Synthesis and characterization of new complexes of the type [Ru(CO)$_2$Cl$_2$ (2-phenyl-1,8-naphthyridine-*kN*) (2-phenyl-1,8-naphthyridine-*kN*′)]. Preliminary applications in homogeneous catalysis

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Novel ruthenium (II) complexes were prepared containing 2-phenyl-1,8-naphthyridine derivatives. The coordination modes of these ligands were modified by addition of coordinating solvents such as water into the ethanolic reaction media. Under these conditions 1,8-naphthyridine (napy) moieties act as monodentade ligands forming unusual [Ru(CO)$_2$Cl$_2$(η^1-2-phenyl-1,8-naphthyridine-*kN*)(η^1-2-phenyl-1,8-naphthyridine-*kN*′)] complexes. The reaction was reproducible when different 2-phenyl-1,8-naphthyridine derivatives were used. On the other hand, when dry ethanol was used as the solvent we obtained complexes with napy moieties acting as a chelating ligand. The structures proposed for these complexes were supported by NMR spectra, and the presence of two ligands in the [Ru(CO)$_2$Cl$_2$(η^1-2-phenyl-1,8-naphthyridine-*kN*)(η^1-2-phenyl-1,8-naphthyridine-*kN*′)] type complexes was confirmed using elemental analysis. All complexes were tested as catalysts in the hydroformylation of styrene showing moderate activity in *N*,*N*′-dimethylformamide.

Keywords: ruthenium complexes; naphthyridine; homogeneous catalysis; styrene hydroformylation

Introduction

Transition metal complexes containing electron-rich ligands have been the focus of several studies in the field of organometallic chemistry of metals in group VIII. Very strong σ-donor ligands such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) have been extensively used in the coordination chemistry of ruthenium and applied in homogeneous catalysis as electron reservoirs in metal complexes or as promoters of catalytic reactions.[1] For example, it has been demonstrated that complexes of the type ruthenium carbonyl with bipyridine or phenanthroline are active catalysts in the water–gas-shift-reaction, and in the hydrogenation of ketones and olefins.[2–4] Also, the [Ru$_3$(CO)$_{12}$/1,10-phenanthroline] system has been found to be active in the hydroformilation of α-olefins.[5]

On the other hand, the 1,8-naphthyridine (napy) ligand is a versatile molecule due to its different coordination modes: monodentade, chelating and bridged. In the case of the Ru^{II}-(bipy)$_2$ type complex, both *cis*-[Ru(bpy)$_2$(1,8-naphthyridine-*kN*)(CH$_3$CN)]PF$_6$ and *trans*- [Ru(bpy)$_2$(1,8-naphthyridine-k^2N,*N*′)](PF$_6$) have been isolated, and their crystal structures and electrochemical properties determined by Nakajima *et al*.[6] These authors have demonstrated that monodentade ruthenium (II) complexes exhibit rapid coordination-site exchange reactions.[7] Also, the 1,8-naphthyridine ligand can place two metal centers so close to each other that bonding, magnetic and/or energy transfer interactions are likely to happen between these metals. Several dinuclear complexes bridged with napy have been examined in this respect.[8–11] Furthermore, napy ligands have shown the ability of forming four-membered chelate rings when the two nitrogen atoms bind to one central metal. This is probably the consequence of the small *bite*

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of 2.2 Å attributed to the 1,8-naphthyridine ligands. An example of this behavior is the $[Ru(napy)_4]^{2+}$ complex.[12–15] Nevertheless, in a previous paper we reported the synthesis of complexes of the type ruthenium–carbonyl in which the1,8-naphthyridine fragments were coordinated in chelating form, demonstrating the great versatility of these ligands.[16]

The complexes derived from 1,8-naphthyridine have been barely studied in homogeneous catalysis reactions in comparison with the 1,10-phenanthroline or 2,2′-bipyridyl derivatives. However, Tanaka and co-workers have developed a ruthenium–naphthyridine complex that transforms carbon dioxide into acetone, which is an important feedstock for the chemical industry.[17] Besides, complexes such as $Ru_2(dmnapy)Cl_4$ (where dmnapy = 2,7-dimethoxy-1,8-naphthyridine) have been found to be active in the catalytic oxidation of alcohols and the epoxidation of *trans*-stilbene.[18]

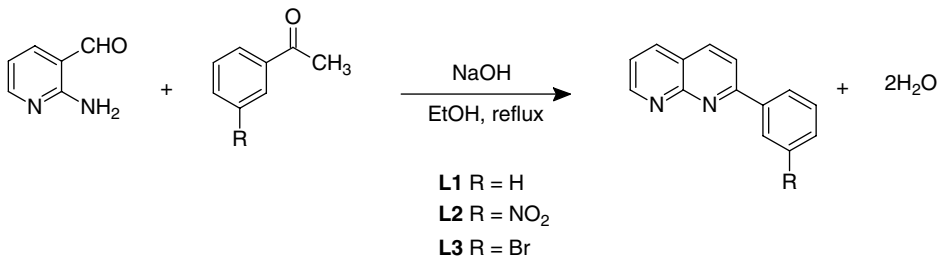
Supported by these arguments, we report here the synthesis of new ruthenium–carbonyl complexes derived from 2-phenyl-1,8-naphthyridine-type ligands, including their first application as homogeneous catalysts in the hydroformylation of styrene

