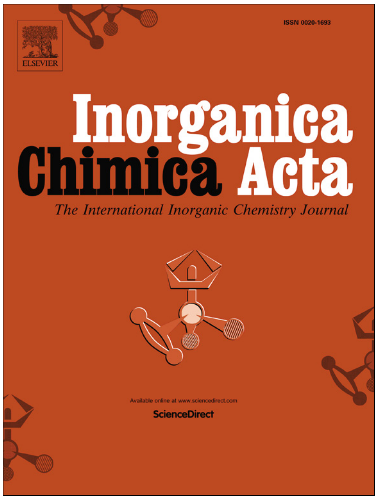

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Synthesis, characterization, density function theory studies and catalytic performances of palladium(II)-*N*-heterocyclic carbene complexes derived from benzimidazol-2-ylidenes

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Abstract

1-Benzyl-3-ethylbenzimidazolium iodide (**1**) and 1-benzyl-3-(2′-nitrilebenzyl)benzimidazolium bromide (**2**) were prepared by the reaction of 1-benzylbenzimidazole with ethyl iodide or 2-bromomethylbenzonitrile to act as *N*-heterocyclic carbene (NHC) precursors. Bis-NHC silver(I) complexes having halide (**3a** and **4a**) as well as hexafluorophosphate (**3b** and **4b**) counterions were yielded by the reaction of NHC precursors with silver(I) oxide. Subsequent reactions of the silver(I) halide/hexafluorophosphate complexes with [$PdCl_2(CNCH_3)_2$] in methanol afforded the NHC palladium(II) complexes (**5** and **6**) *via* carbene transfer method. All synthesized compounds were fully characterized by analytical and spectrometric methods. Preliminary catalytic studies evinced that the nitrile-functionalized palladium(II)-NHC complex **6** is highly active in the oxidation of 1-octene as well as styrene in the presence of aqueous hydrogen peroxide as an oxidizing agent. Both the olefins were oxidized to their corresponding oxidized products with 45–52% conversion with moderate selectivity in the presence of NHC palladium complexes, which acted as oxidation catalysts. In order to investigate the suggested structure of the title complexes, Density Functional Theory was used to find the stable structures of the palladium complexes and their isomers. Geometry parameters, molecular orbital energies, electronic energy, band gap, and vibrational frequencies were calculated.

Key words: Catalytic oxidation, *N*-heterocyclic carbene, Silver(I)-NHC complex, Palladium(II)-NHC complex, DFT study.

1. Introduction

Organometallic chemistry of *N*-heterocyclic carbenes (NHCs) is an emerging field, which from a general point of view exploits both, the catalytical and biological, potentials of transition as well as inner-transition metal carbene complexes [1,2]. As an added advantage, NHCs are easier to functionalize at both the heteroatoms and on azolium ring to tune the associated steric properties. Interestingly, the NHC ligands react with metal centers through strong σ-donation, and therefore form more stable metal-carbene bonds. However, a very lesser degree of π-back-donation from NHCs is also possible [3]. Benzimidazole cores are among the important building units used in the NHC ligand design and supramolecular chemistry of carbene complexes [4]. The benzimidazole-derived NHC complexes are known as robust catalysts in C-C coupling reactions [5]. These metal complexes were used as precursors for the preparation of other transition metal NHC complexes via the technique of transmetallation [6]. The benzimidazole and other functionalized moieties viz., pyridine, pyraole among others, can be integrated as part of many bidentate donors to afford a class of potential catalysts for numerous catalytic reactions ranging from various C-C coupling reactions to olefin polymerizations [7].

Palladium(II) complexes with NHC ligands (Chart 1) are widely used in organometallic chemistry due to their potential catalytic properties and have been successfully applied for olefin oligo/polymerization and metathesis among other reactions [8,9]. A series of allyl-palladium-NHC complexes of dibenzyl or diadementyl substituted azolium salts have shown a unique ability to catalyze selectively the aerobic oxidation of unprotected 1,2- and 1,3-diols, viz., (±)-1,2-propanediol and 2R,3Rbutanediol and (±)-1,3-butanediol, respectively, and a 1:1 mixture of meso/rac-2,4-pentanediol to hydroxy ketones [10]. In a similar example, the catalytic performance of a dibromo palladium complex, which is immobilized on SBA-15 has shown excellent catalytic activity in the aerobic oxidation of benzyl alcohol [11,12]. Based on seminal work with [Pd(NHC)$_2$(halide)$_2$] and related functionalized-NHC complexes that show high selectivity for C-C carbon bond forming and C-H activation reactions, we reasoned that similar planar, palladium(II) based benzimidazole-derived NHC-complexes could provide a promising platform for the activation of carbon-oxygen bond formation in the presence of an oxidizing agent.

<Chart 1 here>

On the other hand, oxidation reactions with hydrogen peroxide, one of the ‘greenest’ terminal oxidants, are of immense significance due to the importance of epoxides in the industrial manufacture of both bulk and fine chemicals [13,14]. In general, the catalytic reactions that use hydrogen peroxide in combination with readily available, non-hygroscopic and relatively non-toxic palladium-derived catalysts are potentially viable for large-scale production in the industries [15]. On this background, we investigated the synthesis of both, functionalized and non-functionalized 1,3-disubstituted benzimidazolium salts and their silver(I) and palladium(II)-NHC complexes. Later complexes were prepared by carbene transfer technique from silver(I) to palladium(II), and were evaluated for their potential in the epoxidation of 1-octene and styrene in the presence of 30% aqueous hydrogen peroxide. Theoretical calculations in general and ‘density functional theory’ in particular was used to predict the best and stable conformation and to shed light on many theoretical parameters for palladium(II) complexes such as the dipole moment, electronic energy, *cis-trans* energy barrier and molecular orbitals. The starting structure was built according to the crystal structure of the complex *trans*-bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]dibromopalladium(II).

