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# Synthesis, Characterization, and Catalytic Hydrogenation Activity of New *N*-Acyl-Benzotriazole Rh(I) and Ru(III) Complexes in [bmim][BF<sub>4</sub>]

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**Abstract:** The hydrogenation activity of new *N*-acyl-benzotriazole Rh(I) and Ru(III) complexes in ionic liquid media is reported in this study. Both complexes were completely soluble in 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF<sub>4</sub>], and they were able to catalyze the hydrogenation of styrene and 1-octene. While ethylbenzene conversion in styrene hydrogenation reached 84% when the Ru complex was used, 100% conversion was obtained with the Rh complex at 393 K in 6 h. Additionally, total conversion in 1-octene hydrogenation reached 100% with the Rh complex in [bmim][BF<sub>4</sub>] media. The hydrogenation of styrene and 1-octene in dimethyl sulfoxide (DMSO) and toluene was also studied to compare the solvent effect on catalytic system. The effect of some catalytic parameters such as temperature, H<sub>2</sub> (g) pressure, and catalyst amount on the conversion was examined, and it was found that the conversion increased parallel to the increasing temperature and H<sub>2</sub> pressure. The recyclability of catalysts was also investigated, and it was revealed that the Rh complex in particular maintained the activity for at least 10 cycles.

**Keywords:** *N*-acyl-benzotriazole; ionic liquid; hydrogenation; catalysis; rhodium; ruthenium

## 1. Introduction

As a reaction media, organic solvents are main consumption inputs in synthetic chemistry. In a chemical reaction, decreasing, or if possible completely removing, the usage of organic solvents is an important goal of green chemistry. For this reason, scientists have discovered several alternatives to conventional reaction media. Among these, ionic liquids are coming into prominence for several of their properties such as thermal stability, low vapor pressure, non-flammability, and so on [1–3]. Ionic liquids (ILs) are non-molecular solvents with low melting points (<100 °C). They are able to dissolve apolar and polar organic, inorganic, and polymeric materials. Various organic reactions are successfully carried out in ionic liquids. Additionally, they are used as reaction media in reactions with transition metals such as oxidation [4,5], hydrogenation [6,7], hydroformylation [8,9], oligomerization [10,11], and so on [12,13]. Chauvin et al. performed the first hydrogenation reaction in ILs ([bmim][BF<sub>4</sub>] or [bmim][SbF<sub>6</sub>]) with [Rh(nbd)(Ph<sub>3</sub>P)<sub>2</sub>]PF<sub>6</sub> (nbd = norbornadiene) complex and reported a higher activity than that in acetone media [14].

Researchers have developed a wide range of metal complexes for use as a catalyst in ILs media. Heterocyclic compounds with at least one O, S, or N atom in the aromatic ring are attractive ligands for transition metal catalysis. Nitrogen containing molecules such as benzimidazole, benzotriazole, indole, and triazole can be coordinated to a metal center as mono-, bi-, ter-, and tetra-dentate ligands. One of these ligands is the 1H-benzotriazole (C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>) molecule, which is an aromatic heterocyclic compound made up of benzene and a triazole ring. The synthesis and catalytic application of

different benzotriazole metal complexes are reported in related literature. Verma et al. synthesized and characterized cheap and thermally stable benzotriazole derivative ligands and their palladium complexes and reported these complexes as efficient catalysts in C–C (Suzuki, Heck, Fujiwara–Moritani, Sonogashira), C–N, and C–S coupling reactions [15]. Das et al. synthesized and characterized 1-(phenylselenomethyl)-1H-benzotriazole (L<sub>1</sub>) and 1-(4-methoxyphenyltelluromethyl)-1H-benzotriazole (L<sub>2</sub>) ligands as well as their Pd(II) and Ru(II) complexes. They reported that both complexes are suitable for C–C coupling reactions (Heck and Suzuki–Miyaura) and catalytic oxidation of alcohols [16].

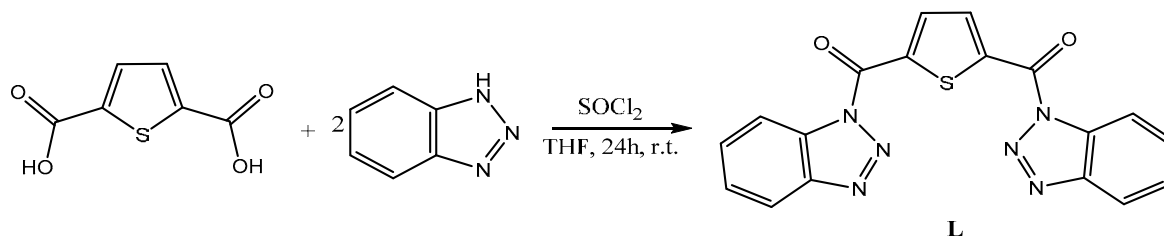
We herein describe the synthesis and characterization of new Rh(I) and Ru(III) complexes ([Rh(COD)L]Cl and [Ru(L)(H<sub>2</sub>O)Cl<sub>3</sub>]) including a *N*-acyl-benzotriazole ligand. We examined the catalytic activity of complexes in hydrogenation reactions in [bmim][BF<sub>4</sub>] used as reaction media. The effect of temperature, H<sub>2</sub> pressure, catalyst amount, and organic solvent on the catalytic activity of complexes was determined. In addition, the reusability of catalysts in styrene hydrogenation was investigated as well.

