ORGANOMETALLICS

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Arene Ruthenium Complexes as Versatile Catalysts in Water in both Transfer Hydrogenation of Ketones and Oxidation of Alcohols. Selective Deuterium Labeling of *rac*-1-Phenylethanol

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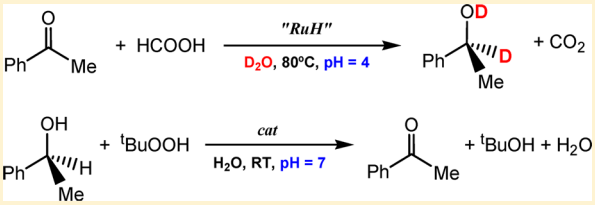
Supporting Information

ABSTRACT: The preparation of three series of arene Ru(II) half-sandwich compounds with the functional ligand 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) is described. The new cationic derivatives have the general formula $[(\eta^6\text{-arene})RuCl(\kappa^2\text{-}N,N\text{-dmobpy})]X$ (arene = benzene, X = Cl^- ([**1**]**Cl**), BF_4^- ([**1**][**BF$_4$**]), TsO^- ([**1**]**TsO**), PF_6^- ([**1**][**PF$_6$**]); arene = *p*-cymene (*p*-cym), X = Cl^- ([**2**]**Cl**), BF_4^- ([**2**][**BF$_4$**]), TsO^- ([**2**]**TsO**), PF_6^- ([**2**][**PF$_6$**]); arene = 2-phenoxy-1-ethanol (phoxet), X = Cl^- ([**3**]**Cl**), BF_4^- ([**3**][**BF$_4$**]), TsO^- ([**3**]**TsO**), PF_6^- ([**3**][**PF$_6$**])). The structures of [**1**]**Cl**, [**1**]**TsO**, [**2**]**TsO**, [**2**][**BF$_4$**], and [**2**][**PF$_6$**] were determined by X-ray crystallography. All of the complexes except the PF_6^- salts were water-soluble, and they behaved as active catalysts in two different processes: the transfer hydrogenation of water-soluble and -insoluble ketones to the corresponding alcohols, using HCOONa as the hydrogen source at pH 4, and the oxidation of *rac*-1-phenylethanol to acetophenone with ^{t}BuOOH at pH 7, both in aqueous solution. For the transfer hydrogenation with *p*-cymene complexes the aqua, formato, and hydride species were detected by means of ^{1}H NMR experiments in D_2O. It was found that the cationic hydrido complex was $[(\eta^6\text{-}p\text{-cymene})RuD(dmobpy)]^+$. The reversible and pH-dependent formation of the hydroxo derivative was also observed. When the catalytic transfer hydrogenation was performed in D_2O, the 1-phenylethanol obtained was selectively deuterated at the benzylic carbon. Mechanistic proposals are also included.



INTRODUCTION

The number of organic reactions catalyzed by half-sandwich Ru(II) arene complexes has increased considerably in the past decade. Relevant examples of this proliferation include the following: hydration of organonitriles,[1] hydration of alkynes,[2] Diels−Alder reactions,[3] alkene metathesis,[4] hydrogenation of alkenes,[5] asymmetric transfer hydrogenation of ketones[6] and imines, and oxidation of alcohols.[7,8] In particular, we are interested in the development of versatile catalysts in aqueous media, for both the transfer hydrogenation of ketones[9,10] and the oxidation of alcohols.[11] Obvious advantages result from the use of water as a solvent, in that it avoids environmental issues related to the use of organic solvents and it also makes the separation of organics products easier.[12,13]

Several procedures are available to achieve the synthesis of organic alcohols. Hydroboration−oxidation of alkenes, hydrolysis of esters, nucleophilic substitution on haloalkanes, and reduction of ketones are well-known procedures. In particular, the reduction of ketones by catalytic transfer hydrogenation has become established as one of the most useful protocols among the latter group of reactions, mainly because it avoids the drawbacks associated with the use of high-pressure molecular hydrogen. 2-Propanol is the preferred hydrogen source in most cases, and Ru-, Rh-, or Ir-based complexes are the most popular catalytic precursors.[14] Moreover, the reaction can be carried out in water using a mixture of HCOONa and HCOOH as the hydrogen source and this approach has evident benefits from an environmental point of view. Species of general formula $[(\eta^6\text{-arene})RuCl(N,N)]^+$ show good activities in this field, provided that they are soluble in water. Several groups have exploited the possibilities of chloro and aqua complexes, of general formula $[(\eta^6\text{-arene})Ru(NN)(X)]^{n+}$ (X = Cl, H_2O; *n* = 1, 2), with remarkable results.[9,10,15]

The oxidation of accessible primary and secondary alcohols to prepare reactive aldehydes and ketones, respectively, is a highly attractive synthetic strategy, and several protocols are known. The classical Jones oxidation uses CrO_3 in sulfuric media to oxidize secondary alcohols to ketones and primary alcohols to aldehydes under water-free conditions or carboxylic acids in wet solvents.[16] Nevertheless, Cr(VI) chemicals are highly toxic, and their use is undesirable. Alternative protocols avoid the use of toxic metals such as chromium, and these can be carried out under very mild conditions. The Corey−Kim

Received: May 29, 2012
Published: August 22, 2012

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

reaction and the Swern reaction are based on the "in situ" generation of the dimethylchlorosulfonium ion, either from *N*-chlorosuccinimide and dimethyl sulfide (Corey–Kim) or from DMSO and oxalyl chloride (Swern), and both involve the use of Et_3N as a base.[17] The Oppenauer oxidation is an aluminum-catalyzed reaction based on hydride transfer from the α-carbon of the corresponding alcohol to the carbonyl carbon of a ketone such as benzophenone.[18] The Dess–Martin oxidation makes use of a hypervalent iodine compound to oxidize alcohols to adehydes or ketones smoothly and selectively in dichloromethane or chloroform at room temperature.[19] Many other oxidants have been used in a variety of Ru-based catalytic systems, namely chloramine-T,[20] benzoquinone,[21] iodosylbenzene,[22] $NaIO_4$,[8] *N*-methylmorpholine *N*-oxide (NMO),[23] and ^{t}BuOOH.[24] The last peroxide is cheap and easy to use. In addition, in some recent reports the efficiencies of different oxidants have been compared.[7,8,25]

Most of these methodologies produce toxic byproducts and employ organic solvents. Therefore, the use of cleaner oxidants, such as hydrogen peroxide[26] and molecular oxygen,[21,27] in the catalytic oxidation of alcohols has been developed to satisfy the demands of greener technologies. Dehydrogenative oxidation of alcohols accompanied by the release of H_2 represents a further step as far as atom efficiency is concerned, since it avoids the use of any oxidant.[28] The application of these strategies in aqueous media is emerging as a safer, cleaner, and cheaper alternative, and it also allows the separation of the organic products and the reuse of the water-soluble catalysts by simple liquid–liquid extraction. Consequently, significant efforts have been dedicated to the design and preparation of robust organometallic catalysts with hydrophilic functions to enhance their water solubility.[29]

In the work described here, we targeted the synthesis and characterization of new arene ruthenium complexes of formula $[(\eta^6\text{-arene})RuCl(NN)]X$ for their use as versatile catalysts in the transfer hydrogenation of water-soluble and -insoluble ketones, with HCOONa as the hydrogen source, and the oxidation of alcohols with ^{t}BuOOH as the oxidant, both in aqueous solutions. The NN ligand 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) was chosen for this study. The introduction of the methoxy groups was carried out with the belief that they could enhance the solubility in water of the corresponding Ru salts in comparison to similar complexes with bpy. At the same time, we relied on the premise that dmobpy could facilitate the activation of the catalytic precursors. It has been reported that bipy, as a π-acceptor ligand, hinders the dissociation of the chloride group in $[(\eta^6\text{-arene})Ru(bipy)Cl]Cl$.[30] In contrast, we predicted that the presence of electron-donating groups (–OMe) in dmobpy should moderate this π-acceptor effect due to the diminished electron-withdrawing ability. This in turn would decrease the positive charge on the metallic center and would make the Cl^- dissociation process more favorable, which would increase the aquation rate.[30]

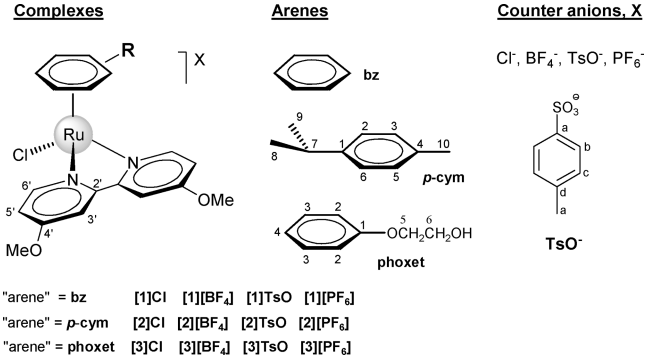
Another aim of the work was to analyze the effect of the counteranion and/or the arene on the water solubility and the catalytic behavior. Thus, different anions (X = Cl^-, BF_4^-, TsO^-, PF_6^-) and three distinct arenes were introduced. In addition to the more commonly used benzene and *p*-cymene arenes, the scarcely explored 2-phenoxy-1-ethanol (phoxet) was also used in the synthesis of the catalytic precursors.[6,31] It was thought that the pendant group could have a positive effect on the catalytic activity, bearing in mind that it has been established that donor groups on the arene ring favor the catalytic behavior in the transfer hydrogenation of ketones.[9,32] This pendant group could also favor water solubility, according to previous studies with phosphine ruthenium systems.[33]

The detection of intermediates in the transfer hydrogenation process was also a goal of this work. In this context, we observed selective deuteration at the benzylic carbon of the phenylethanol obtained in the transfer hydrogenation of acetophenone carried out in D_2O. This finding indicates that the hydride intermediate of the catalytic process undergoes a fast and reversible interchange with D^+ from the solvent.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization of Complexes. The commercial ligand 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) was used to prepare three series of new compounds with the general formula $[(\eta^6\text{-arene})RuCl(\kappa^2\text{-}N,N\text{-dmobpy})]X$ (arene = benzene, X = Cl^- ([**1**]**Cl**), BF_4^- ([**1**][**BF**$_4$]), TsO^- ([**1**]**TsO**), PF_6^- ([**1**][**PF**$_6$]); arene = *p*-cymene (*p*-cym), X = Cl^- ([**2**]**Cl**), BF_4^- ([**2**][**BF**$_4$]), TsO^- ([**2**]**TsO**), PF_6^- ([**2**][**PF**$_6$]); arene = 2-phenoxy-1-ethanol (phoxet), X = Cl^- ([**3**]**Cl**), BF_4^- ([**3**][**BF**$_4$]), TsO^- ([**3**]**TsO**), PF_6^- ([**3**][**PF**$_6$])) (see Scheme 1). The cationic derivatives were obtained in one-pot processes by reacting the appropriate arene starting material with the functional chelating ligand dmobpy and the corresponding silver salt, when necessary, in polar solvents such as methanol, ethanol, 2-propanol, acetonitrile, and water (see the Experimental Section). The monomer $[(\eta^6\text{-benzene})RuCl_2(CH_3CN)]$[34] was used to prepare [**1**]**Cl**, [**1**][**BF**$_4$], [**1**]**TsO**, and [**1**][**PF**$_6$] (eqs 1 and 2 in Scheme 2), whereas dimers of formula $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = *p*-cym,[35] phoxet[31]) were employed to isolate compounds of series **2** and [**3**]**Cl** (eqs 3 and 4 in Scheme 2). Finally, the complexes [**3**]**X** (X = BF_4^-, TsO^-, PF_6^-) were prepared from [**3**]**Cl** according to eq 5 in Scheme 2. The usual workup procedures afforded the new complexes in moderate to good yields (47–88%) as air- and moisture-stable yellow solids. Solubility tests proved that most of the complexes are water-soluble (see Table 1), and this is probably a consequence of both their cationic nature and the presence of the –OMe groups, which can act as hydrogen bond acceptors.[36] However, relevant counterion and arene effects on the solubility can be deduced from these tests. In general, the *p*-cymene derivatives are more soluble. Concerning the anion effect, the chloro salts are the most soluble in the case of benzene or *p*-cymene complexes, while for the arene 2-phenoxy-1-ethanol the solubility is higher for the derivative

Scheme 1. Structures and Numbering Scheme of the New Ru(II) Arene Compounds of General Formula $[(\eta^6\text{-arene})RuCl(\kappa^2\text{-}N,N\text{-dmobpy})]X$ ([1]X, [2]X, and [3]X)



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Scheme 2. Preparation of Compounds of the Series 1−3

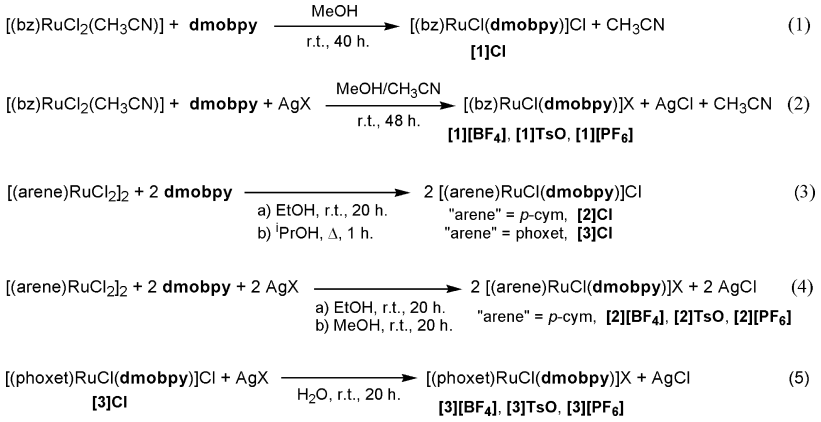


Table 1. Solubility Values in Water at Room Temperature

compd	solubility[a]
[1]Cl	11.1 (23.8)
[1][BF_4]	0.5 (1.0)
[1]TsO	0.7 (1.2)
[2]Cl	11.3 (21.6)
[2][BF_4]	2.9 (5.1)
[2]TsO	5.0 (7.6)
[3]Cl	2.9 (5.5)
[3][BF_4]	2.0 (3.5)
[3]TsO	6.4 (9.7)

[a]Values in mg mL^{-1} (values in parentheses in μmol mL^{-1}).

containing the tosylate anion. The chloro salts [**1**]**Cl** and [**2**]**Cl** have the highest solubilities. In contrast, the PF_6^- salts are poorly soluble in water and they were therefore not used in the catalytic studies.

The new products were fully characterized by ^1H, ^{19}F (for BF_4^- salts), ^{31}P (for PF_6^- salts), and $^{13}C\{^1H\}$ NMR spectroscopy and also by IR spectroscopy, FAB mass spectrometry, molar conductivity, and elemental analysis. The structures of [**1**]**Cl**, [**1**]**TsO**, [**2**]**TsO**, [**2**][BF_4], and [**2**][PF_6] were determined by single-crystal X-ray diffraction.

