

Unusual Crystal Structures of ($R_{Ru}R_C/S_{Ru}R_C$)-(η^6 -*p*-Cymene)Ru Complexes – Diastereomers with Opposite Configuration at the Metal Center in the Unit Cell

Henri Brunner^{*a}, Thomas Neuhierl, and Bernhard Nuber^b

Institut für Anorganische Chemie der Universität Regensburg^a,
Universitätsstraße 31, D-93053 Regensburg, Germany
Fax: (internat.) + 49(0)941/9434439
E-mail: henri.brunner@chemie.uni-regensburg.de

Anorganisch-Chemisches Institut der Universität Heidelberg^b,
In Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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Condensation of (*R*)-2-aminobutanol with salicylaldehyde and 2-pyrrolicarbaldehyde gave the chiral chelate ligands HLL_1^* and HLL_2^* , respectively. The diastereomeric complexes (R_{Ru}, R_C)- and (S_{Ru}, R_C)-[(η^6 -arene)Ru(LL_1^*)Cl], η^6 -arene = *p*-cymene (**1a/1b**), η^6 -arene = benzene (**2a/2b**), and (R_{Ru}, R_C)- and (S_{Ru}, R_C)-[(η^6 -arene)Ru(LL_2^*)Cl], η^6 -arene = *p*-cymene (**3a/3b**), η^6 -arene = benzene (**4a/4b**), which only differ in the ruthenium configuration, were prepared by the reaction of [(η^6 -arene)RuCl₂]₂ with the anion of the corresponding ligand HLL^* . X-ray analyses of **1a/1b** and **3a/**

3b showed a structural peculiarity. The unit cell of these complexes contained diastereomers with the same configuration at the carbon atoms but opposite configuration at the metal centers in a 1:1 ratio. Weak intramolecular O–H...Cl hydrogen bridges were formed in all the complexes. ¹H-NMR studies demonstrated the configurational lability at the Ru center. The iodo complexes (R_{Ru}, R_C)- and (S_{Ru}, R_C)-[(η^6 -*p*-cymene)Ru(LL^*)I], $LL^* = LL_1^*$ (**5a/5b**) and $LL^* = LL_2^*$ (**6a/6b**), were synthesized by halogen exchange.

Introduction

Optically active (η^6 -arene)ruthenium half-sandwich complexes have attracted interest in enantioselective catalysis^{[2][3][4][5]}, including Diels–Alder and olefin isomerization reactions.^{[6][7][8]} There is a series of structural studies on optically active chiral-at-Ru complexes of the type [(η^6 -arene)Ru(LL^*)L] and [(η^6 -arene)Ru(LL^*)L]X, arene = *p*-cymene, mesitylene, benzene, LL^* = anionic or neutral unsymmetrical ligand, L = halide or unidentate ligand, X = anion.^{[9][10][11][12][13][14][15]} Resolution of (η^6 -arene)ruthenium half-sandwich complexes usually is carried out using optically active chelate ligands HLL^* containing optically active amine components. Diastereomers are formed, which only differ in the configuration at the stereogenic Ru atom.

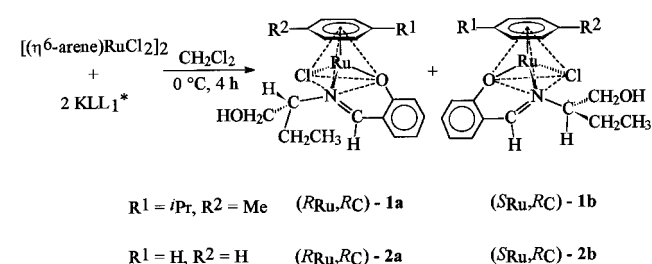
Diastereomers are different molecules. Therefore, ubiquitously, single crystals obtained from a mixture of diastereomers contain only one diastereomer. This, in effect, is the basis of diastereomer separation by crystallization. There are, however, examples, in which the presence of both diastereomers with opposite configuration at the metal center in one crystal is reported.^{[14][15][16]} In the present paper we describe the syntheses and the X-ray structures of

ruthenium half-sandwich complexes, two of which show this structural peculiarity.^[17]

Results and Discussion

2-*N*-[(*R*)-1-Hydroxybut-2-yl]salicylaldimine^[18] (HLL_1^*) was obtained by condensation of (*R*)-2-aminobutanol with salicylaldehyde. HLL_1^* was deprotonated in dichloromethane with KO^{*t*}Bu and [(η^6 -arene)RuCl₂]₂ (arene = *p*-cymene, benzene) was added. The formation of the diastereomeric complexes (R_{Ru}, R_C)- and (S_{Ru}, R_C)-[(η^6 -*p*-cymene)Ru(LL_1^*)Cl] (**1a, b**) and [(η^6 -benzene)Ru(LL_1^*)Cl] (**2a, b**) is depicted in Scheme 1.

