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Synthesis and structure of chiral-at-metal complexes with the ligand (*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline

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Abstract

Half-sandwich complexes of formula [(η^n-ring)MClL]PF_6 [L = (*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline; (η^n-ring)M = (η^5-C_5Me_5)Rh; (η^5-C_5Me_5)Ir; (η^6-*p*-MeC_6H_4*i*Pr)Ru; (η^6-*p*-MeC_6H_4*i*Pr)Os] have been prepared and spectroscopically characterised. The molecular structures of the rhodium and iridium compounds have been determined by X-ray crystallography. The related solvate complexes [(η^5-C_5Me_5)ML(Me_2CO)]$^{2+}$ (M = Rh, Ir) are active catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene.

Keywords: Phosphinoferrocenyloxazoline ligands; Rhodium; Iridium; Ruthenium; Osmium; Asymmetric catalysis; Molecular structures

1. Introduction

Following the pioneering work of Ugi et al. [1,2] many types of ferrocene compounds with planar chirality have been prepared through diastereoselective ortholithiation [3]. In particular, oxazoline moieties have been used as chiral *ortho*-directing groups by several research groups [4–14], chlorodiphenylphosphine being one of the quenching electrophiles commonly employed [4,5,9–12]. The resulting optically active diphenylphosphinoferrocenyloxazolines (see Scheme 1), with both planar and atom-centred elements of chirality, have been used as ligands to build up transition-metal catalysts for a variety of organic processes including allylic substitutions, hydrosilylations or hydrogen transfer reactions, among others [15–18].

We are interested in the synthesis, characterisation and catalytic properties of chiral-at-metal half-sandwich compounds of the platinum group metals [19]. In particular, we have recently shown the ability of phosphinooxazoline–rhodium, or -iridium [19i] and -ruthenium or -osmium [19p] complexes of formula [(η^n-ring)M(phosphinooxazoline)(solvate)]$^{2+}$ to act as catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene. Following these studies, in this paper we describe the preparation of some new diphenylphosphinoferrocenyloxazoline compounds of rhodium, iridium, ruthenium or osmium of formula [(η^n-ring)MClL]PF_6 [L = (*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline (R = *i*Pr in Scheme 1); (η^n-ring)M = (η^5-C_5Me_5)Rh, (**1**); (η^5-C_5Me_5)-Ir, (**2**); (η^6-*p*-MeC_6H_4*i*Pr)Ru, (**3**); (η^6-*p*-MeC_6H_4*i*Pr)Os, (**4**)]. The complexes have been completely characterised by analytical and spectroscopic means including the molecular structure determination of two representative examples, namely [(η^5-C_5Me_5)MClL]PF_6 [M = Rh (**1**), Ir (**2**)], by X-ray diffractometric methods. The related solvate complexes [(η^5-C_5Me_5)ML(Me_2CO)]$^{2+}$ (M = Rh, Ir) are active catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene with good diastereoselectivity and up to 38% enantioselectivity in the major diastereomer.

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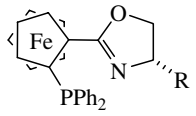


Scheme 1. Diphenylphosphinoferrocenyloxazolines.

2. Results and discussion

Reaction of (*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline (L) with the dimers [{(η^n-ring)MCl}$_2$(μ-Cl)$_2$] in the presence of KPF_6 gave the corresponding air stable complexes [(η^n-ring)MClL]PF_6 [(η^n-ring)M = (η^5-C_5Me_5)Rh (**1**), (η^5-C_5Me_5)Ir (**2**), (η^6-*p*-MeC_6H_4*i*Pr)Ru (**3**), (η^6-*p*-MeC_6H_4*i*Pr)Os (**4**)] in 80–95% isolated yield. The bidentate ligand coordinates through the phosphorus and the oxazoline nitrogen atoms. Therefore, the metal becomes a chiral centre and a pair of diastereomers, epimers at metal, could be formed. The epimer ratio could be determined by ^{1}H NMR integration and this technique also shows that recrystallisation from different solvent mixtures renders different epimer compositions. In overall, diastereomeric excesses of 86% (complex **1**), 87.5% (**2**) and 80% (**3** and **4**), were achieved. The new complexes have been characterised by IR and NMR spectroscopies, mass spectrometry, microanalysis and by the X-ray crystal structure determination of compounds **1** and **2**. Back donation from the second row metals is not so effective as that from the third row metals as can be seen by comparing the chemical shift difference, δP (compound) – δP (free ligand), for compounds **1** and **3** (40–50 ppm) to that for complexes **2** and **4** (2–18 ppm). On the other hand, the ^{31}P NMR resonance appears as a doublet in the rhodium complex **1** due to coupling to the metal. These data unequivocally establish the phosphorus coordination.