2. Experimental

2.1. Reagents and instruments

All the chemicals used for the present investigation were of reagent grade, and the solvents were dried and distilled before use according to the standard protocols. Benzimidazole, benzyl bromide, 2-bromomethy benzonitrile, ethyl iodide, potassium hexafluorophosphate, silver(I) oxide, palladium(II) chloride, 1-octene, styrene and 30% aqueous hydrogen peroxide were purchased from Sigma–Aldrich and used without further purification. 1-Benzylbenzimidazole was prepared according to the literature method [16] with slight modifications. ^{1}H and ^{13}C NMR spectra of all the synthesized compounds were recorded at room temperature using a Bruker 400 MHz spectrometer in d_6-DMSO or d_3-CD_3CN, using TMS as an internal reference. The FTIR spectra of all the compounds were obtained in potassium bromide disks using a Perkin Elmer 2000 system spectrometer in the range 4000–400 cm^{-1}. The melting points were assessed by using a Stuart Scientific SMP-1 (UK) instrument. All reported compounds were analyzed for carbon, hydrogen and nitrogen by the CHN microanalyses using a Perkin Elmer 2400 LS Series

CHN/S analyzer. Olefin oxidized products were analyzed by a Hewlett-Packard 6890N gas chromatograph using an Ultra-1 column and a Hewlett-Packard GC-MSD instrument using an HP5 column.

2.2. Syntheses

*2.2.1. Synthesis of 1-benzyl-3-ethylbenzimidazolium iodide (**1**)*

To a solution of 1-benzylbenzimidazole (0.208 g, 1.0 mmol) in acetonitrile (30 mL), an excess of ethyl iodide (0.21 g, 1.3 mmol) was added while stirring in a 50 mL round bottom flask fitted with a condenser. The resulting reaction mixture was refluxed for 48 h in an oil bath. The solvent was removed under reduced pressure by using a rotary evaporator to afford a beige solid, which was washed with diethyl ether (3 × 5 mL) and dried. Yield: 83.8 %. M.P.: 125.5 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.6 (3H, t J = 7.5 Hz, CH_3), 4.58 (2H, quartet J = 7.5 Hz, CH_2), 5.8 (2H, s, benzylic CH_2), 7.30-7.37 (5H, m, benzyl-H), 7.85-7.93 (2H, m, benzimidazole-H), 8.16-8.23 (2H, m, benzimidazole-H) and 10.0 (H, s, benzimidazole-H2′). ^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ 15.1 (CH_3), 51.7 (CH_2), 53.2 (benzylic CH_2), 125.5 (C2,C6-benzyl), 127.8 (C3,C5-benzyl), 129.3 (C4-benzyl), 135.9 (C1-benzyl), 118.5 (C4-benzimidazole), 118.8 (C5-benzimidazole), 126.9 (C6-benzimidazole), 131.3 (C7-benzimidazole), 131.5 (C8,C9-benzimidazole), and 139.3 (benzimidazolium C2′). FT-IR (KBr disc) cm^{-1}: 2931, 2866 ν(C–H), 1626 ν(C=N, benzimidazole), 1011 ν(C-N, benzimidazole). Anal. Calc. for $C_{16}H_{17}N_2I$: C, 52.8; H, 4.7; N, 7.7. Found: C, 52.3; H, 5.0; 7.3%.

*2.2.2. Synthesis of 1-benzyl-3-(2-benzonitrile)benzimidazolium bromide (**2**)*

This compound was prepared in a manner analogous to that for **1**, only with 2-bromomethyl benzonitrile (0.196 g, 1.0 mmol) instead of ethyl iodide. Preparation, further work up and purifications were done according to the reported method [17]. Yield: 86.2 %. M.P.: 119-120 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 5.85 (2H, s, benzylic CH_2), 6.1 (2H, s, benzonitrile CH_2), 7.3-7.41 (5H, m, Ar-CHbenzyl), 7.7-7.83 (8H, m, Ar-CHbenzonitrile), 7.91-8.0 Ar-CHbenzimidazole), and 10.12 (1H, s, benzimidazolium H2´). ^{13}C{^{1}H}NMR (100 MHz, d_6-DMSO): δ 48.2 (CH_2), 50.1 (CH_2), 111.1 (C≡N), 112.8 (C2,C6-benzyl), 125.4 (C3,C5-benzyl), 126.4 (C4-benzyl), 135.3 (C1-benzyl), 113.8 (C5-benzonitrile), 127.7 (C4-benzonitrile), 130.4 (C3-benzonitrile), 132.3 (C1-benzonitrile), (C2-benzonitrile), 116.5 (C4-benzimidazole), 126.0 (C5-benzimidazole), 130.4 (C6-benzimidazole), 132.9 (C7-benzimidazole), 136.3 (C8,C9-

benzimidazole), 142.9 (benzimidazolium C2′). FT-IR (KBr disc) cm^{-1}: 2943, ~2860 ν(C–H), 2224 ν(C≡N, benzonitrile), 1616 ν(C=N, benzimidazole), ~1010 ν(C-N, benzimidazole). Anal. Calc. for $C_{22}H_{18}N_3Br$: C, 65.4; H, 4.5; N, 10.4. Found: C, 65.3; H, 4.3; 10.8%.

