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Synthesis and characterization of ruthenium (II) carbonyl complexes containing naphthyridine and acetylacetonate ligands and their catalytic activity in the hydrogen transfer reaction

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ABSTRACT

A series of novel complexes of the $Ru(L)_2(CO)_2$ L = 2-(3′ methoxyphenyl)-1,8-naphthyridine (complex **1**), and type $Ru(acac)_2(L)(CO)$ with L = 2-(3′ methoxyphenyl)-1,8-naphthyridine (complex **2**), 2-(2′-bromophenyl)-1,8-naphthyridine (complex **3**) and 2-phenyl-1,8-naphthyridine (complex **4**) was synthesized and characterized. We found that the complexes **2**, **3**, and **4** can be directly synthesized from $Ru_3(CO)_{12}$. The complex $Ru(acac)_2(L)(CO)$ L = 2-(3′ methoxyphenyl)-1,8-naphthyridine (**2**) was characterized by X-ray single crystal analysis which confirms the monodentate coordination mode of the 1,8-naphthyridine derivate and the *cis* arrangement of the acac ligands. Preliminary studies in transfer hydrogenation of acetophenone in the presence of 2-propanol show the good catalytic activity of complex **2** with 92% conversion.

Introduction. Ruthenium polypyridine complexes have been extensively studied, particularly those containing a 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) ligand, and these species have proven to be active catalysts in water gas shift reaction (WGSR) as well as in hydrogenation of ketones [1–3].

In homogeneous catalytic reactions, the presence of a hemi-labile ligand is highly desirable; it allows the catalytic reaction to take place via the formation of a vacant coordination site (monodentate coordination mode). Moreover, inhibition of side reactions and promotion of product elimination from a reaction center are promoted by the bidentate coordination mode. To construct such catalytic systems, the presence of a ligand which can adopt different coordination modes reversibly with little configurational barrier is required. It has been shown that 1,8-naphthyridine (napy) can be coordinated to a metal center as mono- and bi-dentate fashions. The monodentate (*κN1* or *κN8*) and bidentate (κ^2*N1*, *N8*) modes can be rapidly exchanged in solution, a process which depends on the temperature [4].

That is why we are currently developing the chemistry of ruthenium (II) complexes incorporating a 1,8-naphthyridine ligand, their catalytic properties being less explored. However, some studies have shown that ruthenium and rhodium naphthyridine complexes are interesting catalysts in alcohol oxidation and silylformylation of alkynes, respectively [5]. Herein, we report the direct synthesis of novel ruthenium complexes containing a monodentate naphthyridine and two acetylacetonate (acac) ligands as well as their catalytic activity in transfer hydrogenation of acetophenone.

Result and discussion. $[RuCl_2$(2-(3′-methoxyphenyl)-1,8-naphthyridine-*κN1*)(2-(3′-methoxyphenyl)-1,8-naphthyridine-*κN8*)$(CO)_2]$ (**1**) was prepared using the procedure reported by Moya et al. for similar compounds from $[RuCl_2(CO)_2]_n$ and 2-(3′-methoxyphenyl)-1,8-naphthyridine [6]. The treatment of **1** with acetylacetone H(acac) in the presence of a base (Na_2CO_3) yields the new ruthenium complex **2** in 54% yield (Scheme 1). In the alkaline media the two chloro ligands are exchanged by six-membered chelating acac ligands, while the carbon monoxide is released. Complex **2** was characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and X-ray diffraction studies.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ shows singlets at δ 1.81, 1.96, 2.03 and 2.08, attributed to the four non-equivalent acac-Me groups, as well as two singlets at δ 5.27 and 5.35 assigned to the acac-CH protons. The naphthyridine protons give rise to nine signals in the aromatic region (see supplementary material).

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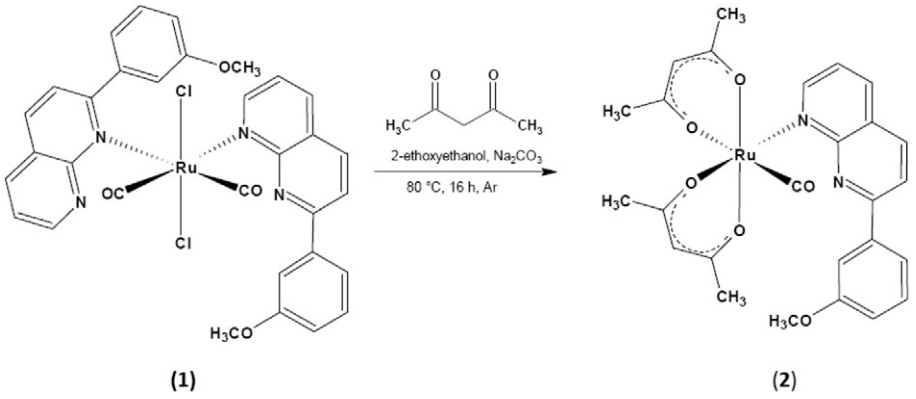


Scheme 1. Synthesis of complex **2**.