Scheme 1

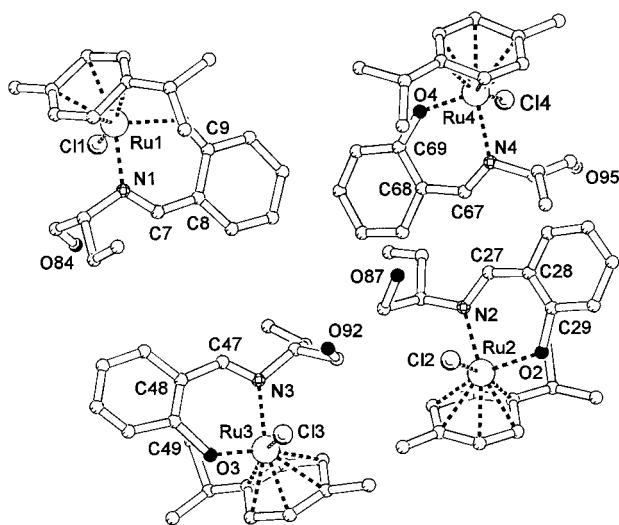


[\diamond] Part 117: See ref. [1].

The ^1H -NMR spectrum of the *p*-cymene complex in CDCl_3 showed the presence of two diastereomers **1a** and **1b** in a ratio of 91:9. As there is no “ β -phenyl effect”^{[13][19]}, no assignment of major/minor isomer to **1a/1b** can be made. The isomer ratio was obtained from the intensities of the singlets of the imine protons at $\delta = 7.75$ and $\delta = 7.85$. There are two doublets at $\delta = 1.15$ and $\delta = 1.26$ for the CHMe_2 groups of the *p*-cymene ligand in the major diastereomer and two doublets at $\delta = 1.08$ and $\delta = 1.24$ for the minor diastereomer indicating their diastereotopicity. Similarly, the benzene complex forms two diastereomers **2a** and **2b**. Integration of the singlets of the imine protons at $\delta = 7.77$ and $\delta = 8.39$ in CDCl_3 gave a ratio of 76:24.

Crystallization of the diastereomeric mixture **1a/1b** from dichloromethane/thf/pentane at 3°C gave triangular plates of X-ray analytical quality. To our surprise the structural study showed the presence of both isomers **1a** and **1b** in the asymmetric unit in a 1:1 ratio. The molecules **1a** and **1b** have the same configuration at the carbon atom but differ in the configuration at the metal center. There are four independent molecules in the unit cell, two with (R_{Ru}) and two with (S_{Ru}) configuration. Figure 1 displays the molecular structure of **1a/1b**.

Figure 1. Crystal structure of $(R_{\text{Ru}}, R_{\text{C}}/S_{\text{Ru}}, R_{\text{C}})-[(\eta^6\text{-}p\text{-cymene})\text{-Ru}(\text{LL}_1^*)\text{Cl}]$ **1a/1b**



In all four independent molecules the chiral Schiff base is bonded through the phenolic oxygen and the imine nitrogen. The stereogenic carbon atom of the chelate ligand has the expected (R_{C}) configuration introduced in the synthesis. The *i*Pr group of the π -bonded *p*-cymene ligand lies above the phenolic oxygen. Thus, the *p*-methyl group is located near the chloride ligand. The oxygen atom of the hydroxymethyl group is oriented towards the chloride ligand. The configuration of the stereogenic ruthenium centers is determined according to the priority sequence $\eta^6\text{-}p\text{-cymene} > \text{Cl} > \text{O} > \text{N}$.^{[20][21][22]} (R) configuration is assigned to Ru1 and Ru2, (S) configuration to Ru3 and Ru4. In the unit cell the pairs of diastereomers Ru1/Ru3 and Ru2/Ru4 are almost centrosymmetric, except the arrangement of the 2-amino-1-yl substituents which have the same (R_{C}) configura-

tion at the stereogenic carbon atom. Selected bond distances and angles are listed in Table 1.

Table 1. Selected bond lengths and angles of **1a/1b**; estimated standard deviations are shown in parentheses

	$R_{\text{Ru}(1)}$	$R_{\text{Ru}(2)}$	$S_{\text{Ru}(3)}$	$S_{\text{Ru}(4)}$
Ru–Cl	2.459(4)	2.467(4)	2.434(4)	2.431(4)
Ru–O	2.153(9)	2.108(10)	1.728(11)	2.028(9)
Ru–N	2.106(11)	2.096(11)	2.134(11)	2.185(12)
Ru–(arene)	1.634(5)	1.680(4)	1.687(4)	1.669(8)
Cl–Ru–O	83.6(3)	86.3(3)	91.5(4)	81.4(3)
Cl–Ru–N	85.4(3)	83.3(3)	83.5(3)	84.1(4)
O–Ru–N	88.8(4)	89.9(4)	90.0(5)	85.9(4)