*2.2.3. Synthesis of bis-(1-benzyl-3-ethylbenzimidazolium)silver(I) iodide/hexafluorophosphate (**3a/3b**)*

A suspension of silver(I) oxide (0.126 g, 0.055 mmol) and benzimidazolium salt **1** (0.365 g, 1 mmol) in methanol (30 mL) were stirred at room temperature for 30 h in a 50 mL round bottom flask wrapped with aluminum foil to exclude light. After which the reaction mixture was filtered through a pad of celite to discard the unreacted silver(I) oxide. Filtrate was evaporated to dryness under reduced pressure using a rotary evaporator to yield off-white silver(I)-NHC halide complex **3a** as a light-sensitive solid. The complex thus obtained was recrystallized by repeated precipitation in methanol and diethyl ether solution. Yield: 67.2 %. M.P.: 202.5 ^{o}C.). ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.45 (6H, t, J = 7.2 Hz, 2×CH_3), 4.55 (4H, quartet J = 7.2 Hz, 2×CH_2), 5.77 (4H, s, benzylic 2×CH_2), 7.26-7.32 (6H, m, 2×benzyl-H), 7.48-7.55 (4H, t, J = 6.0 Hz, 2×benzyl-H), 7.75 (4H, d, J = 7.0 Hz, benzimidazole-H), 7.86 (4H, m, benzimidazole-H). ^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ 16.3 (CH_3), 51.4 (CH_2), 53.8 (benzylic CH_2), 119.1 (C2,C6-benzyl), 125.4 (C3,C5-benzyl), 126.9 (C4-benzyl), 135.8 (C1-benzyl), 118.1 (C4-benzimidazole), 120.2 (C5-benzimidazole), 125.4 (C6-benzimidazole), 132.2 (C7-benzimidazole), 133.7 (C8,C9-benzimidazole), and 182.2 (C2′ benzimidazolium-Ag). FT-IR (KBr disc) cm^{-1}: ~2935, 2872 ν(C–H), ~1620 ν(C=N, benzimidazole), 1073 ν(C-N, benzimidazole). Anal. Calc. for $C_{32}H_{32}N_4IAg$: C, 54.3; H, 4.6; N, 7.9. Found: C, 54.8; H, 5.1; 8.1%. Further, the iodide complex **3a** was directly converted into its hexafluorophosphate counterpart by metathesis reaction using KPF_6 (0.276 g, 1.5 mmol) in 30 mL methanol. The resultant solution was stirred for 2 h during which a gray colored precipitate of **3b** was formed and was left to stand overnight. So obtained hexafluorophosphate complex **3b** was filtered under reduced pressure, washed with distilled water (3 x 5 mL) to remove the unreacted KPF_6, and air dried in dark. Spectral data of the complex **3b** had no or negligible changes compared to its iodide counterpart **3a**. Microanalysis data of the complex is in well agreement with the proposed structure.

2.2.4. Synthesis of bis-[1-benzyl-3-(2-benzonitrile)benzimidazolium]silver(I) bromide

*/hexafluorophosphate (**4a/4b**)*

These complexes were prepared in a manner analogous to that for **3a/3b**, only with the functionalized benzimidazolium salt **2** (0.404 g, 1.0 mmol) instead of non-functionalized salt **1**. Preparation, further work up and purifications of both the complexes were done according to the established procedure [17]. Yield: 55.3 %. M.P.: 221-222 °C. Both, **4a** and **4b**, had almost similar spectral characteristics among which data of the complex **4a** is given. ^{1}H NMR (500 MHz, d_6-DMSO): δ 5.7 (2H, s, benzylic CH_2), 5.95 (2H, s, benzonitrile CH_2), 7.10-7.22 (5H, m, Ar-CHbenzyl) 7.40-7.52 (4H, m, Ar-CHbenzonitrile), 7.65-7.86 (4H, m, Ar-CHbenzimidazole). ^{13}C{1H} NMR (100 MHz, d_6-DMSO): δ 50.3 (CH_2-benzyl), 51.9 (CH_2-benzonitrile), 110.4 (C≡N-nitrile), 117.1 (C2,C6-benzyl), 124.4 (C3,C5-benzyl), 127.2 (C4-benzyl), 133.3 (C1-benzyl), 124.5 (C1-benzonitrile), 128.7 (C3,C4-benzonitrile), 133.7 (C5,C6-benzonitrile), 136.0 (C2-benzonitrile), 128.0 (C4-benzimidazole), 128.9 (C5-benzimidazole), 133.7 (C6-benzimidazole), 139.3 (C7,C8-benzimidazole), 190.35 (d, *J* = 72.5 Hz, C2´ benzimidazolium-Ag). FT-IR (KBr disc) cm^{-1}: ~2940, 2872 ν(C–H), 2223 ν(C≡N, benzonitrile), 1601 ν(C=N, benzimidazole), ~1070 ν(C-N, benzimidazole). Anal. Calc. for $C_{44}H_{34}N_6BrAg$: C, 63.3; H, 4.1; N, 10.1. Found: C, 63.3; H, 4.5; 10.5%. Microanalysis data of the complex **4b** is in well agreement with its empirical formula.

