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Inverted piano-stool dimers of half-sandwich Ru(II) complexes with (*R*)-phenylglycine methylester and (*S*)-phenylalanineamide: An X-ray structural study and preliminary catalytic results

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Abstract

The two new complexes [Ru(η^6-*p*-cymene)(κ^1-*N*-(*rac*)-phenylglycine methylester)Cl_2] (**1**) and [Ru(η^6-*p*-cymene)(κ^2-*N*,*N*′-(*S*)-phenylalanineamido)Cl] (**2**) have been synthesized by reacting [Ru(*p*-cymene)Cl_2]$_2$ with the HCl-free corresponding ligands. The complexes have been fully characterized by spectroscopic and analytical methods, and their solid structures have been determined by single crystal X-ray analysis. Both complexes have a pseudo-tetrahedral geometry: in **1** ruthenium is bound to the nitrogen, to the η^6-coordinated *p*-cymene molecule and to two chloride ligands. In **2** the ligand has lost an amide proton binding ruthenium in a *N*,*N*′ bidentate fashion, the coordination geometry being completed by a η^6-coordinated *p*-cymene molecule and a chloride ligand. The X-ray structure of **1** has revealed the racemization of the ligand, while in **2** the ligand has retained its configuration but, interestingly, the two diasteromers $R_{Ru}S_C$ and $S_{Ru}S_C$ have co-crystallized in the same single crystal. The crystal architecture of **2** is characterized by the presence of two opposite helices of akin diastereoisomers, connected through strong intermolecular hydrogen bonds between the amine and carbonyl groups. ESI-MS of an *i*-PrOH solution of **2** points out that the dimers are maintained also in solution. Complex **2** is an active catalyst for the homogeneous transfer hydrogenation of acetophenone and cyclohexanone in an *i*-PrOH/*t*-BuOK mixture, with TOFs up to 800 and 1000 h^{-1}, respectively.

Keywords: Ruthenium; Hydrogen transfer; N ligands; Helical structures; Amino acids

1. Introduction

The use of α-amino acids or their derivatives as ligands in organometallic chemistry is a well defined topic [1]. Metal complexes with amino acid-type ligands have found applications mainly in bio-inorganic chemistry, for example in the synthesis of peptides [2] or bio-inorganic models [3].

Homogeneous enantioselective catalytic processes promoted by transition metal complexes are elegant ways to obtain important organic molecules with high optical purity. The search of asymmetric supporting ligands able to transfer the chirality to the final organic product is then a fundamental chapter in catalysis. Amino acids or their derivatives represent a cheap and easily available class of chiral ligands, and the literature counts several examples of homogeneous enantioselective processes catalyzed by amino acid based metal complexes [1,4]. However, homogeneous enantioselective catalysts containing amino acid amides have been much less

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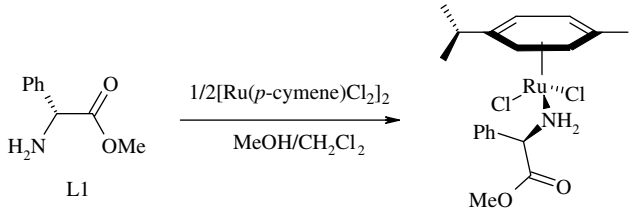
investigated [5]. In this paper, we describe the synthesis, the characterization and the X-ray structure analysis of two new *half-sandwich* ruthenium(II) complexes obtained by using (*R*)-phenylglycine methyl ester (**1**) and (*S*)-phenylalanineamide (**2**) as ligands. Furthermore, a preliminary study on the potentiality of complex **2** as homogeneous catalyst in the hydrogen transfer reaction from *i*-PrOH to ketones is reported.

2. Results and discussion

After neutralization, L1 · HCl reacts with [Ru(*p*-cymene)Cl_2]$_2$ in a methanol/dichloromethane mixture at room temperature leading to complex **1** (Scheme 1).

In order to avoid the hydrolysis of the methyl-ester group of the ligand, the reaction has been conducted under strictly anhydrous conditions. **1** has been isolated as an orange powder, stable in the solid state as well as in open air solutions. The complex has a pseudo-tetrahedral geometry, where ruthenium is bound to the amine group of L1, to two chloride ligands and to a η^6-coordinated *p*-cymene molecule. The exclusion of the ester group from the coordination sphere is evidenced by the strong IR stretching band at 1736 cm^{-1}, equivalent to that of L1 · HCl. The stretching signals of the amine group are in the region 3278–3153 cm^{-1}. In the ^1H NMR spectrum, the most interesting feature is the splitting of the NH_2 signals (two multiplets at 3.04 and 7.07 ppm, respectively), due to the interaction of the nitrogen donor with the metal center; the other signals showing the expected chemical shifts. In order to unequivocally establish the structure of the complex, well shaped single crystals of **1** have been grown in methanol. The X-ray diffraction analysis has confirmed the proposed structure, although pointing out the racemization of the ligand. The metal-promoted activation of protons attached to α-carbons is a known process which, however, takes place at high pH and temperatures, usually [6]. Repeated attempts aimed to detect a Ru-hydride intermediate by NMR experiments were uninformative. More likely, the explanation of the occurred racemization of L1 resides in the presence of a phenyl ring on the α-carbon atom, able to stabilize the incipient carbanion [7] formed upon proton abstraction promoted by traces of free *t*-BuOK. This is supported by the not observed racemization of the ligand during the synthesis of [Ru(η^6-benzene)(L-alaMe)Cl_2] complex [8], where a methyl group is attached to the α-carbon atom.



