

## Synthesis and Intramolecular and Interionic Structural Characterization of Half-Sandwich (Arene)Ruthenium(II) Derivatives of Bis(Pyrazolyl)Alkanes

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Arene ruthenium(II) complexes containing bis(pyrazolyl)methane ligands have been prepared by reacting the ligands  $L'$  ( $L'$  in general; specifically  $L^1 = H_2C(pz)_2$ ,  $L^2 = H_2C(pz^{Me_2})_2$ ,  $L^3 = H_2C(pz^{4Me})_2$ ,  $L^4 = Me_2C(pz)_2$  and  $L^5 = Et_2C(pz)_2$  where  $pz =$  pyrazole) with  $[(arene)RuCl(\mu-Cl)]_2$  dimers (arene = *p*-cymene or benzene). When the reaction was carried out in methanol solution, complexes of the type  $[(arene)Ru(L')Cl]Cl$  were obtained. When  $L^1$ ,  $L^2$ ,  $L^3$ , and  $L^5$  ligands reacted with excess  $[(arene)RuCl(\mu-Cl)]_2$ ,  $[(arene)Ru(L')Cl][(arene)RuCl_3]$  species have been obtained, whereas by using the  $L^4$  ligand under the same reaction conditions the unexpected  $[(p\text{-cymene})Ru(pzH)_2Cl]Cl$  complex was recovered. The reaction of 1 equiv of  $[(p\text{-cymene})Ru(L')Cl]Cl$  and of  $[(p\text{-cymene})Ru(pzH)_2Cl]Cl$  with 1 equiv of  $AgX$  ( $X = O_3SCF_3$  or  $BF_4$ ) in methanol afforded the complexes  $[(p\text{-cymene})Ru(L')Cl](O_3SCF_3)$  ( $L' = L^1$  or  $L^2$ ) and  $[(p\text{-cymene})Ru(pzH)_2Cl]BF_4$ , respectively.  $[(p\text{-cymene})Ru(L^1)(H_2O)][PF_6]_2$  formed when  $[(p\text{-cymene})Ru(L^1)Cl]Cl$  reacts with an excess of  $AgPF_6$ . The solid-state structures of the three complexes,  $[(p\text{-cymene})Ru\{H_2C(pz)_2\}Cl]Cl$ ,  $[(p\text{-cymene})Ru\{H_2C(pz^{4Me})_2\}Cl]Cl$ , and  $[(p\text{-cymene})Ru\{H_2C(pz)_2\}Cl](O_3SCF_3)$ , were determined by X-ray crystallographic studies. The interionic structure of  $[(p\text{-cymene})Ru(L^1)Cl](O_3SCF_3)$  and  $[(p\text{-cymene})Ru(L^1)Cl][(p\text{-cymene})RuCl_3]$  ( $L' = L^1$  or  $L^2$ ) was investigated through an integrated experimental approach based on NOE and pulsed field gradient spin–echo (PGSE) NMR experiments in  $CD_2Cl_2$  as a function of the concentration. PGSE NMR measurements indicate the predominance of ion pairs in solution. NOE measurements suggest that  $(O_3SCF_3)^-$  approaches the cation orienting itself toward the  $CH_2$  moiety of the  $L^1$  ( $H_2C(pz)_2$ ) ligand as found in the solid state. Selected Ru species have been preliminarily investigated as catalysts toward styrene oxidation by dihydrogen peroxide,  $[(p\text{-cymene})Ru(L^1)(H_2O)][PF_6]_2$  being the most active species.

### Introduction

The organometallic chemistry of half-sandwich  $\eta^6$ -arene-ruthenium(II) complexes has been widely developed in the past few years, due to their wide range of potential applications as catalyst precursors for hydrogen transfer,<sup>1</sup> alkene polymerization, ring opening metathesis polymerization,<sup>2</sup> and olefin oxidation.<sup>3</sup> Arene ruthenium compounds also have been extensively investigated for their potent antibacterial and anticancer activity.<sup>4</sup>

Moreover, arene ruthenium compounds belong to a well-established family of robust metal-organic molecules (metal = Ru(II), Rh(III), and Ir(III)) very soluble and stable in water,<sup>5</sup> with many potential advantages such as alleviation of environmental problems associated with the use of organic solvents, industrial applications with the introduction of new biphasic processes,<sup>6</sup> and metal-mediated organic syntheses in water.<sup>7</sup>

The  $\pi$ -ligated arene confers great stability to Ru in the +2 oxidation state, and the characteristic "piano stool" structure offers the possibility to vary the additional donors via substitution of halide(s) with a variety of  $\sigma$ -donors ranging from phosphines<sup>8</sup> to  $\beta$ -diketones,<sup>9</sup> to aliphatic as well as aromatic amines.<sup>1</sup>

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Several works appeared also on the interaction of  $\eta^6$ -arene Ru(II) with tris(pyrazol-1-yl)borates<sup>10</sup> and tris(pyrazol-1-yl)alkanes,<sup>11</sup> the well-known Trofimenko's "scorpionate ligands"; however, it is surprising that no attempts have been made to explore the interaction of  $\eta^6$ -arene-ruthenium(II) fragments with bis(pyrazol-1-yl)alkanes, a family of less used "scorpionates" that shows interesting coordinative features, as reported in our recent review.<sup>12</sup> Herein, we report a systematic investigation of the interaction between arene ruthenium(II) (arene = *p*-cymene and benzene) with several bis(pyrazol-1-yl)alkanes, together with the characterization by single crystal X-ray analyses of some derivatives and NOE<sup>13</sup> and pulsed field gradient spin-echo (PGSE)<sup>14</sup> NMR experiments. The latter techniques were used to investigate the interionic solution structures of the complexes [(*p*-cymene)Ru(L<sup>1</sup>)Cl](O<sub>3</sub>SCF<sub>3</sub>) and [(*p*-cymene)Ru(L<sup>1</sup>)Cl][(p-cymene)RuCl<sub>3</sub>] (L<sup>1</sup> = L<sup>1</sup> or L<sup>2</sup>), which possess an unusual

organometallic counterion, as it is well-recognized that ion-pairing drastically affects the reactivity and structure of ionic organometallics.<sup>15</sup>

## Results and Discussion

**Synthesis and Spectroscopic Characterization of Complexes 1–16.** By the interaction of 1 equiv of the dinuclear [(*p*-cymene)RuCl( $\mu$ -Cl)]<sub>2</sub> with 2 equiv of bis(pyrazol-1-yl)alkanes L' in methanol at room temperature, the derivatives [(*p*-cymene)Ru(L')Cl]Cl **1–5** (L' = L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>, L<sup>4</sup> and L<sup>5</sup>) have been obtained (Scheme 1) as red-brown powders, stable in the air and in solution, and very soluble in water, alcohols, chlorinated solvents, acetone, dmsol and acetonitrile, where they behave as 1:1 electrolytes.<sup>16</sup> In the positive ESI-MS spectra of **1–5** the peak due to the cationic fragment [(*p*-cymene)Ru(L')Cl]<sup>+</sup> is always present as the predominant species.

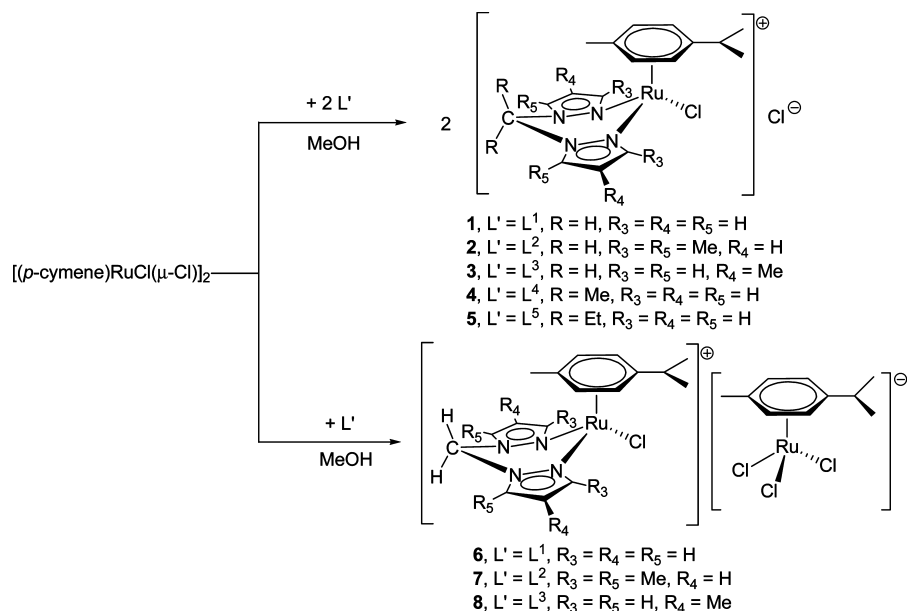
By using equivalent quantities of [(*p*-cymene)RuCl( $\mu$ -Cl)]<sub>2</sub> and L' in methanol at room temperature, the derivatives [(*p*-cymene)Ru(L')Cl][(p-cymene)RuCl<sub>3</sub>] **6–8** (**6**: L' = L<sup>1</sup>; **7**: L' = L<sup>2</sup>; **8**: L' = L<sup>3</sup>), in which the anion is the organometallic [(p-cymene)RuCl<sub>3</sub>]<sup>−</sup> group (Scheme 1), were obtained. Analogous [(Cp\*)M(L')Cl][(Cp\*)MCl<sub>3</sub>] complexes have been previously reported (M = Rh, Ir).<sup>17</sup> Compounds **6–8** are stable in the air and in solution and soluble in water, alcohols, chlorinated solvents, acetone, dmsol and acetonitrile, where they behave as 1:1 electrolytes.<sup>16</sup> Negative ESI-MS spectra of **6–8** show a peak at *m/z* (%) 341 due to anionic [(p-cymene)RuCl<sub>3</sub>]<sup>−</sup> fragment, while positive ESI-MS spectra exhibit always the peak due to the cation and in the spectrum of derivative **8**, also a peak due to the dinuclear species [(p-cymene)Ru(L<sup>1</sup>)Cl]RuCl(OH)]<sup>+</sup>.

