

Synthesis of new Rh(I) and Ru(III) complexes and investigation of their catalytic activities on olefin hydrogenation in green reaction media

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Two new Ru(III) and Rh(I) complexes of N-acyl benzotriazole derivative ligand have been synthesized and characterized. The catalytic activities of complexes were tested on styrene and 1-octene hydrogenation in ionic liquid ([bmim][BF₄]), DMSO and toluene media. For styrene hydrogenation, 100 % ethyl benzene conversion was obtained with Rh(I) complex, while the conversion ratio was found to be 86.6 % with Ru(III) complex. The catalytic experiments were also conducted in DMSO and toluene to make comparison with ionic liquid under the same conditions (393 K and 6h). 1-octene conversion was found to be 94.5 % with Rh(I) complex at 373 K for 1h. The effect of H₂(g) pressure and catalyst amount was also tested on catalytic reactions. Reusability tests of complexes were investigated over five reaction cycles under 10 bar H₂ in [bmim][BF₄]. No activity loss was observed during five cycles with Rh complex.

Keywords: N-acyl benzotriazole, ionic liquid, hydrogenation, rhodium, ruthenium

1. INTRODUCTION

Environmental friendly chemical processes are being important for sustainable chemistry day by day. One of the alternative reaction media as ionic

liquid is the promising solvent appearing at this point. Having numerous advantages rather than organic solvents [1,2] make ionic liquids preferable green media for numerous reaction types [3] (Table 1).

Table 1. Several reaction types studied in ionic liquid

Reaction type	Ionic Liquid	Catalyst	Reference
Hydrogenation	Graphene oxide-[mpim][Cl]	Ionic liquid-Ru cat.	[4]
Friedel-Crafts	[bmim][PF ₆]	Acid catalyst	[5]
Diels-Alder	[emim][Cl]/AlCl ₃	Acid catalyst	[6]
Dimerization	[bmim][Cl]/AlCl ₃	Nickel complex	[7]
Alkylation	Net ₃ HCl/AlCl ₃ /CuCl	No catalyst	[8]
Allylation	[bmim][BF ₄]	Palladium catalyst	[9]
Heck	[bmim][Br], [nbu ₄][Br]	Palladacyl catalyst	[10]
Suzuki coupling	[bmim][BF ₄]	Palladium catalyst	[11]
Hydroformylation	[bmim][PF ₆]	Rhodium catalyst	[12]
Oxidation	[bmim][PF ₆]	Chiral Mn(II) catalyst	[13]

Bidentate ligands have been extensively studied and the catalytic activities of their transition metal complexes have been proved many times [14-17]. Benzotriazole derived ligands are much attractive molecules with their relatively cheap, easily obtainable and good coordination abilities to the metal centers. However, transition metals containing benzotriazole ligands are rarely investigated on catalytic reactions (Table 2). To the best of our knowledge, catalytic reactions conducted in ionic liquid media with N-acyl benzotriazole ligand containing rhodium and ruthenium complexes found to be only one which was reported before by our research group [18].

In this study, two new rhodium and ruthenium complexes having furan bridged N-acyl benzotriazole ligand were synthesized and characterized by elemental analysis, FT-IR, UV-VIS, LC-MS, ¹H-NMR and ¹³C-NMR techniques. The catalytic hydrogenation activities of synthesized complexes were investigated on styrene and 1-octene mainly in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) ionic liquid, besides DMSO and toluene as organic solvents.

2. RESULTS AND DISCUSSION

2.1. Characterization of ligand and complexes

In the FT-IR spectrum of ligand, furan dicarboxylic acid O–H stretching vibration at 3100-

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2882 cm^{-1} disappeared after the substitution via benzotriazole. Also carbonyl (C=O) vibration frequency shifted from 1689 cm^{-1} to 1710 cm^{-1} . Furthermore, C=N stretching vibration of benzotriazole moiety was observed at 1379 cm^{-1} and 1249 cm^{-1} . In the ^1H -NMR spectrum of ligand, furan ring protons were observed at $\delta = 8.34$ ppm as a singlet peak. The doublet peaks observed at $\delta = 8.48$ and 8.24 ppm and triplet peaks at $\delta = 7.78$ and 7.62

ppm were associated with benzotriazole moiety of the ligand. Total nine carbon signals were observed in ^{13}C -NMR because of symmetrical structure of ligand. The carbonyl carbons were observed at $\delta = 154.39$ ppm and the thiophene ring carbon atoms were observed at $\delta = 147.66$ and $\delta = 145.72$ ppm. The other carbon signals were observed between $\delta = 131.98$ and 114.78 ppm.