*2.2.5. Synthesis of bis-(1-benzyl-3-ethylbenzimidazolium)palladium(II) chloride (**5**)*

To a solution of silver(I) bromide complex **3a** (0.355 g, 0.05 mmol) in 20 mL dichloromethane was added $PdCl_2(CH_3CN)_2$ (0.130 g, 0.05 mmol). The reaction mixture was stirred for 14 h at room temperature with the exclusion of light. The resulted suspension was filtered through a pad of celite and the volume of resulting solution was reduced to 4 mL using a rotary evaporator. Further, diethyl ether was added to the solution to yield the desired palladium(II)-NHC complex **5** as a pale brown powder. So obtained complex **5** was recrystallized by the repeated precipitation of the complex in methanol using diethyl ether. This complex exhibits two sets of proton and carbon resonances evidencing the existence of *cis-* and *trans-* isomers of complex **5**. Complex **5** is also obtained from silver hexafluorophosphate complex with almost same yield. Yield: 48.3 %. M.P.: 263-264 °C. ^{1}H NMR (500 MHz, d_3-CD_3CN): δ 1.64 (6H, t *J* = 7.5 Hz, 2×CH_3), 1.85 (6H, t *J* = 7.5 Hz, 2×CH_3), 4.85 (4H, quartet *J* = 7.5 Hz, 2×CH_2), 5.03 (4H, quartet *J* = 7.5 Hz, 2×CH_2), 5.97 (4H, s, benzylic CH_2), 6.19 (4H, s, benzylic CH_2), 7.1-7.21 (6H, m, benzyl-H), 7.34-7.42 (6H, m, benzyl-H), 7.68-7.75 (4H, m, benzimidazole-H) and 7.87-7.94 (4H, m, benzimidazole-H). ^{13}C{1H} NMR (125 MHz, d_3-CD_3CN): δ 16.8, 17.2 (CH_3), 50.2, 50.8 (CH_2), 52.3, 52.7 (benzylic CH_2), 118.6, 119.0, 125.0, 125.4, 126.9, 135.4, 135.8 (Ar-C benzyl), 118.1, 118.3, 120.2, 125.4, 132.2, 132.7, 133.7, (Ar-C benzimidazole), and 178.2 and 178.4 (C2′benzimidazolium-Pd). FT-IR (KBr disc) cm^{-1}: ~2930, ~2870 ν(C–H), 1643 ν(C=N, benzimidazole), 1077 ν(C-N, benzimidazole). Anal. Calc. for $C_{32}H_{32}N_4Cl_2Pd$: C, 59.1; H, 5.0; N, 8.6. Found: C, 59.4; H, 5.1; 8.3%.

*2.2.6. Synthesis of bis-[1-benzyl-3-(2-benzonitrile)benzimidazolium]palladium(II) chloride (**6**)*

To a solution of **4a** (0.418 g, 0.05 mmol) in 20 mL dichloromethne was added $PdCl_2(CH_3CN)_2$ (0.130 g, 0.05 mmol). Following the similar procedure to **5**, functionalized complex **6** was isolated as a brown powder. Complex **6** is also obtained from silver hexafluorophosphate complex with almost same yield. Yield: 56.3%. M.P.: 261-262 °C. ^{1}H NMR (500 MHz, d_3-CD_3CN): δ 6.14 (2H, s, benzylic CH_2), 6.26 (2H, s, benzonitrile CH_2), 7.1-7.22 (5H, m, Ar-CHbenzyl), 7.34-7.46 (4H, m, Ar-CHbenzonitrile), 7.7-7.83 (4H, m, Ar-CHbenzimidazole). ^{13}C{1H} NMR (125 MHz, d_3-CD_3CN): δ 51.5 (CH_2-benzyl), 52.3 (CH_2-benzonitrile), 112.1 (C≡N-nitrile), 118.5 (C2,C6-benzyl), 124.5 (C3,C5-benzyl), 128.2 (C4-benzyl), 132.2 (C1-benzyl), 119.7 (C3-benzonitrile), 123.5 (C4,C5-benzonitrile), 126.7 (C1-benzonitrile), 136.1 (C2-benzonitrile), 127.4 (C4,C7-benzimidazole), 134.1 (C5,C6-benzimidazole), 138.8 (C8,C9-benzimidazole), 174.2 (C2´ benzimidazolium-Pd). FT-IR (KBr disc) cm^{-1}: 2942, 2864 ν(C–H), 2222 ν(C≡N, benzonitrile), 1652 ν(C=N, benzimidazole), 1074 ν(C-N, benzimidazole). Anal. Calc. for $C_{44}H_{34}N_6Cl_2Pd$: C, 64.1; H, 4.2; N, 10.2. Found: C, 63.9; H, 4.5; 10.4%.

2.3. Catalytic activity

The catalytic epoxidation of alkenes viz., 1-octene and styrene, with 30% aqueous hydrogen peroxide was executed in a 25 mL round-bottom flask furnished with a condenser. In a distinctive olefin epoxidation experiment, the flask was loaded with 10 mL of acetone (for 1-octene) or acetonitirle (for styrene), 1.0 mmol alkene, 1.0 mmol hydrogen peroxide, and 1.0 mmol of palladium complex **5** or **6** as catalyst. The oxidation of olefin was carried out in an oil bath with continuous stirring at refluxing temperature for 4 h. At appropriate intervals, aliquots were removed from the reaction mixture and analyzed immediately by GC. Before injecting into the GC, the aliquots were treated with diethyl ether and centrifuged to confiscate unreacted hydrogen peroxide, water and the palladium complex. Further, the organic part was subsequently separated and used for GC analysis. Alkene conversion (%) and the reaction products were quantified using a GC instrument and identified by comparing the retention time of these with the retention time to those of an authentic standard sample.

