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Optically active transition metal complexes. Part 115[1]. Synthesis, crystal structure and properties of chiral (η^5-C_5H_5)Ru complexes with pyrrolecarbaldiminato and salicylaldiminato ligands

Henri Brunner [a,*], Thomas Neuhierl [a], Bernhard Nuber [b]

[a] *Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany*
[b] *Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

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Abstract

The chiral complexes CpRu(LL*)PPh_3, Cp = η^5-C_5H_5, LL*-1 = anion of 2-*N*-[(*S*)-l-phenylethyl]pyrrolecarbaldimine (**1a**/**1b**), LL*-2 = anion of 2-*N*-[(*R*)-hydroxybut-2-yl)]pyrrolecarbaldimine (**2a**/**2b**) and LL*-3 = anion of *N*-[(*S*)-1-phenylethyl]salicylaldimine (**3a**/**3b**), can be prepared by reaction of CpRu$(PPh_3)_2Cl$ and the corresponding ligand HLL* in boiling toluene. An X-ray structure analysis of diastereomerically pure **1a** shows S_{Ru} configuration. The phenyl substituent of the ligand adopts a T-shape arrangement with respect to the Cp ring. The PPh_3 ligand is in a right handed propeller conformation. The activation parameters of the epimerization **1a** $\rightleftharpoons$ **1b** were determined to be $\Delta H^{\neq} = (133 \pm 33)$ kJ mol^{-1} and $\Delta S^{\neq} = (77 \pm 26)$ J K^{-1} mol^{-1}. The equilibrium ratios are **1a**:**1b** = 86:14, **2a**:**2b** = 1:1 and **3a**:**3b** = 88:12, the attractive interaction between the Cp ring and the phenyl substituent of the chiral center in the chelating ligand LL* favoring one diastereomer of the complexes **1a**/**1b** and **3a**/**3b**.

Keywords: Ruthenium; Chiral complexes; Crystal structure

1. Introduction

The catalytic potential of ruthenium(II) complexes is well documented, e.g. in the enantioselective transfer hydrogenation of prochiral ketones [2–5]. Frequently, half-sandwich arene ruthenium(II) complexes have been used as precatalysts [6,7]. The syntheses and the chemistry of a variety of arene half-sandwich ruthenium complexes have been reported [8–11]. There is a manifold of stereochemical studies on optically active complexes [(η^6-Ar)Ru(LL*)X] and [(η^6-Ar)Ru(LL*)L′]PF_6, Ar = *p*-cymene, mesitylene, benzene, LL* = anionic or neutral unsymmetrical ligand, X = halide, L′ = unidentate ligand containing a stereogenic Ru atom [12–22].

In the present paper we transfer these stereochemical investigations from (η^6-Ar)Ru complexes to (η^5-Cp)Ru compounds. Studies on the stereochemical course of reactions and diastereomer equilibria of CpRu complexes are summarized by Consiglio and Morandini [23]. We describe the synthesis and characterization of the complexes [(η^5-C_5H_5)Ru(LL*)PPh_3] (**1**–**3**), in which LL* is the anion of 2-*N*-[(*S*)-1-phenylethyl]pyrrolecarbaldimine, 2-*N*-[(*R*)-hydroxybut-2-yl)]pyrrolecarbaldimine and *N*-[(*S*)-1-phenylethyl]salicylaldimine, respectively [24]. For complex **1**, the diastereomers **1a** and **1b** could be separated. The structure of **1a** was established by an X-ray structure analysis. The rate of the epimerization **1a** $\rightleftharpoons$ **1b** was studied [24].

* Corresponding author. Fax: +49 941 9434439.
[1] For part 114, see [1].

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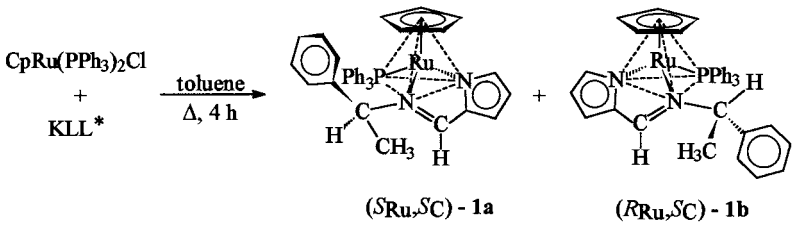


Scheme 1.