For the rhodium and iridium compounds, **1** and **2**, single crystals of the more abundant diastereomer could be obtained by slow diffusion of diethylether into dichloromethane solutions. Both crystal structures are isostructural. A molecular drawing of the rhodium complex is depicted in Fig. 1a; selected molecular parameters for both compounds are listed in Table 1. Both molecules show the expected "three-legged piano-stool" structure with the phosphinoferrocenyloxazoline ligand chelating the metal through P and N donor atoms. An (η^5-C_5Me_5) group occupies three *fac* positions and one chlorine atom completes the coordination sphere of the metals. The absolute configuration of the metal in both complexes is *S* according to the ligand priority sequence [20] (η^5-C_5Me_5) > Cl > P > N. Despite of the isostructural relationship, the electronic and steric differences of the two metals (Rh vs. Ir) produce minor variations at a molecular level; thus, the M–Cl and the M–P bond lengths are statistically shorter in the Ir derivative, showing the greater tendency for electron release of iridium vs. rhodium. On the other side, the M–C(C_5Me_5) bond distances are spread out in a wide range (0.13 Å approx.) and the differences clearly reflect the unlike *trans* influences of the remaining ligands, with the shortest distances (M–C(1)) located *opposite* to the oxazoline nitrogen atom (see Table 1). This effect was also observed in the related rhodium(I) or iridium(I) M(cod)L derivatives containing the same phosphinooxazoline chelate ligand [10,21].

The six-membered M–P(1)–C(23)–C(27)–C(33)–N chelate rings exhibit puckering parameters typical of an envelope conformation (^1E) with the metal out of the metallacycle plane; the total puckering amplitudes are 0.642(4) and 0.625(5) Å for complexes **1** and **2**, respectively [22]. Within experimental error, there is no apparent modification in the bond distances and angles of the ferrocene moieties after coordination [4,10]. Only a clear change in the torsion angle C(23)–C(27)–C(33)–N has been produced upon coordination to allow the nitrogen to approach the metal and the subsequent chelate coordination (−156.3° in the free ligand, −21.76(3) in **1** and −20.78(4) in **2**). The cyclopentadiene rings of the ferrocene present a nearly eclipsed disposition with mean relative rotations of 16.4(3)° and 16.6(4)° in **1** and **2**, respectively. As a relevant topological feature it is worth to mention that, in these diastereomers, the ferrocene moiety is directed away from the M(η^5-C_5Me_5) unit; thus, the metals are at both sides of the mean plane of the quelate ring (defined through

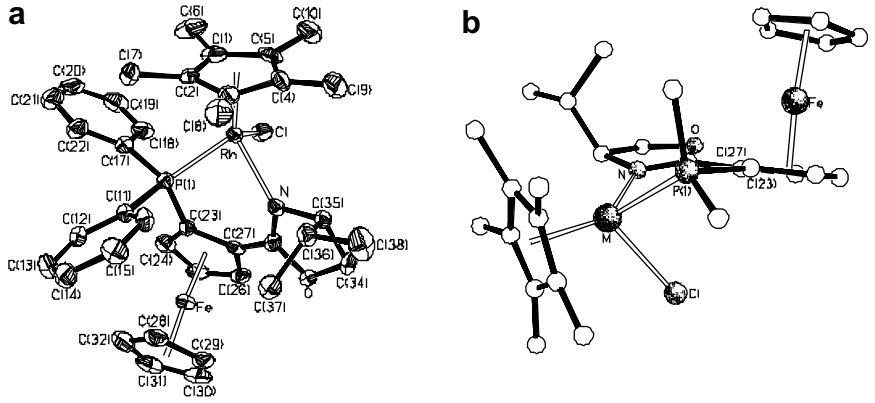


Fig. 1. (a) Molecular view of the cation of complex **1**. (b) Schematic representation showing the envelope conformation of the metallacycle M–P–C–C–C–N and the relative disposition of the ferrocene and M(η^5-C_5Me_5) moieties in complex **1**.