Full assignment of resonances in the ^1H and $^{13}C\{^1H\}$ NMR spectra of every complex was performed using 2D NMR experiments such as gCOSY, NOESY, gHSQC, and gHMBC (see the Experimental Section and Table S11 in the Supporting Information). The ^1H NMR spectra of compounds [**2**]**X** and [**3**]**X** in CD_3OD at room temperature are consistent with C_s-symmetric species (nonstereogenic and achirotopic Ru ion). Thus, the *p*-cymene series shows the characteristic AA′BB′ spin system for the aromatic protons of the arene and homotopic methyl groups for the isopropyl moiety. Similarly, complexes of series **3** exhibit an AA′BB′C spin system for the aromatic protons of the phenoxyethanol ring and homotopic methylene protons for the ethanol arm. Compounds of series **1** only present a singlet for the six equivalent protons of the benzene at around 6 ppm, and consequently, information about the symmetry cannot be inferred in this case. On the other hand, the dmobpy signals were shifted downfield in all the complexes with respect to those of the free ligand, as a consequence of coordination to the metallic center. As expected, $\delta(H^{6'})$ is particularly sensitive to this effect, due to its proximity to the metallic center. Complexes of series **2** and **3** show an equivalent deshielding, $\Delta\delta(H^{6'}) = 0.7$ ppm, whereas complexes of series **1** exhibit a slightly higher displacement, $\Delta\delta(H^{6'}) = 0.8$ ppm. Apparently, the lower π-donor ability of benzene, in comparison to that of *p*-cymene and phenoxyethanol, is compensated by a higher σ-donation from the N,N ligand to the Ru ion. On the other hand, a counteranion effect was not observed on the resonances in CD_3OD. Additional peaks were recorded for the TsO^- anion in the spectra of **1**[**TsO**], **2**[**TsO**], and **3**[**TsO**]. The $^{13}C\{^1H\}$ NMR spectra of all the complexes

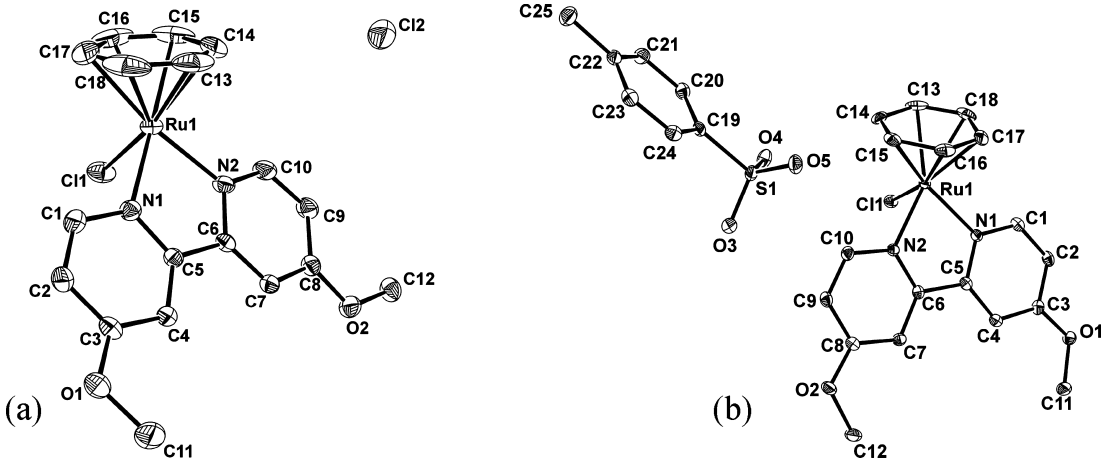


Figure 1. ORTEP diagrams for complexes (a) [**1**]**Cl** and (b) [**1**]**TsO**. Hydrogens have been omitted for clarity.

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

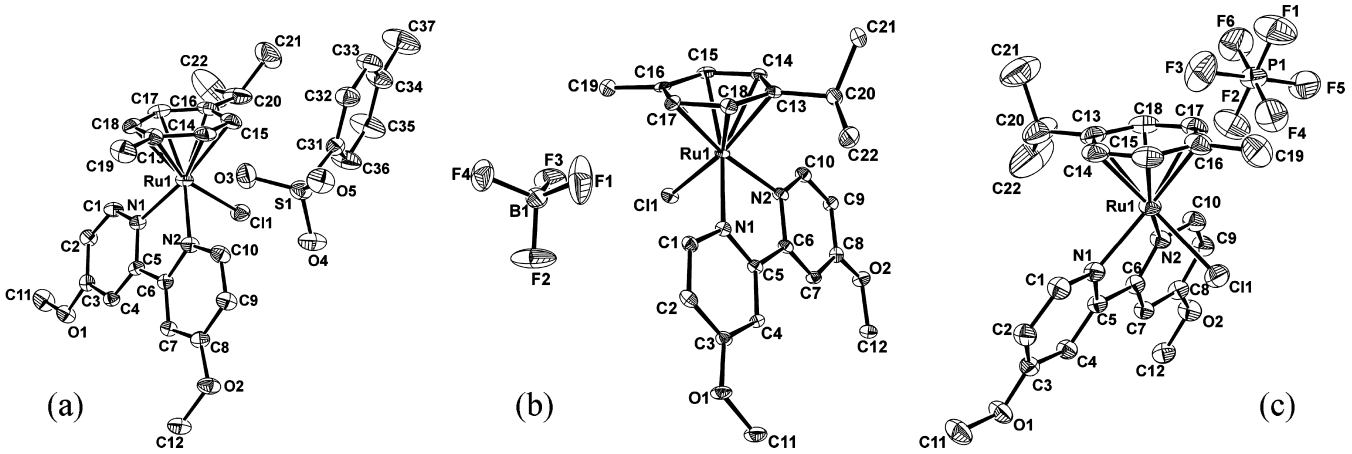


Figure 2. ORTEP diagrams for complexes (a) [2]**TsO**, (b) [2][BF_4], and (c) [2][PF_6]. Hydrogens have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds [1]Cl, [1]TsO·H_2O, [2]TsO, [2][BF_4], and [2][PF_6]

bond length/angle	[1]Cl	[1]TsO·H_2O	[2]TsO	[2][BF_4]	[2][PF_6]
Ru(1)−Cl(1)	2.3989(9)	2.4192(7)	2.409(2)	2.410(1)	2.392(1)
Ru(1)−N(1)	2.085(2)	2.082(2)	2.092(3)	2.085(3)	2.084(3)
Ru(1)−N(2)	2.078(2)	2.075(2)	2.082(3)	2.084(3)	2.091(3)
N(1)−Ru(1)−N(2)	76.19(8)	76.31(7)	76.6(2)	76.4(1)	76.1(1)
N(1)−Ru(1)−Cl(1)	85.22(6)	84.15(5)	84.23(9)	85.25(9)	83.99(8)
N(2)−Ru(1)−Cl(1)	84.80(6)	85.99(5)	84.35(9)	81.09(9)	83.32(9)

Table 3. Selected Geometric Parameters for the Cations of [1]Cl, [1]TsO·H_2O, [2]TsO, [2][BF_4], and [2][PF_6]

complex	range of Ru−C dist (Å)	Ru−centroid (Å)[a]	α(py−py)[b] (deg)	β(dmobpy−"arene")[c] (deg)	γ(Cx−C_{ipso}−Ru−Cl)[d] (deg)
[1]Cl	2.154(3)−2.186(3)	1.685	8.5	53.8	
[1]TsO·H_2O	2.159(2)−2.199(2)	1.672	2.0	60.4	
[2]TsO	2.161(5)−2.237(5)	1.687	1.8	64.3	12.8
[2][BF_4]	2.164(4)−2.210(4)	1.679	6.4	66.9	14.3
[2][PF_6]	2.146(4)−2.225(4)	1.685	2.1	66.4	6.5

[a]Calculated with Mercury, version 2.4.6. [b]Dihedral angle between the two pyridyl rings. [c]Dihedral angle between the arene and the dmobpy ligand. [d]Dihedral angle formed by the atoms Cx−C_{ipso}−Ru−Cl; Cx represents the carbon atom of the methyl ([2]BF_4 or [2]PF_6) or isopropyl ([2]**TsO**) groups of the *p*-cymene ring.

show characteristic signals for dmobpy and the corresponding arenes with symmetry patterns fully consistent with those established by ^{1}H NMR (see the Experimental Section).

The FAB+ mass spectra for complexes of series **1**−**3** all exhibit a characteristic set of peaks for the corresponding cationic unit $[M - X]^+$.

FT-IR spectra were recorded for all complexes and are fully consistent with the formulations described above. All complexes show characteristic bands for the Ru−Cl stretching vibrations at around 280 cm^{-1}. Furthermore, the BF_4^- salts show strong diagnostic peaks at around 1058 cm^{-1} (ν_{B-F}), whereas the TsO^- salts show peaks at around 1212 ($\nu_{as,S=O}$) and 1188 cm^{-1} ($\nu_{as,S=O}$) and the PF_6^- salts at 841 (ν_{P-F}) and 558 cm^{-1} (δ_{F-P-F}).

The molar conductivity measurements (Λ_M) for all the monocationic complexes show that they behave as 1:1 electrolytes in acetonitrile solutions (10^{-3} M) (see the Experimental Section and Table S12 in the Supporting Information).[37]

X-ray Structure Determination. Single crystals of [1]**Cl**, [1]**TsO**, [2]**TsO**, [2][BF_4], and [2][PF_6] were obtained, and the corresponding structures were determined by single-crystal X-ray diffraction analysis. The ORTEP diagrams are shown in Figures 1 and 2. Selected bond lengths and angles are given in Table 2, and relevant crystallographic parameters are given in the Supporting Information. The molecular structures of the five complexes present the classical three-legged piano-stool arrangement with a pseudo-octahedral geometry and display features similar to those of structurally related ruthenium complexes with bpy-type ligands[38,39] such as, for example, [RuCl(*p*-cym)(bpy)]PF_6[39] and [RuCl(bz)(bpy)]Cl.[40]

The ruthenium atom is coordinated to the corresponding η^6-arene ring, which occupies three facial coordination positions, and also to the two nitrogen atoms of the dmobpy ligand and the chloride group. The range of Ru−C distances is shown in Table 3. This range is higher for [2]**TsO** and [2][BF_4]. The Ru−C distances trans to the chloro ligand are generally shorter than those trans to the dmobpy ligand, thus reflecting a higher trans influence of the nitrogenated ligand. The Ru−centroid distances are also included in Table 3. It can be observed that there are no clear differences in these values between the two arenes benzene and *p*-cymene. The Ru−Cl and Ru−N bond lengths and coordination angles are similar to those reported for related arene Ru(II) complexes with bipyridine ligands (Table 2). The two pyridyl rings of the dmobpy ligand are practically coplanar (see dihedral angle in Table 3), and both

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

rings and the chelate ring are also approximately coplanar, as expected for complexes with this type of bidentate ligand. The dihedral angle formed between the arene ring and the mean plane of the dmobpy ligand is higher for the *p*-cymene complexes, possibly for steric reasons (see Table 3). The orientation of the *p*-cymene ring in the corresponding complexes allows the formation of weak hydrogen bonds between the chloride and the methyl ([**2**][BF_4] or [**2**][PF_6]) or isopropyl ([**2**]**TsO**) hydrogen atoms (distances: Cl1−C19 = 3.38 Å in [**2**][BF_4] and 3.33 Å in [**2**][PF_6] and Cl1−C20 = 3.44 Å in [**2**]**TsO**). To quantify the orientation of these groups, we defined the dihedral angle formed by Cx−C_{ipso}−Ru−Cl, where Cx is the carbon atom of the methyl ([**2**][BF_4] or [**2**][PF_6]) or isopropyl ([**2**]**TsO**) groups bonded to the arene ring. It is noteworthy that, although the three derivatives contain the same cation, a different orientation for the *p*-cymene ring was found in [**2**]**TsO** with respect to the other two derivatives.

The methoxy groups in all derivatives exhibit a coplanar conformation with the bpy moiety, indicating a conjugation effect, as usually found for methoxyphenyl groups bearing two ortho H atoms.[41] This situation has also been found in the three reported ruthenium complexes containing the dmobpy ligand.[42] In complexes [**1**]**TsO** and [**2**][BF_4] the two methoxy groups exhibit a convergent orientation, while in the other derivatives these two groups are in a divergent arrangement.

In the crystal structure the different counteranions participate in the formation of hydrogen bonds with several cations (up to 5). In the case of [**2**]**TsO**, there are also hydrogen bonds between the anions.

[**1**]**TsO** crystallizes with one water molecule per unit formula that also participates in the formation of hydrogen bonds. The crystal structure shows metal complex dimers with the two cations in a head-to-tail disposition related by an inversion center. The two cations interact with each other through multiple hydrogen bonds. In particular, each chloride anion behaves as the hydrogen acceptor in four different contacts with the neighbor; thus, eight interactions are observed for each dimer (see Figure 3). This situation may explain the convergent orientation of the two methoxy groups. The methoxy groups of the other derivatives are also involved in different hydrogen bonds with other cations in the crystal structure.

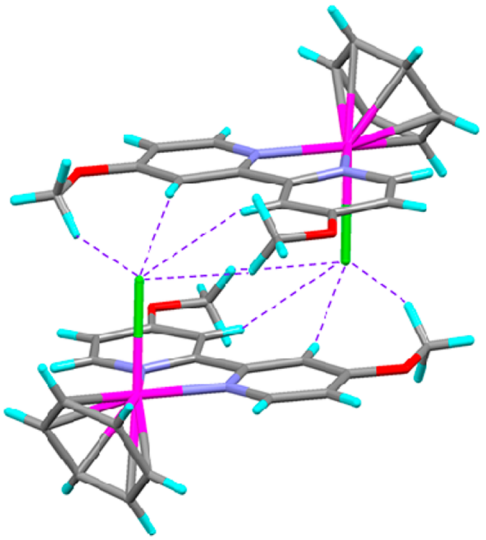
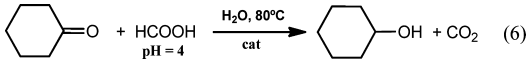


Figure 3. Dimers in the crystal structure of [**1**]**TsO**·H_2O. Hydrogen bonds are indicated with violet dashed lines.

In the case of [**1**]**Cl** there is a $\pi-\pi$ stacking interaction between the benzene rings of two cations that are related by an inversion center. The parameters for this interaction are as follows: distances, Ct−Ct = 3.49 Å and Ct−pl = 3.33 Å; angles, α (angle between planes) = 0° and β (angle formed by the lines Ct−Ct and Ct−pl) = 17° (Ct = centroid, pl = plane).

Catalytic Transfer Hydrogenation of Ketones in Water. The activity of our complexes in the catalytic transfer hydrogenation of cyclohexanone to cyclohexanol in water was explored using a mixture of sodium formate/formic acid (pH 4) as the hydrogen source at 80 °C under a nitrogen atmosphere, according to the conditions established in the bibliography for similar systems (eq 6).[10] First, the corresponding blank and



(6)

control experiments were carried out for this reaction. The formation of product was not detected without catalyst (Table 4, entry 1), in the presence of the free ligand dmobpy (Table 4, entry 2), or in the presence of the starting material [(bz)$RuCl_2(CH_3CN)$] (Table 4, entry 3). The reduction of cyclohexanone to cyclohexanol was then evaluated in the presence of [**1**][BF_4] as the catalytic precursor under different reaction conditions and also with the addition of different additives, as either promoters or inhibitors (Table 4). The first experiment was carried out with a catalyst/substrate ratio of 1/200, with $AgBF_4$ as a potential promoter, and with a reaction time of 20 h (entry 4). A yield of 100% was achieved under these conditions. The experiment was repeated without $AgBF_4$ (entry 5) and the yield remained 100%, thus demonstrating that activation by chloride abstraction is not necessary. When the reaction time was reduced to 8 or 4 h (entries 6 and 7), the yield was reduced to 84 and 26%, respectively, although in the case of entry 6 the TOF was increased. When the catalyst/substrate ratio was changed to 1/500 (20 h), an increase in the TOF value was also achieved and a yield of 100% was obtained (compare entries 5 and 8). In the next experiment NaCl (2.5 mol % with regard to catalyst) was added to hinder the chloride dissociation and the formation of the labile aqua derivative, which could be the putative active species. As expected, a decrease in the yield was observed (compare entries 5 and 9), indicating that activation of the catalyst probably requires dissociation of the chloride. The use of H_2O/MeOH (9/1) as the solvent system diminished the conversion (entry 10). A rough estimation of the pH effect was carried out by using either HCOOH (pH 3) or HCOONa (pH 9) as the only hydrogen source, with yields of 9 and 0% obtained (entries 11 and 12, respectively), thus confirming that a pH of 4 is the best of those tested for our model system. Finally, the catalyst was moderately active when the solvent was changed to H_2O/MeOH (9/1), using HCOONa as the only hydrogen source (entry 13).