Table 2. Several benzotriazole complexes and their catalytic activities

Complex	Substrate	Reaction type	Reference
[(TMCIBTP) ₂ Cu]	L-Lactide	Polymerization	[19]
[(5CBiIBTP)Ni ₂ (OAc) ₂]	CO ₂ + CHO	Copolymerization	[20]
[(C8FuIBTP) ₂ Zn]	Propylene oxide + CO ₂	Coupling	[21]
BiBTP-Zr(IV) alkoxide	Lactide	Ring opening polymerization	[22]
[Rh(COD)L]Cl, [Ru(L)(H ₂ O)Cl ₃]	Styrene, 1-octene, cyclohexene	Hydrogenation	[18]
P-BTA-Cu	Ethyl benzene	Oxidation	[23]
[(C8NNBTP)ZnEt]	Lactide	Ring opening polymerization	[24]

In the FT-IR spectra of [RhL(COD)]Cl complex, carbonyl (C=O) group stretching vibration of ligand shifted to higher wavelength (1718 cm^{-1}) and C-N vibration of benzotriazole moiety appeared at 1285 cm^{-1} . Peak observed at 424 cm^{-1} is dedicated to Rh-N coordination [25]. In the ^1H -NMR of complex, singlet peak of furan ring shifted from 8.34 ppm to 8.27 ppm and doublet peak of free benzotriazole ring shifted to upfield and observed at 8.39 ppm as doublet of doublets after bonding with metal center. The ^1H -NMR signals of cyclooctadiene (COD) emerged at 4.27 and 2.15 ppm as multiple peaks [26]. From the ^{13}C -NMR spectrum of [RhL(COD)]Cl complex, carbonyl carbon (C=O) signal was observed at 170.34 ppm, aromatic ring carbons appeared between 132.12-114.88 ppm values. Additionally, peaks of carbon atoms of COD group were observed at 127.57 and 28.15 ppm. The signals which was observed at 67.03 and 23.89 ppm are related to carbons of solvent (THF) molecule. In the UV-VIS spectrum of the ligand, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand charge transfer transitions were observed at 279 nm and 333 nm. There is no $d \rightarrow d$ transitions after ligand-metal interaction in [RLh(COD)]Cl complex spectra. The molecular ion peaks of rhodium complex was observed at m/z 606.2, which supports the formulation of [RhL(COD)]Cl, as shown by the optimized molecular structure in Figure 1. The magnetic susceptibility measurements of Rh complex indicated that this complex is diamagnetic ($\mu_s = 0$) and the structure of complex is a square planar geometry.

In the FT-IR spectrum of [RuL(H₂O)Cl₃] complex, broad aqua peak observed at 3445 cm^{-1} . Aromatic C-H, carbonyl, aromatic C=C and C-N vibration peaks observed at 3077-2797, 1705, 1531-1455 and 1368-1251 cm^{-1} respectively. Ru-O and Ru-N bond stretching appeared as two new peaks at 450 and 434 cm^{-1} respectively [27]. These peaks indicated that two different ligand coordinated to metal centre. The water is coordinated through the oxygen atom and benzotriazole ligand is coordinated via nitrogen atom. Since [RuL(H₂O)Cl₃] complex was found to be paramagnetic, nuclear magnetic resonance measurement can not be clear as Rh complex but observed signals are suitable for suggested complex structure. The protons of furan ring were observed at 8.12 ppm as singlet peak after metal-ligand interaction. Doublet proton peaks of benzotriazole ring of free ligand, which were observed at 8.48 ppm and 8.24 ppm shown as quartet peak at 7.89 ppm and the other proton peaks also observed as quartet at 7.42 ppm after metal-ligand interaction. The observed peak at 3.77 ppm is related to aqua ligand [28]. In the UV-VIS spectrum of ruthenium complex in DMSO, three absorption bands were observed at 272, 362 and 532 nm. The $\pi \rightarrow \pi^*$ transition of ligand observed at 272 nm in the complex spectrum. M-L charge transfer transition and $d \rightarrow d$ (d^5) transitions of metal were observed 362 and 532 nm respectively. The molecular ion peak of [RuL(H₂O)Cl₃] complex including solvent (THF) observed m/z 663.3. The magnetic susceptibility measurement of the [RuL(H₂O)Cl₃] complex is found to be 1.24 BM and this means that d orbitals have one unpaired electron and the electronic

