Synthesis of chiral-at-metal half-sandwich ruthenium(II) complexes with the CpH(PN$_{Ment}$) tripod ligand

Takashi Tsuno [a,*], Henri Brunner [b], Syushi Katano [a], Naoto Kinjyo [a], Manfred Zabel [b]

[a] *Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, 1-2-1 Izumi-cho, Narashino-schi, Chiba 275-8575, Japan*
[b] *Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany*

Abstract

Treatment of the chiral tripod ligand (L$_{Ment}$,S_C)-CpH(PN$_{Ment}$) with (Ph$_3$P)$_3$RuCl$_2$ in ethanol afforded the two chiral-at-metal diastereomers (L$_{Ment}$,S_C,R_{Ru})- and (L$_{Ment}$,S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru(PPh$_3$)Cl] (70% de) in which the cyclopentadienyl group and the P atom of the ligand coordinated at the metal center. The (L$_{Ment}$,S_C,R_{Ru})-diastereomer was isolated by crystallization from ethanol–pentane and its structure was established by X-ray crystallography. The (L$_{Ment}$,S_C,R_{Ru})-diastereomer epimerized in CDCl$_3$ solution at 60 °C in a first-order reaction with a half-life of 5.66 h. In alcoholic solution epimerization occurred at room temperature. Substitution of the chloride ligand in (L$_{Ment}$,S_C,R_{Ru})- and (L$_{Ment}$,S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru(PPh$_3$)Cl] by nitriles NCR (R = Me, Ph, CH$_2$Ph) in the presence of NH$_4$PF$_6$ gave mixtures of the diastereomers (L$_{Ment}$,S_C,R_{Ru})- and (L$_{Ment}$,S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru(PPh$_3$)NCR]PF$_6$. Treatment of (L$_{Ment}$,S_C,R_{Ru})- and (L$_{Ment}$,S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru(PPh$_3$)Cl] with piperidine or morpholine in the presence of NH$_4$PF$_6$ led to the chiral-at-metal diastereomers (L$_{Ment}$,S_C,R_{Ru})- and (L$_{Ment}$,S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru(PPh$_3$)NH$_3$]PF$_6$ (6% de).
© 2006 Elsevier B.V. All rights reserved.

Keywords: Ruthenium; Chirality; Metal configuration; Half-sandwich complexes; Ammine complexes

1. Introduction

Due to the recent progress in asymmetric organometallic catalysis, enantioselective synthesis has become one of the most effective methods for the preparation of enantiomerically enriched compounds and alternative strategies in this field are highly desired. In three-legged piano-stool complexes of the type [(η^n-Ar)M(LL′)X] (LL′ is a unsymmetrical chelate ligand and X is a monodentate ligand) the metal atom is a chiral center. These compounds have attracted much study in terms of the stereochemistry of substitution reactions at the chiral metal center [1–4]. In particular, there are many chiral-at-metal ruthenium compounds [(η^5-Cp)Ru(LL′)X] some of which can be used as catalysts in organic transformations. As usually the epimerization at the metal center is faster than the catalytic reaction, two

diastereomeric catalysts participate in product formation. Hence, it would be desirable to control the metal configuration in such complexes during catalysis.

The tripod ligands CpH(PN) = *rac*-**1** and CpH-(PN$_{Ment}$) = (L$_{Ment}$,S_C)-**2** (see Scheme 1, top) have three different binding sites, a cyclopentadiene system (CpH), a diphenylphosphanyl group (P), and a pyridine or 2-menth-oxy-substituted pyridine ring (N and N$_{Ment}$) connected by an asymmetric carbon atom. Separation of the CpH-(PN$_{Ment}$)-diastereomers (L$_{Ment}$,S_C) and (L$_{Ment}$,R_C) by fractional crystallization gave (L$_{Ment}$,S_C)-**2** resolved with respect to the asymmetric carbon atom at the branching position [5]. We reported the synthesis of the half-sandwich rhodium complex (L$_{Ment}$,S_C,R_{Rh})-**3** in which the ligand coordinated with Cp, P and N to the metal atom (see Scheme 1, bottom). The (S_C)-configuration of the tripod ligand (L$_{Ment}$,S_C)-**2** enforced (R_{Rh})-configuration at the metal center and inhibited any configuration change at the metal atom including substitution reactions of the Cl
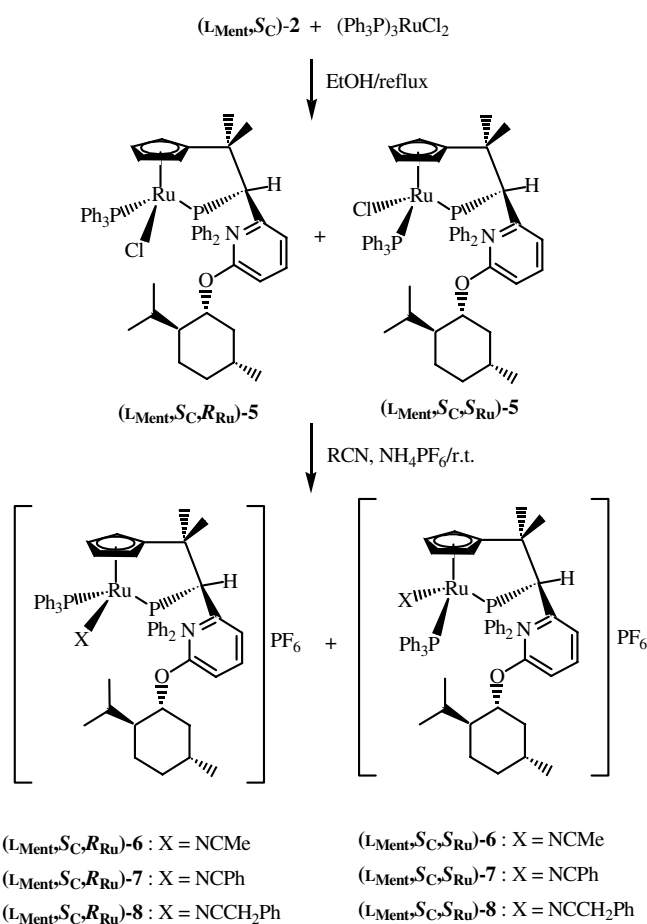
Scheme 1.

Scheme 2.
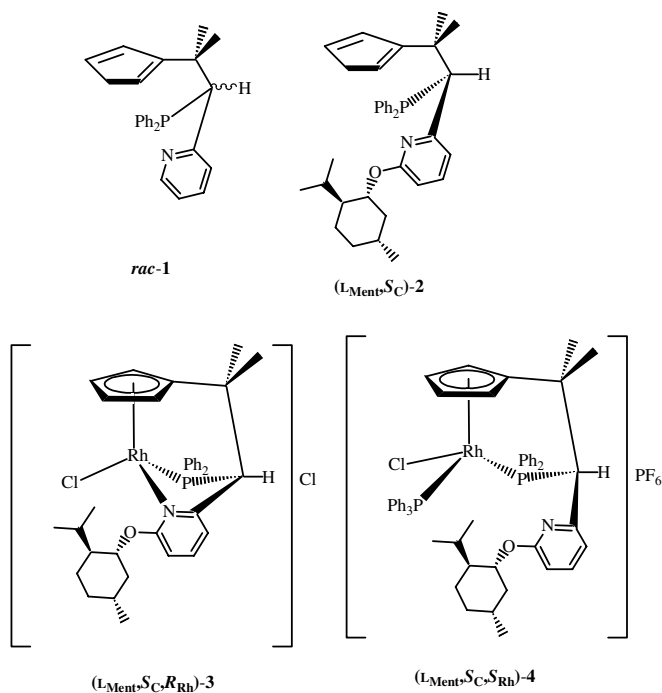
ligand by other halogen and pseudohalogen ligands [5,6]. However, the attempt to replace the Cl ligand by PPh$_3$ resulted in a decoordination of the pyridine part of the ligand which in the product (L$_{Ment}$,S$_C$,S$_{Rh}$)-**4** was only bound to the metal atom by Cp and P (see Scheme 1, bottom). Here we wish to report the synthesis of chiral-at-metal ruthenium complexes with the tripod ligand (L$_{Ment}$,S$_C$)-**2** resolved at the branching asymmetric carbon atom.

