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Cationic arene ruthenium complexes containing chelating 1,10-phenanthroline ligands

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Dedicated to Professor Helmut G. Alt on the occasion of his 60th birthday

Abstract

The monocationic chloro complexes containing chelating 1,10-phenanthroline (phen) ligands $[(arene)Ru(N\cap N)Cl]^+$ (**1**: arene = C_6H_6, N∩N = phen; **2**: arene = C_6H_6, N∩N = 5-NO_2-phen; **3**: arene = *p*-$MeC_6H_4Pr^i$, N∩N = phen; **4**: arene = *p*-$MeC_6H_4Pr^i$, N∩N = 5-NO_2-phen; **5**: arene = C_6Me_6, N∩N = phen; **6**: arene = C_6Me_6, N∩N = 5-NO_2-phen; **7**: arene = C_6Me_6, N∩N = 5-NH_2-phen) have been prepared and characterised as the chloride salts. Hydrolysis of these chloro complexes in aqueous solution gave, upon precipitation of silver chloride, the corresponding dicationic aqua complexes $[(arene)Ru(N\cap N)(OH_2)]^{2+}$ (**8**: arene = C_6H_6, N∩N = phen; **9**: arene = C_6H_6, N∩N = 5-NO_2-phen; **10**: arene = *p*-$MeC_6H_4Pr^i$, N∩N = phen; **11**: arene = *p*-$MeC_6H_4Pr^i$, N∩N = 5-NO_2-phen; **12**: arene = C_6Me_6, N∩N = phen; **13**: arene = C_6Me_6, N∩N = 5-NO_2-phen; **14**: arene = C_6Me_6, N∩N = 5-NH_2-phen), which have been isolated and characterised as the tetrafluoroborate salts. The catalytic potential of the aqua complexes **8**–**14** for transfer hydrogenation reactions in aqueous solution has been studied: complexes **12** and **14** catalyse the reaction of acetophenone with formic acid to give phenylethanol and carbon dioxide with turnover numbers around 200 (80 °C, 7 h). In the case of **12**, it was possible to observe the postulated hydrido complex $[(C_6Me_6)Ru(phen)H]^+$ (**15**) in the reaction with sodium borohydride; **15** has been characterised as the tetrafluoroborate salt, the isolated product [**15**]BF_4, however, being impure. The molecular structures of $[(C_6Me_6)Ru(phen)Cl]^+$ (**1**) and $[(C_6Me_6)Ru(phen)(OH_2)]^{2+}$ (**12**) have been determined by single-crystal X-ray structure analysis of [**1**]Cl and [**12**]$(BF_4)_2$.

Keywords: Arene complexes; Chloro complexes; Aqua complexes; Phenanthroline complexes; Ruthenium

1. Introduction

While classical coordination chemistry is typically considered as aqueous solution chemistry, organometallic chemistry takes place almost exclusively in organic solution. Owing to the high sensitivity of many organometallics towards hydrolysis, the organic solvents employed in most organometallic syntheses and reactions are thoroughly dried prior to use. The rigorous exclusion of water has become a general feature of laboratory techniques in this field, to such an extent that water is rarely considered to be a suitable reaction medium for organometallic complexes. The obvious gap between organometallic and classical coordination chemistry is bridged by a rather small interface of complexes containing both, soft organic and hard aqua ligands. The first complex of this type is presumably the dinuclear cation $[(C_5H_5)_2Ti_2(H_2O)_2O]^{2+}$, synthesised and isolated as the bromide salt by Wilkinson and Birmingham in 1954 and erroneously addressed as $[(C_5H_5)_2Ti(OH)Br] \cdot H_2O$ [1]. The correct nature of this cationic species was established later by IR and nuclear magnetic resonance (NMR) measurements [2] and by a single-crystal

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X-ray structure analysis of the dithionate salt [3]. The existence of arene(aqua)ruthenium complexes was observed NMR-spectroscopically in 1972 by Zelonka and Baird in the reaction of $[(C_6H_6)Ru_2Cl_4]$ with D_2O [4]. The osmium complex $[(C_6H_6)Os(H_2O)_3]^{2+}$ was synthesised by analogy and characterized spectroscopically by Hung et al. [5]. Stebler-Röthlisberger et al. finally succeeded in isolating the cationic benzene aqua complexes $[(C_6H_6)Ru(H_2O)_3]^{2+}$ and $[(C_6H_6)Os(H_2O)_3]^{2+}$ as the tosylate salts; the structure of the triaqua(benzene)ruthenium(II) cation was confirmed by a single-crystal X-ray structure analysis of the sulphate [6].

Since these early reports, the chemistry of organometallic aqua ions of the transition metals has steadily grown since the 1980s. This topic was comprehensively reviewed by Koelle [7]. Related reviews deal with water-soluble organometallics complexed by hydrophilic ligands [8], metal-mediated organic synthesis in water [9] and catalysis by water-soluble organometallic complexes in biphasic systems [10]. Several recent reports deal with transfer hydrogenation of ketones with formate in aqueous media using catalytic systems based on $[(p\text{-}MeC_6H_4\text{-}Pr^i)RuCl_2]_2$ and *N*-(*p*-toluenesulfonyl)-1,2-diphenyl-ethylenediamine [11–14], 2-(*N*-anilinocarboxy)-pyrrolidine [15] or amino-alcohol attached on cyclodextrine [16]. Recently, Ogo et al. reported transfer hydrogenation reactions of ketones with sodium formate to give secondary alcohols, catalysed in aqueous solution by $[(C_6Me_6)Ru(bipy)(OH_2)]^{2+}$ (bipy = 2,2′-bipyridine), the intermediary formato complex $[(C_6Me_6)Ru(bipy)(OCHO)]^{+}$ being isolated and characterised as the formato salt [17]. The postulated hydrido intermediate $[(C_6Me_6)Ru(bipy)H]^{+}$ has also been isolated and characterised as the triflate salt by single-crystal X-ray structure analysis [18].

In this paper we report two series of cationic arene ruthenium complexes containing 1,10-phenanthroline or derivatives thereof as chelating N,N-donor ligands. All these cationic complexes, isolated as chloride or tetrafluoroborate salts, are soluble in water.

2. Results and discussion

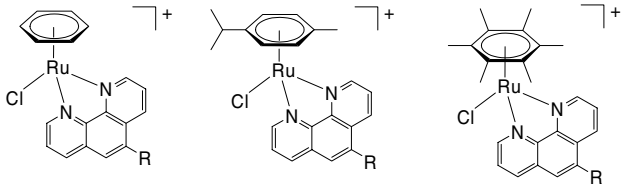
2.1. Synthesis of the chloro complexes $[(arene)Ru(N\cap N)Cl]^{+}$ (1-7)

The dimeric arene ruthenium complexes $[(arene)RuCl_2]_2$ (arene = benzene, *p*-cymene, hexamethylbenzene) react at room temperature in dichloromethane solution with 1,10-phenanthroline (phen) or with its 5-nitro or 5-amino derivatives to give quantitatively the cationic chloro complexes $[(arene)Ru(N\cap N)Cl]^{+}$ (**1**–**7**) containing the corresponding N,N-donor as chelating ligand (Eq. (1)). All cations ares isolated as the chloride salt.

$$1/2\ [(arene)RuCl_2]_2 + N\cap N \rightarrow [(arene)Ru(N\cap N)Cl]^{+} + Cl^{-} \quad (1)$$

	1	2	3	4	5	6	7
arene	C_6H_6	C_6H_6	p-$MeC_6H_4Pr^i$	p-$MeC_6H_4Pr^i$	C_6Me_6	C_6Me_6	$C_6\ Me_6$
N∩N	phen	5-NO_2-phen	phen	5-NO_2-phen	phen	5-NO_2-phen	5-NH_2-phen

The chloride salts of **1**–**7** are yellow-orange solids that dissolve well in water, a property which is used to remove unreacted starting material after the synthetic reaction. As there is a risk of slow hydrolysis in water, the aqueous solution is immediately filtered and then evapourated to dryness to give the analytically pure salts [**1**–**7**]Cl. All compounds have been characterised by ^1H and ^{13}C NMR spectroscopy, mass spectroscopy and elementary analysis. The 1,10-phenanthroline complexes **1** and **3** are already known, they have been reported as early as 1980 by Stephenson et al. [19], however, without structural characterisation. We know present the single-crystal X-ray structure analysis of [**1**]Cl (see Section 2.3).



