



## Ruthenium Aqua Complexes Supported by the Kläui Tripodal Ligand: Synthesis, Structure, and Their Application in Catalytic

## **C-H Oxidation in Water**

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#### Dedication ((optional))

Abstract: Water-soluble ruthenium(III) aqua complexes supported by the Kläui tripodal ligand  $[Co(\eta^5-C_5H_5){P(O)(OEt)_2}_3]^ (L_{OEt}^-)$  have been synthesized and structurally characterized, and their use as catalysts for C-H oxidation in water has been studied. The treatment of [Ru(L<sub>OEt</sub>)Cl<sub>2</sub>(MeCN)] with N-donor ligands afforded the adducts  $[Ru(L_{OEt})Cl_2(L)]$  (L =  $tBuNH_2$  (1), pyridine (2), imidazole (3)). Refluxing [Ru(LOEt)Cl2(MeCN)] in neat tBuNH2 gave the amidine complex [Ru(L<sub>OEt</sub>)Cl<sub>2</sub>{N(H)C(Me)NHtBu}] (4). Chloride abstraction of 1-3 with AgOTs (OTs = tosylate) in 1 M p-toluenesulfonic acid Ru<sup>Ⅲ</sup> afforded water-soluble the diaqua complexes [Ru(L<sub>OEt</sub>)(H<sub>2</sub>O)<sub>2</sub>(L)](OTs)<sub>2</sub> (L= *t*BuNH<sub>2</sub> (5), pyridine (6), imidazole (7)), 4 yielded whereas that for the triaqua complex  $[Ru(L_{OEt})(H_2O)_3](OTs)_2$  (8). The crystal structures of 4, 5, 7, and 8 have been determined. The reduction of 5 with Zn dust in D<sub>2</sub>O gave a diamagnetic Rull species, whereas that in MeCN led to isolation of the  $Ru^{II}$  acetonitrile complex  $[Ru^{II}(L_{OEt})(MeCN)_2(tBuNH_2)](PF_6)$  (9) that has been characterized by X-ray diffraction. The Ru<sup>III</sup> aqua complexes proved to be moderately efficient catalysts for C-H bond oxidation with tert-butyl hydroperoxide in water. For example, the oxidation of ethylbenzene with tert-butyl hydroperoxide in water at room temperature in the presence of 0.1 mol% of 8 afforded acetophenone in ca. 62% yield.

#### Introduction

Water is an ideal solvent for green chemical processes because it is non-toxic, non-flammable, and environmentally benign.<sup>[1]</sup> One advantage of using water as solvent for catalytic reactions is that organic products can be separated and isolated from the reaction mixture easily. Furthermore, it was reported that water can enhance the rate or selectivity of some types of organic reactions that are performed "on water".<sup>[2,3]</sup> In this regard, much effort has been made to synthesize water-soluble metal complexes and explore their catalytic activity in aqueous media.

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Of interest are Ru complexes that are capable of catalyzing a range of organic transformations, including oxidation, alkene isomerization, transfer hydrogenation, alkene metathesis, and cyclopropanation.<sup>[4]</sup> A vast majority of reported water-soluble Ru-based oxidation catalysts are supported by Ndonor ligands such as amines and pyridine and related Nheterocycles.<sup>[5]</sup> For example, Ru<sup>III</sup> complexes with 1,4,7trimethyl-1,4,7-triazacyclononane were found to be efficient catalysts for organic oxidations in aqueous media.<sup>[5b,5c,6]</sup> Yi et al. reported that the pyridine-oxazoline complex [(pymox-[pymox-Me<sub>2</sub> 4,4-dimethyl-2-(2- $Me_2)_2RuCl_2](BF_4)$ = pyridyl)oxazoline] can catalyze the oxidation of benzylic C-H bonds in water at ambient conditions.<sup>[7]</sup> By comparison, less attention has been paid to water-soluble Ru catalysts bearing Odonor ligands that are relevant to the aqua and hydroxo/oxo ligands in aqueous reaction environments.

The Ru aqua ion that contains an electron-rich metal center and labile aqua ligands has attracted attention owing to its interesting organometallic reactivity in aqueous media.<sup>[8]</sup> For example,  $[Ru(H_2O)_6]^{2+}$  has been used as a catalyst for isomerization of allylic compounds and ring-opening metathesis polymerization of cyclo-olefins.<sup>[9,10]</sup> Recently, Mon et al. reported that  $[Ru(H_2O)_6]^{3+}$  can catalyze the iminiation of alcohols but loses the catalytic activity rapidly owing to its instability under the catalytic conditions (90 °C). The catalytic activity of the Ru<sup>III</sup> aqua ion can be preserved upon immobilization of the complex on solid supports.<sup>[11]</sup>



Scheme 1. Structure of the Kläui tripodal ligand LOEt.

