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Optically active transition metal complexes. Part 117:[1] Synthesis, crystal structure and properties of chiral (η^6-arene)ruthenium complexes with *N,O*- and *N,N*-ligands

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Abstract

The complexes [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(NO$_2$pesa)Cl] **2**, [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(oxazsa)Cl] **3** and [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pepy)Cl] **4**, chiral in the chelate ligand and chiral at the ruthenium atom, have been prepared by reaction of [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$ with the anions of the (*S*)-configured bidentate *N,O*- and *N,N*-ligands. [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pesa)I] **5** was synthesized by halide exchange. The diastereomer ratios of compounds **2**–**4** with respect to the stereogenic ruthenium atom are in CDCl$_3$ **2a**:**2b**=81:19, **3a**:**3b**=77:23 and **4a**:**4b**=61:39. Compound **5** is obtained diastereomerically pure. An X-ray structure analysis of **3** shows (R_{Ru},S_C)-configuration

1. Introduction

Half-sandwich (η^6-arene)ruthenium(II) complexes have attracted much interest in recent years. They have proven to be extremely useful in catalytic syntheses, asymmetric as well as non-asymmetric.[2–4] In addition, the pseudo-tetrahedral geometry makes them particularly suitable for the investigation of the stereochemistry at the metal center.[5–7]

In our search for new catalysts of the enantioselective double bond isomerization of cyclic allyl acetals we found that (η^6-arene)ruthenium complexes are surprisingly active and highly stereoselective (see the following paper). Thus, complex **1** (Scheme 1) turned out to be a much better catalyst than the rhodium and ruthenium compounds used up to now.[8] Hence, we have synthesized the compounds **2**–**5** (Scheme 1) to investigate the influence of the chelate ligand on the activity and enantioselectivity of (η^6-arene)ruthenium halides in the catalytic double bond isomerization of 2-*n*-butyl-4,7-dihydro-1,3-dioxepin.

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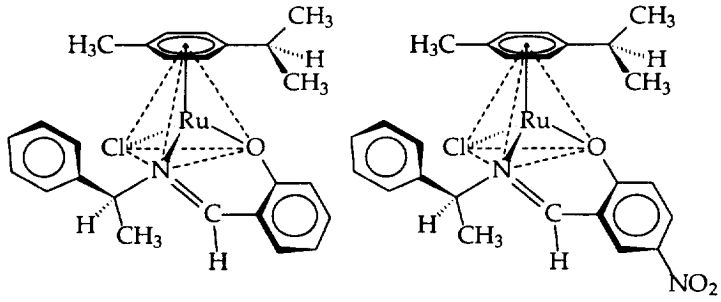
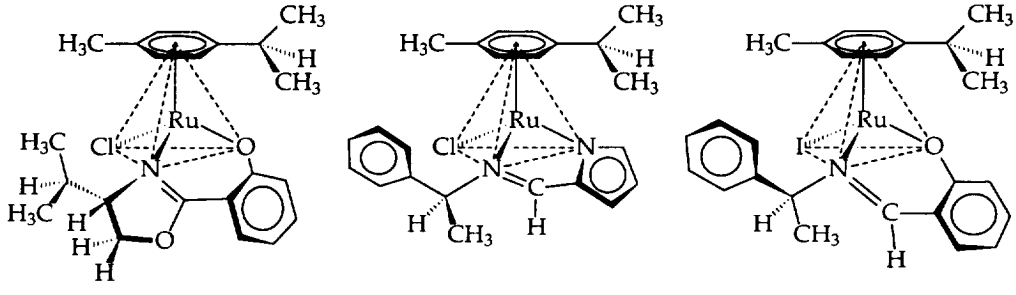


$(R_{Ru},S_C)/(S_{Ru},S_C)$-**1** $(R_{Ru},S_C)/(S_{Ru},S_C)$-**2**

[(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pesa)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(NO$_2$pesa)Cl]



$(R_{Ru},S_C)/(S_{Ru},S_C)$-**3** $(R_{Ru},S_C)/(S_{Ru},S_C)$-**4** (R_{Ru},S_C)-**5**

[(η⁶-^{i}PrC$_6$H$_4$Me)Ru(oxazsa)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pepy)Cl] [(η⁶-^{i}PrC$_6$H$_4$Me)Ru(pesa)I]

Scheme 1. Complexes **1–5** and their abbreviated formulas. Only one diastereomer of each complex is shown