R= H: **1**, NO_2: **2** R= H: **3**, NO_2: **4** R= H: **5**, NO_2: **6**, NH_2: **7**

In all cases, the phenanthroline ligand is coordinated in a η^2-N,N-fashion to the ruthenium centre. In contrast to the symmetrical 1,10-phenanthroline complexes **1**, **3** and **5**, the 5-nitro- and 5-amino-1,10-phenanthroline complexes **2**, **4**, **6** and **7** are chiral; the compounds [**2**]Cl, [**4**]Cl, [**6**]Cl and [**7**]Cl are therefore obtained as a racemic mixture of enantiomers.

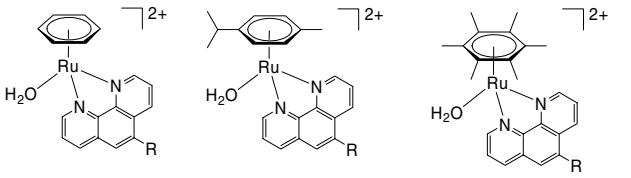
2.2. Synthesis of the aqua complexes $[(arene)Ru(N\cap N)(H_2O)]^{2+}$ (8–14)

The chloro complexes $[(arene)Ru(N\cap N)Cl]^{+}$ (**1**–**7**) undergo hydrolysis in aqueous solution, the reaction, however, being rather slow. The formation of the corresponding aqua complexes $[(arene)Ru(N\cap N)(H_2O)]^{2+}$ (**8** - **14**) can be accelerated and rendered quantitative by

precipitating the chloride formed with silver salt (Eq. (2)). The cations **8**–**14** are isolated as the tetrafluoroborate salts.

$$[(\text{arene})\text{Ru}(\text{N}\cap\text{N})\text{Cl}]^{+} + \text{H}_2\text{O} + \text{Ag}^{+} \rightarrow [(\text{arene})\text{Ru}(\text{N}\cap\text{N})(\text{H}_2\text{O})]^{2+} + \text{AgCl} \quad (2)$$

The aqua complexes **8**–**14** are air-stable yellow solids which crystallise from the aqueous solution. Although **8**–**14** have not been reported in the literature before, we learnt that the hexamethylbenzene derivative **12** has been synthesised and characterised as the hexafluorophosphate salt recently by Ogo and co-workers [20].



R= H: **8**, NO_2: **9** R= H: **10**, NO_2: **11** R= H: **12**, NO_2: **13**, NH_2: **14**

2.3. Molecular structures of $[(C_6Me_6)Ru(phen)(Cl)]^+$ (**1**) and $[(C_6Me_6)Ru(phen)(OH_2)]^{2+}$ (**12**)

The compound [**1**]Cl · 3 H_2O crystallises in the triclinic centrosymmetric space group $P\bar{1}$. The asymmetric unit comprises one molecule of the cationic complex, one chloride counter-anion and three water molecules. The molecular structure of **1** is depicted in Fig. 1. Crystallographic details are given in Table 1, and significant bond lengths and bond angles are listed in Table 2.

Cation **1** consists of a ruthenium atom coordinated to the η^6-benzene ligand, to the two nitrogen atoms of the 1,10-phenanthroline ligand, and to a chlorine atom, the coordination geometry of ruthenium being pseudo-tetrahedral. The Ru atom is situated 1.6783 Å away from the centroid of the C_6H_6 moiety, the interplanar angle between the C_6H_6 and phen planes being 62.69(4)°. Ru–C distances fall within the range 2.1758(17)–2.2105(18) Å. Ru–N distances are similar to those found in $[(C_6H_5(CH_2)_3OH)Ru(phen)]^{2+}$ [21,22], $[(p\text{-}MeC_6H_4\text{-}Pr^i)Ru(phen)(CCH)]^{+}$ [23] and $[(C_6H_5CH_2COOC_2H_5)Ru(phen)Cl]^{+}$ [24]. We note the presence of intermolecular hydrogen bonds in the crystal lattice, between the water molecules themselves and with the neighbouring chloride ion.

The compound [**12**]$(BF_4)_2$ crystallises in the monoclinic centrosymmetric space group $P2_1/n$. The asymmetric unit comprises one molecule of the cationic complex and two tetrafluoroborate counter-anions. The molecular structure of **12** is depicted in Fig. 2. Crystallographic details are given in Table 3, and significant bond lengths and bond angles are listed in Table 4.

	8	**9**	**10**	**11**	**12**	**13**	**14**
arene	C_6H_6	C_6H_6	p-$MeC_6H_4Pr^i$	p-$MeC_6H_4Pr^i$	C_6Me_6	C_6Me_6	C_6Me_6
N∩N	phen	5-NO_2-phen	phen	5-NO_2-phen	phen	5-NO_2-phen	5-NH_2-phen

The structure of the cation consists of a pseudo-tetrahedral arrangement of a ruthenium atom coordinated to the η^6-hexamethylbenzene ligand, to the two nitrogen atoms of the 1,10-phenanthroline ligand, and to the oxygen atom of a water molecule. The Ru atom is situated 1.6970 Å from the centroid of the C_6Me_6 moiety, the interplanar angle between the C_6Me_6 and phen planes being 55.24(6)°. Ru–C distances fall within the range 2.186(2)–2.243(2) Å. Ru–N distances are similar to those found in $[(C_6H_5(CH_2)_3OH)Ru(phen)]^{2+}$ [21,22], $[(p\text{-}MeC_6H_4\text{-}Pr^i)Ru(phen)(CCH)]^{+}$ [23] and $[(C_6H_5CH_2COOC_2H_5)Ru(phen)Cl]^{+}$ [24]. We note the presence of intermolecular hydrogen bonds in the crystal lattice, between the water molecule and the neighbouring BF_4^- ions, the

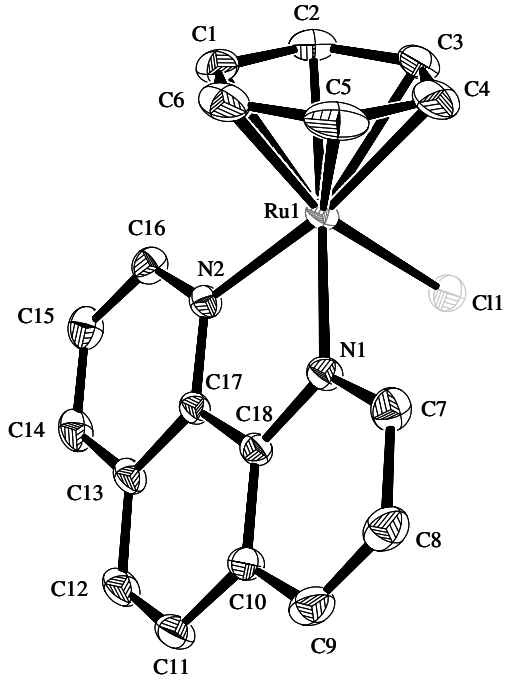


Fig. 1. Molecular structure of cation **1**. The hydrogen atoms and the chloride anion have been omitted for clarity.