Unexpectedly, by using the ligand L<sup>1</sup> and the same conditions employed for the synthesis of derivatives **6–8**, [(*p*-cymene)Ru(pzH)<sub>2</sub>Cl]Cl **9**, where the two neutral pyrazoles arise from C–N breaking in the L<sup>4</sup> ligand, has been recovered from solution.<sup>18</sup> Slow decomposition of complexes containing poly(pyrazolyl)borates has been previously observed to proceed through B–N breaking which generally occurs when at least one arm of the ligand is not coordinated, which makes possible the interaction of water with the B and N atoms of an uncoordinated ring.<sup>18c</sup> However, in this case a less polarized C–N bond is involved in the decomposition process, so that at this stage of the knowledge we cannot propose any hypothesis on the operating mechanism. Compound **9** converts to [(*p*-cymene)Ru(pzH)<sub>2</sub>Cl]BF<sub>4</sub> **10**, through a metathesis reaction with AgBF<sub>4</sub> (Scheme 2). Derivatives **11** and **12** have been synthesized from

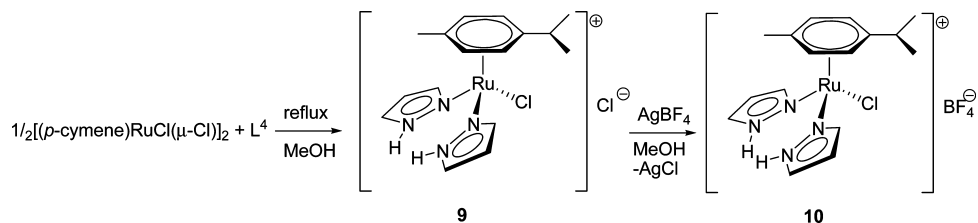
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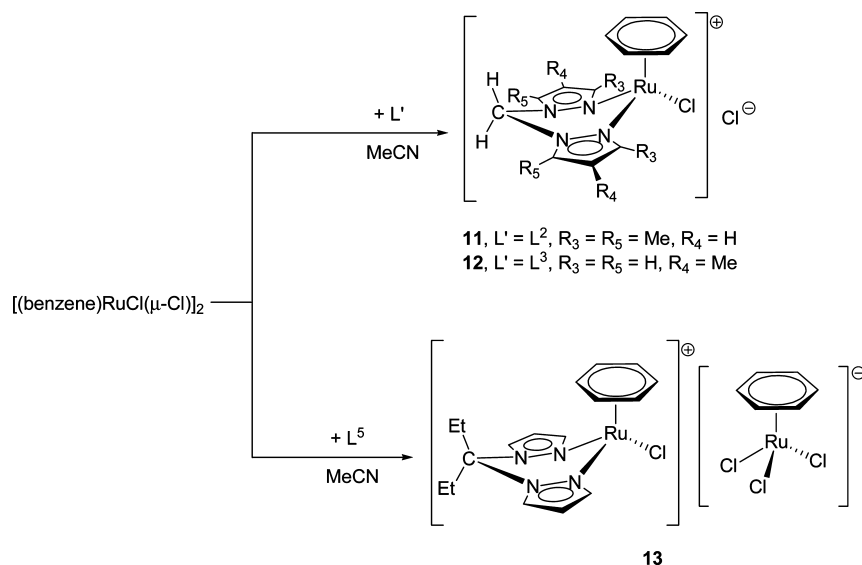
Scheme 1



Scheme 2

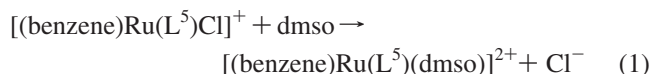


Scheme 3



interaction of an equivalent of  $[(\text{benzene})\text{RuCl}(\mu\text{-Cl})_2]$  with a 2-fold amount of the ligands  $L^2$  and  $L^3$ , respectively, in acetonitrile at room temperature (Scheme 3), the choice of this solvent being dictated by solubility of the dinuclear ruthenium acceptor. Compound **13** has been isolated by using equivalent quantities of  $[(\text{benzene})\text{RuCl}(\mu\text{-Cl})_2]$  and the ligand  $L^5$  in acetonitrile (Scheme 3). Compound **13** is poorly soluble in most solvents, except water and dmsO, where it likely behaves as 1:2 electrolyte,<sup>16,19,20</sup> in

accordance with a successive  $\text{Cl}^-$  displacement by a dmsO molecule from the cationic fragment (eq 1):

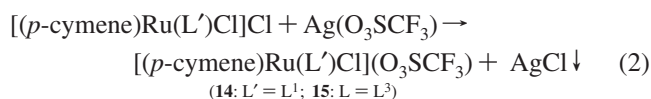


In the far-IR spectra of **1–5** and **9–12** a strong and sharp absorption due to  $\nu(\text{Ru}-\text{Cl})$  has always been found in the range  $270\text{--}300\text{ cm}^{-1}$ , in accordance with the presence of single  $\text{Ru}-\text{Cl}$  bonds.<sup>9</sup> On the contrary, the far-IR spectra of

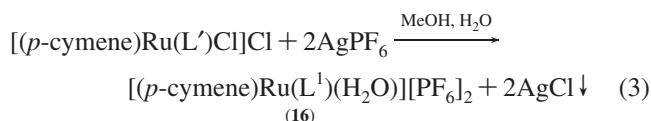
**6–8** and **13** show a very strong but broad absorption below  $300\text{ cm}^{-1}$ , due to overlapped  $\nu(\text{Ru}-\text{Cl})$  stretching modes of the cationic  $[(\text{arene})\text{Ru}(\text{L}')\text{Cl}]^+$  and anionic  $[(\text{arene})\text{RuCl}_3]^-$  fragments. The IR spectra of **9** and **10** show broad bands above  $3200\text{ cm}^{-1}$  due to the N–H stretching of pyrazole and in **10** also two very strong and sharp absorptions at  $1053$  and  $664\text{ cm}^{-1}$  due to ionic  $\text{BF}_4^-$ .<sup>21</sup>

In the  $^1\text{H}$  NMR spectra the geminal methylene protons in bis(pyrazol-1-yl)alkane ligands give the signals expected for an AX spin system in the case of compounds **1**, **3**, **6**, **8** and **15** and for an AB system in the case of compounds **2**, **7**, **11**, **12**, **14**, and **16**, and two resonances have been observed for the bridging  $-\text{CR}_2-$  groups in **4** and **5**, thus indicating a diastereotopic nature of R groups.<sup>17</sup> Accordingly, two resonances due to the methyl carbon atoms of  $\text{Me}_2\text{C}-$  have been detected in the  $^{13}\text{C}\{^1\text{H}\}$  NMR of **4**. Moreover the *p*-cymene protons give rise to resonances due to AA'BB' spin systems. The presence of two different sets of resonances for cymene protons and carbons and only one for bis(pyrazol-1-yl)alkane ligands in  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **6–8** confirms our hypothesis on the existence of both cationic  $[(\text{arene})\text{Ru}(\text{L}')\text{Cl}]^+$  and anionic  $[(\text{arene})\text{RuCl}_3]^-$  fragments. The NMR features of **11** and **12** strictly resemble those of derivatives **1–5**, a quartet being observed in  $^1\text{H}$  NMR spectra for diastereotopic methylene protons, together with a single resonance at ca. 6.00 ppm for protons of  $\pi$ -metal-ligated benzene, whereas in the  $^1\text{H}$  NMR spectrum of **13** two resonances of benzene protons have been detected, in accordance with the presence of the two different benzene fragments in the cation and in the anion.

The external chloride in derivatives **1** and **3** can be replaced by the less-coordinating  $\text{CF}_3\text{SO}_3^-$  anion through a metathesis reaction with silver triflate, derivatives **14** and **15** being easily obtained (eq 2):



Finally, reaction of **1** with 2 equiv of  $\text{AgPF}_6$  gave  $[(p\text{-cymene})\text{Ru}(\text{L}^1)(\text{H}_2\text{O})][\text{PF}_6]_2$ , **16** (eq 3), in which one water molecule, coming from final work up of the reaction mixture, substitutes the chloride in the Ru coordination sphere



Positive ESI-MS spectra of **14** and **15** show the cationic fragment peak, together with additional peaks due to the oxidized species  $\{[(p\text{-cymene})\text{Ru}^{\text{III}}(\text{L}^1)\text{Cl}](\text{O}_3\text{SCF}_3)\}^+$  in the spectrum of **14**, and to a hydride species formulated as  $[(p\text{-cymene})\text{Ru}(\text{L}^3)(\text{H})]^+$  in the spectrum of **15**, arising by breaking of one C–H bond in the bridging methylene of the  $\text{N}_2$ -chelating ligand. Negative ESI-MS spectra of **14** and

**15** show two peaks, the first due to  $(\text{O}_3\text{SCF}_3)^-$  and the second to the aggregate species  $\{[\text{CF}_3\text{SO}_3]_2\text{Na}\}^-$ . The unique substitution of the external chloride in **14** and **15** is supported by the presence of the Ru–Cl stretching mode in their far-IR spectra and by the characteristic absorption in the  $1000\text{--}1200\text{ cm}^{-1}$  region, typical of a not coordinated  $(\text{O}_3\text{SCF}_3)^-$ .<sup>22</sup>

The positive ESI MS spectrum of **16** in MeCN exhibits the more intense signal at  $212.6\text{ m/z}$  assigned to  $[(p\text{-cymene})\text{Ru}(\text{L}^1)(\text{MeCN})]^{2+}$  species in accordance with complete chloride displacement.

