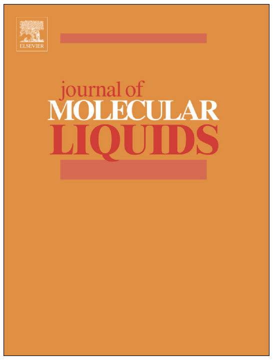

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New Palladium (II) Complexes with Thiophene and Furan Bridged *N*-Acylbenzotriazole Ligands: Synthesis, Characterization and Hydrogenation Activity in Ionic Liquid

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Abstract: Palladium complexes of *N*-Acylbenzotriazole derivative ligands were synthesized and characterized. The catalytic activities of complexes of ([PdL1(OAc)$_2$] and [PdL2(OAc)$_2$]) were investigated in relation to hydrogenation reactions of styrene, 1-octene and cyclohexene in [bmim][BF$_4$] as greener reaction media. 100% ethyl benzene conversion was obtained with both complexes in 1h reaction time. Additionally, 100% 1-octene conversion was reached within the same period of time with [PdL2(OAc)$_2$]) complex. In cyclohexene hydrogenation, product formation reached up to 67% at 363 K with [PdL1(OAc)$_2$] complex. Reusability tests were conducted under the highest product conversion conditions, and both catalysts were found to be efficient up to five cycles for all substrates. The other reaction parameters such as solvent effect, H$_2$ (g) pressure, n_s/n_c ratio were also investigated.

Keywords: N-Acylbenzotriazole, Palladium, Ionic Liquid, Hydrogenation

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1. Introduction

The primary purpose of a chemical reaction is to achieve maximum product yield and selectivity in a short period of time. Unfortunately, it is always not possible to achieve 100% yield and selectivity for every chemical reaction. Catalysts help at this point. Without using a suitable catalyst, reactions generally require much more time and energy during the desired product formation and by-products are observed many times as well. Organometallic compounds can behave as suitable catalysts for several chemical reactions such as hydrogenation [1,2], hydroformylation [3,4], oxidation [5,6] etc offering high product yields and selectivities. The common problems in catalytic reactions are decomposition of expensive catalysts, laborious product isolation, low activities and selectivities, poor reagent and catalyst solubility, and all these problems force the chemists to search alternative solvent systems. ILs can solve not all but most of these problems. Ionic liquids (ILs) are low-melting (<373 K) salts having numerous specialities including thermal stability [7], low vapour pressure [8], non-toxic [9-11] and non-flammability [12]. These specialities make them better alternatives to conventional organic solvents [13,14]. They can solve several inorganic, organic, organometalic and polymeric compounds**.**

N-heterocycles are important compounds thanks to their significant chemical, biological and pharmacological activities [15]. One of these compounds, benzotriazole (Bt) derivatives, has widespread research area for different industrial applications including field-effect transistors [16], light emitting diodes [17], photovoltaic devices [18], solar cells [19] synthetic products [20] and so on. Benzotriazole derivatives have also drawn increasing attention in coordination chemistry due to excellent coordination capability. They are used as N-donor ligand. Most of the Bt derivatives are air and moisture stable compounds, and they are thus preferred ligands for catalytic reactions. For example, Hurtado, J., et al. reported 3,5-bis (benzotriazol-1-ylmethyl) toluene ligand obtained between 3,5-bis (bromomethyl) toluene and benzotriazole reaction. Synthesized ligand was then reacted with [$PdCl_2$(cod)] (cod = 1,5-cyclooctadiene) to form a new palladium complex catalyst for oxidative amination reactions [21]. Wangming, D. et al. synthesized several ruthenium(II) complexes with 2-(benzimidazole-2-yl)-6-(benzotriazole-1-yl)pyridine ligand for examining its catalytic effects on transfer hydrogenation reactions [22].

In this study, we prepared two N-Acyl-benzotriazole derivative ligands via substitution reaction between 1H-benzotriazole and thiophene or furan-2,5-dicarboxylic acid compounds in the presence of chlorinating agent (thionyl chloride), and the one with thiophene-substituted benzotriazole ligand had been reported by our research group[23] before. Synthesized ligands were then reacted with palladium acetate precursor to obtain two new palladium complexes. All the compounds were characterized with FT-IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis techniques. Catalytic activity of complexes was investigated in relation to hydrogenation reactions of some olefins (styrene, 1-octene and cyclohexene) in 1-buthyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]).

2. Experimental

2.1. Materials

All the reagents were commercially obtained (Sigma-Aldrich and Merck) at highest quality and used without further purification. 1-butyl-3-methylimidazolium tetrafluoroborate, thiophene-2,5-dicarboxylic acid and palladium (II) acetate were purchased from Aldrich Chemical Co. 1H-benzotriazole, styrene, 1-octene and cyclohexene were obtained from Merck. Chemical syntheses were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted.

2.2. Measurements

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker (500 MHz) DPX FT spectrometer, using the solvents of $CDCl_3$ and DMSO-d_6. Chemical shifts were expressed in δ (ppm) using TMS as the internal standard. Elemental analysis was conducted using Elementar Vario EL III microanalyzer. The magnetic susceptibility was measured at room temperature (20-28 °C) with a Sherwood Scientific MX-I Model magnetic balance. The melting points were determined on a capillary melting point apparatus Stuart SMP30. FT-IR spectra were recorded with Perkin Elmer Spectrum 100 Spectrometer using KBr discs. Mass spectra were recorded on Agilent LC-MSD Trap SL spectrophotometer. The conversions of products in catalytic hydrogenation 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.