2. Results and discussion

The chiral tripod ligand CpH(PN$_{Ment}$), designated (L$_{Ment}$,S$_C$)-**2**, was prepared according to the published method [5]. The reaction of (L$_{Ment}$,S$_C$)-**2** with (Ph$_3$P)$_3$RuCl$_2$ in ethanol afforded orange crystals in 54% yield. The ^{1}H NMR spectrum of a solution of the crystals in CDCl$_3$ showed two sets of signals (see in Fig. 4) which we assigned to the two diastereomers (L$_{Ment}$,S$_C$,R$_{Ru}$)- and (L$_{Ment}$,S$_C$,S$_{Ru}$)-**5** differing only in the Ru-configuration (see Scheme 2, upper part). This assignment was corroborated by the appearance of two signals in the ^{31}P{^{1}H} NMR spectrum for a coordinated PPh$_3$ ligand at 42.8 (d, $^2J_{P-P} = 35.1$ Hz) and 43.6 ppm (d, $^2J_{P-P} = 35.1$ Hz) and the coordinated PPh$_2$ group of the tripod ligand at 75.0 (d, $^2J_{P-P} = 35.1$ Hz) and 62.8 ppm (d, $^2J_{P-P} = 35.1$ Hz), respectively (ratio 85:15). In boiling benzene the reaction of (L$_{Ment}$,S$_C$)-**2** with (Ph$_3$P)$_3$RuCl$_2$ gave the two diastereomers also in the ratio 85:15.

In the reaction of (L$_{Ment}$,S$_C$)-**2** with (Ph$_3$P)$_3$RuCl$_2$ the cyclopentadiene system of the tripod was transformed into the π-bonded cyclopentadienyl ligand occupying three coordination sites at the Ru atom in (L$_{Ment}$,S$_C$,R$_{Ru}$)- and (L$_{Ment}$,S$_C$,S$_{Ru}$)-**5**. According to the ^{31}P{^{1}H} NMR spectrum another two coordination sites in the half-sandwich complexes were occupied by P atoms. The sixth coordination position, however, was crucial. The ligand for this coordination site could have been the relatively nucleophilic chloride giving the neutral complex [Cp(PN$_{Ment}$)-Ru(PPh$_3$)Cl] **5** (similar to **4**) or the pyridine arm of the tripod ligand giving the ionic complex [Cp(PN$_{Ment}$)-Ru(PPh$_3$)]Cl (similar to **3**). A decision was possible on the basis of the mass spectra. The ESI-MS spectrum in dichloromethane-acetonitrile showed peaks at m/z 900 for [Cp(PN$_{Ment}$)Ru(PPh$_3$)]$^+$ and at m/z 941 for [Cp(PN$_{Ment}$)-Ru(PPh$_3$)NCMe]$^+$ (Fig. 1(a)). These ions do not contain chlorine. However, when the solvent was changed to dichloromethane only, a peak at 935 for [Cp(PN$_{Ment}$)-Ru(PPh$_3$)Cl]$^+$ was observed (Fig. 1(b)) indicating that complexes (L$_{Ment}$,S$_C$,R$_{Ru}$)- and (L$_{Ment}$,S$_C$,S$_{Ru}$)-**5** do contain a coordinated chloride ligand at the metal center. In a previous paper we had reported that the reaction of rac-**1** with (Ph$_3$P)$_3$RuCl$_2$ had given an ionic complex [Cp(PN)Ru(PPh$_3$)]Cl with the tripod ligand binding by Cp, P and N [7]. As in the FD mass spectrum in CH$_2$Cl$_2$ a peak at m/z 781 had been present this complex must be reformulated as the neutral complex [Cp(PN)Ru(PPh$_3$)Cl]
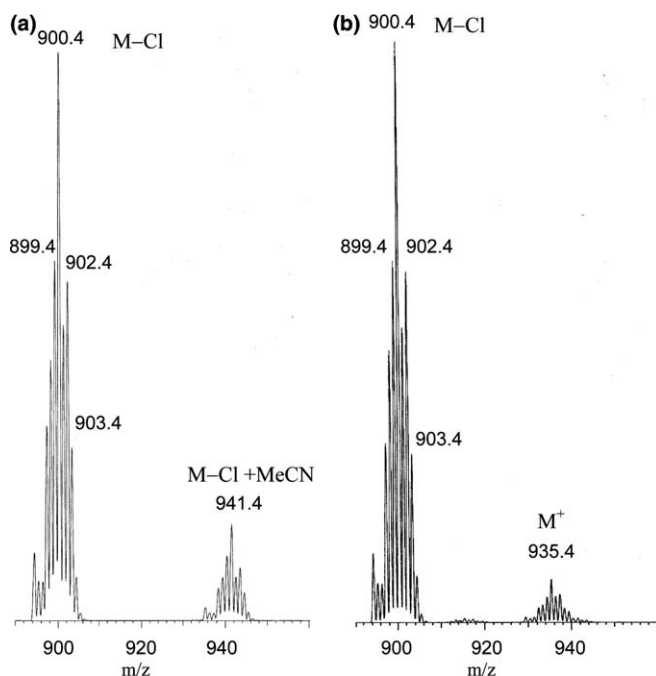
Fig. 1. ESI-MS spectra of **5**: (a) in CH$_2$Cl$_2$–MeCN, (b) in CH$_2$Cl$_2$.

with a coordinated chloride ligand and the tripod ligand binding by Cp and P only similar to complexes **5** of the present study.

Fortunately, slow diffusion of pentane into an ethanol or CH$_2$Cl$_2$ solution of the diastereomers afforded single crystals of the main diastereomer of **5** which an X-ray analysis proved to have (L$_{Ment}$,S$_C$,R$_{Ru}$)-configuration (see Fig. 2) [8]. The X-ray analysis corroborated the presence of the coordinated chloride ligand and the binding of the tripod ligand by Cp and P only.
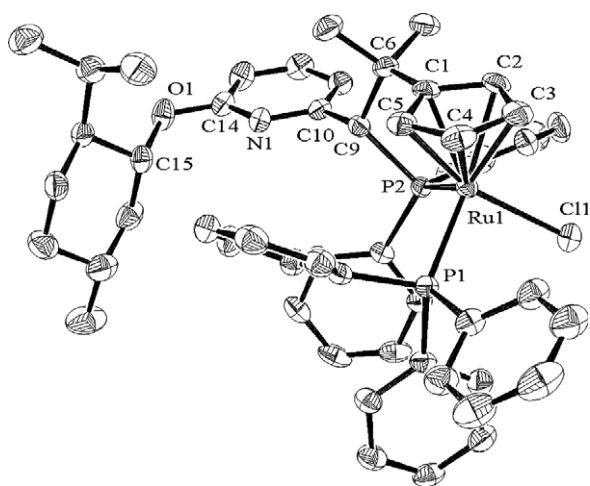
In the CD spectrum of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** a positive Cotton effect was observed at 286 nm in CH$_2$Cl$_2$ (see Fig. 3, solid line) which has the same intensity but opposite sign compared to (L$_{Ment}$,S$_C$,S$_{Rh}$)-**4** probably due to the opposite metal configurations [6].

(L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** was configurationally stable in the solid state. In solution, however, epimerization occurred. When the equilibration of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** (1.02×10^{-2} mol L^{-1}) with respect to the Ru-configuration to give the 85:15-mixture of (L$_{Ment}$,S$_C$,R$_{Ru}$)- and (L$_{Ment}$,S$_C$,S$_{Ru}$)-**5** was monitored by ^{1}H NMR in CDCl$_3$ at 60 °C, a rate constant k was calculated as 3.4×10^{-5} s^{-1} [half-life τ = 5.66 h] (see Fig. 4). The cyclopentadienyl proton at ca. 3 ppm and the methine proton on the chiral carbon atom of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** were observed as broad peaks (see Fig. 4, bottom). Surprisingly, although both proton signals shifted to lower magnetic field during isomerization to (L$_{Ment}$,S$_C$,S$_{Ru}$)-**5**, the signals of these protons appeared as sharp peaks shifted to higher magnetic field with the methine proton resolved as a doublet ($^2J_{P–H}$ = 10.1 Hz) after 2 weeks at room temperature (see Fig. 4, top). In the ^{31}P{^{1}H} NMR spectra a signal change of broad doublets to sharp doublets was also observed. Furthermore, when CD$_3$OD was added to a solution of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** in CDCl$_3$ at room temperature, the ratio of (L$_{Ment}$,S$_C$,R$_{Ru}$)- and (L$_{Ment}$,S$_C$,S$_{Ru}$)-**5** immediately reached the equilibrium state of 85:15.

The configurational lability of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** found in the present study contrasts with the configurational stability of (R$_C$,R$_{Ru}$)- and (R$_C$,S$_{Ru}$)-[CpRu(Prophos)Cl], Prophos = (R)-1,2-bis(diphenylphosphanyl)propane [9,10]. Both compounds have the same coordination frame Cp, P, P′, Cl with the chelate bridge in our complex between Cp and P and in the Prophos complex between P and P′.