Table 1
Selected bond distances (Å) and angles (°) for complexes **1** and **2**

	1	2		1	2
M–Cl	2.4143(17)	2.402(2)	M–C(1)	2.139(8)	2.153(11)
M–N	2.162(5)	2.147(8)	M–C(2)	2.177(6)	2.189(11)
M–P(1)	2.3107(19)	2.290(2)	M–C(3)	2.231(7)	2.213(12)
M–G(1)*	1.845(4)	1.858(6)	M–C(4)	2.268(7)	2.267(10)
			M–C(5)	2.243(7)	2.245(12)
P(1)–C(23)	1.807(6)	1.806(9)	C(23)–C(27)	1.446(9)	1.411(13)
N–C(33)	1.273(8)	1.293(11)	C(27)–C(33)	1.455(9)	1.432(12)
Fe–C(23)	2.038(6)	2.043(9)	Fe–C(28)	2.050(7)	2.042(10)
Fe–C(24)	2.059(7)	2.027(10)	Fe–C(29)	2.056(7)	2.012(12)
Fe–C(25)	2.029(7)	2.015(9)	Fe–C(30)	2.043(7)	2.035(10)
Fe–C(26)	2.029(6)	2.023(9)	Fe–C(31)	2.034(8)	2.018(10)
Fe–C(27)	2.032(6)	2.026(9)	Fe–C(32)	2.048(8)	2.032(11)
Fe–G(2)*	1.637(3)	1.631(4)	Fe–G(3)*	1.650(4)	1.646(5)
Cl–M–P(1)	89.38(6)	89.79(9)	M–P(1)–C(23)	109.1(2)	108.9(3)
Cl–M–N	85.69(15)	83.6(2)	M–N–C(33)	127.4(5)	126.2(6)
Cl–M–G(1)*	117.87(12)	118.17(18)	G(2)*–Fe–G(3)*	174.47(18)	174.8(3)
P(1)–M–N	87.69(15)	88.3(2)	P(1)–C(23)–C(27)	122.2(5)	122.4(7)
P(1)–M–G(1)*	128.06(12)	128.6(2)	C(23)–C(27)–C(33)	126.4(6)	127.2(8)
N–M–G(1)*	134.1(2)	133.7(3)	C(27)–C(33)–N	127.6(6)	128.1(9)
			C(27)–C(33)–O	113.9(6)	115.2(8)

G(1) represents the centroid of the η^5-C_5Me_5 ligand, G(2) the centroid of C(23)–C(27) ring and G(3) the centroid of C(28)–C(32) cyclopentadienyl group.

P(1)–C(23)–C(27)–C(33)–N), with separations of 1.018 and 0.998(5) Å for Rh and Ir, and of ca. −1.47 Å for the iron centre (Fig. 1b). This relative disposition seems to reduce the steric interaction between the C_5Me_5 ligand and the ferrocene moiety and creates an open space for the coordination of a remaining ligand.

While in $CDCl_3$, at room temperature, the metal centre in the ruthenium and osmium complexes **3** and **4** is configurationally stable, the rhodium and iridium complexes **1** and **2** slowly epimerise in the same conditions. Thus, the diastereomeric excess of solutions of **1** or **2** gradually decreases from 98% to 42% or 80% d.e., respectively, after 20 days. In this context, it is interesting to note that the related d^6 half-sandwich compounds of the four metals with phosphinooxazoline ligands are configurationally stable in chloroform, acetone, or methanol, the composition of mixtures of epimers remaining unchanged for days [19i,19p].