Table 1
Crystallographic data for the structure of [**1**](Cl) · $3H_2O$

Chemical formula	$C_{18}H_{20}Cl_2N_2O_3Ru$
Formula weight	484.33
Crystal colour and shape	Orange-red, block
Crystal size (mm)	$0.50 \times 0.50 \times 0.30$
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.0736(8)
b (Å)	12.1389(13)
c (Å)	11.8989(13)
α (°)	71.344(8)
β (°)	79.064(8)
γ (°)	75.533(8)
V (Å^3)	930.59(18)
Z	2
D_{calc} (g cm^{-3})	1.728
μ(Mo Kα) (mm^{-1})	1.150
Temperature (K)	173(2)
F(000)	488
Scan range (°)	$1.95 < \theta < 29.55$
Cell refinement parameters reflections	25554
Reflections measured	17819
Independent reflections	4968
Reflections observed [$I > 2\sigma(I)$]	4830
R_{int}	0.0205
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0221$, wR_2[a]$= 0.0912$
R indices (all data)	$R_1 = 0.0230$, wR_2[a]$= 0.0926$
Goodness-of-fit	0.881
Residual density: max, min $\Delta\rho$ (e Å^{-3})	0.650, −0.885

[a] Structure was refined on F_o^2 : $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2
Selected bond lengths (Å) and angles (°) in [**1**](Cl) · $3H_2O$

Interatomic distances		Bond angles	
Ru(1)–Cl(1)	2.4132(5)	N(1)–Ru(1)–N(2)	77.64(5)
Ru(1)–N(1)	2.0943(14)	N(1)–Ru(1)–Cl(1)	85.42(4)
Ru(1)–N(2)	2.0988(13)	N(2)–Ru(1)–Cl(1)	85.80(4)
Ru(1)–C(1)	2.1843(16)		
Ru(1)–C(2)	2.2105(18)		
Ru(1)–C(3)	2.1873(16)		
Ru(1)–C(4)	2.1864(19)		
Ru(1)–C(5)	2.1758(17)		
Ru(1)–C(6)	2.2024(16)		

distances between the oxygen atom and two fluorine atoms being 2.682(3) and 2.662(2) Å.

2.4. Catalytic application of **8–14** for the transfer hydrogenation of acetophenone with formic acid in aqueous solution

Based on the pioneering study of Ogo et al. on the use of the bypiridine (bipy) complex $[(C_6Me_6)Ru(bipy)(H_2O)]^{2+}$ for the transfer hydrogenation of ketones using formic acid as hydrogen donor in water [18], we checked the catalytic potential of the phenanthroline complexes **8–14** for this reaction using acetophenone as test substrate

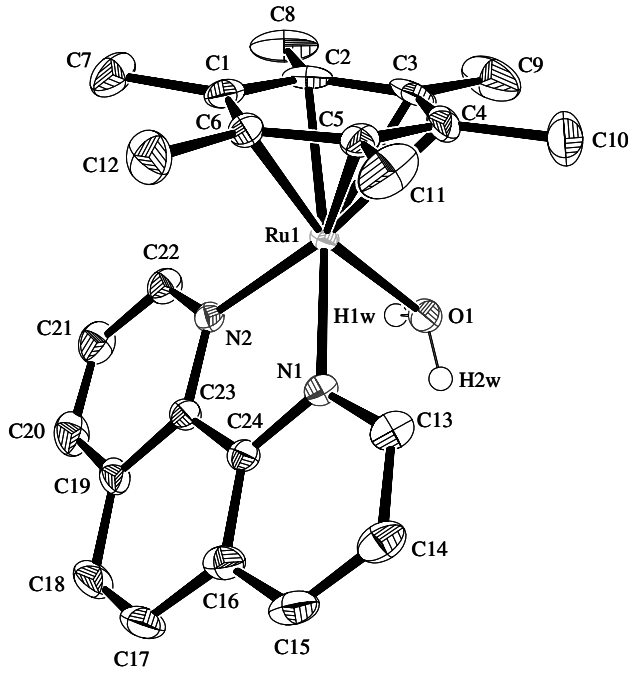


Fig. 2. Molecular structure of **12** with thermal ellipsoids at 50% probability. The hydrogen atoms and the tetrafluoroborate anion are omitted for clarity.

Table 3
Crystallographic data for the structure of [**12**](BF$_4$)$_2$

Chemical formula	$C_{24}H_{28}B_2F_8N_2ORu$
Formula weight	635.17
Crystal colour and shape	Orange-red, block
Crystal size (mm)	$0.50 \times 0.50 \times 0.40$
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.9718(9)
b (Å)	15.0356(9)
c (Å)	16.6949(14)
α (°)	90
β (°)	90.357(10)
γ (°)	90
V (Å^3)	2503.1(3)
Z	4
D_{calc} (g cm^{-3})	1.686
μ(Mo Kα) (mm^{-1})	0.708
Temperature (K)	173(2)
F(000)	1280
Scan range (°)	$2.28 < \theta < 25.90$
Cell refinement parameters reflections	8000
Reflections measured	18219
Independent reflections	4802
Reflections observed [$I > 2\sigma(I)$]	4408
R_{int}	0.0477
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0293$, wR_2[a] $= 0.0754$
R indices (all data)	$R_1 = 0.0321$, wR_2[a] $= 0.0789$
Goodness-of-fit	1.077
Residual density: max, min $\Delta\rho$ (e Å^{-3})	0.731, −0.530

[a] Structure was refined on F_o^2 : $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 4
Selected bond lengths (Å) and angles (°) in [**12**]$(BF_4)_2$

Interatomic distances		Bond angles	
Ru(1)–O(1)	2.1665(16)	N(1)–Ru(1)–N(2)	77.82(7)
Ru(1)–N(1)	2.1074(19)	N(1)–Ru(1)–O(1)	83.83(7)
Ru(1)–N(2)	2.1131(19)	N(2)–Ru(1)–O(1)	84.04(7)
Ru(1)–C(1)	2.216(2)		
Ru(1)–C(2)	2.219(2)		
Ru(1)–C(3)	2.199(3)		
Ru(1)–C(4)	2.233(2)		
Ru(1)–C(5)	2.243(2)		
Ru(1)–C(6)	2.186(2)		

$$MeC(O)Ph + HCOOH \rightarrow MeCH(OH)Ph + CO_2 \quad (3)$$

All phenanthroline complexes **8**–**14** are found to catalyse transfer hydrogenation reactions of ketones in aqueous solution with formic acid as hydrogen source; with acetophenone as substrate, the highest activity is observed for hexamethylbenzene derivatives **12**–**14** (Table 5). A comparison the bipy complex $[(C_6Me_6)Ru(bipy)(H_2O)]^{2+}$ (TON = 196 after 4 h at 70 °C) studied by Ogo et al. [18] shows that the phen analogue **12** is less active (TON = 144 after 48 h at 70 °C) under the same conditions. Substitution of the 5-position of the phenanthroline ligand increases the activity of the hexamethylbenzene ruthenium complex slightly, the activity of **13** and **14** being surprisingly the same, despite the different electronic effects of the 5-nitro or the 5-amino substituent (Table 5).

The pH dependence of the catalytic activity of [**13**]SO_4 was studied for the transfer hydrogenation of acetophenone to give phenylethanol in aqueous solution. As Fig. 3 shows, the best pH conditions were found for pH around 4, which corresponds to the pK_a of the formic acid (3.77). At this pH, formic acid and formate are in 1:1 equilibrium.

The temperature dependence of the catalytic activity of [**13**]SO_4 was also studied for the same reaction. The flattering of the curve (Fig. 4) shows that there is no more significant increase of the TOF beyond 80 °C.

The kinetic plot (Fig. 5) shows that under these conditions the reaction is almost complete after 7 h. The initial turnover frequency calculated in this case, using the best catalyst precursor **13**, is 32 h^{-1}; lower than that found with the bipy analogue (75 h^{-1}) [11].

Table 5
Transfer hydrogenation of acetophenone to phenylethanol using complexes **8**–**14** as catalyst precursors and HCOONa as hydrogen donor in biphasic media at 50 °C at pH 3.8[a]

Catalyst	TON[b,d]	TOF[c,d]	Yield (%)[d]
8	24	0.40	12
9	50	0.83	25
10	40	0.67	20
11	80	1.33	40
12	156	2.60	78
13	164	2.73	82
14	164	2.73	82

[a] Conditions: 50 °C, acetophenone (0.64 mmol) in H_2O (10 ml), catalyst/acetophenone/HCOONa = 1/200/6000, 60 h.
[b] Turnover number: mol of phenylethanol/mol of catalyst.
[c] Initial turnover frequency: mol of phenylethanol/mol of catalyst/h.
[d] Determined by gas chromatography.