2. Results and discussion

The ligands pesaH,[9] NO$_2$pesaH,[b] pepyH[10] and oxazsaH[11] and the complexes [(η⁶-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$[12] and **1**[13] were prepared according to reported procedures. For the synthesis of compounds **2** and **3**, NO$_2$pesaH and oxazsaH, respectively, were deprotonated with KO^{t}Bu in methylene chloride. After addition of [(η⁶-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$ at 0°C the solution was stirred for 3 h. The diastereomeric complexes (S_{Ru},S_C)- and (R_{Ru},S_C)-[(η⁶-*p*-^{i}PrC$_6$H$_4$Me)Ru(NO$_2$pesa)Cl] **2a/2b** and (S_{Ru},S_C)- and (R_{Ru},S_C)-[(η⁶-*p*-^{i}PrC$_6$H$_4$Me)Ru(oxazsa)Cl] **3a/3b**, differing only in the configuration at the ruthenium atom, were formed. After recrystallization, the analytically pure complexes were obtained as dark red crystals or as an orange microcrystalline powder, respectively. [(η⁶-*p*-^{i}PrC$_6$H$_4$Me)Ru(pepy)Cl] **4** was prepared according to the corresponding benzene derivative.[6d] PepyH was deprotonated with sodium hydride in methylene chloride. After adding [(η⁶-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$ at −15°C, the solution was stirred for 3 h. The resulting mixture was purified by column chromatography. Complex **4** was dissolved in methylene chloride:ethyl acetate (1:1) and crystallized by adding ether and petroleum ether. Complex **5** was synthesized from **1** by halide exchange. Stirring of **1** with a ten-fold excess of sodium iodide for 1 h gave compound **5** as a red powder in almost quantitative yield.

Complexes **1–4** are mixtures of diastereomers. The ratio in solution can be determined by ^{1}H NMR spectroscopy. Complex **1** is known to exhibit a ratio **1a**:**1b**=87:13 in CDCl$_3$.[14] For **2**, integration of the doublets of the methyl protons of the 1-phenylethyl group at 1.99 and 1.79 ppm gives a ratio of **2a**:**2b**=81:19 in CDCl$_3$. In the major diastereomer, the cymene protons are shifted to a higher field

compared to the minor diastereomer. This parallels the behavior of the majority of (η^6-arene)ruthenium and other half-sandwich complexes. There is a face-on orientation of the phenyl group of the 1-phenylethyl substituent towards the arene or cyclopentadienyl ligand in the favored diastereomer, causing an attractive interaction, the 'β-phenyl effect'.[15] Due to this face-on orientation, the arene ligand lies in the magnetic anisotropy cone of the phenyl group of the (*S*)-1-phenylethyl substituent. Hence, *R*-configuration is assigned to the ruthenium atom in the major diastereomer.

None of the signal pairs of the salicyloxazoline complex **3** is separated sufficiently to allow an accurate measurement of the diastereomeric ratio. An estimation on the basis of half of the AA'BB' system of the cymene protons of one diastereomer in relation to the total of the three oxazoline protons afforded an approximate ratio **3a**:**3b**≈77:23. The ^{1}H NMR shows the presence of approximately 0.5 equiv. of methylene chloride. This result was verified by the elemental analysis and the X-ray structure analysis.

For the pyrroleimine complex **4** the integration of the doublets of the methyl substituent of the chelate ligand at 1.86 and 1.65 ppm yields a ratio **4a**:**4b**=61:39 in the solvent $CDCl_3$. As the configuration at the metal center in (η^6-arene)ruthenium complexes with pyrroleimine ligands turned out to be much more stable than with salicylimine ligands,[d] the temperature dependence of the diastereomer ratio of complex **4** was investigated. A solid sample of **4** was dissolved in CD_2Cl_2 below −70°C. At −70°C the ^{1}H NMR showed a diasteromer ratio of ca. 25:75. In a second sample the ratio was ca. 29:71. This difference is probably due to the duration of the dissolution process which took ca. 1 h at −70°C. After 22 h at room temperature, the ratio was 71:29. It did not change on cooling to −70°C. Obviously, epimerization is slow at −70°C, becoming fast at higher temperatures.

The iodide compound **5** shows only the signals of one stereoisomer in $CDCl_3$, whereas in similar iodide compounds a mixture of diastereomers was found.[16] The configuration of the ruthenium atom in the only diastereomer of complex **5** was assigned on the basis of the above mentioned 'β-phenyl effect'. Therefore, (R_{Ru},S_C)-configuration is ascribed to the observed diastereomer of **5** (Scheme 1).