Single crystals suitable for X-ray diffraction were grown by slow evaporation from a chloroform solution of **2**, its molecular structure is shown in Fig. 1, in which the two acac ligands and the napy ligand are coordinated in a monodentate fashion. The compound crystallizes in a monoclinic crystal system. The geometry around the Ru center is pseudo-octahedral with a monodentate naphthyridine, a carbon monoxide and two (κ^2-*O, O′*) acac ligands which are not equivalents and *cis* relative to each other. The Ru–O (2.05–2.09 Å) bond lengths are similar to those found for the complex *cis*-Ru(acac)$_2$(meso-BESE), (where BESE is 1,2-bis(ethylsulfinyl)ethane = EtS(O)(CH$_2$)$_2$S(O)Et) [7]. The acac bite angles O(3)–Ru(1)–O(5) [84.63(7)°], O(4)–Ru(1)–O(6) [84.76(7)°] and O(5)–Ru(1)–O(4) [85.37(7)°], are smaller than expected, probably due to the coordination of the 2-phenyl substituted naphthyridine moiety. Ru(1)–C(26)–O(2) [179.2 (2)°] angle is nearly linear and the Ru(1)–N(1) [2.092 (2) Å], Ru(1)–C(26) [1.825 (2) Å] and C(26)–O(2) [1.158 (3) Å] distances are in the expected range [8].

This synthetic route to **2** is, however, not straightforward and requires the tedious preparation of **1** [RuCl$_2$(2-phenyl-1,8-naphthyridine-$\kappa N1$)(2-phenyl-1,8-naphthyridine-$\kappa N8$)(CO)$_2$] derivatives. We found a one-pot synthesis to Ru(acac)$_2$(napy-$\kappa N8$)(CO) complexes derivate, which consists of reacting Ru$_3$(CO)$_{12}$ with 2-(2′-bromophenyl)-1,8-naphthyridine (complex **3**) or 2-phenyl-1,8-naphthyridine (complex **4**) in refluxing THF, in the presence of H(acac) and Na$_2$CO$_3$ (Scheme 2). The reaction afforded two new products, which were isolated in 26% (**3**) and 45% (**4**) yields, respectively as pure compounds after purification by column chromatography. The ^{1}H and ^{13}C NMR spectra of **3** are consistent with the proposed structure, i.e. a *cis* arrangement of the acac ligands, as observed for **2**. For example, the acac resonances of **3** appear in the ^{13}C NMR spectrum (CDCl$_3$) at δ 27.36, 27.45, 27.89 and 28.15 (methyl groups) and δ 185.74, 187.89, 187.97 and 189.61 (C(O)) for **3**. The CO ligand appears typically at δ 209.71 and the Br-napy ligand gives rise to nine signals. The NMR data of **4** are very similar to those of **3**, in