2. [CpRu(LL*)PPh$_3$] (1a/1b), LL* = anion of 2-*N*-[(*S*)-1-phenylethyl]pyrrolecarbaldimine

2-*N*-[(*S*)-1-Phenylethyl]pyrrolecarbaldimine (HLL*-1) was prepared from 2-pyrrolecarbaldehyde and (*S*)-1-phenylethylamine. Deprotonation of HLL*-1 was carried out with KO^{t}Bu in toluene. After addition of CpRu(PPh$_3$)$_2$Cl, the solution was refluxed for 4 h. The diastereomeric complexes (S_{Ru}, S_C)- and (R_{Ru}, S_C)-[CpRu(LL*)PPh$_3$] (**1a**/**1b**), differing only in the configuration at the ruthenium atom, were formed (Scheme 1).

After filtration, concentration and addition of petroleum ether, a yellow powder precipitated at −25°C. Integration of the singlet signals of the Cp protons at 3.88 and 4.16 ppm in the ^{1}H-NMR spectrum gave a ratio **1a**:**1b** = 86:14 at this stage of the work-up procedure. There is a large difference between the Cp signals of **1a** and **1b** of 0.28 ppm. The Cp singlet of **1a** experiences a high-field shift due to the inner magnetic anisotropy beam of the phenyl substituent of LL* [25], called the 'β-phenyl effect' and corroborated by the X-ray structure analysis described below. All the ^{1}H-NMR signals of the neutral complexes (η^5-C$_5$H$_5$)Ru(LL*)PPh$_3$] (**1a**) and (**1b**) are shifted to high-field compared with the corresponding cationic complexes [(η^6-C$_6$H$_6$)Ru(LL*)PPh$_3$]$^+$ [19]. The highest shift is observed for the methine and imine protons.

Crystallization of the diastereomeric mixture **1a**/**1b** from toluene:pentane (1:2) gave pure **1a** as yellow prisms of X-ray analytical quality. The residue of the mother liquor was crystallized from toluene/pentane, the solid obtained was discarded and the residue of the new mother liquor was collected. After four repetitions of this procedure, a subsequent column chromatography on silica gel with toluene gave the complex **1b** with a diastereomeric purity of **1a**:**1b** = 8:92.

In order to determine the absolute configuration of the Ru atom in **1a** a single crystal X-ray structure analysis was carried out. Details of the data collection and structure refinement are given in Table 1. Selected bond distances and angles are listed in Table 2. In Fig. 1 an ORTEP plot of the molecular structure of **1a** is shown.

In complex **1a** the asymmetric carbon atom of the chelate ligand has the expected S_C configuration. The configuration of the stereogenic ruthenium center is S_{Ru} according to the priority sequence η^5-C$_5$H$_5$ > P > N (imine) > N (pyrrolate) [26–28]. The phenyl substituent Ph4 is in a T-shape arrangement with respect to the Cp1 ring, causing an attractive Cp/Ph interaction, the 'β-phenyl effect' [25]. The distance of the centroids of Cp1 and Ph4 is 4.74 Å. The ring normals include an angle of 51.3° [29,30]. In complex **1a**, the PPh$_3$ ligand adopts a right handed propeller conformation.

The conversion of diastereomerically pure **1a** into the equilibrium mixture **1a** ⇌ **1b** was monitored in benzene-d$_6$ solution by ^{1}H-NMR spectroscopy. When a

Table 1
Summary of crystal data, data collection and structure refinement[a] for complex **1a**