Results and Discussion

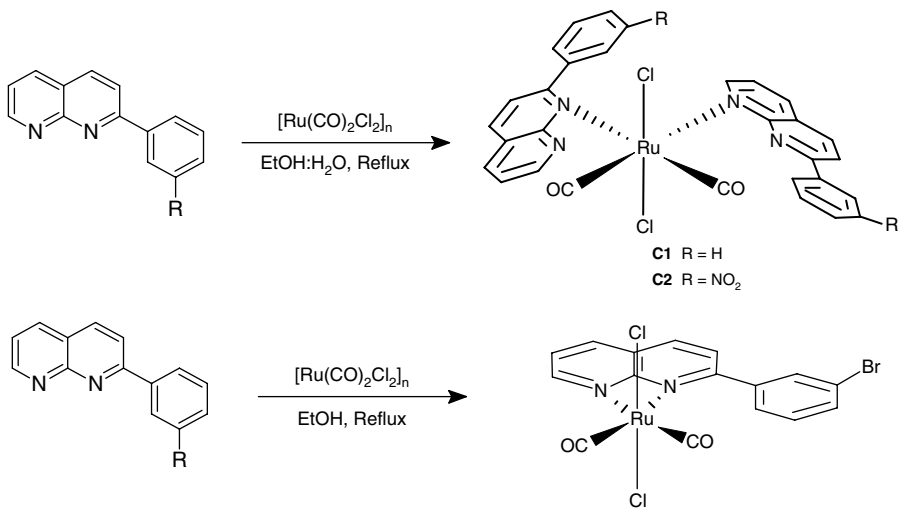
Synthesis of the ligands

Synthesis of the 2-phenyl-1,8-naphthyridine type ligands

The synthesis of 2-phenyl-1,8-naphthyridine, **L1,** and 2-(3′-nitrophenyl)-1,8-naphthyridine, **L2,** starts with the preparation of 2-aminonicotinaldehyde.[19] This material reacts with acetophenone, an enolizable ketone and 3′-nitroacetophenone, respectively, through a Friedländer condensation in alkaline ethanol medium (Scheme 1). When the first ketone was used, 2-phenyl-1,8-naphthyridine was the resulting product, but when 3′-nitroacetophenone was used, the resulting product was 2-(3′-nitrophenyl)-1,8-naphthyridine. Both solids were obtained in good yield, and they proved stable in air at room temperature and soluble in chlorinated solvents, such as chloroform and dichloromethane. The ligands were characterized by ^{1}H-NMR spectroscopy, showing the typical chemical shifts of aromatic groups localized in the two positions of the substituted 1,8-naphthyridine,[16] namely H_a, δ 9.10 (R = H) and 9.15 (R = NO_2). In both cases, this signal appears as a doublet of doublets, which presumably is the consequence of the coupling with the H_b protons (δ 7.47 and 7.54 for R = H and R = NO_2 respectively) and H_c (δ 8.22 and 8.24 for R = H and R = NO_2 respectively). Protons H_b and H_c also appear as doublets of doublets. The protons H_d (δ 8.02 and 8.10 for R = H and R = NO_2) and H_e (δ 8.28 and 8.39 for R = H and R = NO_2) are registered as doublets. The differences observed in the chemical shifts of 1,8-naphthyridines are due to the influence of the nitro group, which is more electron-withdrawing than hydrogen; this produces a deshielding effect on the protons in 2-(3′-nitrophenyl)-1,8-naphthyridine. This effect is dramatic for the phenyl protons. Thus, when R = H, the H_i proton appears at δ 8.29, but with R = NO_2 this signal appears at δ 9.09. The same behavior was observed in the corresponding ^{13}C-NMR spectra. The assignment of the signals, in every case, was confirmed by ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC spectroscopy.



Scheme 1. Friedländer condensation reaction to obtain the ligands.



Scheme 2. Synthesis of the new complexes using an ethanol-water mixture (top) and using only ethanol (bottom).

Synthesis of the complexes

The synthesis of the complexes *trans*-Cl-*cis*-(CO)-[$Ru(CO)_2Cl_2(\eta^1$-2-phenyl-1,8-naphthyridine-*kN*) (η^1-2-phenyl-1,8-naphthyridine-*kN*′)] (**1**), and *trans*-Cl-*cis*-(CO)-[$Ru(CO)_2Cl_2(\eta^1$-2-(3′nitro-phenyl)-1,8-naphthyridine-*kN*)(η^1-2-(3′-nitro-phenyl)η^1-1,8-naphthyridine-*kN*′)] (**2**) was carried out via reaction of $[Ru(CO)_2Cl_2]_n$[20] with **L1** and **L2,** respectively (Scheme 2, top). The selection of the solvent is crucial in order to modify the reaction product. For instance, in previous work[16] we had $[Ru(CO)_2Cl_2]_n$ reacting with ligands derived from 1,8-naphthyridine in ethanol, and the product obtained was *trans*-Cl-*cis*-(CO)-[$Ru(CO)_2Cl_2$(N–N)], where N–N is a naphthyridine ligand. In this case the naphthyridine is coordinated in a chelating way. However, Boelrijk