2.4. DFT Calculations

The structures of the isomers of the present palladium complexes were built based on the crystal structure of the complex *trans*-bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]dibromopalladium(II)) in which, similarly, the palladium is in square-planar geometry with a substituted benzimidazole-based NHC ligand field [18]. Gaussian 09 [19] was employed to execute all the theoretical calculations. 6-31G(d,p) basis set was engaged for the atoms C, H, N and Cl, whereas Pd was demonstrated with LANL2DZ basis set. The optimization was achieved without any restriction in symmetry or internal coordinates. Frequencies calculations have shown no imaginary frequency; and hence the optimized structures of all the isomers are in their optimum minima. These structures were involved to calculate the full set of the molecular orbitals, however, it is focused on the orbitals through HOMO-2 to LUMO+2 along with the band gap energy as this the difference between the HOMO and LUMO set of orbitals, (LUMO-HOMO).

3. Results and discussion

In the present article new palladium(II)-NHC-complexes of a functionalized and a non-functionalized benzimidazol-2-lyidene moiety are reported. Both, benzimidazolium salts and carbene-complexes are air and moisture stable, while silver-complexes were light sensitive. The use of a nitrile-functionality of the benzimidazolium salt is to know the coordination mode of the ligand, however, this found away from the metal center. Palladium(II)-NHC complexes were used as homogeneous catalysts for the olefin epoxidation reactions is in the focus of our work. CHN elemental analysis data of all the reported compounds is in well agreement with their suggested structures. So far, only a limited number of palladium(II)-NHC complexes suitable for olefin oxidation reactions have been studied, nevertheless, nitrile-functionalized complexes employed in olefin epoxidation reactions is presented for the first time.

3.1. Syntheses

N-alkyl- or aryl- or aryl-alkyl substituted benzimidazolium salts are typically prepared by reacting benzimidazole with alkyl- or aryl- or aryl-alkyl halide in stoichiometric ratio in the presence of a strong base like sodium hydroxide [16]. Further, *N,N'*-disubstituted benzimidazolium salts are prepared by the reaction of one equivalent of the corresponding N-substituted benzimidazoles with one equivalent of alkyl- or aryl-halide [20]. This method was successfully utilized to synthesize both, non-functionalized and functionalized, benzimidazolium compounds as shown in Scheme 1. Refluxing 1-benzylbenzimidazole with ethyl iodide or 2-bromomethylbenzonitrile in 1,4-dioxane for 2 days afforded the desired 1-benzyl-3-ethylbenzimidazolium iodide (**1**) and 1-benzyl-3-(2'-benzonitrile)-benzimidazolium bromide (**2**), respectively, as white powders in competitively good yield.

< Scheme 1 here >

< Scheme 2 here >

Further, direct reaction of two equivalents of benzimidazolium salts (**1** and **2**) with [$PdCl_2(CH_3CN)_2$] stirred at different temperatures in different solvents for different periods of time results in no palladium complex formation. Conversely, the reaction of an imidazolium salt with palladium acetate could yield palladium NHC complex [21]. Therefore, we followed the technique of transmetallation to prepare the targeted palladium NHC complexes [22]. Reactions of salts **1** and **2** with silver(I) oxide in methanol at room temperature for 30 h yielded colorless silver-NHC halide complexes **3a** [Ag(non-functionalized-NHC)$_2$]I and **4a** [Ag(nitrile-functionalized-NHC)$_2$]Br, respectively as shown in Scheme 2. Later, these complexes were treated with excess potassium hexafluorophosphate in methanol for 4 h at room temperature to afford silver-NHC hexafluorophosphate complexes **3b** [Ag(non-functionalized-NHC)$_2$]PF_6 and **4b** [Ag(nitrile-functionalized-NHC)$_2$]PF_6, in good yields.

The importance of silver-NHC complexes is apparent in their common use as a carbene transfer agent in the preparation of other transition and inner-transition metal NHC complexes [23,24]. Reaction of **3a** and **4a** with [$PdCl_2(CH_3CN)_2$] in methanol at room temperature for 12 h afforded palladium complexes **5** [Pd(non-functionalized-NHC)$_2$$Cl_2$] and **6** [Pd(nitrile-functionalized-NHC)$_2$$Cl_2$], respectively (Scheme 3), which is as a result of acetonitrile replacement at palladium(II) and halide migration to Ag(I). The yields obtained with this carbene transfer method were lower (48.3% for **5**, 56.3% for **6**), and the same inference is observed in the similar studies when aforementioned route is used for the preparation of palladium-NHC complexes [25].

< Scheme 3 here >

3.2. Spectral characterization

The formation of the benzimidazolium salts and their silver and palladium-NHC complexes in each step can be nicely traced by ^{1}H and ^{13}C NMR, and FTIR spectroscopic techniques followed by microanalysis data. The successful formation of the benzimidazolium salts **1** and **2** was corroborated by characteristic downfield signals at δ 10.0 and 10.12 for the benzimidazolium N-CH-N protons (C2H), respectively. The identity of these NHC precursors **1** and **2** was further evaluated by characteristic downfield signals of benzimidazolium carbene carbon resonances (C2) at δ 139.3 and 142.9, respectively. Apart from these characteristic proton and carbon resonances, spectra of salts also evidenced the presence of benzylic (C12H for **1**, C10H and C17H for **2**), aliphatic (C10H, C11H for **1**) and other aromatic (C4H-C7H, C14H-C18H of **1** and C4H-C7H, C12H-C16H, C19H-C22H of **2**) proton and carbon resonances which are in well agreement with the similar reported compounds [26,27].