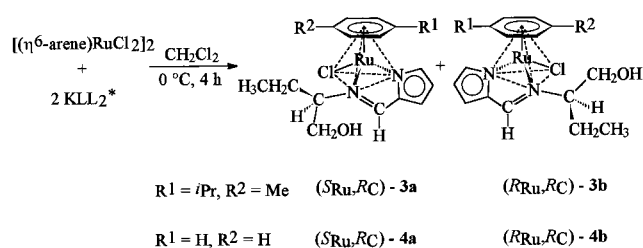
The bond distances and angles are similar to those observed in related complexes.^{[13][14]} However there is a very short Ru3–O3 distance. The complexes with (S_{Ru}) configuration show longer Ru–N distances, whilst the Ru–Cl and Ru–O distances are smaller than in complexes with (R_{Ru}) configuration. The distances of the oxygen atoms to the chloride ligands are: O84...Cl1 3.24 Å, O87...Cl2 3.20 Å, O92...Cl3 3.01 Å, and O95...Cl4 3.13 Å. Weak O–H...Cl hydrogen bridges are described for O...Cl distances between 2.92 and 3.18 Å.^[23] The formation of these O–H...Cl hydrogen bridges may be the driving force which orients the OH groups of the (*R*)-2-aminobut-1-yl substituents towards the chloride ligands.

The X-ray structure analysis demonstrated the presence of both diastereomers **1a** and **1b** in the crystal in a 1:1 ratio. However, the ^1H -NMR spectrum of crystals dissolved in CDCl_3 at room temperature showed a 91:9 ratio which did not change after stirring for 1 d at r.t. Furthermore, crystals of the complex **1a/1b** were dissolved at -80°C in CD_2Cl_2 . Integration of the low temperature ^1H -NMR spectrum gave a diastereomer ratio of 95:5, proving the configurational lability at the metal center even at -80°C . Thus, the equilibrium **1a** \rightleftharpoons **1b** must have been established during the solution procedure at -80°C which took 1 h. Obviously, the energy barrier of the epimerization at the Ru atom in **1a/1b** is very low as observed for similar compounds with related chiral salicylaldiminato ligands.^{[12][13]} Surprisingly, however, crystallization of a solution in which one of the two diastereomers is dominant, gives a 1:1 ratio of **1a/1b** in the crystal lattice.

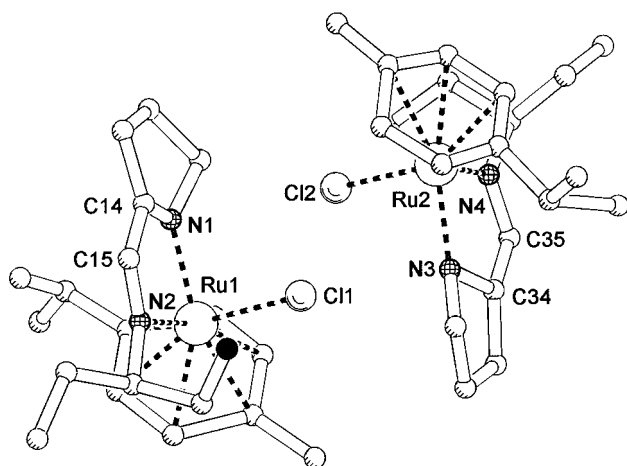
Condensation of (*R*)-2-aminobutan-1-ol with 2-pyrrolicarbaldehyde afforded the ligand 2-*N*-[(*R*)-1-hydroxybut-2-yl]-pyrrolicarbaldehyde^{[17][24]} (HLL_2^*). The formation of the diastereomeric complexes ($R_{\text{Ru}}, R_{\text{C}}$)- and ($S_{\text{Ru}}, R_{\text{C}}$)-[($\eta^6\text{-}p\text{-cymene}$)Ru(LL_2^*)Cl] (**3a, b**) and [($\eta^6\text{-benzene}$)Ru(LL_2^*)Cl] (**4a, b**) is depicted in Scheme 2.

The ^1H -NMR spectrum of **3a/3b** in CDCl_3 showed a diastereomer ratio of 1:1, which did not change after refluxing for 3 h. A measurement in $[\text{D}_6]\text{acetone}$ demonstrated that solvent polarity had no influence on the equilibrium ratio. The diastereomer ratio of 79:21 in CDCl_3 for the complexes **4a, b** was similar to the ratio found for the complexes **2a, b** (76:24).

Scheme 2



From a mixture of CH_2Cl_2 , thf, and pentane crystals of the complex **3a/3b** suitable for X-ray structure analysis were obtained. There are two independent molecules in the unit cell with opposite configurations at the Ru centers. The molecular structure of **3a/3b** is shown in Figure 2.