To develop robust oxygen-based Ru catalysts, we sought to synthesize Ru aqua complexes supported by chelating oxygen ligands. Specifically, Ru aqua complexes containing hydrolytically stable Kläui tripodal ligand  $[Co(\eta^{5}-C_5H_5)\{P(O)(OEt)_2\}_3]^-$  (LoEt\*, Scheme 1)<sup>[12]</sup> were synthesized. Previous studies have shown that the  $\{RuL_{OEt}\}$  core is compatible with a variety of hydrocarbyl ligands, including alkynyl, carbene, vinylidene, allenylidene;<sup>[13]</sup> however, very few Ru-LoEt aqua complexes have been reported. Power et al.

synthesized the oxo-bridged dinuclear  $Ru^{IV}$  aqua complex  $[\{Ru(L_{OEt})(H_2O)\}_2(\mu-O)_2]^{2+}$  from  $[RuO_4]$  and  $NaL_{OEt}$  in  $H_2SO_4$ . Deprotonation of  $[\{Ru(L_{OEt})(H_2O)\}_2(\mu-O)_2]^{2+}$  gave a hydroxo species that was oxidized to a  $Ru^{\vee}$  oxo complex,  $[\{Ru(L_{OEt})(O)\}_2(\mu-O)_2]^{1/4]}$  Nevertheless, the aqueous chemistry of lower valent  $Ru-L_{OEt}$  aqua complexes has not been studied.

As our continuous effort to explore the catalytic chemistry of Ru in oxygen-rich ligand environments, we synthesized watersoluble Ru<sup>III</sup> aqua complexes [Ru(L<sub>OEI</sub>)(H<sub>2</sub>O)<sub>2</sub>(L)]<sup>2+</sup> and [Ru(L<sub>OEI</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup> by chloride abstraction of [Ru(L<sub>OEI</sub>)Cl<sub>2</sub>(L)] (L = N-donor ligand) in water. Reduction of the Ru<sup>III</sup>-L<sub>OEt</sub> aqua complexes with Zn to afford Ru<sup>II</sup> solvento complexes has been studied. The catalytic performance of the Ru<sup>III</sup> aqua complexes in aqueous phase C-H bond oxidation with *tert*-butyl hydroperoxide has been investigated.

#### **Results and Discussion**

#### Synthesis of [Ru(LOEt)Cl2(L)] complexes

reported previously, the acetonitrile ligand in As [Ru(L<sub>OEt</sub>)Cl<sub>2</sub>(MeCN)] can be substituted by N-donor ligands easily.<sup>[15]</sup> Thus, the treatment of [Ru(L<sub>OEt</sub>)Cl<sub>2</sub>(MeCN)] with 1 equivalent of N-donor ligand L in tetrahydrofuran (THF) at reflux followed by column chromatography afforded air-stable  $[Ru(L_{OEt})Cl_2(L)]$  (L = tBuNH<sub>2</sub> (1), pyridine (2), imidazole (3)) in ca. 80% yield (Scheme 2). Complexes 1-3 are soluble in common organic solvents except hexanes. The IR spectrum of 1 displayed two  $\nu(\text{N-H})$  bands at 3222 and 3286  $\text{cm}^{\text{-1},[^{15}]}$  whereas a single v(N-H) band at 3144 cm<sup>-1</sup> was found for **3**.



## $\label{eq:scheme 2. Syntheses of Ru-LoEt complexes with N-donor, aqua and acetonitrile ligands.$

On the other hand, refluxing [Ru(LOEt)Cl2(MeCN)] in neat tBuNH<sub>2</sub> afforded the amidine complex  $[Ru(L_{OEt})Cl_2{N(H)C(Me)NHtBu}]$  (4) instead of the amine adduct. Complex 4 is soluble in common organic solvents including hexanes. The IR spectrum of 4 showed two bands at 3312 and 3379 cm<sup>-1</sup> that are tentatively assigned as the N-H stretches of the amide and imine groups, respectively. The amidine group was apparently formed by the nucleophilic attack of the MeCN ligand by tBuNH<sub>2</sub>. The formation of amidine ligands from metal nitrile complexes is well documented.<sup>[16]</sup> The Ru<sup>III</sup> center in [Ru(L<sub>OEt</sub>)Cl<sub>2</sub>(MeCN)] is believed to act as a Lewis acid, facilitating the nucleophilic attack of the nitrile ligand. A similar pathway has been proposed for the formation of  $[W(NtBu)_{2}{N(H)C(Me)NHtBu}(C_{2}B_{9}H_{11})]$ from  $[W(NtBu)_2(NHtBu)(C_2B_9H_{11})]$ .<sup>[17]</sup> Also, solvolysis of  $[RuCl_3(Hind)_2(H_2O)]$  (Hind = indazole) in MeCN afforded [RuCl<sub>3</sub>(Hind){HN=C(Me)ind}] that further reacted with MeCN to vield the bis(amidine) complex [RuCl<sub>2</sub>{HN=C(Me)ind}<sub>2</sub>]Cl.<sup>[18]</sup>

The crystal structure of **4** is shown in Figure 1. The Ru center is bonded to three P=O groups, two chlorides and the imino group of the amidine ligand in a *pseudo* octahedral coordination geometry. The average Ru-O (2.081 Å) and Ru-Cl (2.331 Å) distances in **4** compare well with those in [Ru(L<sub>OEt</sub>)Cl<sub>2</sub>(MeCN)] (2.074 and 2.327 Å, respectively).<sup>[15]</sup> The Ru-N distance of 2.024(3) Å is similar to that in [RuCl<sub>2</sub>{HN=C(Me)ind}<sub>2</sub>]Cl (2.043(3) Å).<sup>[18]</sup> The N(1)-C(31) (1.310(5) Å) and N(2)-C(31) (1.334(5) Å) distances of the amidine ligand in **4** are quite similar, and the N(1), N(2) and C(31) atoms are approximately coplanar, indicative of Conjugation in the N(1)-C(31)-N(2) unit.