A single crystal X-ray structure analysis was carried out for the salicyloxazoline complex **3**. X-Ray quality crystals were grown by diffusion of ether into a methylene chloride solution of **3**. 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 a PLATON plot of the molecular structure of **3** is shown.

In complex **3** 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^6-*p*-^{i}PrC$_6$H$_4$Me)>Cl>O>N.[17] There are no unusual bond distances or angles. The two *iso*-propyl substituents are almost parallel to each other with their methine protons pointing towards each other. The distance of the two methine protons of these groups is only a little larger than the sum of the van der Waals radii. The distance between the chlorine atom and H6 of the neighboring molecule amounts to 2.619 Å and points to an intermolecular hydrogen bond.[18]

3. Experimental

The ruthenium complexes were prepared under an atmosphere of dry nitrogen using standard Schlenk techniques. IR spectra: Perkin–Elmer 1000PC FT-IR. Mass spectra: field desorption method (Finnigan MAT 95). ^{1}H and ^{13}C NMR spectra: Bruker AC-250 spectrometer. Polarimetric measurements: Perkin–Elmer 241 instrument. Melting points: Büchi SMP 20.

Table 1
Summary of crystal data, data collection and structure refinement[a] for complex **3a**

Elemental formula	$C_{22}H_{28}ClNO_2Ru \cdot 0.5\ CH_2Cl_2$
M	474.99
Crystal system	tetragonal
Space group	$P4_32_12$ (No. 96)
Crystal colour, shape	orange-red needles
Crystal size (mm^3)	0.15 × 0.25 × 0.80
a (Å)	13.867(2)
b (Å)	13.867(2),
c (Å)	23.971(5)
V (Å^3)	4611
Z	8
Density (g cm^{-3})	1.49
$F(000)$	2123
μ (mm^{-1})	0.93
h,k,l ranges	0 to 17, 0 to 17, 0 to 29
2 θ range (°)	3.0 - 50.0
Total no. of unique reflections	4062
No. of observed reflections $I > 2.5\sigma_I$	2758
Min./max. transmission factors	0.92, 1.00
No. of reflections, 2 θ range (°) for empirical absorption correction	6, 7.0 < θ < 42.0
No. of least-squares parameters	255
shift/esd-max.	0.03
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	-0.80, 1.35
R[b]	0.055
R_w[b]	0.047

[a] Syntex R3 diffractometer: Mo-K_α radiation (λ = 0.71073 Å); 293 K.
[b] $R = \Sigma\,||F_o| - |F_c||\ /\ \Sigma|F_o|$; $R_w = \Sigma\,||F_o| - |F_c||\,w^{1/2}\ /\ \Sigma|F_o|\,w^{1/2}$.

Table 2
Selected bond length and angles of **3a**; estimated standard deviations are shown in parentheses

Ru(1)-C(1)	2.157(10)	Ru(1)-Cl(1)	2.429(2)
Ru(1)-C(2)	2.157(10)	Ru(1)-N(1)	2.092(7)
Ru(1)-C(3)	2.156(9)	Ru(1)-O(1)	2.049(6)
Ru(1)-C(4)	2.214(10)	Cl(1)-Ru(1)-O(1)	84.4(2)
Ru(1)-C(5)	2.162(9)	Cl(1)-Ru(1)-N(1)	85.8(2)
Ru(1)-C(6)	2.157(8)	O(1)-Ru(1)-N(1)	86.7(3)

3.1. *[(η^6-p-^{i}PrC$_6$H$_4$Me)Ru(NO$_2$pesa)Cl] 2*

N-[(*S*)-1-Phenylethyl]-4-nitrosalicylaldimine, NO_2pesaH, (568 mg, 2.10 mmol), was dissolved in methylene chloride. After adding KO^{t}Bu (257 mg, 2.29 mmol), the mixture was stirred for 1 h at room temperature. The suspension was cooled to 0°C and [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$ (612 mg, 1.00 mmol) was added. After stirring for 3 h and filtration through Celite, the solution was evaporated. The red solid was washed twice with 10 ml of acetone:petroleum ether (1:8) and three times with 10 ml of petroleum