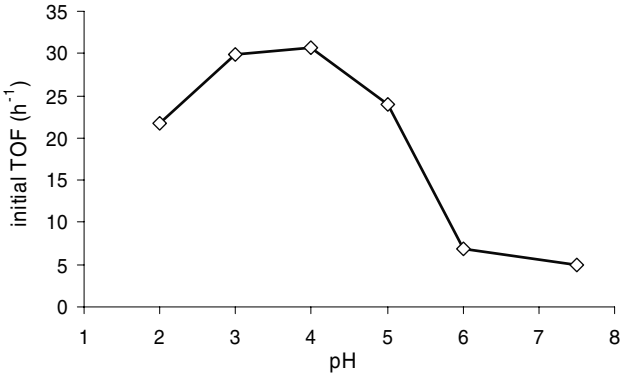


Fig. 3. Initial turnover frequency versus pH plot for the transfer hydrogenation of acetophenone (0.64 mmol) using [**13**]SO_4 (3.2 μmol) with HCOONa (19.2 mmol) in water (10 ml) at 80 °C.

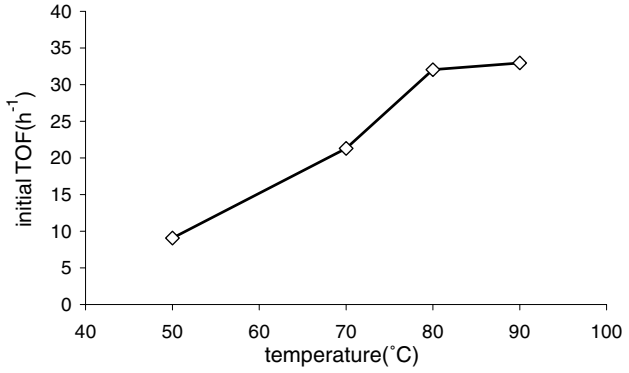


Fig. 4. Initial turnover frequency versus temperature plot for the transfer hydrogenation of acetophenone (0.64 mmol) using [**13**]SO_4 (3.2 μmol) with HCOONa (19.2 mmol) in water (10 ml) at pH 3.8.

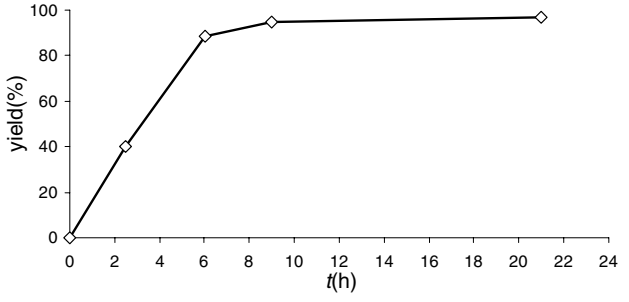
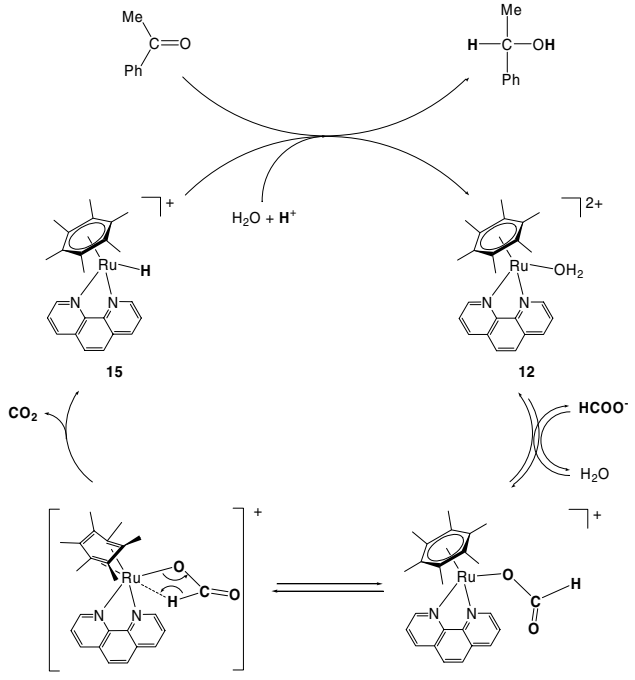


Fig. 5. Conversion versus time plot for the transfer hydrogenation of acetophenone (0.64 mmol) using [**13**]SO_4 (3.2 μmol) with HCOONa (19.2 mmol) in water (10 ml) at 80 °C at pH 3.8.

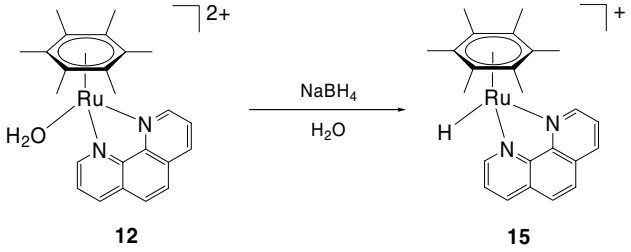
According to a mechanistic scheme worked out by Ogo et al. for the analogous bipy complexes [17], the aqua complex **12** should react with the formate anion to give the corresponding complex which – after rearrangement involving also the arene ligand – eliminates CO_2 to give the hydrido complex **15**, which is supposed to reduce the ketone in the presence of acid to give the corresponding alcohol, restoring the aqua complex **12** (Scheme 1). In the case of the bipy analogues, Ogo et al. succeded in isolating the formato intermediate [17] and also the hydrido intermediate [18]. The strange observation that the nitro and the amino derivatives **13** and **14** have the same catalytic activity (Table 5), which cannot be explained on the basis of the Ogo mechanism, remains to be studied in detail.

In order to check the implication of the hydrido complex **15** in the catalytic process, we tried to synthesise this postulated species by reaction of the aqua complex **12** in aqueous solution with sodium borohydride (Scheme 2). Indeed, the hydrido complex **15** is observed in this reaction, the isolated product [**15**]BF_4 has been characterized by NMR and mass spectroscopy. However, it was never obtained in a pure form, but contained small quantities of [**12**]$(BF_4)_2$.

The hydrido complex **15** obtained was employed in the transfer hydrogenation of acetophenone in the same conditions as for **12** (described in Fig. 4). The initial TOF observed is almost the same in both cases (7.46 h^{-1} for **15** and 6.86 h^{-1} for **12**), as expected for two species being involved in the same catalytic cycle (Scheme 1).



Scheme 1. Postulated catalytic cycle according to Ogo et al. [17].



Scheme 2. Formation of the hydrido complex **15** by reaction of the aqua complex **12** with $NaBH_4$ in water.

In the case of the aqua complexes **8**–**11** and **13**–**14**, the reaction with $NaBH_4$ in water only leads to decomposition, obviously because the corresponding hydrido complexes are less stable under the reaction conditions, although the substituted phenanthroline derivatives **13** and **14** show comparable (even slightly higher) catalytic activity as **12**.

3. Experimental

3.1. General

All manipulations were carried out in an inert atmosphere using standard Schlenk techniques and freshly distilled solvents saturated with nitrogen prior to use. The starting materials $[(arene)RuCl_2]_2$ [25] and 5-NH_2-phen [26] were prepared according to the published methods. All other reagents were commercially available and were used without further purification. NMR spectra were recorded on a Bruker 400 MHz spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate in D_2O as ^{13}C locking agent. Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. Microanalyses were carried out by the Laboratoire de Chimie Pharmaceutique, Université de Genève and by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Switzerland).

3.2. Preparation of the chloro complexes $[(arene)Ru(N\cap N)Cl]^+$ (arene = C_6H_6, p-$MeC_6H_4Pr^i$, or C_6Me_6 and N∩N = phen, 5-NO_2-phen or 5-NH_2-phen)

Two equivalents (0.30 mmol) of the appropriate phenanthroline were added to a suspension of [(arene)$RuCl_2]_2$ (0.15 mmol) in dichloromethane (30 ml). The mixture was stirred for 3 h at room temperature, during this time the colour changed from orange to yellow. After evaporation to dryness, the residue was dissolved in water, the solution was filtered and evaporated to dryness giving the product in quantitative yield.

3.2.1. $[(C_6H_6)Ru(phen)(Cl)]Cl$ ([**1**]Cl)

Anal. Calc. for $C_{18}H_{14}N_2Cl_2Ru$: C, 50.24; H, 3.28; N, 6.51. Found: C, 50.36; H, 3.19; N, 6.48%. ^1H NMR

(400 MHz, δ, D_2O): 6.17 (s, C_6H_6), 7.92 (s, H_{5-6} *phen*), 7.99 (dd, $J = 5.4$ Hz, $J = 8.4$ Hz, H_{3-8} *phen*), 8.62 (d, $J = 8.4$ Hz, H_{4-7} *phen*), 9.77 (d, $J = 5.4$ Hz, H_{2-9} *phen*). ^{13}C NMR (400 MHz, δ, D_2O): 86.96 (C_6H_6), 126.63 (C_{3-8}*phen*), 127.62 (C_{5-6} *phen*), 130.98 ($C_{4'-6'}$ *phen*), 139.47 (C_{4-7} *phen*), 146.08 ($C_{1'-10'}$ *phen*), 155.62 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 395, cation **1**.