Figure 1. Molecular structure of 4. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths [Å] and angles [°]: Ru-O(L\_{OEI}) 2.070(2)-2.092(2), Ru-Cl 2.3300(8) and 2.3328(9), Ru-N(1) 2.024(3), N(1)-C(31) 1.310(5), N(2)-C(31) 1.334(5), N(2)-C(33) 1.476(5); C(31)-N(1)-Ru(1) 133.5(3), N(1)-C(31)-N(2) 118.3(3), N(1)-C(31)-C(32) 119.5(4), N(2)-C(31)-C(32) 122.2(4), C(31)-N(2)-C(33) 130.7(3).

#### Ru<sup>III</sup>-L<sub>OEt</sub> aqua complexes

Attempts to abstract the chloride ligands in 1-3 with Ag<sup>I</sup> salts such as AgOTs (OTs = tosylate) and AgOTf (OTf = triflate) in organic solvents such as tetrahydrofuran and CH<sub>2</sub>Cl<sub>2</sub> were unsuccessful. However, the chlorides in 1-3 can be removed with Ag<sup>I</sup> salts in acidic solutions readily. Thus, the treatment of 1 with 2 equivalents of AgOTs in 1 M p-toluenesulfonic acid at reflux afforded the Ru<sup>Ⅲ</sup> diaqua complex [Ru(L<sub>OEt</sub>)(H<sub>2</sub>O)<sub>2</sub>(*t*BuNH<sub>2</sub>)](OTs)<sub>2</sub> (5) in 80% yield (Scheme 2). Similarly,  $[Ru(L_{OEt})(H_2O)_2(L)](OTs)_2$  (L = pyridine (6), imidazole (7)) were synthesized from 2 and 3, respectively. Complexes 5-7 are air-stable in both the solid state and solution. They are soluble in both water and common organic solvents except hexanes.

Complexes 5 and 7 have been characterized by singlecrystal X-ray diffraction. The structures of the complex cations in 5 and 7 are shown in Figures 2 and 3, respectively; selected bond lengths are collected in Table 1. The geometry around the Ru center in 5 and 7 is *pseudo* octahedral with bond angles in the range of 84.00-97.60° and 87.13-92.39°, respectively. The average Ru-O(LOEt) bond distances in 5 and 7 are 2.035 Å and 2.031 Å, respectively (Table 1), which are slightly shorter than that in **1** (av. 2.074 Å).<sup>[15]</sup> The Ru-OH<sub>2</sub> bond distances in **5** (av. 2.034 Å) and 7 (av. 2.060 Å) are comparable to those of reported Ru<sup>III</sup> aqua complexes, e.g. [Ru(H<sub>2</sub>O)<sub>6</sub>](OTs)<sub>3</sub> (av. 2.029 Å),<sup>[19]</sup> [RuTp(OH)(H<sub>2</sub>O)<sub>2</sub>](OTf) (av. 2.075 Å) (Tp<sup>-</sup> - A = hydridotris(pyrazolyl)borate).<sup>[20]</sup> The Ru-N distance of 7 (2.023 Å) is similar to that in *trans*-[RuCl<sub>2</sub>(In)<sub>4</sub>]CI (In = indazole, av. 2.068 Å).<sup>[21]</sup>

By contrast, the treatment of **4** with 2 equivalents of AgOTs in 1 M *p*-toluenesulfonic acid at reflux led to the isolation of the triaqua complex  $[Ru(L_{OE1})(H_2O)_3](OTs)_2$  (**8**) in 85% yield. It seems likely that in *p*-toluenesulfonic acid, the amidine ligand in **8** is protonated to give the amidinium cation that can be easily dissociated from the Ru center. Similar to **5-7**, complex **8** is soluble in both water and common organic solvents except hexanes.

The structure of the complex cation in **8** is depicted in Figure 4. The complex features a *fac*-{Ru(H<sub>2</sub>O)<sub>3</sub>} fragment that is similar to that in [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>. The bond angles around the Ru center are in the range of 85.36-93.03°. The slight deviation from the ideal octahedral geometry can be attributed to the H-bonds between the coordinated aqua ligands and the TsO<sup>-</sup> anions. The average Ru-O(L<sub>OEt</sub>) and Ru-O(H<sub>2</sub>O) distances in **8** are 2.017 and 2.049 Å, respectively (Table 1). By comparison, the average Ru-O distance in [Ru(H<sub>2</sub>O)<sub>6</sub>](OTs)<sub>3</sub> is 2.029 Å.<sup>[19]</sup>

| (5), imidazole (7), H <sub>2</sub> O (8)). |          |          |           |
|--|----------|----------|-----------|
|  | 5        | 7        | 8         |
| Ru-O(trans to L)                           | 2.070(2) | 2.027(3) |           |
| Ru-O( <i>cis</i> to L)                     | 2.028(3) | 2.037(3) | av. 2.017 |
|  | 2.006(2) | 2.028(3) |           |
| Ru-OH <sub>2</sub>                         | 2.041(2) | 2.042(3) | av. 2.049 |

**Table 1.** Selected bond lengths [Å] for  $[Ru(L_{OEt})(H_2O)_2(L)](OTs)_2$  (L =  $tBuNH_2$ (5) imidazole (7) H<sub>2</sub>O (8))



Figure 2. Structure of the complex cation in 5. Hydrogen atoms except those of the  $BuNH_2$  and aqua ligands are omitted for clarity. The ellipsoids are drawn at 30% probability level.