Elemental formula	$C_{36}H_{33}N_2PRu$
M	625.71
Crystal system	rhombic
Space group	*D*2/4, *P*2.12.12.1 (No 19)
Crystal color, shape	yellow prisms
Crystal size (mm^3)	0.10 × 0.20 × 0.40
a (Å)	9.774(3)
b (Å)	15.65(1)
c (Å)	19.163(7)
γ (°)	90.00
V (Å^3)	2932(3)
Z	4
Density (g cm^{-3})	1.42
F(000)	1288
μ (mm^{-1})	0.62
h, *k*, *l* ranges	0–12, 0–19, 0–23
2θ range (°)	3.0–50.0
Total no. of unique reflections	2934
No. of observed reflections $I > 2.5\sigma(I)$	1844
Min, max transmission factors	0.94, 1.00
No. of reflections, 2θ range (°) for empirical absorption correction	6, 8.0 < 2θ < 31.0
No. of least-squares parameters	361
Shift/estimated S.D.-max	0.003
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	−0.64, 0.57
R[b]	0.059
R_w[b]	0.045
Goodness-of-fit S[b]	1.42

[a] SYNTEX R3 diffractometer: Mo–K$_\alpha$ radiation (λ = 0.71073 Å); 293 K.

[b] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = \Sigma||F_o|-|F_c||w^{1/2}/\Sigma|F_o|w^{1/2}$, $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Table 2
Selected bond length and angles of **1a**; estimated S.D. are shown in parentheses

Bond lengths (Å)	
Ru(1)–P(1)	2.292(3)
Ru(1)–N(1)	2.056(11)
Ru(1)–N(2)	2.127(11)
Ru(1)–C(32)	2.148(13)
Ru(1)–C(33)	2.188(19)
Ru(1)–C(34)	2.186(19)
Ru(1)–C(35)	2.203(15)
Ru(1)–C(36)	2.149(17)
Bond angles (°)	
P(1)–Ru(1)–N(1)	90 0(3)
P(1)–Ru(1)–N(2)	89.8(3)
N(1)–Ru(1)–N(2)	76.7(4)

sample of **1a** was dissolved and stirred at r.t. for 72 h, it did not interconvert to **1b**. However, at higher temperatures, epimerization took place. Samples were thermostated at 61.0, 64.2, 67.5 and 71.0°C for given periods of time. Then the reactions were stopped by cooling. The subsequent ^{1}H-NMR spectra were measured at 21°C. To determine the ratios **1a**:**1b**, the Cp singlets were integrated. Analysis was performed with the function $\ln\{([A_0]-[A_\infty])/([A]-[A_\infty])\} = kt$. The equilibrium concentrations $[A_\infty]$ (**1a**:**1b** = 84.8:15.2 for 61°C and 83.8:16.2 for 71°C) were measured after 18 h of thermostating. The reactions turned out to be first-order. No decomposition products could be detected in the ^{1}H-NMR spectra. The half-lives for the approach to the equilibrium **1a** $\rightleftharpoons$ **1b** in C_6D_6 ranged between $\tau_{1/2}$ = 114 min (61°C) and $\tau_{1/2}$ = 28.4 min (71°C). The results are listed in Table 3.

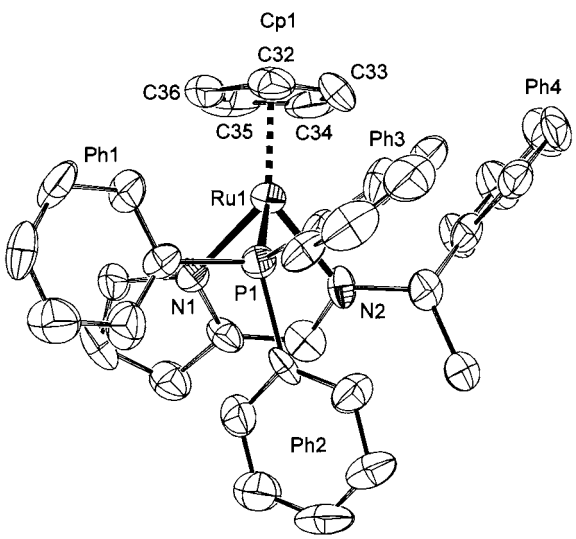


Fig. 1. ORTEP diagram of **1a** showing the labeling scheme used. Ellipsoids are drawn at the 40% probability level; hydrogen atoms have been omitted for clarity.