2.3. Synthesis of ([5-(Benzotriazole-1-carbonyl)-thiophen-2-yl]-benzotriazol-1-yl-methanone) ligand (L1)

Ligand (**L_1**) was synthesized as described previously [23] (Figure 1). The solution of 1H-Benzotriazole (5.6 g, 0.047 mol) in THF was cooled to 273 K, and $SOCl_2$ (1 mL, 0.013 mol) was added dropwise to the solution under nitrogen atmosphere. The solution was mixed for 30 minutes, and then the solution of thiophene-2,5-dicarboxylic acid (1.0 g, 0.0058 mol) in THF was added. The mixture was stirred at room temperature for 24

h. At the end of the reaction, the mixture was filtered, and the solvent was removed under vacuum. The residue was dissolved in dichloromethane and extracted with 6 N HCl (3 x 10 mL). The organic phase was dried over anhydrous $MgSO_4$ and evaporated. Ligand was obtained as a white solid. Yield: 82.2%, m.p.: 513 K. Anal. Calc. (%) for $C_{18}H_{10}N_6O_2S$: 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 (cm^{-1}): 1695, 1368, 1223. ^{1}H-NMR: (500 MHz, $CDCl_3$, δ ppm): 8.65 (2H, s), 8.46 (2H, d, J=8.25 Hz), 8.25 (2H, d, J=8.25 Hz), 7.78 (2H, t, J=7.46 Hz), 7.62 (2H, t, J=7.46 Hz), ^{13}C-NMR: (500 MHz, $CDCl_3$, δ ppm): 159.02, 146.03, 141.72, 137.20, 131.98, 130.94, 126.84, 120.60, 114.83.

2.4. Synthesis of ([5-(Benzotriazole-1-carbonyl)-furan-2-yl]-benzotriazol-1-yl-methanone) ligand (L2)

Ligand (L2) was synthesized from the reaction between furan-2,5-dicarboxylic acid and 1H-benzotriazole according to the same procedure described for L1. White solid. Yield: 70%, m.p.: 536 K. Anal. Calc. (%) for $C_{18}H_{10}N_6O_3$: 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}H-NMR: (500 MHz, $CDCl_3$, δ ppm): 8,48 (2H, d, ^{3}J=8,27), 8,34 (2H, s), 8,24(2H, d, ^{3}J=8,28), 7,78 (2H, t, ^{3}J=7,33), 7,62 (2H, t, ^{3}J=7,34). ^{13}C-NMR:(500 MHz, $CDCl_3$, δ ppm): 154,39 C(a), 147,66 C(b), 145,72 C(c), 131,98 C(d), 131,06 C(e), 126,90 C(f), 124,41 C(g), 120,52 C(h), 114,78 C(ı)

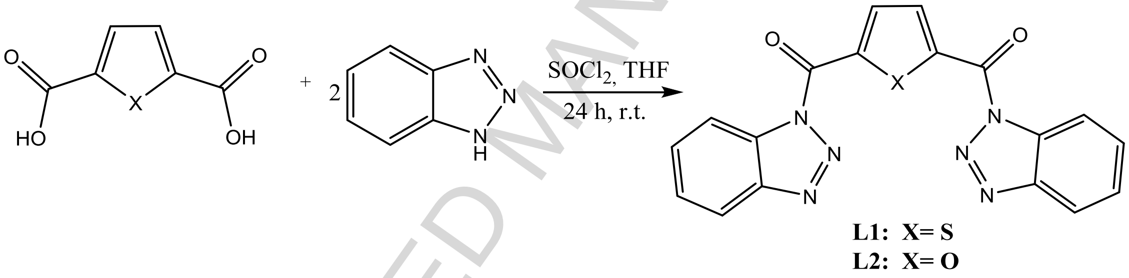


Figure 1: Synthesis procedure of L1 and L2 ligands

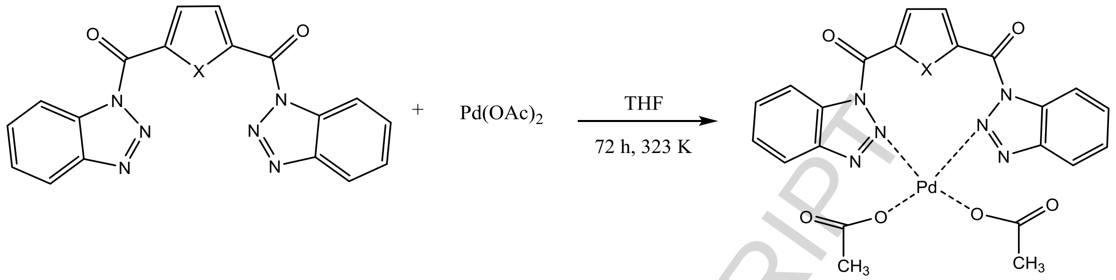
2.5. Synthesis of [PdL1(OAc)$_2$]