**Intramolecular Characterization in Solution through NOE NMR Experiments.** The complexes **6**, **7**, and **14** were characterized in solution by mono- and bidimensional  $^1\text{H}$  NMR spectroscopies.  $^1\text{H}$ -NOESY spectrum of complex **14** (Figure 1) shows dipolar interactions between  $\text{CH}^{\text{up}}$  and resonances of cymene ligand and between proton 3 and cymene resonances (red arrows). Also dipolar interactions are present between  $\text{CH}^{\text{down}}$  and 5 protons (dark arrows). On the contrary,  $\text{CH}^{\text{up}}$  does not interact with 5, neither  $\text{CH}^{\text{down}}$  with cymene protons. These observations are consistent with the preferential presence in solution of the boat conformer illustrated in Figure 1. In this conformation the pyrazolyl rings are positioned far away from the encumbered cymene fragment. The same conformation of the metallacycle  $\text{M}(\text{N}=\text{N})_2\text{C}$  is observed in the solid state structures of complexes **1**, **3**, and **14**.

**NMR Interionic Structure in Solution. (a) PGSE Measurements.**  $^1\text{H}$  and  $^{19}\text{F}$ -PGSE NMR experiments were carried out for complexes **6**, **7**, and **14** in  $\text{CD}_2\text{Cl}_2$ , using tetrakis-(trimethylsilyl) silane (TMSS) as internal standard. PGSE measurements allowed the translational self-diffusion coefficients ( $D_t$ ) for both cationic ( $D_t^+$ ) and anionic ( $D_t^-$ ) moieties to be determined (Table 1). From the measured self-diffusion coefficients ( $D_t$ ), the average hydrodynamic radius ( $r_H$ ) of the diffusing particles were derived taking advantage of the Stokes–Einstein equation (4):

$$D_t = \frac{kT}{c\pi\eta r_H} \quad (4)$$

where  $k$  is the Boltzman constant,  $T$  is the temperature,  $c$  is a numerical factor, and  $\eta$  is the solution viscosity (Table 1).  $D_t$  data were treated taking all the methodological precautions described in our recent paper.<sup>23</sup> From the average hydrodynamic radii of the aggregates, assumed to be spherical, their volumes ( $V_H^+$  and  $V_H^-$ ) were obtained (Table 1). The observed hydrodynamic sizes of anion and cation appear to be similar in all concentration ranges for all samples indicating that even intimate adducts are mainly present in solution. Although the observed  $V_H^\pm$  are significantly higher than the Van der Waals ( $V_{\text{vdw}}$ ) ones for ion pairs [ $V_{\text{vdw}}$  (**14**) =  $350\text{ \AA}^3$ ], the latter are reasonably predominant in  $\text{CD}_2\text{Cl}_2$  as observed for similar rhodium derivatives<sup>17</sup> and ruthenium diimine complexes.<sup>24</sup> We have recently seen that  $V_{\text{vdw}}$

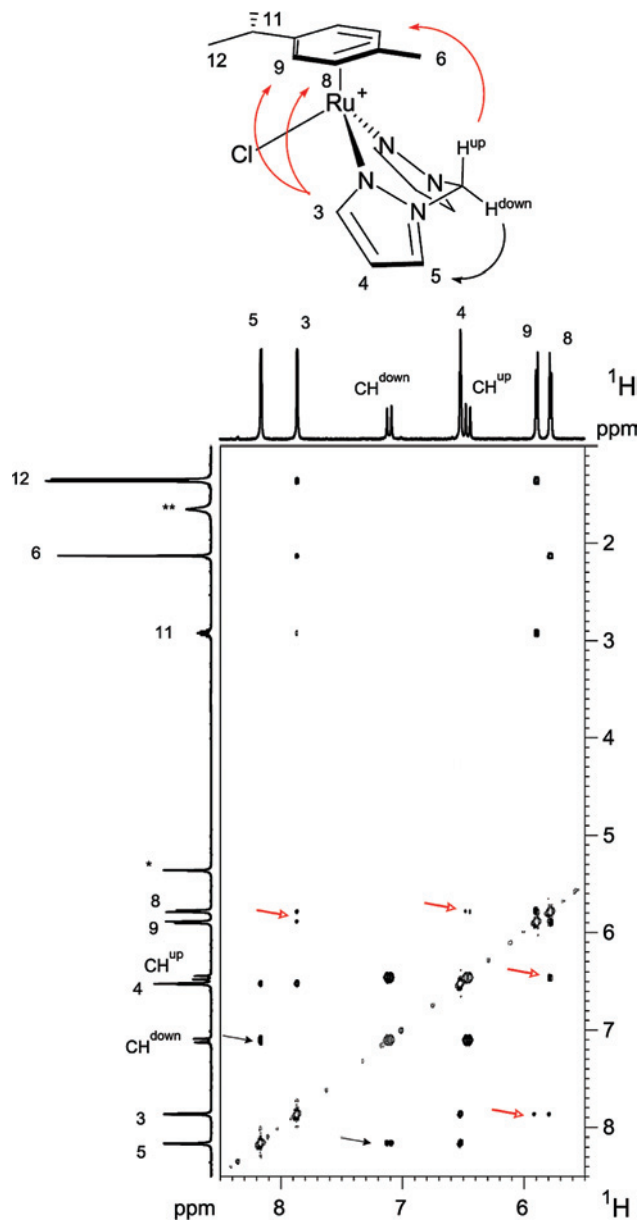
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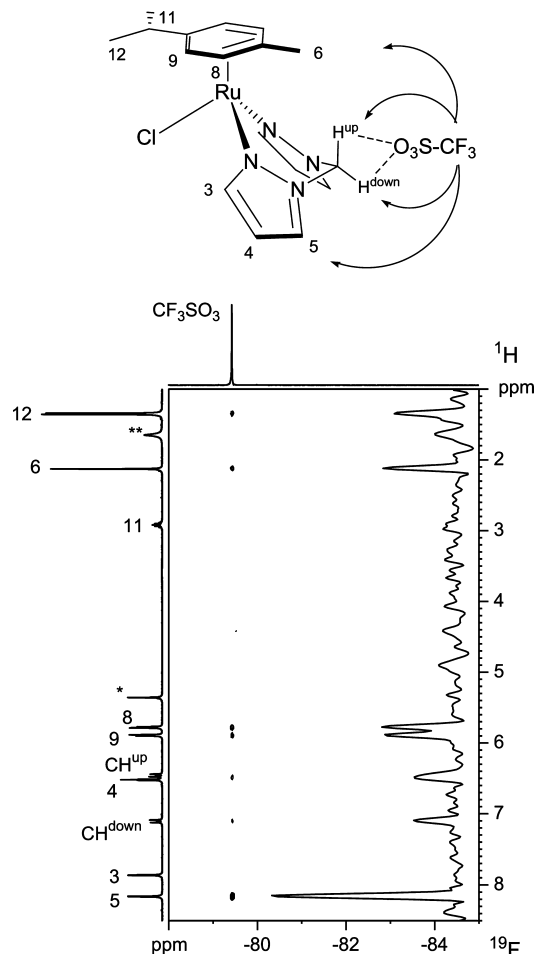


**Figure 1.** A section of the  $^1\text{H}$ -NOESY NMR spectrum (400.13 MHz, 296 K,  $\text{CD}_2\text{Cl}_2$ ) of the complex **14**. \* denotes the residue of non-deuterated solvent. \*\* denotes the  $\text{H}_2\text{O}$  resonance.

**Table 1.** Diffusion Coefficients ( $10^{10} D_t \text{ m}^2 \text{ s}^{-1}$ ), Hydrodynamic Radius ( $r_H$ , Å) and Hydrodynamic Volume ( $V_H$ , Å $^3$ ) for Complexes **6**, **7** and **14** in  $\text{CD}_2\text{Cl}_2$  ( $\epsilon_r$  at 25 °C is equal to 8.93) as a Function of Concentration (C, mM)

entry	$D_t^+$	$D_t^-$	$r_H^+$	$r_H^-$	$V_H^+$	$V_H^-$	C
<b>6</b>							
3	9.1	9.7	5.9	5.6	872	740	0.2
4	9.1	9.1	5.9	5.9	860	860	1
5	8.7	8.6	5.9	5.9	870	860	9
6	8.5	8.5	6.0	6.0	895	891	23
<b>7</b>							
7	9.1	9.5	5.9	5.7	840	760	0.2
8	8.8	9.2	6.0	5.7	890	790	2
9	8.8	8.8	5.9	5.9	880	880	4
10	8.6	8.6	6.0	6.0	900	900	20
<b>14</b>							
1	10.3	10.2	5.3	5.3	630	609	0.2
2	9.4	9.6	5.7	5.6	760	725	11

usually underestimates  $V_H$  by a factor that critically depends on the presence of inlets on the molecular surface.<sup>25</sup>



**Figure 2.**  $^{19}\text{F}$ ,  $^1\text{H}$ -HOESY NMR spectrum (376.65 MHz, 296 K,  $\text{CD}_2\text{Cl}_2$ ) of complex **14**. On the right the column projection is reported. \* denotes the residue of non-deuterated solvent. \*\* denotes the  $\text{H}_2\text{O}$  resonance.