configuration is $t_{2g}^5 e_g^0$. According to the results, geometry of paramagnetic $[RuL(H_2O)Cl_3]$ complex suggested as octahedral. Based on all spectroscopic

results, ligand and complex structures were given in Figure 1.

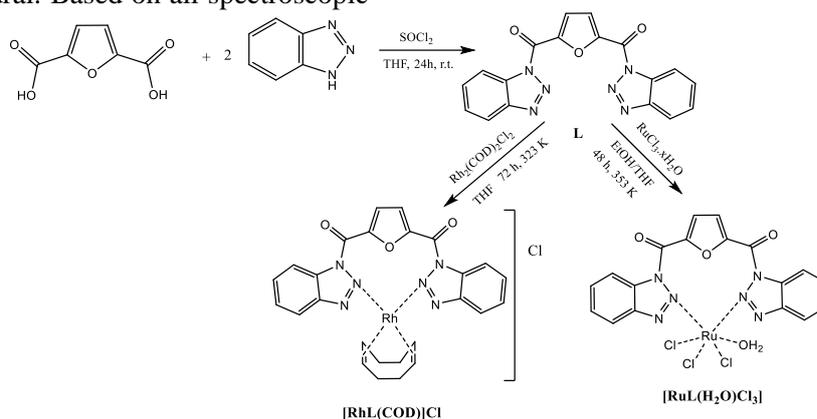


Figure 1. Synthesis and suggested structures of ligand (L) and complexes.

2.2. Hydrogenation activity of complexes

To test the solubility of complexes, catalyst (10 mg) and solvent (IL, DMSO or Toluene) were mixed together in a high pressure reactor via sapphire windows. Sapphire windows provide for monitoring solubility of complexes. It was found that both of complexes are soluble in all solvent media under 10-60 bar $H_2(g)$ between 323-393 K temperatures. During catalytic reactions, catalyst, substrate and solvent were added to the reaction vessel, then reactor was heated to the reaction temperature. Reactor was purged three times with argon gas and then filled with H_2 gas. After the reaction finished, products were extracted with hexane and analyzed by gas chromatography.

2.2.1. Catalytic activity of rhodium catalyst

Styrene and 1-octene were selected as olefin in all catalytic hydrogenation reactions. The results obtained with $[RhL(COD)]Cl$ are given in Table 3. Experiments were conducted with different H_2 pressures, catalyst amount and temperature (Entries 1-12). With a view to testing the temperature effect on hydrogenation of styrene, experiments were conducted between 363-393K in 1 hour reaction time (Entries 1-4). Results indicated that increasing reaction temperature lead to increasing product conversion as expected. The highest product conversion was 50.1 % at 393 K, under 10 bar H_2 pressure (Entry 4). When the reaction time extended to 6 hours, ethyl benzene formation reached to 100 % (Entry 5).

To determine the solvent effect, experiments were conducted in DMSO and toluene besides ionic liquid media (Entries 6-7). It was found that ethyl benzene conversion was high in $[bmim][BF_4]$ than in other organic solvents. Also, activity of catalyst in toluene is better than DMSO.

The effect of H_2 pressure on styrene hydrogenation was tested under 10, 30 and 60 bar pressures at 373 K (Entries 2, 8, 9) in 1h. It was observed that the product formation increased with the pressure and substrate completely converted to ethyl benzene both at 30 and 60 bar $H_2(g)$.

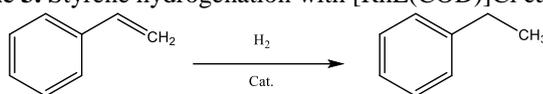
To investigate the effect of s/c ratio, catalytic experiments were performed three different values as 103, 173 and 518 at 10 bar H_2 at 393 K in 6h (Entries 5, 10, 11). The ethyl benzene conversion was higher at 518 s/c ratio and TON value was reached to 457 at this conditions (Entry 10).