Table 3
Results of the kinetic measurements of the epimerization of **1a** in C_6D_6 ($c = 2.26 \cdot 10^{-4}$ mol l^{-1})

Temperatre (°C)	k ($\times 10^4$) (s)	$\tau_{1/2}$ (min)	$[A_\infty]$ (%)
71.0 ± 0.2	4.07 ± 0.03	28.4 ± 0.2	83.8 ± 0.1
71.0 ± 0.2[a]	3.95 ± 0.07	29.2 ± 0.5	83.8 ± 0.1
67.5 ± 0.1	2.62 ± 0.05	44.1 ± 0.8	84.2 ± 0.1
64.2 ± 0.1	1.53 ± 0.02	75.3 ± 0.8	84.7 ± 0.1
61.0 ± 0.1	1.02 ± 0.02	114 ± 2	84.8 ± 0.1

[a] With a 15-molar excess of PPh_3.

The activation parameters $\Delta H^{\neq} = (133 \pm 33)$ kJ mol^{-1} and $\Delta S^{\neq} = (77 \pm 26)$ J K^{-1} mol^{-1} were obtained by the plot $\ln(k/T) = f(1/T)$ according to the equation $\ln(k/T) = -(\Delta H^{\neq}/RT) + (\Delta S^{\neq}/R) + \ln(k_B/h)$. The data are in accord with a dissociative mechanism (dissociation of PPh_3 or of one of the ends of the chelate ligand LL*) [31,32]. There were no differences in the rate constants in the presence of a 15-molar excess of free PPh_3 in agreement with the suggested reaction pathway.

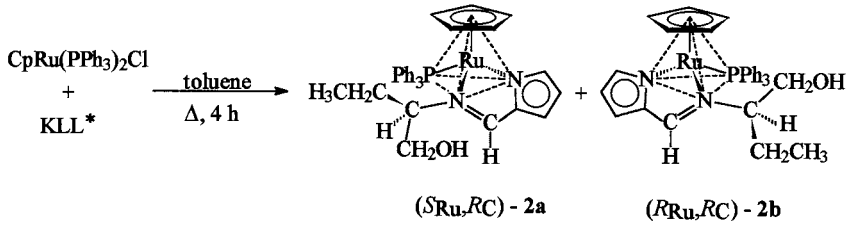
3. [CpRu(LL*)PPh$_3$] (2a/2b), LL* = anion of 2-*N*-[(*R*)-1-hydroxybut-2-yl)]pyrrolecarbaldimine

2-*N*-[(*R*)-1-Hydroxybut-2-yl)]pyrrolecarbaldimine (HLL*-2) was obtained by condensation of (R)-2-aminobutanol with 2-pyrrolecarbaldebyde. HLL*-2 was deprotonated in toluene with KO^{t}Bu. After adding $CpRu(PPh_3)_2Cl$, the solution was refluxed for 4 h. The formation of the diastereomeric complexes (S_{Ru}, R_C)- and (R_{Ru}, R_C)-[CpRu(LL*)PPh$_3$] (**2a**, **2b**) is shown in Scheme 2.

The solution was filtered and crystallized from toluene/petroleum ether at −25°C. The ^{1}H-NMR spectrum of the sample obtained showed the equilibrium ratio **2a**:**2b** = 1:1, which did not change after refluxing for 4 h in toluene. Thus, there are no stabilizing interactions, such as the β-phenyl effect in the complexes **1a**/**1b.** The isomers **2a** and **2b** could not be separated by chromatography or by crystallization.

4. [CpRu(LL*)PPh$_3$] (3a/3b), LL* = anion of *N*-[(*S*)-1-phenylethyl]salicylaldimine

N-[(*S*)-1-Phenylethyl]salicylaldimine (HLL*-3) was prepared from salicylaldehyde and (*S*)-1-phenylethylamine. HLL*-3 was deprotonated with KO^{t}Bu in toluene and $CpRu(PPh_3)_2Cl$ was added. The solution was refluxed for 4 h, giving the diastereomeric complexes (R_{Ru}, S_C) and (S_{Ru}, S_C)-[CpRu(LL*)PPh$_3$] (**3a**/**3b**) (Scheme 3).



Scheme 2.