**NMR Interionic Structure in Solution. (b) NOE Measurements.** The anion-cation relative orientation in solution for complex **14** was determined by detecting dipolar interionic interactions in the  $^{19}\text{F}$ ,  $^1\text{H}$ -HOESY NMR spectrum at room temperature (Figure 2). The derived data were treated taking into account that the volumes of the NOE cross peaks are proportional to  $(n_I n_S / n_I + n_S)$  where  $n_I$  and  $n_S$  are the number of equivalent I and S nuclei, respectively (Table 2).<sup>26</sup> In the  $^{19}\text{F}$ ,  $^1\text{H}$ -HOESY NMR spectrum, strong contacts were observed between F-atoms of the counterion and 5 resonance of the bis(pyrazolyl)methane ligand. Medium-size contacts were detected with cymene resonances (6, 8, 9, and 12) and the  $\text{CH}_{\text{up}}$  and  $\text{CH}_{\text{down}}$  resonances while the anion did not show any interaction with protons 4 and 3 of the bis(pyrazolyl)methane ligand. All these observations indicate that  $\text{CF}_3\text{SO}_3^-$  is located close to the  $\text{CH}_2$ -moiety between the two 5 protons (Figure 2), as previously observed for rhodium com-

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**Table 2.** Relative NOE Intensities Determined by Arbitrarily Fixing at 1 the Intensity of the NOE(s) between the Anion Resonances and 5 Resonances for Complex **14**

resonance	intensity
5	1
CH <sub>down</sub>	0.38
CH <sub>up</sub>	0.45
8 and 9	0.57
6	0.25
12	0.21
3	not detectable

**Table 3.** Selected Bond lengths (Å) and Angles (°) for **1**, **3**, and **14**

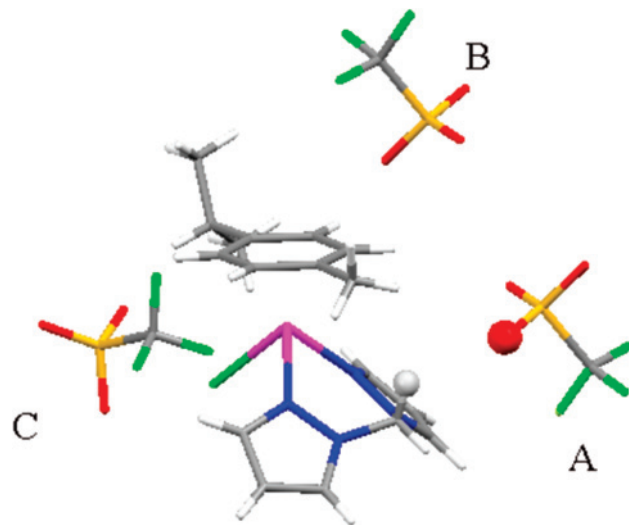
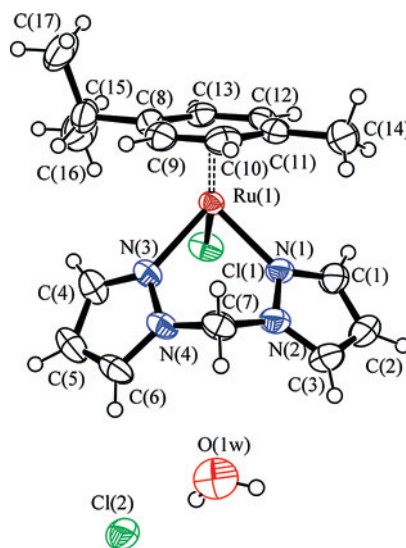
	<b>1</b>	<b>3</b>	<b>14</b>
Ru(1)–N(1)	2.103(1)	2.099(2)	2.103(2)
Ru(1)–N(3)	2.105(1)	2.101(2)	2.096(2)
Ru(1)–C(8)	2.212(2)	2.222(3)	2.219(2)
Ru(1)–C(9)	2.163(2)	2.172(3)	2.192(2)
Ru(1)–C(10)	2.197(2)	2.184(3)	2.176(2)
Ru(1)–C(11)	2.225(2)	2.204(3)	2.208(2)
Ru(1)–C(12)	2.192(2)	2.191(3)	2.188(2)
Ru(1)–C(13)	2.171(2)	2.193(3)	2.180(2)
Ru(1)–Cl(1)	2.4029(5)	2.3995(8)	2.4062(5)
Ru(1)–Cl(centroid)	1.679	1.679	1.679
N(3)–Ru(1)–N(1)	84.78(6)	83.13(9)	84.66(6)
N(3)–Ru(1)–Cl(1)	83.82(4)	85.42(6)	83.78(5)
N(1)–Ru(1)–Cl(1)	85.13(4)	85.95(8)	85.80(5)

plexes,<sup>17</sup> octahedral Ru(II),<sup>27</sup> and square-planar Pd(II) and Pt(II)<sup>28</sup> complexes. Standing in this position the anion can also interact with the resonances of the cymene ligand (Figure 2).

This single cation–anion orientation in solution, deduced by NOE studies, is in agreement with that observed in the solid state. In the solid state of complex **14** the cation is surrounded by three nearest anions (Figure 3). Two anions (**B** and **C** in Figure 3) are located close to the cymene moieties far away from the methylene protons of the nitrogen ligand; the other one (**A** in Figure 3) stays close to the methylene protons on the side of cymene undergoing an electrostatic interaction C–H<sup>δ+</sup>···O<sup>δ-</sup>. We suggest that position **A** is preferentially maintained in solution because of such electrostatic interaction.

For complex **6**, containing the [(*p*-cymene)RuCl<sub>3</sub>]<sup>+</sup> counterion, the <sup>1</sup>H-NOESY NMR spectrum does not show any interionic dipolar interactions between the cymene resonance of the anion and the cationic protons. This suggests that the [(*p*-cymene)RuCl<sub>3</sub>]<sup>+</sup> species approaches the cation orienting the three Cl-legs of the “piano-stool” toward the cation and, plausibly, toward the partially positive CH<sub>2</sub>-moiety<sup>17,27,28</sup> of the cation.

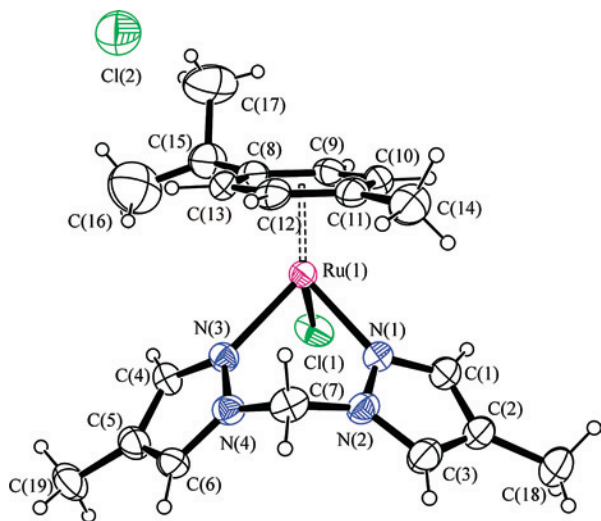
**X-ray Diffraction Studies.** The crystal structures of **1**, **3**, and **14** are shown in Figures 4–6. Complexes **1** and **14** differ from one another in the nature of the counterion which is Cl<sup>–</sup> in **1** and CF<sub>3</sub>SO<sub>3</sub><sup>–</sup> in **14**, respectively, whereas in the

**Figure 3.** Three relevant anion–cation orientations (A, B, C) found in the solid state for compound **14**. For orientation A the oxygen atom and the hydrogen atom of the CH<sub>2</sub> moiety involved in the electrostatic C–H<sup>δ+</sup>···O<sup>δ-</sup> interaction are represented in ball and stick.**Figure 4.** ORTEP drawing of complex **1**. Ellipsoids are drawn at the 50% probability level.

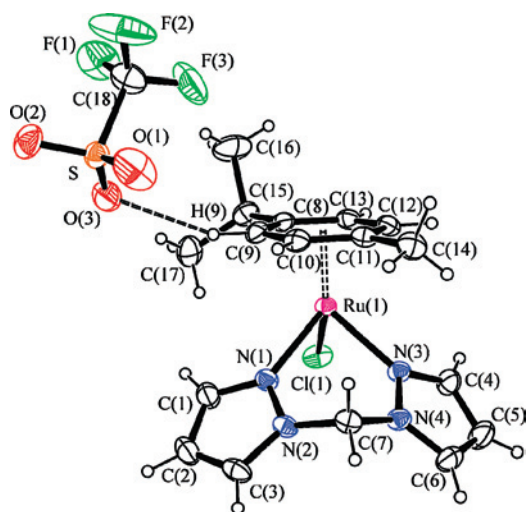
cation complex **3** the two pyrazolyl rings belonging to the bispyrazolylmethane ligand have methyl groups in 3 positions and the counterion is a chloride ligand as in **1**. The ruthenium atom has a distorted octahedral geometry with the η<sup>6</sup> bound arene ring of the *p*-cymene ligand occupying three facial sites, one chloride and a chelating bis(pyrazolyl)methane ligand. The Ru–C(*p*-cymene) average bond lengths are 2.193, 2.194, and 2.194 Å for **1**, **3**, and **14**, respectively [range: 2.163(2)–2.225(2) Å]. In all three cationic complexes the chelating bis(pyrazolyl)methane ligand gives rise to a six-membered metallacycle adopting a boat conformation (Figure 2) with the bite angle N(1)–Ru–N(3) of 84.78(6), 83.13(9), and 84.66(6)° for **1**, **3**, and **14**, respectively. The pyrazolyl rings make mutual dihedral angles of 51.67(8), 56.6(2), and 52.30(8)° for **1**, **3**, and **14**, respectively, being the largest angle in the cationic complex with the bulkier substituted pyrazolyl groups. The Ru–N bond lengths are almost identical [range 2.096(2)–2.105(1) Å] and the Ru–Cl

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**Figure 5.** ORTEP drawing of complex **3**. Ellipsoids are drawn at the 30% probability level.



**Figure 6.** ORTEP drawing of complex **14**. Ellipsoids are drawn at the 30% probability level.

distances fall in the narrow range 2.3995(8)–2.4062(5) Å. These values are in agreement with what it is usually observed in related compounds. Overall, the three cation complexes show only slight structural differences that can be ascribed also to crystal packing effects.

In the asymmetric unit of **1** a crystallization water molecule is located in the vicinity of one methylenic hydrogen [H(7a)] [H(7a)⋯Ow 2.33(1) Å; C(7)⋯Ow 3.262(3) Å; C(7)–H(7a)⋯Ow 161(1)°] thus establishing a weak hydrogen bond.