Reusability of catalyst was tested under the best conversion conditions (393 K, 10 bar H_2 , 6 h). Results are given in Figure 2. After each cycle, remaining product(s) and substrate were extracted with hexane at least three times, not to observe any residue. It was found that there was no activity loss after five cycles.

To determine the catalytic effect of $[RhL(COD)]Cl$ complex on hydrogenation of 1-octene, experiments were conducted between 333-373 K temperatures in 1h reaction time (Entries 1-5). Results are given in Table 4. The best conversion (94.5 %) and n-octane selectivity were obtained at 373 K, under 10 bar H_2 (Entry 5). The solvent effect in 1-octene hydrogenation reactions also investigated and total conversion did not go over 48.7% in DMSO and it remained only 32% in toluene media (Entries 6, 7).

Reusability test of $[RhL(COD)]Cl$ catalyst in 1-octene hydrogenation was conducted at 373 K, under 10 bar H_2 in 1h reaction time (Figure 3). It is detected that catalyst can be reused at least five times with only 5% activity loss and more importantly n-octane selectivity was found to be higher in the first three cycles than the others (Entries 2, 3).

Table 3. Styrene hydrogenation with [RhL(COD)]Cl catalyst



Entry	T(K)	Styrene			Ethyl benzene		
		P _{H2} (Bar)	t(h)	n _s /n _c	Total conv. (%)	TON	TOF
1	363	10	1	103	18.3	19	19
2	373	10	1	103	28.5	30	30
3	383	10	1	103	45.2	47	47
4	393	10	1	103	50.1	52	52
5	393	10	6	103	100	105	18
6 ^a	393	10	6	103	36.1	38	6
7 ^b	393	10	6	103	65.1	68	11
8	373	30	1	103	100	105	105
9	373	60	1	103	100	105	105
10	393	10	6	518	87.3	457	76
11	393	10	6	173	98.2	171	29
12 ^c	393	10	6	103	55.2	55	9

[Reaction cond.: n_{cat.} = 8.30 x 10⁻⁶ mol, n_{styr.} = 8.69 x 10⁻⁴ mol, V_{solv.} = 0,5 mL, P_{H2} = 10 Bar], ^aDMSO, ^bToluene, ^cCat. = [Rh₂Cl₂(COD)₂]

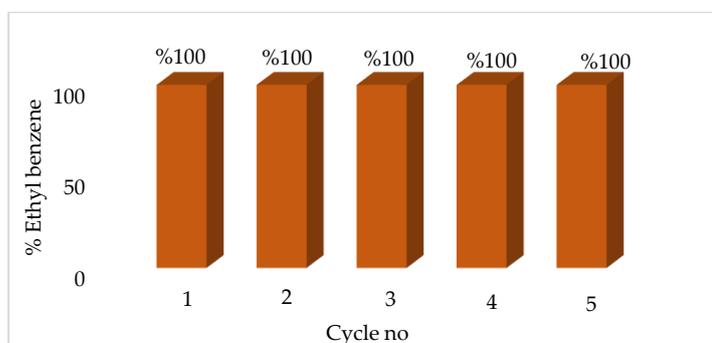
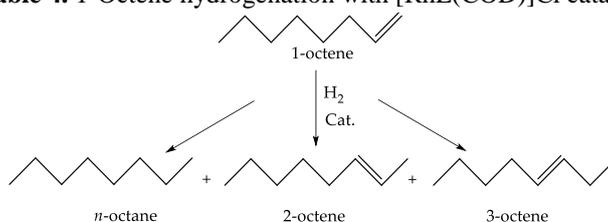


Figure 2. Reusability of [RhL(COD)]Cl catalyst in styrene hydrogenation

[Reaction cond.: T = 393 K, P_{H2} = 10 Bar, n_{sub.} = 8,69 x 10⁻⁴, n_{cat.} = 8,30 x 10⁻⁶ mol, s/c = 103, t = 6 h]