Catalyst Screening. In a second set of experiments, ruthenium complexes [**1**]**X**−[**3**]**X** (X = Cl^-, BF_4^-, TsO^-) were tested as precatalysts in the transfer hydrogenation of cyclohexanone using the conditions shown in entry 5 in Table 4. In this way, the influence of the arene and the counteranion could be evaluated. Derivatives with PF_6^- were not used in this study because of their low solubility in water. Complexes [**1**]**X**−[**3**]**X** (X = Cl^-, BF_4^-, TsO^-) were totally soluble in the

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

Table 4. Catalytic Transfer Hydrogenation of Cyclohexanone to Cyclohexanol Using [1][BF_4] under Different Reaction Conditions[a]

entry	cat.	H source	solvent	additive	cat./S	yield (%)	t (h)	TON	TOF (h^{-1})
1		HCOOH/HCOONa	H_2O			0	20	0	0
2	dmobpy	HCOOH/HCOONa	H_2O		1/200	0	20	0	0
3	[bzRuCl$_2$(CH_3CN)]	HCOOH/HCOONa	H_2O		1/200	0	20	0	0
4	[**1**][BF_4]	HCOOH/HCOONa	H_2O	$AgBF_4$[b]	1/200	100	20	200	10
5	[**1**][BF_4]	HCOOH/HCOONa	H_2O		1/200	100	20	200	10
6	[**1**][BF_4]	HCOOH/HCOONa	H_2O		1/200	84	8	168	21
7	[**1**][BF_4]	HCOOH/HCOONa	H_2O		1/200	26	4	52	13
8	[**1**][BF_4]	HCOOH/HCOONa	H_2O		1/500	100	20	500	25
9	[**1**][BF_4]	HCOOH/HCOONa	H_2O	NaCl[c]	1/200	83	20	166	8.3
10	[**1**][BF_4]	HCOOH/HCOONa	H_2O/MeOH (9/1)		1/200	79	20	158	7.9
11	[**1**][BF_4]	HCOOH[d]	H_2O		1/200	9	20	18	0.9
12	[**1**][BF_4]	HCOONa	H_2O		1/200	0	20	0	0
13	[**1**][BF_4]	HCOONa	H_2O/MeOH (9/1)		1/200	44	20	88	4.4

[a]Control experiments are also included. Conditions: T = 80 °C, cat./S/HCOONa = 1/200/6000, 1.6 μmol of cat., 5 mL of H_2O (except for entry 8, cat./S/HCOONa = 1/500/6000), pH 4 (adjusted with HCOOH). [b]$AgBF_4$ was added to an aqueous solution of the catalyst, which contained HCOOH/HCOONa, before the substrate. [c]NaCl (2.5% with regard to catalyst). [d]cat./S/HCOOH = 1/200/200. TON: turnover number = (mol of ketone converted to alcohol)/(mol of catalyst). TOF: turnover frequency = (mol of product)/((mol of precatalyst) h) (calculated at the end of the reaction).

reaction conditions. It was verified that the dimers [(*p*-cym)$RuCl_2$]$_2$ and [(phoxet)$RuCl_2$]$_2$ were completely inactive in this transformation. The activity of [(bz)$RuCl_2$]$_2$ was not assessed, due to its insolubility in aqueous media. All of the complexes [**1**]**X**−[**3**]**X** (X = Cl^-, BF_4^-, TsO^-) gave full conversion to the expected product after 20 h of reaction (see Table 5). The activity of the complex [(*p*-cym)RuCl(bpy)]Cl, similar to [**1**]**Cl** but with a bpy ligand, was also analyzed. The yield was lower (78%) than that obtained with [**1**]**Cl** (entries 3 and 4), and this shows the beneficial effect of the methoxy groups on the nitrogenated ligand. Several attempts to recycle the catalyst were made, but the catalytic efficiency was much lower in the second cycle.

Table 5. Transfer Hydrogenation of Cyclohexanone to Cyclohexanol Using Different Precatalysts[a]

entry	complex	yield (%) (t (h))	TON	TOF (h^{-1})
1	[(*p*-cym)$RuCl_2$]$_2$	0 (20)	0	0
2	[(phoxet)$RuCl_2$]$_2$	0 (20)	0	0
3	[(*p*-cym)RuCl(bpy)]Cl	78 (20)	156	7.8
4	[**1**]**Cl**	100 (20)	200	10
5	[**1**][BF_4]	100 (20)	200	10
6	[**1**]**TsO**	100 (20)	200	10
7	[**2**]**Cl**	100 (20)	200	10
8	[**2**][BF_4]	100 (20)	200	10
9	[**2**]**TsO**	100 (20)	200	10
10	[**3**]**Cl**	100 (20)	200	10
11	[**3**][BF_4]	100 (20)	200	10
12	[**3**]**TsO**	100 (20)	200	10

[a]Conditions: T = 80 °C, pH 4, cat./S/HCOONa =1/200/6000, 1.6 μmol of cat., 5 mL of H_2O. TON: turnover number = (mol of ketone converted to alcohol)/(mol of catalyst) (calculated after 20 h). TOF: (mol of product)/((mol of precatalyst) h) (calculated after 20 h).

In order to obtain a yield of less than 100% so that we could carry out a comparative analysis of the different precatalysts, the activities of all the complexes were determined again after 8 h of reaction (Table 6). In this block of trials the *p*-cymene complexes gave the highest yields of cyclohexanol, with full conversions for reactions in the presence of [**2**]**Cl** and [**2**]**TsO**

Table 6. Transfer Hydrogenation of Cyclohexanone to Cyclohexanol Using Different Precatalysts[a]

entry	complex	yield (%) (t (h))	TON	TOF (h^{-1})
1	[$RuCl_2$(*p*-cym)]$_2$	0 (8)	0	0
2	[$RuCl_2$(phoxet)]$_2$	0 (8)	0	0
3	[**1**]**Cl**	49 (8)	98	12
4	[**1**][BF_4]	84 (8)	168	21
5	[**1**]**TsO**	53 (8)	106	13
6	[**2**]**Cl**	100 (8)	200	25
7	[**2**][BF_4]	87 (8)	174	22
8	[**2**]**TsO**	100 (8)	200	25
9	[**3**]**Cl**	76 (8)	152	19
10	[**3**][BF_4]	48 (8)	96	12
11	[**3**]**TsO**	62 (8)	124	16
12	[**2**]**Cl**	70 (4)	140	35
13	[**2**][BF_4]	69 (4)	138	35
14	[**2**]**TsO**	90 (4)	180	45

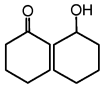
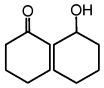
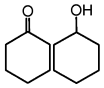
[a]Conditions: T = 80 °C, cat./S/HCOONa = 1/200/6000, 1.6 μmol of cat., 5 mL of H_2O, pH 4 (adjusted with HCOOH). TOF: (mol of product)/((mol of precatalyst) h) (calculated at the end of the reaction). No additive was used in any of these experiments.

and an 87% yield for [**2**][BF_4] (Table 6, entries 6−8). The benzene and phenoxyethanol derivatives gave lower yields (entries 3−5 and 9−11), thus confirming an arene effect on the catalytic activity. Two different arguments must be considered to explain these results. As previously stated, it has been reported[10] that electron-donating substituents have a beneficial effect on the transformation rate, a situation that supports the hypothesis of η^4 transition states postulated by Ogo.[10] This may explain the different performances of *p*-cymene and benzene derivatives. On the other hand, the pendant −OCH_2CH_2OH group on the phenoxyethanol ring could, a priori, compete with the hydrogen donor (formate) or the substrate for a position in the coordination sphere, thus neutralizing the electron-donating effect of this substituent and accounting for the reduced activity of the phenoxyethanol catalysts with respect to the *p*-cymene derivatives.

Finally, the reaction time was shortened once again, from 8 to 4 h, for reactions performed in the presence of the *p*-cymene

dx.doi.org/10.1021/om3004702 | Organometallics 2012, 31, 6106−6123

Table 7. Transfer Hydrogenation of Different Substrates Using $[1][BF_4]$[a]

Entry	Substrate	Products	Cat	Yield % (t, h)	TON	TOF (h^{-1})
1			**[1][BF$_4$]**	84 (8)	168	21
2			**[1][BF$_4$]**	100 (20)	200	10
3			No	0/0 (20)	0	0
4			**[1][BF$_4$]**	48/2 (8)	100[e]	12.5
5			**[1][BF$_4$]**	63/17 (20)	160[e]	8
6			No	0 (20)	0	0
7			**[1][BF$_4$]**	83 (8)	166	21
8			**[1][BF$_4$]**	100 (20)	200	10
9[b]			**[1][BF$_4$]**	83 (20)	166	8.3
10			No	0 (20)	0	0
11			**[1][BF$_4$]**	55 (8)	110	13.8
12			**[1][BF$_4$]**	94 (20)	188	9.4

[a]Conditions: T = 80 °C, cat./S/HCOONa =1/200/6000, 1.6 μmol of cat., 5 mL of H_2O, pH 4 (adjusted with HCOOH). [b]Addition of HCOOH was avoided (the pH was not adjusted to 4), and a H_2O/MeOH (9/1) mixture was used as solvent. TOF: (mol of product)/((mol of precatalyst) h) (calculated at the end of the reaction).

derivatives ([**2**]**X**) in order to improve the comparison of the three precatalysts and to obtain higher TOF values (Table 6, entries 12−14). Thus, we can conclude that [**2**]**TsO** is the most active precatalyst of this family, with a TOF value of 45 h^{-1}, after 4 h.

Comparison of the three different groups of experiments (entries 3−5, 6−8, and 12−14) allows us to establish the effect of the counteranion. This effect is not uniform for the three series. The derivatives that perform best are those with tetrafluoroborate, chloride, and tosylate for the benzene, phenoxyethanol, and *p*-cymene series, respectively. The results obtained for the catalyst [**2**]**OTs** are similar to those of other similar previously reported systems[10,11] if the TOF at the end of the reaction is used for the comparison.

Substrate Scope. The scope of the transformation was investigated with three other substrates: cyclohexenone (soluble in water), 3-pentanone (moderately soluble in water), and acetophenone (sparingly soluble in water) using the $[1][BF_4]$ precatalyst. Cyclohexenone was chosen to compare the activity of the catalysts in the hydrogenation of ketone or olefin double bonds. The results are shown in Table 7. It was concluded that the ruthenium complexes tested are rather tolerant with regard to the substrate, and the three compounds were reduced under the conditions used. Control experiments for the three substrates were run in order to prove that reaction did not take place in the absence of catalysts (entries 3, 6, and 10).

Total conversion to the alcohol was obtained with acetophenone (entry 8), and a yield of 94% was achieved in the case of 3-pentanone (entry 12) after 20 h of reaction. The tests with a reaction time of 8 h (entries 1, 7, and 11) showed the following order of reactivity: cyclohexanone ≅ acetophenone > 3-pentanone. The straight-chain ketone is converted to the corresponding alcohol less efficiently than the cyclic ketone, possibly due to steric reasons. The data shown in entry 9 demonstrate that, as previously observed, the yield is lower when the pH is not adjusted to 4.

The reduction of cyclohexenone was effectively achieved by $[1][BF_4]$, and two products, cyclohexanone and cyclohexanol, were detected, meaning that both the alkene and carbonyl functions are reduced under these conditions (entries 4 and 5, Table 7). The presence of cyclohexanone and not cyclohexenol indicates that the alkene functionality is reduced more easily.

Stability of Complex ***2·BF$_4$*** *in Aqueous Solution: Aquation−Anation Equilibrium, Basic Hydrolysis, and Reactivity in the Presence of HCOONa.* In order to obtain information about the mechanism of the transfer hydrogenation process and to detect possible intermediates or active species, we studied by means of ^{1}H NMR the stability of different

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

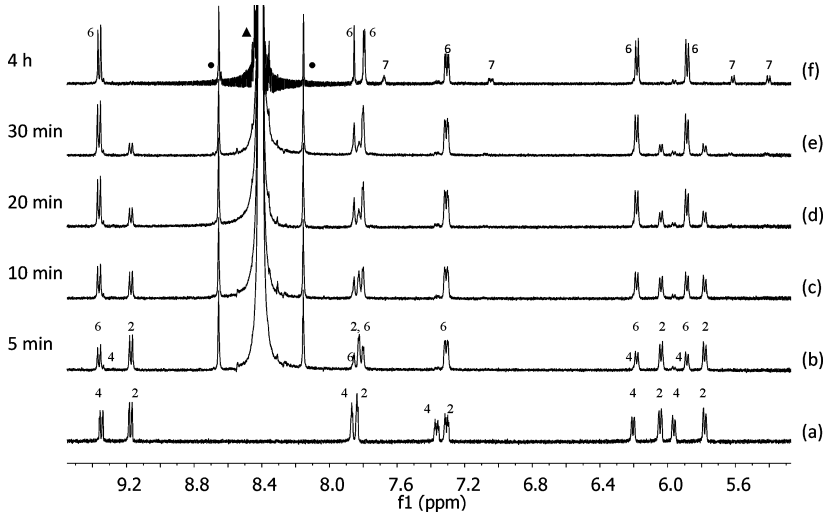


Figure 4. Reaction of [**2**][BF_4] with HCOONa in D_2O at 25 °C: (a) downfield area of the ^1H NMR spectrum of [**2**][BF_4] in D_2O; (b–f) Evolution with time of the same sample after adding an excess of HCOONa (and HCOOH to adjust to pH 4.35). Labeling of signals: [(*p*-cym)Ru(Cl)(dmobpy)]$^+$ (**2**); [(*p*-cym)Ru(D_2O)(dmobpy)]$^{2+}$ (**4**); [(*p*-cym)Ru(HCOO)(dmobpy)]$^+$ (**6**); [(*p*-cym)Ru(D)(dmobpy)]$^+$ (**7**); (▲) $HCOO^-$; (●) ^{13}C satellites.

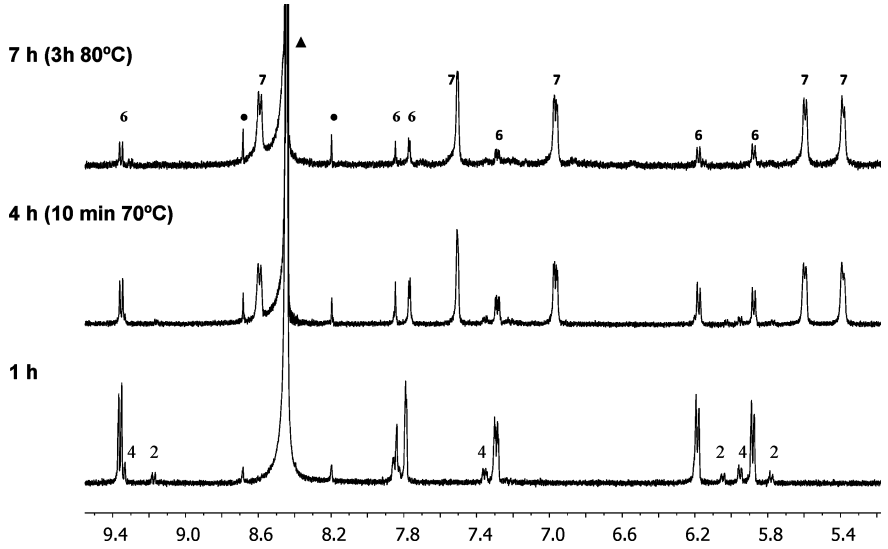


Figure 5. Evolution of the formate complex **6** in D_2O with time and temperature at pH 7: (a) downfield area of the ^1H NMR spectrum of **6** with traces of **2** and **4** in D_2O; (b) evolution of the same sample after 4 h and 10 min of heating; (c) after 3 h more at 80 °C. Labeling of signals: [(*p*-cym)Ru(Cl)(dmobpy)]$^+$ (**2**); [(*p*-cym)Ru(D_2O)(dmobpy)]$^{2+}$ (**4**); [(*p*-cym)Ru(HCOO)(dmobpy)]$^+$ (**6**); [(*p*-cym)Ru(D)(dmobpy)]$^+$ (**7**); (▲) $HCOO^-$; (●) ^{13}C satellites.

complexes in aqueous solution and also the effect of the addition of HCOONa to acidic or basic solutions of [**2**][BF_4].

First, the ^1H NMR spectrum of [**2**][BF_4] in D_2O was recorded at 25 °C to study the corresponding aquation/anation equilibrium. Two sets of peaks were observed immediately after preparation of the sample (<5 min) and these are assigned to [**2**][BF_4] and a new species **4**, with an integration ratio of 52:48 (Figure 4a). The sample was allowed to stabilize for 20 min, but further changes were not detected, suggesting that equilibrium concentrations are reached quickly. An excess of NaCl was then added to the sample and a new spectrum was recorded, which contained one set of peaks. Consequently, the surviving signals can be assigned to the parent chloro complex [**2**][BF_4] and the resonances that were no longer observed to the corresponding aqua cation [(*p*-cym)Ru(OD_2)(dmobpy)]$^{2+}$ (**4**). This assignment is consistent with that reported for similar systems, where aqua complexes show resonances that are displaced to higher frequencies in comparison to those of the parent chloro complexes.[43,44] In conclusion, dissociation of the chloride group in complex **2** is highly favored in water and the corresponding aquation/anation equilibrium is reversible. Indeed, it is well-known that protic solvents facilitate the dissociation of chloro ligands by providing strong hydrogen-bond donors.[45] Similar reversible equilibria were observed in D_2O for [**1**][BF_4], [**2**]**TsO**, and [**3**]**TsO**. The respective Ru–Cl/Ru–OD_2 species coexist with molar ratios of 27/73, 56/44, and 44/56, according to NMR integration.

These studies confirm that for the catalytic activity of the species of the type [(arene)RuCl(NN)]X, the isolation of the corresponding aqua derivatives is not necessary because activation of the chloro precursors takes place easily in water.