3.2.2. [(C_6H_6)Ru(5-NO_2-phen)(Cl)]Cl ([**2**]Cl)

Anal. Calc. for $C_{18}H_{13}N_3O_2Cl_2Ru \cdot 0.2\ CH_2Cl_2$: C, 44.40; H, 2.74; N, 8.54. Found: C, 44.28; H, 2.77; N, 867%. ^1H NMR (400 MHz, δ, D_2O): 6.29 (s, C_6H_6), 8.22 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_8 5-NO_2-*phen*), 8.24 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_3 5-NO_2-*phen*), 8.97 (d, $J = 8.4$ Hz, H_7 5-NO_2-*phen*), 9.16 (s, H_6 5-NO_2-*phen*), 9.37 (d, $J = 8.6$ Hz, H_4 5-NO_2-*phen*), 10.00 (d, $J = 5.4$ Hz, H_2 5-NO_2-*phen*), 10.02 (d, $J = 5.4$ Hz, H_9 5-NO_2-*phen*). ^{13}C NMR (400 MHz, δ, D_2O): 83.71 (C_6H_6), 126.32 ($C_{4'}$ 5-NO_2-*phen*), 130.03 (C_6 5-NO_2-*phen*), 130.24 ($C_{6'}$ 5-NO_2-*phen*), 130.34 (C_8 5-NO_2-*phen*), 130.46 (C_3 5-NO_2-*phen*), 138.92 (C_4 5-NO_2-*phen*), 143.99 (C_7 5-NO_2-*phen*), 146.67 ($C_{10'}$ 5-NO_2-*phen*), 148.91 (C_5 5-NO_2-*phen*), 150.23 ($C_{1'}$ 5-NO_2-*phen*), 159.47 (C_2 5-NO_2-*phen*), 161.17 (C_9 5-NO_2-*phen*). ESI-MS (*m*/*z*): 440, cation **2**.

3.2.3. [(*p*-$MeC_6H_4Pr^i$)Ru(phen)(Cl)]Cl ([**3**]Cl)

Anal. Calc. for $C_{22}H_{22}N_2Cl_2Ru$: C, 54.32; H, 4.56; N, 5.76. Found: C, 54.51; H, 4.62; N, 5.83%. ^1H NMR (400 MHz, δ, D_2O): 0.80 (d, $J = 6.9$ Hz, $CH(CH_3)_2$), 2.07 (s, CH_3), 2.47 (hept, $J = 6.9$ Hz, $CH(CH_3)_2$), 5.87 (d, $J = 6.4$ Hz, C_6H_4), 6.09 (d, $J = 6.4$ Hz, C_6H_4), 7.63 (s, H_{5-6} *phen*), 7.91 (dd, $J = 5.4$ Hz, $J = 8.4$ Hz, H_{3-8} *phen*), 8.44 (d, $J = 8.4$ Hz, H_{4-7} *phen*), 9.65 (d, $J = 5.4$ Hz, H_{2-9} *phen*). ^{13}C NMR (400 MHz, δ, D_2O): 20.72 (CH_3), 23.68 ($CH(CH_3)_2$), 33.25 ($CH(CH_3)_2$), 86.63 (C_6H_4), 88.80 (C_6H_4), 105.71 (C_6H_4), 107.00 (C_6H_4), 129.06 (C_{3-8} *phen*), 129.84 (C_{5-6} *phen*), 133.04 ($C_{4'-6'}$ *phen*), 141.49 (C_{4-7} *phen*), 147.96 ($C_{1'-10'}$ *phen*), 157.82 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 451, cation **3**.

3.2.4. [(*p*-$MeC_6H_4Pr^i$)Ru(5-NO_2-phen)(Cl)]Cl ([**4**]Cl)

Anal. Calc. for $C_{22}H_{21}N_3O_2Cl_2Ru \cdot 0.4\ CH_2Cl_2$: C, 47.59; H, 3.89; N, 7.43. Found: C, 47.58; H, 4.36; N, 7.45%. ^1H NMR (400 MHz, δ, D_2O): 0.90 (d, $J = 6.9$ Hz, $CH(CH_3)_2$), 2.13 (s, CH_3), 2.56 (hept, $J = 6.9$ Hz, $CH(CH_3)_2$), 5.97 (d, $J = 6.4$ Hz, C_6H_4), 6.19 (d, $J = 6.4$ Hz, C_6H_4), 8.13 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_8 5-NO_2-*phen*), 8.14 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_3 5-NO_2-*phen*), 8.85 (d, $J = 8.4$ Hz, $H_7$5-NO_2-*phen*), 9.00 (s, H_6 5-NO_2-*phen*), 9.22 (d, $J = 8.6$ Hz, $H_4$5-NO_2-*phen*), 9.85 (d, $J = 5.4$ Hz, H_2 5-NO_2-*phen*), 9.88 (d, $J = 5.4$ Hz, H_9 5-NO_2-*phen*). ^{13}C NMR (400 MHz, δ, D_2O): 20.67 (CH_3), 23.68 ($CH(CH_3)_2$), 33.33 ($CH(CH_3)_2$), 87.16 (C_6H_4), 87.02 (C_6H_4), 106.09 (C_6H_4), 107.94 (C_6H_4), 126.19 ($C_{4'}$ 5-NO_2-*phen*), 129.96 (C_6 5-NO_2-*phen*), 130.25 ($C_{6'}$ 5-NO_2-*phen*), 130.30 (C_8 5-NO_2-*phen*), 130.33 (C_3 5-NO_2-*phen*), 138.70 (C_4 5-NO_2-*phen*), 143.76 (C_7 5-NO_2-*phen*), 146.61 ($C_{10'}$ 5-NO_2-*phen*), 148.47 (C_5 5-NO_2-*phen*), 149.75 ($C_{1'}$ 5-NO_2-*phen*), 159.26 (C_2 5-NO_2-*phen*), 160.96 (C_9 5-NO_2-*phen*). ESI-MS (*m*/*z*): 496, cation **4**.

3.2.5. [(C_6Me_6)Ru(phen)(Cl)]Cl([**5**]Cl)

Anal. Calc. for $C_{24}H_{26}N_2ClRu$: C, 56.03; H, 5.09; N, 5.45. Found: C, 56.23; H, 4.96; N, 5.51%. ^1H NMR (400 MHz, δ, D_2O): 2.06 (s, Me_3), 7.90 (s, H_{5-6} *phen*), 8.02 (dd, $J = 5.4$ Hz, $J = 8.4$ Hz, H_{3-8} *phen*), 8.58 (d, $J = 8.4$ Hz, H_{4-7} *phen*), 9.29 (d, $J = 5.4$ Hz, H_{2-9} *phen*). ^{13}C NMR (400 MHz, δ, D_2O): 17.61 ($C_6(CH_3)_6$), 98.46 ($C_6(CH_3)_6$), 129.04 (C_{3-8} *phen*), 130.03 (C_{5-6} *phen*), 132.96 ($C_{4'-6'}$ *phen*), 141.27 (C_{4-7} *phen*), 148.23 ($C_{1'-10'}$ *phen*), 155.74 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 479, cation **5**.