Table 4. 1-Octene hydrogenation with [RhL(COD)]Cl catalyst



Entry	Cycle No	T(K)	Total conv. (%)	Products (%)			TON	TOF
				(n-octane)	(2-octene)	(3-octene)		
1		333	35.8	32.6	1.8	1.3	27	27
2		343	67.2	63.7	2.0	1.5	52	52
3		353	71.1	62.3	5.5	3.2	55	55
4		363	86.4	78.3	4.9	3.1	66	66
5		373	94.5	82.8	8.8	1.9	73	73
6 ^a		373	48.7	21.6	19.7	7.4	37	37
7 ^b		373	32.0	17.4	8.8	5.8	25	25
8	2	373	93.9	93.9	0	0	73	73
9	3	373	92.8	92.8	0	0	71	71
10	4	373	91.7	84.5	4.1	3.1	70	70
11	5	373	90.8	83.2	4.2	3.4	70	70

[Reaction cond.: n_{cat.} = 8.30 x 10⁻⁶ mole, n_{1-oct.} = 6.37 x 10⁻⁴ mole, n_s/n_c = 77, V_{solv.} = 0,5 mL, P_{H2} = 10 Bar, t = 1 h], ^aDMSO, ^bToluene, ^ccat = [Rh₂Cl₂(COD)₂]

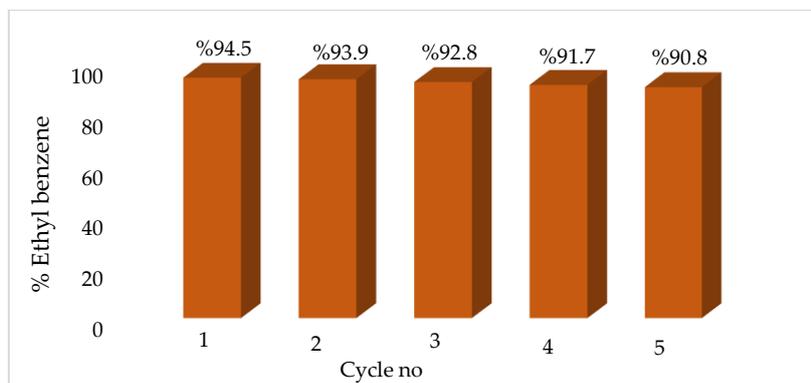


Figure 3. Reusability of [RhL(COD)]Cl catalyst in 1-octene hydrogenation
[Reaction cond.: T= 373 K, P_{H₂}= 10 Bar, n_{sub.}= 8,37 x 10⁻⁴, n_{cat.}= 8,30 x 10⁻⁶ mol, s/c= 77, t= 1 h]

2.2.2. Catalytic activity of ruthenium catalyst

[RuL(H₂O)Cl₃] catalyst activity was tested on styrene hydrogenation between 353-393 K temperatures in 1h reaction times (Entries 1-6). All other conditions being the same, reaction temperature has positive effect on catalytic reaction. Reaction time increased to 6 h for the determine time effect and it was observed that there is no significant change in the total conversion value. At this conditions, catalytic tests were also performed at organic solvent media and To investigate the solvent effect on catalytic reaction, experiments were conducted in toluene and DMSO under 10 bar H₂ at 393 K and these solvents have negative effect on

hydrogenation reactions. Ethyl benzene conversion reached to 23.4% in toluene while only 12 % in DMSO (Entries 7,8). [bmim][BF₄] was detected the best reaction media for [RuL(H₂O)Cl₃] catalyst at styrene hydrogenation.

To test the H₂ pressure effect on catalytic reactions, experiments were conducted under 10, 30 and 60 bar H₂ pressures at 353 K (Entries 1, 9-10) and H₂ pressure had negative effect over catalytic reaction. This may be due to the decreased the solubility of [RuL(H₂O)Cl₃] complex. All of these experiments were performed with s/c ratio 100. When the s/c ratio increased TON was reached the best value (185) in 6h at 393K (Entry 11).