**Figure 3.** Structure of the complex cation in **7**. Hydrogen atoms except those of the aqua and imidazole ligands are omitted for clarity. The ellipsoids are drawn at 30% probability level.



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Figure 4. Structure of the complex cation in 8. Hydrogen atoms except those in the aqua ligands are omitted for clarity. The ellipsoids are drawn at 30% probability level.

#### **Reduction of 5**

Ru<sup>II</sup> aqua complexes are of interest because the Ru<sup>II</sup> aqua ion has been used as a catalyst for organic transformations in water.<sup>[8-10]</sup> Therefore, we sought to prepare Rull-LOEt aqua complexes by reduction of the Ru<sup>III</sup> precursors. The reduction of 8 with Zn dust in water under argon afforded a purple species. However, this purple complex is very water-soluble, rendering its extraction into organic solvents very difficult. Thus, the reduction of 5 that is more soluble in organic solvents was attempted. The Zn reduction of 5 in water under argon afforded a purple species that could be obtained as an air-sensitive, hygroscopic solid after extraction into CH<sub>2</sub>Cl<sub>2</sub> and precipitation with hexanes. The <sup>1</sup>H NMR spectrum of the red complex in D<sub>2</sub>O displayed sharp signals attributable to the  $L_{OEt}$  [ $\delta$  = 1.22 (m), 1.31 (m), 4.01 (m), 4.19 (m) and 5.22 (s) ppm] and  $tBuNH_2$  [ $\delta$  = 1.27 (s) ppm] ligands along with the resonances of the tosylate anion. The N-H signal of the tBuNH<sub>2</sub> ligand was not observed presumably owing to the rapid H/D exchange of the amine with water. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed resonances at  $\delta$  = 120 and 123 ppm that are typical for Ru<sup>II</sup>-L<sub>OEt</sub> complexes.<sup>[22]</sup> The NMR spectral data indicate that the Zn reduction of 5 afforded a diamagnetic Ru<sup>II</sup> aqua species, presumably  $[Ru(L_{OEt})(tBuNH_2)(H_2O)_2]^+$ . Unfortunately, despite many attempts, we were not able to crystallize this air-sensitive Rull aqua complex for structure determination.

To show that a Ru<sup>II</sup> complex was formed by Zn reduction of **5**, we attempted the reduction of **5** with Zn in MeCN in the presence of NH<sub>4</sub>PF<sub>6</sub>, which led to the isolation of the Ru<sup>II</sup> solvento complex [Ru(L<sub>OEt</sub>)(MeCN)<sub>2</sub>(*t*BuNH<sub>2</sub>)](PF<sub>6</sub>) (**9**). The <sup>1</sup>H NMR spectrum of **9** in (CD<sub>3</sub>)<sub>2</sub>CO displayed sharp signals attributable to the L<sub>OEt</sub> and *t*BuNH<sub>2</sub> ligands along with a singlet at  $\delta$  = 2.80 ppm due to the coordinated MeCN ligands.

Complex 9 has been characterized by X-ray diffraction. The structure of the complex cation in **9** is depicted in Figure 5. The Ru-O(L<sub>OEt</sub>) distances (av. 2.105 Å) are slightly longer than those of the Ru<sup>III</sup> complexes **4**, **5** and **7** (2.006(2)-2.070(2) Å). The Ru-NCMe distance (1.971(3) Å) in **9** is shorter than the those in [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(MeCN)<sub>3</sub>]<sup>+</sup> (av. 2.083 Å)<sup>[23]</sup> and [RuTp(MeCN)<sub>3</sub>]<sup>+</sup> (av. 2.045 Å),<sup>[24]</sup> indicating that there is strong back-bonding between the acetonitrile ligands and the Ru<sup>III</sup> center. Accordingly, the C-N distances of the acetonitrile ligands in **9** (av. 1.142 Å) are slightly longer than those in [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(MeCN)<sub>3</sub>]<sup>+</sup> (av. 1.131 Å)<sup>[23]</sup> and [RuTp(MeCN)<sub>3</sub>]<sup>+</sup> (av. 1.124 Å) are slightly longer than those in [Ru( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(MeCN)<sub>3</sub>]<sup>+</sup> (av. 1.131 Å)<sup>[23]</sup> and [RuTp(MeCN)<sub>3</sub>]<sup>+</sup> (av. 1.124 Å)<sup>[24]</sup>. These results are consistent with the trend of donor strength of the 6-electron ligand Cp<sup>-</sup> < Tp<sup>-</sup> < L<sub>OEt</sub>·[<sup>24]</sup> The Ru-N distance of the *t*BuNH<sub>2</sub> ligand in **9** (2.106(3) Å) is comparable to those in the Ru<sup>III</sup> analogues **1** (2.109(9) Å) and **5** (2.100(3) Å).