3.2.6. [(C_6Me_6)Ru(5-NO_2-phen)(Cl)]Cl ([**6**]Cl)

Anal. Calc. for $C_{24}H_{25}N_3O_2Cl_2Ru$: C, 51.53; H, 4.50; N, 7.51. Found: C, 51.48; H, 4.62; N, 7.52D_2O): 2.11 (s, Me_6), 8.21 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_8 5-NO_2-*phen*), 8.22 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_3 5-NO_2-*phen*), 8.87 (d, $J = 8.4$ Hz, H_7 5-NO_2-*phen*), 9.08 (s, H_6 5-NO_2-*phen*), 9.26 (d, $J = 8.6$ Hz, H_4 5-NO_2-*phen*), 9.44 (d, $J = 5.4$ Hz, H_2 5-NO_2-*phen*), 9.48 (d, $J = 5.4$ Hz, H_9 5-NO_2-*phen*). ^{13}C NMR (400 MHz, δ, D_2O): 17.64 ($C_6(CH_3)_6$), 98.94 ($C_6(CH_3)_6$), 125.95 ($C_{4'}$ 5-NO_2-*phen*), 130.04 (C_6 5-NO_2-*phen*), 130.11 ($C_{6'}$ 5-NO_2-*phen*), 130.28 (C_8 5-NO_2- *phen*), 130.35 (C_3 5-NO_2-*phen*), 138.37 (C_4 5-NO_2-*phen*), 143.41 (C_7 5-NO_2-*phen*), 146.73 ($C_{10'}$ 5-NO_2-*phen*), 148.67 (C_5 5-NO_2-*phen*), 149.96 ($C_{1'}$ 5-NO_2-*phen*), 157.20 (C_2 5-NO_2-*phen*), 158.88 (C_9 5-NO_2-*phen*). ESI-MS (*m*/*z*): 524, cation **6**.

3.2.7. [(C_6Me_6)Ru(5-NH_2-phen)(Cl)]Cl ([**7**]Cl)

Anal. Calc. for $C_{24}H_{27}N_3Cl_2Ru$: C, 54.44; H, 5.14; N, 7.94. Found: C, 54.62; H, 5.03; N, 7.88%. ^1H NMR (400 MHz, δ, D_2O): 2.08 (s, Me_3), 7.03 (s, H_6 5-NH_2-*phen*), 7.83 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_8 5-NH_2-*phen*), 8.04 (dd, $J = 5.4$ Hz, $J = 8.7$ Hz, H_3 5-NH_2-*phen*), 8.25 (d, $J = 8.4$ Hz, H_7 5-NH_2-*phen*), 8.70 (d, $J = 8.6$ Hz, H_4 5-NH_2-*phen*), 9.00 (d, $J = 5.4$ Hz, H_2 5-NH_2-*phen*), 9.32 (d, $J = 5.4$ Hz, H_9 5-NH_2-*phen*). ^{13}C NMR (400 MHz, δ, D_2O): 17.60 ($C_6(CH_3)_6$), 98.42 ($C_6(CH_3)_6$), 107.56 (C_6 5-NH_2-*phen*), 126.52 ($C_{4'}$ 5-NH_2-*phen*), 126.80 (C_8 5-NH_2-*phen*), 128.02 (C_3 5-NH_2-*phen*), 128.91 (C_7 5-NH_2-*phen*), 134.49 (C_4 5-NH_2-*phen*), 136.00 ($C_{10'}$ 5-NH_2-*phen*), 138.41 ($C_{6'}$ 5-NH_2-*phen*), 145.54 (C_5 5-NH_2-*phen*), 148.94 ($C_{1'}$ 5-NH_2-*phen*), 151.81 (C_2 5-NH_2-*phen*), 155.71 (C_9 5-NH_2-*phen*). ESI-MS (*m*/*z*): 494, cation **7**.

3.3. Preparation of the aqua complexes $[(arene)Ru(N\cap N)(OH_2)]^{2+}$ (arene = C_6H_6, p-MeC_6H_4Pr, or C_6Me_6 and N∩N = phen, 5-nitro-phen or 5-amino-phen)

A mixture of the appropriate chloro complex $[(arene)Ru(N\cap N)(Cl)]^+$ (0.2 mmol) and one equivalent of silver sulphate (0.2 mmol, 62.4 mg) in water (30 ml) was stirred for 1 h in the dark at room temperature. After this time, the white precipitate (AgCl) was removed by filtration from the yellow solution. Solid $NaBF_4$ was added until it did not dissolve any more and a yellow precipitate appeared. Then the suspension was centrifuged, the solid was dissolved in 10 ml of dry acetonitrile and filtered on celite to eliminate the excess of $NaBF_4$. After evaporation of the solvent, the tetrafluoroborate salt was obtained as a yellow-orange powder in quantitative yield.

3.3.1. $[(C_6H_6)Ru(phen)(OH_2)](BF_4)_2$ ([**8**]$(BF_4)_2$)

Anal. Calc. for $C_{18}H_{16}N_2OB_2F_8Ru$: C, 39.24; H, 2.93; N, 5.08. Found: C, 39.15; H, 2.96; N, 4.92%. ^{1}H NMR (400 MHz, δ, D_2O): 6.36 (s, C_6H_6), 8.17 (dd, J = 5.4 Hz, J = 8.4 Hz, H_{3-8} *phen*), 8.19 (s, H_{5-6} *phen*), 8.88 (d, J = 8.4 Hz, H_{4-7} *phen*), 10.02 (d, J = 5.4 Hz, H_{2-9} *phen*). ^{13}C NMR (400 MHz, δ, D_2O): 83.75 (C_6H_6), 124.67 (C_{3-8} *phen*), 125.64 (C_{5-6} *phen*), 128.96 ($C_{4'-6'}$ *phen*), 138.38 (C_{4-7} *phen*), 144.46 ($C_{1'-10'}$ *phen*), 153.77 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 377, cation **8**.

3.3.2. $[(C_6H_6)Ru(5\text{-}NO_2\text{-}phen)(OH_2)](BF_4)_2$ ([**9**]$(BF_4)_2$)

Anal. Calc. for $C_{18}H_{15}N_3O_3B_2F_8Ru$: C, 36.27; H, 2.54; N, 7.05. Found: C, 36.45; H, 2.63; N, 7.09%. ^{1}H NMR (400 MHz, δ, D_2O): 6.25 (s, C_6H_6), 8.15 (dd, J = 5.4 Hz, J = 8.7 Hz, H_8 *5-NO_2-phen*), 8.17 (dd, J = 5.4 Hz, J = 8.7 Hz, H_3 *5-NO_2-phen*), 8.87 (d, J = 8.4 Hz, H_7 *5-NO_2-phen*), 9.03 (s, H_6 *5-NO_2-phen*), 9.25 (d, J = 8.6 Hz, H_4 *5-NO_2-phen*), 9.95 (d, J = 5.4 Hz, H_2 *5-NO_2-phen*), 9.98 (d, J = 5.4 Hz, H_9 *5-NO_2-phen*). ^{13}C NMR (400 MHz, δ, D_2O): 87.35 (C_6H_6), 123.84 ($C_{4'}$ *5-NO_2-phen*), 124.03 (C_6 *5-NO_2-phen*), 127.56 ($C_{6'}$ *5-NO_2-phen*), 127.85 (C_8 *5-NO_2-phen*), 127.89 (C_3 *5-NO_2-phen*), 136.47 (C_4 *5-NO_2-phen*), 141.56 (C_7 *5-NO_2-phen*), 144.18 ($C_{10'}$ *5-NO_2-phen*), 146.49 (C_5 *5-NO_2-phen*), 147.79 ($C_{1'}$ *5-NO_2-phen*), 157.16 (C_2 *5-NO_2-phen*), 158.87 (C_9 *5-NO_2-phen*). ESI-MS (*m*/*z*): 440, cation **9**.

3.3.3. $[(p\text{-}MeC_6\mathbf{H_4}Pr^i)Ru(phen)(OH_2)](BF_4)_2$ ([**10**]$(BF_4)_2$)

Anal. Calc. for $C_{22}H_{24}N_2OB_2F_8Ru$: C, 43.52; H, 3.92; N, 4.61. Found: C, 43.69; H, 4.12; N, 4.49%. ^{1}H NMR (400 MHz, δ, D_2O): 0.90 (d, J = 6.9 Hz, $CH(CH_3)_2$), 2.23 (s, CH_3), 2.52 (hept, J = 6.9 Hz, CH $(CH_3)_2$), 6.21 (d, J = 6.4 Hz, C_6H_4), 6.41 (d, J = 6.4 Hz, C_6H_4), 8.19 (dd, J = 5.4 Hz, J = 8.4 Hz, H_{3-8} *phen*), 8.20 (s, H_{5-6} *phen*), 8.88 (d, J = 8.4 Hz, H_{4-7} *phen*), 9.98 (d, J = 5.4 Hz, H_{2-9} *phen*). ^{13}C NMR (400 MHz, δ, D_2O): 20.38 (CH_3), 23.68 ($CH(CH_3)_2$), 33.19 ($CH(CH_3)_2$), 85.90 (C_6H_4), 89.32 (C_6H_4), 103.80 (C_6H_4), 106.59 (C_6H_4), 129.48 (C_{3-8} *phen*), 130.46 (C_{5-6} *phen*), 133.69 ($C_{4'-6'}$ *phen*), 143.06 (C_{4-7} *phen*), 148.79 ($C_{1'-10'}$ *phen*), 158.35 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 433, cation **10**.