Scheme 1. Synthesis of complex **1**.

The crystal structure of **1** (Fig. 1) shows that the coordination geometry of the [RuNCl_2(η^6-C_6)] moiety, summarized in Table 1, may be described as tetrahedral by considering the center (Cy) of the η^6-*p*-cymene aromatic ring as the fourth ligand position. In fact, the

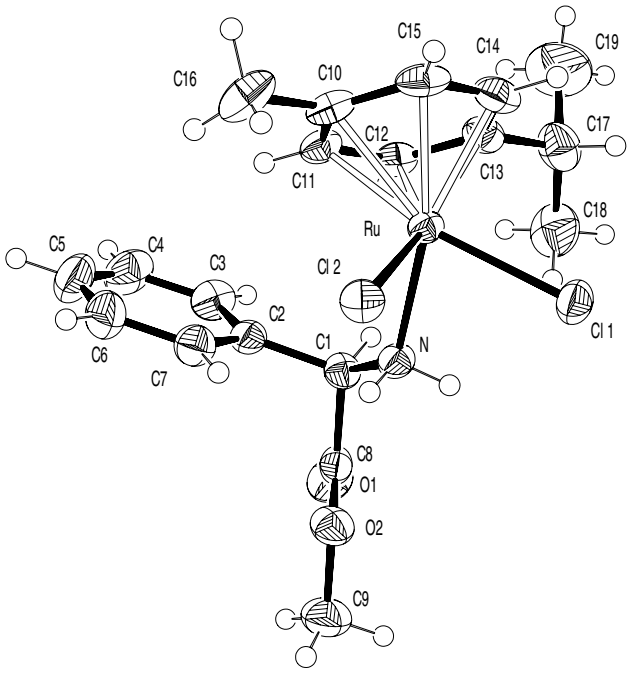


Fig. 1. Perspective view and labeling scheme of **1**. Thermal ellipsoids drawn at the 50% probability level.

Table 1
Coordination bond lengths (Å) and angles (°) for **1** and **2**

1			
Ru–N	2.165(1)	N–Ru–Cl2	81.69(4)
Ru–(C10–C15)	2.156(1)–2.203(1)	N–Ru–Cl1	81.67(4)
Ru–Cy	1.64	Cl2–Ru–Cl1	87.23(1)
Ru–Cl2	2.4139(4)	Cy–Ru–N	134
Ru–Cl1	2.4206(4)	Cy–Ru–Cl1	126
		Cy–Ru–Cl2	129
2			
B		A	
Ru1–N1	2.058(9)	Ru2–N3	2.053(9)
Ru1–N2	2.125(8)	Ru2–N4	2.133(9)
Ru1–(C10–C15)	2.15(1)–2.20(1)	Ru2–(C29–C34)	2.16(1)–2.27(1)
Ru1–Cl1	2.435(3)	Ru2–Cl2	2.438(3)
Ru1–Cy1	1.65	Ru2–Cy2	1.70
N1–Ru1–N2	76.8(3)	N3–Ru2–N4	76.7(3)
N1–Ru1–Cl1	86.6(3)	N3–Ru2–Cl2	87.8(3)
N2–Ru1–Cl1	82.8(2)	N4–Ru2–Cl2	82.6(3)
Cy1–Ru1–N1	131	Cy2–Ru2–N3	131
Cy1–Ru1–N2	133	Cy2–Ru2–N4	132
Cy1–Ru1–Cl1	128	Cy2–Ru2–Cl2	128

Ru–C distances relative to the *p*-cymene coordination range from 2.170(2) to 2.203(1) Å, with Ru–Cy = 1.665(1)Å.

The overall shape of **1** may thus be defined as a piano-stool geometry. The large steric hindrance of *p*-cymene produces a remarkable distortion in the tetrahedral coordination geometry, by widening the Cy–Ru–N and Cy–Ru–Cl angles and tightening the N–Ru–Cl ones. The *p*-cymene is oriented so that the C10–C16 bond to the methyl group is eclipsed to the Ru–Cl2 bond (C16–C10–Ru–Cl2 = −11.6(2)°). The most relevant conformational degrees of freedom of L1 in **1** are the rotations around the Ru–NH_2 bond and the NH_2–CH bond, which, taken together, determine the orientation of the aromatic group of the phenylglycine residue relatively to the *p*-cymene ligand. As regards the former, in **1** the N–H bonds belonging to the mono-hapto –NH_2 group are eclipsed with respect to the Ru–Cl bonds (Cl2–Ru–N–C1 = 126.2(1)°), while the latter is characterized by torsion angle Ru–N–C1–C2 = −60.5(2)°. These values show that the ligand aromatic residue is oriented towards the *p*-cymene methyl end, giving an edge-to-face intramolecular contact between the *p*-cymene aromatic C–H groups and the L1 π electron density (H11···C2 = 2.70 Å). In examining the crystal packing of **1** it is convenient to refer to the distribution of the shortest Ru···Ru contacts, in order to analyze how the complex molecules are paired by intermolecular interactions (Fig. 2).