## 2. Results and Discussion

### 2.1. Characterization of Ligand and Complexes

#### 2.1.1. Ligand Characterization

Ligand (L) was obtained with a nucleophilic reaction between 1H-benzotriazole and thiophene-2,5-dicarboxylic acid (Figure 1). In the FT-IR spectrum of ligand, the O–H stretching vibration of thiophene-2,5-dicarboxylic acid at 3000–3100 cm<sup>−1</sup> disappeared after the reaction with benzotriazole. The carbonyl stretching vibration of free dicarboxylic acid shifted from 1662 to 1695 cm<sup>−1</sup>. Additionally, C=N stretching vibration in triazole ring was observed at 1368 and 1223 cm<sup>−1</sup> values (see Supplementary Materials, Figure S1).



**Figure 1.** Synthesis of *N*-acyl-benzotriazole ligand. (THF = Tetrahydrofuran, L = Ligand).

In the <sup>1</sup>H NMR spectra, thiophene protons were observed at  $\delta = 8.65$  ppm as a singlet peak. The doublet peaks at  $\delta = 8.46$  and 8.25 ppm and triplet peaks at  $\delta = 7.78$  and 7.62 ppm were associated with the benzotriazole moiety of the ligand. Due to its symmetrical nature, the ligand with 18 carbon atoms was observed to have nine carbon signals in its C NMR spectrum. The carbonyl carbons were observed at  $\delta = 159.02$  ppm, and the carbon atoms belonging to the thiophene ring were observed at  $\delta = 146.03$  and 137.2 ppm. The other carbons were observed to be between  $\delta = 141.7$  and 114.8 ppm.

#### 2.1.2. Rhodium Complex Characterization

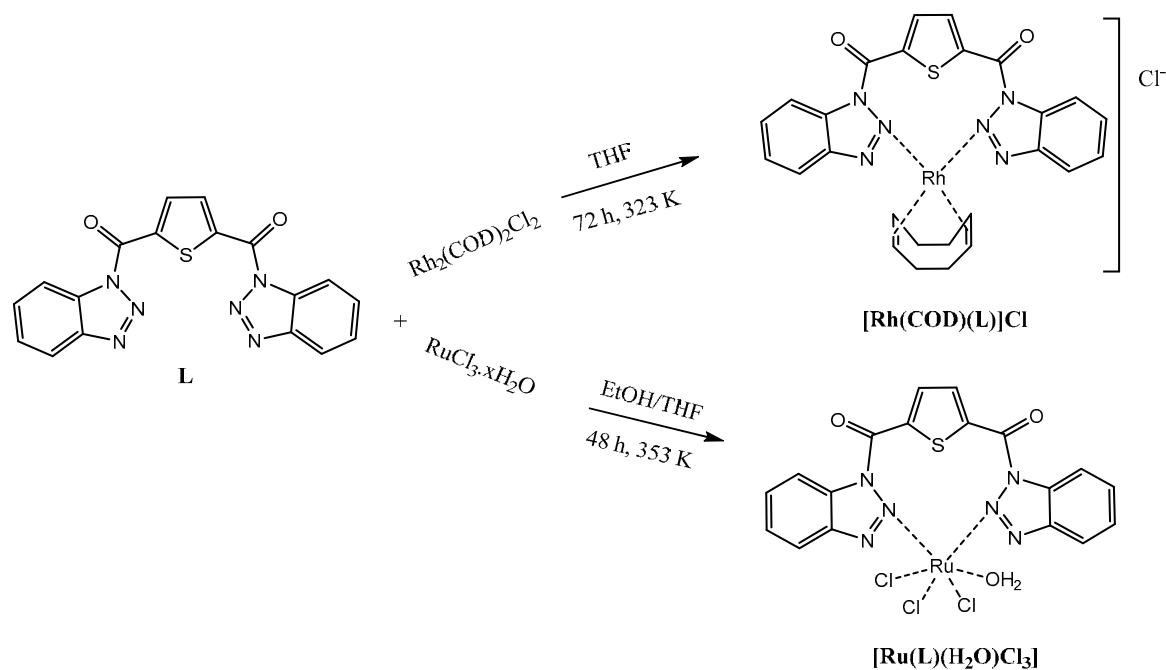
In the FT-IR spectra, the Rh–N stretching vibration was observed at 423 cm<sup>−1</sup> as a new peak, which indicated that the ligand coordinated to the metal center via the second nitrogen atom, N(2), of triazole moiety [17]. C=O and C–N vibrations of the ligand at 1689 and 1222 cm<sup>−1</sup> were also observed in complex spectrum (see Supplementary Materials, Figure S2).