Figure 2. Crystal structure of $(R_{Ru}, R_C/S_{Ru}, R_C)-[(\eta^6-p\text{-cymene})\text{-Ru}(\text{LL}_2^*)\text{Cl}]$ **3a/3b**

The chiral Schiff base is coordinated through the pyrrole nitrogen and the imine nitrogen. The stereogenic carbon atom of the chelate ligand has the expected (R_C) configuration. The iPr group of the cymene ring is located in the vicinity of the imine nitrogen. Both methyl groups of the iPr substituent tend away from the chelate ring and the p -methyl group fills the space between the imine nitrogen and the chloride ligand. The oxygen atom of the hydroxymethyl group is oriented towards the chloride ligand. Both molecules are arranged in a quasi centrosymmetric manner. However, there is no real centrosymmetry due to the given (R_C) configuration at the stereogenic carbon atoms. According to the priority sequence $\eta^6\text{-}p\text{-cymene} > \text{Cl} > \text{N}(\text{imine}) > \text{N}(\text{pyrrolate})$ the configuration of the stereogenic ruthenium centers is (S) for Ru1 and (R) for Ru2. Selected bond distances and angles are listed in Table 2.

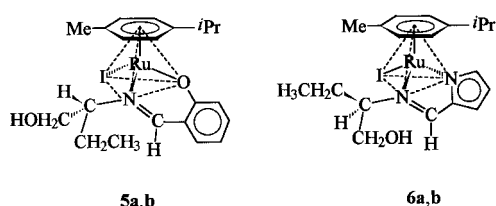
The bond lengths and angles are similar to those observed in related complexes.^[12] The distances of the oxygen atoms to the chloride ligands are $\text{O1}\cdots\text{Cl1}$ 3.28 Å and $\text{O2}\cdots\text{Cl2}$ 3.00 Å, indicating the formation of weak $\text{O}\cdots\text{H}\cdots\text{Cl}$ hydrogen bridges as observed for **1a/1b**.

The dissociation of the chloride ligand in ruthenium half-sandwich complexes^{[12][13][25][26][27]} can be used for halogen exchange reactions.^[27] Stirring the complexes **1a/1b** in

Table 2. Selected bond lengths and angles of **3a/3b**; estimated standard deviations are shown in parentheses

	$R_{Ru(1)}$	$S_{Ru(2)}$
Ru–Cl	2.481(11)	2.361(10)
Ru–N(pyr)	2.082(26)	2.041(26)
Ru–N(imine)	2.137(27)	2.119(27)
Ru–(arene)	1.626(14)	1.711(17)
Cl–Ru–N(pyr)	84.7(7)	84.8(7)
Cl–Ru–N(imine)	85.8(7)	84.4(8)
N(pyr)–Ru–N	75.3(10)	80.1(10)

MeOH in the presence of a 10 M excess of NaI for 1 h at rt gave the complexes $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}_1^*)\text{I}]$ (**5a, b**) (Scheme 3) in nearly quantitative yield.

Scheme 3. Structural formulae of the iodo complexes **5a/5b, 6a/6b**. Only one diastereomer is shown

There were hardly differences in the chemical shifts of the iodo complex **5a/5b** and the chloro complex **1a/1b**. In the iodo complex the p -methyl group of the cymene ligand was shifted 0.17 ppm to low field, whereas the imine proton was shifted 0.16 ppm to high field relative to the chloro complex. The diastereomer ratio of **5a, b** (88:12) was similar to that found for **1a, b** (91:9). Thus, the exchange of the p -cymene ligand in **1** for benzene in **2** had a much stronger impact on the diastereomer ratio than the exchange of chloride in **1** for iodide in **5**.

The preparation of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}_2^*)\text{I}]$ (**6a/6b**) (Scheme 3) from **3a/3b** was carried out as described for the system **1** \rightarrow **5**. In the FD mass spectrum of **6a/6b** only the peak of the iodo complex was detected confirming quantitative halogen exchange. The integration of the imine protons at $\delta = 7.44$ and 7.48 in CDCl_3 gave a diastereomer ratio of 65:35.