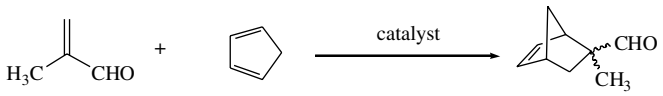
2.1. Catalytic Diels–Alder reactions

Diels–Alder reactions are classical pattern reactions that play an important role in the construction of complicated molecules with stereochemical control [23]. Recently, in addition to the more common titanium, aluminum, or boron catalysts, some transition-metal and lanthanide complexes have been described as promising catalysts for this reaction [24]. Cationic ruthenium [19c,19e,19l,19p,25] and, to a lesser extension, rhodium [19b,19e,19i,26], iridium [19d,19i,26b] and osmium [19p,27] complexes with NO, NN, OP, NP, or PP bidentate ligands have been successfully used as asymmetric catalysts for Diels–Alder reactions.

The chloride compounds **1**–**4** were not active as catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene. Most probably the coordinative saturation of the metallic centre in these complexes avoids catalysis. To obtain complexes with a vacant or with a more labile ligand in the metal sphere, we treated the solvates [28] [{(η^n-ring)M(Me_2CO)$_3$}(BF_4)$_2$ with 1 equiv. of L. For the *p*-cymene Ru or Os derivatives, the resulting solutions consist of intractable mixtures of chelate and bridging ferrocenylphosphinooxazoline containing compounds. For the pentamethylcyclopentadienyl Rh or Ir derivatives, the solutions were vacuum-dried and the NMR spectra of the resulting residues, in $(CD_3)_2CO$, at room temperature, strongly indicate the formation of the solvate complexes [(η^5-C_5Me_5)ML(Me_2CO)]$^{2+}$. Thus, the ^{1}H NMR spectra show the presence of the PN and C_5Me_5 ligands in a 1:1 molar ratio, the ^{13}C NMR spectra exhibited the expected resonances for the PN coordinated ligand [29] and in the ^{31}P NMR spectra a doublet centred at 31.0 ppm, with a $^1J_{RhP}$ coupling constant of 142.8 Hz (rhodium complex) and a singlet at 7.7 ppm (iridium complex), support the coordination of the phosphorus to the metal. Interestingly, only one set of sharp resonances was observed in all these spectra, indicating either the presence of only one diastereomer or that a rapid exchange involving the two possible epimers at metal is taking place.

In situ prepared dichloromethane solutions of these solvates are active catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene. Table 2 summarizes the results. Precatalyst:methacrolein 5:100 and cyclopentadiene:methacrolein 6:1 molar ratios were used in all cases. Enantioselectivities up to 38% were achieved and, as expected, better *exo*:*endo* and enantioselectivities were obtained at lower temperatures. The preferential *exo* adduct obtained was (1*S*,2*R*,4*S*)-2-methylbicyclo[2.2.1]-hept-5-ene-2-carbaldehyde. The iridium derivative is more active than the rhodium one. Thus, for example, while with the iridium

Table 2
Enantioselective Diels–Alder reaction of methacrolein with cyclopentadiene catalysed by the solvate complexes in dichloromethane



Entry	Precatalyst	T (°C)	t (h)	Yield (%)	Isomer ratio *exo*:*endo*	E.e. *exo* (%)	E.e. *endo* (%)
1	–	RT	1	0.5	–	–	–
2	Rhodium solvate	RT	2	91	86:14	4	14
3	Rhodium solvate	−20	168	75	91:9	18	36
4	Iridium solvate	RT	1	94	87:13	8	10
5	Iridium solvate	−20	48	92	91:9	16	38

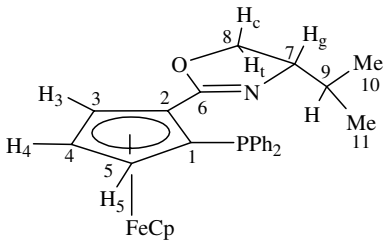
compound, 80% conversion was achieved after 0.5 h of reaction, at RT, only 54% conversion was obtained with the rhodium complex in the same conditions. A similar trend was observed at −20 °C. However, similar diastereo and enantioselectivities have been achieved with both catalysts. In summary, the solvates $[(\eta^5\text{-}C_5Me_5)ML(Me_2CO)]^{2+}$ (M = Rh, Ir) are active catalysts for the Diels–Alder reaction between methacrolein and cyclopentadiene with good diastereoselectivity but poor enantioselectivity.