Figure 5. Structure of complex cation in 9. Hydrogen atoms are omitted for clarity. The ellipsoids are drawn at 30% probability level. Selected bond lengths [Å] and angles [°]: Ru-O( $L_{OEI}$ ) av. 2.105, Ru-N(1) 2.106(3), Ru-N(2) 1.971(3), Ru-N(3) 1.971(3), N(1)-C(31) 1.494(4), N(2)-C(41) 1.143(4), N(3)-C(51) 1.141(4); C(31)-N(1)-Ru(1) 127.2(2), C(41)-N(2)-Ru(1) 174.4(3), C(51)-N(3)-Ru(1) 174.6(3).

#### Ru-catalyzed C-H oxidation in water

The catalytic activity of water-soluble Ru-LOEt aqua complexes in aqueous-phase oxidation of hydrocarbons has been studied. The Ru<sup>III</sup> agua complexes are capable of catalyzing C-H bond oxidation with tert-butyl hydroperoxide (TBHP) in water, and the results are summarized in Table 2. Among the Ru aqua complexes synthesized, the triaqua complex 8 appears to be the most active oxidation catalyst. For example, the oxidation of ethylbenzene with TBHP in water at room temperature with 0.1 mol% of 8 afforded acetophenone in 62% yield that is higher than those for the diaqua analogues 5-7 (ca. 25%) under the same conditions. Unlike ethylbenzene, the oxidation of cumene with 8 afforded a 12.5:1 mixture of the alcohol and ketone products with a total yield of ca. 81%. As expected, aliphatic hydrocarbons that possess stronger C-H bonds are more difficult to oxidize than for alkylbenzenes. The Ru-catalyzed oxidation of cyclohexane with TBHP afforded ca. 1:2 mixture of cyclohexanol and cyclohexanone with a total yield of 14%, whereas that of adamantane gave a ca. 3:1 mixture of 1- and 2-adamanantol with a total yield of 33%. The tertiary C-H bonds of adamantane were oxidized preferentially over the secondary ones owing to the lower C-H bond strength.

The possibility of using other terminal oxidants such as H<sub>2</sub>O<sub>2</sub> and cerium(IV) ammonium nitrate (CAN) for the Rucatalyzed C-H oxidation has been explored. Treatment of ethylbenzene and  $\mathbf{8}$  in water with  $H_2O_2$  led to immediate formation of a large amount of gas bubbles, presumably oxygen; however, no oxidation of ethylbenzene was found. Therefore it appears that  $\mathbf{8}$  is a catalyst for the decomposition of  $H_2O_2$  to oxygen, possibly via an Ru oxo or peroxo intermediate that cannot undergo oxo transfer to ethylbenzene. Additional work is required to elucidate the mechanism of 8-catalyzed decomposition of H<sub>2</sub>O<sub>2</sub>. Meanwhile, the addition of CAN to an aqueous solution of 8 led to transfer of the LOEt ligand from Ru to Ce, and formation of the known compound [Ce(L<sub>OEt</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>[25]</sup> along with an unidentified Ru-containing species. This result shows the high affinity of the electrophilic Ce<sup>IV</sup> ion for the oxygen tripod ligand.

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| Table 2. Ru-ca   | atalyzed C-H oxi            | dations with TB | HP in water <sup>[a]</sup> . |                                 |    |    |    |    |
|------------------|-----------------------------|-----------------|------------------------------|---------------------------------|----|----|----|----|
| Entry            | Substrate                   | Catalyst        | Time (h)                     | Product, % Yield <sup>[b]</sup> |    |    |    |    |
| 1                |                             | 5               | 16                           |                                 |    |    | 24 |    |
| 2                |                             | 6               | 16                           | 0                               |    |    | 25 |    |
| 3                |                             | 7               | 16                           |                                 |    | 25 |    |    |
| 4                |                             | 8               | 16                           |                                 |    |    | 62 |    |
| 5 <sup>[c]</sup> |                             | 8               | 16                           |                                 |    | 0  |    |    |
| 6                | $\mathbf{i} \in \mathbf{i}$ | 8               | 16                           | UH UH                           | 75 | 0  |    | 6  |
| 7                | $\bigcirc$                  | 8               | 64                           | OH                              | 4  |    |    | 10 |
| 8                |                             | 8               | 16                           | OH                              | 25 | Ā  | ОН | 8  |
| 9                |                             | 8               | 16                           | 0 2                             | ОН | 10 | o  | 85 |

<sup>[a]</sup> Catalytic conditions: catalyst (0.16 μmol), substrate (0.16 mmol), TBHP (58 μL, 5.5 M in decane, 0.32 mmol) in H<sub>2</sub>O (3 mL), 25 °C, under N<sub>2</sub>. <sup>[b]</sup> Product yield based on the substrate used was determined by GLC. <sup>[c]</sup> Addition of 1 equivalent of 2,6-di-*tert*-butyl-4-methylphenol.