Palladium acetate (100 mg, 0.45 mmol) was dissolved in 50 mL THF and added to the ligand solution (180 mg, 0.48 mmol in 20 mL THF) at 323 K for 30 minutes. The mixture was stirred at room temperature for 72 h under nitrogen atmosphere. The precipitated brown solid was isolated by filtration and washed with THF (3 x 10 mL) and then dried under vacuum (Scheme 2). Yield 42 %, (120 mg), m.p.: > 593 K decomp. Anal. Calc. (%) for $C_{22}H_{16}N_6O_6SPd$: C=44.1; H=2.6; S=5.4; N=14.0. Found: C=44.8; H=2.9; S=5.1; N=13.7. LC-MS, m/z (calc./found): 670.1/660.1 FT-IR (cm^{-1}): 1695, 1508, 1368, 533, 427 ^{1}H-NMR: (500 MHz, d^6-DMSO, δ ppm): 8.65(2H, s), 8.40 (2H, d, J=8.23), 8.38(4H, dd, J_1=12.3 Hz, J_2=8.23 Hz), 7.89 (2H, t, J=7.50), 7.72 (2H, t, J=7.70), 1.91 (3H, s) ^{13}C-NMR: (500 MHz, d^6-DMSO, δ ppm): 162.85, 140.24, 138.80, 134.88, 133.68, 114.95, 97.69, 84.81, 67.51, 66.26, 23.95

2.6. Synthesis of [PdL2(OAc)$_2$]

[PdL2(OAc)$_2$] was synthesized with the same procedure described above (Figure 2). Dark brown solid. Yield 53 %, m.p.: > 593 K decomp. Anal. Calc. (%) for $C_{22}H_{16}N_6O_6SPd$: C=45.3; H=2.7; N=14.4. Found: C=44.6; H=2.4; N=14.7. LC-MS, m/z (calc./found): 654.1/661.3 FT-IR (cm^{-1}): 1720, 1577, 1330, 523, 434 ^{1}H-NMR: (500

MHz, d^6-DMSO, δ ppm): 8,15 (2H, s), 8,08 (2H, d, ^{3}J=8,39), 7,92 (2H, d, ^{3}J=8,34), 7,59 (2H, t, ^{3}J=7,38), 7,45 (2H, t, ^{3}J=7,56), 2,09 (3H, s, asetat). ^{13}C-NMR: (500 MHz, d^6-DMSO, δ ppm): 202,2, 159,94, 148,24, 147,91, 118,51, 104,52, 97,67, 66,35, 33,76, 24,07, 21,73.



[PdL1(OAc)$_2$]: X=S
[PdL2(OAc)$_2$]: X=O

Figure 2: Synthesis and possible structures of complexes

2.5. Characterization of ligands and complexes

In this study, the ligands acting as a bidentate ligand and coordinates to the palladium centre. Detailed description and characterization of L1 had been published previously.

Therefore, we here explain [PdL1(OAc)$_2$] characterization. In the IR spectrum of [PdL1(OAc)$_2$] complex, Pd-N and Pd-O (from acetate oxygen) peaks were observed at 533 cm^{-1} and 427 cm^{-1}, respectively. Formation of the Pd-N bond indicates that ligand coordinated to the metal center via nitrogen atoms (See Supplemantary Materials, Figure S1). In the ^{1}H-NMR spectra of the L1 ligand, the aromatic protons of the N-acyl benzotriazole moiety appeared to be two triplet (7.62 ppm and 7.78 ppm) and two doublet (8.25 ppm and 8.46 ppm), and the thiophene protons appeared to be a single peak (8.65 ppm) because of the symmetrical nature of the ligand (See Supplemantary Materials, Figure S2). In the ^{1}H-NMR spectra of [PdL1(OAc)$_2$] complex, benzotriazole protons appeared to be doublet of doublets at 8.38 ppm and triplets at 7.89 and 7.72 ppm. Also, we noted the presence of a singlet at 1.91 ppm corresponding to CH_3 protons of acetate ligand (See Supplemantary Materials, Figure S3). In the ^{13}C-NMR spectrum of the L1 ligand had nine signals between 159.02-114.83 ppm due to the symmetrical nature of ligand. The signal located at 159.02 ppm corresponds to the carbonyl group. The signals located at 146.03 and 137.2 ppm corresponding to thiophene carbons. The carbons of benzotriazole ring appeared to be between 140.24-66.26 ppm(See Supplemantary Materials, Figure S4). In ^{13}C-NMR spectrum of [PdL1(OAc)$_2$] complex, carbon signal of C=O shifted to 162.85 ppm. The methyl carbon of the acetate ligand appeared to be at 23.95 ppm (See Supplemantary Materials, Figure S5).