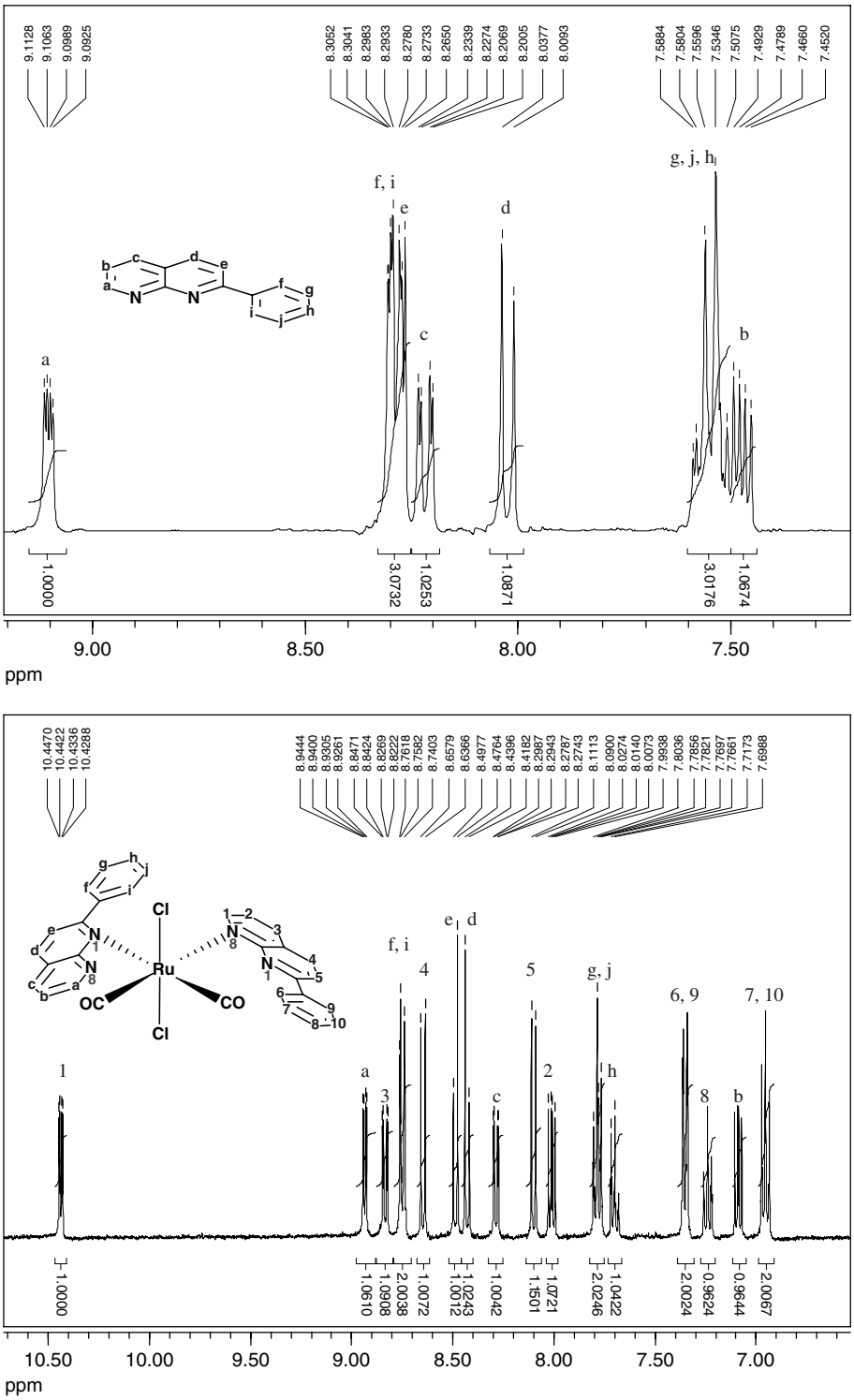


Figure 1. ^{1}H-NMR (400 MHz, acetone-d_6) spectra for the complex **1** (bottom) and. ^{1}H-NMR for **L1** ligand (top).

et al.[18] have reported the effects that coordinating solvents, such as water or acetonitrile, can provide in the coordination of 1,8-naphthyridine. Whereas the 1,8-naphthyridine in alcohol acts as a chelating ligand, in water or acetonitrile it acts as a monocoordinating ligand.

The addition of water to alcohol might imply a possible N-protonation. However this possibility must be ruled out because the ^{1}H-NMR spectrum is not affected. It is more likely that the presence of water produces the modification of the coordination in the metal center.

In order to modify the product of the reaction upon changing the solvent, we carried out the synthesis using an ethanol–water mixture (9:1) to force the naphthyridine to behave as a monocoordinating ligand. The syntheses were accomplished using reflux under a nitrogen atmosphere for 24 h. The reaction of $[Ru(CO)_2Cl_2]_n$ with **L1** yielded complex **1**. The ^{1}H-NMR spectrum