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106–6123

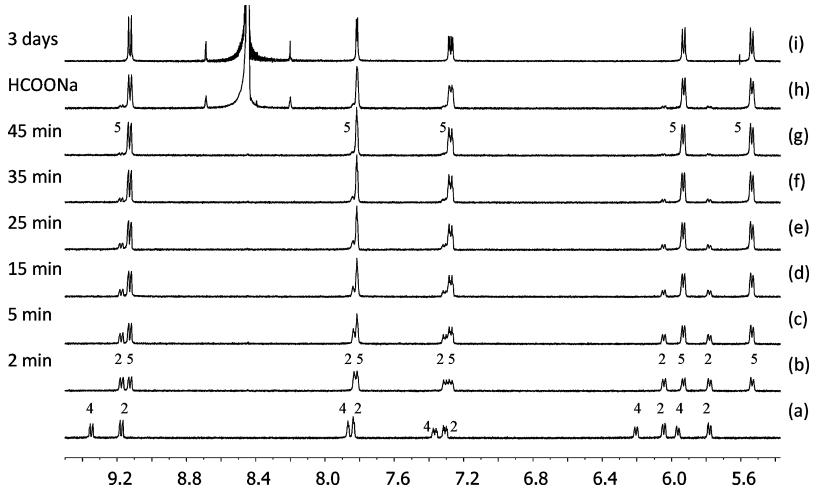


Figure 6. (a) Downfield area of the ^{1}H NMR spectrum of [**2**][$\mathbf{BF_4}$] in D_2O at 25 °C, (b–g) evolution with time of the same sample after adding an excess of KOH (pH >13), and (h, i) the same sample after adding HCOONa, showing no reaction with anion $HCOO^-$. Labels: [(*p*-cym)Ru(Cl)(dmobpy)]$^+$ (**2**); [(*p*-cym)Ru(OD_2)(dmobpy)]$^{2+}$ (**4**); [(*p*-cym)Ru(OD)(dmobpy)]$^+$ (**5**).

In an additional experiment, we added an equimolar amount of HCOOH to an equilibrated solution of [**2**][$\mathbf{BF_4}$] in D_2O at room temperature (containing a 56/44 mixture of **2** and **4**) in an NMR tube. In this case, however, reaction evidence was not detected. In a separate experiment an excess of HCOONa was added to an equilibrated solution of [**2**][$\mathbf{BF_4}$] in D_2O. The pH value was adjusted to 4.35 with HCOOH, and the subsequent evolution was monitored (see Figure 4). Two sets of new signals (**6** and **7**) of increasing intensity were observed together with those of **2** and **4**, which decreased correspondingly. The formation of species **6** is very fast and initially took place at the expense of the aqua cation **4**, the resonances of which also decreased rapidly at the beginning (the species distribution after 5 min was determined by integration, with 59/5/36 ratios for **2**/**4**/**6**). The simultaneous appearance of a singlet at 7.85 ppm, assigned to a coordinated formate anion, allowed us to formulate **6** as the formato cation [(*p*-cym)Ru(OOCH)-(dmobpy)]$^+$. After 10 min, a clear decrease in the chloro complex **2** was also observed, compound **6** continued to be formed, and the first evidence of **7** was detected. Finally, the system seemed to reach an equilibrium after 4 h, with **6** and **7** as the main species in an 86/13 ratio along with trace amounts of **2** and **4**. Signals for **7** appeared shifted upfield relative to the other species, an observation consistent with the formation of a hydride complex according to the literature examples for similar systems.[43] However, a Ru–H resonance was not detected at low frequencies. As explained below, compound **7** is the species [(*p*-cym)Ru(D)(dmobpy)]$^+$. In conclusion, this sequence of reactions can explain the formation of the active species and the different intermediates in the possible mechanism for the hydrogen transfer reaction of ketones. An excess of acetophenone was subsequently added in order to prove that either species **6** or **7** were catalytically active in the transfer hydrogenation of the carbonyl substrate. Signals of **7** disappeared immediately, and *rac*-1-phenylethanol was formed slowly at room temperature with a yield of 77%, after 6 days (estimated by integration).

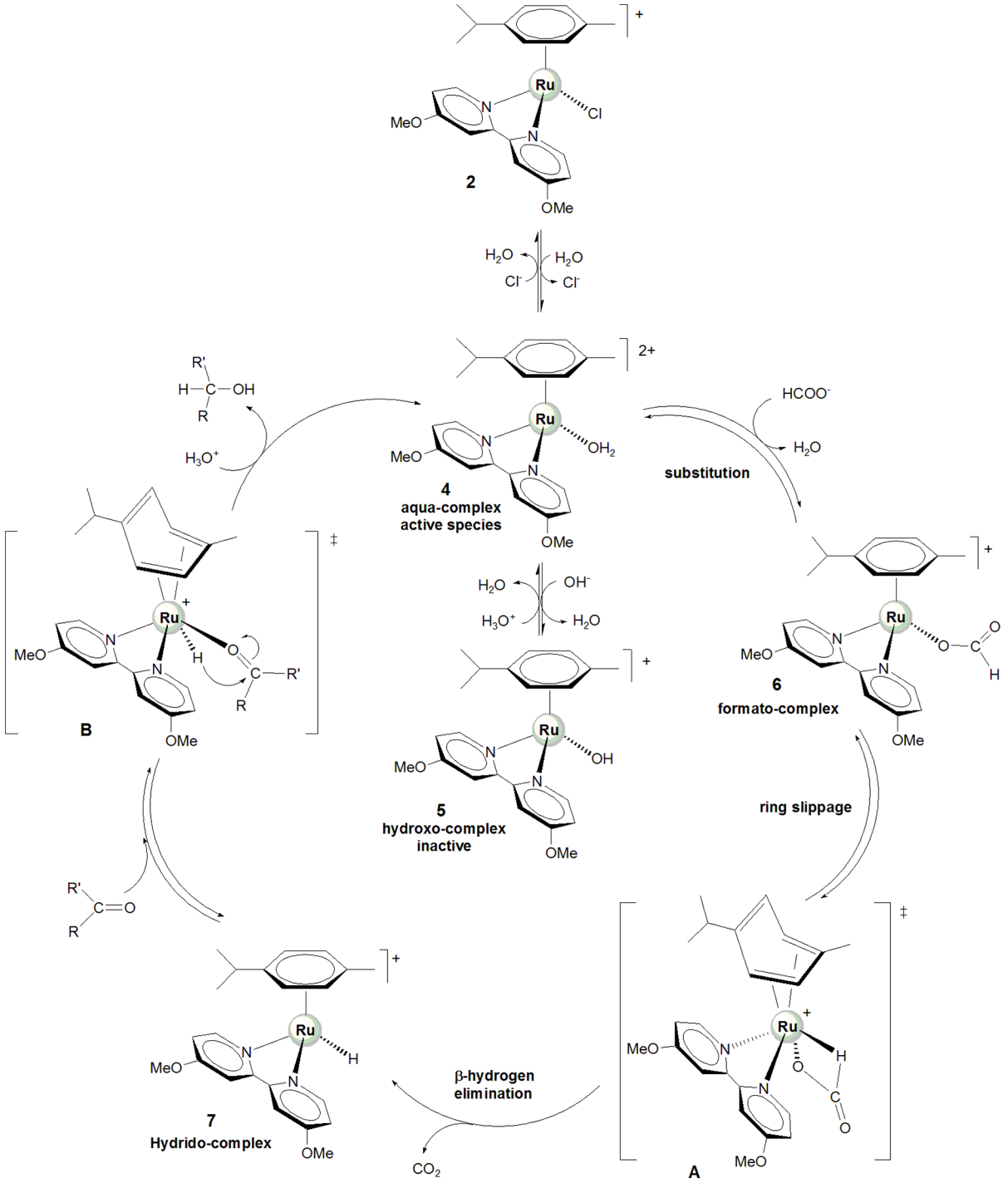
In order to increase the amount of **7** and taking into account the results by Ogo et al.,[10] who demonstrated that the formation of the corresponding hydride from [(η^6-C_6Me_6)Ru-(bpy)(H_2O)]SO_4 is favored at pH 7–8 and at high temperatures, we performed two similar experiments involving the addition of an excess of HCOONa to an equilibrated solution of [**2**][$\mathbf{BF_4}$] in D_2O, but at pH 7.5 at either 25 °C or 80 °C. At 25 °C, the species **6** and **7** were also detected, but in this case the proportion of the hydride **7** was higher (**6**/**7** = 69/31). Furthermore, at 80 °C species **7** was the major component of the reaction mixture (see Figure 5). Once more, the Ru–H resonance of this compound was not visible at high field.

In order to obtain information about the dependence of the behavior of the catalysts on pH, an excess of solid KOH (pH >13) was added to an NMR sample of [**2**][$\mathbf{BF_4}$] in D_2O at 25 °C and the evolution of the system was monitored by ^{1}H NMR for 40 min (see Figure 6). Signals attributed to the aqua species Ru–OD_2 were almost completely suppressed after 5 min of reaction, and a new set of resonances, assigned to the new species **5**, was observed along with those of decreasing amounts of **2**. In fact, peaks due to the Ru–Cl derivative **2** also disappeared during the next 30 min to produce a spectrum in which the only visible signals corresponded to **5**. Protons of **5** were more shielded than those of **2** and **4**, and **5** was formulated as the hydroxo complex [(*p*-cym)Ru(OD)-(dmobpy)]$^+$. Next, an excess of HCOONa was added to this sample but no further changes took place, even after 3 days. This finding demonstrates that the Ru–OD derivative was very inert with regard to substitution processes, and this situation is consistent with the results of previous studies.[46] The reversibility of the basic hydrolysis equilibrium was probed by performing two additional experiments. First, an excess of solid KOH (pH >13) was added to an NMR sample of [**2**][$\mathbf{BF_4}$] in D_2O at 25 °C and, when the reaction was complete (after 40 min), an excess of $HClO_4$ (pH <1) was also added to confirm that the hydroxo derivative **5** is able to regenerate **4** as the only species. In a parallel NMR test, KOH (pH >13) and HCl (pH <1) were successively added to show that the hydroxo species **5** can also regenerate the chloride derivative **2** under acidic conditions (Figure S1, Supporting Information).

Taking into account the preceding results, we postulate the catalytic cycle reflected in Scheme 3 for the transfer hydrogenation of ketones in the presence of complexes of the type [(arene)Ru(Cl)(dmobpy)]$^+$. Initially, the chloro complex **2** (the catalytic precursor) undergoes aquation to give **4**, which is the active species in the catalytic cycle. Then, in the presence of the formate anion complex **6** is formed as the result of a

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106–6123

Scheme 3. Proposed Mechanism for the Transfer Hydrogenation of Carbonyl Substrates, Using HCOONa as the Hydrogen Donor and Complex [2]X as the Catalyst



substitution reaction. In the next step β-hydrogen elimination gives rise to the hydrido derivative **7**, via transition state **A**, where the arene undergoes partial slippage to generate a vacant site in the coordination sphere and the formate proton interacts with the metallic center. This key step would involve evolution of CO_2, and this has also been assumed by other groups for similar processes.[39,43] Finally, the coordination of the ketone is followed by hydride transfer in the transition state **B**, and then the alcohol is formed after protonation (in acidic media) and the aqua complex is regenerated. A possible alternative to **B** is an outer-sphere transition state similar to that proposed by Ogo.[10]

Furthermore, we have shown that the system is pH dependent, since the reversible formation of unreactive **5** at high pH leads to a dead end (see the interior part of the cycle in Scheme 3).

Deuterium Labeling and H/D Exchange. As anticipated previously, the Ru−H resonance of species **7** was not visible in the ^{1}H NMR spectrum (D_2O), likely as a consequence of deuteration. In an effort to demonstrate the hydride nature of **7**, we repeated the experiment described in Figure 5, using a

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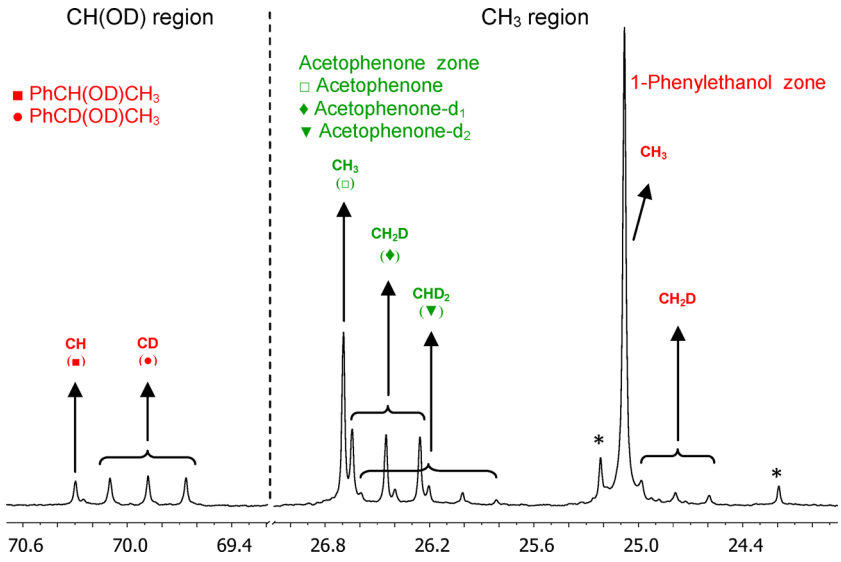


Figure 7. High-field region of the $^{13}C\{^1H\}$ NMR spectrum for acetophenone-*d*, acetophenone-d_2, and 1-*rac*-phenylethanol-d_2. The asterisk indicates impurities.

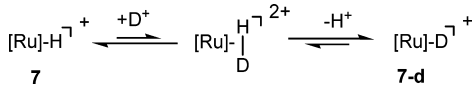
D_2O/H_2O mixture (1/1). Thus, the corresponding ^1H NMR spectrum for the reaction of [**2**][BF_4] with HCOONa (80 °C, 4 h, D_2O/H_2O) showed a broad signal at −6.2 ppm, which we ascribed to the Ru−H. The integration of this resonance is significantly lower than that corresponding to 1H, indicating that this group is partially deuterated in this media.

Moreover, we indirectly proved the involvement of the Ru−D group of **7** in the transfer hydrogenation process through the hydrogenation of acetophenone in D_2O, which led to deuterium incorporation in the resulting *rac*-1-phenylethanol (an excess of acetophenone was added to the NMR tube under the conditions of the spectrum in Figure 4f at 25 °C). Interestingly, in the corresponding ^1H NMR (D_2O, 25 °C) spectrum of this alcohol the resonances for the CH(OH) group were not detected (possibly obscured by the residual H_2O) and a singlet was observed for the methyl signal (the expected $^3J_{HD}$ was smaller than the width of the signal at medium height), suggesting deuteration of the benzylic carbon. In order to fully characterize this product, a transfer hydrogenation experiment was carried out in D_2O at 80 °C and pH 4. The water-insoluble organic products were removed and dissolved in $CDCl_3$, and the ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded. The ^1H NMR spectrum showed signals for a mixture of acetophenone and *rac*-1-phenylethanol (molar ratio 56/44), particularly a quartet with an anomalously low integration (0.21H instead of the expected 1H) for the CH group of the alcohol. The $^{13}C\{^1H\}$ NMR spectrum validated the selective deuteration of 1-*rac*-phenylethanol, as three lines of equal intensity were observed at 69.9 ppm for the −CD group (see Figure 7). Although the relative integration in ^{13}C spectra cannot be considered as a valuable measure for the molar ratio of the species, the difference in intensity for the CD and residual CH resonances at around 70 ppm implies that deuteration is dominant over this position of the alcohol. As far as the aromatic resonances are concerned, evidence for the existence of CD groups in these positions was not obtained. The signal of the CH_3 group appears at around 25 ppm as a singlet, but at higher field a resonance consisting of three lines of equal intensity can be assigned to a CDH_2 group (see Figure 7). Deuteration in this position is unexpected for a hydrogen transfer process. The reason this process occurs is apparent if we consider the appearance of the Me signal for the residual acetophenone (56% by integration) in both the ^1H and the $^{13}C\{^1H\}$ NMR spectra (Figure 7 and Figure S2 (Supporting Information)). Resonances for the respective isotopomers with CH_3, CDH_2, and CD_2H groups are visible. It is well-known that this group can be readily deuterated in an acidic medium through keto−enol tautomerism. Once the Me groups of the substrate have been partially deuterated, the observation of deuterium in the Me group of the phenylethanol is easily understood. Conditions for a full conversion experiment are described in the Experimental Section.