In the IR spectrum of L2 ligand, the O-H stretching vibration of dicarboxylic acid disappeared after benzotriazole substitution. Vibrations observed at 3176-3134 cm^{-1} were related to aromatic C-H bonds. Carbonyl stretching frequency shifted from 1689 cm^{-1} to 1710 cm^{-1} after substitution with benzotriazole. C-N stretching and bending vibration peaks were observed at 1379 cm^{-1} and 1249-1212 cm^{-1}, respectively (See Supplemantary Materials, Figure S6). After the complex formation, peaks observed at

1330 and 1223 cm^{-1} were dedicated to coordination which occurred via nitrogen atom of L2 ligand. Eventually, frequency shifting for about 49 cm^{-1} value was observed. Pd-O vibration of acetate ion was also observed at 434 cm^{-1} (See Supplemantary Materials, Figure S7). In the 1H-NMR spectrum of L2 ligand, aromatic protons of benzotriazole part were observed as two triplet (7.62-7.78 ppm) and two doublet (8.24-8.48 ppm) signals. Singlet peak observed at 8.34 ppm was related to furan protons signal (See Supplemantary Materials, Figure S8). In the [PdL2(OAc)$_2$] complex spectrum, proton signals of furan ring shifted from 8.34 ppm to 8.15 ppm. Additionally, two triplet peaks of free ligand at 7.62 ppm and 7.78 ppm shifted to 7.45 ppm and 7.59 ppm. After the complexation, two doublet proton peaks of benzotriazole ring at 8.24 ppm and 8.48 ppm appeared at 7.62 ppm and 7.78 ppm respectively. The acetate group peaks were observed at 2.09 ppm as singlet signal (See Supplemantary Materials, Figure S9). ^{13}C-NMR spectrum of L2 ligand contains nine carbon signals between 154.3-114.7 ppm. The carbonyl (C=O) carbon signal was observed at 154.3 ppm. The carbon atoms of furan ring were observed at 147.6 ppm and 124.4 ppm. The other carbon signals between 145.7-114.7 ppm were related to benzotriazole group (See Supplemantary Materials, Figure S10). In the ^{13}C-NMR, the spectrum of [PdL2(OAc)$_2$] complex was observed to have eleven signals between 202.2-21.7 ppm values. The aromatic carbon signals pf complex were observed between 159.9-104.5 ppm. The signals observed at 21.7 ppm and 202.2 ppm were associated with methyl and carbonyl carbon of complex acetate ion (See Supplemantary Materials, Figure S11).

The UV-VIS spectrum of complexes and ligands were taken with DMSO solutions between 200-800 nm range. For L1 ligand, $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ intra ligand transitions were observed at 262, 281 and 335 nm. After the formation of [PdL1(OAc)$_2$] complex, these transitions shifted to lower wavelength (251 and 331 nm) (See Supplemantary Materials, Figure S12). The transitions observed at 252, 279 and 333 nm for L2 ligand shifted to 265 and 320 nm in the [PdL2(OAc)$_2$] complex spectra (See Supplemantary Materials, FigureS13). Any d-d transitions of both complexes were not observed from spectra because of d^8 electronic configurations of metal ions.

The mass spectra of [PdL1(OAc)$_2$] complex showed the molecular ion peak at *m/z* 661.4. This value indicates that the solvent molecule tetrahydrofuran (THF) was trapped in the complex structure (See Supplemantary Materials, Figure S14). The same situation was observed also for [PdL2(OAc)$_2$] complex with close *m/z* value as *m/z* 661.3 (See Supplemantary Materials, Figure S15). The magnetic susceptibility measurement of complexes was performed according to the method of Evans with a Gouy balance. The experimental magnetic susceptibility values were equal to zero for both complexes. This indicated that the complexes were diamagnetic with all electrons paired and that both of the geometries were square planar. In line with all these characterization studies, the proposed structures of complexes can be seen in Figure 2.

2.6. Catalytic studies

Catalytic hydrogenation experiments were carried out using a 100 mL stainless steel high pressure reactor (Parr Inc. 4590 micro Bench Top with 4842 process controller) containing a magnetic bar, temperature controller and sapphire window for viewing. Before this, each experiment reactor was first cleaned, and substrate, catalyst and ionic liquid were then placed into the reactor. The reactor was tightly closed and flushed with nitrogen gas to displace any air inside. The reactor was heated to reaction temperature, and hydrogen gas was introduced into the reactor. After the reaction ended, hydrogen gas was depressurized with valves and product(s) extracted with n-hexane from ionic liquid media; then, the organic solution was directly analyzed by gas chromatography.

We also investigated reusability of catalysts. For this purpose, when the main reaction was completed, catalyst was removed from ionic liquid via extraction with DMSO, filtered and washed with acetone and diethylether and dried at 333 K. Fresh reactants and catalyst was added to reactor for the next reaction cycle.

2.7. Solubility Tests of Complexes in IL

Qualitative solubility of complex in [bmim][BF_4] was investigated by visual observation under different temperatures (303-383 K). For this purpose, 1 mL [bmim][BF_4] and 10 mg catalyst was placed in a test tube, mixed and heated to desired temperature. The solution was stirred for one hour, and solubility was observed by visual observation. Both complexes were found to be insoluble in [bmim][BF_4] and to act as a heterogeneous catalyst during the catalytic reactions.

3. Results and discussion

The objective of the catalytic study presented here was to develop an environmentally friendly catalytic system for the hydrogenation of some olefins. For this purpose, in this study, we synthesized two new Pd complexes for use as hydrogenation catalysts. In addition, we also aimed at using ionic liquid as reaction media. The results obtained are presented below.

