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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$_5$Me$_5$)Rh; (η^5-C$_5$Me$_5$)Ir; (η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru; (η^6-*p*-MeC$_6$H$_4$*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$_5$Me$_5$)ML(Me$_2$CO)]$^{2+}$ (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$_5$Me$_5$)Rh, (**1**); (η^5-C$_5$Me$_5$)-Ir, (**2**); (η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru, (**3**); (η^6-*p*-MeC$_6$H$_4$*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$_5$Me$_5$)MClL]PF$_6$ [M = Rh (**1**), Ir (**2**)], by X-ray diffractometric methods. The related solvate complexes [(η^5-C$_5$Me$_5$)ML(Me$_2$CO)]$^{2+}$ (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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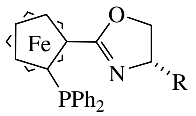

Scheme 1. Diphenylphosphinoferrocenyloxazolines.

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$_5$Me$_5$)Rh (**1**), (η^5-C$_5$Me$_5$)Ir (**2**), (η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru (**3**), (η^6-*p*-MeC$_6$H$_4$*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$_5$Me$_5$) 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$_5$Me$_5$) > 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$_5$Me$_5$) 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$_5$Me$_5$) unit; thus, the metals are at both sides of the mean plane of the quelate ring (defined through

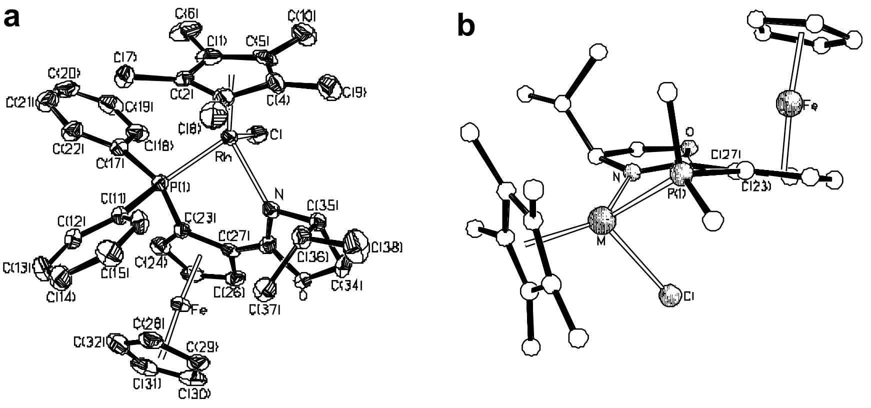

Fig. 1. (a) Molecular view of the cation of complex **1**. (b) Schematic representation showing the envelope conformation of the metallacycle M–P–C–C–C–N and the relative disposition of the ferrocene and M(η^5-C$_5$Me$_5$) moieties in complex **1**.