3.3.4. $[(p\text{-}MeC_6H_4Pr^i)Ru(5\text{-}NO_2\text{-}phen)(OH_2)](BF_4)_2$ ([**11**]$(BF_4)_2$)

Anal. Calc. for $C_{22}H_{23}N_3O_3B_2F_8Ru$: C, 40.52; H, 3.55; N, 6.44. Found: C, 40.35; H, 3.72; N, 6.52%. ^{1}H NMR (400 MHz, δ, D_2O): 0.92 (d, J = 6.9 Hz, *CH* $(CH_3)_2$), 2.16 (s, CH_3), 2.58 (hept, J = 6.9 Hz, $CH(CH_3)_2$), 6.00 (d, J = 6.4 Hz, C_6H_4), 6.21 (d, J = 6.4 Hz, C_6H_4), 8.17 (dd, J = 5.4 Hz, J = 8.7 Hz, H_8 *5-NO_2-phen*), 8.18 (dd, J = 5.4 Hz, J = 8.7 Hz, H_3 *5-NO_2-phen*), 8.89 (d, J = 8.4 Hz, H_7 *5-NO_2-phen*), 9.06 (s, H_6 *5-NO_2-phen*), 9.27 (d, J = 8.6 Hz, H_4 *5-NO_2-phen*), 9.88 (d, J = 5.4 Hz, H_2 *5-NO_2-phen*), 9.91 (d, J = 5.4 Hz, H_9 *5-NO_2-phen*). ^{13}C NMR (400 MHz, δ, D_2O): 18.38 (CH_3), 21.37 ($CH(CH_3)_2$), 31.04 ($CH(CH_3)_2$), 84.87 (C_6H_4), 86.75 (C_6H_4), 103.86 (C_6H_4), 105.61 (C_6H_4), 123.95 ($C_{4'}$ *5-NO_2-phen*), 127.72 (C_6 *5-NO_2-phen*), 127.75 ($C_{6'}$ *5-NO_2-phen*), 128.00 (C_8*5-NO_2-phen*), 128.04 (C_3 *5-NO_2-phen*), 136.45 (C_4 *5-NO_2-phen*), 141.52 (C_7 *5-NO_2-phen*), 144.36 ($C_{10'}$ *5-NO_2-phen*), 146.20 (C_5 *5-NO_2-phen*), 147.50 ($C_{1'}$ *5-NO_2-phen*), 156.97 (C_2 *5-NO_2-phen*), 158.67 (C_9 *5-NO_2-phen*). ESI-MS (*m*/*z*): 496, cation **11**.

3.3.5. $[(C_6Me_6)Ru(phen)(OH_2)](BF_4)_2$ ([**12**]$(BF_4)_2$)

Anal. Calc. for $C_{24}H_{28}N_2OB_2F_8Ru$: C, 45.38; H, 4.44; N, 4.41. Found: C, 45.19; H, 4.32; N, 4.29%. ^{1}H NMR (400 MHz, δ, D_2O): 2.22 (s, Me_6), 8.19 (s, H_{5-6} *phen*), 8.21 (dd, J = 5.4 Hz, J = 8.4 Hz, H_{3-8} *phen*), 8.84 (d, J = 8.4 Hz, H_{4-7} *phen*), 9.59 (d, J = 5.4 Hz, H_{2-9} *phen*). ^{13}C NMR (400 MHz, δ, D_2O): 17.64 ($C_6(CH_3)_6$), 98.30 ($C_6(CH_3)_6$), 129.36 (C_{3-8} *phen*), 130.44 (C_{5-6} *phen*), 133.38 ($C_{4'-6'}$ *phen*), 145.59 (C_{4-7} *phen*), 149.00 ($C_{1'-10'}$ *phen*), 156.28 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 461, cation **12**.

3.3.6. $[(C_6Me_6)Ru(5\text{-}NO_2\text{-}phen)(OH_2)](BF_4)_2$ ([**13**]$(BF_4)_2$)

Anal. Calc. for $C_{24}H_{27}N_3O_3B_2F_8Ru$: C, 42.38; H, 4.00; N, 6.18. Found: C, 42.57; H, 4.06; N, 6.15%. ^{1}H NMR (400 MHz, δ, D_2O): 2.20 (s, Me_6), 8.31 (dd, J = 5.4 Hz, J = 8.7 Hz, H_8 *5-NO_2-phen*), 8.34 (dd, J = 5.4 Hz, J = 8.7 Hz, H_3 *5-NO_2-phen*), 9.02 (d, J = 8.4 Hz, H_7 *5-NO_2-phen*), 9.20 (s, H_6 *5-NO_2-phen*), 9.41 (d, J = 8.6 Hz, H_4 *5-NO_2-phen*), 9.70 (d, J = 5.4 Hz, H_2 *5-NO_2-phen*), 9.72 (d, J = 5.4 Hz, H_9 *5-NO_2-phen*). ^{13}C NMR (400 MHz, δ, D_2O): 15.34

($C_6(CH_3)_6$), 96.37 ($C_6(CH_3)_6$), 123.92 ($C_{4'}$ *5-NO$_2$-phen*), 128.00 (C_6 *5-NO$_2$-phen*), 128.15 ($C_{6'}$ *5-NO$_2$-phen*), 128.27 (C_8 *5-NO$_2$-phen*), 128.32 (C_3 *5-NO$_2$-phen*), 137.19 (C_4 *5-NO$_2$-phen*), 142.28 (C_7 *5-NO$_2$-phen*), 144.61 ($C_{10'}$ *5-NO$_2$-phen*), 147.10 (C_5 *5-NO$_2$-phen*), 148.38 ($C_{1'}$ *5-NO$_2$-phen*), 155.41 (C_2 *5-NO$_2$-phen*), 157.09 (C_9 *5-NO$_2$-phen*). ESI-MS (*m*/*z*): 524, cation **13**.

3.3.7. [(C$_6$Me$_6$)Ru(5-NH$_2$-phen)(OH$_2$)](BF$_4$)$_2$ ([**14**](BF$_4$)$_2$)

Anal. Calc. for $C_{24}H_{23}N_3B_2F_8Ru$: C, 44.33; H, 4.50; N, 6.46. Found: C, 44.28; H, 4.42; N, 6.35%. ^{1}H NMR (400 MHz, δ, D_2O): 2.17 (s, Me_3), 7.25 (s, H_6 *5-NH$_2$-phen*), 7.95 (dd, J = 5.4 Hz, J = 8.7 Hz, H_8 *5-NH$_2$-phen*), 8.16 (dd, J = 5.4 Hz, J = 8.7 Hz, H_3 *5-NH$_2$-phen*), 8.44 (d, J = 8.4 Hz, H_7 *5-NH$_2$-phen*), 8.88 (d, J = 8.6 Hz, H_4 *5-NH$_2$-phen*), 9.23 (d, J = 5.4 Hz, H_2 *5-NH$_2$-phen*), 9.55 (d, J = 5.4 Hz, H_9 *5-NH$_2$-phen*). ^{13}C NMR (400 MHz, δ, D_2O): 15.30 ($C_6(CH_3)_6$), 95.87 ($C_6(CH_3)_6$), 105.81 (C_6 *5-NH$_2$-phen*), 124.51 ($C_{4'}$ *5-NH$_2$-phen*), 126.03 (C_8 *5-NH$_2$-phen*), 126.87 (C_3 *5-NH$_2$-phen*), 132.38 (C_7 *5-NH$_2$-phen*), 134.88 (C_4 *5-NH$_2$-phen*), 137.31 ($C_{10'}$ *5-NH$_2$-phen*), 141.80 ($C_{6'}$ *5-NH$_2$-phen*), 143.53 (C_5 *5-NH$_2$-phen*), 147.29 ($C_{1'}$ *5-NH$_2$-phen*), 150.06 (C_2 *5-NH$_2$-phen*), 153.90 (C_9 *5-NH$_2$-phen*). ESI-MS (*m*/*z*): 494, cation **14**.