The two closest Ru···Ru distances are related to an inverted piano-stool arrangement (Fig. 2, A–B pair) assisted by C–H···Cl2(i) contacts (Ru···Ru(i) = 5.68 Å, C···Cl = 3.590(2) Å, Cy–Ru···Ru(i) = 78°, i = $-x, -y, 2-z$), and to a different centrosymmetric pair (Fig. 2, A–C pair) based on –NH···Cl1(ii) hydrogen bonds (Ru···Ru(ii) = 6.80 Å, N···Cl(ii) = 3.517(2) Å, N–H···Cl(ii) = 145(2)°, ii = $-x, -y, 1-z$). Brunner has individuated the inverted piano-stool motif as a common molecular recognition pattern in (*p*-cymene)RuXYZ complexes. In particular, this motif has been invoked to justify the remarkable trend to co-crystallization shown by piano-stool diastereoisomeric pairs [9], and this issue will be further considered in discussing the crystal structure of **2**.

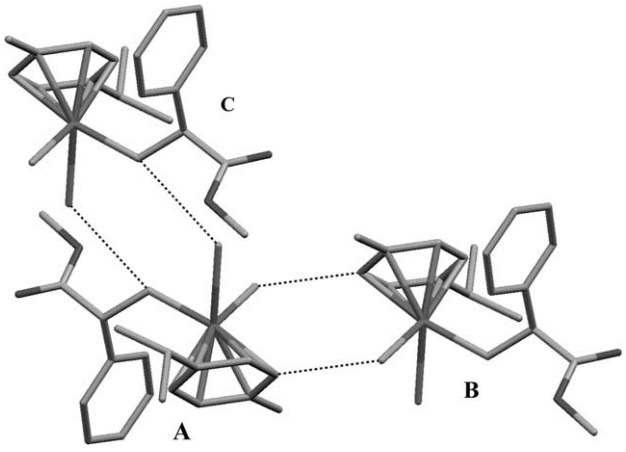
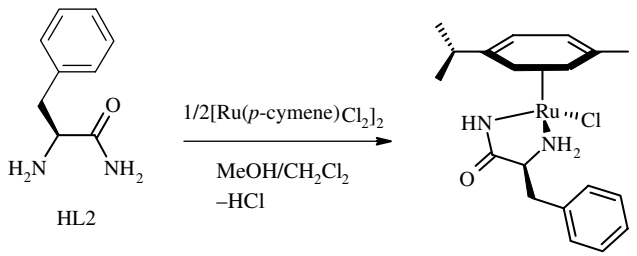


Fig. 2. Molecular aggregation in the crystal structure of **1**. A–B = inverted piano-stool dimer; A–C = hydrogen bonded dimer.

HL2 reacts with [Ru(*p*-cymene)Cl_2]$_2$ under the same experimental conditions as for **1**, leading to complex **2** (Scheme 2).

The product is stable in the solid state as well as in open air solutions. The ligand shows a bidentate behavior, binding the metal through the amine and amide nitrogens. The complexation occurs with elimination of a HCl molecule, consequent to the monodeprotonation of the amide nitrogen, and then L1 acts as an anionic *N,N′* bidentate ligand. The pseudo-tetrahedral coordination is completed by a chloride ligand and a η^6-coordinated *p*-cymene ring. The IR spectrum shows a strong stretching band of the amide C=O group at 1581 cm^{-1} [10], while the stretching of the NH bonds originates an unresolved band in the region 3285–3115 cm^{-1}. The ^{1}H NMR spectrum recorded in CD_3OD shows the presence of two diastereomers (see Section 4); at room temperature they are in a 75:25 ratio. The formation of pairs of diastereomers is common for *half-sandwich* Ru(II) complexes of the three-legged piano-stool type containing chiral bidentate ligands: in complexes of general formula Ru(arene)(LL′)X (X = halogen or other unidentate ligand) the formally monohapto coordination of the *p*-cymene ring renders the metal a stereogenic center. Thus, in the presence of an enantiomerically pure ligand, in the present case having an S_C configuration, the two diastereomers $R_{Ru}S_C$ and $S_{Ru}S_C$ arise. Interestingly, the X-ray diffraction analysis carried out on a single crystal of **2** obtained at 5 °C from a dichloromethane solution, showed the presence of both diastereomers. Contrarily to ligand L1, the X-ray analysis of **2** indicates that L2 has retained its configuration at the stereogenic carbon atom. To the best of our knowledge, this is the first example of an α-amino (primary)amide Ru(II) complex of the three-legged piano-stool type structurally characterized. The presence of two diasteromers in the same crystal is an interesting feature already observed for other Ru(η^6-arene)(LL′)Cl type complexes, and about 20 examples



Scheme 2. Synthesis of complex **2**.

are reported in the literature [9]; the majority of them deals with complexes of general formula [Ru(η^6-*p*-cymene)(salicylaldiminate-ligand)Cl], and only in one case the ligand is *N*,*N*′ [11]. This co-crystallization is usually based on a sort of molecular recognition within inverted piano-stool dimers. This feature is evidenced in Fig. 3, where the crystal structure of the two independent diastereomers $S_{Ru}S_C$ (molecule A, Ru2) and $R_{Ru}S_C$ (molecule B, Ru1) present in the asymmetric unit of **2** is reported.