3.1. Styrene hydrogenation in IL

The effects of various parameters such as temperature, H_2(g) pressure, reaction medium, catalyst amount and reaction time on the hydrogenation reactions of styrene were investigated. We also investigated the reusability of the palladium catalysts. The data obtained can be seen in Table 1 and Table 2**.**

Table 1. Hydrogenation of styrene by [PdL1$(OAc)_2$] complex

Ent.	T(K)	P_{H2} (Bar)	t(h)	n_s/n_c	Total Conv. (%)	TON	TOF(h^{-1})
1	313	10	1	103	3.8	4	4
2	323	10	1	103	14.9	15	15
3	333	10	1	103	28.8	30	30
4	343	10	1	103	52.7	55	55
5	353	10	1	103	100	104	104
6	323	30	1	103	46.8	49	49
7	323	60	1	103	75.4	78	78
8	353	10	0.25	103	23.5	24	92
9	353	10	0.5	103	35.6	37	74
10	353	10	0.75	103	54.4	57	75
11	353	10	1	172	100	172	172
12	353	10	1	515	65	338	338
13[b]	353	10	1	103	100	104	104
14[c]	353	10	1	103	100	104	104
15[d]	353	10	1	103	90.1	94	94

[a] Reaction conditions: $n_{cat.} = 8.36x10^{-6}$ mol, $n_{styr.} = 8.69x10^{-4}$ mol, $V_{solv.}$ = 0.5 mL, P_{H2} = 10 bar; [b] DMSO; [c] Toluene; [d] cat.= [Pd$(OAc)_2$].

For [PdL1(OAc)$_2$] complex, the effects of reaction temperature were investigated in the range of 313 K to 353 K, and the other reaction parameters were kept constant (P_{H2}=10 bar, sub./cat.=103). It was observed that the conversion value reached from 3.8 % to 100 % with the increasing temperature in 1h (Entries 1-5). As a result of the increasing reaction temperature, higher energizing molecules can easily exceed the activation energy required to form the desired product and increase the product yield. Hence, the optimal reaction temperature was found to be 353 K.

We studied four different reaction times to determine the optimal reaction time in the hydrogenation of styrene (Entries 5, 8-10). 100 % ethylbenzene formation was obtained in 1 h at 353 K. Hence, the remaining catalytic experiments were conducted in 1 hour reaction time.

To investigate the effects of the hydrogen pressure, experiments were carried out at 10, 30 and 60 bar H_2(g) pressures at 323 K in 1h. According to the results, the hydrogen pressure had a strong effect on ethyl benzene conversion. TON value increased from 15 to 78 as shown in entries 2, 6 and 7. In order to determine the catalyst amount effect on styrene hydrogenation reactions, three different n_s/n_c ratios were selected (Entries 5,11,12) at 393 K in 1h. The conversion of ethylbenzene increased from 65% to 100% when the n_s/n_c ratio decreased from 515 to 172. Reusability and recovery of catalyst from the reaction media are important issues for catalytic systems. The reusability of [PdL1(OAc)$_2$] complex was investigated for the five cycles under the optimal reaction conditions (353 K, 10 bar H_2 and 1 h), and catalyst activity retained over 96% without observing significant deactivation for at least three cycles (Figure 1).

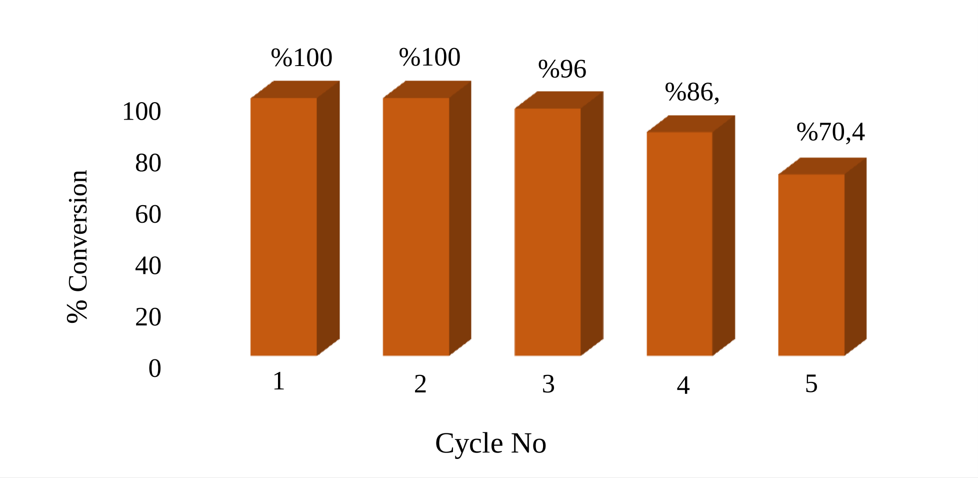


Fig 1. Reusability of [PdL1(OAc)$_2$] catalyst in styrene hydrogenation. Reaction conditions: T = 353 K, PH_2= 10 bar, $n_{sub.}$ = 8.69 × 10^{-4}, $n_{cat.}$ = 8.36 × 10^{-6} mol, n_s/n_c = 103, t = 1 h.