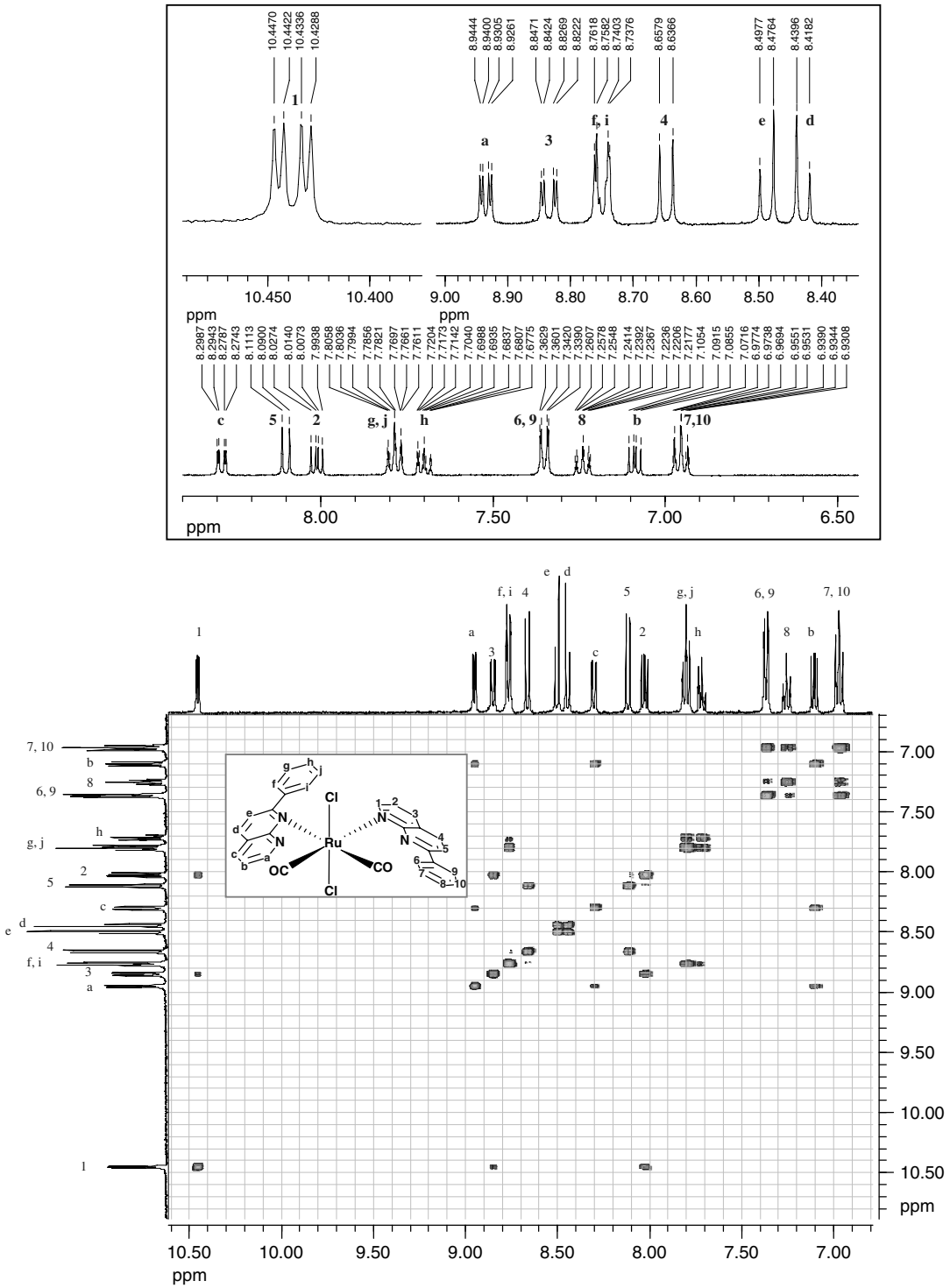


Figure 2. Expanded ^{1}H-NMR spectra of the complex **1** (top) and its ^{1}H-^{1}H COSY (400 MHz, acetone-d_6).

for this product (Fig. 1, bottom) shows a total of 20 signals when compared with the 10 signals shown by the uncoordinated ligand (Fig. 1, top). This suggests the existence of two ligand units coordinated to the ruthenium atom. The nonequivalence of the protons is a strong evidence that the naphthyridine is behaving as a monocoordinating ligand which binds to the metal through one nitrogen atom.

The chemical shifts suggest that one of the ligands is coordinated to ruthenium through nitrogen 1 and the other is coordinated through nitrogen 8. This was confirmed by analyzing the chemical shifts of the different protons. For instance, proton H_1 appears at δ 10.44. This deshielding is due to the coordination to the metal through nitrogen 8. On the contrary, proton H_a appears at δ 8.94. This shift is similar to that observed in the uncoordinated ligand (δ 9.10), which clearly indicates that the ligand is not coordinated through nitrogen 8 but through nitrogen 1 since H_e appears at δ 8.49 and H_5 at δ 8.10 with a clear influence of the metal center. In a similar way, proton H_i (δ 8.75) is localized at a lower field than H_6 (δ 7.35) because of its proximity to the ruthenium atom.

The ^{1}H-NMR assignments were confirmed by ^{1}H–^{1}H-COSY spectroscopy (Figure 2). The spectrum shows H_a, H_b and H_c protons (which are doublets of doublets) coupling with themselves; the same happens with H_d and H_e (both doublets). Similar behavior is observed for H_1, H_2 y H_3 (analogous to H_a, H_b and H_c) and H_4 and H_5 protons (analogous to H_d and H_e). The multiplicities either for protons designed by small letters or for those designed by numbers (assigned in a arbitrary way) are the same, but with different chemical shifts. In order to check if the results obtained by us are reproducible, we synthesized another complex by reacting $[Ru(CO)_2Cl_2]_n$ with 2-(3′-nitrophenyl)-1,8-naphthyridine. This yielded the complex **2**, which, in a way similar to that in the previous case, has the 1,8-naphthyridine coordinated as a monodentate ligand. In addition, when the previous reaction was repeated using only ethanol as solvent (scheme 2, bottom), the complex **4** obtained had only one naphthyridine moiety (the product shows only nine signals in ^{1}H-NMR). The reproducibility of this synthesis is dependent on the solvent since when wet ethanol was used traces of complex **1** were obtained together with the principal product, which is the complex **4** with the 1,8-naphthyridine moiety coordinated in a chelating manner. However, when the reaction was performed in dry ethanol, e.g. with 2-(3′-bromophenyl)-1,8-naphthyridine ligand **L3** (this one was prepared like **L1**, for more details see Experimental section), we obtained the complex **3** in good yield. The ^{1}H-NMR (Fig. 3) and COSY ^{1}H–^{1}H of this complex are in agreement with the proposed formula (Scheme 2) showing a similar pattern to the one observed in 1,8-naphthyridine coordinated ligands.