3. Experimental

All solvents were dried over appropriate drying agents, distilled under N_2 and degassed prior to use. All preparations have been carried out under nitrogen. Infrared spectra were obtained as Nujol mulls with a Nicolet 550 spectrometer. The C, H, and N analyses were carried out with a Perkin–Elmer 240B microanalyzer. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on a Varian UNITY 300 spectrometer [299.9 (^{1}H), 121.4 (^{31}P) and 75.4 (^{13}C) MHz]. Chemical shifts are expressed in ppm upfield from $SiMe_4$ (^{1}H, ^{13}C) or 85% H_3PO_4 in D_2O (^{31}P). FAB$^+$ mass spectra were recorded on a VG Autospec spectrometer. The precursors $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (M = Rh [30], Ir [29]) and $[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)MCl\}_2(\mu\text{-}Cl)_2]$ (M = Ru [31], Os [32]) and the ligand (*S*)-2-[(S_p)-2-(diphenylphosphino)ferrocenyl]-4-isopropyloxazoline [4,5,9,10,12] were prepared according to published procedures.

3.1. Preparation of $[(\eta^5\text{-}C_5Me_5)MClL]PF_6$ [M = Rh (1), Ir (2)]

Under argon, to a suspension of $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ (0.17 mmol) in methanol (10 mL), 176.5 mg (0.37 mmol) of L and 67.5 mg (0.37 mmol) of KPF_6 were added. An orange precipitate is almost instantaneously formed which was filtered off, washed with cold methanol and air-dried. By vacuum-concentration of the filtrate, a second fraction was obtained which was collected on a glass frit, washed with Et_2O and air-dried. The resulting filtrate was vacuum-evaporated to dryness and the residue extracted with CH_2Cl_2. A third fraction precipitates by addition of Et_2O, which was collected by filtration, washed with cold Et_2O and air-dried.



Labelling for NMR assignments

Compound **1**: Representative yield: first fraction 75% (d.e., 98%), second fraction 8% (d.e., 80%), third fraction 12% (d.e., 50%). Anal. Calc. for $C_{38}H_{43}ClF_6FeNOP_2Rh$: C, 50.7; H, 4.8; N, 1.6. Found: C, 50.35; H, 5.5; N 1.7%.

Major epimer: ^{1}H NMR ($CDCl_3$, RT): $\delta = 0.96$, 1.16 (2 × d, 6H, $J = 6.9$ Hz, Me_2 *i*Pr), 1.36 (d, 15H, $J_{HP} = 3.9$ Hz, C_5Me_5), 2.25 (dsp, 1H, $J = 6.9$, 2.5 Hz, CH *i*Pr), 3.55 (s, 5H, Cp), 4.20–4.23 (m, 1H, H_g), 4.42 (t, 1H, $J = 9.2$ Hz, $H_{c/t}$), 4.52 (dd, 1H, $J = 9.2$, 3.7 Hz, $H_{t/c}$), 4.57 (br s), 4.73 (t, $J = 2.5$ Hz) 4.89 (br s) (3H, H_3, H_4, H_5), 7.43–8.01 (m, 10H, Ph_2). ^{13}C NMR ($CDCl_3$, RT): $\delta = 9.38$ (d, $J = 0.9$ Hz, C_5Me_5), 14.36, 18.30 (C_{10}, C_{11}), 29.32 (C_9), 68.04 (C_8), 71.59 (d, $J = 17.5$ Hz, C_2), 71.90 (br s, Cp + $C_{3/4}$), 71.95 (C_7), 72.78 (d, $J = 6.9$, C_5), 77.01 ($C_{4/3}$), 80.58 (d, $J = 50.7$ Hz, C_1), 101.73 (dd, $J = 6.4$, 2.3 Hz, C_5Me_5) 128.27, 128.92, 129.39, 132.16, 132.24, 133.37, 133.91, 135.49 (Ph_2), 172.67 (C_6). ^{31}P NMR ($CDCl_3$, RT): $\delta = 32.32$ (d, $J = 142.9$ Hz), −145.34 (sp, $J = 716.5$ Hz, PF_6). FAB$^+$ MS: 754 (M^+, 100%), 598 (80). IR (Nujol): 617.6 cm^{-1} ν(C=N).