Experimental Section

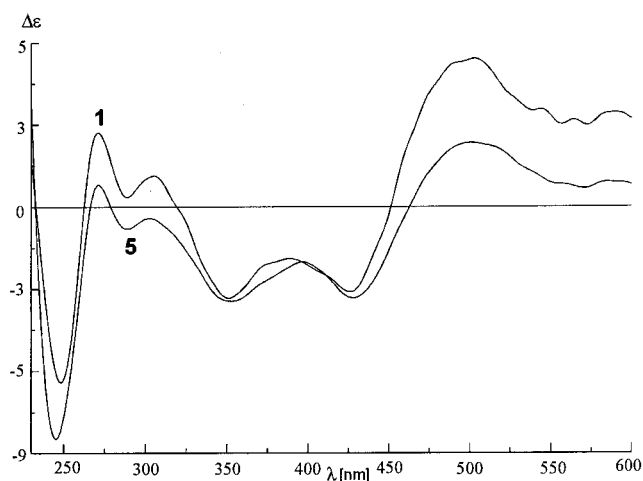
General Remarks: Preparation of the ruthenium complexes was carried out under an atmosphere of dry nitrogen with standard Schlenk techniques. – IR spectra: Beckman IR 4240 spectrometer. – Mass spectra: field desorption method (Finnigan MAT 95). – ^1H -NMR spectra: Bruker ARX 400 spectrometer (400 MHz). – UV/Vis spectroscopy: Kontron Uvikon 922 spectrophotometer. – CD spectra Jasco J-710 spectrophotometer. – Polarimetric measurements: Perkin-Elmer 241 instrument. – Melting points: Büchi SMP 20. Elemental analyses: microanalytical laboratory of the University of Regensburg. – $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ ^[28–30] and $[(\eta^6\text{-benzene})\text{RuCl}_2]_2$ ^{[28][29][30]} were prepared as published from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. 2- N -[(R)-1-hydroxybut-2-yl]salicylaldehyde^[18] (HLL*-**1**) and 2- N -[(R)-1-hydroxybut-2-yl]pyrrolecarbaldehyde^{[17][24]} (HLL*-**4**) were synthesized by the literature methods. –

X-ray structure analyses: Syntex R3 diffractometer, Mo- K_α radiation, $T = 296$ K. Solution by direct methods using the program SHELXTL Plus (release 4.2/800), PC version. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (e-mail: crysdata@fiz-karlsruhe.de) on quoting the respective depository CSD number (vide infra).

Preparation of the Complexes $[(\eta^6\text{-arene})\text{Ru}(\text{LL}^*)\text{Cl}]$: 2.07 mmol of the appropriate ligand HLL* was dissolved in abs. CH_2Cl_2 and KOtBu (2.07 mmol) was added. The mixture was stirred for 1 h at room temp. After adding CH_2Cl_2 the mixture was cooled to 0°C . $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ (1.00 mmol) was added and the solution was stirred for 4 h at 0°C . The solution was filtered through Celite and concentrated. The product was precipitated quantitatively by slow addition of petroleum ether with stirring. The red microcrystalline residue was washed with petroleum ether and dried.

$[(\eta^6\text{-p-Cymene})\text{Ru}(\text{LL}_1^*)\text{Cl}]$ (1a, b**):** Yield: 705 mg (83%), m.p. 136°C (decomp.). – IR (KBr): $\tilde{\nu} = 1615\text{ cm}^{-1}$ (C=N), 1600, 1540, 1470 (C=C). – $[\alpha]^{24}_D$ ($c = 0.14$, CHCl_3) (589 nm) +770, (578 nm) +1025, (546 nm) +1277. – UV/Vis ($c = 1.32 \cdot 10^{-4}\text{ mol l}^{-1}$, CH_2Cl_2) λ_{max} (lg ϵ) = 277 nm (3.67). – CD data ($c = 1.80 \cdot 10^{-4}\text{ mol l}^{-1}$, CH_2Cl_2) λ_{max} ($\Delta\epsilon$) = 248 nm (−6.40), 261 (0.0), 271 (2.71), 305 (1.14), 320 (0.0), 351 (−3.31), 426 (−3.11), 450 (0.0), 503 (5.41). – ^1H NMR (CDCl_3): $\delta = 1.15$ (m, 6 H, CH_3 , $\text{CH}_3\text{-iPr}$), 1.26 (d, $J = 6.9$ Hz, 3 H, $\text{CH}_3\text{-iPr}$), 1.97 (m, 2 H, CH_2CH_3), 2.25 (s, 3 H, $\text{CH}_3\text{-cymene}$), 2.75 (sept, $J = 6.9$ Hz, 1 H, CH-iPr), 3.71 (m, 1 H, CH), 3.98 (m, 1 H, HCHOH), 4.44 (m, 1 H, HCHOH), 4.99/5.40 (AB, d, $J = 5.7$ Hz, 2 H, H-cymene), 5.46/5.47 (AB, d, $J = 6.5$ Hz, 2 H, H-cymene), 6.44 (m, 1 H, $\text{H}^{\text{A-sal}}$), 6.95 (m, 2 H, $\text{H}^{\text{B,H-sal}}$), 7.19 (m, 1 H, $\text{H}^{\text{F-sal}}$), 7.75 (7.85, 9%) (s, 1 H, N=CH). – MS-FD (EtOH); m/z (%): 463 (100) $[\text{M}^+]$ rel. to ^{102}Ru . – $\text{C}_{21}\text{H}_{28}\text{ClNO}_2\text{Ru}$ (462.98): calcd. C 54.48, H 6.10, N 3.03; found C 54.24, H 6.31, N 3.04.