The reaction of salts **1** and **2** with silver oxide could proceed smoothly in methanol at mild condition, giving preferably the *anti*-configured NHC-silver halide complexes **3a** and **4a**. While further forms complexes **3b** and **4b** *via* salt metathesis reactions with KPF_6. ^{1}H-NMR spectrum of silver complexes in d_6-DMSO reveals the complete disappearance of the resonances for the acidic C2H-benzimidazole protons, evidencing the successful formation of the desired NHC-silver complexes **3a/b** and **4a/b**. Further, their ^{13}C NMR spectra also display noteworthy downfield shifted resonances for the benzimidazolium carbene carbon nuclei to δ 182.2 and 190.35 (C2 for **3a** and C2 for **4a**), thus pointing to successful NHC-silver complex formation. Interestingly, the latter resonance is an apparent doublet centered at δ 190.35 with coupling constant 72.5 Hz. This resonance is presumably due to the coupling between the carbene carbon of complex **4a** and two isotopes of silver, viz., ^{109}Ag and ^{107}Ag nuclei. Almost similar results were observed in the literature for benzimidazole-derived silver-NHC complexes [28]. Apart from these major changes, spectra of these complexes also evidenced the presence of resonances for other aliphatic and aromatic protons and carbon nuclei.

Furthermore, the formation of palladium-NHC complexes **5** and **6** was verified using ^{1}H and ^{13}C NMR spectroscopy, which showed almost similar pattern to that of silver-NHC complexes with slight variations in the peak positions and their integration values. A bit complicated ^{1}H and ^{13}C NMR spectrum of complex **5** was mainly attributed to a dynamic process in solution. Both the spectra evidenced the presence of two sets of resonances for each proton and carbon, which confirmed the existence of *cis-* and *trans-* isomers in solutions. While complex **6** did not show any isomerism in solution mainly due to more rigid palladium-carbene carbon bond, presumably that originates from nitrile-functionality. Also, the steric factors originating from the substitutions perhaps influenced the formation of rigid palladium-carbene carbon bond. Apart from this, appearance of an apparent carbene carbon resonance at δ 178.2 and 174.2 in the ^{13}C NMR spectra of palladium complexes **5** and **6**, (C2) respectively, indicating the successful formation of desired complexes [29,30].

Finally, benzimidazolium salts and carbene complexes were also monitored by FTIR spectral technique over the range 4000–400 cm^{-1}, to ensure their successful formation. Spectra of the benzimidazolium salts show strong absorption bands at around 1010, 1610, and 2860 and 2930 cm^{-1} corresponding to the stretching vibrations of benzimidazole C-N, C=N and C-H modules, respectively. In the case of salt **2**, a sharp band with medium intensity was observed at 2222 cm^{-1} due to the stretching vibrations of nitrile functionality (C≡N). However, in the complex FTIR spectra, the band due to benzimidazole ring C-N and C=N vibrations showed a negative shifts indicating the formation of carbene-complexes. Interestingly, in the case of silver and palladium complexes of salt **2**, nitrile starching vibrations remained unaffected indicating the presence of aforementioned functionality away from the coordination spear.

3.3. Catalytic epoxidation studies

The activities of the palladium-NHC complexes, **5** and **6**, were tested in the oxidation of 1-octene and styrene. Both, the catalyzed oxidations of 1-octene as well as styrene, were carried out with aqueous hydrogen peroxide to give mixture of oxidized products in different ratio. Control experiments revealed that the presence of hydrogen peroxide and palladium complexes **5** and **6** were all essential for the oxidation of aforementioned olefins. Later, the olefin oxidation character of both the palladium complexes over both the substrates was proven by conducting the similar experiments with benzimidazolium salts **1** and **2**, and their respective silver complexes **3a** and **4a**. Since no significant catalytic activity was detected by compounds **1-4**, hence the oxidation activities of the two palladium complexes were considered truly by the insertion of palladium center.

3.3.1. Epoxidation of 1-octene

Taking into account the oxidation of 1-octene, both the palladium complexes were active (Scheme 4). As evident from the Table 1, the conversion and the selectivity values of both the complexes were comparable. While the catalytic oxidation of 1-octene by these palladium complexes did not occur at room temperature even in the presence of excess hydrogen peroxide. Essentially, since palladium-carbene moieties, in both the cases, are almost similar but they are having non-functionalized and nitrile-functionalized benzimidazolium cores, which are not sensitive to the olefin oxidation. Therefore, they show a comparable behavior in terms of activity and selectivity towards 1-octene. However, the nitrile-functionalized palladium complex **6** showed a higher conversion value (51.2%) with reference to the non-functionalized complex **5** (47.3%) at 70 ^{o}C, which might be originated by the increased steric bulk due to the four benzyl substitution around the palladium center. Such difference can also be ascribed to the formation of isomers in solution, which is quite difficult to evaluate. Nevertheless, the activity of these palladium-carbene complexes found comparable with the heterogeneous catalysts of first row transition metals reported by us [31] as well as by others [32,33].

< Scheme 4 here >

< Table 1 here >

In terms of selectivity, non-functionalized palladium complex **5** displayed slightly better results than its functionalized counterpart. Major product in the oxidation of 1-octene by complexes **5** and **6** was the 1,2-octanediol showing *ca.* 63.2 and 51.8% selectivity, respectively, after 4 h of reaction. The other main product was the 2-octanone formed with the *ca.* 34.7 and 45.7% selectivity along with *ca.* 2.1 and 2.5% of 1,2-epoxyoctane, respectively. This behavior of product formation suggests that a similar reactivity takes place at both the palladium centers with a narrow difference in the acidic character originating from the functionalization. Graphs of substrate conversion and product formation by complexes **5** and **6** as a function of time are shown in Figures 1 and 2, respectively. It is found that the yield of 1,2-octanediol increased as the reaction time is increased in both the cases. It is well known that the formation of 1,2-

octanediol from its epoxy counterpart, 1,2-epoxyoctane, is catalyzed by acidic species. Therefore, it is speculated that, palladium complexes **5** and **6** possess acid sites when activated with oxidant, showed high yields of 1,2-octanediol. Almost similar catalytic performances are displayed by palladium-NHC complexes having almost similar ligand field [31a].