**Catalytic Studies.** Among the catalysts which have potential for use in selective oxidations, ruthenium takes a special position owing to its versatility. Compounds **1**, **6**, and **16** were investigated as catalysts toward styrene oxidation by H<sub>2</sub>O<sub>2</sub> (see Experimental Section for details). All reactions were run with 1.0 mol % of Ru catalyst/substrate ratio. The preliminary tests (Table 5) show that compounds **1** and **16** are active in the homogeneous oxidation of styrene whereas compound **6** is inactive in the reaction conditions used (entries 3 and 10). Compound **16**, containing the dicationic fragment [(*p*-cymene)Ru(L<sup>1</sup>)(H<sub>2</sub>O)]<sup>2+</sup>, is more

effective than **1**, resulting in higher yields of styrene conversion. When the catalytic experiments were carried out in MeOH we have generally observed the formation of the two regional isomers 2-methoxy-1-phenyl-ethanol and 2-methoxy-2-phenyl-ethanol, as confirmed by gas-chromatography–mass spectrometry, likely arising from the oxirane ring-opening by MeOH.<sup>29</sup> Longer reaction times does not improve the yield of the conversion of styrene to 2-methoxy-1-phenyl-ethanol and 2-methoxy-2-phenyl-ethanol (entry 7). When the catalytic experiments have been carried out with a strong excess of H<sub>2</sub>O<sub>2</sub> (entry 8) the styrene conversion increases, but the reaction is less selective and formation of benzaldehyde, α-methoxyphenylacetic acid and methylbenzoate has been observed. On the other hand in acetone, when strong excess of H<sub>2</sub>O<sub>2</sub> has been employed, benzaldehyde is the unique product (entry 12). In this solvent higher amounts of Ru catalyst improves the styrene conversion only slightly (entry 13).

We have also recorded ESI-MS spectra of the solutions derived from the experiments carried out by using **16** as catalysts and MeOH as solvent, where we have detected two major species containing Ru fragments: the peak at 449 *m/e* (maximum of the isotopic cluster) well agrees with the calculated distribution expected for [Ru(cymene)(L<sup>1</sup>)(MeOH)(OOH)]<sup>+</sup>, possible intermediate in the H<sub>2</sub>O<sub>2</sub> activation, whereas the peak at 608 *m/e* could be assigned to a dinuclear species of composition {[Ru(cymene)]<sub>2</sub>⋯(O–O)(styrene)}<sup>+</sup>. These results, although not conclusive, evidenced the existence in solution of a ruthenium species containing coordinated cymene and pyrazolylalkane also in the drastic conditions employed in the catalytic test.

Further investigations are currently ongoing in our laboratory to optimize yields and conditions.<sup>30</sup>

## Conclusions

We have successfully synthesized a number of arene ruthenium(II) bis(pyrazolyl)methane complexes of formula [(arene)Ru(L')Cl]Cl, [(arene)Ru(L')Cl][(arene)RuCl<sub>3</sub>], [(*p*-cymene)Ru(L')Cl](O<sub>3</sub>SCF<sub>3</sub>) and [(*p*-cymene)Ru(L<sup>1</sup>)(H<sub>2</sub>O)][PF<sub>6</sub>]<sub>2</sub> that have been fully characterized by analytical and spectroscopic techniques. In particular ESI MS spectroscopy has been demonstrated an effective technique for the detection of the species existing in solution. The interionic structure of [(*p*-cymene)Ru(L')Cl](O<sub>3</sub>SCF<sub>3</sub>) and [(*p*-cymene)Ru(L')Cl][(arene)RuCl<sub>3</sub>] was investigated through an integrated experimental approach based on NOE and PGSE NMR experiments in CD<sub>2</sub>Cl<sub>2</sub> as a function of the concentration. Preliminary catalytic experiments showed that [(*p*-cymene)Ru(L<sup>1</sup>)(H<sub>2</sub>O)][PF<sub>6</sub>]<sub>2</sub> is the most active species toward styrene oxidation by dihydrogen peroxide.

## Experimental Section

**Materials and Methods.** All chemicals were purchased from Aldrich (Milwaukee, WI) and used as received. All the reactions and manipulations were performed under dry nitrogen atmosphere

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**Table 4.** Crystal Data and Experimental Details for **1**·H<sub>2</sub>O, **3** and **14**

compound	<b>1</b>	<b>3</b>	<b>14</b>
formula	C <sub>17</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> Ru·H <sub>2</sub> O	C <sub>19</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>4</sub> Ru	C <sub>18</sub> H <sub>22</sub> ClF <sub>3</sub> N <sub>4</sub> O <sub>3</sub> RuS
fw	472.37	482.41	567.98
<i>T</i> , K	293(2)	293(2)	293(2)
$\lambda$ , Å	0.71073	0.71073	0.71073
crystal symmetry	monoclinic	monoclinic	monoclinic
space group	<i>C2/c</i> (No. 15)	<i>P2<sub>1</sub>/c</i> (No. 14)	<i>P2<sub>1</sub>/c</i> (No. 14)
<i>a</i> , Å	26.5531(9)	15.715(1)	7.4027(4)
<i>b</i> , Å	10.2129(3)	10.5640(7)	14.5879(8)
<i>c</i> , Å	14.9574(5)	14.3798(9)	20.7934(12)
$\alpha$ , °	90	90	90
$\beta$ , °	96.249(1)	106.996(1)	95.3380(10)
$\gamma$ , °	90	90	90
cell volume, Å <sup>3</sup>	4032.1(2)	2283.0(3)	2235.7(2)
<i>Z</i>	8	4	4
<i>D<sub>c</sub></i> , Mg m <sup>-3</sup>	1.556	1.404	1.687
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	1.055	0.930	0.966
<i>F</i> (000)	1920	984	1144
crystal size/ mm	0.15 × 0.18 × 0.25	0.16 × 0.28 × 0.38	0.23 × 0.27 × 0.33
$\theta$ limits, °	1.54–28.75	2.56–26.99	1.71–28.62
reflections collected	17213 ( $\pm h, \pm k, \pm l$ )	17898 ( $\pm h, \pm k, \pm l$ )	19112 ( $\pm h, \pm k, \pm l$ )
unique obs. reflections [ <i>F<sub>o</sub></i> > 4 $\sigma$ ( <i>F<sub>o</sub></i> )]	4714 [R(int) = 0.0163]	4823 [R(int) = 0.0271]	5370 [R(int) = 0.0192]
goodness-of-fit-on <i>F</i> <sup>2</sup>	1.065	1.001	1.073
<i>R</i> <sub>1</sub> ( <i>F</i> ) <sup>a</sup> , <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.0209, 0.0548	0.0328, 0.0889	0.0248, 0.0655
largest diff peak and hole, e Å <sup>-3</sup>	0.371 and -0.429	0.836 and -0.461	0.460 and -0.289

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2} \text{ where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP] \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

**Table 5.** Oxidation of Styrene with H<sub>2</sub>O<sub>2</sub> (in 1:5 Ratio) Using **1**, **6**, and **16** as Catalysts<sup>a</sup>

entry	catalyst	time [h]	solvent	products	conversion <sup>b</sup> mol%	selectivity <sup>c</sup> mol%
1	<b>1</b>	12	MeOH	2-methoxy-1-phenyl-ethanol	25	25
				2-methoxy-2-phenyl-ethanol		75
2	<b>1</b>	6	MeOH	2-methoxy-1-phenyl-ethanol	24	25
				2-methoxy-2-phenyl-ethanol		75
3	<b>6</b>	12	MeOH	2-methoxy-1-phenyl-ethanol		68
4	<b>16</b>	12	MeOH	2-methoxy-1-phenyl-ethanol	62	32
				2-methoxy-2-phenyl-ethanol		68
5	<b>16<sup>d</sup></b>	12	MeOH	2-methoxy-1-phenyl-ethanol	53	25
				2-methoxy-2-phenyl-ethanol		75
6	<b>16</b>	6	MeOH	2-methoxy-1-phenyl-ethanol	54	30
				2-methoxy-2-phenyl-ethanol		70
7	<b>16</b>	24	MeOH	2-methoxy-1-phenyl-ethanol	52	26
				2-methoxy-2-phenyl-ethanol		74
8	<b>16<sup>d</sup></b>	12	MeOH	2-methoxy-1-phenyl-ethanol	67	52
				2-methoxy-2-phenyl-ethanol		1.5
				benzaldehyde		24
				methylbenzoate		4.5
				( <i>R</i> )-(-)- $\alpha$ -methoxyphenylacetic acid		18
9	<b>1</b>	12	MeCN			
10	<b>6</b>	12	MeCN			
11	<b>16</b>		MeCN			
12	<b>16</b>	12	acetone	benzaldehyde	34	>99
13	<b>16<sup>e</sup></b>	12	acetone	benzaldehyde	38	>99

<sup>a</sup> To a stirred mixture of styrene (0.25 mmol) and Ru catalyst (0.0025 mmol) in methanol (1.5 mL) was added as one portion aqueous hydrogen peroxide [0.121 g, 35% (w/w), 1.25 mmol] and the reaction mixture was stirred under nitrogen at ambient temperature for 12 h. <sup>b</sup> Determined by GLC analysis based on the starting styrene using an internal standard. <sup>c</sup> Determined by GLC analysis based on the converted styrene. <sup>d</sup> Aqueous hydrogen peroxide in strong excess [0.220 g, 35% (w/w), 2.05 mmol]. <sup>e</sup> 2.0 mol % of catalyst.

and solvents were degassed prior to use; however, the reaction can also be performed in the air, but the products will invariably contain one or two water molecules, likely dispersed in the solid lattice, as observed in the crystallographic studies (see below) carried out on single crystals of one derivative, obtained from slow evaporation of chloroforms solutions performed in air. Solvent evaporations were always carried out under vacuum using a rotary evaporator. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 torr). Elemental analyses (C, H, N) were performed in-house with a Fison Instrument 1108 CHNS-O Elemental analyzer. IR spectra were recorded from 4000 to 200 cm<sup>-1</sup> with a Perkin-Elmer System 2000 FT-IR instrument. <sup>1</sup>H, <sup>19</sup>F, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a VXR-300 Varian instrument operating at room temperature (300 MHz for <sup>1</sup>H, 75.5

MHz for <sup>13</sup>C and 282.2 MHz for <sup>19</sup>F). H and C chemical shifts ( $\delta$ ) are reported in parts per million (ppm) from SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C calibration by internal deuterium solvent lock). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m. One- and two-dimensional <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P NMR spectra were measured on Bruker DRX 400 spectrometers. Referencing is relative to TMS (<sup>1</sup>H and <sup>13</sup>C), CCl<sub>3</sub>F (<sup>19</sup>F), and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). NMR samples were prepared dissolving the suitable amount of compound in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub>. Melting points are uncorrected and were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus. The electrical conductivity measurements ( $\Lambda_m$ , reported as  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) of acetonitrile solutions of the complexes were taken with a Crison CDTM 522 conductimeter at room temperature. The positive and negative electrospray mass



spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent grade acetonitrile. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1.<sup>31</sup> Peaks containing ruthenium(II) ions are identified as the center of an isotopic cluster.