In the <sup>1</sup>H NMR of the Rh complex, the singlet proton peak of thiophene shifted to  $\delta = 8.56$  ppm after the coordination to metal center. Two doublet peaks of benzotriazole shifted to  $\delta = 8.39$  ppm as a doublet of doublets. Additionally, two triplet peaks shifted to  $\delta = 7.89$  and 7.71 ppm in the complex

spectrum. The two new peaks observed at  $\delta = 4.26$  and  $2.14$  ppm are related to the 1,5-cyclooctadiene (COD) protons [18]. Additionally, the two singlet peaks at  $\delta = 3.62$  and  $1.76$  ppm are related to the solvent protons. The carbonyl (C=O) carbon signal was observed at  $159.13$  ppm, and the carbon atoms of the COD (cyclooctadiene) group were observed at  $127.59$  and  $27.93$  ppm. The other carbon signals appeared between  $145.8$  and  $115.01$  ppm.

In the UV-Vis spectrum of the ligand, the three absorption bands were observed at  $262$ ,  $281$ , and  $335$  nm, which could be attributed to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  intra-ligand charge transfer transitions. The spectrum of the Rh(I) complex displayed three absorption bands at  $252$ ,  $281$ , and  $329$  nm, which could be attributed to ligand metal charge transfer (LMCT) transitions. No  $d \rightarrow d$  transition was observed at  $200$ – $800$  nm.

The mass spectra of Rh(I) complex showed the molecular ion peaks at  $m/z$   $661.4$  and agree very well with the formula weights of the complex including the solvent (THF, tetrahydrofuran) molecule. This confirms the proposed structures of this complex as a 1:1; M/L complex (see Supplementary Materials, Figure S4). The magnetic susceptibility of the Rh complex was measured according to the Evans method and was found to be zero. This result indicated that the complex is diamagnetic ( $\mu_s = 0$ ) consistent with square planar geometry. Eventually, the possible structure of the Rh complex is suggested as in Figure 2.



**Figure 2.** Synthesis and possible structures of the complexes.

### 2.1.3. Ruthenium Complex Characterization

In the FT-IR spectrum of the Ru complex, the Ru–N stretching vibration was observed at  $434\text{ cm}^{-1}$ , which demonstrated that the ligand coordinated to the metal center via the nitrogen atom of the triazole moiety. The Ru–O stretching vibration was observed at  $450\text{ cm}^{-1}$  in the IR spectra, and the signal at  $4.95$  ppm in the  $^1\text{H}$  NMR spectra indicated that the aqua ligand coordinated to the metal center via the oxygen atom. Additionally, the carbonyl (C=O) and C–N stretching vibrations of the ligand were observed at  $1705$ ,  $1368$ , and  $1251\text{ cm}^{-1}$ , respectively (see Supplementary Materials, Figure S3).

In the  $^1\text{H}$  NMR spectra of the ruthenium complex, the aromatic proton signals of the thiophene moiety shifted from  $\delta = 8.65$  ppm to  $\delta = 7.73$  ppm, and the proton signals of the benzotriazole moiety shifted to higher frequencies ( $\delta = 7.93$  ppm and  $7.46$  ppm) after the M–L interaction. According to the literature, the singlet signal at  $\delta = 3.42$  ppm is dedicated to the aqua ligand in the complex structure [19].

In the  $^{13}\text{C}$  NMR spectra, the C=O group signals were observed at 162.85 ppm, and the other aromatic carbon signals appeared between 140.2 and 115.4 ppm.

In the UV-Vis spectrum of the Ru complex, three absorption bands were observed at 272, 362, and 532 nm in dimethyl sulfoxide (DMSO). The intensive band at 272 nm results from intramolecular  $\pi \rightarrow \pi^*$  transitions. Free ligand  $n \rightarrow \pi^*$  transitions shifted from 335 to 362 nm due to a nitrogen-metal charge transfer. Additionally, the  $d \rightarrow d$  transition of octahedral complex was observed at 532 nm.

Ru(III) complex showed the molecular ion peaks at  $m/z$  645.1. The calculated mass of Ru(III) complex was 644.9. The observed data were in good agreement with the proposed molecular formula that is  $[\text{Ru}(\text{L})(\text{H}_2\text{O})\text{Cl}_3]$ . In addition to the molecular ion peaks, the spectra exhibit other peaks assignable to various fragments arising from the thermal cleavage of the complexes (see Supplementary Materials, Figure S5). The magnetic susceptibility of the complex was measured as 1.26 BM, which means that d orbitals had one unpaired electron around the metal center ( $t_{2g}^5 e_g^0$ ) and that the complex geometry was octahedral.

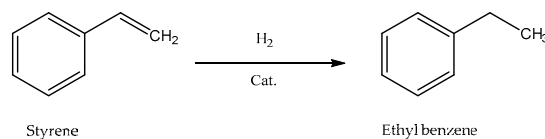
## 2.2. Hydrogenation Activity of Complexes

In order to investigate the solubility of complexes in IL media, 10 mg of catalyst and 1 mL of  $[\text{bmim}][\text{BF}_4]$  were put in a high-pressure reactor. The solubility of the catalyst was viewed through a sapphire window of the reactor. Both complexes were found to be homogeneously soluble in  $[\text{bmim}][\text{BF}_4]$  at certain pressures (10–60 bar) and at certain temperatures (323–393 K). In a typical hydrogenation reaction, catalyst, substrate, and IL were added to the reactor, and the reaction vessel was then purged with argon gas. The solution was heated to the reaction temperature, and  $\text{H}_2$  (g) was pressurized into the reactor. After the reaction, the products were extracted with hexane and analyzed with gas chromatography (GC).