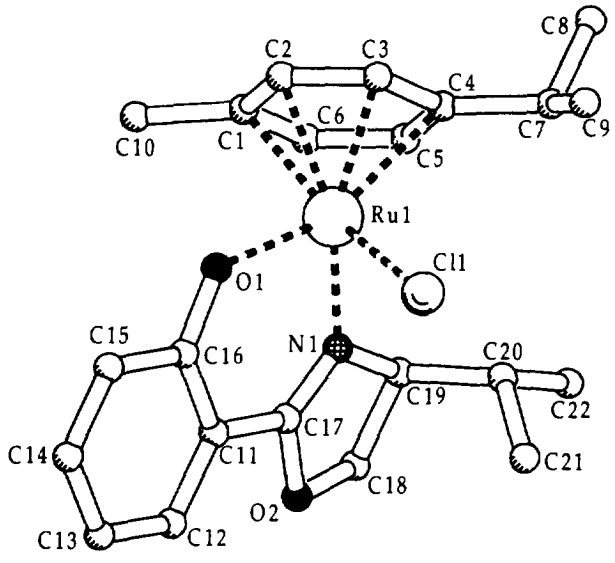


Fig. 1. PLATON plot of **3a** showing the labeling scheme used. Hydrogen atoms have been omitted for clarity

ether and dried. The product was dissolved in methylene chloride (5 ml) and ether was added (5 ml). The complex precipitated at room temperature.

Yield 510 mg (0.94 mmol, 47%). The following analytical data refer to the 81:19 mixture of **2a**:**2b**. M.p. 235–237°C (decomp.). IR (KBr): 1625 (C=N), 1548, 1311 (NO_2) cm^{-1}. ^1H NMR data for the less preferred diastereomer are given in parentheses, when different to the preferred diastereomer. ^1H NMR (250 MHz, $CDCl_3$): 8.09–7.82 (m, 2H, sal-*H3*, sal-*H5*), 8.02 (s, 1H, N=C*H*), 7.68–7.32 (m, 5H, *Ph*), 6.92 (6.86) (d, $^3J_{H6,H5}$=9.3 Hz, 1H, sal-*H6*), 5.88 (5.70) (q, $^3J_{CH,CH_3}$=7.0 Hz, 1H, C*H*CH_3), 5.36/5.24 (5.61/5.46) (AB, ^3J=6.3 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 5.01/4.81 (5.40/5.17) (AB, ^3J=5.6 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 2.66 (2.82) (sept, $^3J_{CH,CH_3}$=6.9 Hz, 1H, C*H*-^{i}Pr), 2.17 (2.20) (s, 3H, CH_3-cym), 1.79 (1.99) (d, $^3J_{CH_3,CH}$=7.0 Hz, CHCH_3), 1.18 (1.28) (d, $^3J_{CH_3,CH}$=6.9 Hz, CH_3–^{i}Pr), 1.04 (1.16) (d, $^3J_{CH_3,CH}$=6.9 Hz, CH_3–^{i}Pr). $[\alpha]_D^{20}$=−410 (c=0.4, $CHCl_3$). Anal. calcd for $C_{25}H_{27}ClN_2O_3Ru$ (540.03): C, 55.60; H, 5.04; N, 5.19. Found: C, 55.26; H, 5.15; N, 5.18. FD MS (CH_2Cl_2): m/z (%)=540 (M, 100), rel. to ^{102}Ru.

3.2. *[(η⁶-p-^{i}PrC$_6$H$_4$Me)Ru(oxazsa)Cl] 3*

(4*S*)-2-(2-Hydroxyphenyl)-4-isopropyl-2-oxazoline (432 mg, 2.10 mmol), KO^{t}Bu (257 mg, 2.29 mmol) and [(η⁶-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$ (612 mg, 1.00 mmol) were reacted and worked up as described for **2**. The orange solid was dissolved in 15 ml of methylene chloride. Ether (40 ml) and petroleum ether (40 ml) were added. Complex **3** crystallized at −30°C. Recrystallization from 10 ml of methylene chloride/ether at room temperature afforded the product as an orange microcrystalline solid. A quantity (0.5 equiv.) of methylene chloride was found in the crystals.

Yield 915 mg (1.93 mmol, 97%). The following analytical data refer to the 77:23 mixture of **3a**:**3b**. M.p. 194–195°C (decomp.). IR (KBr): 1622 (C=N) cm^{-1}. ^1H NMR data for the less preferred diastereomer are given in parentheses, when different to the preferred diastereomer. ^1H NMR (250 MHz, $CDCl_3$): 7.39 (dd, $^3J_{H3,H4}$=8.0 Hz, $^4J_{H3,H5}$=1.9 Hz, 1H, sal-*H3*), 7.12 (ddd, $^3J_{H5,H6}$=8.6 Hz, $^3J_{H5,H4}$=6.8 Hz, $^4J_{H5,H3}$=1.9 Hz, 1H, sal-*H5*), 6.92 (ddd, $^3J_{H6,H5}$=8.6 Hz, $^4J_{H6,H4}$=1.2 Hz, $^5J_{H6,H3}$=0.5 Hz, 1H, sal-*H6*), 6.35 (ddd, $^3J_{H4,H3}$=8.0 Hz, $^3J_{H4,H5}$=6.8 Hz, $^4J_{H4,H6}$=1.2 Hz, 1H, sal-*H4*), 5.43 (bs, 2H, *H2/H3*- or