Table 1 lists the most relevant geometric features of the two molecules, which cocrystallize in the acentric polar space group $I4_1$. In both cases the ruthenium coordination is tetrahedral, by considering the chlorine ligand, the amidic and aminic nitrogen atoms of the bidentate ligand, and the geometric centre (Cy) of the *p*-cymene aromatic ring as the four donors. In both molecules the coordination to the deprotonated amidic donor is stronger than to the aminic group. The *N*,*N*′ chelation of L2 to Ru generates a five membered chelation ring, with bite angles N–Ru–N = 76.8(3)° in A and B, while the remaining coordination angles on Ru are larger than the corresponding ones in **1**. The opposite absolute configuration of the metal in A and B results in a different orientation of the Ru–Cl bond relatively to the C–H bond of the chiral carbon atom (C2 and C21, respectively, for A and B). Both bonds are axially oriented with respect to the chelation rings, but they are in *anti* configuration in B, and *syn* in A. The *p*-cymene is always coordinated with the methyl end pointing towards the chlorine ligand (C16–C11–Ru1–Cl1 = −20.6(9)°, C16···Cl1 = 3.55(1) Å; C35–C34–Ru2–Cl2 = −23.5(9)°, C35···Cl2 = 3.56(1) Å). Diastereomers A and B cocrystallize by forming an inverted piano-stool dimer, wherein A and B are related by a non-crystallographic operation mimicking a center of inversion, so that the aromatic *p*-cymene moieties lie parallel on opposite sides relatively to the metal atoms. It has been suggested [9] that the stability of this inverted piano-stool recognition pattern is the reason of the relevant occurrence of diastereomers cocrystallization for Ru(η^6-arene)XYZ complexes, with electronegative X and Y. The inversion operation is required in order to create contacts between complementary groups on A and B: C29···O1 = 3.41(1), C10···O2 = 3.36(1), N1···Cl2 = 3.490(8), and N3···Cl1 = 3.481(8) Å. This non-crystallographic operation acts locally between the metal centers of the A–B dimer so that the two molecules show opposite chirality on the metals. However, due to the enantiomeric purity of L2, the symmetry relation cannot be extended to the entire molecular pair, but it is confined to the central core, inside the limit defined by the chiral carbons. The two resulting $S_{Ru}S_C$ and $R_{Ru}S_C$ complexes are in close contact, with Ru1···Ru2 = 5.14 Å, Cy–Ru–Ru′–Cy′ = 179°, and Cy–Ru–Ru′ = 111°, which are quite typical values for this kind of pattern [9]. The next shortest

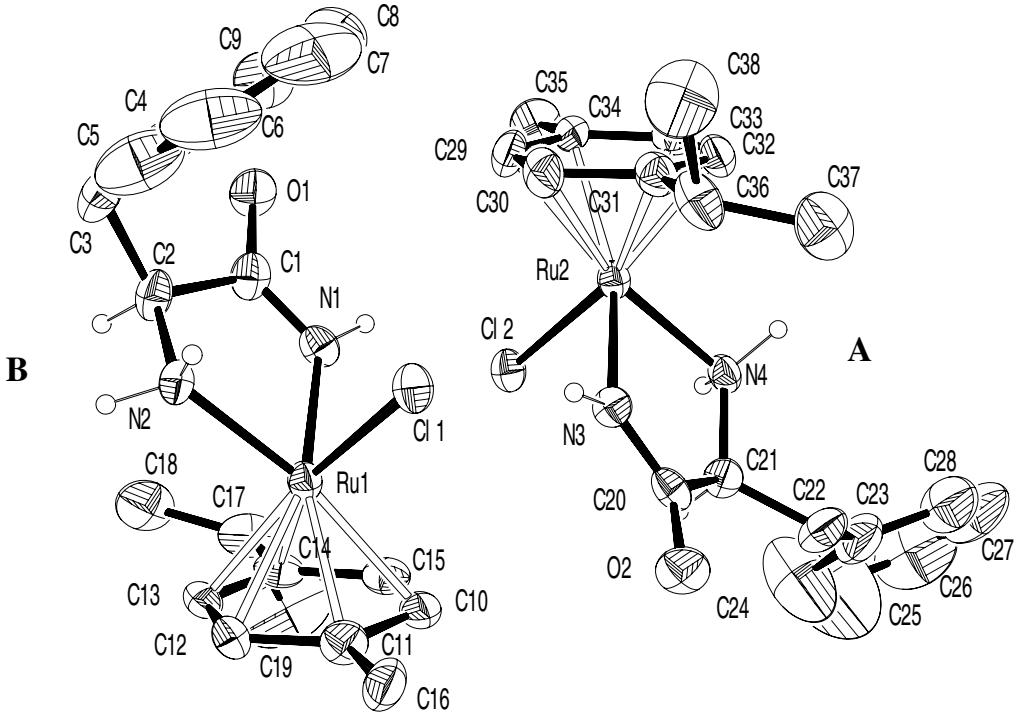


Fig. 3. Perspective view and labeling of the two diastereomers $S_{Ru}S_C$ (molecule A) and $R_{Ru}S_C$ (molecule B) co-crystallized in **2**. Thermal ellipsoids at the 30% probability level, hydrogens omitted with the exception of those bonded to N and to chiral C atoms. Molecules A and B form an inverted piano-stool pair.