The red solution was filtered and concentrated. After addition of petroleum ether, an analytically pure red powder precipitated at −25°C. Integration of the singlet signals of the Cp protons at 3.84 and 4.23 ppm gave the equilibrium ratio **3a**:**3b** = 88:12 after refluxing for 4 h in toluene. The difference of the Cp signals is 0.39 ppm. In the favored complex **3a** the Cp singlet is shifted to high-field due to the magnetic anisotropy of the phenyl substituent in LL* [25]. In polarimetric measurements, the neutral complex **3a** exhibits the same optical rotation as the ionic complex (R_{Ru}, S_C)-[(η^6-C_6H_6)Ru(LL*)PPh_3]PF_6 [16,18]. On this basis *R*-configuration was assigned to the ruthenium center in **3a**. Comparison of the ^{1}H-NMR spectrum of **3a** with the ^{1}H-NMR spectrum of (R_{Ru}, S_C)-[(η^6-C_6H_6)Ru-(LL*)PPh_3]PF_6 shows that the imine proton and all the protons of the salicyl ring in **3a** are shifted to high-field. The highest shift is observed for the protons in the 3- and 4-position of the phenolate system. Attempts to separate the isomers **3a** and **3b** by chromatography or crystallization were unsuccessful

5. Experimental

Preparation of the ruthenium complexes under an atmosphere of dry nitrogen with standard Schlenk techniques. IR spectra: Beckman IR 4240 spectrometer. Mass spectra: field desorption method (Finnigan MAT 95). ^{1}H-NMR spectra: Bruker ARX 400 spectrometer. CD spectra: Jasco J-710 spectrophotometer. Polarimetric measurements: Perkin-Elmer 241 instrument. Melting points: Büchi SMP 20. $CpRu(PPh_3)_2Cl$ was prepared as published [33] from $RuCl_3 \cdot xH_2O$, cyclopentadiene and triphenyhphosphane. 2-*N*-[(*S*)-1-Phenylethyl]pyrrolecarbaldimine [34,35] and *N*-[(*S*)-1-phenylethyl]salicylaldimine [36,37] were prepared by the literature methods.

5.1. Preparation of 2-N-[(R)-1-hydroxybut-2-yl)]pyrrolecarbaldimine (HLL*-2)

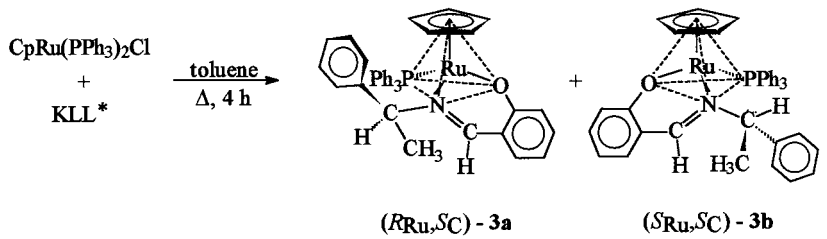
2-Pyrrolecarbaldehyde (2.44 g, 25.7 mmol) and sodium sulfate (2.41 g) were suspended in absolute toluene (30 ml). After adding (R)-2-aminobutanol (2.4 ml, 2.28 g, 25.6 mmol), the mixture was refluxed for 1 h. The mixture turned orange. The sodium sulfate was filtered off and the solvent was evaporated. At 50°C the residue was dissolved in toluene (10 ml) and petroleum ether (5 ml) was added. At −25°C colorless needles crystallized, which were washed with cold petroleum ether and diethylether. Yield: 2.60 g (15.6 mmol, 61%), m.p. 86–87°C. Anal. found: C, 65.03; H, 8.60; N, 16.79. $C_9H_{14}N_2O$ (166.2) Calc.: C, 65.04; H, 8.49; N, 16.84%. EI-MS: *m*/*z* 166 (M, 26), 135 ([M-CH_2OH], 100). IR: (cm^{-1}, KBr): 1640 vs (C=N). ^{1}H-NMR (250 MHz, $CDCl_3$, TMS): δ (ppm, *J* (Hz)) 0.81 (t, $^3J_{HH}$ 7.4, 3H, CH_3); 1.45 (m, 2H, CH_2CH$_3$); 3.07 (m, 1H, C*H*); 3.78 (m, 2H, CH_2OH); 6.12 (dd, $^3J_{HH}$ 3.6, $^3J_{HH}$ 2.6, 1H, H^4-pyrr); 6.18 (dd, $^3J_{HH}$ 3.6, $^4J_{HH}$ 1.4, 1H, H^3-pyrr); 6.85 (bs, 1H, H^5-pyrr); 7.57 (s, 1H, N=C*H*). $[\alpha]^{22}$ ($= 100\alpha/lc$, with α (°) the observed rotation, *l* (dm) the path length and *c* (g/100 ml solution) the concentration) (*c* = 1.08, $CHCl_3$): (589 nm) −266, (578 nm) −285, (546 nm) −350.