### 2.2.1. Catalytic Activity of Rhodium Catalyst

The hydrogenation activity of the Rh complex was tested on two different substrates (styrene and 1-octene). The experimental results are presented in Tables 1 and 2. For the purpose of investigating the temperature effect on styrene hydrogenation, the experiments were performed at six different temperature values (Entries 1–6). The best ethyl benzene conversion was found to be 39.7% at 393 K in 1 h (Entry 6). When the reaction time was increased to 6 h, the conversion value reached 100% (Entry 7). In order to determine the solvent effect on the catalytic system, the experiments were also performed in DMSO and toluene under optimum reaction conditions (393 K, 10 bar  $\text{H}_2$ , 6 h). The total conversion reached 100% in toluene, but it was only 22.9% in DMSO (Entries 7–9). The results indicated that rhodium complex activity was found higher in toluene and ionic liquid than in DMSO. Because of these results, it can be stated that the potential coordination of DMSO molecules to the metal center changes the catalytic route and that the effectiveness of the catalyst thus decreases in DMSO media. In order to determine the  $\text{H}_2$  pressure effect on styrene hydrogenation, the catalytic reactions were conducted under 10-, 30-, and 60-bar pressures at 343 K in 1 h. The product conversion and turnover frequency (TOF) reached its highest value under 60-bar  $\text{H}_2$  (Entry 11).

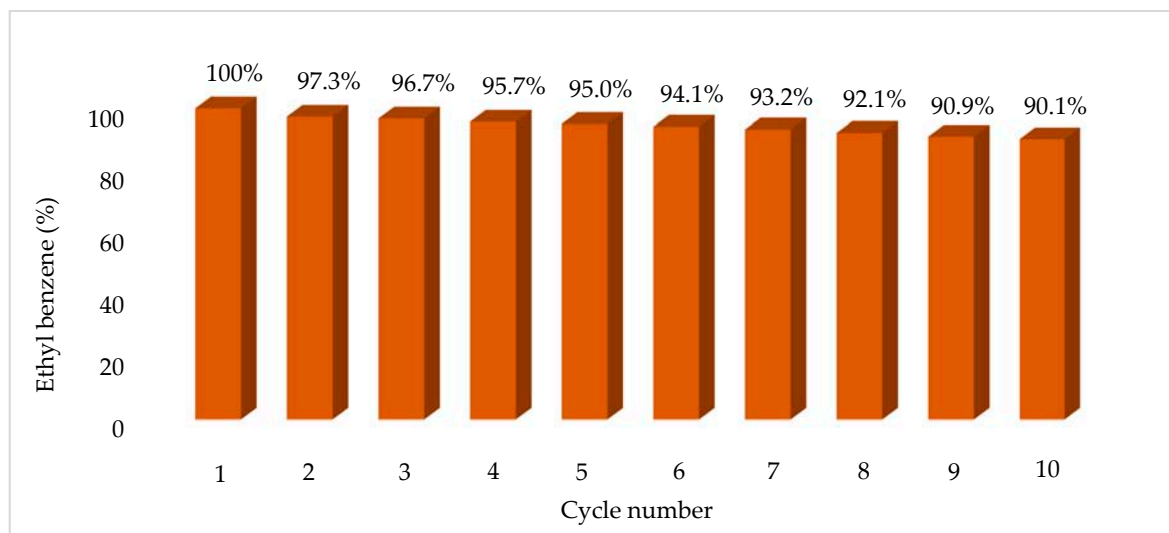
We studied three different  $n_s/n_c$  ratios to determine the effect of the catalyst amount at 393 K and 10-bar  $\text{H}_2$  on styrene hydrogenation. It was observed that the total conversion increased in line with the increasing catalyst amount and that the highest TOF value was obtained with a  $n_s/n_c$  ratio of 531 in 6 h (Entry 12). The results can be seen in Table 1.

**Table 1.** Styrene hydrogenation with [Rh(COD)L]Cl catalyst <sup>a</sup>. TOF (Turnover Frequency); TON (Turnover Number).

Entry	<i>T</i> (K)	<i>P</i> <sub>H<sub>2</sub></sub> (bar)	<i>t</i> (h)	<i>n</i> <sub>s</sub> / <i>n</i> <sub>c</sub>	Total Conversion (%)	TON	TOF
1	343	10	1	106	18.3	20	20
2	353	10	1	106	19.2	21	21
3	363	10	1	106	24.4	26	26
4	373	10	1	106	24.6	26	26
5	383	10	1	106	35.8	38	38
6	393	10	1	106	39.7	43	43
7	393	10	6	106	100	107	18
8 <sup>b</sup>	393	10	6	106	22.9	25	4
9 <sup>c</sup>	393	10	6	106	100	107	18
10	343	30	1	106	41.6	45	45
11	343	60	1	106	63.4	68	68
12	393	10	6	531	43.5	233	39
13	393	10	6	177	82.4	148	25
14 <sup>d</sup>	393	10	6	106	78.6	85	14

<sup>a</sup> Reaction conditions:  $n_{\text{cat.}} = 8.09 \times 10^{-6}$  mol,  $n_{\text{styr.}} = 8.69 \times 10^{-4}$  mol,  $V_{\text{solv.}} = 0.5$  mL,  $P_{\text{H}_2} = 10$  bar; <sup>b</sup> DMSO; <sup>c</sup> toluene; <sup>d</sup> cat. = [Rh<sub>2</sub>Cl<sub>2</sub>(COD)<sub>2</sub>].