3.4. Preparation of the hydrido complex [(C$_6$Me$_6$)Ru(phen)H]$^+$ (**15**)

A solution of 30 mg (0.047 mmol) of [(C_6Me_6)Ru(phen)(OH_2)][BF_4]$_2$ ([**12**](BF_4)$_2$) in 10 ml of water was saturated with argon by bubbling for 1 h. After this time, solid $NaBH_4$ (0.06 mmol, 2.3 mg) was added slowly (in 10 portions) to the orange solution, while maintaining the argon bubbling. The solution turned brown, and then a brown precipitate appeared, which was isolated by centrifugation and dried in vacuo. This solid contained [**15**]BF_4 contaminated by a small amount of [**12**](BF_4)$_2$.

3.4.1. [(C$_6$Me$_6$)Ru(phen)(H)](BF$_4$) ([15]BF$_4$)

^{1}H NMR (400 MHz, δ, CD_3OD): -6.69 (s, hydride), 2.32 (s, Me_3), 7.92 (dd, J = 5.4 Hz, J = 8.4 Hz, H_{3-8} *phen*), 8.13 (s, H_{5-6} *phen*), 8.63 (d, J = 8.4 Hz, H_{4-7}*phen*), 9.10 (d, J = 5.4 Hz, H_{2-9}*phen*). ^{13}C NMR (400 MHz, δ, CD_3OD): 17.58 ($C_6(CH_3)_6$), 97.79 ($C_6(CH_3)_6$), 129.32 (C_{3-8} *phen*), 130.15 (C_{5-6} *phen*), 133.04 ($C_{4'-6'}$ *phen*), 141.27 (C_{4-7} *phen*), 148.23 ($C_{1'-10'}$ *phen*), 155.72 (C_{2-9} *phen*). ESI-MS (*m*/*z*): 445, cation **15**.

3.5. Single crystal X-ray structure analyses

An orange-red crystal of compound [**1**]Cl was mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite-monochromator. Data collection was performed at −100 °C using Mo Kα radiation (λ = 0.71073 Å). 240 exposures (2 min per exposure) were obtained at an image plate distance of 100 mm, 120 frames with $\varphi = 0°$ and $0 < \omega < 180°$, and 120 frames with $\varphi = 90°$ and $0 < \omega < 180°$, with the crystal oscillating through 1.5° in ω. The resolution was $D_{min} - D_{max}$ 17.78–0.72 Å. This compound crystallised in a triclinic cell ($P\bar{1}$). The molecular formula of this compound is [RuCl(C_6H_6)(phen)]Cl · $3H_2O$. The structure was solved by direct methods using the program SHELXS-97 [27] and refined by full matrix least squares on F^2 with SHELXL-97 [28]. The six hydrogen atoms of the water molecules were derived from difference Fourier maps and refined with the O–H distance constrained to the theoretical value, the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied using MULABS (PLATON03 [29], T_{min} = 0.58735, T_{max} = 0.84261). The figure was drawn with ORTEP [30].

An orange-red crystal of compound [**12**](BF_4)$_2$ was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator. Data collection was performed at −100 °C using Mo Kα radiation (λ = 0.71073 Å). 190 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 190°$ and with the crystal oscillating through 1° in φ. The resolution was $D_{min} - D_{max}$ 12.45–0.81 Å. This compound crystallised in a monoclinic cell (space group $P2_1/n$). The molecular formula of this compound is [Ru(η^6-C_6Me_6)(phen)(OH_2)](BF_4)$_2$. The structure was solved by direct methods using the program SHELXS-97 [27] and refined by full matrix least squares on F^2 with SHELXL-97 [28]. The two hydrogen atoms H1w and H2w of the water ligand were derived from difference Fourier maps and refined with the O–H distances constrained to the theoretical value, the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. The figure was drawn with ORTEP [30].

3.6. Transfer hydrogenation catalysis

The transfer hydrogenation reactions of acetophenone (0.64 mmol) using **8**–**14** as their sulphate salts (3.2 μmol) with HCOONa (19.2 mmol) were carried out in water (10 ml) at pH 3.8 using a buffer of HCOOH/HCOONa under inert atmosphere. The reaction was quenched by cooling the mixture to 0 °C. The products were extracted by Et_2O and identified (and turnover were determined) by gas chromatography. The pH was monitored using a pH meter (Mettler

Toledo InLab® 413). The initial turnover frequencies were determined for all the catalytic reactions by using the turnover frequencies at 20% of conversion for the hydrogenation reaction of the acetophenone to phenylethanol.

4. Supplementary data

CCDC-258437 [**1**]$Cl \cdot 3H_2O$ and 258438 [**12**]$(BF_4)_2$ contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif,by emailing data_request@ccdc.cam.ac.uk,or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033.

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References

[1] G. Wilkinson, J.M. Birmingham, J. Am. Chem. Soc. 76 (1954) 4281.
[2] K. Doppert, J. Organomet. Chem. 178 (1979) C3.
[3] U. Thewalt, G. Schleußner, Angew. Chem. 90 (1978) 559.
[4] R.A. Zelonka, M.C. Baird, Can. J. Chem. 50 (1972) 3063.
[5] Y. Hung, W.-J. Kung, H. Taube, Inorg. Chem. 20 (1981) 457.
[6] M. Stebler-Röthlisberger, W. Hummel, P.-A. Pittet, H.-B. Bürgi, A. Ludi, A.E. Merbach, Inorg. Chem. 27 (1988) 1358.
[7] U. Koelle, Coord. Chem. Rev. 135/136 (1994) 623.
[8] M. Barton, J.D. Atwood, J. Coord. Chem. 24 (1991) 43.
[9] A.G. Samuelson, Curr. Sci. 63 (1992) 547.
[10] W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem., Int. Ed. Engl. 32 (1993) 1524.
[11] X. Wu, X. Li, W. Hems, F. King, J. Xiao, Org. Biomol. Chem. 2 (2004) 1818.
[12] Y. Ma, H. Liu, L. Chen, X. Cui, J. Zhu, J. Deng, Org. Lett. 5 (2003) 2103.
[13] X. Li, X. Wu, W. Chen, F.E. Hancock, F. King, J. Xiao, Org. Lett. 6 (2004) 3321.
[14] P.N. Liu, J.G. Deng, Y.Q. Tu, S.H. Wang, Chem. Commun. (2004) 2070.
[15] H.Y. Rhyoo, H.-J. Park, W.H. Suh, Y.K. Chung, Tetrahedron Lett. 43 (2002) 269.
[16] A. Schlatter, M.K. Kundu, W.-D. Woggon, Angew. Chem. Int. Ed. 43 (2004) 6731.
[17] S. Ogo, T. Abura, Y. Watanabe, Organometallics 21 (2002) 2964.
[18] S. Ogo, K. Uehara, T. abura, Y. Watanabe, S. Fukuzumi, Organometallics 23 (2004) 3047.
[19] D.R. Robertson, I.W. Robertson, T.A. Stephenson, J. Organomet. Chem. 202 (1980) 309.
[20] S. Ogo, personal communication.
[21] T. Ohnishi, Y. Miyaki, H. Asano, H. Kurosawa, Chem. Lett. (1999) 809.
[22] Y. Miyaki, T. Onishi, H. Kurosawa, Inorg. Chim. Acta 300–302 (2000) 369.
[23] C. Menéndez, D. Morales, J. Pérez, V. Riera, D. Miguel, Organometallics 20 (2001) 2775.
[24] R. Stodt, S. Gencaslan, I.M. Müller, W. Sheldrick, Eur. J. Inorg. Chem. (2003) 1873.
[25] M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.
[26] D. Garcia-Fresnadillo, G. Orellana, Helv. Chim. Acta 84 (2001) 2708.
[27] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[28] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[29] A.L. Spek, J. Appl. Cryst. 36 (2003) 7.
[30] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.