5.2. Preparation of the [CpRu(LL*)PPh3] complexes 1–3

The corresponding ligands (1.25 mmol) were dissolved in absolute toluene (90 ml) and KO^{t}Bu (141 mg, 1.25 mmol) was added. The mixture was stirred for 1 h at r.t. After adding $CpRu(PPh_3)_2Cl$ (828 mg, 1.14 mmol) the solution was refluxed for 4 h. The solution was filtered through Celite and concentrated. Then 2.5 ml of petroleum ether were added. At −25°C the complexes precipitated.

5.2.1. 1a/1b, LL* = anion of 2-N-[(S)-1-phenylethyl]pyrrolecarbaldimine

Yield, 577 mg (0.92 mmol, 81%). The following analytical data refer to **1a**. M.p. 198°C (decomp.). Anal. found: C, 69.47; H, 5.36; N, 4.37. $C_{36}H_{33}N_2PRu$ (625.7) Calc.: C, 69.11; H 5.32; N, 4.48%. FD-MS (toluene): *m*/*z* 626 (M, 100), rel. to ^{102}Ru. IR (cm^{-1}, KBr): 1580 vs (C=N), 1430 s (PPh_3). $[\alpha]^{25}$ (*c* = 0.39, $CHCl_3$): (589 nm) −388, (578 nm) −414, (546 nm) −543. NMR data for **1b** are added in parentheses, when different to **1a**. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.90 (1.56) (d, $^3J_{HH}$ 6.9, 3H, CH_3); 3.88 (4.16) (s, 5H, η^5-C_5H_5); 4.94 (4.67) (q, $^3J_{HH}$ 6.9, 1H, C*H*); 6.14



Scheme 3.

(6.06) (dd, $^3J_{HH}$ 3.7, $^3J_{HH}$ 1.6, 1H, H^4-pyrr); 6.67 (6.56) (ddd, $^3J_{HH}$ 3.7, $^4J_{HH}$ 1.6, $^5J_{HP}$ 1.2, 1H, H^3-pyrr); 6.95 (6.86) (d, $^3J_{HH}$ 1.6, 1H, H^5-pyrr); 7.07 (m, 6H, H^{ortho}-PPh_3); 7.22 (m, 1H, H^{para}-Ph); 7.24–7.33 (m, 9H, H-PPh_3); 7.33 (m, 2H, H^{meta}-Ph), 7.35 (m, 2H, H^{ortho}-Ph); 7.51 (7.41) (d, $^4J_{HP}$ 2.1, 1H, N=CH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 ext.): 56.2 (51.6) (s). CD data **1a** ($c = 1.37 \cdot 10^{-4}$ mol l^{-1}, CH_2Cl_2): λ_{max} ($\Delta\varepsilon$ [l mol^{-1} cm^{-1}]): 244 (−18.9); 287 (−9.46); 335 (18.6); 393 (−15.5). CD data (**1b** 92% diastereomeric purity) ($c = 1.37 \cdot 10^{-4}$ mol l^{-1}, CH_2Cl_2): 242 (10.3); 291 (6.4); 332 (−9.5); 403 (6.2).

Crystallization of **1a**: 50 mg of **1a**/**1b** were dissolved in 3.2 ml of toluene. After addition of 1.6 ml of pentane, yellow prisms of pure **1a** crystallized at −25°C. The residue from the respective mother liquor was recrystallized four times from toluene/pentane. After column chromatography with toluene, **1b** was obtained in 92% diastereomeric purity.