< Figure 1 here >

< Figure 2 here >

3.3.2. Epoxidation of styrene

Palladium complexes, **5** and **6**, were also tested as catalysts in the epoxidation with styrene with hydrogen peroxide as terminal oxidant. Both the palladium complexes were active in the epoxidation of styrene. Both, benzimidazolium salts **1** and **2**, and their silver-carbene complexes **3a** and **4a**, did not induce product formation in the presence and absence of oxidant. Unlike the formation of mixed products in the case of 1-octene, with styrene complexes **5** and **6** showed formation of single product, i.e., styrene epoxide. However, the conversion of styrene found much lesser compared to heterogeneous catalysts [34,35]. Therefore, it is predicted that the activity associated with these palladium complexes is mainly because of the insertion of palladium center. While the palladium complexes **5** and **6** did not catalyze styrene epoxidation at room temperature even after for long time, and even at 70 ^{o}C after 2 h in the presence of excess hydrogen peroxide. The palladium complexes, **5** and **6**, catalyzed the oxidation of styrene in the presence of hydrogen peroxide at 70 ^{o}C after 3 h with 6.5 and 8%, and after 4 h displayed 7.5 and 9% conversion, respectively. Further, even after prolonged reaction time, complexes did not show any further increase in the conversion rate even with the varied oxidant to catalyst ratio. This could be ascribed to the deactivation of active species at higher temperature. In order to optimize the reaction condition to increase the percentage of substrate conversion, we tried the catalytic styrene epoxidation reactions with different solvents at different temperatures, unfortunately all reactions were ended with negative results.

*3.4. Theoretical study using DFT method for complexes **5** and **6***

A structurally similar palladium(II) complex with two un/substituted benzimidazole, *trans*-bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]dibromopalladium(II), was reported by Gökçe and coworkers [19]. In this complex, the palladium center was coordinated by two bromido and two benzimidazole-based NHC ligands. The benzyl and the pentafluorobenzyl substitutions on each benzimidazole core are forming a *trans-* conformation. Since the present palladium(II) complexes **5** and **6** possess similar architectures forming a complex with two substituted benzimidazole-based NHCs and two chlorido ligands, it is appropriate to build the present palladium complexes accordingly. B3LYP, as one of the density functional methods, was used to optimize the starting structures. The common bond distances, angles and dihedral angles were compared with the crystal structure of the similar compound [18] from the literature.

< Table 2 here >

As depicted in Table 2, the values of the dipole moment of the complex **5** in the *cis-* and *trans-* conformations are less than 0.5 Debye. The dipole moment of the complex **6** in the *cis-* conformation is much higher than its *trans-* conformer, which shows the difference in the charge distribution between the two conformations. In contrast, the energy difference or the band gap between the HOMO and LUMO of the four isomers of both the palladium complexes are very close with a value around 1.7 eV.

The electronic energies of the optimized complexes in the *cis-* and *trans-* conformations with the *cis-trans* energy barrier are listed in Table 3. Interestingly, the energy difference between these two conformations for the complex **5** is less than 0.5 kcal/mol and the *trans-* isomer is more stable with that value. The *cis-* conformation of the complex **6** is more stable than the *cis-* conformation with an energy barrier of -11.8 kcal/mol.

< Table 3 here >

The optimized structures of the present palladium complexes were used to calculate the energies of the molecular orbitals (MOs). In order to have a general idea about the molecular orbitals, a number of orbitals beside the HOMO and LUMO orbitals are shown in Figure 3. The figure showing the molecular orbitals through HOMO-2 to LUMO+2 and the band gaps for the *cis-* and *trans-* conformations for the complexes **5** and **6**. The band gaps for the two complexes **5** and **6** are close to 1.7 eV.

< Figure 3 here >

The molecular density distribution through the molecular orbital is reflecting the contribution of each atom in the molecular orbital. The localization of the density for the HOMO and LUMO orbitals for the palladium complexes **5** and **6** are summarized in Figures 4 and 5, respectively. Interestingly, the density localization is identical for the corresponding molecular orbitals for these two complexes. The highest contribution for the HOMO molecular orbital for the two isomers is attributed to the lone pairs on the chlorido ligands. In the LUMO orbital, in addition to the localized density from the palladium and the two chlorido ligands, there is some contribution from the carbene of the benzimidazole groups, as shown in Figures 4 and 5.

< Figure 4 here >

< Figure 5 here >

4. Conclusions

Two non-symmetrically substituted benzimidazolium salts as NHC precursors can be efficiently complexed with silver(I) in good yields. Owing to the easier crystallization of the silver-carbene complexes with bulkier anions like hexaflurophosphate anion, halide complexes were converted into their hexaflurophosphate counterparts by salt metathesis reaction. Palladium-carbene complexes of the NHC precursors were prepared by the carbene transfer reaction using silver complexes. Both, benzimidazolium salts and their carbene-complexes, were evaluated as catalysts for oxidation of olefins viz., 1-octene and styrene, using hydrogen peroxide as terminal oxidant. Both the palladium complexes showed moderate substrate conversion values in the range 47-51% with good selectivity. However, in the case of styrene epoxidation, percentage conversion of substrate found much lesser compared to heterogonous catalysts. DFT calculations have shown that the *cis* and *trans* energy barrier of the complex **5** is close to 0.5 kcal/mol and the *trans* isomer is more stable while the energy barrier for the complex **6** is -11.8 kcal/mol, hence the *cis* conformation found more stable.