**Syntheses. [(*p*-cymene)Ru(L<sup>1</sup>)Cl]Cl (1).** [(Ru(*p*-cymene)Cl<sub>2</sub>)<sub>2</sub>] (0.306 g, 0.5 mmol) was dissolved in methanol (20 mL) and stirred 30 min, then L<sup>1</sup> (0.148 g, 1.0 mmol) was added to the red solution which immediately changed to orange. After 24 h stirring at room temperature the clear orange solution was evaporated to dryness and redissolved in diethyl ether (5 mL). Slow evaporation afforded a brown powder, which was washed with *n*-hexane and dried under reduced pressure and identified as derivative **1**. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmso. Yield 65%. Mp 158–160 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 129.3  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>17</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 44.94; H, 4.88; N, 12.33. Found: C, 44.62; H, 4.98; N, 12.05%. IR (nujol, cm<sup>-1</sup>): 3103m  $\nu$ (C<sub>arom</sub>-H), 1516m  $\nu$ (C=N + C=C), 465m, 445s, 418m, 399s  $\nu$ (Ru-C), 297s  $\nu$ (Ru-Cl), 247m  $\nu$ (Ru-N). <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$ , 1.26d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.04s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.83m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.01m (4H, AA'BB' spin system, <sup>4</sup>J<sub>AA'</sub>: 6.2 Hz, <sup>3</sup>J<sub>AB</sub>: 8.8 Hz, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.33dd (2H, H<sub>4</sub> of L<sup>1</sup>), 8.08d, 6.94d (2H, AX spin system, <sup>2</sup>J<sub>AX</sub>: 14.7 Hz, H<sub>2</sub>C- of L<sup>1</sup>), 7.72d (2H, H<sub>5</sub> of L<sup>1</sup>), 8.48d (2H, H<sub>3</sub> of L<sup>1</sup>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.6 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.5 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.8 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 63.6 (s, H<sub>2</sub>C- of L<sup>1</sup>), 83.8, 86.1, 101.0, 105.7 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 108.5 (s, C<sub>4</sub> of L<sup>1</sup>), 136.1 (s, C<sub>5</sub> of L<sup>1</sup>), 146.3 (s, C<sub>3</sub> of L<sup>1</sup>). ESI-MS (MeCN) (+): *m/z* (%) = 419 (100) [(*p*-cymene)Ru(L<sup>1</sup>)Cl]<sup>+</sup>, 873 (10) [(*p*-cymene)Ru(L<sup>1</sup>)Cl]<sub>2</sub>Cl<sup>+</sup>.

**[(*p*-cymene)Ru(L<sup>2</sup>)Cl]Cl (2).** Derivative **2** has been synthesized as for **1**. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmso. Yield 53%. Mp 166–167 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 108.0  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 49.41; H, 5.92; N, 10.98. Found: C, 49.11; H, 5.99; N, 11.12%.

**[(*p*-cymene)Ru(L<sup>3</sup>)Cl]Cl (3).** Derivative **3** has been synthesized as for **1**. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmso. Yield 73%. Mp 159–160 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 119.8  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>19</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 47.31; H, 5.43; N, 11.61. Found: C, 47.04; H, 5.60; N, 11.24%.

**[(*p*-cymene)Ru(L<sup>4</sup>)Cl]Cl (4).** Derivative **4** has been synthesized as for **1**. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmso. Yield 69%. Mp 127–130 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 124.1  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>19</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 47.31; H, 5.43; N, 11.61. Found: C, 47.44; H, 5.55; N, 11.50%.

**[(*p*-cymene)Ru(L<sup>5</sup>)Cl]Cl (5).** Derivative **5** has been synthesized as for **1**. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmso. Yield 76%. Mp 165–166 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 126.4  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>21</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 49.41; H, 5.92; N, 10.98. Found: C, 49.23; H, 5.98; N, 11.12%.

**[(*p*-cymene)Ru(L<sup>1</sup>)Cl][(p-cymene)RuCl<sub>3</sub>] (6).** [(*p*-cymene)RuCl( $\mu$ -Cl)]<sub>2</sub> (0.612 g, 1.0 mmol) was dissolved in methanol (20 mL) and stirred 30 min, then L<sup>1</sup> (0.148 g, 1.0 mmol) was added to the red solution which immediately changed to orange. After 24 h stirring at room temperature the clear orange solution was evaporated to

dryness and the residue extracted into chloroform (5 mL). Slow evaporation afforded a red-brown powder, which was washed with *n*-hexane and dried under reduced pressure. The powder was identified as derivative **6**. Yield 62%. Mp 191–193 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 134.2  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>27</sub>H<sub>36</sub>Cl<sub>4</sub>N<sub>4</sub>Ru<sub>2</sub>: C, 42.64; H, 4.77; N, 7.37. Found: C, 42.52; H, 4.85; N, 7.58%. IR (nujol, cm<sup>-1</sup>): 3111m, 3085m  $\nu$ (C<sub>arom</sub>-H), 1518m, 1505m  $\nu$ (C=C + C=N), 476w, 461m, 446w, 418m, 400w  $\nu$ (Ru-C), 288vs br (Ru-Cl), 254sh, 247s  $\nu$ (Ru-N). <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$ , 1.26d, 1.33d (12H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 1.98s, 2.27s (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.82m, 3.16m (2H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.37m (4H, AA'BB' spin system, <sup>4</sup>J<sub>AA'</sub>: 6.0 Hz, <sup>3</sup>J<sub>AB</sub>: 43.5 Hz, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.80m (4H, AA'BB' spin system, <sup>4</sup>J<sub>AA'</sub>: 5.2 Hz, <sup>3</sup>J<sub>AB</sub>: 7.8 Hz, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.29q (2H, H<sub>4</sub> of L<sup>1</sup>), 7.23dbr, 6.32dbr (2H, AX spin system, <sup>2</sup>J<sub>AX</sub>: 14.6 Hz, H<sub>2</sub>C- of L<sup>1</sup>), 7.64d (2H, H<sub>5</sub> of L<sup>1</sup>), 8.24d (2H, H<sub>3</sub> of L<sup>1</sup>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.7, 19.0 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.5 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.7, 31.0 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 67.1, 68.3 (s, H<sub>2</sub>C- of L<sup>1</sup>), 79.9, 81.9, 83.5, 86.2, 96.8, 100.8, 101.3, 105.5 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 108.3 (s, C<sub>4</sub> of L<sup>1</sup>), 136.8 (s, C<sub>5</sub> of L<sup>1</sup>), 145.8 (s, C<sub>3</sub> of L<sup>1</sup>). ESI-MS (MeCN) (+): *m/z* (%) = 419 (100) [(*p*-cymene)Ru(L<sup>1</sup>)Cl]<sup>+</sup>, 572 (85) [(*p*-cymene)Ru(L<sup>1</sup>)Cl]-RuCl(OH)]<sup>+</sup>. ESI-MS (MeCN) (-): *m/z* (%) = 341 (20) [(*p*-cymene)RuCl<sub>3</sub>]<sup>-</sup>.

**[(*p*-cymene)Ru(L<sup>2</sup>)Cl][(p-cymene)RuCl<sub>3</sub>] (7).** Derivative **7** has been synthesized as for **6**. Yield 64%. Mp 165–167 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 127.1  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>31</sub>H<sub>44</sub>Cl<sub>4</sub>N<sub>4</sub>Ru<sub>2</sub>: C, 45.59; H, 5.43; N, 6.86. Found: C, 45.34; H, 5.38; N, 6.77%.

**[(*p*-cymene)Ru(L<sup>3</sup>)Cl][(p-cymene)RuCl<sub>3</sub>] (8).** Derivative **8** has been synthesized as for **6**. Yield 67%. Mp 120 °C dec  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 123.0  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>29</sub>H<sub>40</sub>Cl<sub>4</sub>N<sub>4</sub>Ru<sub>2</sub>: C, 44.17; H, 5.11; N, 7.10. Found: C, 44.10; H, 5.05; N, 6.98%.