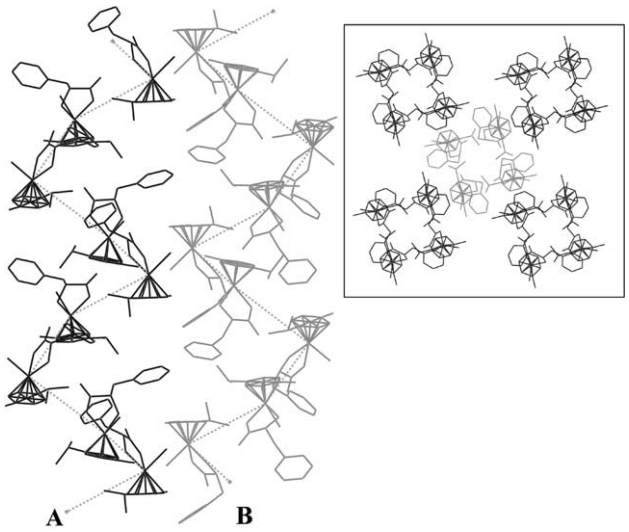


Fig. 4. Helical structure of hydrogen bonded chains in **2**. The opposite handness of the chains formed by A (left handed) and B (right handed) is evidenced by a dotted line linking the metal atoms. The pair of molecules A–B in the center of the figure form an inverted piano-stool dimer (fifth molecules from the top). The packing of the chains is shown in the inset.

Ru···Ru contacts are larger than 6.7 Å. Most interesting is the organization of the crystal architecture. Each diastereomer is in fact part of a helix of akin molecules based on the strong hydrogen bonds N2–H···O1(i) (N···O = 2.78(1) Å, N–H···O = 163(7)°, i = $y + 1/2, 1-x, z-1/4$) for B and N4-H···O2(ii) (N···O = 2.84(1) Å, N–H···O = 161(6)°, ii = $y + 1, -x + 1/2, z + 1/4$) for A. Both helices A and B are generated by the 4_1 symmetry operator, with pitch $c = 14.572(1)$ Å (Fig. 4), but they have opposite handness, right-handed for B and left-handed for A.

The helix handness is governed by metal configuration, so that all the chlorine ligands stick outside from the corners of the chains. The intra-chain packing of L2 is the main difference between the two diastereomeric helices A and B. Helices interact in the crystal through the inverted piano-stool dimers located at each 90° turn of the helix, so that each helix is surrounded by four helices of opposite type, packed in antiparallel mode.

The formation of **2** has been monitored by ESI-MS in *i*-PrOH, dissolving HL2 · HCl, [Ru(*p*-cymene)Cl_2]$_2$ and KOH in a 2:1:2 molar ratio ([Ru] = 10^{-3}). Within 60 minutes the reaction is completed (disappearance of the signal belonging to [Ru(*p*-cymene)Cl_2]$_2$) and the ESI(+) spectrum shows a signal centered at $m/z = 399$, attributable to $[\mathbf{2} - Cl]^+$, and another one at $m/z = 435$, attributable to $[\mathbf{2} + H^+]^+$. Importantly, the dimeric units seem maintained in *i*-PrOH solution; in fact, as it is shown in Fig. 5, the spectrum exhibits two ion signals at m/z 869 and 907 accounting for the presence of the dimeric form of **2** as $[2\mathbf{2} + H^+]^+$ and $[2\mathbf{2} + K^+]^+$, respectively (cone voltage: 50 V, see Section 4). These experimental isotope clusters were in agreement with the theoretical masses and reconstructed singly charged ESI isotope patterns. These data agree well with the re-

