



Synthesis of a bimetallic P–N bridged rhodium (I)–ruthenium (II) complex: Application in the hydroformylation reaction



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ABSTRACT

The reaction of $[\text{Rh}(\text{acac})(\text{PPh}_2\text{Py})_2]$ (acac = acetylacetonate, $\text{PPh}_2\text{Py} = 2$ -(diphenylphosphino)pyridine) with $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3][\text{OTf}]$ ($\text{Cp}^* =$ pentamethylcyclopentadienyl, $\text{OTf} =$ trifluoromethanesulfonate) provides a cationic bimetallic complex $[\text{Cp}^*\text{Ru}(\text{PPh}_2\text{Py})_2\text{Rh}(\text{acac})][\text{OTf}]$, in which a ruthenium–rhodium coordinate (dative covalent) bond is formed. The structure was ascertained by single crystal X-ray diffraction. The catalytic performances of the bimetallic complex were evaluated in the hydroformylation reaction of 1-octene and compared to those of the *in situ* formed catalysts and the mononuclear counterparts. The catalysis results point out that the bimetallic complex is fragmenting under hydroformylation conditions, which was confirmed by NMR analysis.

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1. Introduction

Bimetallic complexes, whether homo- or heterobimetallic, have attracted considerable interest in recent years because they often present a different reactivity from that of mononuclear counterparts. Several reviews have highlighted the great variety of complexes synthesized and the large number of stoichiometric reactions for which they have showed different reactivity from mononuclear complexes [1,2]. However, their use as catalysts is limited [3]. Today, even if many issues remain still to rationalize in bimetallic catalysis, it has been clearly shown that the combination of two metal centres in catalysis can affect the activity, even the selectivity of the reaction and/or allow easy recovery of the catalyst [4–9].

In this context we decided to explore the reactivity of new bimetallic complex with the aim to establish a relationship between structure and catalytic properties. We have prepared a new cationic rhodium–ruthenium complex linked by a P, N ligand. The most interesting use of bimetallic complexes as catalysts is in tandem reactions [10,11]. In that direction, the use of a bimetallic system composed by ruthenium and rhodium complexes as

catalysts in the tandem hydroformylation/hydrogenation of terminal olefins was reported by Nozaki [12]. The authors produce alcohols from alkenes under syngas in high yield (up to 90%) in a one-pot reaction. Taking into account this result we decided to test the rhodium–ruthenium bimetallic complex synthesised in the hydroformylation of 1-octene.

2. Results and discussion

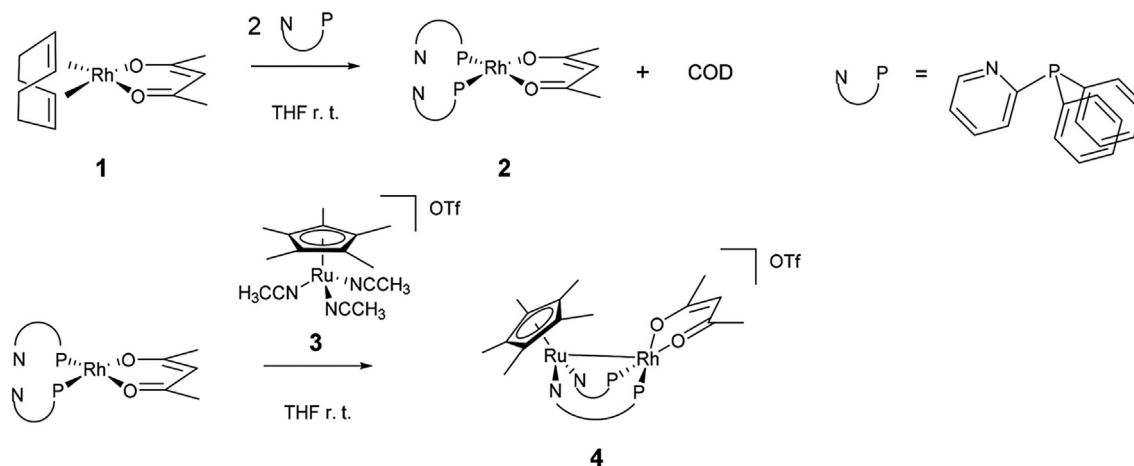
Treatment of $[\text{Rh}(\text{acac})(\text{COD})]$ (acac = acetylacetonate, COD = 1,5 cyclooctadiene) with two equivalents of 2-(diphenylphosphino)pyridine (PPh_2Py) in THF (tetrahydrofuran) at room temperature for 1 h provided the rhodium complex (**2**) as an orange solid in 83% yield (Scheme 1). The ^1H NMR spectrum recorded in THF- d_6 showed the presence of two singlets at 1.36 and at 5.19 ppm attributed to the acetylacetonate moiety. Furthermore, a series of six multiplets are visible in the range of 7.00–8.23 ppm, and are assigned to the protons of the PPh_2Py ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a doublet at 54.74 ppm with a rhodium–phosphorus coupling constant of 193.4 Hz. The IR spectrum showed two bands at 1572 and 1514 cm^{-1} typical from the acac moiety.