H4/H5-cym), 5.35/4.97 (AB, ^3J=5.7 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 4.55–4.33 (m, 3H, NC*H*, OCH_2), 2.81 (sept, $^3J_{CH,CH_3}$=6.9 Hz, C*H*–^{i}Pr-cym), 2.73–2.64 (m, 1H, C*H*–^{i}Pr-ox), 2.25 (s, 3H, CH_3-cym), 1.27 (d, $^3J_{CH_3,CH}$=6.9 Hz, CH_3–^{i}Pr-cym), 1.17 (d, $^3J_{CH_3,CH}$=6.9 Hz, CH_3–^{i}Pr-cym), 1.00 (d, $^3J_{CH_3,CH}$=7.2 Hz, CH_3–^{i}Pr-ox), 0.81 (d, $^3J_{CH_3,CH}$=7.2 Hz, CH_3–^{i}Pr-ox). ^{13}C NMR (62.9 MHz, $CDCl_3$): 168.7 (sal-*C1*), 162.4 (sal-*C2*), 133.8 sal-*C5*), 129.1 (sal-*C3*), 123.1 (sal-*C6*), 113.4 (sal-*C4*), 108.4 (ox-*C2*), 101.5 (cym-*C4*), 97.0 (cym-*C1*), 85.1, 83.4, 80.9, 79.8 (cym-*C2*, -*C3*, -*C5*, -*C6*), 76.0 (ox-*C4*), 66.9 (ox-*C5*), 30.6 (*C*H–^{i}Pr-cym), 29.9 (*C*H–^{i}Pr-ox), 22.7, 21.8 (*C*H_3–^{i}Pr-cym), 19.8 (*C*H_3–^{i}Pr-ox), 18.7 (*C*H_3), 14.9 (*C*H_3–^{i}Pr-ox). $[\alpha]_D^{20}$=+733 (c=0.4, $CHCl_3$). Anal. calcd for $C_{22}H_{28}ClNO_2Ru$ (474.99): C, 55.63; H, 5.94; N, 2.95. Calcd for $C_{22}H_{28}ClNO_2Ru \cdot 0.5CH_2Cl_2$: C, 52.23; H, 5.65; N, 2.71. Found: C, 52.32; H, 5.74; N, 2.70. FD MS (CH_2Cl_2) m/z (%)=475 (M, 100), rel. to ^{102}Ru.

3.3. [(η^6-p-^{i}*PrC*$_6$*H*$_4$*Me)Ru(pepy)Cl] 4*

Sodium hydride (127 mg, 5.29 mmol) was suspended in 70 ml of methylene chloride at 0°C. After adding a cooled solution of 2-*N*-[(*S*)-1-phenylethyl]pyrrolcarbaldimine (1.05 g, 5.32 mg) in 2 ml methylene chloride, the mixture was stirred for 2 h. Subsequently, the solution was cooled to −15°C and [(η^6-*p*-^{i}PrC$_6$H$_4$Me)RuCl$_2$]$_2$ (1.07 g, 1.75 mmol) was added. After 3 h, the dark brown suspension was filtered through Celite and the solution was evaporated. The residue was purified by column chromatography (SiO_2, methylene chloride:ethyl acetate=1:1). The solution was concentrated to 10 ml. Then 50 ml of ether and 200 ml of petroleum ether were added. At −30°C the complex precipitated.