It is noteworthy that the selective labeling of the hydrogenated substrate supports two impressive facts: (i) the putative intermediate of the hydrogenation, monohydride **7**, must be deuterated in the hydride position by D_2O, and (ii) more importantly, this deuteration must be very fast—at least as fast as the hydride transfer to the benzophenone. Ready H/D exchange in the hydride position of metal hydride derivatives is a known process that is postulated to occur through dihydrogen species.[47] This means that the monohydride **7** is quickly deuterated in D_2O in a reversible way, forming a transient dihydrogen Ru(HD) intermediate. Very few examples of the protonation of hydride species with this reversible behavior have been described. Stabilization of the dihydrogen species and their evolution to give the homolytic cleavage of H_2 to give classical dihydrides, or the release of this molecule, are more common ways of evolution. In the absence of other information, we postulate that the formic acid added to the reaction is the protonating agent that transfers deuterons from D_2O. In contrast to a hypothetical direct deuteration from water, our proposal is based on the acidity of this agent as compared with that of water. As stated, it is very interesting that the H/D interchange process in **7** is faster than the proton/deuterium incorporation in the reaction product, 1-phenylethanol. This situation allows practically total deuterium incorporation in the benzylic position of this alcohol. Given this possibility, it is necessary to consider a lateral equilibrium in the mechanism proposed in Scheme 3, starting from **7** and concerning the H/D exchange of this species (see Scheme 4).

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

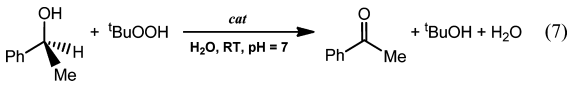
Scheme 4. Mechanism Proposed for the Deuteration of Species 7



The selective deuterium or tritium labeling of organic substrates is currently a very active research field with applications in spectroscopy, mechanistic studies, and medicine.[48,49] The processes described in this work allow the incorporation of deuterium from a cheap and green source (water), and this is a very attractive characteristic. Very few examples of such a process have been reported to date, and many that have been described occur only under very stringent reaction conditions.[49,50]

The results discussed above open the possibility of new experimental routes focused on the selective deuterium labeling of new substrates bearing not only C═O functionalities but also C═C groups. This latter aspect is supported by the results obtained in this work concerning the hydrogenation of cyclohexenone. Work aimed at addressing these questions is planned in our research group in the near future.

Catalytic Oxidation of Alcohols in Water. Inspired by the search for versatile catalysts that could be active in different catalytic transformations, and based on the studies reported by Süss-Fink[11] and Singh,[7,8] we tested the activity of a selection of our complexes in the catalytic oxidation of *rac*-1-phenylethanol with ^{t}BuOOH in aqueous media (see eq 7 and Table 8). A



blank experiment was initially run in the absence of metallic species to rule out any possible activity attributable to a noncatalytic reaction (Table 8, entry 1). A number of experiments were then carried out to evaluate the performance of several catalytic precursors, namely [**1**][BF_4], [**2**][BF_4], and [**3**][BF_4] and the precursors [(*p*-cym)$RuCl_2$]$_2$ and [(phoxet)-$RuCl_2$]$_2$ (entries 2, 6, 9, 13, and 18). To our surprise, the conversion of *rac*-1-phenylethanol to acetophenone (%) after 3 h was complete in all cases and [**1**][BF_4] (entry 9) exhibited a conversion close to this value (98%). To the best of our knowledge, this is the first time that water-soluble Ru complexes have been described as versatile catalytic precursors for both the transfer hydrogenation of ketones and the oxidation of alcohols in aqueous media, despite the fact that specific precursors are known for each of these catalytic processes.

Reactions with shorter times (1 h, 0.5 h) and higher substrate/catalyst ratios (10^4) were also performed. The tests enabled better comparisons to be made. It was concluded that [**2**][BF_4] and [**3**][BF_4] were more active than [**1**][BF_4] and gave TOF values of 9000 and 8400 h^{-1} (measured at the end of the reaction). The results for the dimeric species [(*p*-cym)$RuCl_2$]$_2$ and [(phoxet)$RuCl_2$]$_2$ were even more satisfactory, giving 100% yields for reaction times of either 1 or 0.5 h and TOF values as high as 53 000 h^{-1} for shorter reaction times on using a substrate/catalyst ratio of 10^4 (entries 6 and 10). It is noteworthy that yields of about 90% were achieved in times as short as 10 min. One relevant result obtained in this work is that these easily made dimeric species are very active without the need for a specific additional ligand.

Table 8. Catalytic Oxidation of *rac*-1-Phenylethanol to Benzophenone Using the Oxidants ^{t}BuOOH and H_2O_2 and the Catalysts [$RuCl_2$(*p*-cym)]$_2$, [$RuCl_2$(phoxet)]$_2$, [1**][BF_4], [**2**][BF_4], and [**3**][BF_4]**[a]

entry	cat.	oxidant	S/cat.	yield (%) (*t* (h))	TON	TOF (h^{-1})
1	none	^{t}BuOOH		0 (3)		
2	[(*p*-cym)$RuCl_2$]$_2$	^{t}BuOOH	10^3	100 (3)	1000	333
3	[(*p*-cym)$RuCl_2$]$_2$	^{t}BuOOH	10^3	100 (1)	1000	1000
4	[(*p*-cym)$RuCl_2$]$_2$	^{t}BuOOH	10^3	100 (0.5)	1000	2000
5	[(*p*-cym)$RuCl_2$]$_2$	^{t}BuOOH	10^4	100 (1)	10000	10000
6	[(*p*-cym)$RuCl_2$]$_2$	^{t}BuOOH	10^4	89 (10 min)	8900	53400
7	[(phoxet)$RuCl_2$]$_2$	^{t}BuOOH	10^3	100 (1)	1000	1000
8	[(phoxet)$RuCl_2$]$_2$	^{t}BuOOH	10^3	100 (0.5)	1000	2000
9	[(phoxet)$RuCl_2$]$_2$	^{t}BuOOH	10^4	100 (1)	10000	10000
10	[(phoxet)$RuCl_2$]$_2$	^{t}BuOOH	10^4	88 (10 min)	8800	52800
11	[**1**][BF_4]	^{t}BuOOH	10^3	98 (3)	980	327
12	[**1**][BF_4]	^{t}BuOOH	10^3	85 (1)	850	850
13	[**1**][BF_4]	^{t}BuOOH	10^3	62 (0.5)	620	1240
14	[**1**][BF_4]	^{t}BuOOH	10^4	69 (1)	6900	6900
15	[**1**][BF_4]	^{t}BuOOH	10^3	100 (3)	1000	333
16	[**2**][BF_4]	^{t}BuOOH	10^3	84 (1)	840	840
17	[**2**][BF_4]	^{t}BuOOH	10^3	67 (0.5)	670	1340
18	[**2**][BF_4]	^{t}BuOOH	10^4	100 (3)	10^4	3333
19	[**2**][BF_4]	^{t}BuOOH	10^4	90 (1)	9000	9000
20	[**3**][BF_4]	^{t}BuOOH	10^3	100 (3)	1000	333
21	[**3**][BF_4]	^{t}BuOOH	10^3	100 (1)	1000	1000
22	[**3**][BF_4]	^{t}BuOOH	10^3	65 (0.5)	650	1300
23	[**3**][BF_4]	^{t}BuOOH	10^4	84 (1)	8400	8400
24	[**3**][BF_4]	H_2O_2	10^3	0 (3)		

[a]Conditions: reactions carried out at room temperature, pH 7, oxidant/S/cat = 4000/1000/1 or 40 000/10 000/1, 1 μmol of cat., 5 mL of H_2O. The yield was determined by ^{1}H NMR and GC for every experiment. Caution: gas formation and high pressures were observed for those experiments with oxidant/S/cat. = 40 000/10 000/1, which were carried out using 5 mL of H_2O.

Finally, the reaction was tested using H_2O_2 as the oxidant and [**2**][BF_4] as the catalytic precursor, but in this case the conversion was zero, showing that H_2O_2 is not an appropriate oxidant with our systems (see entry 24, Table 8). Additional experiments are ongoing in our laboratory to extend the reaction scope to other alcohols.

CONCLUSIONS

A new family of organometallic Ru(II) arene (benzene, *p*-cymene, 2-phenoxy-1-ethanol) complexes with the commercial ligand 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) were synthesized. Most of these compounds are water-soluble, due to a combination of their cationic nature and the presence of −OMe groups in the ligand. It was found that the arene and the counteranion have an influence on the solubility values. The complexes were active as catalysts in aqueous media, in both the transfer hydrogenation of water-soluble and -insoluble ketones to the corresponding alcohols (with HCOONa as the

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

hydrogen source) and the oxidation of alcohols to the corresponding ketones (using ^{t}BuOOH as the oxidant). Yields of 100% were obtained in these reactions. To our knowledge, this constitutes the first example in which Ru complexes have shown this versatility in aqueous solution.

In the alcohol oxidation process it was demonstrated that the dimeric species $[(p\text{-cym})RuCl_2]_2$ and $[(phoxet)RuCl_2]_2$ exhibit a very high activity (TOF = 53 000 h^{-1}). This is a very important finding, considering that these compounds are easily made and the presence of an additional ligand is not necessary.

The most active precatalysts in the transfer hydrogenation process were the *p*-cymene derivatives, and among these, the ones that contained the tosylate anion gave rise to the highest TOF values. The activity of the catalysts was very dependent on the pH. A pH value of 4 was found to be the most favorable. In any case, from the results described here and those from previous studies, it seems clear that the presence of the nitrogenated ligand in the Ru precursors is essential for their catalytic performance in the transfer hydrogenation of ketones. The activity of a similar precursor containing a bpy ligand without the methoxy groups was lower, thus showing the beneficial effect of these groups. Moreover, the Ru−Cl complexes with dmobpy undergo easy activation (aquation) in water, meaning that it is not necessary to isolate the corresponding aqua derivatives to achieve good catalytic activities.

A number of ^{1}H NMR experiments allowed the detection of several intermediates in the transfer hydrogenation process, including formate and hydride species. Furthermore, the reversible formation of hydroxo derivatives in alkaline media and their inertness to substitution reactions was also observed. On the basis of all these results, a catalytic mechanism was formulated.

It has been demonstrated that the hydride species is quickly deuterated in a reversible way in the presence of D_2O and formic acid, forming a transient dihydrogen $Ru(X_2)$ (X = H, D) intermediate. This deuteration is faster than the hydrogenation process on benzophenone and allows the selective deuteration of phenylethanol at the benzylic carbon. This process opens up new possibilities for the selective deuteration of different unsaturated organic substrates.

EXPERIMENTAL SECTION

General Methods and Starting Materials. *Starting Materials.* $RuCl_3{\cdot}xH_2O$ was purchased from Apollo Scientific Ltd. and used as received. $[(\eta^6\text{-}C_6H_6)RuCl_2(CH_3CN)]$[34] or $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = benzene, *p*-cymene,[35] phenoxyethanol[31]), were prepared according to literature procedures. $AgBF_4$, AgTsO, $AgPF_6$, and the ligand 4,4′-dimethoxy-2,2′-bipyridine (dmobpy) were purchased from Aldrich and used without further purification. Ketones and alcohols were purchased from Aldrich. Deuterated solvents were obtained from SDS and Euriso-top. The aqueous solutions were prepared with doubly deionized water from a Millipore Q apparatus (APS; Los Angeles, CA).

General Methods. All synthetic manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer 2400 CHN microanalyzer. The analytical data for the new complexes were obtained from crystalline samples when possible. In some cases the data were totally accurate, but in others the agreement of calculated and found values for carbon was >0.4%, so that solvent molecules were introduced in the molecular formulas to improve agreement. In any case, all the complexes were obtained in enough analytic purity to be used as starting materials. IR spectra were recorded on a Nicolet Impact 410 spectrophotometer (4000−400 cm^{-1} range) as KBr pellets and on a Jasco FT/IR-6300 spectrophotometer (630−150 cm^{-1} range) as Nujol mulls deposited on a polyethylene film. FAB mass spectra (position of the peaks in Da) were recorded with an Autospec spectrometer. The isotopic distribution of the heaviest set of peaks matched very closely that calculated for the formulation of the complex cation in every case. NMR samples were prepared under a nitrogen atmosphere by dissolving the suitable amount of compound in 0.5 mL of the respective oxygen-free deuterated solvent, and the spectra were recorded at 298 K (unless otherwise stated) on a Varian Unity Inova-400 (400 MHz for ^{1}H; 161.9 MHz for ^{31}P; 100.6 MHz for ^{13}C). Typically, 1D ^{1}H NMR spectra were acquired with 32 scans into 32 k data points over a spectral width of 16 ppm. ^{1}H and $^{13}C\{^1H\}$ chemical shifts were internally referenced to TMS via 1,4-dioxane in D_2O (δ 3.75 ppm and δ 67.19 ppm, respectively) or via the residual ^{1}H and ^{13}C signals of the corresponding solvents, CD_3OD (δ 3.31 ppm and δ 49.00 ppm) and $(CD_3)_2CO$ (δ 2.05 ppm and δ 29.84 ppm), according to the values reported by Fulmer et al.[51] Chemical shift values are reported in ppm and coupling constants (J) in Hertz. The splitting of proton resonances in the reported ^{1}H NMR data is defined as s = singlet, d = doublet, t = triplet, st = pseudotriplet, q = quartet, sept = septet, m = multiplet, and bs = broad singlet. All ^{31}P resonances were referenced to 85% H_3PO_4 at 0 ppm. 2D spectra were recorded using standard pulse−pulse sequences. For COSY spectra, a standard pulse sequence, an acquisition time of 0.214 s, a pulse width of 10 μs, a relaxation delay of 1 s, 16 scans, and 512 increments were used. The NOE difference spectra were recorded with 5000 Hz, an acquisition time of 3.27 s, a pulse width of 90°, a relaxation delay of 4 s, and an irradiation power of 5−10 dB. The probe temperature (±1 K) was controlled by a standard unit calibrated with a methanol reference. All NMR data processing was carried out using MestReNova version 6.1.1.

pH Measurement. The pH values of NMR samples in D_2O were measured at room temperature before and after recording the NMR spectra, using a Metrohm 16 DMS Titrino pH meter fitted out with a combined glass electrode and a 3 M KCl solution as a liquid junction, which was calibrated with Radiometer Analytical SAS buffer solutions at pH 1.679, 2.000, 4.005, 6.865, 7.000, and 7.413. No correction was applied for the effect of deuterium on the glass electrode.

X-ray Crystallography. A summary of crystal data collection and refinement parameters for all compounds is given in the Supporting Information.

Single crystals of **[1]Cl**, **[1]TsO**, **[2]TsO**, **[2][BF$_4$]**, and **[2][PF$_6$]** were obtained by liquid−liquid diffusion or evaporation experiments from the following solvent systems: methanol/diethyl ether (**[1]Cl**), H_2O (**[1]TsO·H$_2$O**), methanol/diethyl ether (**[2]TsO**), methanol (**[2][BF$_4$]**), and acetone (**[2][PF$_6$]**) respectively. The single crystals were mounted on a glass fiber and transferred to a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.710 73 Å). The highly redundant data sets were integrated using SAINT[52] and corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements with the program SADABS.[53]

The software package SHELXTL version 6.10[54] was used for space group determination, structure solution, and refinement by full-matrix least-squares methods based on F^2. A successful solution by direct methods provided most non-hydrogen atoms from the *E* map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless specified otherwise. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. For the molar conductimetry measurements, the Λ_M values are given in S cm^2 mol^{-1} and were obtained at room temperature for 10^{-3} M solutions of the corresponding complexes in CH_3CN, using a CRISON 522 conductimeter equipped with a CRISON 5292 platinum conductivity cell.