Minor epimer: ^{1}H NMR ($CDCl_3$, RT): $\delta = 0.90$, 0.97 (2 × d, 6H, $J = 6.6$ Hz, Me_2 *i*Pr), 1.27 (d, 15H, $J = 3.9$ Hz, C_5Me_5), 2.56 (m, 1H, CH *i*Pr), 4.0 (s, 5H, Cp). ^{31}P NMR ($CDCl_3$, RT): $\delta = 23.74$ (d, $J = 147.2$ Hz).

Compound **2**: Representative yield: first fraction 70% (d.e., 98%), second fraction 13% (d.e., 70%), third fraction 9% (d.e., 60%). Calc. for $C_{38}H_{43}ClF_6FeIrNOP_2$: C, 46.1; H, 4.4; N, 1.4. Found: C, 46.2; H, 3.8; N, 2.1%.

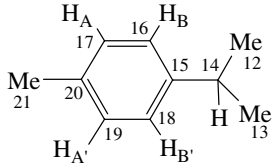
Major epimer: ^{1}H NMR ($CDCl_3$, RT): $\delta = 0.96$, 1.15 (2 × d, 6H, $J = 6.9$ Hz, Me_2 *i*Pr), 1.36 (d, 15H, $J = 2.5$ Hz,

C_5Me_5), 2.23 (dsp, 1H, $J = 6.9$, 2.5 Hz, CH *i*Pr), 3.56 (s, 5H, Cp), 4.09–4.14 (m, 1H, H_g), 4.42 (t, 1H, $J = 9.3$ Hz, $H_{c/t}$), 4.53–4.58 (m, 2H), 4.76–4.78 (m, 1H), 4.91–4.93 (m, 1H) ($H_{t/c}$, H_3, H_4, H_5), 7.39–7.51 (m, 3H), 7.74–7.79 (m, 5H), 7.92–7.99 (m, 2H) (Ph_2). ^{13}C NMR ($CDCl_3$, RT): $\delta = 9.06$ (C_5Me_5), 14.46, 18.00 (C_{10}, C_{11}), 28.96 (C_9), 68.32, 71.35 (d, $J = 16.1$ Hz), 72.10 (d, $J = 7.8$ Hz), 72.00 (Cp), 72.54 (d, $J = 6.4$ Hz), 73.51 (C_7), 77.50 (br s, C_8), (C_2–C_5), 81.27 (d, $J = 59.0$ Hz, C_1), 95.55 (d, $J = 2.3$ Hz, C_5Me_5), 128.15, 129.03, 129.24, 131.90, 132.02, 133.41, 133.95, 135.76 (Ph_2), 172.68 (C_6). ^{31}P NMR ($CDCl_3$, RT): $\delta = 0.76$ (s), −145.27 (sp, $J = 716.5$ Hz, PF_6). FAB^+ MS: 844 (M^+, 100%), 688 (75), 598 (80), 154 (20). IR (Nujol): 1618.0 cm^{-1} ν(C=N).

Minor epimer: ^1H NMR ($CDCl_3$, RT): $\delta = 2.11$ (s, 15H, C_5Me_5), 2.46 (m, 1H, CH *i*Pr), 4.03 (s, 5H, Cp). ^{31}P NMR ($CDCl_3$, RT): $\delta = -5.05$ (s).

3.2. Preparation of [(η^6-*p*-MeC_6H_4iPr)MClL]PF_6 [M = Ru (3), Os (4)]

Under argon, to a solution of [{(η^6-*p*-MeC_6H_4*i*Pr)-MCl}$_2$(μ-Cl)$_2$] (0.17 mmol) in methanol (5 mL) 177.0 mg (0.37 mmol) of L and 67.7 mg (0.37 mmol) of KPF_6 were added. The resulting orange solution was refluxed during 2 h and, then, the solvent vacuum-evaporated. The residue was extracted with CH_2Cl_2. The solution was concentrated and addition of Et_2O produced the precipitation of the product as an orange powder.