Yield 1.24 g (2.6 mmol, 74%). The following analytical data refer to the 61:39 mixture of **4a**:**4b**. M.p. 221–223°C (decomp.). IR (KBr): 1584/1578 (C=N) cm^{-1}. ^{1}H NMR data for the less preferred diastereomer are given in parentheses, when different to the preferred diastereomer. ^{1}H NMR (250 MHz, $CDCl_3$): 7.70 (s, 1H, N=C*H*), 7.50–7.29 (m, 6H, *Ph*, pyr-*H5*), 6.64 (dd, $^3J_{H3,H4}$=3.9 Hz, $^4J_{H3,H5}$=1.0 Hz, 1 H, pyr-*H3*), 6.23 (dd, $^3J_{H4,H3}$=3.9 Hz, $^3J_{H4,H5}$=1.8 Hz, 1H, pyr-*H4*), 5.40 (4.99) (q, $^3J_{CH,CH_3}$=7.0 Hz, 1H, C*H*CH$_3$), 5.37/4.82 (5.45/4.89) (AB, ^3J=6.0 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 5.04/4.57 (5.09/4.14) (AB, ^3J=5.7 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 2.39 (sept, $^3J_{CH,CH_3}$=6.9 Hz, 1H, C*H*–^{i}Pr), 2.03 (2.09) (s, 3H, CH_3-cym), 1.65 (1.86) (d, $^3J_{CH_3,CH}$=7.0 Hz, CHCH_3), 0.98 (0.94) (d, $^3J_{CH_3,CH}$=6.9 Hz, CH_3-^{i}Pr), 0.71 (0.61) (d, $^3J_{CH_3,CH}$=6.7 Hz, CH_3–^{i}Pr). $[\alpha]_D^{20}$=−26 (c=0.5, $CHCl_3$). Anal. calcd for $C_{23}H_{27}ClN_2Ru$ (468.01): C, 59.03; H, 5.82; N, 5.99. Found: C, 59.01; H, 5.80; N, 5.97. FD MS (CH_2Cl_2): m/z (%)=468 (M, 100), rel. to ^{102}Ru.

3.4. [(η^6-p-^{i}*PrC*$_6$*H*$_4$*Me)Ru(pesa)I] 5*

[(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pesa)Cl] (101 mg, 0.20 mmol) and sodium iodide (300 mg, 2.00 mmol) were dissolved in 20 ml of methanol and stirred for 3 h. The solvent was evaporated, the residue was dissolved in 5 ml of methylene chloride and filtered through Celite. Evaporation afforded complex **5** as a red powder.

Yield 111 mg (0.19 mmol, 95%). ^{1}H NMR (250 MHz, $CDCl_3$): 7.86 (s, 1H, N=C*H*), 7.52–7.38 (m, 5H, *Ph*), 7.19 (ddd, $^3J_{H5,H6}$=8.6 Hz, $^3J_{H5,H4}$=6.8 Hz, $^4J_{H5,H3}$=1.8 Hz, 1H, sal-*H5*), 6.99 (dd, $^3J_{H3,H4}$=7.7 Hz, $^4J_{H3,H5}$=1.8 Hz, 1H, sal-*H3*), 6.95 (d, $^3J_{H6,H5}$=8.6 Hz, 1H, sal-*H6*), 6.45 (ddd, $^3J_{H4,H3}$=7.7 Hz, $^3J_{H4,H5}$=6.8 Hz, $^4J_{H4,H6}$=1.0 Hz, 1H, sal-*H4*), 5.89 (q, $^3J_{CH,CH_3}$=7.0 Hz, 1H, C*H*CH$_3$), 5.53/5.02 (AB, ^3J=5.9 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 5.11/4.66 (AB, ^3J=5.6 Hz, 2H, *H2/H3*- or *H4/H5*-cym), 2.81 (sept, $^3J_{CH,CH_3}$=7.0 Hz, C*H*-^{i}Pr), 2.28 (s, 3H, CH_3-cym), 1.79 (d, $^3J_{CH,CH_3}$=7.0 Hz, CHCH_3), 1.19 (d, $^3J_{CH_3,CH}$=7.0 Hz, CH_3–^{i}Pr), 1.03 (d, $^3J_{CH_3CH}$=7.0 Hz, CH_3–^{i}Pr). Anal. calcd for $C_{25}H_{28}INORu$ (586.48):

C, 51.20; H, 4.81; N, 2.39. Found: C, 50.85; H, 4.85; N, 2.27. FD MS (methylene chloride): m/z (%)=587 (M, 100), rel. to ^{102}Ru.

3.5. Crystallography

X-Ray diffraction data were collected at 20°C with a Syntex-Nicolet R3 diffractometer using Mo-K_α radiation (λ=0.71073 Å) with a graphite monochromator. The data were collected in the ω mode. The structure was solved using the Patterson–Fourier method with SHELXTL PLUS (release 4.2/800), PC version.[19] The hydrogen atoms were added in calculated positions with the option HFIX. The absolute configuration was checked on the basis of η=0.9(2). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen (e-mail: crysdata@FIZ-karlsruhe.de) on quoting the depository CSD 408759.

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