The Ru-catalyzed oxidation of ethylbenzene with TBHP was completely quenched when radical scavengers such as 2,6di-*tert*-butyl-4-methylphenol was added to the reaction mixture, indicating that the catalytic reaction involves a radical intermediate. Therefore, we believe that the active species in the Ru-catalyzed oxidation is an alkylperoxo radical derived from TBHP, instead of a Ru=O complex. Accordingly, the Ru-catalyzed oxidation of cyclohexene with TBHP led to oxidation of the allylic C-H bonds and formation of cyclohexen-2-one as major product, instead of the epoxide. A possible mechanism for the Ru-catalyzed oxidation of ethylbenzene by TBHP is shown in Scheme 3.



Scheme 3. Possible mechanism for the Ru-catalyzed oxidation of ethylbenzene with TBHP.

#### Conclusions

In summary, we have synthesized water-soluble Ru<sup>III</sup>-L<sub>OEt</sub> aqua complexes by the chloride abstraction of  $[Ru(L_{OEt})(Cl)_2(L)]$  (L = N-donor ligand) with AgOTs in *p*-toluenesulfonic acid. Refluxing  $[Ru(L_{OEt})Cl_2(MeCN)]$  in neat  $tBuNH_2$  gave a Ru<sup>III</sup> amidine complex that is a precursor to a Ru<sup>III</sup> triaqua complex. Reduction of  $[Ru(L_{OEt})(tBuNH_2)(H_2O)_2]^{2+}$  with Zn in water and acetonitrile led to formation of Ru<sup>III</sup> aqua and acetonitrile complexes, respectively. The Ru<sup>IIII</sup> aqua complexes were found to be moderately efficient catalysts for C-H oxidation of hydrocarbons with TBHP in water, presumably via a radical intermediate(s). The investigation of the catalytic activity of water-soluble Ru-L<sub>OEt</sub> aqua complexes in other organic transformations in aqueous media is underway.

#### **Experimental Section**

**General:** All manipulations were carried out under dinitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled before usage. NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400 and 162 MHz for <sup>1</sup>H and <sup>31</sup>P, respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H), CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub> (<sup>19</sup>F) and H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), respectively. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental

analyses were performed by Medac Ltd., Surrey, UK. The compounds  $[Ru(L_{OEt})Cl_2(MeCN)]$  and  $[Ru(L_{OEt})Cl_2(tBuNH_2)]$  (1)<sup>[15]</sup> were prepared as described elsewhere. All other reagents were purchased from standard commercial sources and used without further purification.

Preparations of  $[Ru(L_{OEt})Cl_2(L)]$  (L = pyridine (2), imidazole (3)): These complexes were prepared according to a previously published method.<sup>[15]</sup> A solution of  $[Ru(L_{OEt})Cl_2(MeCN)]$  (100 mg, 0.134 mmol) and 1 equivalent of L (0.134 mmol) in tetrahydrofuran (8 mL) was refluxed overnight. The solvent was removed *in vacuo*. Column chromatography on silica using ethyl acetate/hexane as eluent afforded orange crystals. For **2**: Yield: 85 mg (81 %). IR (KBr, cm<sup>-1</sup>): 1380-1480 [v(C-N)]. C<sub>22</sub>H<sub>40</sub>Cl<sub>2</sub>CoNO<sub>9</sub>P<sub>3</sub>Ru (785.97) calcd. C 33.60, H 5.13, N 1.78; found C 33.60, H 5.08, N 1.76. For **3**: Yield: 75 mg (72 %). IR (KBr, cm<sup>-1</sup>): 3144 [v(N-H)], 1388-1484 [v(C-N)]. C<sub>20</sub>H<sub>39</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>9</sub>P<sub>3</sub>Ru (774.96) calcd. C 30.98, H 5.07, N 3.61; found C 31.07, H 5.05, N 3.55.

Preparation of [Ru(L<sub>0Et</sub>)Cl<sub>2</sub>{NHC(CH<sub>3</sub>)NH*t*Bu}] (4): A solution of 1 (100 mg, 0.134 mmol) in neat *tert*-butylamine (10 mL) was refluxed overnight. The solvent was removed *in vacuo*. Column chromatography on silica using ethyl acetate/hexane as eluent afforded red crystals. Yield: 85 mg (77 %). IR (KBr, cm<sup>-1</sup>): 3312, 3379 [v(N-H)]. C<sub>23</sub>H<sub>49</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>9</sub>P<sub>3</sub>Ru (821.04) calcd. C 33.63, H 6.01, N 3.41; found C 33.71, H 5.99, N, 3.43.