Labelling for NMR assignments

Compound **3**: Yield 80–90% (d.e., 80%). Calc. for $C_{38}H_{43}ClF_6FeNOP_2Ru$: C, 50.9; H, 4.7; N, 1.6. Found: C, 51.1; H, 6.0; N, 1.8%. ^1H NMR ($CDCl_3$, RT): $\delta = 0.83$, 1.01 (2 × d, 6H, $J = 6.6$ Hz, Me_2 *i*Pr L), 0.95, 1.13 (2 × d, 6H, $J = 6.9$ Hz, Me_2 *i*Pr ring), 1.95 (s, 3H Me ring), 2.07 (bsp, 1H, CH *i*Pr L), 2.93 (sp, 1H, CH *i*Pr ring), 4.04 (s, 5H, Cp), 4.50–4.55 (m, 3H, H_c, H_g, H_t), 4.60 (br s, 1H), 4.80 (t, 1H, $J = 2.6$ Hz), 5.14 (br s, 1H) (H_3, H_4, H_5), 4.70, 5.56 (AB system, 2H, $J = 6.2$ Hz, H_A, H_B), 5.60, 5.85 (AB system, 2H, $J = 6.0$ Hz, $H_{A'}$, $H_{B'}$), 6.86–6.96 (m, 2H, Ph_2), 7.35–7.40 (m, 3H, Ph_2), 7.56–7.66 (m, 3H, Ph_2), 8.19–8.25 (m, 2H, Ph_2). ^{13}C NMR ($CDCl_3$, RT, selected signals): $\delta = 70.30$ (d, $J_{PC} = 47.4$ Hz, C_1), 72.34 (s, Cp), 170.38 (d, $J_{PC} = 2.3$ Hz, C_6). ^{31}P NMR ($CDCl_3$, RT): $\delta = 24.96$ (s), −145.27 (sp, $J = 716.5$ Hz, PF_6). FAB^+ MS: 752 (M^+−MeC_6H_4*i*Pr, 100%). IR (Nujol): 1624.1 cm^{-1} ν(C=N).

Compound **4**: Yield 80–90% (d.e., 80%). Calc. for $C_{38}H_{43}ClF_6FeNOOsP_2$: C, 46.3; H, 4.3; N, 1.4. Found: C, 46.85; H, 5.0; N, 1.7%. ^1H NMR ($CDCl_3$, RT): $\delta = 0.86$, 1.00 (2 × d, 6H, $J = 6.6$ Hz, Me_2 *i*Pr L), 0.98, 1.08 (2 × d, 6H, $J = 6.9$ Hz, Me_2 *i*Pr ring), 1.70 (bsp, 1H, CH *i*Pr L), 1.96 (s, 3H, Me ring), 2.69 (sp, 1H, CH *i*Pr ring), 4.08 (s, 5H, Cp), 4.43–4.58 (m, 3H, H_c, H_g, H_t), 4.64 (br s, 1H), 4.87 (t, 1H, $J = 2.6$ Hz), 5.19 (br s, 1H) (H_3, H_4, H_5), 4.98, 5.74 (AB system, 2H, $J = 3.9$ Hz, H_A, H_B), 5.65, 6.07 (AB system, 2H, $J = 5.0$ Hz, $H_{A'}$, $H_{B'}$), 6.76–6.86 (m, 2H, Ph_2), 7.33–7.39 (m, 3H, Ph_2), 7.58–7.63 (m, 3H, Ph_2), 8.10–8.16 (m, 2H, Ph_2). ^{13}C NMR ($CDCl_3$, RT, selected signals): $\delta = 70.03$ (d, $J_{PC} = 53.9$ Hz, C_1), 72.40 (s, Cp), 169.83 (s, C_6). ^{31}P NMR ($CDCl_3$, RT): $\delta = -15.08$ (s), −145.27 (sp, $J = 716.5$ Hz, PF_6). FAB^+ MS: 842 (M^+, 100%) 686 (86%). IR (Nujol): 1624.1 cm^{-1} ν(C=N).