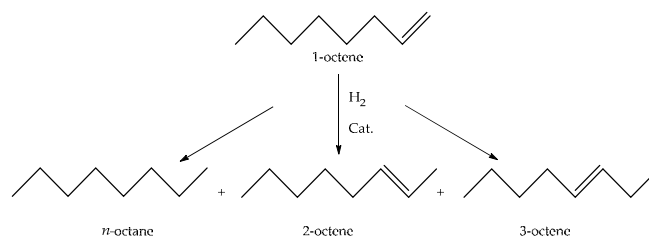
The reusability of the catalyst was also tested in styrene hydrogenation during the 10 cycles at 393 K and 10-bar H<sub>2</sub> pressure for 6 h. After the catalytic reaction, the substrate and product(s) were removed from the IL with *n*-hexane. Afterward, fresh substrate was added to the reaction media to operate the next cycle. Following 10 cycles, an approximate decrease of 10% was observed in the activity of the Rh catalyst. Figure 3 presents the results obtained from the recycle experiments.

**Figure 3.** Reusability of [Rh(COD)L]Cl catalyst in styrene hydrogenation. Reaction conditions: *T* = 393 K, *P*<sub>H<sub>2</sub></sub> = 10 bar,  $n_{\text{sub.}} = 8.69 \times 10^{-4}$ ,  $n_{\text{cat.}} = 8.09 \times 10^{-6}$  mol,  $n_s/n_c = 106$ , *t* = 6 h.

In order to evaluate the activity of the rhodium complex in 1-octene hydrogenation, catalytic experiments were performed at temperatures ranging from 323 to 383 K (Entries 1–7) under 10-bar H<sub>2</sub> pressure for 1 h (Table 2). It was found that the total conversion gradually increased in line with

the increasing temperature and reached 100% at 383 K (Entry 7). Additionally, the isomerization products of 1-octene were observed during these experiments. The distribution of the products can be seen in Table 2. The product distribution at 383 K consisted of 62.5% *n*-octane, 26.6% 2-octene, and 10.9% 3-octene, so selectivity to *n*-octane of catalyst was found to be higher compared with the other isomerization products. 1-octene hydrogenation reactions were also performed in DMSO and toluene. The total conversion was found to be 55.2% and 81.3% at 383 K in DMSO and toluene, respectively (Entries 8 and 9).

**Table 2.** 1-Octene hydrogenation with [Rh(COD)L]Cl catalyst <sup>a</sup>.



Entry	T (K)	Total Conversion (%)	Products (%)			TON	TOF
			( <i>n</i> -Octane)	(2-Octene)	(3-Octene)		
1	323	10.5	3.7	4.2	2.5	83	83
2	333	20.8	5.9	9.1	5.8	16	16
3	343	28.9	15.2	7.7	6.0	23	23
4	353	36.8	18.2	11.1	7.5	29	29
5	363	65.1	30.7	20.4	14.1	51	51
6	373	86.7	46.0	24.3	16.4	68	68
7	383	100	62.5	26.6	10.9	79	79
8 <sup>b</sup>	383	55.2	27.2	17.7	10.3	43	43
9 <sup>c</sup>	383	81.3	52.3	18.4	10.6	64	64
10 <sup>d</sup>	383	62.9	31.3	18.2	13.4	49	49

<sup>a</sup> Reaction conditions:  $n_{\text{cat.}} = 8.09 \times 10^{-6}$  mol,  $n_{1\text{-oct.}} = 6.37 \times 10^{-4}$  mol,  $n_s/n_c = 79$ ,  $V_{\text{solv.}} = 0.5$  mL,  $P_{\text{H}_2} = 10$  bar,  $t = 1$  h; <sup>b</sup> DMSO; <sup>c</sup> toluene; <sup>d</sup> cat. = [Rh<sub>2</sub>Cl<sub>2</sub>(COD)<sub>2</sub>].

### 2.2.2. Catalytic Activity of Ruthenium Catalyst

The catalytic activity of the ruthenium catalyst was investigated between 363 and 393 K temperatures in styrene hydrogenation. The experimental results are presented in Table 3. The highest ethyl benzene conversion value (34.8%) was obtained at 393 K in 1 h (Entry 4). When the reaction time was increased to 6 h, the conversion reached 84.3% under the same conditions (Entry 5). The catalytic activity of the complex was also tested in organic solvents. It was found that the ethyl benzene conversion was only 19.1% in DMSO, while it was 43.1% in toluene at 393 K (Entries 6 and 7). For this reason, the order of the Ru complex activity in solvents could be suggested to be as [bmim][BF<sub>4</sub>] > toluene > DMSO.