**[(*p*-cymene)Ru(pzH)<sub>2</sub>Cl]Cl (9).** Derivative **9** has been synthesized in an attempt to isolate a derivative of L<sup>4</sup> analogous to **6–8**, by stirring at reflux a methanol (20 mL solution of [(*p*-cymene)RuCl( $\mu$ -Cl)]<sub>2</sub> (0.612 g, 1.0 mmol) and L<sup>3</sup> (0.176 g, 1.0 mmol) for 24 h. Then the clear orange solution was evaporated to dryness and the residue extracted into chloroform (5 mL). Slow evaporation afforded a red-brown powder, which was washed with *n*-hexane and dried under reduced pressure and identified as derivative **9**. Yield 62%. Mp 128–130 °C.  $\Lambda_M$  (acetonitrile, 10<sup>-3</sup> M): 115.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Anal. Calcd. for C<sub>16</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 43.44; H, 5.01; N, 12.67. Found: C, 43.11; H, 5.14; N, 12.21%. IR (nujol, cm<sup>-1</sup>): 3439m br, 3260m br  $\nu$ (N-H), 3067m  $\nu$ (C<sub>arom</sub>-H), 1532m, 1508m  $\nu$ (C=N + C=C), 461m, 448m, 422m, 403m, 393m  $\nu$ (Ru-C), 293s  $\nu$ (Ru-Cl), 242s  $\nu$ (Ru-N). <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$ , 1.09d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 1.72s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.10m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.96mbr (4H, AA'BB' spin system, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.03t (2H, H<sub>4</sub> of pzH), 7.75d (2H, H<sub>5</sub> of pzH), 8.02d (2H, H<sub>3</sub> of pzH), 14.5br (2H, N-H of pzH).

**[(*p*-cymene)Ru(pzH)<sub>2</sub>Cl]BF<sub>4</sub> (10).** Derivative **10** has been synthesized by addition of an equivalent of AgBF<sub>4</sub> to a methanol solution of an equivalent of **9**, filtration to separate the precipitate silver chloride and elimination of solvent in a rotary evaporator. The crude product has been identified as **10**, and its analytical and spectral data are in accordance with those reported previously in the literature (see compound **19** in ref 18a).

**[(benzene)Ru(L<sup>2</sup>)Cl]Cl (11).** Derivative **11** has been synthesized similarly to **1**, by interaction of L<sup>2</sup> with [(benzene)RuCl( $\mu$ -Cl)]<sub>2</sub> in acetonitrile, the choice of solvent being dictated by solubility of the latter. It is very soluble in water, alcohols, chlorinated solvents,

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acetonitrile and dmsO. Yield 68%. Mp 238–242 °C.  $\Lambda_M$  (acetonitrile,  $10^{-3}$  M):  $120.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd. for  $\text{C}_{17}\text{H}_{22}\text{Cl}_2\text{N}_4\text{Ru}$ : C, 44.94; H, 4.88; N, 12.33. Found: C, 45.03; H, 4.96; N, 12.02%.

[(benzene)Ru(L<sup>3</sup>)Cl]Cl (**12**). Derivative **12** has been synthesized as for **1**. It is very soluble in water, alcohols, chlorinated solvents, acetonitrile and dmsO. Yield 79%. Mp 246–247 °C.  $\Lambda_M$  (acetonitrile,  $10^{-3}$  M):  $122.1 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd. for  $\text{C}_{15}\text{H}_{18}\text{Cl}_2\text{N}_4\text{Ru}$ : C, 42.26; H, 4.26; N, 13.14. Found: C, 41.98; H, 4.36; N, 13.01%.

[(benzene)Ru(L<sup>5</sup>)Cl][(benzene)RuCl<sub>3</sub>] (**13**). Derivative **13** has been synthesized as for **6**. It is soluble only in water and dmsO. Yield 80%. Mp 210 °C dec  $\Lambda_M$  (dmsO,  $10^{-3}$  M):  $66.8 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd. for  $\text{C}_{23}\text{H}_{28}\text{Cl}_4\text{N}_4\text{Ru}_2$ : C, 39.22; H, 4.01; N, 7.95. Found: C, 39.10; H, 3.91; N, 7.78%. IR (nujol,  $\text{cm}^{-1}$ ): 3064w  $\nu(\text{C}_{\text{arom}}-\text{H})$ , 1590w br  $\nu(\text{C}=\text{N} + \text{C}=\text{C})$ , 445m br, 414w, 377w, 361m  $\nu(\text{Ru}-\text{C})$ , 321s, 283s  $\nu(\text{Ru}-\text{Cl})$ , 256m  $\nu(\text{Ru}-\text{N})$ . <sup>1</sup>H (dmsO-*d*<sub>6</sub>):  $\delta$ , 0.48t, 0.99t (6H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 2.31q, 2.90q (4H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 5.95s, 6.15s (12H, C<sub>6</sub>H<sub>6</sub>), 6.74t (2H, H<sub>5</sub> of L<sup>5</sup>), 8.39d (2H, H<sub>5</sub> of L<sup>5</sup>), 8.52d (2H, H<sub>3</sub> of L<sup>5</sup>). <sup>1</sup>H (D<sub>2</sub>O):  $\delta$ , 0.46t br, 1.00t br (6H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 2.30q br, 2.79q br (4H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 5.76s br, 6.05s br, 6.15s br (12H, C<sub>6</sub>H<sub>6</sub>), 6.57br, 6.64br (2H, H<sub>5</sub> of L<sup>5</sup>), 8.10br, 8.15br (2H, H<sub>5</sub> of L<sup>5</sup>), 8.31br, 8.45br (2H, H<sub>3</sub> of L<sup>5</sup>). <sup>13</sup>C{<sup>1</sup>H} (dmsO-*d*<sub>6</sub>):  $\delta$ , 7.3, 8.4 (s, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 25.7 (s, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 84.8 (s, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C- of L<sup>5</sup>), 86.8, 87.6 (s, C<sub>6</sub>H<sub>6</sub>), 108.0 (s, C<sub>4</sub> of L<sup>5</sup>), 135.9 (s, C<sub>5</sub> of L<sup>5</sup>), 151.0 (s, C<sub>3</sub> of L<sup>5</sup>).

[(*p*-cymene)Ru(L<sup>1</sup>)Cl](O<sub>3</sub>SCF<sub>3</sub>) (**14**). Compound **1** (0.227 g, 0.5 mmol) was dissolved in methanol (20 mL), then AgCF<sub>3</sub>SO<sub>3</sub> (0.128 g, 0.5 mmol) was added to the red solution. A colorless precipitate immediately afforded. After 1 h stirring at room temperature the reaction mixture was filtered off to remove the precipitate AgCl, the filtrate was evaporated to dryness and the residue extracted into chloroform (5 mL). Slow evaporation afforded a brown powder, which was washed with *n*-hexane and dried under reduced pressure and identified as **14**. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmsO. Yield 94%. Mp 177–180 °C.  $\Lambda_M$  (acetonitrile,  $10^{-3}$  M):  $131.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{22}\text{ClF}_3\text{N}_4\text{O}_3\text{RuS}$ : C, 38.06; H, 3.90; N, 9.86; S, 5.64. Found: C, 37.85; H, 4.03; N, 9.54; S, 5.88%. IR (nujol,  $\text{cm}^{-1}$ ): 3074w  $\nu(\text{C}_{\text{arom}}-\text{H})$ , 1538w, 1508m  $\nu(\text{C}=\text{N} + \text{C}=\text{C})$ , 1155s, 724s, 632s  $\nu(\text{SO}_3\text{CF}_3)$ , 458m, 450m, 420w, 404m  $\nu(\text{Ru}-\text{C})$ , 296s  $\nu(\text{Ru}-\text{Cl})$ , 265m, 236m  $\nu(\text{Ru}-\text{N})$ . <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$ , 1.32d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.10s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.87m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.89m (4H, AA'BB' spin system, <sup>4</sup>J<sub>AA'</sub>: 5.8 Hz, <sup>3</sup>J<sub>AB</sub>: 18.4 Hz, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.45dd (2H, H<sub>4</sub> of L<sup>1</sup>), 6.88m (2H, AB spin system, <sup>2</sup>J<sub>AB</sub>: 15.0 Hz, H<sub>2</sub>C- of L<sup>1</sup>), 7.80d (2H, H<sub>5</sub> of L<sup>1</sup>), 8.18d (2H, H<sub>3</sub> of L<sup>1</sup>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.5 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.4 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.9 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 63.5 (s, H<sub>2</sub>C- of L<sup>1</sup>), 84.0, 85.5, 100.6, 106.2 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 109.0 (s, C<sub>4</sub> of L<sup>1</sup>), 135.8 (s, C<sub>5</sub> of L<sup>1</sup>), 146.8 (s, C<sub>3</sub> of L<sup>1</sup>). ESI-MS (MeCN) (+): *m/z* (%) = 419 (100) [(*p*-cymene)Ru(L<sup>1</sup>)Cl]<sup>+</sup>, 567 (7) [(*p*-cymene)Ru(III)-(L<sup>1</sup>)Cl]CF<sub>3</sub>SO<sub>3</sub><sup>+</sup>. ESI-MS (MeCN) (-): *m/z* (%) = 149 (100) [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, 321 (62) [(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>Na]<sup>-</sup>.