Fig. 2. Molecular structure of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles and torsion angles (°): Ru1–Cl1 2.4626(8), Ru1–P1 2.3219(7), Ru1–P2 2.3056(6), Ru1–C1 2.170(3), Ru1–C2 2.210(3), Ru1–C3 2.230(3), Ru1–C4 2.227(3), Ru1–C5 2.167(3); Cl1–Ru1–P1 91.85(3), Cl1–Ru1–P2 97.17(2), P1–Ru1–P2 100.87(2), Ru1–P2–C9 101.08(8); Cl1–Ru1–P2–C(9) −159.90(8), P1–Ru1–P2–C9 106.81(8), Ru1–P2–C9–C6 42.66(18), Ru1–P2–C9–C10 179.20(19).

Fig. 3. CD spectra of (L$_{Ment}$,S$_C$,R$_{Ru}$)-**5** (——) and a mixture (88:12) of (L$_{Ment}$,S$_C$,R$_{Ru}$)- and (L$_{Ment}$,S$_C$,S$_{Ru}$)-**6** (·····) in CH$_2$Cl$_2$.
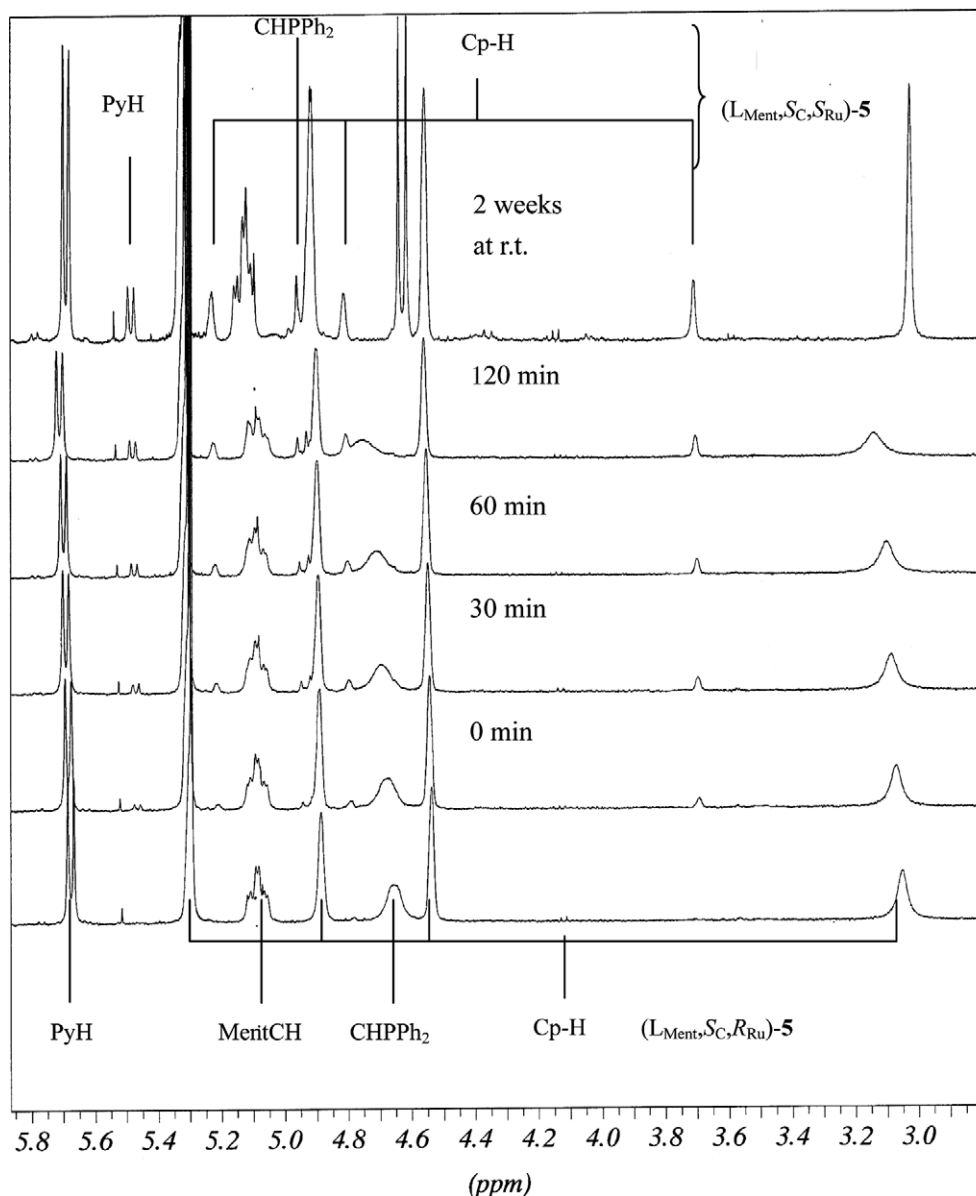
Fig. 4. Time resolved ^{1}H NMR spectra of isomerization of (L_{Ment}, S_C, R_{Ru})-**5** to (L_{Ment}, S_C, S_{Ru})-**5** at 60 °C in CDCl$_3$.

Whereas in our case the diastereomer ratio in the synthesis both in ethanol and in benzene was under thermodynamic control (see above), Consiglio et al. assigned the diastereomer ratio of 60:40 in their synthesis in refluxing benzene to kinetic control [9]. They state that their complex did not show epimerization in toluene at 80 °C for 96 h, but they claim epimerization in C$_6$D$_5$Cl at 80 °C. Furthermore, Consiglio et al. used their Prophos complex in methanol solution as the starting material for substitution reactions, which overwhelmingly occurred with retention of configuration at the Ru atom [11,12]. In contrast, our compound (L_{Ment}, S_C, R_{Ru})-**5** epimerized readily in alcoholic solution at room temperature probably due to the ancillary effect of the dangling pyridine ligand. An alternative explanation of the higher configurational stability of Consiglio's Prophos complex (R_C, S_{Ru})-[CpRu(Prophos)Cl] could be the

small chelate angle P–Ru–P' of 82.9° resisting widening necessary in any transition state for a change of the Ru configuration. The P1–Ru–P2 angle in (L_{Ment}, S_C, R_{Ru})-**5** is 100.87°. Conversely, in (L_{Ment}, S_C, R_{Ru})-**5** the Cp–Ru–P2 (Cp = ring centroid) angle to the tethered PPh$_2$ group and the Cp–Ru–P1 angle to the PPh$_3$ ligand are 113.16° and 117.90°, respectively. These angles are smaller than the Cp–Ru–P and Cp–Ru–P' angles in the Prophos complex (129.5° and 131.3°) [9].

The reaction of the racemic tripod CpH(PN) *rac*-**1** lacking the 2-menthoxy substituent with (Ph$_3$P)$_3$RuCl$_2$ in the presence of NH$_4$PF$_6$ had given the complex [Cp(PN)Ru-(PPh$_3$)]PF$_6$ in which the tripod was bonded by Cp, P and N [7]. We tried to synthesize the same type of complex with the resolved tripod CpH(PN$_{Ment}$) (L_{Ment}, S_C)-**2**. However, the reaction of the diastereomers (L_{Ment}, S_C, R_{Ru})- and

(L_{Ment},S_C,S_{Ru})-**5** with NH_4PF_6 in CH_2Cl_2 afforded yellow-black powders the ^1H NMR spectra of which showed only broad signals. Obviously, the N_{Ment} part of the tripod cannot coordinate at the metal center due to steric repulsion between the bulky 2-menthoxy moiety and the triphenylphosphane ligand.