Table 5. Styrene hydrogenation with [RuL(H₂O)Cl₃] catalyst

Entry	T(K)	P _{H₂} (Bar)	t(h)	s/c	Total conv. (%)	TON	TOF
1	353	10	1	100	29.1	29	29
2	363	10	1	100	38.6	39	39
3	373	10	1	100	39.9	40	40
4	383	10	1	100	44.5	45	45
5	393	10	1	100	81.1	82	82
6	393	10	6	100	86.6	88	15
7a	393	10	6	100	12	12	2
8b	393	10	6	100	23.4	24	4
9	353	30	1	100	21.4	22	22
10	353	60	1	100	13.7	14	14
11	393	10	6	500	36.6	185	31
12	393	10	6	167	43.1	73	12
13c	393	10	6	100	42.1	43	7

[Reaction cond.: n_{cat.}= 8.58 x 10⁻⁶ mol, n_{styr.}= 8.69 x 10⁻⁴ mol, V_{solv.}= 0,5 mL, P_{H₂}=10 Bar] ^aDMSO, ^bToluene, ^ccat= RuCl₃.x H₂O

Reusability of [RuL(H₂O)Cl₃] catalyst on styrene hydrogenation were tested during five cycles under 10 bar H₂ at 393 K for 6h (Figure 4). Conversion of

ethyl benzene was found to be 86.6 % at first cycle and after decreased gradually to 78.1 % at the last cycle.

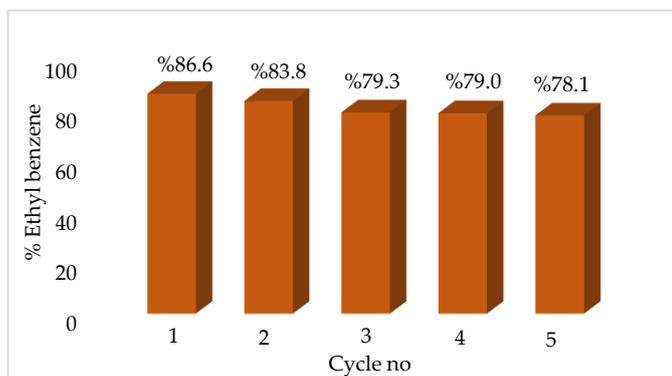


Figure 4. Reusability of [RuL(H₂O)Cl₃] catalyst in styrene hydrogenation
[Reaction cond.: T= 393 K, P_{H₂}= 10 Bar, n_{sub.}= 8.69 x 10⁻⁴, n_{cat.}= 8.58 x10⁻⁶ mol, s/c= 100, t= 6 h]

To investigate the catalytic activity of [RuL(H₂O)Cl₃] complex on 1-octene hydrogenation, experiments were conducted between 353-393 K under 10 bar H₂ in 1h. The results are given in Table 6. Catalyst activity gradually increased from 353 K to 373 K. Conversion decreased at higher temperatures. There may be the catalyst is decomposed at high temperatures. The most effective

reaction temperature was found to be as 373 K and the total conversion reached to 44.1 % (Entry 3). The selectivity of catalyst to n-octane was higher at all temperature degrees. Catalyst had almost no activity in organic solvents as compared with ionic liquid media and the activity was found to be only 10.6 % in toluene (Entries 6, 7).

Table 6. 1-Octene hydrogenation with [RuL(H₂O)Cl₃] catalyst

Entry	Cycle No	T(K)	Total conv. (%)	Products(%)			TON	TOF
				(n-octane)	(2-octene)	(3-octene)		
1		353	27.4	19.9	5.2	2.2	20	20
2		363	35.1	24.2	7.5	3.4	26	26
3		373	44.1	26.0	12.7	5.3	33	33
4		383	18.1	16.4	1.7	0	13	13
5		393	12.3	12.3	0	0	9	9
6 ^a		373	0	0	0	0	0	0
7 ^b		373	10.6	1.9	5.4	3.3	8	8
8	2	373	45.7	25.4	13.8	6.4	34	34
9	3	373	54.0	39.9	9.4	4.6	40	40
10	4	373	59.1	49.4	6.6	3.1	44	44
11	5	373	45.9	36.0	6.9	2.9	34	34

[Reaction cond.: n_{cat.}= 8.58 x10⁻⁶ mol, n_{1-oct.}= 6.37 x 10⁻⁴ mol, n_s/n_c= 74, V_{solv.}= 0,5 mL, P_{H₂}=10 Bar, t=1 h] ^aDMSO, ^bToluene, ^ccat= RuCl₃.x H₂O

[RuL(H₂O)Cl₃] activity in 1-octene hydrogenation was monitored during five cycle under 10 bar H₂ at 373 K for 1h reaction time (Figure 5) and it was shown that product conversion gradually increased from 44.1% to 59.1% at fourth

step (59.1 %). The reason of increase is that the catalyst gains activity with temperature. It was found that the catalyst was deactivated after this cycle and conversion decreased to 45.9 %.