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

Synthesis of Complexes. *[(η^6-benzene)RuCl(dmobpy)]Cl* (**[1]Cl**). In a 100 mL Schlenk flask, dmobpy (74.2 mg, 0.343 mmol) was added under a nitrogen atmosphere to a suspension of [(η^6-bz)-$RuCl_2(CH_3CN)$] (100 mg, 0.343 mmol) in degassed methanol (20 mL). The mixture was stirred at room temperature for 40 h. The solvent was then removed under vacuum, and the residue was washed with *n*-hexane and dried under vacuum to produce a yellow solid. Yield: 0.136 g (0.29 mmol, 85%). M_r ($C_{18}H_{18}N_2O_2Cl_2Ru$) = 466.3278 g/mol. Anal. Calcd for $C_{18}H_{18}N_2O_2Cl_2Ru{\cdot}2.5H_2O$: C, 42.28; H, 5.53; N, 5.48. Found: C, 42.51; H, 4.125; N, 5.833. ^{1}H NMR (400 MHz, CD_3OD): δ 9.27 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.05 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.29 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 6.07 (s, 6H, H-bz), 4.09 (s, 6H, H^{OMe}) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 170.09 (s, 2C, $C^{4'}$), 158.04 (s, 2C, $C^{2'}$), 157.40 (s, 2C, $C^{6'}$-dmobpy), 114.77 (s, 2C, $C^{5'}$), 111.28 (s, 2C, $C^{3'}$), 87.77 (s, 6C, C-bz), 57.53 (s, 2C, -OMe) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3065 (m, ν_{CH,sp^2}), 3031 (m), 1620 (s, $\nu_{C=C+C=N}$), 1615 (s, $\nu_{C=C+C=N}$), 1558 (m), 1497 (s, $\nu_{C=C+C=N}$), 1435 (s, $\nu_{C=C+C=N}$), 1339 (m), 1316 (m), 1270 (s), 1255 (s), 1232 (s, $\nu_{as,OMe}$), 1047 (s, $\nu_{s,OMe}$), 1029 (s), 1004 (m), 886 (w), 842 (m), 629 (w), 587 (w). FT-FIR (Nujol, cm^{-1}; selected bands): 379 (w), 303 (w), 278 (w), 254 (w). MS (FAB+, CH_3OH): m/z (%) 431 (17) ([M − Cl]$^+$). Molar conductivity (CH_3CN): 120 S cm^2 mol^{-1}. Solubility: soluble in water, methanol, ethanol, and acetonitrile and slightly soluble in acetone and dichloromethane.

[(η^6-benzene)RuCl(dmobpy)]BF_4 (**[1][BF$_4$]**). In a 100 mL Schlenk flask protected from light, [(η^6-bz)$RuCl_2(CH_3CN)$] (100 mg, 0.343 mmol) was dissolved in a degassed methanol/acetonitrile mixture (9 mL/9 mL), under a nitrogen atmosphere. Then, $AgBF_4$ (66.8 mg, 0.343 mmol) was added, and the suspension was stirred overnight in the dark at room temperature. Solid AgCl was removed by filtration, and the resulting solution was treated with dmobpy (74.2 mg, 0.343 mmol) and stirred overnight at room temperature. Then, the volume of the solution was reduced under vacuum to just 2 mL to precipitate a yellow solid that was collected by filtration and dried under vacuum. Yield: 0.125 g (0.24 mmol, 70.4%). M_r ($C_{18}H_{18}N_2O_2ClRuBF_4$) = 517.6698 g/mol. Anal. Calcd for $C_{18}H_{18}N_2O_2ClRuBF_4{\cdot}0.5H_2O$: C, 41.05; H, 3.64; N, 5.32. Found: C, 40.89; H, 3.664; N, 5.724. ^{1}H NMR (400 MHz, CD_3OD): δ 9.27 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.05 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.28 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 6.07 (s, 6H, H-bz), 4.09 (s, 6H, H^{OMe}) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 169.75 (s, 2C, $C^{4'}$), 157.84 (s, 2C, $C^{2'}$), 157.61 (s, 2C, $C^{6'}$), 114.77 (s, 2C, $C^{5'}$), 111.43 (s, 2C, $C^{3'}$), 87.71 (s, 6C, C-bz), 57.84 (s, 2C, −OMe) ppm. ^{19}F NMR (376 MHz, CD_3OD): δ −155.35 (s, ^{10}B−F, BF_4^-), −155.40 (s, ^{11}B−F, BF_4^-) ppm. Integration ratio (1/4) in agreement with the isotopic distribution for ^{10}B/^{11}B (20/80). FT-IR (KBr, cm^{-1}; selected bands): 3089 (w, ν_{CH,sp^2}), 3032 (w), 1620 (s, $\nu_{C=C+C=N}$), 1616 (s, $\nu_{C=C+C=N}$), 1559 (m), 1495 (s, $\nu_{C=C+C=N}$), 1440 (s, $\nu_{C=C+C=N}$), 1343 (m), 1314 (m), 1268 (s), 1253 (s), 1235 (s, $\nu_{as,OMe}$), 1062 (s, $\nu_{d,BF}$), 1048 (s, $\nu_{s,OMe}$), 1032 (s), 1006 (m), 894 (w), 841 (m), 629 (w), 588 (w), 522 (m, δ_{BF}). FT-FIR (Nujol, cm^{-1}; selected bands): 374 (w), 308 (w), 280 (m), 250 (w). MS (FAB+, CH_3OH): m/z (%) 431 (10) ([M − BF_4]$^+$). Molar conductivity (CH_3CN): 126 S cm^2 mol^{-1}. Solubility: soluble in water, ethanol, acetonitrile, and dichloromethane and slightly soluble in acetone and methanol.

[(η^6-benzene)RuCl(dmobpy)]OTs (**[1]OTs**). In a 100 mL Schlenk flask protected from light, [(η^6-bz)$RuCl_2(CH_3CN)$] (100 mg, 0.343 mmol) was dissolved in a degassed methanol/acetonitrile mixture (9 mL/9 mL), under a nitrogen atmosphere. Then, AgOTs (95.7 mg, 0.343 mmol) was added, and the suspension was stirred for 2 h in the dark, at room temperature. The precipitate of AgCl was removed by filtration, and the resulting solution was treated with dmobpy (74.2 mg, 0.343 mmol) and stirred overnight at room temperature. Then, the solvents were removed under vacuum. The solid residue was washed with diethyl ether (10 mL) and dried under vacuum to produce a yellow solid. Yield: 0.160 g (0.27 mmol, 77.5%). M_r ($C_{25}H_{25}N_2O_5ClSRu$) = 602.0706 g/mol. Anal. Calcd for $C_{25}H_{25}N_2O_5ClSRu{\cdot}1.5H_2O$: C, 47.73; H, 4.49; N, 4.45. Found: C, 47.85; H, 4.349; N, 5.021. ^{1}H NMR (400 MHz, CD_3OD): δ 9.27 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.04 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.70 (m, 2H, H^b-OTs), 7.28 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 7.22 (m, 2H, H^c-OTs), 6.06 (s, 6H, H-bz) 4.08 (s, 6H, H^{OMe}), 2.36 (s, 3H, H^e-OTs) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) 170.06 (s, 2C, $C^{4'}$), 158.02 (s, 2C, $C^{2'}$), 157.41 (s, 2C, $C^{6'}$), 143.65 (s, 1C, C^a-TsO^-), 141.61 (s, 1C, C^d-TsO^-), 129.79 (s, 2C, C^c-TsO^-), 126.97 (s, 2C, C^b-TsO^-), 114.77 (s, 2C, $C^{5'}$), 111.27 (s, 2C, $C^{3'}$), 87.77 (s, 6C, C-bz), 57.53 (s, 2C, −OMe), 21.30 (s, 1C, C^e-TsO^-) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3078 (m, ν_{CH,sp^2}), 2991 (w, ν_{CH,sp^3}), 1620 (s, $\nu_{C=C+C=N}$), 1615 (s, $\nu_{C=C+C=N}$), 1559 (m), 1495 (s, $\nu_{C=C+C=N}$), 1440 (s, $\nu_{C=C+C=N}$), 1343 (m), 1268 (m), 1253 (s), 1232 (s, $\nu_{as,OMe}$), 1216 (vs, $\nu_{as,S=O}$), 1195 (vs, $\nu_{as,S=O}$), 1121 (m), 1049 (s, $\nu_{s,OMe}$), 1032 (s, TsO^-), 1011 (s, TsO^-), 856 (m), 840 (m), 819 (m, TsO^-), 682 (s, TsO^-), 569 (s, TsO^-). FT-FIR (Nujol, cm^{-1}; selected bands): 376 (w), 305 (w), 281 (m), 249 (w). MS (FAB+, CH_3OH): m/z (%) 431 (47) ([M − TsO]$^+$). Molar conductivity (CH_3CN): 107 S cm^2 mol^{-1}. Solubility: soluble in water, methanol, and acetonitrile and poorly soluble in acetone, ethanol, and dichloromethane.

[(η^6-benzene)RuCl(dmobpy)]PF_6 (**[1][PF$_6$]**). In a 100 mL Schlenk flask protected from light, [(η^6-bz)$RuCl_2(CH_3CN)$] (100 mg, 0.343 mmol) was dissolved in a degassed methanol/acetonitrile mixture (10 mL/10 mL), under a nitrogen atmosphere. Then, $AgPF_6$ (86.7 mg, 0.343 mmol) was added, and the suspension was stirred for 2 h in the dark, at room temperature. The precipitate of AgCl was removed by filtration, and the resulting solution was treated with dmobpy (74.2 mg, 0.343 mmol) and stirred overnight at room temperature. Then, the solvents were removed under vacuum. The solid residue was washed with diethyl ether (10 mL) and dried under vacuum to produce a yellow solid. Yield: 0.160 g (0.28 mmol, 81%). M_r ($C_{18}H_{18}N_2O_2ClRuPF_6$) = 575.843 g/mol. Anal. Calcd for $C_{18}H_{18}N_2O_2ClRuPF_6$: C, 37.55; H, 3.15; N, 4.86. Found: C, 37.50; H, 3.28; N, 5.04. ^{1}H NMR (400 MHz, CD_3OD): δ 9.27 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.05 (d, J = 2.7 Hz, 2H, $H^{3'}$), 7.29 (dd, J = 6.6, 2.7 Hz, 2H, $H^{5'}$), 6.07 (s, 6H, bz), 4.08 (s, 6H, H^{OMe}) ppm. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.42 (d, J = 6.6 Hz, 2H, $H^{6'}$-dmobpy), 8.16 (d, J = 2.8 Hz, 2H, $H^{3'}$-dmobpy), 7.32 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$-dmobpy), 6.20 (s, 6H, bz), 4.12 (s, 6H, H^{OMe}-dmobpy) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3COCD_3) 169.26 (s, 2C, $C^{4'}$), 157.41 (s, 2C, $C^{2'}$), 157.31 (s, 2C, $C^{6'}$), 114.35 (s, 2C, $C^{5'}$), 110.94 (s, 2C, $C^{3'}$), 87.47 (s, 6C, C-bz), 57.51 (s, 2C, −OMe) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_3COCD_3): δ −143.17 (sept, J = 708 Hz, 1P, PF_6^-) ppm. ^{19}F NMR (376 MHz, CD_3COCD_3): δ −72.99 (d, J = 708 Hz, 6F, PF_6^-) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3096 (m, ν_{CH,sp^2}), 3041 (m), 2948 (m, ν_{CH,sp^3}), 1619 (s, $\nu_{C=C+C=N}$), 1561 (m), 1495 (s, $\nu_{C=C+C=N}$), 1471 (m), 1441 (s, $\nu_{C=C+C=N}$), 1342 (m), 1315 (m), 1289 (m), 1270 (s), 1254 (s), 1234 (s, $\nu_{as,OMe}$), 1048 (s, $\nu_{s,OMe}$), 1031 (s), 1006 (w), 841 (vs, ν_{P-F}), 741 (w), 558 (s, δ_{F-B-F}). FT-FIR (Nujol, cm^{-1}; selected bands): 374 (w), 307 (w), 280 (m), 248 (w). MS (FAB+, CH_3OH): m/z (%) 431 (32) ([M − PF_6]$^+$). Molar conductivity (CH_3CN): 140 S cm^2 mol^{-1}. Solubility: soluble in acetone and acetonitrile and partially soluble in methanol, ethanol, and dichloromethane.

*[(η^6-*p*-cymene)RuCl(dmobpy)]Cl* (**[2]Cl**). In a 100 mL Schlenk flask, dmobpy (70.5 mg, 0.326 mmol) was added under a nitrogen atmosphere to a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (100 mg, 0.163 mmol) in degassed ethanol (30 mL). The mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the solid residue was washed with *n*-hexane (2 × 5 mL) and dried under vacuum, to produce a yellow solid. Yield: 152.5 mg (0.3 mmol, 89.4%). M_r ($C_{22}H_{26}N_2O_2Cl_2Ru$) = 522.435 g/mol. Anal. Calcd for $C_{22}H_{26}N_2O_2Cl_2Ru{\cdot}2H_2O$: C, 47.32; H, 5.41; N, 5.02. Found: C, 47.37; H, 4.91; N, 5.04. ^{1}H NMR (400 MHz, CD_3OD): δ 9.19 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.06 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.30 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 6.02 (d, J = 6.4 Hz, 2H, $H^{2,6}$-cym), 5.76 (d, J = 6.4 Hz, 2H, $H^{3,5}$-cym), 4.09 (s, 6H, H^{OMe}), 2.62 (sept, J = 6.9 Hz, 1H, H^7-cym), 2.26 (s, 3H, H^{10}-cym), 1.06 (d, J = 6.9 Hz, 6H, $H^{8,9}$-cym) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 170.03 (s, 2C, $C^{4'}$), 157.82 (s, 2C, $C^{2'}$), 157.30 (s, 2C, $C^{6'}$), 114.97 (s, 2C, $C^{5'}$), 111.28 (s, 2C, $C^{3'}$), 105.05 (s, 1C, C^1-cym), 104.81 (s, 1C, C^4-cym), 87.53 (s, 2C, $C^{2,6}$-cym), 84.64 (s, 2C, $C^{3,5}$-cym), 57.54 (s, 2C, C^{OMe}), 32.33 (s, 1C, C^7-cym), 22.31 (s, 2C, $C^{8,9}$-cym), 18.98 (s, 1C, C^{10}-cym) ppm. FT-IR

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

(KBr, cm^{-1}; selected bands): 3027 (w, ν_{CH,sp^2}), 2971 (w, ν_{CH,sp^3}), 1614 (vs, $\nu_{C=C+C=N}$), 1558 (m), 1496 (s, $\nu_{C=C+C=N}$), 1422 (s), 1346 (m), 1317 (w), 1281 (s), 1255 (w), 1231 (s, $\nu_{as,OMe}$), 1046 (s, $\nu_{s,OMe}$), 1031 (m), 1017 (m), 864 (w), 840 (m). FT-FIR (Nujol, cm^{-1}; selected bands): 381 (w), 303 (w), 279 (m), 250 (w). MS (FAB+, CH_3OH): m/z (%) 487 (100) ($[M - Cl]^+$); 353 (25) ($[M - Cl - cym]^+$). Molar conductivity (CH_3CN): 109 S cm^2 mol^{-1}. Solubility: soluble in water, methanol, ethanol, dichloromethane, and acetonitrile and poorly soluble in acetone.

Synthesis of [(η^6-p-cymene)RuCl(dmobpy)]BF_4 ([2][BF_4]). In a 100 mL Schlenk flask protected from light, $AgBF_4$ (63.5 mg, 0.326 mmol) was added under a nitrogen atmosphere to a solution of $[(\eta^6$-p-cymene)$RuCl_2]_2$ (100 mg, 0.163 mmol) in degassed ethanol (30 mL). The mixture was stirred for 2 h in the dark, at room temperature. The precipitate of AgCl was removed by filtration. Then, the ligand dmobpy (70.5 mg, 0.326 mmol) was added and the mixture was stirred overnight at room temperature. The volume of the resulting solution was reduced under vacuum to 10 mL, and *n*-hexane (40 mL) was added to fully precipitate a yellow solid, which was collected by filtration and dried under vacuum. Yield: 140 mg (0.24 mmol, 76%). M_r ($C_{22}H_{26}N_2O_2ClBF_4Ru$) = 573.777 g/mol. Anal. Calcd for $C_{22}H_{26}N_2O_2ClBF_4Ru$: C, 46.05; H, 4.57; N, 4.88. Found: C, 46.34; H, 4.51; N, 4.48. ^{1}H NMR (400 MHz, CD_3OD): δ 9.18 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.06 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.29 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 6.02 (d, J = 6.4 Hz, 2H, $H^{2,6}$), 5.75 (d, J = 6.4 Hz, 2H, $H^{3,5}$), 4.09 (s, 6H, H^{OMe}), 2.62 (sept, J = 6.9 Hz, 1H, H^7), 2.26 (s, 3H, H^{10}), 1.06 (d, J = 6.9 Hz, 6H, $H^{8,9}$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 170.02 (s, 2C, $C^{4'}$), 157.81 (s, 2C, $C^{2'}$), 157.29 (s, 2C, $C^{6'}$), 115.00 (s, 2C, $C^{5'}$), 111.25 (s, 2C, $C^{3'}$), 105.03 (s, 1C, C^1-cym), 104.82 (s, 1C, C^4-cym), 87.53 (s, 2C, $C^{2,6}$-cym), 84.64 (s, 2C, $C^{3,5}$-cym), 57.53 (s, 2C, C^{OMe}), 32.33 (s, 1C, C^7-cym), 22.31 (s, 2C, $C^{8,9}$-cym), 18.98 (s, 1C, C^{10}-cym) ppm. ^{19}F NMR (376 MHz, CD_3OD): δ −155.35 (s, $^{10}B-F$, BF_4^-), −155.40 (s, $^{11}B-F$, BF_4^-) ppm. Integration ratio (1/4) in agreement with the isotopic distribution for $^{10}B/^{11}B$ (20/80). FT-IR (KBr, cm^{-1}; selected bands): 3076 (w, ν_{CH,sp^2}), 2963 (w, ν_{CH,sp^3}), 1615 (vs, $\nu_{C=C+C=N}$), 1558 (m), 1497 (s, $\nu_{C=C+C=N}$), 1479 (m), 1423 (m), 1346 (m), 1281 (s), 1255 (w), 1229 (s, $\nu_{as,OMe}$), 1083 (s), 1065 (s, $\nu_{d,BF}$), 1046 (s, $\nu_{s,OMe}$), 1032 (m), 1017 (m), 864 (w), 839 (m), 522 (w, δ_{BF}). FT-FIR (Nujol, cm^{-1}; selected bands): 303 (w), 282 (m), 252 (w). MS (FAB+, CH_3OH): m/z (%) 487 (100) ($[M - BF_4]^+$); 353 (31) ($[M - BF_4 - cym]^+$). Molar conductivity (CH_3CN): 143 S cm^2 mol^{-1}. Solubility: soluble in methanol and acetonitrile and poorly soluble in water, acetone, ethanol, and dichloromethane.