Next, the reaction of diastereomerically pure (L_{Ment},S_C,R_{Ru})-**5** and NH_4PF_6 in the presence of acetonitrile was investigated giving mixtures of the diastereomers (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru-(PPh$_3$)NCMe]PF$_6$ **6** in 91% yield (76% de) (see Scheme 2). The CD spectrum of the mixture of (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**6** is shown in Fig. 3 (dotted line). It has been reported that both (S_C,R_{Ru})- and (S_C,S_{Ru})-[CpRu(Pro-phos)NCMe]PF$_6$ were stereospecifically obtained by substitution of the corresponding diastereomers (S_C,R_{Ru})- and (S_C,S_{Ru})-[CpRu(Prophos)Cl] with acetonitrile in the presence of NH$_4$PF$_6$ [11,12]. However, in our case complex **6** was isolated as a mixture of diastereomers. When benzonitrile and phenylacetonitrile were used as monodentate ligands and reacted with the mixture of the diastereomers (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**5** and NH$_4$PF$_6$, a mixture of the diastereomers of (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-[Cp(PN$_{Ment}$)Ru(PPh$_3$)NCR]PF$_6$ **7** (R = Ph) and **8** (R = CH$_2$Ph) was obtained. The diastereomeric excess decreased in the order **6** (76% de) > **7** (56% de) > **8** (44% de). In the ESI-MS spectra of these nitrile complexes a cation peak containing the corresponding coordinated nitrile was observed, when dichloromethane was used as the solvent. Small amounts of single crystals of **8** were obtained by recrystallization from CH$_2$Cl$_2$-ether. The X-ray analysis proved the (L_{Ment},S_C,R_{Ru})-configuration (see Fig. 5) [13]. There is a strong resemblance between the structures of (L_{Ment},S_C,R_{Ru})-**5** and (L_{Ment},S_C,R_{Ru})-**8**. As shown in Fig. 5, the phenyl group of phenylacetonitrile bends towards the ruthenium center minimizing space filling.
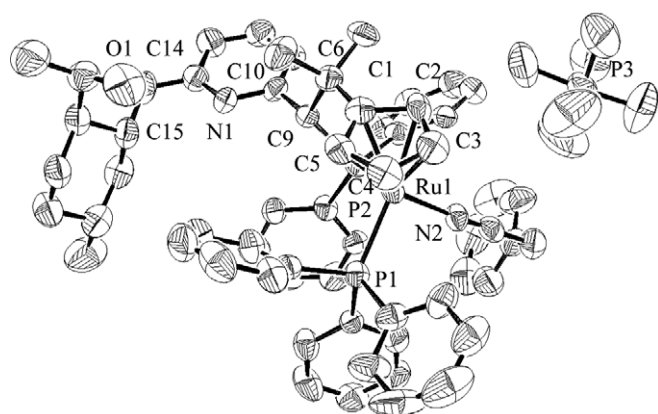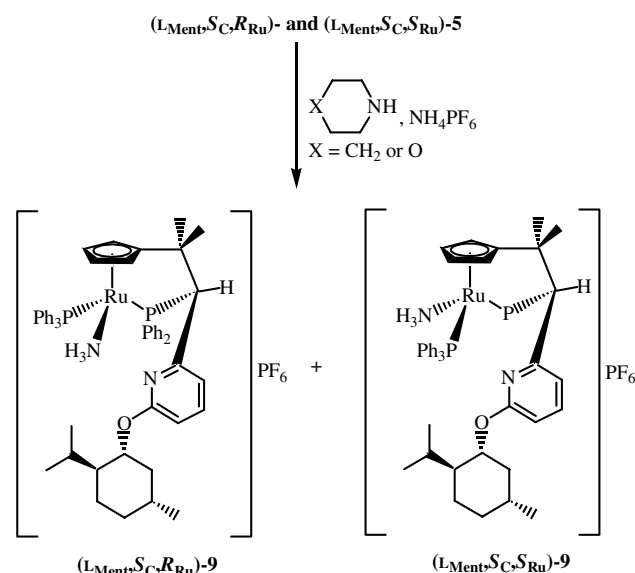
Using amines such as piperidine and morpholine as monodentate ligands we expected a stereospecific substitution of the chloride ligand in (L_{Ment},S_C,R_{Ru})-**5** due to the formation of a hydrogen bond between the incoming amines and the nitrogen of the dangling pyridine. However, both reactions of (L_{Ment},S_C,R_{Ru})-**5** with piperidine and morpholine, respectively, and NH$_4$PF$_6$ gave a mixture of diastereomers of the same compound (54% yield for piperidine; 63% for morpholine). The IR spectra showed N–H bands at 3356 and 3282 cm^{-1} [14]. In the ESI-MS spectrum in dichloromethane a cation of m/z 917 was observed which corresponded to [Cp(PN$_{Ment}$)Ru(PPh$_3$)-NH$_3$]$^+$. This suggests that the product was (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**9** with ammonia coordinated to the ruthenium center corroborated by the data of the elemental analysis (see Scheme 3). It has been reported that an ammine–ruthenium(II) complex [CpRu(PPh$_3$)$_2$NH$_3$]PF$_6$ was prepared by the reaction of [CpRu(PPh$_3$)$_2$Cl] with NH$_4$PF$_6$ in the presence of thallium(I) carbonate in methanol [14]. In this reaction, the thallium(I) cation scavenged the chloride anion and the carbonate ion removed a proton from the ammonium ion. The ammonia formed coordinated to the metal center. Similarly, in our case the amines piperidine and morpholine abstracted a proton from the ammonium ion of the additive NH$_4$PF$_6$ and the resulting ammonia replaced the chloride ligand in (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**5** to give (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**9**. The ratio of the diastereomers of **9** was determined to be 57:43 by ^{31}P{^{1}H} NMR analysis (6% de).

3. Experimental

3.1. General

All manipulations and reactions were carried out under an inert atmosphere of dry nitrogen or dry argon using

Fig. 5. Molecular structure of (L_{Ment},S_C,R_{Ru})-**8**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles and torsion angles (°): Ru1–N2 2.018(5), Ru1–P1 2.305(2), Ru1–P2 2.330(2), Ru1–C1 2.230(7), Ru1–C2 2.270(6), Ru1–C3 2.233(5), Ru1–C4 2.191(5), Ru1–C5 2.180(6); N2–Ru1–P1 93.7(2), N2–Ru1–P2 91.5(1), P1–Ru1–P2 102.00 (6), Ru1–P2–C9 102.02(2); N2–Ru1–P2–C(9) −159.4(2), P1–Ru1–P2–C9 106.5(2), Ru1–P2–C9–C6 42.1(4), Ru1–P2–C9–C10 179.2(4).

Scheme 3.

standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Melting points: Büchi SMP 20 or Yazawa micro hot stage (uncorrected). Mass spectra: Thermoquest Finnigan TSQ 7000. ^{1}H and ^{31}P{^{1}H} NMR: Bruker Avance-400 spectrometer (TMS as an internal standard for ^{1}H, H_3PO_4 as an external standard for ^{31}P). CD spectra: JASCO J-710 spectrophotometer. IR spectra: Beckman IR 4240 or BIO-RAD FTS 60A spectrometer. X-ray structure analysis: STOE-IPDS (Mo-$K\alpha$ radiation, 173 K, $\lambda = 0.71073$ Å, Oxford cryosystems cooler, graphite monochromator) or Rigaku RAXIS-RAPID (Cu-$K\alpha$ radiation, 296 K, $\lambda = 1.5419$ Å) diffractometers. (L_{Ment},S_C)-2,2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl-6-[(1R,2S,5R)-menthoxy]-pyridine (L_{Ment},S_C)-**2** was prepared as published [6]. $(Ph_3P)_3RuCl_2$ was commercially available.

3.1.1. $(L_{Ment},S_C,R_{Ru})/(L_{Ment},S_C,S_{Ru})$-[Chloro{2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine}triphenylphosphane]-ruthenium(II) (L_{Ment},S_C,R_{Ru})-5 and (L_{Ment},S_C,S_{Ru})-5