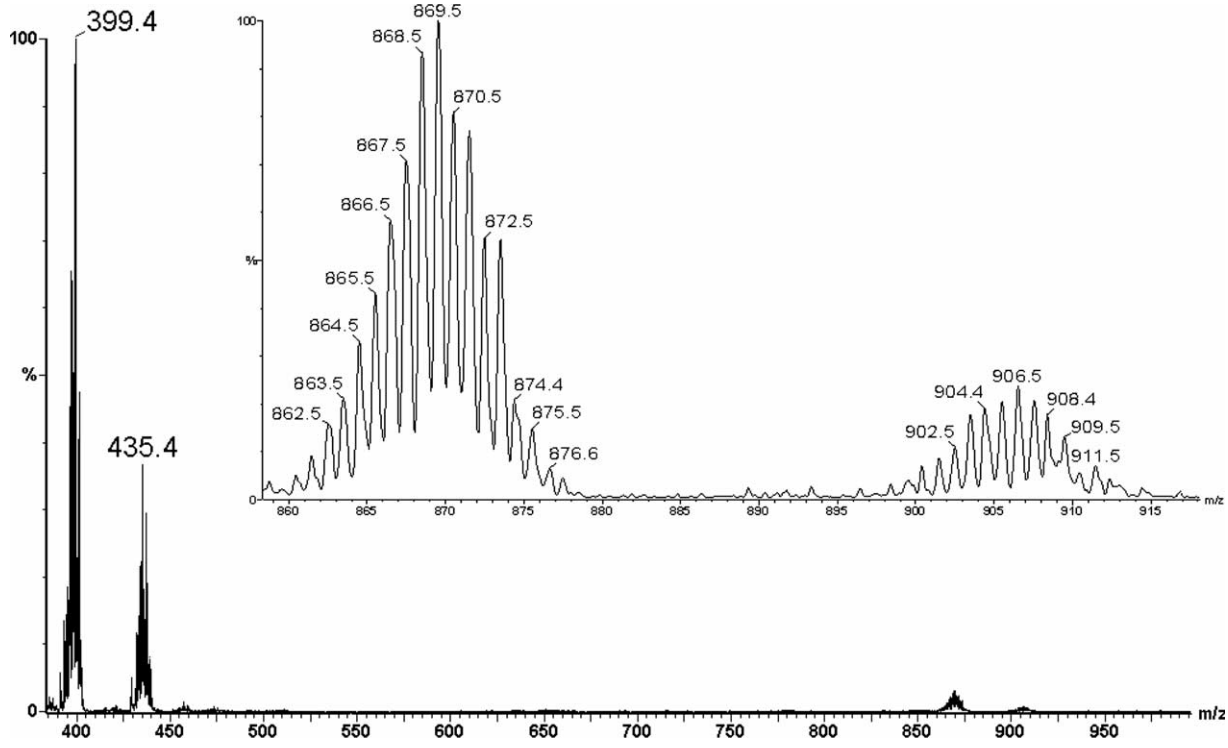


Fig. 5. ESI(+) mass spectra of the pre-catalyst **2** acquired at a cone voltage of 50 V after 60 min. In the inset are shown the ion signals at m/z 869 and 907 attributable to the $[2M + H^+]^+$ and $[2M + K^+]^+$ adduct ions from the dimeric form of **2**, respectively.

cently observed tendency of neutral α-amino amidate (Noyori's catalysts) and acidate half-sandwich Ru(II) complexes to form dimers in solution. PGSE (pulsed field gradient spin-echo) NMR technique [12], has evidenced that the aggregation tendency is maintained in several solvents, *i*-PrOH included.

Chiral vicinal diamines or chiral aminoalcohols are important classes of supporting ligands for enantioselective homogeneous catalysis. These ligands have been extensively used in the Ru(II) catalyzed asymmetric hydrogen transfer reaction from alcohols to ketones, leading to exceptionally high enantiomeric excesses [13]. Phenylalanine amide contains two NH_2 groups connected through a chiral backbone, and then complex **2** can be considered a good candidate as catalyst for the asymmetric hydrogen transfer reaction. The use of amino acid amides as chiral supporting ligands for hydrogen transfer reduction counts a limited number of recent examples, dealing with proline derivatives [14] and dipeptide-analogue ligands [15]. Moreover, no information are available on the structure of the pre-catalyst since they are generated in situ, usually. With this in mind, we were particularly interested in testing complex **2** as catalyst for the hydrogen transfer reaction from *i*-PrOH to ketones. We chose two different ketones as substrate, one prochiral (acetophenone) and one not-prochiral (cyclohexanone). The catalytic experiments were conducted in dry *i*-PrOH, at two different temperatures (room temperature or 80 °C), using *t*-BuOK as co-catalyst and a Ru:ketones:base = 1:1000:2 molar ratio. The catalytic results are collected in Table 2.

Already at room temperature complex **2** is an active catalyst in the hydrogenation of acetophenone, leading to 75% conversion after 6 hours of reaction (entry 1). When the temperature is raised to 80 °C, after 1 hour of reaction a 80% conversion has been observed (entry 2). Regrettably, the ees are negligible in both cases. With cyclohexanone at 80 °C the complete conversion to cyclohexanol has been obtained after 1 h of reaction (entry 3). Although in the case of acetophenone the ee is far to be satisfactory, the TOFs are significant (up to 1000 h^{-1} in the case of cyclohexanone). In fact, the productivity of **2** is much greater than those of parent complexes, to say those generated with proline-derivatives [14] and the preformed amino acidato *half-sandwich* Ru(II) complexes [16].

The not observed enantioselectivity in the acetophenone reduction, seems easily ascribable to the contemporary presence of both diastereoisomers of complex **2** in solution, although the ratio between the two enantiomers of 1-phenylethanol does not correspond to the ratio between the two diastereomers of **2**, as established by ^{1}H NMR. This could indicate a labile metal configuration, as demonstrated for amino acidato *half-sandwich* complexes by Carmona et al. [16c,17]. The preparation of Ru(II) complexes containing other amino amide ligands designed with the aim of improving the enantioselectivity of the hydrogen transfer reaction, and the possible understanding of the role of the dimers on the catalysis, is currently under way in our laboratory.

3. Conclusions

We have prepared and structurally characterized two *half-sandwich* Ru(II) complexes containing amino acid derivatives. The unusual cocrystallization of the two diastereomers $R_{Ru}S_C$ and $S_{Ru}S_C$ has been observed with complex **2**, having (*S*)-phenylalanineamide as ligand. This occurs through an inverted piano-stool dimer motif and each diastereomers belongs to a helix of akin molecules. The two helixes have opposite handness defined by the metal configuration, left-handed for the $S_{Ru}S_C$ isomer and right-handed for the $R_{Ru}S_C$ isomer. The dimeric units seem maintained in *i*-PrOH solutions, as evidenced by ESI-MS analysis. Complex **2** is an active catalyst in the hydrogen transfer reaction of ketones (cyclohexanone and acetophenone) in *i*-PrOH/*t*-BuOK, leading to high TOF values.