For [PdL2(OAc)$_2$] complex, temperature effect was investigated between 313 K to 363 K under constant hydrogen pressure (10 Bar), reaction time (1 h) and sub./cat. ratio (100) (Entries 1-6). According to the results, ethylbenzene conversion increased from 13.9% to 100% with the increasing reaction temperature. We determined the optimal reaction temperature for [PdL2(OAc)$_2$] complex as 363 K. H_2 pressure effect experiments were carried out at minimum conversion temperature as 323 K in order to observe whether there was an increase in the conversion value of the desired product with the rising hydrogen pressure. When the pressure increased from 10, 30 and finally

60 bar, ethylbenzene conversion was found to increase from 28.4%, 93.7% and finally to 100%, respectively (Entries 2,7,8).

Table 2. Hydrogenation of styrene by [PdL2(OAc)$_2$] complex

Ent.	**T(K)**	**P_{H2} (Bar)**	**t(h)**	**n_s/n_c**	**Total Conv. (%)**	**TON**	**TOF(h^{-1})**
1	313	10	1	100	13.9	14	14
2	323	10	1	100	28.4	29	29
3	333	10	1	100	38	38	38
4	343	10	1	100	43.6	44	44
5	353	10	1	100	74.6	75	75
6	363	10	1	100	100	101	101
7	323	30	1	100	93.7	95	95
8	323	60	1	100	100	101	101
9	353	10	1	167	73.4	124	124
10	353	10	1	500	45.6	230	230
11[b]	363	10	1	100	100	101	101
12[c]	363	10	1	100	100	101	101
13[d]	363	10	1	100	92,7	93	93

[a] Reaction conditions: $n_{cat.} = 8.59 \times 10^{-6}$ mol, $n_{styr.} = 8.69 \times 10^{-4}$ mol, $V_{solv.} = 0.5$ mL, [b] DMSO; [c] Toluene; [d] cat.= [Pd(OAc)$_2$].

In order to test the effect of n_s/n_c ratio on styrene hydrogenation reactions, experiments were carried out with the n_s/n_c values of 100, 167 and 500. According to the results, the highest TON value (TON=230) was obtained with n_s/n_c =500 at 353 K in 1h (Entries 5, 9, 10).

To test the effect of solvent type on catalytic reactions, toluene and DMSO were selected as non-polar and polar solvents. The results indicated that catalytic cycle does not depend on the solvent polarity under the same conditions (353 K, 10 bar H_2 and 1h reaction time) (Entries 6, 11, 12).

As for the testing of [PdL2(OAc)$_2$] catalyst reusability, experiments were conducted for five cycles with the same catalyst under optimal reaction conditions (363 K, 10 bar and 1 h). Catalyst was found to be effective over five cycles without loss of its activity. Catalyst reusability results are given in Figure 2.

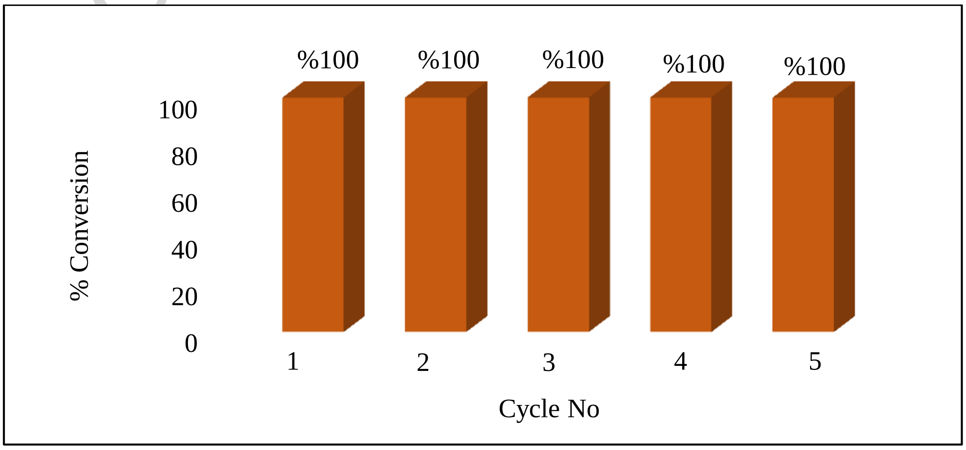


Fig 2. Reusability of [PdL2(OAc)$_2$] catalyst in styrene hydrogenation. Reaction conditions: T = 363 K, P$_{H_2}$= 10 bar, $n_{sub.} = 8.69 \times 10^{-4}$, $n_{cat.} = 8.59 \times 10^{-6}$ mol, $n_s/n_c = 100$, t = 1 h.

3.2. 1-Octene Hydrogenation in IL

1-octene was chosen as a terminal olefin in catalytic experiments. The results are given in Table 2. n-octane is the desired hydrogenation product of 1-octene. Conversion to internal alkenes as 2-octene and 3-octene (byproduct) was also observed in some cases.

In order to study the effect of temperature on catalyst activity of [PdL1(OAc)$_2$] catalyst, the experiments were conducted at 4 different temperatures (333-363 K). The catalyst activity was found to be very low at 333 K with only 2.4% n-octane formation. Increasing reaction temperature from 343 to 363 K resulted in an increase in n-octane selectivity from 10.9% to 86.7% and in an increase in the total conversion value.

Reusability tests of the same catalyst were performed at 363 K in 1h as shown in Table 2. The conversion rate was found to be about 80% for the first four cycles and to decrease to 65.7% at the last cycle.