To a suspension of $(Ph_3P)_3RuCl_2$ (1.22 g, 1.27 mmol) in absolute ethanol (70 mL) was added a solution of (L_{Ment},S_C)-**2** (754 mg, 1.32 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was refluxed for 3 h and then cooled to room temperature. After evaporation of the solvent, the residue was chromatographed on silica gel using 25% EtOAc–petroleum ether (40/60) as an eluent to give a crude diastereomer mixture of (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**5**. Crystallization from CH_2Cl_2-pentane afforded (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**5** in 54% yield (651 mg) as orange crystals. Diastereomerically pure (L_{Ment},S_C,R_{Ru})-**5** was obtained by slow recrystallization from CH_2Cl_2–pentane or ethanol–pentane at room temperature. Mp. 158–159 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, signals of the (L_{Ment},S_C,S_{Ru})-isomer given in brackets if distinguishable): $\delta = 7.83$ (t, $^3J = 8.5$ Hz, 2H, Ph), [7.41 (t, $^3J = 7.2$ Hz, 2H, Ph)], 7.60–6.80 (m, 21H, Ph), [7.72–6.80 (m, 21H, Ph)], 6.88 (t, $^3J = 7.6$ Hz, 1H, Py–H^4), 6.64 (t, $^3J = 7.6$ Hz, 2H, Ph), [6.79 (t, $^3J = 7.4$ Hz, 1H, Py–H^4)], 6.43 (d, $^3J = 7.6$ Hz, 1H, Py–H$^{3/5}$), [6.41 (d, $^3J = 7.5$ Hz, 1H, Py–H$^{3/5}$)], 5.66 (d, $^3J = 7.6$ Hz, 1H, Py–H$^{3/5}$), [5.45 (d, $^3J = 7.5$ Hz, 1H, Py–H$^{3/5}$)], 5.26 (s, 1H, Cp–H), [5.19 (s, 1H, Cp–H)], 5.10 (dt, $^3J = 4.3$ Hz, $^3J = 10.7$ Hz, 1H, OCH), [4.96 (dt, $^3J = 4.3$ Hz, $^3J = 10.7$ Hz, 1H, OCH)], 4.86 (s, 1H, Cp–H), [5.09 (s, 1H, Cp–H)], 4.59 (d, $^2J_{P-H} = 10.2$ Hz, 1H, PPh$_2$CHPy), [4.92 (d, $^2J_{P-H} = 11.0$ Hz, 1H, PPh$_2$CHPy)], 4.58 (s, 1H, Cp–H), 3.06 (s, 1H, Cp–H), [3.77 (s, 1H, Cp–H)], 2.35 (br d, $J = 11.0$ Hz, 1H, Ment), 2.07–1.98 (m, 1H, Ment), 1.87–1.50 (m, 6H, Ment), 1.28 (s, 3H, CH$_3$), [1.18 (s, 3H, CH$_3$)], 1.17–1.10 (m, 1H, Ment), 1.07 (d, $^3J = 6.7$ Hz, 3H, CH$_3$), [0.93 (d, 3H, $^3J = 6.5$ Hz, 3H, CH$_3$)], 1.01 (s, 3H, CH$_3$), [1.07 (s, 3H, CH$_3$)], 0.90 (d, $^3J = 7.0$ Hz, 3H, CH$_3$), [0.99 (d, $^3J = 7.0$ Hz, 3H, CH$_3$)], 0.73 (d, $^3J = 7.0$ Hz, 3H, CH$_3$), [0.72 (d, $^3J = 7.0$ Hz, 3H, CH$_3$)] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 300 K, signals of

the (L_{Ment},S_C,S_{Ru})-isomer given in brackets if distinguishable): 162.12 (s, Py–C^2), 153.84 (d, $J_{C-P} = 6.9$ Hz, P–Ar–C), 138.32 (d, $J_{C-P} = 12.2$ Hz, P–Ar–CH), 137.34 (s, Py–CH), [137.43 (s, Py–CH)], 135.11–126.53 (m, Ar–C, Ar–CH, Py–CH, Py–C), 119.63 (s, Py–CH), 109.32 (s, Py–CH), [109.45 (s, Py–CH)], 86.32 (s, $J_{C-P} = 4.6$ Hz, Cp), 80.43 (br d, $J_{C-P} = 9.9$ Hz, Cp), 79.14 (br d, $J_{C-P} = 11$ Hz, Cp), 76.2 (s, Cp), 74.84 (d, $J_{C-P} = 19.8$ Hz, P–CH), 73.96 (s, Ment–CH), [74.14 (s, Ment–CH)], 60.00 (s, Cp), 47.63 (s, Ment–CH), 41.15 (s, Ment–CH$_2$), [40.87 (s, Ment–CH$_2$)], 38.19 (d, $^2J_{C-P} = 7.6$ Hz, CpCMe$_2$), [37.86 (d, $^2J_{C-P} = 6.1$ Hz, CpCMe$_2$)], 34.63 (s, Ment–CH$_2$), 31.87 (s, Ment–CH), [31.45 (s, Ment–CH)], 30.04 (d, $^3J_{C-P} = 17.5$ Hz, CpCMe_2), 29.71 (s, CpCMe_2), 26.37 (s, Ment–CH), 23.96 (s, Ment–CH$_2$), 23.12 (s, Ment–CH), 22.45 (s, Ment–Me), [22.18 (s, Ment–Me)], 20.72 (s, Ment–Me), [20.80 (s, Ment–Me)], 16.77 (s, Ment–Me), [16.97 (s, Ment–Me)] ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): (L_{Ment},S_C,R_{Ru})-**5**: $\delta = 42.8$ (d, $^2J_{P-P} = 35.1$ Hz, 1P), 62.8 (d, $^2J_{P-P} = 35.1$ Hz, 1P) ppm; (L_{Ment},S_C,S_{Ru})-**5**: $\delta = 43.6$ (d, $^2J_{P-P} = 35.1$ Hz, 1P), 75.0 (d, $^2J_{P-P} = 35.1$ Hz, 1P) ppm. MS spectra were shown in Fig. 1. $C_{54}H_{58}ClNOP_2Ru \cdot (CH_2Cl_2)_{1/2}$ (978.0): Calc. C, 66.93; H, 6.08; N, 1.43. Found: C, 66.60; H, 6.34; N, 1.31%.

3.1.2. $(L_{Ment},S_C,R_{Ru})/(L_{Ment},S_C,S_{Ru})$-⟨[Acetonitrile{2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine}-triphenylphosphane]ruthenium(II)⟩-hexafluorophosphate (L_{Ment},S_C,R_{Ru})-6 and (L_{Ment},S_C,S_{Ru})-6

To a solution of (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**5** (156 mg, 0.167 mmol, ratio 85:15) in a mixture of acetonitrile (5 mL) and CHCl$_3$ (15 mL) was added NH$_4$PF$_6$ (67 mg). The mixture was stirred for 18 h at room temperature and then evaporated in vacuo. The residue was washed with CHCl$_3$ and the filtrate was evaporated to give (L_{Ment},S_C,R_{Ru})- and (L_{Ment},S_C,S_{Ru})-**6** in 91% yield (158 mg) as light yellow crystals. Mp. 159–163 °C. IR (KBr): $v = 2245$ (CN) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 300 K, signals of the (L_{Ment},S_C,S_{Ru})-isomer given in brackets if distinguishable): $\delta = 7.90$–6.90 (m, 24H, Ph, Py–H^4), 6.71 (t, $^3J = 7.6$ Hz, 2H, Ph), [6.82 (t, $^3J = 7.1$ Hz, 2H, Ph)], 6.44 (d, $^3J = 8.3$ Hz, 1H, Py–H$^{3/5}$), [6.45 (d, $^3J = 8.1$ Hz, 1H, Py–H$^{3/5}$)], 5.67 (s, 1H, Cp–H), [5.75 (s, 1H, Cp–H)], 5.44 (d, $^3J = 7.6$ Hz, 1H, Py–H$^{3/5}$), [5.90 (br s, 1H, Py–H$^{3/5}$)], 5.21 (d, $^4J_{P-H} = 1.4$ Hz, 1H, Cp–H), [5.53 (s, 1H, Cp–H)], 4.92 (m, 1H, OCH), 4.76 (s, 1H, Cp–H), [4.62 (s, 1H, Cp–H)], 4.44 (d, $^2J_{P-H} = 11.2$ Hz, 1H, PCHPy), [4.91 (d, $^2J_{P-H} = 10.8$ Hz, 1H, PCHPy)], 4.01 (s, 1H, Cp–H), [4.10 (s, 1H, Cp–H)], 2.16 (br d, $^3J = 11.4$ Hz, 1H, Ment–H), 2.07–2.01 (m, 1H, Ment–H), 2.00 (s, 3H, CH$_3$CN), 1.83–1.50 (m, 4H, Ment–H), 1.52 (s, 3H, CH$_3$), [1.36 (s, 3H, CH$_3$)], 1.30–0.95 (m, 3H, Ment–H), 1.15 (s, 3H, CH$_3$), [1.23 (s, 3H, CH$_3$)], 1.02 (d, $^3J = 6.6$ Hz, 3H, CH$_3$), [1.16 (d, $^3J = 7.0$ Hz, 3H, CH$_3$)], 0.91 (d, $^3J = 7.0$ Hz, 3H, CH$_3$), [0.87 (d, $^3J = 7.0$ Hz, 3H, CH$_3$)], 0.75 (d, $^3J = 7.0$ Hz, 3H, CH$_3$), [0.65 (d,