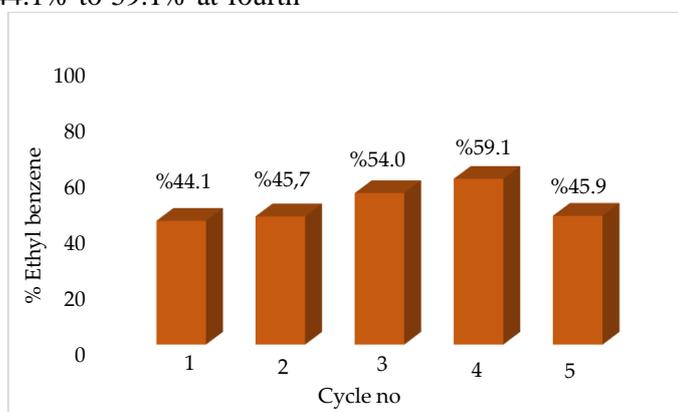


Figure 5. Reusability of [RuL(H₂O)Cl₃] catalyst in 1-octene hydrogenation
[Reaction cond.: T= 373 K, P_{H₂}= 10 Bar, n_{sub.}= 6,37 x 10⁻⁴, n_{cat.}= 8,58 x10⁻⁶ mol, s/c= 74, t= 1 h]

To test the activity of metal precursors, All catalytic experiments were conducted with $[\text{Rh}_2\text{Cl}_2(\text{COD})_2]$ and $\text{RuCl}_{3,x}\text{H}_2\text{O}$ in $[\text{bmim}][\text{BF}_4]$. The main aim of this study is whether or not ligand has positive effect on catalytic experiments. The results showed that metal precursors are less effective than complexes under the same conditions.

3. MATERIALS AND METHODS

3.1. General

All the reagents were commercially obtained (Sigma-Aldrich and Merck) and used without further purification. Ligand and complexes synthesis was carried out under inert (nitrogen) atmosphere using standard schlenk techniques. The catalytic reactions were performed in a 100 mL stainless steel high pressure reactor (Parr inst.) containing a magnetic bar, temperature controller and sapphire window. FT-IR spectra were recorded with Perkin Elmer Spectrum 100 Spectrometer using KBr. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on Bruker (500 MHz) DPX FT spectrometer. Mass spectra were recorded on Agilent LC-MSD Trap SL spectrophotometer. Elemental analysis was conducted using Elementar Vario EL III micro analyzer device. Melting points were measured with a Stuart SMP-30 melting point apparatus. Magnetic susceptibility measurements were performed with the Sherwood Scientific MK-1 device. The product conversions in catalytic reactions were determined with Thermo Finnigan Trace GC using a Permabond SE-54-DF-0.25 25 m x 0.32 mm ID column and using helium as carrier gas.

3.2. Synthesis of ligand and complexes

Synthesis procedure of ligand and its rhodium and ruthenium complexes are summarized in Figure 1. Benzotriazole ligand and complexes were successfully prepared with good yields. Synthesized compounds are solid and stable during laboratory storage and the complexes are found to be soluble in mentioned solvents under studied conditions.

3.2.1. Ligand synthesis. Ligand synthesis procedure was following as described before using furan-2,5-dicarboxylic acid instead of thiophene-2,5-dicarboxylic acid [18]. White solid (Figure 1). Yield: %70 (1.8 g), m.p.: 536 Anal. Calc. (%) for $\text{C}_{18}\text{H}_{10}\text{N}_6\text{O}_3$: C=60.3; H=2.8; N=23.4. Found: C=59.4; H=2.5; N=23.2. FT-IR (cm^{-1}): 1710, 1379, 1249. $^1\text{H-NMR}$: (500 MHz, CDCl_3 , δ ppm): 8,48 (2H, d, $^3\text{J}=8,27$), 8,34 (2H, s), 8,24(2H, d, $^3\text{J}=8,28$), 7,78 (2H, t, $^3\text{J}=7,33$), 7,62 (2H, t, $^3\text{J}=7,34$). $^{13}\text{C-NMR}$:(500 MHz, CDCl_3 , δ ppm): 154,39, 147,66, 145,72, 131,98, 131,06, 126,90, 124,41, 120,52, 114,78.