Table 3. Hydrogenation of 1-octene by [PdL1(OAc)$_2$] complex

Ent.	**T(K)**	**Cycle No**	**Total Conv. (%)**	**Products (%)**			**TON**	**TOF (h^{-1})**
				(n-octane)	**(2-octene)**	**(3-octene)**		
1	333		2.4	2.4	------	------	2	2
2	343		15.6	10.9	3.1	1.6	12	12
3	353		81.7	58.3	15.3	8.1	62	62
4	363	1	95.6	86.7	6.9	2.0	73	73
5[b]	363		91.2	35.7	38.1	17.4	69	69
6[c]	363		100	100	0	0	76	76
7	363	2	87.9	55.9	21.6	10.4	67	67
8	363	3	84.2	51.3	19.2	13.7	64	64
9	363	4	79.3	45.4	21.4	12.4	60	60
10	363	5	65.7	38.3	17.2	10.2	50	50

[a] Reaction conditions: $n_{cat.} = 8.36 \times 10^{-6}$ mol, $n_{1\text{-}oct.} = 6.37 \times 10^{-4}$ mol, n_s/n_c=76, $V_{solv.}$ = 0.5 mL, P_{H2} = 10 bar, t=1h, [b] DMSO, [c] Toluene.

To test the effectivity of [PdL2(OAc)$_2$] catalyst on 1-octene hydrogenation, experiments were conducted between 323 K - 353 K temperatures. Catalyst activity was found to be lower at 323 K than at other temperatures (Entry 1). It was found that the increasing reaction temperature had a positive effect on hydrogenation reactions under the same conditions (10 Bar H_2, 1 h reaction time). The highest conversion rate was obtained at 353 K in 1 h reaction time with 100% n-octane formation (Entry 4).

Catalyst reusability was tested under 10 Bar H_2(g) over five cycles at 353 K in 1 h reaction time period. Approximately 30% catalyst activity loss was found for the last cycle on 1-octene hydrogenation reaction (Entries 7-10).

Table 4. Hydrogenation of 1-octene by [PdL2(OAc)$_2$] complex

Ent.	T(K)	Cycle No	Total Conv. (%)	Products (%)			TON	TOF (h^{-1})
				(n-octane)	(2-octene)	(3-octene)		
1	323	1	16.5	12.5	2.6	1.5	12	12
2	333		21.8	16.6	3.1	2.1	16	16
3	343		61.1	51.4	6.3	3.2	45	45
4	353		100	98.2	1.8	0	74	74
5[b]	353		56.7	29.0	17.9	9.7	42	42
6[c]	353		100	69.9	23.8	6.3	74	74
7	353	2	100	98.7	1.3	0	74	74
8	353	3	100	99.0	1.0	0	74	74
9	353	4	100	95.7	2.8	1.5	74	74
10	353	5	95.7	85.7	7.4	2.6	71	71

[a] Reaction conditions: $n_{cat.} = 8.59 \times 10^{-6}$ mol, $n_{1\text{-}oct.} = 6.37 \times 10^{-4}$ mol, $n_s/n_c = 74$, $V_{solv.} = 0.5$ mL, $P_{H2} = 10$ bar, t=1h [b] DMSO; [c] Toluene.

3.3. Cyclohexene Hydrogenation in IL

Cyclohexene was hydrogenated to cyclohexane with [PdL1(OAc)$_2$] complex in catalytic conditions. The results obtained are given in Table 5. The catalytic efficiency of complex on cyclohexene hydrogenation was investigated with temperatures ranging from 333 K to 373 K (Entries 1-5). It was observed that the activity of catalyst increased gradually to 363 K and then decreased at 373 K suddenly. The reason for the decrease in activity is thought to be the decomposition of catalyst at higher temperatures. The highest conversion value (TOF= 79) was observed at 363 K, under 10 Bar $H_2(g)$ in 1 hour reaction time (Entry 4).

Solvent effect of [PdL1(OAc)$_2$] catalyst on 1-octene hydrogenation led to nearly 100% product formation in toluene when compared to polar DMSO with only 5.6% product formation (Entries 6,7). This means DMSO molecules can coordinate to the metal center and affect the catalytic cycle under these conditions.

Reusability of the same catalyst on cyclohexene hydrogenation was investigated at 363 K in 1 h reaction time (Table 5). It was found that catalyst activity decreased at each cycle and conversion values decreased from 67.1% to 13.7% for the last cycle (Entries 1, 8-11).

Table 5. Hydrogenation of cyclohexene by [PdL1(OAc)$_2$] complex

Entry	T (K)	Cycle No	Conv. (%)	TON	TOF (h^{-1})
1	333	1	0	0	0
2	343		22.5	27	27
3	353		51.3	61	61
4	363		67.1	79	79
5	373		41.1	49	49
6[b]	363		5.6	7	7

7^c	363		98.1	116	116
8	363	2	37.8	45	45
9	363	3	26.7	32	32
10	363	4	16.9	20	20
11	363	5	13.7	16	16

[a] Reaction conditions: $n_{cat.}$ = 8.36 × 10^{-6} mol, $n_{cyc.}$ = 9.87× 10^{-4} mol, n_s/n_c=118, $V_{solv.}$ = 0.5 mL, P_{H2} = 10 bar, t=1h, [b] DMSO; [c] Toluene.