$^3J = 6.9$ Hz, 3H, CH$_3$)] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 300 K, signals of the (L$_{Ment}$,S_C,S_{Ru})-isomer given in brackets if distinguishable): 162.32 (s, Py–C^2), [162.36 (s, Py–C^2)], 152.84 (d, $J_{C–P} = 8.2$ Hz, P–Ar–C), [153.20, br d, $J_{C–P} = 10.0$ Hz, P–Ar–C], 137.90 (s, Py–CH), [137.90 (s, Py–CH)], 135.36 (d, $J_{C–P} = 11.4$ Hz, P–Ar–CH), [136.68 (d, $J_{C–P} = 11.4$ Hz, P–Ar–CH)], 135.50 (d, $J_{C–P} = 38.1$ Hz, P–Ar–C), 133.13 (d, $J_{C–P} = 10.7$ Hz, P–Ar–CH), 132.60 (d, $J_{C–P} = 7.6$ Hz, P–Ar–CH), [132.50 (d, $J_{C–P} = 9.9$ Hz, P–Ar–CH)], 132.52–122.05 (m, P–Ar–C, P–Ar–CH, Py–C, Py–CH, CN), 118.60 (s, Py–CH), [119.14 (s, Py–CH)], 110.01 (s, Py–CH), [110.10 (s, Py–CH)], 90.30 (s, Cp), [88.32 (d, $J_{C–P} = 5.1$ Hz, Cp)], 81.70 (d, $J_{C–P} = 5.1$ Hz, Cp), [83.85 (d, $J_{C–P} = 5.1$ Hz, Cp)], 78.53 (d, $J_{C–P} = 8.7$ Hz, Cp–CH), [70.25 (d, $J_{C–P} = 9.2$ Hz, Cp)], 75.95 (d, $J_{C–P} = 19.7$ Hz, P–CH), [73.61 (d, $J_{C–P} = 21.3$ Hz, P–CH)], 74.73 (s, Ment–CH), [74.16 (br s, Ment–CH)], 61.50 (s, Cp), [65.87 (br s, Cp)], 47.50 (s, Ment–CH), [47.50 (s, Ment–CH)], 40.90 (s, Ment–CH$_2$), [40.73 (s, Ment–CH$_2$)], 38.40 (d, $^2J_{C–P} = 8.0$ Hz, CpCMe$_2$), [38.22 (d, $^2J_{C–P} = 6.7$ Hz, CpCMe$_2$)], 34.51 (s, Ment–CH$_2$), [34.44 (s, Ment–CH$_2$)], 31.63 (s, Ment–CH), [31.20 (s, Ment–CH)], 29.28 (d, $^3J_{C–P} = 19.1$ Hz, CpCMe_2), [29.48 (d, $^3J_{C–P} = 19.4$ Hz, CpCMe_2)], 29.22 (s, CpCMe_2), [29.22 (s, CpCMe_2)], 26.31 (s, Ment–CH), [26.40 (s, Ment–CH)], 24.01 (s, Ment–CH$_2$), [23.77 (s, Ment–CH$_2$)], 23.20 (s, Ment–CH), [21.90 (s, Ment–CH)], 22.29 (s, Ment–Me), [22.18 (s, Ment–Me)], 20.70 (s, Ment–Me), [20.91 (s, Ment–Me)], 16.95 (s, Ment–Me), [17.13 (s, Ment–Me)], 2.55 (s, CH_3CN), [3.96 (s, CH_3CN)] ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): (L$_{Ment}$,S_C,R_{Ru})-**6**: $\delta = 48.2$ (d, $^2J_{P–P} = 30.9$ Hz, 1P), 70.5 (d, $^2J_{P–P} = 30.9$ Hz, 1P), −143.5 (septet, $^1J_{P–F} = 712.3$ Hz, 1P) ppm; (L$_{Ment}$,S_C, S_{Ru})-**6**: $\delta = 48.2$ [overlapping with (L$_{Ment}$,S_C,R_{Ru})-**6** signal], 77.4 (br d, $^2J_{P–P} = 24.4$ Hz, 1P), −143.5 (septet, $^1J_{P–F} = 712.3$ Hz, 1P) ppm. ESI-MS (CH$_2$Cl$_2$, rel. int.) m/z = 941 (M, 18), 900 (M−MeCN, 100). C$_{56}$H$_{61}$F$_6$N$_2$OP$_3$Ru (1086.1): Calc. C, 61.93; H, 5.66; N, 2.58. Found: C, 61.85; H, 5.85; N, 2.58%.

3.1.3. (L$_{Ment}$,S_C,R_{Ru})/(L$_{Ment}$,S_C,S_{Ru})-⟨[Benzonitrile{2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine}-triphenyl-phosphane]ruthenium(II)⟩-hexafluorophosphate (L$_{Ment}$,S_C,R_{Ru})-7 and (L$_{Ment}$,S_C,S_{Ru})-7

Procedure as for **6**. Yield 49%. Mp. 156 °C. IR (KBr): $v = 2229$ (CN) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 273 K), signals of the (L$_{Ment}$,S_C,S_{Ru})-isomer given in brackets if distinguishable): $\delta = 7.69$–6.90 (m, 28H, Ph, Py–H^4), 6.71 (t, $^3J = 6.7$ Hz, 2H, Ph), [6.81 (t, $^3J = 7.0$ Hz, 2H, Ph)], 6.46 (d, $^3J = 8.4$ Hz, 1H, Py–H$^{3/5}$), [6.52 (d, $^3J = 7.3$ Hz, 1H, Py–H$^{3/5}$)], 5.80 (s, 1H, Cp–H), [5.80 (s, 1H, Cp–H)], 5.90 (d, $^3J = 7.4$ Hz, 1H, Py–H$^{3/5}$), [6.08 (br s, 1H, Py–H$^{3/5}$)], 5.30 (s, 1H, Cp–H), [5.30 (s, 1H, Cp–H)], 4.89 (dt, $^3J = 4.2$ Hz, $^3J = 11.0$ Hz, 1H, OCH), 4.85 (s, 1H, Cp–H), [4.72 (s, 1H, Cp–H)], 4.58 (d, $^2J_{P–H} = 11.1$ Hz, 1H, PyCHPPh$_2$), [4.98 (d, $^2J_{P–H} = 11.5$ Hz, 1H, PyCHPPh$_2$)], 4.14 (s, 1H, Cp–H), [4.14 (s, 1H, Cp–H)], 2.20–0.70 (m, 9H, Ment–H), 1.15 (s, 3H, CH$_3$), [1.29 (s, 3H, CH$_3$)], 1.18 (s, 3H, CH$_3$), [1.03 (s, 3H, CH$_3$)], 1.02 (d, $^3J = 6.4$ Hz, 3H, CH$_3$), 0.91 (d, $^3J = 6.9$ Hz, 3H, CH$_3$), [0.88 (d, $^3J = 7.1$ Hz, 3H, CH$_3$)], 0.74 (d, $^3J = 6.8$ Hz, 3H, CH$_3$), [0.62 (d, $^3J = 7.1$ Hz, 3H, CH$_3$)] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 300 K, signals of the (L$_{Ment}$,S_C,S_{Ru})-isomer given in brackets if distinguishable): 162.31 (s, Py–C), [162.69 (s, Py–C)], 152.67 (d, $J_{C–P} = 7.6$ Hz, P–Ar–C), 137.91 (s, Py–CH), [138.06 (s, Py–CH)], 136.73–123.36 (m, Ar–C, Ar–CH, Py–CH, Py–C, CN), 119.29 (s, Py–CH), [118.78 (s, Py–CH)], 110.06 (s, Py–CH), 91.30 (d, $J_{C–P} = 3.1$ Hz, Cp), [88.76 (d, $J_{C–P} = 6.1$ Hz, Cp)], 81.35 (d, $J_{C–P} = 2.9$ Hz, Cp), [84.03 (d, $J_{C–P} = 3.1$ Hz, Cp)], 79.28 (d, $J_{C–P} = 5.1$ Hz, Cp), [70.99 (d, $J_{C–P} = 5.1$ Hz, Cp)], 75.40 (d, $J_{C–P} = 19.8$ Hz, P–CH), [73.66 (d, $J_{C–P} = 25.2$ Hz, P–CH)], 74.65 (s, Ment–CH), [74.33 (s, Ment–CH)], 62.77 (s, Cp), [67.04 (br s, Cp)], 47.52 (s, Ment–CH), [47.47 (s, Ment–CH)], 40.90 (s, Ment–CH$_2$), [40.65 (s, Ment–CH$_2$)], 38.29 (d, $^2J_{C–P} = 6.9$ Hz, CpCMe$_2$), [38.44 (d, $^2J_{C–P} = 7.6$ Hz, CpCMe$_2$)], 34.53 (s, Ment–CH$_2$), [34.44 (s, Ment–CH$_2$)], 31.64 (s, Ment–CH), [31.17 (s, Ment–CH)], 29.32 (d, $^3J_{C–P} = 19.1$ Hz, CpCMe_2), 26.39 (s, Ment–CH), [26.29 (s, Ment–CH)], 23.98 (s, Ment–CH$_2$), [23.82 (s, Ment–CH$_2$)], 23.06 (s, Ment–CH), [21.92 (s, Ment–CH)], 22.32 (s, Ment–Me), [22.13 (s, Ment–Me)], 20.73 (s, Ment–Me), [21.00 (s, Ment–Me)], 16.96 (s, Ment–Me), [17.26 (s, Ment–Me)] ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 273 K): (L$_{Ment}$,S_C,R_{Ru})-**7**: $\delta = 69.9$ (br s, 1P), 48.3 (d, $^2J_{P–P} = 31.7$ Hz, 1P), −142.9 (septet, $^1J_{P–F} = 717.4$ Hz, 1P) ppm; (L$_{Ment}$,S_C,S_{Ru})-**7**: $\delta = 78.1$ (br s, 1P), 49.5 (br s, 1P), −142.9 (septet, $^1J_{P–F} = 717.4$ Hz, 1P) ppm. ESI-MS (CH$_2$Cl$_2$, rel. int.): m/z = 1003 (M, 4), 900 (M−PhCN, 100). C$_{61}$H$_{63}$F$_6$N$_2$OP$_3$Ru (1148.2): Calc. C, 63.81; H, 5.53; N, 2.44. Found: C, 63.66; H, 5.98; N, 2.62%.