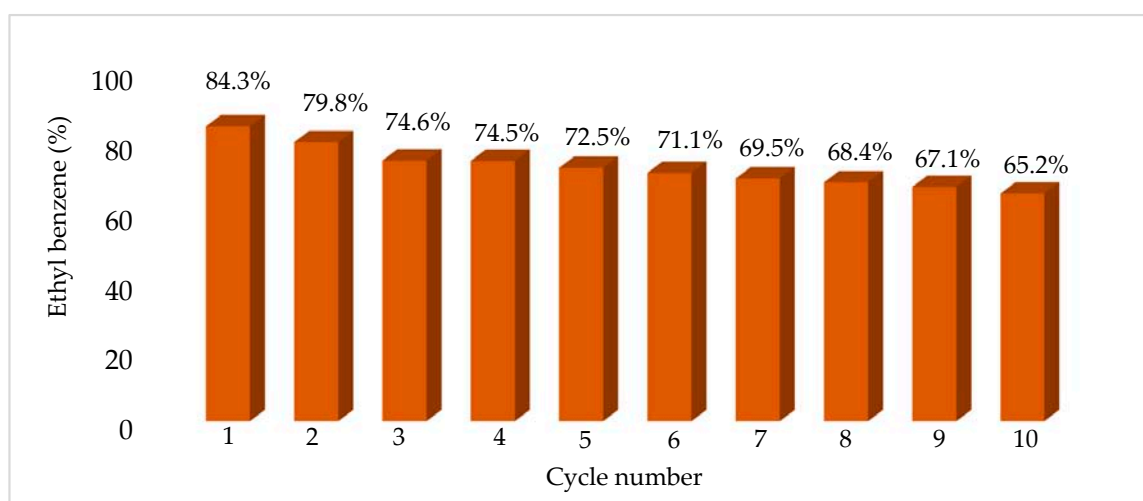
In order to investigate the H<sub>2</sub> pressure effect on styrene hydrogenation, catalytic experiments were conducted at 10-, 30-, and 60-bar H<sub>2</sub> pressures at 373 K. The conversion value was found to increase sharply from 43.1% under 10-bar H<sub>2</sub> pressure to 95.7% under 30 bar and to reach 100% at 60-bar in 1 h (Entry 9). For the purpose of determining the  $n_s/n_c$  ratio effect, catalytic experiments were performed with three different values (515, 172, and 103) at 393 K. The best ethyl benzene conversion (84.3%) was obtained with  $n_s/n_c = 103$  for 6 h (Entry 12).

Reusability tests of the ruthenium catalyst in styrene hydrogenation were performed at 393 K and 10-bar H<sub>2</sub> for 6 h during the 10 cycles (Figure 4). The ethyl benzene conversion found to be 84.3% in the first cycle decreased approximately 20% in the last cycle.

**Table 3.** Styrene hydrogenation with [Ru(L)(H<sub>2</sub>O)Cl<sub>3</sub>] catalyst <sup>a</sup>.

Entry	<i>T</i> (K)	<i>P</i> <sub>H<sub>2</sub></sub> (bar)	<i>t</i> (h)	<i>n</i> <sub>s</sub> / <i>n</i> <sub>c</sub>	Total Conversion (%)	TON	TOF
1	363	10	1	103	12.6	13	13
2	373	10	1	103	22.2	23	23
3	383	10	1	103	22.9	24	24
4	393	10	1	103	34.8	36	36
5	393	10	6	103	84.3	88	15
6 <sup>b</sup>	393	10	6	103	19.1	20	3
7 <sup>c</sup>	393	10	6	103	43.1	45	7
8	373	30	1	103	95.7	100	100
9	373	60	1	103	100	104	104
10	393	10	6	515	47.2	246	41
11	393	10	6	172	54.9	95	16
12 <sup>d</sup>	393	10	6	103	71.6	75	12

<sup>a</sup> Reaction conditions:  $n_{\text{cat.}} = 8.69 \times 10^{-6}$  mol,  $n_{\text{styr.}} = 8.69 \times 10^{-4}$  mol,  $V_{\text{solv.}} = 0.5$  mL,  $P_{\text{H}_2} = 10$  bar; <sup>b</sup> DMSO; <sup>c</sup> toluene; <sup>d</sup> cat. = RuCl<sub>3</sub>·*x*H<sub>2</sub>O.



**Figure 4.** Reusability of [Ru(L)(H<sub>2</sub>O)Cl<sub>3</sub>] catalyst in styrene hydrogenation. Reaction conditions:  $T = 393$  K,  $P_{\text{H}_2} = 10$  bar,  $n_{\text{sub.}} = 8.69 \times 10^{-4}$ ,  $n_{\text{cat.}} = 8.35 \times 10^{-6}$  mol,  $n_{\text{s}}/n_{\text{c}} = 103$ ,  $t = 6$  h.

The ruthenium catalyst was found ineffective for 1-octene hydrogenation between 373 and 393 K under 10-bar H<sub>2</sub> pressure (Table 4). The total conversion only reached about 5% in 6 h at 393 K (Entry 3). In addition, the complex activity was tested in DMSO and toluene, and the best activity was obtained in toluene (total conversion = 53.7%, Entry 5).