[(η^6-p-cymene)RuCl(dmobpy)]OTs ([2]OTs). In a 100 mL Schlenk flask protected from light, AgOTs (91.0 mg, 0.326 mmol) was added under a nitrogen atmosphere to a solution of $[(\eta^6$-p-cymene)$RuCl_2]_2$ (100 mg, 0.163 mmol) in degassed ethanol (30 mL). The mixture was stirred for 2 h in the dark at room temperature. The precipitate of AgCl was removed by filtration. Then, the ligand dmobpy (70.5 mg, 0.326 mmol) was added and the mixture was stirred overnight at room temperature. The solvent of the resulting solution was removed under vacuum, and the solid residue was washed with *n*-hexane (20 mL) and dried under vacuum to produce a yellow solid. Yield: 140.5 mg (0.21 mmol, 66.6%). M_r ($C_{29}H_{33}N_2O_5ClSRu$) = 658.1778 g/mol. Anal. Calcd for $C_{29}H_{33}N_2O_5ClSRu{\cdot}H_2O$: C, 51.51; H, 5.22; N, 4.14. Found: C, 51.51; H, 5.63; N, 4.01. ^{1}H NMR (400 MHz, CD_3OD): δ 9.18 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.05 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.71 (m, 2H, H^b-OTs), 7.29 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 7.23 (m, 2H, H^c-OTs), 6.02 (d, J = 6.4 Hz, 2H, $H^{2,6}$-cym), 5.75 (d, J = 6.4 Hz, 2H, $H^{3,5}$-cym), 4.08 (s, 6H, H^{OMe}), 2.61 (sept, J = 6.9 Hz, 1H, H^7-cym), 2.37 (s, 3H, H^e-OTs), 2.25 (s, 3H, H^{10}-cym), 1.05 (d, J = 6.9 Hz, 6H, $H^{8,9}$-cym) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 169.99 (s, 2C, $C^{4'}$), 157.79 (s, 2C, $C^{2'}$), 157.33 (s, 2C, $C^{6'}$), 143.67 (s, 1C, C^a-OTs), 141.62 (s, 1C, C^d-OTs), 129.81 (s, 2C, C^c-OTs), 126.98 (s, 2C, C^b-OTs), 114.99 (s, 2C, $C^{5'}$), 111.26 (s, 2C, $C^{3'}$), 105.02 (s, 1C, C^4-cym), 104.79 (s, 1C, C^1-cym), 87.53 (s, 2C, $C^{2,6}$-cym), 84.63 (s, 2C, $C^{3,5}$-cym), 57.55 (s, 2C, C^{OMe}), 49.00, 32.32 (s, 1C, C^7-cym), 22.32 (s, 2C, $C^{8,9}$-cym), 21.30 (s, 1C, C^e-OTs), 18.99(s, 1C, C^{10}-cym) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3068 (w, ν_{CH,sp^2}), 2967 (w, ν_{CH,sp^3}), 1615 (vs, $\nu_{C=C+C=N}$), 1558 (m), 1496 (s, $\nu_{C=C+C=N}$), 1472 (m), 1441 (m), 1421 (m), 1343 (m), 1283 (s), 1255 (w), 1231 (s, $\nu_{as,OMe}$), 1214 (vs, $\nu_{as,S=O}$), 1196 (vs, $\nu_{as,S=O}$), 1121 (m), 1048 (s, $\nu_{s,OMe}$), 1033 (s, TsO^-), 1011 (s, TsO^-), 864 (w), 841 (m), 819 (m, TsO^-), 682 (s, TsO^-), 568 (s, TsO^-). FT-FIR (Nujol, cm^{-1}; selected bands): 368 (w), 303 (w), 289 (m), 253 (w). MS (FAB+, CH_3OH): m/z (%) 487 (100) ($[M - TsO]^+$); 353 (19) ($[M - TsO - cym]^+$). Molar conductivity (CH_3CN): 121 S cm^2 mol^{-1}. Solubility: soluble in methanol and acetonitrile and poorly soluble in water, acetone, ethanol, and dichloromethane.

[(η^6-p-cymene)RuCl(dmobpy)]PF_6 ([2][PF_6]). In a 100 mL Schlenk flask protected from light, $AgPF_6$ (82.6 mg, 0.326 mmol) was added under a nitrogen atmosphere to a solution of $[(\eta^6$-p-cymene)$RuCl_2]_2$ (100 mg, 0.163 mmol) in degassed methanol (20 mL). The mixture was stirred for 2 h in the dark at room temperature. The precipitate of AgCl was removed by filtration. Then, the ligand dmobpy (70.5 mg, 0.326 mmol) was added and the mixture was stirred overnight at room temperature. The resulting solution was concentrated under vacuum to a final volume of 10 mL, and diethyl ether was added (30 mL) to precipitate a yellow solid, which was collected by filtration and dried under vacuum. Yield: 113.5 mg (0.18 mmol, 55.0%). M_r ($C_{22}H_{26}N_2O_2ClPF_6Ru$) = 631.9366 g/mol. Anal. Calcd for $C_{22}H_{26}N_2O_2ClPF_6Ru$: C, 41.81; H, 4.15; N, 4.43. Found: C, 41.92; H, 4.28; N, 4.45. ^{1}H NMR (400 MHz, CD_3OD): δ 9.18 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.06 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.30 (dd, J = 6.6 Hz, 2.8 Hz, 2H, $H^{5'}$), 6.02 (d, J = 6.4 Hz, 2H, $H^{2,6}$), 5.75 (d, J = 6.4 Hz, 2H, $H^{3,5}$), 4.09 (s, 6H, -OMe), 2.60 (sept, J = 6.9 Hz, 1H, H^7), 2.26 (s, 3H, H^{10}), 1.06 (d, J = 6.9 Hz, 6H, $H^{8,9}$) ppm. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.32 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.14 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.32 (dd, J = 6.6 Hz, 2.8 Hz, 2H, $H^{5'}$), 6.14 (d, J = 6.4 Hz, 2H, $H^{2,6}$), 5.88 (d, J = 6.3 Hz, 2H, $H^{3,5}$), 4.12 (s, 6H, -OMe), 2.75 (sept, J = 6.9 Hz, 1H, H^7), 2.28 (s, 3H, H^{10}), 1.10 (d, J = 6.9 Hz, 6H, $H^{8,9}$) ppm. ^{13}C NMR (101 MHz, CD_3COCD_3): δ 169.21 (s, 2C, $C^{4'}$), 157.25 (s, 2C, $C^{2'}$), 157.14 (s, 2C, $C^{6'}$), 114.58 (s, 2C, $C^{5'}$), 110.92 (s, 2C, $C^{3'}$), 104.81 (s, 1C, C^1), 104.06 (s, 1C, C^4), 86.95 (s, 2C, $C^{2,6}$), 84.39 (s, 2C, $C^{3,5}$), 57.46 (s, 2C, −OMe), 31.82 (s, 1C, C^7), 22.30 (s, 2C, $C^{8,9}$), 18.89 (s, 1C, C^{10}) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, CD_3COCD_3): δ −143.15 (sept, J = 708 Hz, 1P, PF_6^-) ppm. ^{19}F NMR (376 MHz, CD_3COCD_3): δ −72.99 (d, J = 708 Hz, 6F, PF_6^-) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3087 (w, ν_{CH,sp^2}), 2971 (w, ν_{CH,sp^3}), 2932 (w), 1620 (vs, $\nu_{C=C+C=N}$), 1614 (vs, $\nu_{C=C+C=N}$), 1561 (m), 1495 (s, $\nu_{C=C+C=N}$), 1475 (s), 1421 (s), 1340 (m), 1314 (w), 1281 (s), 1254 (w), 1230 (s, $\nu_{as,OMe}$), 1047 (s, $\nu_{s,OMe}$), 1031 (m), 879 (m), 841 (vs, ν_{P-F}), 558 (s, δ_{F-B-F}). FT-FIR (Nujol, cm^{-1}; selected bands): 375 (w), 290 (m), 248 (w). MS (FAB+, CH_3OH): m/z (%) 487 (43) ($[M - PF_6]^+$). Molar conductivity (CH_3CN): 127 S cm^2 mol^{-1}. Solubility: soluble in acetone, partially soluble in methanol, ethanol, and dichloromethane, and poorly soluble in water.

[(η^6-phoxet)RuCl(dmobpy)]Cl ([3]Cl). In a 100 mL Schlenk flask under a nitrogen atmosphere, $[(\eta^6$-phoxet)$RuCl_2]_2$ (90 mg, 0.145 mmol) was dissolved in degassed isopropyl alcohol (6 mL). The ligand dmobpy (62.7 mg, 0.29 mmol) was added, and the mixture was refluxed at 80 °C for 1 h. The resulting solution was concentrated to 2 mL under vacuum; the solid was collected by filtration and dried under vacuum to produce a dark yellow solid. Yield: 0.1242 g (0.24 mmol, 81.4%). M_r ($C_{20}H_{22}N_2O_4Cl_2Ru$) = 526.3802 g/mol. Anal. Calcd for $C_{20}H_{22}N_2O_4Cl_2Ru{\cdot}0.5H_2O$: C, 44.87; H, 4.33; N, 5.23. Found: C, 44.76; H, 4.373; N, 5.117. ^{1}H NMR (400 MHz, CD_3OD): δ 9.19 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.04(d, J = 2.8 Hz, 2H, $H^{3'}$), 7.29 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 6.27 (dd, J = 6.7, 5.5 Hz, 2H, H^3-phoxet), 5.64 (d, J = 6.7 Hz, 2H, H^2-phoxet), 5.50 (t, J = 5.5 Hz, 1H, H^4-phoxet), 4.13(m, 2H, H^5-phoxet), 4.08 (s, 6H, H^{OMe}), 3.86 (m, 2H, H^6-phoxet) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 169.96 (s, 2C, $C^{4'}$), 158.04 (s, 2C, $C^{2'}$), 156.93 (s, 2C, $C^{6'}$), 139.56 (s, 1C, C^1-phoxet), 114.71 (s, 2C, $C^{5'}$), 111.12 (s, 2C, $C^{3'}$), 95.48 (s, 2C, C^2-phoxet), 73.92 (s, 1C, C^4-phoxet), 72.92 (s, 1C, C^5-phoxet), 65.78 (s, 2C, C^3-phoxet), 60.89 (s, 1C, C^6-phoxet), 57.49 (s, 2C, −OMe) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3182 (w), 3064 (w, ν_{CH,sp^2}), 2924 (w, ν_{CH,sp^3}), 1614 (vs, $\nu_{C=C+C=N}$), 1558 (m), 1530 (s, phoxet), 1496 (s, $\nu_{C=C+C=N}$), 1469 (m), 1425 (m), 1351 (m), 1281 (vs), 1235 (s, $\nu_{as,OMe}$), 1048 (s, $\nu_{s,OMe}$), 1030 (m), 1019 (m), 864 (m), 839 (m), 665 (m, phoxet). FT-

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

FIR (Nujol, cm^{-1}; selected bands): 374 (w), 303 (w), 274 (m), 247 (w). MS (FAB+, CH_3OH): m/z (%) 491 (12) ($[M - Cl]^+$). Molar conductivity (H_2O): 158 S cm^2 mol^{-1}. Solubility: soluble in water and methanol and poorly soluble in acetone, ethanol, dichloromethane, and acetonitrile.

General Procedure for the Synthesis of [3][BF_4] and [3]TsO. In a 100 mL Schlenk flask protected from light, the corresponding silver salt AgX (0.190 mmol) was added under a nitrogen atmosphere to a solution of [(η^6-phoxet)RuCl(dmobpy)]Cl (100 mg, 0.190 mmol) in distilled/degassed water (5 mL). The mixture was stirred overnight in the dark, at room temperature. The precipitate of AgCl was removed by filtration, and the resulting solution was evaporated to dryness under vacuum. The solid residue was washed with diethyl ether (2 × 5 mL) and dried under vacuum to produce a yellow solid.

[(η^6-phoxet)RuCl(dmobpy)]BF_4 ([3][BF_4]). $AgBF_4$ (37 mg, 0.190 mmol) and [(η^6-phoxet)RuCl(dmobpy)]Cl (100 mg, 0.190 mmol). Yield: 0.0485 g (0.084 mmol, 44.2%). M_r ($C_{20}H_{22}N_2O_4ClBF_4Ru$) = 577.7222 g/mol. Anal. Calcd for $C_{20}H_{22}N_2O_4ClBF_4Ru$: C, 41.58; H, 3.84; N, 4.85. Found: C, 41.57; H, 4.37; N, 4.89. ^{1}H NMR (400 MHz, CD_3OD): δ 9.19 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.04 (d, J = 2.7 Hz, 2H, $H^{3'}$), 7.28 (dd, J = 6.6, 2.7 Hz, 2H, $H^{5'}$), 6.27 (dd, J = 6.7, 5.5 Hz, 2H, H^3-phoxet), 5.64 (d, J = 6.7 Hz, 2H, H^2-phoxet), 5.49 (t, J = 5.5 Hz, 1H, H^4-phoxet), 4.13 (m, 2H, H^5-phoxet), 4.08 (s, 6H, H^{OMe}), 3.86 (m, 2H, H^6-phoxet) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 169.95 (s, 2C, $C^{4'}$), 158.04 (s, 2C, $C^{2'}$), 156.92 (s, 2C, $C^{6'}$), 139.55 (s, 1C, C^1-phoxet), 114.70 (s, 2C, $C^{5'}$), 111.12 (s, 2C, $C^{3'}$), 95.48 (s, 2C, C^2-phoxet), 73.92 (s, 1C, C^4-phoxet), 72.91 (s, 1C, C^5-phoxet), 65.77 (s, 2C, C^3-phoxet), 60.89 (s, 1C, C^6-phoxet), 57.49 (s, 2C, −OMe) ppm. ^{19}F NMR (376 MHz, CD_3OD): δ −155.20 (s, $^{10}B-F$, BF_4^-), −155.25 (s, $^{11}B-F$, BF_4^-), ppm. Integration ratio (1/4) in agreement with the isotopic distribution for $^{10}B/^{11}B$ (20/80). FT-IR (KBr, cm^{-1}; selected bands): 3083 (w, ν_{CH,sp^2}), 2925 (w, ν_{CH,sp^3}), 1620 (vs, $\nu_{C=C+C=N}$), 1560 (m), 1524 (s, phoxet), 1496 (s, $\nu_{C=C+C=N}$), 1470 (m), 1425 (m), 1345 (m), 1267 (s), 1256 (s), 1234 (s, $\nu_{as,OMe}$), 1069 (s, $\nu_{d,B-F}$), 1050 (s, $\nu_{s,OMe}$), 1031 (s), 922 (m), 864 (m), 853 (m), 838 (m), 668 (m, phoxet), 521 (w, δ_{F-B-F}). FT-FIR (Nujol, cm^{-1}; selected bands): 376 (w), 301 (w), 281 (m), 253 (w), 248 (w). MS (FAB+, CH_3OH): m/z (%) 491 (13) ($[M - BF_4]^+$). Molar conductivity (H_2O): 158 S cm^2 mol^{-1}. Solubility: soluble in water, methanol, and ethanol and slightly soluble in acetone, dichloromethane, and acetonitrile.