3.1.4. (L$_{Ment}$,S_C,R_{Ru})/(L$_{Ment}$,S_C, S_{Ru})-⟨[Phenylacetonitrile-{2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine}-triphenylphosphane]ruthenium(II)⟩-hexafluorophosphate (L$_{Ment}$,S_C,R_{Ru})-8 and (L$_{Ment}$,S_C,S_{Ru})-8

Procedure as for **6**. Yield 71%. Mp. 141 °C. IR (KBr): $v = 2265$ (CN) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 300 K, signals of the (L$_{Ment}$,S_C,S_{Ru})-isomer given in brackets if distinguishable): $\delta = 7.80$–6.85 (m, 29H, Ph, Py–H^4), 6.75 (d, $^3J = 7.6$ Hz, 2H, NCCH$_2$Ph–H$^{2/6}$), 6.45 (d, $^3J = 7.6$ Hz, 1H, Py–H$^{3/5}$), [6.28 (d, $^3J = 7.6$ Hz, 1H, Py–H$^{3/5}$)], 5.82 (s, 1H, Cp–H), [5.82 (s, 1H, Cp–H)], 5.54 (d, $^3J = 7.3$ Hz, 1H, Py–H$^{3/5}$), [5.54 (br s, 1H, Py–H$^{3/5}$)], 5.38 (s, 1H, Cp–H), [5.67 (s, 1H, Cp–H)], 4.96 (dt, $^3J = 4.2$ Hz, $^3J = 10.8$ Hz, 1H, OCH), 4.66 (br s, 1H, Cp–H), [4.66 (br s, 1H, Cp–H)], 4.54 (d, $^2J_{P–H} = 10.8$ Hz, 1H, PyCHPPh$_2$), [4.92 (d, $^2J_{P–H} = 11.5$ Hz, 1H, PyCHPPh$_2$)], 3.94 (d, $^2J = 18.6$ Hz, 1H, CHCN), [3.56 (d, $^2J = 18.6$ Hz, 1H, CHCN)], 3.88 (d, $^2J = 18.6$ Hz, 1H, CHCN), [2.97 (d, $^2J = 18.6$ Hz, 1H, CHCN)], 3.68 (s, 1H, Cp–H), [3.76 (s, 1H, Cp–H)], 2.20–

0.70 (m, 9H, Ment–H), 1.39 (s, 3H, CH$_3$), [1.21 (s, 3H, CH$_3$)], 1.09 (s, 3H, CH$_3$), [1.05 (s, 3H, CH$_3$)], 1.05 (d, ^3J = 6.6 Hz, 3H, CH$_3$), 0.90 (d, ^3J = 7.6 Hz, 3H, CH$_3$), [0.86 (d, ^3J = 7.1 Hz, 6H, CH$_3$)], 0.73 (d, ^3J = 6.8 Hz, 3H, CH$_3$), [0.62 (d, ^3J = 7.1 Hz, 3H, CH$_3$)] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 300 K, signals of the (L$_{Ment}$,S_C,R_{Ru})-isomer given in brackets if distinguishable): 162.28 (s, Py–C), [162.35 (s, Py–C)], 152.69 (d, J_{C-P} = 7.9 Hz, P–Ar–C), 137.75 (s, Py–CH), [138.00 (s, Py–CH)], 138.63–123.13 (m, Ar–C, Ar–CH, Py–CH, Py–C, CN), 119.28 (s, Py–CH), [118.57 (s, Py–CH)], 109.94 (s, Py–CH), [110.04 (s, Py–CH)], 90.46 (d, J_{C-P} = 3.8 Hz, Cp), [89.22 (br s, Cp)], 82.85 (d, J_{C-P} = 2.3 Hz, Cp), 79.93 (d, J_{C-P} = 7.6 Hz, Cp), 75.44 (d, J_{C-P} = 19.0 Hz, P–CH), [73.66 (d, J_{C-P} = 25.2 Hz, P–CH)], 74.47 (s, Ment–CH), [74.31 (s, Ment–CH)], 62.33 (s, Cp), [66.75 (br s, Cp)], 47.52 (s, Ment–CH), [47.47 (s, Ment–CH)], 40.96 (s, Ment–CH$_2$), [40.66 (s, Ment–CH$_2$)], 38.12 (d, $^2J_{C-P}$ = 6.9 Hz, CpCMe$_2$), [38.46 (d, $^2J_{C-P}$ = 7.6 Hz, CpCMe$_2$)], 34.53 (s, Ment–CH$_2$), [34.46 (s, Ment–CH$_2$)], 31.74 (s, Ment–CH), [31.17 (s, Ment–CH)], 29.66 (d, $^3J_{C-P}$ = 19.8 Hz, CpCMe_2), 25.63 (s, PhCH_2), [23.92 (s, PhCH_2)], 26.36 (s, Ment–CH), [22.15 (s, Ment–CH)], 23.98 (s, Ment–CH$_2$), [23.82 (s, Ment–CH$_2$)], 22.90 (s, Ment–CH), [21.92 (s, Ment–CH)], 22.37 (s, Ment–Me), [22.84 (s, Ment–Me)], 20.69 (s, Ment–Me), [20.96 (s, Ment–Me)], 16.83 (s, Ment–Me), [17.22 (s, Ment–Me)] ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 300 K): (L$_{Ment}$,S_C,R_{Ru})-**8**: δ = 70.0 (br d, $^2J_{P-P}$ = 29.7 Hz, 1P), 48.4 (d, $^2J_{P-P}$ = 29.7 Hz, 1P), −142.8 (septet, $^1J_{P-F}$ = 718.5 Hz, 1P) ppm; diastereomer (L$_{Ment}$,S_C,S_{Ru})-**8**: δ = 78.0 (br d, $^2J_{P-P}$ = 30.0 Hz, 1P), 49.4 (br d, $^2J_{P-P}$ = 30.0 Hz, 1P), −142.8 (septet, $^1J_{P-F}$ = 718.5 Hz, 1P) ppm. ESI-MS (CH$_2$Cl$_2$, rel. int.): m/z = 1017 (M, 5), 900 (M–PhCH$_2$CN, 100). C$_{62}$H$_{65}$F$_6$N$_2$OP$_3$Ru (1148.2): Calc. C, 64.08; H, 5.64; N, 2.41. Found: C, 63.71; H, 6.00; N, 2.47%.