**Table 4.** 1-Octene hydrogenation with [Ru(L)(H<sub>2</sub>O)Cl<sub>3</sub>] catalyst <sup>a</sup>.

Entry	<i>T</i> (K)	Total Conversion (%)	Products (%)			TON	TOF
			( <i>n</i> -Octane)	(2-Octene)	(3-Octene)		
1	373	2.5	2.5	0	0	2	0.3
2	383	3.2	3.2	0	0	2	0.4
3	393	4.4	4.4	0	0	3	0.6
4 <sup>b</sup>	393	6	1.8	0	0	5	0.8
5 <sup>c</sup>	393	53.7	11.5	28.4	13.8	41	7
6 <sup>d</sup>	393	75.5	65.8	7.2	2.5	58	10

<sup>a</sup> Reaction conditions:  $n_{\text{cat.}} = 8.69 \times 10^{-6}$  mol,  $n_{1\text{-oct.}} = 6.37 \times 10^{-4}$  mol,  $n_{\text{s}}/n_{\text{c}} = 76$ ,  $V_{\text{solv.}} = 0.5$  mL,  $P_{\text{H}_2} = 10$  bar,  $t = 6$  h; <sup>b</sup> DMSO; <sup>c</sup> toluene; <sup>d</sup> cat. = RuCl<sub>3</sub>·*x*H<sub>2</sub>O.



We also investigated the performance of metal precursors ( $[\text{Rh}_2\text{Cl}_2(\text{COD})_2]$  and  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ) in  $[\text{bmim}][\text{BF}_4]$ . These studies are intended to provide a fundamental understanding of the effect of the ligand on activity. For styrene hydrogenation reaction, lower TOF values were obtained with both metal precursors. However,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  showed activity in 1-octene hydrogenation, while our complex was found to be ineffective. Therefore, we observed that the ligand has a positive effect on the catalytic reaction in IL.

### 3. Materials and Methods

#### 3.1. General

All the reagents were commercially obtained (Sigma-Aldrich Co., St. Louis, MO, USA and Merck Co., Darmstadt, Germany) at the highest quality and used without further purification. The synthesis of ligand and complexes was carried out under a nitrogen atmosphere using standard reaction techniques. The catalytic reactions were performed in a 100-mL stainless steel high-pressure reactor (Parr inst., Moline, IL, USA) containing a magnetic bar, temperature controller, and a sapphire window for viewing.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 500 MHz DPX FT (Bruker Co., Ettlingen, Germany) spectrometer. Chemical shifts were expressed in  $\delta$  (ppm) using Tetramethyl Silane (TMS) as the internal standard. Elemental analysis was conducted using a Elementar Vario EL III microanalyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany) device. FT-IR spectra were recorded with a Perkin Elmer Spectrum 100 Spectrometer (Perkin Elmer Inc., Waltham, MA, USA) using KBr discs. Mass spectra were recorded on an Agilent LC-MSD Trap SL spectrophotometer (Agilent Tech., Santa Clara, CA, USA). Melting points were measured with a Stuart SMP-30 melting point apparatus (Biby Scientific Ltd., Staffordshire, UK). Magnetic susceptibility measurements were performed with the Sherwood Scientific MK-1 device (Sherwood Scientific, Cambridge, UK). The product conversions in the catalytic reactions were determined with Thermo Finnigan Trace GC (Thermo Fischer Scientific Inc., Waltham, MA, USA) using a Permabond SE-54-DF-0.25 25 m  $\times$  0.32 mm ID column and using helium as carrier gas.

#### 3.2. Synthesis of Ligand and Complexes

##### 3.2.1. Ligand Synthesis

1H-benzotriazole (5.6 g, 0.047 mol) was dissolved in 20 mL of THF and then cooled to 273 K. Thionyl chloride (1.0 mL) was added dropwise to this solution under a nitrogen atmosphere for 30 min. A thiophene-2,5-dicarboxylic acid (1.0 g, 0.0058 mol) solution in 30 mL of THF was added to the first solution and stirred at room temperature for 24 h. At the end of the reaction, the solution was filtered, and the residue was dried under vacuum. For purification, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and extracted with 6N HCl ( $3 \times 10$  mL). The organic phase was dried over anhydrous  $\text{MgSO}_4$  and evaporated with a rotary evaporator. The ligand was obtained as a white solid (Figure 1). Yield: 82% (1.8 g), mp: 513 K. Anal. Calcd (%) for  $\text{C}_{18}\text{H}_{10}\text{N}_6\text{O}_2\text{S}$ : C = 57.8; H = 2.7; S = 8.6; N = 22.5. Found: C = 58.1; H = 2.5; S = 8.3; N = 22.8. FT-IR ( $\text{cm}^{-1}$ ): 1695, 1368, 1223.  $^1\text{H}$  NMR: (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 8.65 (2H, s), 8.46 (2H, d,  $^3J = 8.251$ ), 8.25 (2H, d,  $^3J = 8.251$ ), 7.78 (2H, t,  $^3J = 7.46$ ), 7.62 (2H, t,  $^3J = 7.46$ ).  $^{13}\text{C}$  NMR: (500 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 159.02, 146.03, 141.72, 137.2, 131.98, 130.94, 126.84, 120.60, 114.83.