5.2.2. *2a*/*2b*, *LL* = anion of 2-N-[(R)-1-hydroxybut-2-yl)]pyrrolecarbaldimine*

The following analytical data refer to the 1:1 mixture of **2a**/**2b**. Yield: 376 mg (0.63 mmol, 61%), m.p. 181°C (decomp.). Anal. found: C, 64.99; H, 5.67; N, 4.66. $C_{32}H_{33}N_2OPRu$ (593.7) Calc.: C, 64.74; H, 5.60; N, 4.72%. FD-MS (CH_2Cl_2): m/z 594 (M, 100), rel. to ^{102}Ru. IR (cm^{-1}, KBr): 1580 vs (C=N). NMR data for **2b** are added in parentheses, when different to **2a**. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.73 (0.97) (t, $^3J_{HH}$ 7.2 (7.4), 3H, CH_3); 1.49 (1.79) (m, 2H, CH_2CH$_3$); 3.29 (3.79) (m, 2H, CH_2OH); 3.59 (3.86) (m, 1H, CH); 4.30 (4.32) (s, 5H, η^5-C$_5H_5$); 6.11 (m, 1H, H^4-pyrr); 6.63 (6.68) (dd, $^3J_{HH}$ 2.5, $^4J_{HH}$ 1.3, 1H, H^3-pyrr); 6.74 (6.85) (bs, 1H, H^5-pyrr); 6.92–7.01 (m, 5H, H-PPh_3); 7.20–7.30 (m, 10H, H-PPh_3); 7.44 (7.54) (d, $^4J_{HP}$ 2.1 (2.2), 1H, N=CH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 ext.): 51.6 (52.8) (s).

5.2.3. *3a*/*3b*, *LL* = anion of N-[(S)-1-phenylethyl]salicylaldimine*

The following analytical data refer to the 88:12 mixture of **3a**/**3b**. Yield: 420 mg (0.64 mmol, 64%), m.p. 129°C (decomp.). Anal. found: C, 69.88; H 5.19; N, 2.07. $C_{38}H_{34}NOPRu$ (652.7) Calc.: C, 69.92; H, 5.25; N, 2.15%. FD-MS (CH_2Cl_2): m/z 653 (M, 100), rel. to ^{102}Ru. IR (cm^{-1}, KBr): 1610 vs (C=N), 1440 s (PPh_3). NMR data for **3b** are added in parentheses, when different to **3a**. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 0.91 (0.86) (d, $^3J_{HH}$ 7.1 (7.0), 3H, CH_3); 3.84 (4.23) (s, 5H, η^5-C$_5H_5$); 5.30 (5.19) (q, $^3J_{HH}$ 7.1, 1H, CH); 6.20 (6.02) (ddd, $^3J_{HH}$ 7.8, $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.1, 1H, H^4-sal); 6.53 (6.46) (dd, $^3J_{HH}$ 8.7, $^4J_{HH}$ 1.1, 1H, H^6-sal); 6.77 (6.89) (dd, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.9, 1H, H^3-sal); 6.97 (6.84) (ddd, $^3J_{HH}$ 8.7, $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.9, 1H, H^5-sal); 7.27–7.33 (m, 14H, H-Ph, H-PPh_3); 7.41–7.46 (m, 6H, H-Ph, H-PPh_3); 7.79 (7.72) (d, $^4J_{HP}$ 1.4 (2.2), 1H, N=CH). $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 ext.): 53.8 (46.6) (s). $[\alpha]^{23}$ ($c = 0.14$, CH_2Cl_2): (589 nm) −355, (578 nm) −413, (546 nm) −701.

5.3. Crystallography

The details of the crystal structure determination are summarized in Table 1. X-ray diffraction data were collected at 20°C with a SYNTEX R3 diffractometer using Mo–K_α radiation ($\lambda = 0.71073$ Å) with a graphite-crystal monochromator. Cell constants were obtained with 18 reflections in the range $5.0° < 2\theta < 17.0°$. The data were collected in the θ–2θ mode. The structure was solved using the Patterson-Fourier method with SHELXTL PLUS (release 4.2/ 800), PC version [38]. The hydrogen atoms were added in calculated positions with the option HFIX. The absolute configuration was checked on the basis of $\eta = 1.1(2)$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository CSD number CSD-408327.

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