4. Experimental

4.1. General methods

All reactions were performed under an atmosphere of dry nitrogen, employing standard Schlenk techniques. Solvents were dried prior to use and stored over molecular sieves and under nitrogen. Elemental analysis (C, H, N) were performed by using a Carlo Erba Mod. EA 1108 apparatus. Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer in the range

Table 2
Catalytic data for the hydrogen transfer reactions catalyzed by complex **2**[a]

Entry	Substrate	*T* (°C)	Time (h)	Conversion (%)	TON[b]	TOF[c]	ee (%)
1	Acetophenone	r.t.	6	75	750	125	6(R)
2	Acetophenone	80	1	80	800	800	6(R)
3	Cyclohexanone	80	1	100	1000	1000	–

[a] Ru/substrate/*t*-BuOK molar ratio = 1:1000:2.
[b] TON = mole product/mole catalyst.
[c] TOF = (mole product/mole catalyst) h^{-1}.

4000–400 cm^{-1}, by using KBr disks. ^1H NMR spectra were obtained at 300 K on a Bruker 300 FT spectrometer, by using $SiMe_4$ as internal standard. The GC analyses have been performed by means of a Dani HP 3800 flame-ionization instrument, equipped with a CP Chirasil Dex CB capillary column. The GC conditions were: oven temperature from 90 to 190 °C with an increment of 15 °C/min.; retention times: acetophenone = 4.9 min, (*R*)-1-phenylethanol = 5.7 min, (*S*)-1-phenylethanol = 5.8 min. The ESI-MS spectra were acquired with a Quattro LC triple quadrupole instrument (Micromass, Manchester, UK) equipped with an electrospray interface (Micromass). ESI-MS analysis were performed by operating the mass spectrometer in positive ion (PI) mode acquiring mass spectra over the scan range *m*/*z* 100–1300 using a step size of 0.1 Da and a scan time of 1.2 s. The operating parameters of interface were as follows: source temperature 70 °C, desolvation temperature 70 °C, ES (+) voltage 3.0 kV, cone voltage 50 V, rf lens 0.3 V.

The hydrochloride forms of enantiomerically pure (*R*)-phenylglycine methylester (L1 · HCl) and *S*-phenylalanine amide (HL2 · HCl) were purchased by Aldrich, while $[Ru(p\text{-cymene})Cl_2]_2$ was synthesized following a literature reported method [18]. Acetophenone (Aldrich) and cyclohexanone (CarloErba) have been utilized as received.

5. Preparation of the Ru(II) complexes

5.1. [Ru(η^6-p-cymene)(κ^1-N-L1)Cl_2] (1)

198 mg (0.9 mmol) of L1 · HCl and 100 mg (0.9 mmol) of *t*-BuOK were dissolved in 30 ml of methanol at room temperature; *n*-pentane was added and KCl was filtered-off. A dichloromethane solution (15 ml) of $[Ru(p\text{-cymene})Cl_2]_2$ (300 mg, 0.5 mmol) was then added and the resulting orange solution was stirred at room temperature for four hours. An orange solid precipitated. This was filtered-off, washed with diethyl ether and dried in vacuum. A further crop of solid was recovered from the refrigerated mother liquor. Red crystals suitable for X-ray analysis were obtained by re-crystallization in methanol. Yield: 240 mg (78%). M.p.: 168–170 °C. Anal. calc. for $C_{19}H_{23}Cl_2NO_2Ru$: C, 48.41; H, 5.34; N, 2.97. Found: C, 48.57; H, 5.32; N, 2.93%. ^1H NMR ($CDCl_3$): δ 1.27 (d, 3H, *p*-cymene, $^3J_{HH} = 7Hz$), 1.32 (d, 3H, *p*-cymene, $^3J_{HH} = 7Hz$), 2.16 (s, 1H, C*H*(Ph)NH_2), 2.23 (s, 3H, *p*-cymene), 3.04 (m, 1H, NH), 2.93 (m, 1H, *p*-cymene), 3.77 (s, 3H, C(O)OCH3), 5.27 (d, 1H, *p*-cymene, $^3J_{HH} = 6Hz$), 5.33 (d, 1H, *p*-cymene, $^3J_{HH} = 6Hz$), 5.48 (m, 2H, *p*-cymene), 7.42 (m, 5H, Ph), 7.72 (m, 1H, NH). IR: 3278-3219-3153 $\nu(NH_2)$, 1736 ν(C=O ester), 1260 ν(C=O ester).