Figure 3. CD spectra of the chloride and iodide complexes **1a, b** (91:9) and **5a, b** (88:12) in dichloromethane. [$c(\mathbf{1}) = 1.80 \cdot 10^{-4}\text{ mol l}^{-1}$, $c(\mathbf{5}) = 1.59 \cdot 10^{-4}\text{ mol l}^{-1}$]



Crystals for X-ray analysis were obtained from a mixture of CH_2Cl_2 , thf, and pentane at 3°C . X-ray structure analysis of $(R_{\text{Ru}}, R_{\text{C}}/S_{\text{Ru}}, R_{\text{C}})\text{-}[(\eta^6\text{-p-cymene})\text{Ru}(\text{LL}_1^*)\text{Cl}]$: dark red triangular plates, crystal size $0.25 \times 0.45 \times 0.55\text{ mm}^3$, monoclinic, space group C_2^2 , $P2_1$ (no 4), $a = 7.715(2)$, $b = 17.859(4)$, $c = 29.359(8)$ Å, $\beta = 94.90(2)^\circ$, $V = 4031(2)\text{ Å}^3$, $Z = 4$, $d_{\text{calc}} = 1.52\text{ g cm}^{-3}$, empirical absorption correction (7 reflections $4.6^\circ < 2\theta < 41.2^\circ$), ω scans, 2θ range $3.0^\circ < 2\theta < 59.0^\circ$, Friedel pairs $3.0^\circ < 2\theta < 35.0^\circ$,

transmission factors 0.86–1.00, $\mu = 0.93\text{ mm}^{-1}$, $F(000) = 1896$; 13919 unique, 8505 observed reflections [$I > 2.5\sigma(I)$]. Parameters blocked 4-115, total 457; $R = 0.074$, $R_w = 0.067$, residual electron density $4.60/-2.00\text{ e Å}^{-3}$. CSD 408883.

$[(\eta^6\text{-benzene})\text{Ru}(\text{LL}_1^*)\text{Cl}]$ (2a, b**):** Yield: 363 mg (72%), m.p. 167°C (decomp.). – IR (KBr): $\tilde{\nu} = 1620\text{ cm}^{-1}$ (C=N), 1600, 1540, 1470 (C=C). – $[\alpha]^{20}_D$ ($c = 0.12$, CH_2Cl_2) (589 nm) +920, (578 nm) +1111, (546 nm) +1547. – CD data ($c = 1.48 \cdot 10^{-4}\text{ mol l}^{-1}$, CH_2Cl_2) λ_{max} ($\Delta\epsilon$) = 247 nm (−2.30), 269 (0.0), 282 (0.18). – NMR data for the minor diastereomer are added in parentheses when different to the major diastereomer. ^1H NMR (CDCl_3): $\delta = 1.16$ (0.92) (t, $J = 7.2$ (7.4) Hz, 3 H, CH_3), 2.00 (m, 2 H, CH_2CH_3), 3.76 (m, 1 H, CH), 3.99 (m, 1 H, HCHOH), 4.51 (m, 1 H, HCHOH), 5.60 (s, 6 H, H-benzene), 6.48 (m, 1 H, $\text{H}^{\text{A-sal}}$), 6.98 (m, 2 H, $\text{H}^{\text{B,H-sal}}$), 7.22 (m, 1 H, $\text{H}^{\text{F-sal}}$), 7.77 (8.39) (s, 1 H, N=CH). – MS-FD (CH_2Cl_2); m/z (%): 407 (100) $[\text{M}^+]$ rel. to ^{102}Ru . – $\text{C}_{17}\text{H}_{20}\text{ClNO}_2\text{Ru}$ (406.87): calcd. C 50.18, H 4.95, N 3.44; found C 50.55, H 5.29, N 3.85.