3.3. Catalysis

Catalyst precursors were prepared by adding one equivalent of L to an acetone solution of [{(η^5-C_5Me_5)M(Me_2-CO)$_3$}(BF_4)$_2$ (M = Rh, Ir). The resulting solution was vacuum-dried and the resulting microcrystalline solid used as catalyst precursor. A solution of the corresponding precursor (0.025 mmol) in 2 mL of dry CH_2Cl_2 was prepared under argon. Methacrolein (0.5 mmol) in 2 mL of CH_2Cl_2 and freshly distilled cyclopentadiene (3 mmol) in 2 mL of CH_2Cl_2 were added consecutively by syringe. The reaction was monitored by gas chromatography (GC). Yields and *exo*:*endo* ratios were determined by GC analysis. The reaction mixture was concentrated to *ca.* 0.3 mL, filtered through silica gel, and washed with CH_2Cl_2/hexane (1/1, v/v) before the determination of the enantiomeric purity. Enantiomeric excesses (e.e.) were determined by integration of the aldehyde proton of both enantiomers in ^1H NMR spectra, using Eu(hfc)$_3$ in *ca.* 0.3 ratio as a chiral shift reagent. The absolute configuration of the major adduct was assigned by comparing the sign of $[\alpha]^D$ with that of the literature [33].

3.4. X-ray structure determination

A summary of crystal data, data collection and refinement parameters for the structural analysis is given in Table 3. Data for **1** and **2** were collected at low temperature (150 and 173 K) with a Siemens-Stoe AED-2 or a Bruker SMART APEX diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). For **1**, three standard reflections were monitored throughout data collection to check crystal and instrument stability; no significant intensity variations were observed. In the case of **2**, data were measured through the use of CCD recording of ω rotation frames (0.3° each). Data were integrated with the Stoe REDU4 (**1**) and Bruker SAINT programs (**2**) [34] and corrected for Lorentz and polarization effects. Absorption correction was applied by using the XPREP [35] and SADABS [36] routine. Structures were solved by direct methods and completed by subsequent difference Fourier tech-

Table 3
Crystal data, data collection and refinement for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{38}H_{43}ClF_6FeNOP_2Rh$	$C_{38}H_{43}ClF_6Fe\ IrNOP_2$
F_w	899.88	989.17
Crystal size (mm)	$0.34 \times 0.27 \times 0.11$	$0.17 \times 0.16 \times 0.07$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	11.544(2)	11.5377(10)
b (Å)	12.033(2)	12.0098(11)
c (Å)	14.806(2)	14.8298(13)
β (°)	112.860(14)	112.689(2)
V (Å^3)	1895.2(6)	1895.9(3)
Z	2	2
D_{calc} (g cm^{-3})	1.577	1.733
μ (mm^{-1})	1.035	4.105
θ Range for data collection	1.91–25.02°	1.91–28.77°
Number of measured reflections	7782	12868
Number of unique reflections (R_{int})	6658 (0.0411)	7945 (0.0665)
Minimum, maximum transmission factor	0.760, 0.892	0.510, 0.750
Number of data/ restraints/parameter	6658/37/463	6360/37/463
$R(F)$ ($F^2 \geqslant 2\sigma(F^2)$)	0.0466	0.0534
$wR(F^2)$ (all data)	0.1093	0.1055
S (all data)	1.027	0.941

niques. Refinement on F^2 was carried out by full-matrix least-squares (SHELXL-97) [37]. All non-hydrogen atoms, except F atoms in the PF_6 anions, were refined with anisotropic displacement parameters. A model of disorder based on two alternate positions was assumed for the PF_6^-. Geometric restraints were applied to the disordered anion during the structure refinement. The hydrogen atoms were included in calculated positions according to their geometry and refined riding on carbon atoms. The absolute structures were determined on the basis of the Flack parameters 0.01(3) (**1**), 0.009(9) (**2**) and using the internal reference of the asymmetric carbon atom in phosphinoferrocenyloxazoline ligand.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 616204 (**1**) and 616205 (**2**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK or e-mail: deposit@ccdc.cam.ac.uk Supplementary data associated with this article (a molecular view of complex **2**) can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.003.

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