Complex **2** reacts with one equivalent of $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3][\text{OTf}]$ ($\text{Cp}^* =$ pentamethylcyclopentadienyl, $\text{OTf} =$ trifluoromethanesulfonate) (**3**) in THF at room temperature for 30 min to give the rhodium–ruthenium complex (**4**, Scheme 1). Compound **4** was obtained in 88% yield as a brown solid. The ^1H NMR spectrum

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Scheme 1. Synthesis of bimetallic complex 4.

recorded in THF- d_8 showed two singlets at 1.83 and 5.70 ppm corresponding to the acetylacetonate ligand. Both signals are downfield shifted with respect to those of complex 2. A singlet attributed to the methyl groups of the Cp* moiety appeared at 1.20 ppm. A set of multiplets are visible in the range of 6.95–7.72 ppm attributed to the protons of the phosphine ligand. Moreover, a doublet appeared at 9.70 ppm with a coupling constant of 5.4 Hz, attributed to the proton in alpha position with respect to the nitrogen atom of the pyridine moiety. We note that this doublet is approximately downfield shifted by 1.5 ppm relative to same signal of complex 2. This change of the chemical shift indicates the coordination of the pyridine group to the ruthenium atom. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a doublet at 41.92 ppm with a rhodium–phosphorus coupling constant of 167.5 Hz. In addition, the IR spectrum showed two bands at 1574 and 1518 cm^{-1} attributed to the presence of the acac moiety, one band at 1031 cm^{-1} attributed to the presence of the Cp* and finally a strong band at 1264 cm^{-1} characteristic of the triflate counterion.

Single crystals of 4 suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of the complex in THF (Fig. 1). The structure confirmed the formation of the binuclear complex 4 and revealed the presence of a ruthenium–rhodium bond of 2.901(1) Å [13,14]. Loss of the three coordinated acetonitrile ligands from the ruthenium atom results in a coordinative unsaturation which is alleviated by formation of a coordinate (dative covalent) ruthenium–rhodium bond. Taking into account the metals oxidation states (Rh(I) and Ru(II)) a dative $\text{Rh} \rightarrow \text{Ru}$ bond is needed to give to the ruthenium atom its preferred 18e- configuration. The rhodium atom presents a slightly distorted square planar geometry (without taking into account the Rh–Ru bond, $\text{P–Rh–O} = 178.69(8)^\circ$ and $169.86(8)^\circ$). The rhodium is coordinated to the acac ligand and to two phosphorus atoms. The ruthenium (II) atom shows a typical three legged piano-stool geometry with the ruthenium atom being coordinated by two nitrogen atoms of the pyridine moiety of the PPh₂Py ligand and one coordination site occupied by the rhodium atom. Crystal data and refinement parameters are given in Table 1.

The catalytic activity of this novel bimetallic ruthenium–rhodium complex was tested in the hydroformylation reaction of 1-octene (Scheme 2), the results are summarized in Table 2.

In general, all the conditions tested attained high conversions of 1-octene in 3 h. However, isomerisation was high (up to 9%) and alkane formation was observed (up to 14%). Higher conversions were observed in THF and *i*PrOH than in toluene. In both solvents some aldehyde hydrogenation was obtained (up to 4% of alcohol):

at 80 °C for *i*PrOH, however producing high quantity of acetal as by-product, and at 120 °C for THF. The low *l/b* ratio obtained in all cases (*l/b* \approx 3) clearly indicates that the ruthenium organometallic ligand is not anymore acting as such [15,16] pointing out the fragmentation of the bimetallic complex.

To shed light on that point and on the catalytic species operating in the reaction we carried out an NMR experiment under CO/H₂ pressure. A solution of bimetallic complex 4 in THF- d_8 was placed on a quick pressure valve NMR tube. The tube was pressurized with 5 bar of a mixture of CO/H₂ (1/1) and heated at 60 °C for 15 min and 3 h. After 15 min heating at 60 °C the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was recorded at room temperature. The spectrum revealed the disappearance of the doublet at 41.92 ($J_{\text{Rh–P}} = 167.5$ Hz) corresponding to

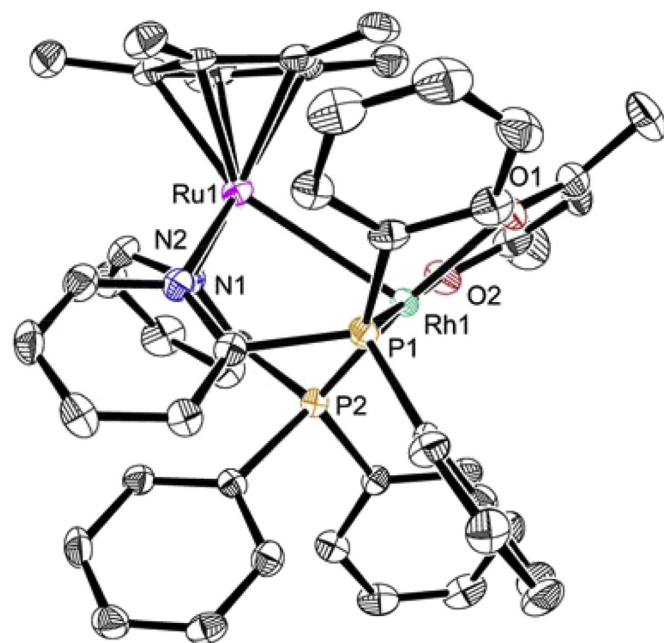


Fig. 1. Structure model of bimetallic complex 4. Thermal ellipsoids are drawn at the 50% probability level. Counterion, solvates and hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Ru1–Rh1 = 2.901(1); Ru1–N1 = 2.166(3); Ru1–N2 = 2.190(3); Rh1–P1 = 2.207(1); Rh1–P2 = 2.211(1); Rh1–O1 = 2.060(3); Rh1–O2 = 2.073(2); P1–Rh1–O2 = 178.69(8); P2–Rh1–O1 = 169.86(8); N1–Ru1–Rh1 = 87.70(9); N2–Ru1–Rh1 = 87.09(9); N2–Ru1–N1 = 91.55(12).

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