$[(\eta^6\text{-p-cymene})\text{Ru}(\text{LL}_2^*)\text{Cl}]$ (3a, b**):** Yield: 615 mg (72%), m.p. 157°C (decomp.). – IR (KBr): $\tilde{\nu} = 1660\text{ cm}^{-1}$ (C=N), 1580, 1460 (C=C). – $[\alpha]^{20}_D$ ($c = 0.11$, CH_2Cl_2) (589 nm) +68, (578 nm) +75, (546 nm) +95. – UV/Vis ($c = 4.21 \cdot 10^{-5}\text{ mol l}^{-1}$, CH_2Cl_2) λ_{max} (lg ϵ) = 324 nm (4.22). – NMR data for the second diastereomer are added in parentheses when different to the first diastereomer. Intensities are related to the corresponding peaks. ^1H NMR (CDCl_3): $\delta = 0.80$ (0.94) (d, $J = 6.9$ Hz, 3 H, $\text{CH}_3\text{-iPr}$), 1.06 (t, $J = 7.4$ Hz, 3 H, CH_3), 1.14 (m, 6 H, CH_3 , $\text{CH}_3\text{-iPr}$), 1.28 (d, $J = 6.9$ Hz, 3 H, $\text{CH}_3\text{-iPr}$), 1.75 (1.93) (m, 2 H, CH_2CH_3), 2.23 (2.26) (s, 3 H, $\text{CH}_3\text{-cymene}$), 2.57 (sept, $J = 6.9$ Hz, 1 H, CH-iPr), 3.50 (4.12) (m, 1 H, CH), 3.66 (4.04) (m, 2 H, CH_2OH), 5.26 (m, 3 H, H-cymene), 5.34 (d, $J = 6.2$ Hz, 1 H, H-cymene), 5.47 (d, $J = 6.2$ Hz, 1 H, H-cymene), 5.64 (m, 2 H, H-cymene), 5.75 (d, $J = 6.1$ Hz, 1 H, H-cymene), 6.32 (m, 1 H, $\text{H}^{\text{A-pyrr}}$), 6.67 (m, 1 H, $\text{H}^{\text{B-pyrr}}$), 7.44 (m, 1 H, $\text{H}^{\text{F-pyrr}}$), 7.57 (7.61) (s, 1 H, N=CH). – MS-FD (acetone); m/z (%): 436 (100) $[\text{M}^+]$ rel. to ^{102}Ru . – $\text{C}_{19}\text{H}_{27}\text{ClN}_2\text{ORu}$ (435.96): calcd. C 52.35, H 6.24, N 6.43; found C 52.24, H 6.46, N 6.38.

Crystals of **3a/3b** for X-ray analysis were obtained from a mixture of CH_2Cl_2 , thf, and pentane at 3°C . X-ray structure analysis of $(R_{\text{Ru}}, R_{\text{C}}/S_{\text{Ru}}, R_{\text{C}})\text{-}[(\eta^6\text{-p-cymene})\text{Ru}(\text{LL}_2^*)\text{Cl}]$: orange-red needles, crystal size $0.08 \times 0.10 \times 0.08\text{ mm}^3$, monoclinic, space group C_2^2 , $P2_1$ (no 4), $a = 10.036(3)$, $b = 9.415(3)$, $c = 21.132(7)$ Å, $\beta = 101.44(2)^\circ$, $V = 1957(1)\text{ Å}^3$, $Z = 2$, $d_{\text{calc}} = 1.48\text{ g cm}^{-3}$, empirical absorption correction (8 reflections $4.2^\circ < 2\theta < 35.2^\circ$), ω scans, 2θ range $3.0^\circ < 2\theta < 50.0^\circ$, Friedel pairs $3.0^\circ < 2\theta < 42.0^\circ$, transmission factors 0.86–1.00, $\mu = 0.95\text{ mm}^{-1}$, $F(000) = 896$; 5465 unique, 3069 observed reflections [$I > 2.5\sigma(I)$]. Parameters 213; $R = 0.119$, $R_w = 0.096$, residual electron density $1.93/-2.47\text{ e Å}^{-3}$. CSD 408884.

$[(\eta^6\text{-benzene})\text{Ru}(\text{LL}_2^*)\text{Cl}]$ (4a, b**):** Yield: 340 mg (66%), m.p. 110°C (decomp.). – IR (KBr): $\tilde{\nu} = 1620\text{ cm}^{-1}$ (C=N), 1580, 1435 (C=C). – $[\alpha]^{20}_D$ ($c = 0.17$, CH_2Cl_2) (589 nm) −321, (578 nm) −381, (546 nm) −669. – NMR data for the second diastereomer are added in parentheses when different to the first diastereomer. ^1H NMR (CDCl_3): $\delta = 1.06$ (1.12) (t, $J = 7.4$ Hz, 3 H, CH_3), 1.79 (1.92) (m, 2 H, CH_2CH_3), 3.55 (m, 1 H, CH), 3.72 (m, 1 H, HCHOH), 3.92 (m, 1 H, HCHOH), 5.70 (5.62) (s, 6 H, $\eta^6\text{-C}_6\text{H}_6$), 6.34 (dd, $J = 3.8$ Hz, $J = 1.1$ Hz, 1 H, $\text{H}^{\text{A-pyrr}}$), 6.71 (dd, $J = 3.8$ Hz, $J = 1.1$ Hz, 1 H, $\text{H}^{\text{B-pyrr}}$), 7.53 (broad, 1 H, $\text{H}^{\text{F-pyrr}}$), 7.59 (7.62) (s, 1 H, N=CH). – MS-FD (acetone); m/z (%): 380 (100) $[\text{M}^+]$ rel. to ^{102}Ru . – $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{ORu}$ (379.85): calcd. C 45.28, H 5.32, N 7.04; found C 45.00, H 5.12, N 6.33.

Preparation of the complexes $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}^*)\text{I}]$: 0.15 mmol of the appropriate ruthenium complex (**1a**, **b**) or (**3a**, **b**) was dissolved in abs. MeOH (15 ml). NaI (1.5 mmol) was added. The solution was stirred for 1 h at r.t. The solvent was evaporated and the red residue was dissolved in CH_2Cl_2 and filtered. After removing the solvent an analytically pure red powder was obtained in nearly quantitative yield.

