y, Kawano H, Arai T, Saburi M, Yoshikawa S, Akutagawa S (1985) J Chem Soc Chem Commun 922
- [7] Ohta T, Takaya H, Kitamura M, Nagai K, Noyori R (1987) J Org Chem 52: 3174

- [8] Takaya H, Ohta T, Sayo N, Kumobayashi H, Akutagawa S, Inoue S, Kasahara I, Noyori R (1987) J Am Chem Soc 109: 1596
- [9] Mashima K, Kusano K, Ohta T, Noyori R, Takaya H (1989) J Chem Soc Chem Commun 1208
- [10] Masamune S, Choy W, Peterson JS, Sita LR (1985) Angew Chem 97: 1; Angew Chem Int Ed Engl 24: 1
- [11] Spitzer J (1998) Dissertation, University of Regensburg
- [12] (1970) Inorg Chem 9: 1
- [13] Bennett MA, Wilkinson G (1959) Chem Ind (London) 1516
- [14] Bernal I, Reisner GM, Brunner H, Riepl G (1983) Inorg Chim Acta 103: 179
- [15] Terentev AP, Potapov VM (1958) Zh Obsch Khim 28: 1161; J Gen Chem USSR 28: 1220
- [16] Smith HE, Cook SL, Warren ME (1964) J Org Chem 29: 2265

Received October 12, 1998. Accepted November 6, 1998