5.2. [Ru(η^6-p-cymene)(κ^2-N,N′-L2)Cl] · 1/2H_2O (2)

130 mg (0.6 mmol) of HL2 · HCl and 67 mg (0.6 mmol) of *t*-BuOK were dissolved in 30 ml of methanol. A dichloromethane solution (15 ml) of $[Ru(p\text{-cymene})Cl_2]_2$ (200 mg, 0.3 mmol) was then added and the resulting orange solution was stirred at room temperature for four hours. The solvents were then removed in vacuum and the residue was treated with dichloromethane filtering the KCl off. The remaining red light solution is refrigerated at 5 °C obtaining red prismatic crystals. After filtration, a further crop of solid (orange powder) was obtained by treating the mother liquor with diethyl ether. Yield: 230 mg (75%). M.p.: 227–229 °C. Anal. calc. for $C_{19}H_{25}ClN_2ORu \cdot 1/2H_2O$: C, 51.52; H, 5.92; N, 6.32. Found: C, 51.83; H, 5.78; N, 6.56%. ^1H NMR (CD_3OD): major diastereomer δ 1.23 (d, 3H, *p*-cymene, $^3J_{HH} = 7Hz$), 1.32 (d, 3H, *p*-cymene, $^3J_{HH} = 7Hz$), 2.03 (sbr, 1H, NH), 2.09 (s, 3H, *p*-cymene), 2.43 (m, 2H, CH_2), 2.70 (m, 1H, *p*-cymene), 3.07 (dd, 1H, C*H*(Bz)NH_2, $^2J_{HH} = 4.3Hz$), 5.55 (d, 1H, *p*-cymene, $^3J_{HH} = 6Hz$), 5.65 (d, 1H, *p*-cymene, $^3J_{HH} = 5.8$ Hz), 6.11 (d, 1H, *p*-cymene, $^3J_{HH} = 5.8Hz$), 6.50 (d, 1H, *p*-cymene, $^3J_{HH} = 6Hz$), 7.32–7.09 (m, 7H, Ph + NH_2); minor diastereomer δ 1.16 (d, 3H, *p*-cymene, $^3J_{HH} = 6.9Hz$), 5.20 (dbr, 2H, *p*-cymene, $^3J_{HH} = 5.7Hz$), 5.42 (dbr, 2H, *p*-cymene, $^3J_{HH} = 4.7Hz$). IR: 3285–3115 (NH), 1581 (C=O amide).

6. X-ray structures

Single crystals of **1** and **2** were mounted on glass fibers and X-ray diffraction data were collected on a Bruker-Siemens SMART AXS 1000 equipped with CCD detector, using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data collection details are: crystal to detector distance = 5.0 cm, 2424 frames collected (complete sphere mode), time per frame = 30 s, oscillation $\Delta\Phi = 0.300°$. Crystal decay resulted negligible in both cases. Data reduction was performed up to $d = 0.70$ and 0.90 Å for **1** and **2**, respectively, by the SAINT package [19] and data were corrected for absorption effects by the SADABS [20] procedure ($T_{max} = 1.000$, $T_{min} = 0.788$ for **1** and $T_{max} = 1.000$, $T_{min} = 0.848$ for **2**). The phase problem was solved by direct methods [21] and refined by full-matrix least-squares on all F^2 [22], implemented in the WINGX package [23]. Anisotropic displacement parameters were refined for all non-hydrogen atoms, while hydrogen atoms were introduced in calculated positions, except for amine and amide hydrogens, which were located from Fourier maps and refined isotropically. A partially occupied (50%) water molecule completes the asymmetric unit contents for **2**. Absolute structure for **2** was assessed by Flack's parameter = −0.11(7). Final maps were featureless. Use of the

Table 3
Crystal data and structure refinement for **1** and **2**

Identification code	**1**	**2**
Empirical formula	$C_{19}H_{25}Cl_2NO_2Ru$	$[C_{19}H_{25}ClN_2ORu]_2 \cdot 0.5H_2O$
Formula weight	471.37	876.86
Wavelength (Å)	0.71069	0.71069
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$I41$
Unit cell dimensions		
a (Å)	9.7100(9)	23.701(2)
b (Å)	9.7898(9)	
c (Å)	10.772(1)	14.572(1)
α (°)	97.595(2)	
β (°)	97.369(2)	
γ (°)	104.982(2)	
Volume (Å^3)	966.28(15)	8186(1)
Z	2	8
D_{calc} (Mg/m^3)	1.620	1.423
Absorption coefficient (mm^{-1})	1.100	0.905
$F(000)$	480	3592
θ Range for data collection (°)	1.94–30.38	1.21–23.29
Reflections collected	13585	36794
Data/restraints/parameters	5254/0/238	5917/9/438
Goodness-of-fit on F^2	1.038	1.163
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0209$, $wR_2 = 0.0534$	$R_1 = 0.0359$, $wR_2 = 0.1001$
R indices (all data)	$R_1 = 0.0244$, $wR_2 = 0.0549$	$R_1 = 0.0520$, $wR_2 = 0.1182$
Largest ΔF maximum/minimum (e Å^{-3})	0.481/−0.455	0.909/−0.306

Cambridge Crystallographic Database [24] facilities was made for structure discussion. Data collection and refinement results are summarized in Table 3.

7. Hydrogen transfer reactions

0.05 mmol of **2** was dissolved in 5 ml of *i*-PrOH and the solution thermostated at the desired temperature (room temperature or 80 °C). An *i*-PrOH solution (5 ml) of the ketone (50 mmol) was added and after a hour an *i*-PrOH solution (5 ml) of *t*-BuOK (0.1 mmol, 11 mg) was added. After an additional hour of reaction a small portion of the reactant solution was withdrawn, quenched with water, extracted with diethyl ether, eluted through a short silica column with diethyl ether and finally analyzed by GC.

8. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 270629 for compound **1** and CCDC No. 270628 for compound **2**.

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