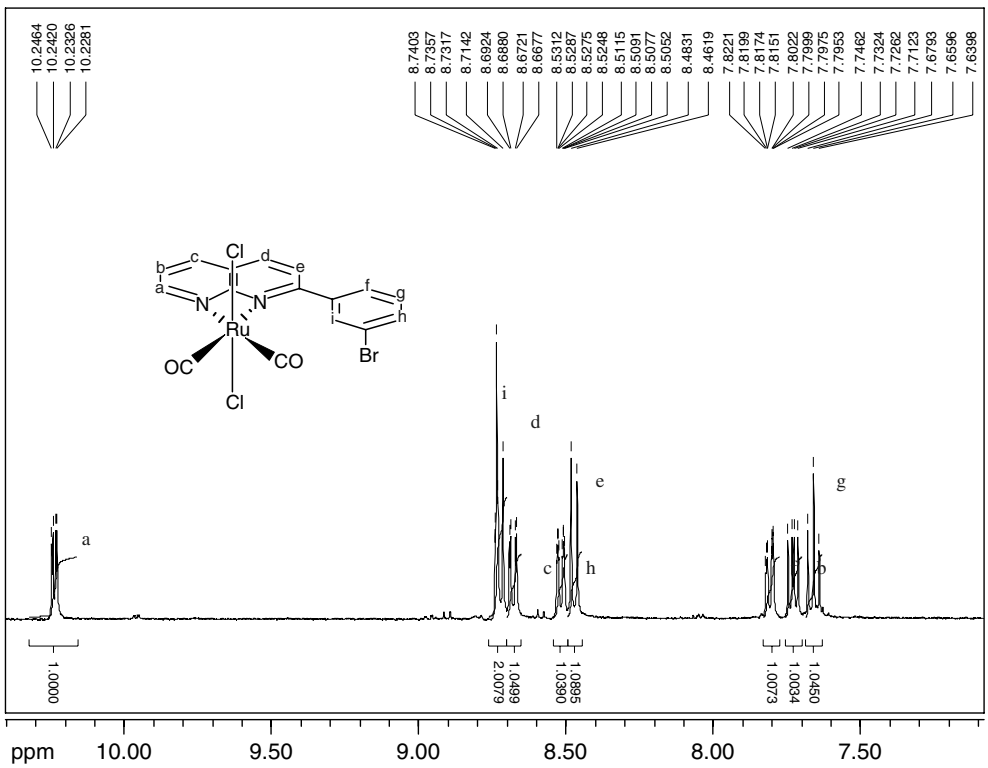
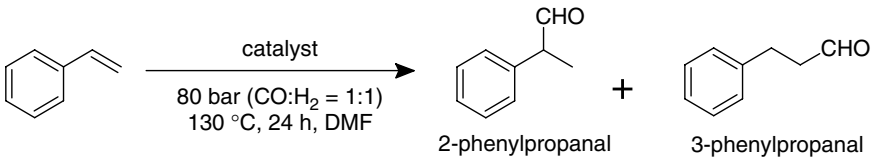
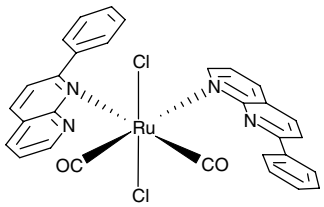
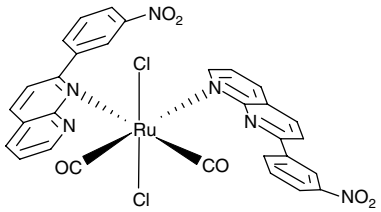
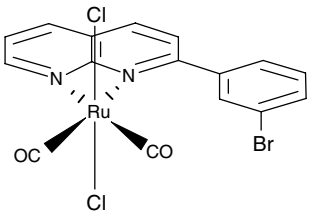


Figure 3. ^{1}H-NMR (400 MHz, acetone-d_6) spectra of the complex **3**.



Scheme 3. Hydroformylation of styrene using the new complexes as catalysts.

Table 1. Conversion of aldehydes in the hydroformylation of styrene

Catalyst	Total conversion of aldehydes (%)	CHO Conversion (%)	CHO Conversion (%)	*n*-Selectivity[a] (%)
	26.73	14.67	12.06	45
	41.75	17.11	24.63	64
	50.69	24.85	25.84	51

[a] *n*-Selectivity = 3-phenylpropanal/total aldehydes.

Hydroformylation of styrene

In order to test the catalytic potential of the new complexes, two of them were assayed in the hydroformylation reaction of styrene. The reaction was carried out under 80 bar of synthesis gas ($CO/H_2 = 1:1$) at 130 °C in the presence of catalytic amounts of complexes **1** or **2** in *N*,*N*′-dimethylformamide (DMF) (Scheme 3). The expected products were 2-phenylpropanal (branched) and 3-phenylpropanal (*n*-aldehyde), as shown in Table 1. In the case of complex **2**, the NO_2 group debilitates the Ru–CO bond, rendering it more reactive towards the incoming styrene, thus increasing the overall conversion to aldehydes. However, in this case the linear aldehyde is sterically favored with respect to the branched isomer. This indicates that the structural effects by the R groups on the naphthyridine ligands are important, which together with the exact nature of the mechanism, is currently the focus of the ongoing investigation. Indeed one the few examples of thoroughly studied mechanisms of Ru complexes with nitrogen-containing ligands have been reported by Frediani *et al*.[21] The hydroformilation activities for 1-hexene reported in this work are in the range of 8–33%, with a high selectivity towards the lineal product.