Preparation of  $[Ru(L_{OEI})(H_2O)_2(L)][OTS]_2$  (L = Bu'NH<sub>2</sub> (5), pyridine (6), imidazole (7)): A solution of  $[Ru(L_{OEI})Cl_2(L)]$  (0.102 mmol) and 2 equivalents of AgOTs (0.205mmol) in 1 M *p*-toluenesulfonic acid (20 mL) was refluxed overnight. The AgCl formed was filtered off and extracted with CH<sub>2</sub>Cl<sub>2</sub> and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.The volatiles were pumped off and washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane afforded yellow crystals. For **5**: Yield: 90 mg (81 %). IR (KBr, cm<sup>-1</sup>): 3143, 3228 [v(N-H)]. C<sub>35</sub>H<sub>64</sub>CoNO<sub>17</sub>P<sub>3</sub>RuS<sub>2</sub> (1088.12) calcd. C 38.64, H 5.93, N 1.29; found C 36.53, H 5.52, N, 1.11. For **6**: Yield: 85 mg (76 %). IR (KBr, cm<sup>-1</sup>): 1390-1477 [v(C-N)]. C<sub>36</sub>H<sub>56</sub>CoNO<sub>17</sub>P<sub>3</sub>RuS<sub>2</sub> (1094.07) calcd. C 39.53, H 5.34, N 1.28; found C 38.67, H 5.62, N 1.22. For **7**: Yield: 85 mg (76 %). IR (KBr, cm<sup>-1</sup>): 3120 [v(N-H)], 1389-1490 [v(C-N)]. C<sub>34</sub>H<sub>57</sub>CoN<sub>2</sub>O<sub>17</sub>P<sub>3</sub>RuS<sub>2</sub> (1083.07) calcd. C 37.71, H 5.31, N 2.59; found C 36.97, H 5.41, N 2.51.

**Preparation of [Ru(L**<sub>OEt</sub>)(H<sub>2</sub>**O**)<sub>3</sub>](**OTs**)<sub>2</sub>(8): A solution of **5** (80 mg, 0.097 mmol) and 2 equivalents of AgOTs (60 mg, 0.214 mmol) in 1 M *p*-toluenesulfonic acid (20 mL) was refluxed overnight. The AgCl formed was filtered off and extracted with CH<sub>2</sub>Cl<sub>2</sub> and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The volatiles were pumped off and washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane afforded yellow crystals. Yield: 85 mg (85 %). C<sub>31</sub>H<sub>55</sub>CoO<sub>18</sub>P<sub>3</sub>RuS<sub>2</sub> (1033.04) calcd. C 36.05, H 5.37; found C 35.57, H 4.35.

**Reduction of 5 with Zn in water:** A mixture of **5** (10 mg) and zinc dust (100 mg) in D<sub>2</sub>O (2 mL) was stirred at room temperature under argon for 5 min. The solution changed from yellow to purple gradually. NMR spectroscopy indicated that the purple species, which could be isolated as a solid upon extraction with CH<sub>2</sub>Cl<sub>2</sub> and precipitation with hexanes, is a diamagnetic complex, presumably a Ru<sup>II</sup> aqua complex. We have not

been able to obtain satisfactory elemental analysis for this purple complex owing to its air-sensitivity and hydroscopic nature.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, D<sub>2</sub>O):  $\delta$  = 1.22 (overlapping t, 12H, CH<sub>3</sub>), 1.27 (s, 9H, *t*Bu), 1.31 (t, 6H, CH<sub>3</sub>), 4.01 (m, 8H, CH<sub>2</sub>), 4.19 (m, 4H, CH<sub>2</sub>), 5.22 (s, 5H, Cp), 7.34 (d, 2H, OTs), 7.66 (d, 2H, OTs). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, D<sub>2</sub>O):  $\delta$  = 120.54 (m), 122.95 (m).

**Preparation of [Ru<sup>II</sup>(L**<sub>OEt</sub>)(MeCN)<sub>2</sub>(tBuNH<sub>2</sub>)](PF<sub>6</sub>) (9): A mixture of **5** (100 mg, 0.092 mmol) and Zn dust (500 mg) in acetonitrile (10 mL) was stirred overnight at room temperature. NH<sub>4</sub>PF<sub>6</sub> (15 mg, 0.092 mmol) was added and the mixture was stirred for 2 h. The solvent was removed in *vacuo*, and the residue was washed with hexane. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane afforded red crystals that were suitable for X-ray diffraction study. Yield: 75 mg (86 %). <sup>1</sup>H NMR [400 MHz, CDCl<sub>3</sub>, 25 °C, (CD<sub>3</sub>)<sub>2</sub>CO]: δ = 1.21 (s, 9H, *t*Bu), 1.26-1.32 (overlapping t, 18H, CH<sub>3</sub>), 2.80 (s, 9H, MeCN), 2.86 (br, 2H, NH<sub>2</sub>), 4.05-4.18 (m, 12H, CH<sub>2</sub>), 5.08 (s, 5H, Cp) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR [162 MHz, CDCl<sub>3</sub>, (CD<sub>3</sub>)<sub>2</sub>CO]: δ = 120.1 (s, L<sub>OEt</sub>), -144.41, (quintet, PF<sub>6</sub><sup>-</sup>) ppm. C<sub>25</sub>H<sub>52</sub>CoF<sub>6</sub>N<sub>3</sub>O<sub>9</sub>P<sub>4</sub>Ru (937.09) calcd. C 32.06, H 5.60, N 4.49; found C 31.85, H 5.45, N 4.58.

General procedure of the Ru-catalyzed C-H oxidation : A mixture of Ru aqua complex (0.16 µmol), hydrocarbon substrate (0.16 mmol) and TBHP (5.5 M in decane, 58 µL, 0.32 mmol) in water (3 mL) was stirred in air for 16-48 h in a 10 mL screw capped vial equipped with a magnetic stirring bar. The reaction mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The yields of the oxidized products were determined by GLC using bromobenzene as internal standard.