[(η^6-phoxet)RuCl(dmobpy)]OTs ([3]OTs). AgTsO (52 mg, 0.190 mmol) and [(η^6-phoxet)RuCl(dmobpy)]Cl (100 mg, 0.190 mmol). Yield: 0.0875 g (0.132 mmol, 69.6%). M_r ($C_{27}H_{29}N_2O_7ClSRu$) = 662.123 g/mol. Anal. Calcd for $C_{27}H_{29}N_2O_7ClSRu$: C, 48.98; H, 4.41; N, 4.23. Found: C, 48.71; H, 4.45; N, 4.33. ^{1}H NMR (400 MHz, CD_3OD): δ 9.19 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.04 (d, J = 2.8 Hz, 2H, $H^{3'}$), 7.71 (m, 2H, H^b-OTs^-), 7.28 (dd, J = 6.6, 2.8 Hz, 2H, $H^{5'}$), 7.23 (m, 2H, H^c-OTs^-), 6.27 (dd, J = 6.4, 5.5 Hz, 2H, H^3-phoxet), 5.64 (d, J = 6.4 Hz, 2H, H^2-phoxet), 5.49 (t, J = 5.5 Hz, 1H, H^4-phoxet), 4.12 (m, 2H, H^5-phoxet), 4.08 (s, 6H, H^{OMe}), 3.85 (m, 2H, H^6-phoxet), 2.37 (s, 3H, H^e-OTs^-) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 169.95 (s, 2C, $C^{4'}$), 158.04 (s, 2C, $C^{2'}$), 156.92 (s, 2C, $C^{6'}$), 139.55 (s, 1C, C^1-phoxet), 129.81 (s, 2C, C^c-OTs), 126.98 (s, 2C, C^b-OTs), 114.70 (s, 2C, $C^{5'}$), 111.12 (s, 2C, $C^{3'}$), 95.48 (s, 2C, C^2-phoxet), 73.92 (s, 1C, C^4-phoxet), 72.91 (s, 1C, C^5-phoxet), 65.77 (s, 2C, C^3-phoxet), 60.89 (s, 1C, C^6-phoxet), 57.49 (s, 2C, −OMe) ppm. Some peaks are missing due to low-quality spectrum. FT-IR (KBr, cm^{-1}; selected bands): 3083 (w, ν_{CH,sp^2}), 2966 (w, ν_{CH,sp^3}), 1620 (vs, $\nu_{C=C+C=N}$), 1614 (vs, $\nu_{C=C+C=N}$), 1559 (m), 1527 (s, phoxet), 1497 (s, $\nu_{C=C+C=N}$), 1470 (m), 1444 (m), 1422 (m), 1344 (m), 1263 (vs), 1219 (vs, $\nu_{as,S=O}$), 1187 (vs, $\nu_{as,S=O}$), 1122 (m), 1101 (s), 1049 (s, $\nu_{s,OMe}$), 1034 (s, TsO^-), 1011 (s, TsO^-), 913 (w), 853 (m), 802 (m, TsO^-), 683 (s, TsO^-), 668 (w, phoxet), 568 (s, TsO^-). FT-FIR (Nujol, cm^{-1}; selected bands): 376 (w), 301 (w), 281 (m), 247 (w). MS (FAB+, CH_3OH): m/z (%) 491 (11) ($[M - TsO]^+$). Molar conductivity (H_2O): 58 S cm^2 mol^{-1}. Solubility: soluble in water and methanol, poorly soluble in ethanol and dichloromethane, and insoluble in acetone.

[(η^6-phoxet)RuCl(dmobpy)]PF_6 ([3][PF_6]). In a 100 mL Schlenk flask protected from light, $AgPF_6$ (38.4 mg, 0.152 mmol) was added under a nitrogen atmosphere to a solution of [(η^6-phoxet)RuCl-(dmobpy)]Cl (80 mg, 0.152 mmol) in distilled and degassed water (5 mL). The mixture was stirred overnight in the dark, at room temperature. The precipitate of AgCl was removed by filtration. The solid residue was extracted with acetone, and both the organic and aqueous solutions were combined and evaporated to dryness under vacuum. The resulting solid was washed with n-hexane (2 × 5 mL) and dried under vacuum to produce a yellow solid. Yield: 0.0421 g (0.066 mmol, 43.6%). Yield: 0.0421 g (0.066 mmol, 44.5%). M_r ($C_{20}H_{22}N_2O_4ClPF_6Ru$) = 635.896 g/mol. Anal. Calcd for $C_{20}H_{22}N_2O_4ClPF_6Ru$: C, 37.78; H, 3.49; N, 4.41. Found: C, 37.45; H, 3.19; N, 4.93. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 9.32 (d, J = 6.6 Hz, 2H, $H^{6'}$), 8.12 (d, J = 2.6 Hz, 2H, $H^{3'}$), 7.33 (dd, J = 6.6, 2.6 Hz, 2H, $H^{5'}$), 6.41 (dd, J = 6.7, 5.5 Hz, 2H, H^3-phoxet), 5.73 (d, J = 6.7 Hz, 2H, H^2-phoxet), 5.62 (t, J = 5.5 Hz, 1H, H^4-phoxet), 4.27 (m, 2H, H^5-phoxet), 4.11 (s, 6H, H^{OMe}-dmobpy), 3.88 (m, 2H, H^6-phoxet) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_3COCD_3): δ 169.15 (s, 2C, $C^{4'}$), 157.43 (s, 2C, $C^{2'}$), 156.78 (s, 2C, $C^{6'}$), 139.43 (s, 1C, C^1-phoxet), 114.29 (s, 2C, $C^{5'}$), 110.77 (s, 2C, $C^{3'}$), 95.01 (s, 1C, C^2-phoxet), 73.71 (s, 1C, C^4-phoxet), 72.81 (s, 1C, C^5-phoxet), 65.45 (s, 1C, C^3-phoxet), 60.75 (s, 1C, C^6-phoxet), 57.43 (s, 2C, −OMe) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, acetone): δ −143.17 (sept, J = 708 Hz, 1P, PF_6^-) ppm. ^{19}F NMR (376 MHz, acetone): δ −72.99 (d, J = 708 Hz, 6F, PF_6^-) ppm. FT-IR (KBr, cm^{-1}; selected bands): 3083 (w, ν_{CH,sp^2}), 2948 (w, ν_{CH,sp^3}), 1621 (vs, $\nu_{C=C+C=N}$), 1561 (m), 1533 (s, phoxet), 1496 (s, $\nu_{C=C+C=N}$), 1471 (m), 1453 (m), 1422 (m), 1343 (m), 1280 (s), 1269 (s), 1255 (s), 1233 (s, $\nu_{as,OMe}$), 1050 (s, $\nu_{s,OMe}$), 1032 (m), 841 (vs, ν_{P-F}), 667 (m, phoxet), 559 (s, δ_{F-B-F}). FT-FIR (Nujol, cm^{-1}; selected bands): 377 (w), 300 (w), 280 (m), 276 (m), 251 (w). MS (FAB+, CH_3COCH_3): m/z (%) 491 (18) ($[M - PF_6]^+$). Molar conductivity (CH_3CN): 141 S cm^2 mol^{-1}. Solubility: soluble in acetone and partially soluble in water and dichloromethane.

Catalytic Transfer Hydrogenation of Ketones. A Radley Carousel 12 Reaction Station was used to run sets of experiments simultaneously under similar conditions. In a typical experiment for the catalytic transfer hydrogenation of ketones to the corresponding secondary alcohols, the procedure was as follows: the ketone (0.32 mmol) was dissolved in degassed/distilled water (5 mL). Then, the hydrogen source HCOONa (9.6 mmol), and complexes of series **1**, **2**, or **3** (1.6 μmol), as the catalysts, were added under a nitrogen atmosphere. The pH was adjusted to a value of 4 with HCOOH (1 M), or KOH (1 M). The solutions were stirred at 80 °C for the given time. Then, the reaction mixtures were cooled in the refrigerator to quench the reaction, and a fraction of the crude product was analyzed by ^{1}H NMR (D_2O/1,4-dioxane). In addition, the organic products of the main fraction were extracted with diethyl ether and identified by GC, on a Hewlett-Packard 5890 Series II equipment, using an HP-FFAP (12 m × 0.2 mm × 0.33 mm) capillary column. The yield of alcoholic products (%) was determined by integration of ^{1}H NMR signals and GC peaks. All the experiments were carried out twice.

Catalytic Transfer Hydrogenation of acetophenone in D_2O. Selective Deuteration Experiments. In an NMR tube, acetophenone (50 μL, 51.5 mg, 0.43 mmol) was dissolved in degassed D_2O (0.5 mL) under a nitrogen atmosphere. Then, HCOONa (0.8865 g, 13 mmol) and [**2**][BF_4] (2.5 mg, 4.4 μmol) were added. The pH was adjusted to a value of 4 with HCOOH (1 M). The solutions were stirred at 80 °C for the given time (24−72 h). The reaction mixture was cooled in the refrigerator to quench the reaction, and the supernatant organic phase was taken with a Pasteur pipet and dissolved in $CDCl_3$. The sample was analyzed by ^{1}H NMR and ^{13}C NMR ($CDCl_3$, 25 °C). The yield of alcoholic products (%) was determined by integration of ^{1}H NMR signals.

rac-1-Phenylethanol-d_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 5H, Ph), 4.88 (m, 0.4H, CHOD), 2.59 (s, 0.08H, OH), 1.49 (s, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.89 (s, 1C, C^i-Ph), 128.61 (s, 2C, Ph), 127.58 (s, 1C, Ph), 125.51 (s, 2C, Ph), 70.43 (s, CHOD); 70.01 (m, $^1J_{CD}$ = 21.97 Hz, CDOD), 25.21 (s, 1C, CH_3) ppm.

dx.doi.org/10.1021/om3004702 | *Organometallics* 2012, 31, 6106−6123

Catalytic Oxidation of 1-*rac*-Phenylethanol with ^{t}BuOOH or H_2O_2. *Caution*! Gas formation and high pressures were observed for those experiments with oxidant/S/cat. = 40 000/10 000/1 that were carried out using 5 mL of H_2O.

A Radley Carousel 12 Reaction Station was used to run sets of experiments simultaneously under similar conditions. In a typical experiment for the catalytic oxidation of 1-*rac*-phenylethanol to acetophenone using the molar ratio oxidant/S/cat. = 4000/1000/1, the procedure was as follows: the alcohol (1 mmol) was dissolved in degassed/distilled water (5 mL). Then the oxidant, ^{t}BuOOH (4 mmol) or H_2O_2 (5 mmol), and the catalyst, [**1**]**X**, [**2**]**X**, or [**3**]**X** (1 μmol), were added under a nitrogen atmosphere. The pH was adjusted to a value of 7 with HCl (1 M) or KOH (1 M). The solutions were stirred at room temperature for 3 h. Finally, the reaction mixtures were cooled in the refrigerator to quench the reaction, and a fraction of the crude product was analyzed by ^{1}H NMR (D_2O/1,4-dioxane). Furthermore, the organic products of the main fraction were extracted with diethyl ether and identified by GC, on a Hewlett-Packard 5890 Series II equipment using an HP-FFAP (12 m × 0.2 mm × 0.33 mm) capillary column. The yield of ketonic products (%) was determined by integration of ^{1}H NMR signals and GC peaks. All the experiments were carried out twice, and the yield data were expressed as averaged values. For those experiments with the molar ratio oxidant/S/cat. = 40 000/10 000/1 two phases were obtained; therefore, the reaction mixtures were cooled in the refrigerator to quench the reaction, the organic phase was separated, and the aqueous phase was extracted with *n*-hexane. Both organic phases were mixed, and a fraction was diluted with diethyl ether and analyzed by GC.

Aqueous Solution Chemistry. The *aquation−anation equilibrium* and the *basic hydrolysis of the Ru^{II} chloro complex* [**2**][**BF$_4$**] were monitored by ^{1}H NMR spectroscopy. The spectra were recorded for 18 mM solutions in D_2O at various time intervals and the signals referenced to TMS via 1,4-dioxane as an internal reference (δ 3.75 ppm). The relative amounts of the Ru^{II} chloro complex and the aqua derivative were determined by integration of the respective ^{1}H resonances. Aquation−anation experiments for [**1**][**BF$_4$**], [**2**]**TsO**, and [**3**]**TsO** were done in a similar way.

*[(η^6-p-cymene)Ru(OD$_2$)(dmobpy)]$^{2+}$ (**4**).* ^{1}H NMR (400 MHz, D_2O): δ 9.34 (d, J = 6.6 Hz, 2H, H$^{6'}$), 7.86 (d, J = 2.7 Hz, 2H, H$^{3'}$), 7.36 (dd, J = 6.6, 2.7 Hz, 2H, H$^{5'}$), 6.20 (d, J = 6.5 Hz, 2H, H^{2,6}), 5.96 (d, J = 6.5 Hz, 2H, H^{3,5}), 4.07 (s, 6H, H^{OMe}), 2.48 (sept, J = 6.9 Hz, 1H, H^7), 2.20 (s, 3H, H^{10}), 0.95 (d, J = 6.9 Hz, 6H, H^{8,9}) ppm.

*[(η^6-p-cymene)Ru(OD)(dmobpy)]$^+$ (**5**).* ^{1}H NMR (400 MHz, D_2O): δ 9.13 (d, J = 6.7 Hz, 2H, H$^{6'}$), 7.82 (s, 2H, H$^{3'}$), 7.28 (d, J = 6.7 Hz, 2H, H$^{5'}$), 5.93 (d, J = 5.8 Hz, 2H, H^{2,6}), 5.54 (d, J = 5.8 Hz, 2H, H^{3,5}), 4.05 (s, 6H, H^{OMe}), 2.40 (sept, J = 6.8 Hz, 1H, H^7), 2.23 (s, 3H, H^{10}), 0.85 (d, J = 6.8 Hz, 6H, H^{8,9}) ppm.

*Reaction of **[2][BF$_4$]** (18 mM) with HCOONa (180 mM) and Addition of Acetophenone.* An excess of HCOONa (6 mg, 9 × 10^{-2} mmol) was added to a solution of [**2**][**BF$_4$**] (5 mg, 9 × 10^{-3} mmol) in D_2O (0.5 mL) in an NMR tube, and the pH was set at 4.35 by addition of HCOOH. The subsequent reaction was monitored by ^{1}H NMR spectroscopy during 24 h. Then, acetophenone (3 mg, 2.7 × 10^{-5} mmol) was added to the mixture and the evolution was monitored again.

*[(η^6-p-cymene)Ru(OOCH)(dmobpy)]$^+$ (**6**).* ^{1}H NMR (400 MHz, D_2O): δ 9.36 (d, J = 6.6 Hz, 2H, H$^{6'}$), 7.85 (s, 1H, HCOO), 7.80 (d, J = 2.7 Hz, 2H, H$^{3'}$), 7.31 (dd, J = 6.6, 2.7 Hz, 2H, H$^{5'}$), 6.18 (d, J = 6.4 Hz, 2H, H^{2,6}), 5.89 (d, J = 6.4 Hz, 2H, H^{3,5}), 4.04 (s, 6H, H^{OMe}), 2.49 (sept, J = 6.9 Hz, 1H, H^7), 2.12 (s, 3H, H^{10}), 0.95 (d, J = 6.9 Hz, 6H, H^{8,9}) ppm.

Observation of the Hydrido complex 7 by ^{1}H NMR. An excess of HCOONa (1 mg, 1.56 × 10^{-2} mmol) was added to a solution of [**2**][**BF$_4$**] (1.5 mg, 2.6 × 10^{-3} mmol) in a 1/1 D_2O/H_2O mixture (0.5 mL) using an NMR tube, and the pH was set at 7. Then the tube was heated to 80 °C for 4 h. A ^{1}H NMR spectrum was recorded for the resulting solution, and the main product was assigned to the hydride complex **7**.

*[(η^6-p-cymene)Ru(D)(dmobpy)]$^+$ (**7**).* ^{1}H NMR (400 MHz, D_2O): δ 8.60 (d, 2H), 7.51 (d, 2H), 6.97 (m, 2H), 5.60 (d, 2H), 5.39 (d, 2H), 3.95 (s, 3H, MeO), 2.63 (sept, J = 6.9 Hz, 1H), 2.22 (s, 3H, Me), 1.11 (d, J = 6.9 Hz, 6H) ppm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and CIF files giving relevant crystallographic parameters for all the X-ray structures together with figures giving NMR figures and tables giving characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the MINECO of Spain (project CTQ2011-24434, FEDER Funds).

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