$[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}_1^*)\text{I}]$ (**5a**, **b**): m.p. 80°C (decomp.). – $[\alpha]^{21}$ ($c = 0.08$, CHCl_3) (589 nm) +29, (578 nm) –29, (546 nm) –29. – UV/Vis ($c = 1.27 \cdot 10^{-4}$ mol l^{-1} , CH_2Cl_2) λ_{max} (lg ϵ) = 270 nm (3.92), 293 (3.92). – CD data ($c = 1.59 \cdot 10^{-4}$ mol l^{-1} , CH_2Cl_2) λ_{max} ($\Delta\epsilon$) = 245 nm (–8.47), 264 (0.0), 271 (0.81), 279 (0.0), 302 (–0.41), 353 (–3.44), 428 (–3.32), 461 (0.0), 501 (2.33). – NMR data for the minor diastereomer are added in parentheses when different to the major diastereomer. ^1H NMR (CDCl_3): $\delta = 1.12$ (0.91) (t, $J = 7.4$ (7.5) Hz, 3 H, CH_3), 1.16 (d, $J = 6.8$ Hz, 3 H, $\text{CH}_3\text{-}i\text{Pr}$), 1.29 (d, $J = 6.8$ Hz, 3 H, $\text{CH}_3\text{-}i\text{Pr}$), 2.00 (m, 2 H, CH_2CH_3), 2.42 (2.35) (s, 3 H, $\text{CH}_3\text{-cymene}$), 2.88 (sept, $J = 6.8$ Hz, 1 H, $\text{CH-}i\text{Pr}$), 3.74 (m, 1 H, CH), 4.26 (m, 2 H, CH_2OH), 4.89/5.49 (AB, d, $J = 5.3$ Hz, 2 H, $H\text{-cymene}$), 5.30/5.62 (AB, d, $J = 5.7$ Hz, 2 H, $H\text{-cymene}$), 6.42 (m, 1 H, $H^A\text{-sal}$), 6.92 (m, 2 H, $H^B, H^C\text{-sal}$), 7.15 (m, 1 H, $H^D\text{-sal}$), 7.59 (7.66) (s, 1 H, N=CH). – MS-FD (CH_2Cl_2); m/z (%): 555 (100) $[\text{M}^+]$ rel. to ^{102}Ru , 428 (20) $[\text{M}^+ - \text{I}]$. – $\text{C}_{21}\text{H}_{28}\text{INO}_2\text{Ru}$ (554.43): calcd. C 44.06, H 5.28, N 2.45; found C 44.22, H 5.20, N 2.29.

$[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}_2^*)\text{I}]$ (**6a**, **b**): m.p. 67°C (decomp.). – $[\alpha]^{21}$ ($c = 0.09$, CH_2Cl_2) (589 nm) +215, (578 nm) +244, (546 nm) +429. – NMR data for the minor diastereomer are added in parentheses when different to the major diastereomer. ^1H NMR (CDCl_3): $\delta = 0.94$ (0.79) (d, $J = 6.9$ Hz, 3 H, $\text{CH}_3\text{-}i\text{Pr}$), 1.10 (1.05) (t, $J = 7.4$ Hz, 3 H, CH_3), 1.17 (1.25) (d, $J = 6.9$ Hz, 3 H, $\text{CH}_3\text{-}i\text{Pr}$), 1.75 (m, 1 H, HCHCH_3), 1.97 (m, 1 H, HCHCH_3), 2.43 (2.49) (s, 3 H, $\text{CH}_3\text{-cymene}$), 2.66 (t, $J = 6.9$ Hz, 1 H, OH), 2.74 (3.02) (sept, $J = 6.9$ Hz, 1 H, $\text{CH-}i\text{Pr}$), 3.64 (3.34) (m, 1 H, CH), 3.95 (3.51) (m, 1 H, HCHOH), 4.26 (4.07) (m, 1 H, HCHOH), 5.19/5.31 (AB, d, $J = 5.8$ Hz, 2 H, $H\text{-cymene}$), 5.25/5.46 (AB, d, $J = 6.1$ Hz, 2 H, $H\text{-cymene}$), 6.32 (m, 1 H, $H^A\text{-pyrr}$), 6.70 (m, 1 H, $H^B\text{-pyrr}$), 7.37 (m, 1 H, $H^C\text{-pyrr}$), 7.44 (7.48) (s, 1 H, N=CH). – MS-FD (CH_2Cl_2); m/z (%): 528 (100) $[\text{M}^+]$ rel. to ^{102}Ru . – $\text{C}_{19}\text{H}_{27}\text{I-N}_2\text{ORu}$ (527.41): calcd. C 39.23, H 4.77, N 4.57; found C 40.15, H 4.99, N 4.49.

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