In order to evaluate the catalytic activity of [PdL2(OAc)$_2$] complex on cyclohexene hydrogenation, experiments were conducted between 333-383 K under 10 bar H_2(g), in 1h reaction time. The results are given in Table 6. Catalyst activity was found to be increase with reaction temperature, and the highest activity was obtained at 373 K as 42.5% rather than 383 K (Entry 5). The reason for the activity decrease at 383 K is dedicated to degeneration of the structure of the complex. The highest TON value was reached at 373 K in 6 hour reaction time as 73 (Entry 7). Considering the solvent effect, catalyst is more effective in apolar toluene than DMSO media, and the conversion was found to be 47.3% at 353 K in 1 hour in toluene.

Catalyst reusability was tested under the most productive conditions (373 K, 6 h), and approximately 15% activity loss was found to be from 55.3% to 41.3% after five cycles (Entries 7, 11-14).

Table 6. Hydrogenation of cyclohexene by [PdL2(OAc)$_2$] complex

Entry	**T (K)**	**Cycle No**	**T (h)**	**Conv. (%)**	**TON**	**TOF (h^{-1})**
1	333		1	10.5	12	12
2	343		1	18.1	21	21
3	353		1	27.1	31	31
4	363		1	36.3	42	42
5	373		1	42.5	49	49
6	383		1	28.6	33	33
7	373	1	6	63.1	73	12
9^b	353		1	2.8	3	3
10^c	353		1	47.3	54	54
11	373	2	6	55.3	64	12
12	373	3	6	50.4	58	11
13	373	4	6	44.8	51	10
14	373	5	6	41.3	47	9

[a] Reaction conditions: $n_{cat.}$ = 8.59 × 10^{-6} mol, $n_{cyc.}$ = 9.87× 10^{-4} mol, n_s/n_c=115, $V_{solv.}$ = 0.5 mL, P_{H2} = 10 bar, [b] DMSO; [c] Toluene.

4. Conclusion

In this study, two new N-Acyl benzotriazole palladium complexes containing thiophene and furan ring were synthesized and characterized. The activity of complexes for some olefins hydrogenation reactions in [bmim][BF_4] was investigated. The activity of [PdL1(OAc)$_2$] complex was found to be close to [PdL2(OAc)$_2$] especially on styrene hydrogenation under the same conditions. Little activity difference was observed on 1-

octene and cyclohexene hydrogenations between two catalysts. Both catalysts can be active in organic solvents besides green reaction media. Additionally, [PdL2(OAc)$_2$] catalyst can be reused up to five times on styrene hydrogenation reactions without loss of its activity.

We also investigated the performance of metal precursor (Pd(OAc)$_2$) in [bmim][BF$_4$]. For both complexes, lower TOF values were obtained with (Pd(OAc)$_2$). This indicates new ligands have a positive effect on the catalytic activity of metal.

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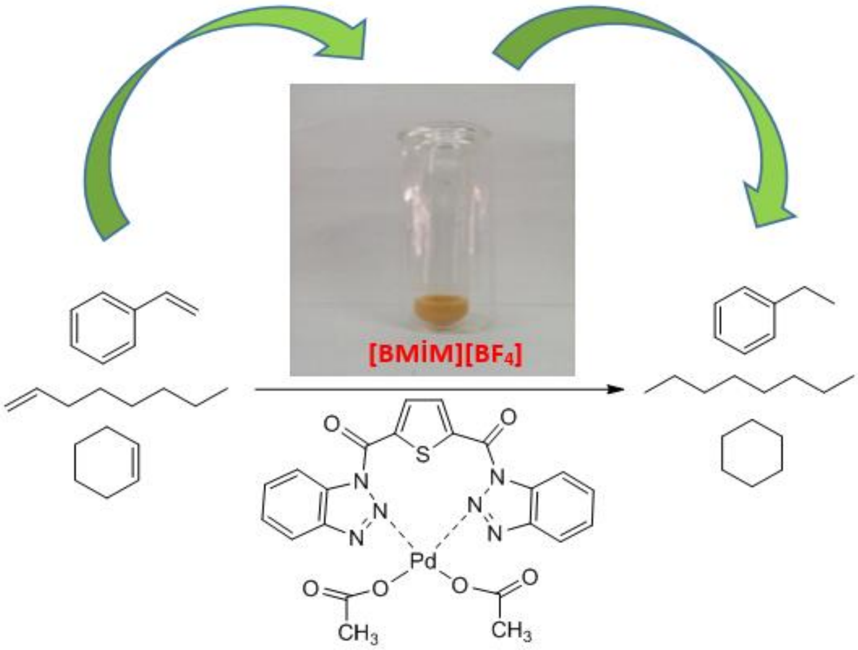

Graphical abstract

Highlights:

- New benzotriazole derived thiophene and furan ligands and their palladium complexes has been synthesized and characterized.
- Catalytic activity of complexes was tested on some olefins hydrogenations and 100 % ethyl benzene formation was observed within 1 hour in [bmim][BF_4] with both complexes.
- [PdL2($(OAc)_2$)] complex can be reused up to five times on styrene hydrogenation without loss of its activity.