$RuCl_3$ hydrated and $Ru_3(CO)_{12}$ have been used as catalysts in the hydroformilation of olefin with nonattractive activities.[22] The activities for the hydroformilation reported by us in this work are similar to those reported for 1-hexene[21] and propene[23] (with conversions in the range of 30–50%).

Experimental

Materials and measurements

$RuCl_3 \cdot nH_2O$, acetophenone, 3′-nitroacetophenone and 3′-bromoacetophenone from Aldrich were used as received. Deuterated solvents, acetone-d_6, chloroform-*d* and dichloromethane-d_2 were purchased from Aldrich and used as received. Absolute ethanol used for the C3 preparation was dried over activated magnesium. The ruthenium (II) polymer, $[Ru(CO)_2Cl_2]_n$[20] and 2-aminonicotinaldehyde[19] were prepared using a literature method. IR spectra as KBr pellets were recorded on an FT-IFS 66v Fourier spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker FT-NMR 400 MHz spectrometer. The chemical shifts were referenced to the residual ^{1}H-NMR signals of the deuterated solvents, 2.05, 7.26 and 5.32 ppm for acetone-d_6, chloroform-*d* and dichloromethane-d_2, respectively, and were reported vs tetramethylsilane (TMS). The yields of the organic compounds (catalytic assays) were obtained by GC (Agilent 6890N GC).

Preparation of the ligands

2-Phenyl-1,8-naphthyridine, **L1**

A mixture of 2-aminonicotinaldehyde (500 mg, 4.10 mmol), acetophenone (492 mg, 4.10 mmol) and sodium hydroxide (three pellets) was dissolved in absolute ethanol (30 mL) and placed in a

round-bottomed flask (150 mL) containing a stir bar. The mixture was refluxed for 4 h under nitrogen. After cooling, a red solution was obtained, the ethanol was evaporated and distilled water was added. After shaking the flask for 5 min, an orange solid precipitated, which was dissolved in dichloromethane and treated with activated charcoal for 1 h. The mixture was filtered and treated with $MgSO_4$ for 20 min. The suspension was filtered, evaporated and the residue recrystallized from ether as a yellow solid (785 mg; 3.81 mmol). Yield, 93%; m.p. 102 °C. ^{1}H-NMR (300 MHz, CD_2Cl_2) δ 9.10 (dd, H_a, $J = 4.2, 2.1$ Hz), 7.47 (dd, H_b, $J = 8.1, 4.2$ Hz), 8.22 (dd, H_c, $J = 8.1, 2.1$ Hz), 8.02 (d, H_d, $J = 8.6$ Hz), 8.28 (d, H_e, $J = 8.6$ Hz), 8.29 (m, H_f), 7.55 (m, H_g), 7.55 (m, H_h), 8.29 (m, H_i), 7.55 (m, H_j). ^{13}C-NMR (75 MHz, CD_2Cl_2) δ 160.52, 156.71, 154.36, 139.31, 138.48 (2C), 137.30, 130.55, 129.38 (2C), 128.27, 122.37, 122.31, 120.10. Anal. calcd for $C_{14}H_{10}N_2 \cdot 0.25\ H_2O$ (%): C, 79.79; N, 13.29; H, 5.02. Found (%): C, 79.77; N, 13.27; H, 4.97.

2-(3′-nitrophenyl)-1,8-naphthyridine, **L2**

A mixture of 2-aminonicotinaldehyde (500 mg; 4.10 mmol), 3′-nitroacetophenone (676 mg; 4.10 mmol), and sodium hydroxide (three pellets), was dissolved in absolute ethanol (30 ml) and placed in a round-bottomed flask (150 mL) containing a stir bar. The mixture was refluxed for 4 h under nitrogen. After the system had cooled, a white solid was separated by filtration, washed and recrystallized from hot ethanol and ethyl ether (1008 mg; 4.02 mmol). Yield, 98%; m.p. 215 °C. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 9.15 (dd, H_a, $J = 4.2, 2.1$ Hz), 7.54 (dd, H_b, $J = 8.1, 4.2$ Hz), 8.28 (dd, H_c, $J = 8.1, 2.1$ Hz), 8.10 (d, H_d, $J = 8.4$ Hz), 8.39 (d, H_e, $J = 8.4$ Hz), 8.34 (ddd, H_f, $J = 8.3, 2.3, 1.1$ Hz), 7.75 (t, H_g, $J = 8.1$ Hz), 8.67 (ddd, H_h, $J = 7.8, 1.7, 1.1$ Hz), 9.09 (t, H_i, $J = 2.0$ Hz). ^{13}C-NMR (75 MHz, CD_2Cl_2) δ 157.97, 156.54, 154.95, 149.48, 141.03, 139.28, 137.45, 134.16, 130.51, 124.99, 123.06, 123.00, 122.90, 119.82. MS, $m/z = 251$ (100%, $C_{14}H_9N_3O_2^+$). IR (KBr), νNO 1523; 1346 cm^{-1}. Anal. calcd for $C_{14}H_9N_3O_2$ (%): C, 66.93; N, 16.72; H, 3.65. Found (%): C, 66.65; N, 16.70; H, 3.57.