3.1.5. (L$_{Ment}$,S_C,R_{Ru})/(L$_{Ment}$,S_C,S_{Ru})-⟨[Ammine{2-(2-cyclopentadienyl-1-diphenylphosphanyl-2-methylprop-1-yl)-6-[(1R,2S,5R)-menthoxy]pyridine}-triphenylphosphane]ruthenium(II)⟩-hexafluorophosphate (L$_{Ment}$,S_C,R_{Ru})-9 and (L$_{Ment}$,S_C,S_{Ru})-9

A mixture (85:15) of (L$_{Ment}$,S_C,R_{Ru})-**5** and (L$_{Ment}$,S_C,S_{Ru})-**5** (150 mg, 0.160 mmol) was dissolved in CH$_2$Cl$_2$. To the solution was added NH$_4$PF$_6$ (330 mg, 1.01 mmol) and then stirred for 30 min at room temperature. To the suspension was added amine (1.00 mmol). The mixture was stirred for 24 h and filtrated. The mother liquor was evaporated in vacuo. The residue was chromatographed on silica gel using EtOAc/ether (1:1, v/v) as an eluent to give (L$_{Ment}$,S_C,R_{Ru})-**9** and (L$_{Ment}$, S_C,S_{Ru})-**9** (57:43 ratio; 54% from piperidine; 63% from morpholine). Mp. 153 °C. IR (KBr): v = 3356, 3283 (NH) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 273 K, signals of the (L$_{Ment}$,S_C,R_{Ru})-isomer given in brackets if distinguishable): δ = 7.91–6.60 (m, 26H, Ph, Py–H^4), 6.45 (d, ^3J = 7.9 Hz, 1H, Py–H$^{3/5}$), [6.43 (d, ^3J = 7.9 Hz, 1H, Py–

H$^{3/5}$)], 5.82 (br s, 1H, Py–H$^{3/5}$), 5.62 (s, 1H, Cp–H), [5.39 (s, 1H, Cp–H)], 5.34 (s, 1H, Cp–H), [5.21 (s, 1H, Cp–H)], 4.97 (d, $^2J_{P-H}$ = 11.0 Hz, 1H, PCHPy), [4.23 (d, $^2J_{P-H}$ = 13.4 Hz, 1H, PCHPy)], 4.76 (s, 1H, Cp–H), [5.06 (s, 1H, Cp–H)], 4.71 (m, 1H, OCH), [4.88 (dt, ^3J = 4.3 Hz, ^3J = 10.4 Hz, 1H, OCH)], 4.06 (s, 1H, Cp–H), [4.32 (s, 1H, Cp–H)], 2.34–0.80 (m, 12H, Ment–H, NH$_3$), 1.25 (s, 3H, CH$_3$), [1.20 (s, 3H, CH$_3$)], 1.10 (s, 3H, CH$_3$), [1.10 (s, 3H, CH$_3$)], 0.90 (d, ^3J = 6.7 Hz, 3H, CH$_3$), [0.99 (d, ^3J = 6.7 Hz, 3H, CH$_3$)], 0.86 (d, ^3J = 7.3 Hz, 3H, CH$_3$), [0.91 (d, ^3J = 7.0 Hz, 3H, CH$_3$)], 0.65 (d, ^3J = 7.3 Hz, 3H, CH$_3$), [0.74 (d, ^3J = 6.7 Hz, 3H, CH$_3$)] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 300 K, signals of the (L$_{Ment}$,S_C,S_{Ru})-isomer given in brackets if distinguishable): 162.38 (s, Py–C^2), [162.49 (s, Py–C^2)], 153.18 (d, J_{C-P} = 9.2 Hz, P–Ar–C), [153.28, d, J_{C-P} = 7.6 Hz, P–Ar–C], 137.78 (s, Py–CH), [137.78 (s, Py–CH)], 136.75–122.41 (m, P–Ar–C, P–Ar–CH, Py–C, Py–CH), 118.47 (s, Py–CH), [118.82 (s, Py–CH)], 110.04 (s, Py–CH), [110.10 (s, Py–CH)], 87.79 (d, J_{C-P} = 5.3 Hz, Cp), 82.31 (d, J_{C-P} = 6.1 Hz, Cp), 74.07 (s, Ment–CH), [75.16 (s, Ment–CH)], 73.40 (d, J_{C-P} = 21.3 Hz, P–CH), 68.33 (d, J_{C-P} = 10.7 Hz, Cp), 58.95 (s, Cp), [64.46 (br s, Cp)], 47.55 (s, Ment–CH), 40.92 (s, Ment–CH$_2$), [40.76 (s, Ment–CH$_2$)], 37.96 (d, $^2J_{C-P}$ = 6.1 Hz, CpCMe$_2$), [38.43 (d, $^2J_{C-P}$ = 8.4 Hz, CpCMe$_2$)], 34.53 (s, Ment–CH$_2$), [34.47 (s, Ment–CH$_2$)], 31.63 (s, Ment–CH), [31.18 (s, Ment–CH)], 28.99 (d, $^3J_{C-P}$ = 18.3 Hz, CpCMe_2), [29.62 (d, $^3J_{C-P}$ = 19.1 Hz, CpCMe_2)], 26.47 (s, Ment–CH), [26.35 (s, Ment–CH)], 24.01 (s, Ment–CH$_2$), [23.77 (s, Ment–CH$_2$)], 23.20 (s, Ment–CH), [21.90 (s, Ment–CH)], 22.24 (s, Ment–Me), [23.73 (s, Ment–Me)], 20.67 (s, Ment–Me), [20.89 (s, Ment–Me)], 17.02 (s, Ment–Me), [17.11 (s, Ment–Me)] ppm. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 273 K): (L$_{Ment}$,S_C,R_{Ru})-**9**: δ = 76.5 (d, $^2J_{P-P}$ = 30.1 Hz, 1P), 51.5 (d, $^2J_{P-P}$ = 30.1 Hz, 1P), −143.2 (septet, $^1J_{P-F}$ = 713.6 Hz, 1P) ppm; (L$_{Ment}$,S_C,S_{Ru})-**9**: δ = 79.1 (br s, 1P), 52.4 (br s, 1P), −143.2 (septet, $^1J_{P-F}$ = 713.6 Hz, 1P) ppm. ESI-MS (CH$_2$Cl$_2$, rel. int.): m/z = 917 (M, 5), 900 (M−NH$_3$, 100). C$_{54}$H$_{61}$F$_6$N$_2$OP$_3$Ru (1062.1): Calc. C, 61.07; H, 5.79; N, 2.64. Found: C, 61.19; H, 5.61; N, 2.66%.

4. Supplementary material

Acknowledgement

References

[1] H. Brunner, Eur. J. Inorg. Chem. (2001) 905.

[2] G. Consiglio, F. Morandini, Chem. Rev. 87 (1987) 761.

[3] H. Brunner, Angew. Chem., Int. Ed. 38 (1999) 1194.

[4] H. Brunner, Adv. Organomet. Chem. 18 (1980) 151.

[5] H. Brunner, A. Köllnberger, A. Mehmood, T. Tsuno, M. Zabel, Organometallics 23 (2004) 4006.

[6] H. Brunner, A. Köllnberger, A. Mehmood, T. Tsuno, M. Zabel, J. Organomet. Chem. 689 (2004) 4244.

[7] H. Brunner, C. Valério, M. Zabel, New J. Chem. 24 (2000) 275.

[8] Crystal data for (L_{Ment},S_C,R_{Ru})-**5**: $C_{54}H_{58}ClNOP_2Ru$, FW; 935.47, monoclinic, $P2_1$, $a = 14.0085(14)$ Å, $b = 13.2789(8)$ Å, $c = 14.4258(13)$ Å, $\beta = 101.792(11)°$, $V = 2626.8(4)$ Å^3, $Z = 2$, $D_C = 1.183$ g cm^{-3}, abs. coeff. = 0.445 mm^{-1}, θ range; 2.13–25.83°, temperature 173(1) K, $F(0\,0\,0) = 976$, number of reflections/unique = 10042/10042, R_1/wR_2 ($I > 2\sigma I$) = 0.0288/0.0740, R_1/wR_2 (all data) = 0.0306/0.0747, largest difference peak/hole = 0.551/−1.005 e Å^3, GOF = 1.034.

[9] F. Morandini, G. Consiglio, B. Straub, G. Ciani, A. Sironi, J. Chem. Soc., Dalton Trans. (1983) 2293.

[10] G. Consiglio, F. Morandini, F. Bangerter, Inorg. Chem. 21 (1982) 455.

[11] F. Morandini, G. Consiglio, V. Lucchini, Organometallics 4 (1985) 1202.

[12] F. Morandini, G. Consiglio, G. Ciani, A. Sironi, Inorg. Chim. Acta 82 (1984) L27.

[13] Crystal data for (L_{Ment},S_C,R_{Ru})-**8**: $C_{62}H_{65}F_6N_2OP_3Ru$, FW 1162.19, monoclinic, $P2_1$, $a = 14.427(1)$ Å, $b = 13.607(1)$ Å, $c = 14.624(1)$ Å, $\beta = 103.516(4)°$, $V = 2791.5(3)$ Å^3, $Z = 2$, $D_C = 1.183$ g cm^{-3}, abs. coeff. = 3.614 mm^{-1}, θ range; 3.1–68.3°, temperature 296.1 K, $F(0\,0\,0) = 12046$, number of reflections/unique = 5314/5004, R/wR ($I > 2\sigma(I)$) = 0.0440/0.0460, largest difference peak/hole = 0.69/−0.64 e Å^3, GOF = 2.250.

[14] F.M. Conroy-Lewis, S.J. Simpson, J. Organomet. Chem. 396 (1990) 83.