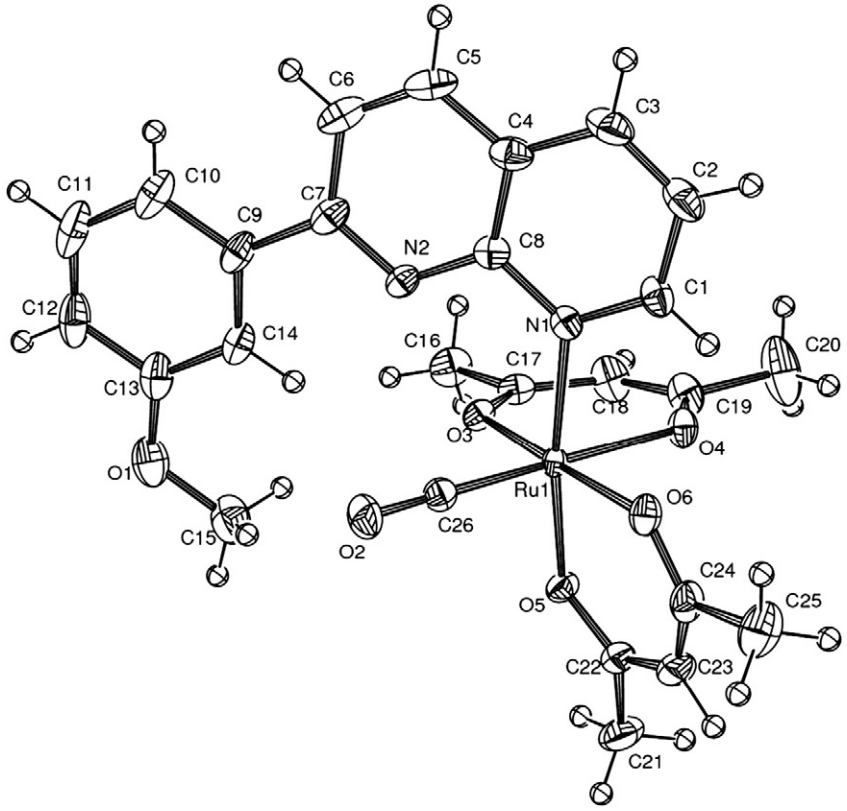
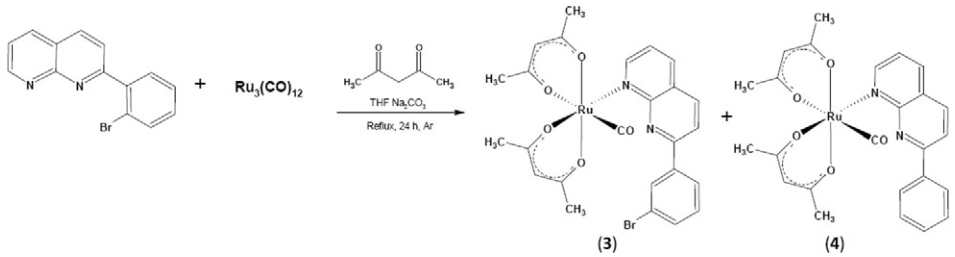


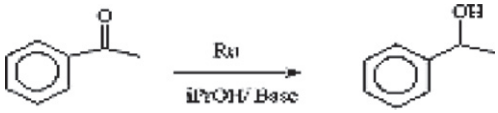
Fig. 1. ORTEP drawing (50% probability) of the complex **2**. Crystallization solvent has been omitted for clarity.



Scheme 2. Synthesis of complexes **3** and **4**.

Table 1
Transfer hydrogenation of acetophenone catalyzed by Ru(acac)$_2$(napy-κ*N8*)(CO) complexes.

	% Conversion$^{\sigma}$		
Reaction time (h)	2	3	4
1	48	17	58
2	86	38	79
3	92	53	90



$_{\sigma}$Conversion of acetophenone to 1-phenylethanol.

agreement with a similar arrangement of the coordinated ligands. However, note that complex **4** underwent a dehalogenation process, as indicated by the presence of ten protons for the napy ligand in the aromatic region. Similarly, when $Ru_3(CO)_{12}$ was reacting with 2-phenyl-1,8-naphthyridine, compound **4** was obtained in a good yield.

Recently catalytic activities displayed by ruthenium complexes containing polypyridine ligands were reported. It was found that compounds containing nitrogen ligands showed high conversions [9]. Consequently the catalytic behavior of the complexes prepared in this work was analyzed. The catalytic activities of **2**, **3**, and **4** compounds were tested in hydrogen transfer reaction of acetophenone to 1-phenylethanol using 2-propanol as hydrogen donor (Table 1). The results are listed in Table 1. The complexes are effective catalysts, **2** appears to be the more active. On the other hand, lower activity shown by **3** might be explained considering an effect of steric hindrance by the *ortho*-Br substituted ligand. In short, we have synthesized and characterized a series of new Ru(acac)$_2$(napy-κ*N8*)(CO) complexes. We have shown that these complexes are directly accessible from $Ru_3(CO)_{12}$ and the appropriate naphthyridine ligand. The preliminary results in transfer hydrogenation reactions are promising and further studies are currently under way. The conversion between 53 and 92% after 3 h reaction has been found.

Conclusion. New complexes type Ru(acac)$_2$(L)CO (L = naphthyridine ligands) have been synthesized by one-pot reaction using $Ru_3(CO)_{12}$, acac and naphthyridine derivate ligands. The compounds were characterized by resonance magnetic nuclear and elemental analysis. The ruthenium compounds show two *cis*-acac configurations and the naphthyridine derivate ligand coordination in a monodentate fashion. The complexes showed moderate activity as catalysts in the hydrogen transfer reaction, and compound **2** showed a conversion of 92%.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.09.028.

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