X-ray Crystallography: Crystallographic data and refinement details for complexes 4, 5, 7, 8 and 9 are listed in Table 3. The diffraction intensity data of complexes 4.8 and 9 were collected with a Rigaku GeminiTM Ultra X-ray Diffractometer with monochromatized Cu-K $\alpha$  radiation ( $\lambda$  = 1.54178 Å) at 173 K. The diffraction intensity data of complexes 5 and 7 were collected with a Rigaku GeminiTM Ultra X-ray Diffractometer with monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 298 and 173 K, respectively. Diffraction data of 4, 5, 7, 8 and 9 were collected and processed using the CrysAlisPro software (Rigaku, 2012). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all complexes were performed using the Olex2 software package<sup>[26]</sup> (which embedded SHELXTL<sup>[27]</sup>). All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F<sup>2</sup>. All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms expect noted separately. All the pictures of molecules were made using XP implemented in SHELXTL.<sup>[27]</sup> CCDC 1518063-1518067 contain the supplementary crystallography data for complexes 4, 5, 7, 8 and 9, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data\_request/cif.

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|                                       | 4   | 5                               | 7                    | 8                              | 9                  |
|---------------------------------------|---|---------------------------------|----------------------|--------------------------------|--------------------|
| Formula                               | C <sub>23</sub> H <sub>49</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>9</sub> P <sub>3</sub> Ru | $C_{35}H_{64}CoNO_{17}P_3RuS_2$ | C34H57C0N2O17 P3RuS2 | $C_{31}H_{55}CoO_{18}P_3RuS_2$ | C25H51C0F6N3O9P4Rt |
| Fw                                    | 821.45  | 1087.90                         | 1082.85              | 1032.78                        | 935.57             |
| Crystal system                        | Orthorhombic  | Monoclinic                      | Triclinic            | Monoclinic                     | Monoclinic         |
| Space group                           | P212121   | P21/n                           | P-1                  | P21/c                          | P21/c              |
| a (Å)                                 | 9.29600(10)   | 13.495(2)                       | 12.6505(3)           | 14.1735(2)                     | 12.6543(2)         |
| b (Å)                                 | 9.80870(10)   | 20.066(3)                       | 13.2608(4)           | 11.8583(2)                     | 19.6468(3)         |
| c (Å)                                 | 37.7852(3)  | 19.005(3)                       | 15.2470(4)           | 26.3816(4)                     | 16.1874(2)         |
| α, (°)                                | 90  | 90                              | 82.115(2)            | 90                             | 90                 |
| β, (°)                                | 90  | 104.503(2)                      | 83.070(2)            | 99.5550(10)                    | 94.3630            |
| γ, (°)                                | 90  | 90                              | 64.310(3)            | 90                             | 90                 |
| V (Å <sup>3</sup> )                   | 3445.32(6)  | 4982.5(14)                      | 2277.78(11)          | 4372.54(12)                    | 4012.79(10)        |
| Z                                     | 4   | 4                               | 2                    | 4                              | 4                  |
| $ ho_{calcd}$ (g cm <sup>-1</sup> )   | 1.584   | 1.450                           | 1.579                | 1.569                          | 1.549              |
| <i>T</i> (K)                          | 173   | 298                             | 173                  | 173                            | 173                |
| <i>F</i> (000)                        | 1692  | 2260                            | 1118                 | 2132                           | 1916               |
| $\mu$ (mm <sup>-1</sup> )             | 10.472  | 0.880                           | 0.963                | 8.304                          | 8.467              |
| No. of reflns                         | 19875   | 29898                           | 10420                | 27527                          | 24576              |
| lo. of indep reflns                   | 6091  | 10596                           | 8056                 | 8418                           | 7727               |
| Rint                                  | 0.0402  | 0.0509                          | 0.0415               | 0.0431                         | 0.0487             |
| GoF <sup>[a]</sup>                    | 1.006   | 1.011                           | 1.003                | 1.004                          | 1.002              |
| $1^{[b]}, WR_2^{[c]}(I > 2\sigma(I))$ | 0.0297, 0.0749  | 0.0519, 0.1178                  | 0.0507, 0.1092       | 0.0286, 0.0710                 | 0.0379, 0.0955     |
| R₁, wR₂ (all data)                    | 0.0305, 0.0756  | 0.0982, 0.1306                  | 0.0667, 0.1176       | 0.0309, 0.0727                 | 0.0446, 0.1006     |

#### Acknowledgments

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**Keywords:** Ruthenium • Aqua complex • Aqueous media • C-H oxidation

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Water-soluble ruthenium aqua complexes supported by the Kläui tripodal ligand have been synthesized and structurally characterized, and their application as catalysts for C-H oxidation of hydrocarbons in water has been studied.

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#### Aqua Complexes

Yat-Ming So, \* Kang-Long Wong, Herman H. Y. Sung, Ian D. Williams, and Wa-Hung Leung\*

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Ruthenium Aqua Complexes Supported by the Kläui Tripodal Ligand: Synthesis, Structure, and Their Application in Catalytic Oxidation in Water