[(*p*-cymene)Ru(L<sup>3</sup>)Cl](O<sub>3</sub>SCF<sub>3</sub>) (**15**). Derivative **15** has been synthesized as for **14**, by using derivative **3** and AgCF<sub>3</sub>SO<sub>3</sub>. It is very soluble in water, alcohols, chlorinated solvents, acetone, acetonitrile and dmsO. Yield 96%. Mp 181–182 °C.  $\Lambda_M$  (acetonitrile,  $10^{-3}$  M):  $123.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd. for  $\text{C}_{20}\text{H}_{26}\text{ClF}_3\text{N}_4\text{O}_3\text{RuS}$ : C, 40.30; H, 4.40; N, 9.40; S, 5.38. Found: C, 40.12; H, 4.33; N, 9.16; S, 5.46%. IR (nujol,  $\text{cm}^{-1}$ ): 3065w  $\nu(\text{C}_{\text{arom}}-\text{H})$ , 1534w, 1506m  $\nu(\text{C}=\text{N} + \text{C}=\text{C})$ , 1154s, 721s, 632s

$\nu(\text{SO}_3\text{CF}_3)$ , 452m, 440m, 418w, 402m  $\nu(\text{Ru}-\text{C})$ , 291s  $\nu(\text{Ru}-\text{Cl})$ , 254m, 243m  $\nu(\text{Ru}-\text{N})$ . <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$ , 1.33d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.06s (6H, C<sub>4</sub>-CH<sub>3</sub> of L<sup>3</sup>), 2.10s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.88m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.84m (4H, AA'BB' spin system, <sup>4</sup>J<sub>AA'</sub>: 5.8 Hz, <sup>3</sup>J<sub>AB</sub>: 18.1 Hz, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.44d, 6.95d (2H, AX spin system, <sup>2</sup>J<sub>AX</sub>: 14.6 Hz, H<sub>2</sub>C- of L<sup>3</sup>), 7.58d (2H, H<sub>5</sub> of L<sup>3</sup>), 7.90d (2H, H<sub>3</sub> of L<sup>3</sup>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 9.1 (s, C<sub>4</sub>-CH<sub>3</sub> of L<sup>3</sup>), 18.5 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.4 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 30.9 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 63.5 (s, H<sub>2</sub>C- of L<sup>3</sup>), 83.9, 85.5, 100.4, 106.1 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 119.0 (s, C<sub>4</sub> of L<sup>3</sup>), 134.5 (s, C<sub>5</sub> of L<sup>3</sup>), 147.7 (s, C<sub>3</sub> of L<sup>3</sup>). ESI-MS (MeCN) (+): *m/z* (%) = 447 (100) [(*p*-cymene)Ru(L<sup>3</sup>)Cl]<sup>+</sup>, 412 (18) [(*p*-cymene)Ru(L<sup>3</sup>)(H)]<sup>+</sup>. ESI-MS (MeCN) (-): *m/z* (%) = 149 (100) [CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup>, 321 (62) [(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>Na]<sup>-</sup>.

[(*p*-cymene)Ru(L<sup>1</sup>)(H<sub>2</sub>O)][PF<sub>6</sub>]<sub>2</sub> (**16**). Derivative **16** has been synthesized as for **14**, by using 1 equiv of **1** and 2 equiv of AgPF<sub>6</sub>. After 1 h stirring at room temperature the reaction mixture was filtered off to remove the precipitate AgCl, the filtrate was evaporated to dryness and the residue was extracted into chloroform (5 mL). Slow evaporation afforded a thick yellow paste, which was finally treated with 5 mL of water to give a yellow powder, which was dried under reduced pressure and identified as **16**. It is very soluble in alcohols, acetonitrile and dmsO and sparingly soluble in chlorinate solvents and water. Yield 85%. Mp 123–126 °C.  $\Lambda_M$  (acetonitrile,  $10^{-3}$  M):  $226 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Anal. Calcd. for  $\text{C}_{17}\text{H}_{24}\text{F}_{12}\text{N}_4\text{OP}_2\text{Ru}$ : C, 29.53; H, 3.50; N, 8.10. Found: C, 29.75; H, 3.65; N, 8.03%. IR (nujol,  $\text{cm}^{-1}$ ): 3638w, 3560–3450br (O–H), 3143w, 3079w  $\nu(\text{C}_{\text{arom}}-\text{H})$ , 1627br (O–H) 1523m  $\nu(\text{C}=\text{N} + \text{C}=\text{C})$ , 820vs, 759s (PF<sub>6</sub>). <sup>1</sup>H (CD<sub>3</sub>CN):  $\delta$ , 1.30d (6H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.12s (3H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 2.89m (1H, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 5.90m (2H, AB spin system, <sup>2</sup>J<sub>AB</sub>: 14.8 Hz, H<sub>2</sub>C- of L<sup>1</sup>) 6.11m (4H, AA'BB' spin system, <sup>4</sup>J<sub>AA'</sub>: 6.6 Hz, <sup>3</sup>J<sub>AB</sub>: 32.6 Hz, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 6.04t (2H, H<sub>4</sub> of L<sup>1</sup>), 6.67m (2H, H<sub>2</sub>O), 8.05d (2H, H<sub>5</sub> of L<sup>1</sup>), 8.13d (2H, H<sub>3</sub> of L<sup>1</sup>). <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>):  $\delta$ , 18.7 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 22.5 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 31.9 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 64.0 (s, H<sub>2</sub>C- of L<sup>1</sup>), 86.8, 87.6, 105.9, 111.2 (s, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-CH(CH<sub>3</sub>)<sub>2</sub>), 110.5 (s, C<sub>4</sub> of L<sup>1</sup>), 137.7 (s, C<sub>5</sub> of L<sup>1</sup>), 149.3 (s, C<sub>3</sub> of L<sup>1</sup>). <sup>19</sup>F (CD<sub>3</sub>CN):  $\delta$ , -74.0s [1], -72.1s [2]. (s ESI-MS (MeCN) (+): *m/z* (%) = 419 (12) [(*p*-cymene)Ru(L<sup>1</sup>)Cl]<sup>+</sup>, 403 (50) [(*p*-cymene)Ru(L<sup>1</sup>)F]<sup>+</sup>, 212.6 (10) [(*p*-cymene)Ru(L<sup>1</sup>)(MeCN)]<sup>+2</sup>, 192 (13) [(*p*-cymene)Ru(L<sup>1</sup>)]<sup>+2</sup>.

All spectroscopic IR and NMR data of derivatives **2–5**, **7–8**, and **11–12**, which are analogous to those of **1** and **6**, are available as Supporting Information.

**NOE Measurements.** The <sup>1</sup>H-NOESY<sup>32</sup> NMR experiments were acquired by the standard three-pulse sequence or by the PFG version.<sup>33</sup> Two-dimensional <sup>19</sup>F,<sup>1</sup>H-HOESY NMR experiments were acquired using the standard four-pulse sequence or the modified version.<sup>34</sup> The number of transients and the number of data points was chosen according to the sample concentration and to the desired final digital resolution. Semiquantitative spectra were acquired using a 2s relaxation delay and 800 ms mixing times.

**PGSE Measurements.** All the PGSE NMR measurements were performed at 296 K without spinning by using the standard stimulated echo pulse sequence<sup>35</sup> on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil.

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The dependence of the resonance intensity ( $I$ ) on a constant waiting time and on a varied gradient strength ( $G$ ) is described by eq 5:

$$\ln \frac{I}{I_0} = -(\gamma\delta)^2 D_t \left( \Delta - \frac{\delta}{3} \right) G^2 \quad (5)$$

where  $I$  = intensity of the observed spin echo,  $I_0$  = intensity of the spin echo without gradients,  $D_t$  = diffusion coefficient,  $\Delta$  = delay between the midpoints of the gradients,  $\delta$  = length of the gradient pulse, and  $\gamma$  = magnetogyric ratio.

The shape of the gradients was rectangular, their duration ( $\delta$ ) was 4–5 ms, and their strength ( $G$ ) was varied during the experiments. The semilogarithmic plots of  $\ln(I/I_0)$  vs  $G^2$  were fitted using a standard linear regression algorithm, and an  $R$  factor better than 0.99 was always obtained. Different values of  $\Delta$ , “ $nt$ ” (number of transients) and number of different gradient strengths ( $G$ ) were used for different samples.

The self-diffusion coefficient  $D_t$ , that is directly proportional to the slope of the regression line obtained by plotting  $\ln(I/I_0)$  vs  $G^2$  (eq 5), was estimated by measuring the proportionality constant, using a sample of HDO (5%) in  $D_2O$  (known diffusion coefficient in the range 274–318 K)<sup>36</sup> in the same exact condition as the sample of interest using TMSS as internal standard.  $D_t$  data were treated as described in the literature.<sup>23</sup>

The measurement uncertainty was estimated by determining the standard deviation of  $m$  by performing experiments with different  $\Delta$  values. Standard propagation of error analysis yielded a standard deviation of approximately 3–4% in the hydrodynamic radius and 10% in the hydrodynamic volumes.

**X-ray Structural Determinations.** The X-ray intensity data were measured on a Bruker SMART 2000 CCD area detector diffractometer for **1** and on a Bruker SMART Apex II CCD area detector diffractometer for **3** and **14**. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different  $\omega$  regions, and eventually refined against all data. For all crystals, a full sphere of reciprocal space was scanned by  $0.3^\circ\omega$  steps. The software SMART<sup>37</sup> was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program,<sup>37</sup> and an empirical absorption correction was applied using SADABS.<sup>38</sup> The structures were solved by direct

methods (SIR 97)<sup>39</sup> and subsequent Fourier syntheses and refined by full-matrix least-squares on  $F^2$  (SHELXTL),<sup>40</sup> using anisotropic thermal parameters for all non-hydrogen atoms. Crystals of complex **1** showed the presence of one crystallization water molecule in the asymmetric unit. In **3**, some disorder was detected for the chlorine anion which was refined over three sites yielding occupation factors of 80, 14 and 6%, respectively. All hydrogen atoms were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters,  $U(H) = 1.2 U_{eq}(C)$  [ $U(H) = 1.5 U_{eq}(C-Me)$ ], and allowed to ride on their carrier carbons. Crystal data and details of the data collection for all structures are reported in Table 4. Molecular graphics were generated using SCHAKAL<sup>41</sup> and Mercury.<sup>42</sup>

**General Procedure for catalytic Oxidation of Styrene by  $H_2O_2$ .** Styrene (0.25 mmol, 0.026 g) and **16** (0.0025 mmol, 0.0016 g) were dissolved in methanol (1.5 mL). Aqueous hydrogen peroxide [0.1214 g, 35% (w/w), 1.25 mmol] was then added as one portion and the reaction mixture was stirred under nitrogen at ambient temperature for 12 h. Then a small portion (20  $\mu$ L) of the resultant solution was diluted to 1 mL and analyzed by GC-MS. Control experiments without either the catalyst or  $H_2O_2$  were performed under identical conditions. An identical reaction procedure was performed also in acetone as solvent. The data obtained in both methanol and acetone by using compounds **1**, **6**, and **16** as catalysts are reported in Table 5.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of **1**, **3**, **14**, Figures 1S and 2S, IR and NMR data of compounds **2–5**, **7–8**, and **11–12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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