2-(3′-bromophenyl)-1,8-naphthyridine, **L3**

A mixture of 2-aminonicotinaldehyde (500 mg; 4.10 mmol), 3′-bromoacetophenone (1169 mg; 4.10 mmol) and sodium hydroxide (three pellets) was dissolved in absolute ethanol in (30 mL) and placed in a round-bottomed flask (150 mL) containing a stir bar. The mixture was refluxed for 4 h under nitrogen. After the system had cooled, a red solution was obtained. This was evaporated to half volume, then water was added and a brown solid was obtained (994 mg; 3.49 mmol) with enough purity for the synthesis of its ruthenium carbonyl complex. In order to obtain an analytical sample, the solid was recrystallized from acetone yielding a clear brown solid. Yield, 85%; m.p. 82 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.14 (dd, H_a, $J = 4.1$; $J = 2.0$ Hz), 7.48 (dd, H_b, $J = 8.2$; $J = 4.1$ Hz), 8.20 (m, H_c), 7.96 (d, H_d, $J = 8.4$ Hz), 8.26 (d, H_e, $J = 8.4$ Hz), 7.60 (dt, H_f, $J = 7.9$; $J = 0.9$ Hz), 7.38 (t, H_g, $J = 7.9$ Hz), 8.20 (m, H_h), 8.51 (s, H_i).

Preparation of the complexes

Trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^1-2-phenyl-1,8-naphthyridine-kN)(η^1-2-phenyl-1,8-naphthyridine-kN′)], (***1***)*

In a 150 mL round-bottomed flask fitted with a reflux condenser the following were added in the indicated order: 2-phenyl-1,8-naphthyridine (481 mg, 2.34 mmol), $[Ru(CO)_2Cl_2]_n$ (500 mg; 2.34 mmol) and ethanol:water 9 : 1 (30 mL). The mixture was refluxed under nitrogen for 24 h, forming a solid. After this the compound was separated and washed with chloroform. Finally, the residue was recrystallized from ethanol, yielding an orange compound (688 mg; 1.08 mmol). Yield, 92%; m.p. 257 °C. ^{1}H-NMR (400 MHz, acetone-d_6) δ 10.44 (dd, H_1, $J = 5.4, 1.9$ Hz), 8.01 (dd, H_2, $J = 8.0, 5.4$ Hz), 8.83 (dd, H_3, $J = 8.1, 1.9$ Hz), 8.65 (d, H_4, $J = 8.5$ Hz), 8.10 (d, H_5, $J = 8.5$ Hz), 7.35 (dd, H_6, $J = 8.4, 1.2$ Hz), 6.95 (m, H_7), 7.24 (tt, H_8, $J = 7.4, 1.2$ Hz), 7.35 (dd, H_9, $J = 8.4, 1.2$ Hz), 6.95 (m, H_{10}), 8.94 (dd, H_a, $J = 5.5, 1.7$ Hz), 7.09 (dd, H_b, $J = 8.0, 5.5$ Hz), 8.29 (dd, H_c, $J = 8.0, 1.7$ Hz), 8.43 (d, H_d, $J = 8.6$ Hz), 8.49 (d, H_e, $J = 8.6$ Hz), 8.75 (m, H_f), 7.78 (m, H_g), 7.70 (tt, H_h, $J = 7.4, 1.2$ Hz), 8.75 (m, H_i), 7.78 (m, H_j). IR (KBr) νCO 2049; 1984 cm^{-1}. Anal. calcd for $C_{30}H_{20}N_4O_2Cl_2Ru \cdot 0.5H_2O$ (%): C, 55.45; N, 8.62; H, 3.26. Found (%): C, 55.30; N, 8.18; H, 2.80.

Trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^1-2-(3′-nitrophenyl)-1,8-naphthyridine-kN)(η^1-2-(3′-nitrophenyl)-1,8-naphthyridine-kN′)], (***2***)*

2-(3′-Nitrophenyl)-1,8-naphthyridine (587 mg, 2.34 mmol), $[Ru(CO)_2Cl_2]_n$ (500 mg; 2.34 mmol) and ethanol : water (9 : 1; 30 ml) were successively added to a round-bottomed flask (150 mL) provided with a reflux condenser. The mixture was refluxed under nitrogen for 24 h, forming a solid. After this the compound was washed with chloroform and recrystallized from ethanol, yielding a yellow complex (760 mg; 1.04 mmol). Yield, 89%; m.p. 256 °C. ^{1}H-NMR (400 MHz, acetone-d_6) δ 10.44 (dd, H_1, $J = 5.3, 1.9$ Hz), 8.09 (dd, H_2, $J = 8.1, 5.3$ Hz), 8.91 (m, H_3), 8.17 (d, H_4, $J = 8.5$ Hz), 8.77 (d, H_5, $J = 8.5$ Hz), 7.67 (ddd, H_6, $J = 7.8, 1.7, 1.1$ Hz), 7.32 (t, H_7, $J = 8.0$ Hz), 8.15 (m, H_8), 8.27 (m, H_9), 8.92 (m, H_a), 8.27 (m, H_b), 7.07 (dd, H_c, $J = 8.0, 5.5$ Hz), 8.40 (d, H_d, $J = 8.5$ Hz), 8.48 (d, H_e, $J = 8.5$ Hz), 8.56 (ddd, H_f, $J = 7.9, 1.8, 1.0$ Hz), 8.13 (m, H_g), 9.11 (ddd, H_h, $J = 7.9, 1.8, 1.0$ Hz), 9.49 (t, H_i, $J = 2.0$ Hz). IR (KBr) νCO 2053; 1989 cm^{-1}. Anal. calcd for $C_{30}H_{18}N_6O_6Cl_2Ru$ (%): C, 49.33; N, 11.50; H, 2.48. Found (%): C, 48.75; N, 11.24; H, 2.61.

Trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^2-2-(3′-bromophenyl)-1,8-naphthyridine-k^{2}N,N′)], (***3***)*

In a 150 mL round-bottomed flask provided with a reflux condenser the following were added in the indicated order: 2-(3′-bromophenyl)-1,8-naphthyridine (666 mg, 2.34 mmol), $[Ru(CO)_2Cl_2]_n$ (500 mg, 2.34 mmol) and dry ethanol. The mixture was refluxed under nitrogen for 24 h forming a solid. After this the compound was washed with acetone. Finally the residue was recrystallyzed from hot chloroform yielding a brown solid. (1165 mg, 2.27 mmol). Yield, 97%; m.p. 312 °C. ^{1}H-NMR (400 MHz, acetone-d_6) δ 10.24 (dd, H_a, $J = 5.6$; $J = 1.9$ Hz), 7.73 (dd, H_b, $J = 8.1$; $J = 5.6$ Hz), 8.68 (dd, H_c, $J = 8.1$; $J = 1.9$ Hz), 8.47 (d, H_d, $J = 8.6$ Hz), 8.73 (d, H_e, $J = 8.6$ Hz), 7.81 (ddd, H_f, $J = 7.9$; $J = 1.9$; $J = 0.9$ Hz), 7.66 (t, H_g, $J = 7.9$ Hz), 8.52 (ddd, H_h, $J = 7.9$; $J = 1.5$; $J = 1.1$ Hz), 8.74 (t, H_i, $J = 1.6$ Hz). IR (KBr) νCO 2057; 1980 cm^{-1}. Anal. calcd for $C_{16}H_9N_2O_2Cl_2BrRu$ (%): C, 37.16; N, 5.42; H, 2.53. Found (%): C, 37.32; N, 4.99; H, 1.98.

Trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^2-2-(3′-nitrophenyl)-1,8-naphthyridine-k^{2}N,N′)], (***4***)*

In a round-bottomed flask (150 mL) provided with a reflux condenser were added: 2-(3′-nitrophenyl)-1,8-naphthyridine (586 mg, 2.34 mmol), $[Ru(CO)_2Cl_2]_n$ (500 mg, 2.34 mmol) into 30 mL dry

ethanol. The mixture was refluxed under nitrogen for 24 h forming a solid. After this compound washed with ethanol and hot chloroform to obtained a soft pink solid (1030 mg, 2.27 mmol); yield, 92%; m.p. 312 °C. ^{1}H-NMR (400 MHz, acetone-d_6) δ 9.99 (dd, H_a, $J = 5.5$; $J = 1.8$ Hz), 8.09 (dd, H_b, $J = 8.1$; $J = 5.5$ Hz), 9.01 (dd, H_c, $J = 8.1$; $J = 1.8$ Hz), 8.71 (d, H_d, $J = 8.5$ Hz), 8.98 (d, H_e, $J = 8.5$ Hz), 8.50 (ddd, H_f, $J = 8.2$; $J = 2.2$; $J = 0.9$ Hz), 7.99 (t, H_g, $J = 8.0$ Hz), 8.92 (ddd, H_h, $J = 7.9$; $J = 1.7$; $J = 1.0$ Hz), 9.18 (t, H_i, $J = 2.0$ Hz). IR (KBr) νCO 2065; 1989 cm^{-1}.

Catalytic assays

Hydroformylation of styrene catalyzed by trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^1-2-phenyl-1,8-naphthyridine-kN) (η^1-2-phenyl-1,8-naphthyridine-kN′)], (***1***)*

In a Schlenk flask complex **1** (25 mg; 0.04 mmol), DMF (40 mL) and styrene (833 mg; 8.0 mmol) were added. The solution was placed in a 100 ml stainless autoclave. After this it was purged with nitrogen and vacuum, and CO (40 bar) and H_2 (40 bar) were added at 25 °C, and the mixture was magnetically stirred at 130 °C for 24 h. 2-Phenylpropanal and 3-phenylpropanal were obtained by GC in yields of 14.7 and 12.1%, respectively.

Hydroformylation of styrene catalyzed by η^1-trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^1-2-(3′-nitrophenyl)-1,8-naphthyridine-kN)(η^1-2-(3′-nitrophenyl)-1,8-naphthyridine-kN′)], (***2***)*

In a Schlenk flask the complex **2** (29 mg; 0.04 mmol), DMF (40 mL) and styrene (833 mg; 8.0 mmol) were added. The solution was placed in a 100 mL stainless autoclave. After this it was purged with nitrogen and vacuum, CO (40 bar) and H_2 (40 bar) were introduced at 25 °C, and the mixture was magnetically stirred at 130 °C for 24 h. 2-Phenylpropanal and 3-phenylpropanal were obtained by GC in yields of 28.85 and 24.84%, respectively.

Hydroformylation of styrene catalyzed by trans-*Cl*-cis-*(CO)-[Ru(CO)$_2$Cl$_2$(η^2-2-(3′-bromophenyl)-1,8-naphthyridine-k^{2}N,N′)] (***3***)*

To a Schlenk flask complex **3** (21 mg; 0.04 mmol), DMF (40 mL) and styrene (833 mg; 8.0 mmol) were added. The solution was placed in a 100 mL stainless autoclave. After this it was purged with nitrogen and vacuum was applied, and CO (40 bar) and H_2 (40 bar) were introduced at 25 °C, and the mixture was magnetically stirred at 130 °C for 24 h. 2-Phenylpropanal and 3-phenylpropanal were obtained by GC in yields of 17.1 and 24.7%, respectively.

Acknowledgments

The authors acknowledge the financial support provided by Fondecyt-Chile (project 1085135) and CEPEDEQ Universidad de Chile. Juana Gajardo and Juan C. Araya acknowledge their doctoral fellowships provided by Conicyt-Chile and Ecos-Chile-France program.

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