3.2.2. Synthesis of $[\text{RhL}(\text{COD})]\text{Cl}$ catalyst.

Ligand (L) (220 mg, 0.6 mmole) was dissolved in THF (20 mL), and $\text{Rh}_2(\text{COD})_2\text{Cl}_2$ (150 mg, 0.3 mmole) solution in 5 mL THF was added slowly to the first solution. The solution was stirred during 72 h at 323 K. When the reaction completed, the mixture was filtered, and the yellow product was washed with cold THF and dried under vacuum (Figure 2). Yield: 53% (200 mg, 0.33 mmole) m.p.: 458-461 K. Anal. Calc. (%) for $\text{C}_{26}\text{H}_{22}\text{ClN}_6\text{O}_2\text{SRh}$: C=51.6; H=3.6; N=13.9. Found: C=50.4; H=3.1; N=14.1. LC-MS, m/z (calc./found): 602.3/606.2 FT-IR (cm^{-1}): 1718, 1379, 1285, 424. $^1\text{H-NMR}$: (500 MHz, d^6 -DMSO, δ ppm): (500 MHz, d^6 -DMSO, δ ppm): 8,39 (3H, dd, $^3\text{J}=8,27$), 8,27 (2H, s), 7,89 (2H, t, $^3\text{J}=7,67$), 7,71 (2H, t, $^3\text{J}=7,67$), 4,27 (2H, t), 2,15 (4H, m). $^{13}\text{C-NMR}$: (500 MHz, d^6 -DMSO, δ ppm):170,34, 131,73, 125,25, 125,04, 120,82, 119,19, 118,87, 114,88, 68,71, 67,03, 28,15, 23,89.

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

The ligand (175 mg, 0.49 mmol) was dissolved in ethanol/THF (1:1, 40 mL) mixture and heated for complete solubility, then $\text{RuCl}_{3,x}\text{H}_2\text{O}$ (100 mg, 0.48 mole) solution in THF (5 mL) was added dropwise to the solution. The mixture was stirred at 353 K for 36 h. After completion of reaction, precipitated black solid was filtered, washed with cold ethanol and dried under vacuum (Figure 2). Yield: 83% (230 mg, 0.39 mmole), m.p.:>593 K (decomp.). Anal. Calc. (%) for $\text{C}_{18}\text{H}_{12}\text{Cl}_3\text{N}_6\text{O}_3\text{SRu}$: C=37.0; H=2.0; N=18.3. Found: C=36.3; H=2.2; N=18.5. LC-MS, m/z (calc./found): 654.9/663.3 FT-IR (cm^{-1}): 3445, 1706, 451, 434. $^1\text{H-NMR}$: (500 MHz, d^6 -DMSO, δ ppm): 8,12 (s, 2H), 7,89 (5H, q, $^3\text{J}=4,0$), 7,42 (5H, q, $^3\text{J}=4,0$) $^{13}\text{C-NMR}$: (500 MHz, d^6 -DMSO, δ ppm): 177,26, 141,81, 139,96, 130,18, 125,92, 117,31, 115,47, 56,13, 14,82.

CONCLUSIONS

In this study, two new benzotriazole derived Rh and Ru complexes were synthesized and characterized successfully. The catalytic hydrogenation activities of synthesized complexes were tested in styrene and 1-octene substrates in $[\text{bmim}][\text{BF}_4]$ as green solvent and also conventional organic solvents. The results indicated that ionic liquid media more effective in hydrogenation catalytic reactions for $[\text{RhL}(\text{COD})]\text{Cl}$ and $[\text{RuL}(\text{H}_2\text{O})\text{Cl}_3]$ catalysts rather than conventional organic solvents. The activity and n-octane selectivity of rhodium complex was found higher than ruthenium complex for both of substrate (styrene and 1-octene). Besides. $[\text{RhL}(\text{COD})]\text{Cl}$ complex can be used several times without any loss of activity.

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