##### 3.2.2. Synthesis of $[\text{Rh}(\text{COD})\text{L}]\text{Cl}$ Catalyst

For the synthesis of the rhodium catalyst, the ligand (L) (304 mg, 0.8 mmol) was dissolved in THF (20 mL), and a  $\text{Rh}_2(\text{COD})_2\text{Cl}_2$  (200 mg, 0.4 mmol) solution in 5 mL of THF was added slowly to the ligand solution. The mixture was stirred at 323 K for 72 h. At the end of the reaction, the reaction mixture was filtered, and the yellow product was washed with cold THF and dried under vacuum (Figure 2). Yield: 73% (470 mg) mp: 573–578 K. Anal. Calcd (%) for  $\text{C}_{26}\text{H}_{22}\text{ClN}_6\text{O}_2\text{SRh}$ : C = 50.3; H = 3.6; S = 5.2; N = 13.5. Found: C = 50.1; H = 3.7; S = 5.3; N = 13.3. LC-MS,  $m/z$  (calcd/found):



655.1/661.4 FT-IR ( $\text{cm}^{-1}$ ): 1689, 1222, 423.  $^1\text{H}$  NMR: (500 MHz,  $d^6$ -DMSO,  $\delta$  ppm): 8.56 (2H, s), 8.39 (6H, dd,  $^3J = 24.09, 8.28$ ), 7.89 (4H, t,  $^3J = 7.68$ ), 7.71 (4H, t,  $^3J = 7.62$ ), 4.26 (2H, t,  $^3J = 7.03$ ), 2.14 (4H, m).  $^{13}\text{C}$  NMR: (500 MHz,  $d^6$ -DMSO,  $\delta$  ppm): 159.13, 145.87, 141.24, 137.77, 132.02, 131.77, 127.59, 120.88, 115.01, 30.67, 27.98.

### 3.2.3. Synthesis of $[\text{Ru}(\text{L})(\text{H}_2\text{O})\text{Cl}_3]$

The ligand (183 mg, 0.48 mmol) was dissolved in a mixture of ethanol and THF (1:1, 20 mL), and a  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (100 mg, 0.48 mol) solution in THF (5 mL) was added dropwise to the solution. The mixture was stirred at 353 K for 48 h. The precipitated black solid was filtered, washed with cold ethanol, and dried under vacuum (Figure 2). Yield: 63% (146 mg), mp > 598 K (decomp.). Anal. Calcd (%) for  $\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{N}_6\text{O}_3\text{SRu}$ : C = 36.4; H = 2.2; S = 5.3; N = 14.0. Found: C = 36.3; H = 2.1; S = 5.3; N = 14.1. LC-MS,  $m/z$  (calcd/found): 644.9/645.1 FT-IR ( $\text{cm}^{-1}$ ): 1705, 450, 434.  $^1\text{H}$  NMR: (500 MHz,  $d^6$ -DMSO,  $\delta$  ppm): 7.93 (3H, q,  $^3J = 4.51$ ), 7.80 (1H, d,  $^3J = 3.80$ ), 7.75 (1H, d,  $^3J = 3.80$ ), 7.73 (1H, s), 7.46 (4H, q,  $^3J = 4.56$ ), 4.95 (2H)  $^{13}\text{C}$  NMR: (500 MHz,  $d^6$ -DMSO,  $\delta$  ppm): 162.97, 140.27, 137.19, 134.13, 133.71, 129.01, 128.32, 125.86, 115.46.

## 4. Conclusions

In the present study, the Rh(I) and Ru(III) complexes consisting of *N*-acyl-benzotriazole ligand were synthesized and characterized. These complexes were found to be effective catalysts in styrene and 1-octene hydrogenation in IL ([BMIM][BF<sub>4</sub>]). The results revealed that the rhodium complex activity was higher than the ruthenium complex activity both in styrene hydrogenation and in 1-octene hydrogenation. In styrene hydrogenation, the best ethyl benzene conversions were obtained in ionic liquid as well as in the apolar organic solvent (toluene) with the Rh complex. Moreover, *n*-octane selectivity of the Rh complex was found to be higher than the other isomerization products (2-octene and 3-octene). It was also found that the catalytic activity of the two complexes increased parallel to the increasing reaction temperature. At the same time, the increasing hydrogen pressure had a positive effect on the catalytic reactions.

The present study primarily aimed at immobilizing synthesized homogenous catalysts in ionic liquid media so as to recover and reuse the complexes. Based on these results, it can be stated that rhodium complexes can be reused up to ten times with little activity loss in styrene hydrogenation reactions.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4344/6/9/147/s1](http://www.mdpi.com/2073-4344/6/9/147/s1), Figure S1: Free ligand FT-IR spectrum, Figure S2: Rh complex FT-IR spectrum, Figure S3: Ru complex FT-IR spectrum, Figure S4: Rh complex LC-MS spectrum, Figure S5: Ru complex LC-MS spectrum.

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