Acknowledgments

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Appendix A. Supplementary material

Bar diagrams showing percentage conversion of 1-octene and percentage selectivity as a function of time are given in the supplementary material.

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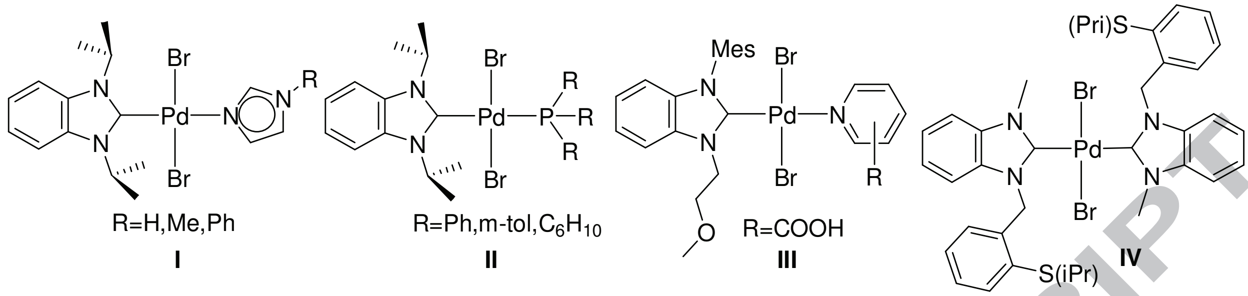
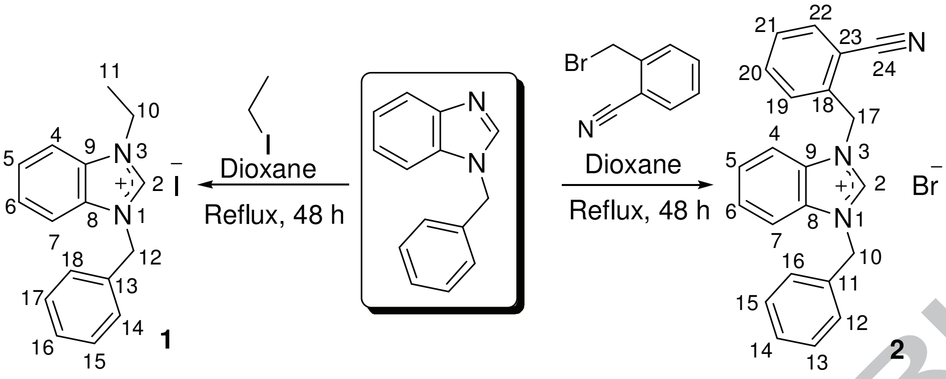
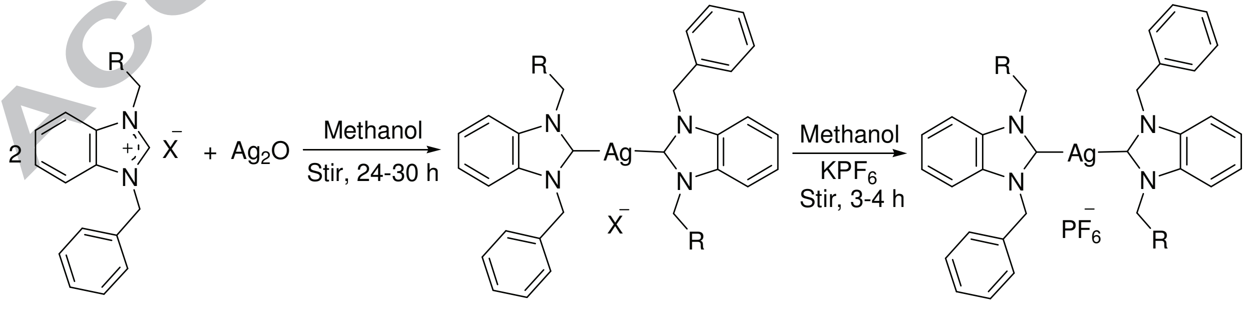
Chart 1. Catalytically active benzimidazole-derived Pd(II)-NHC complexes.



Scheme 1. Synthesis of benzimidazol-2-ylidenes.



Scheme 2. Synthesis of bis(carbene)-Ag complexes.

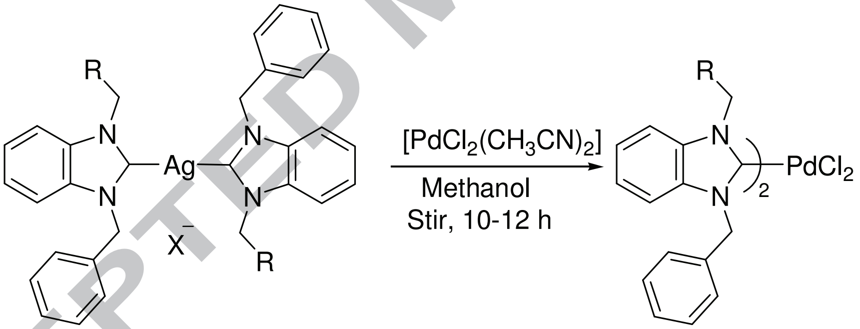


1: R=CH_3, X=I
2: R=2-CN-Ph, X=Br

3a: R=CH_3, X=I
4a: R=2-CN-Ph, X=Br

3b: R=CH_3
4b: R=2-CN-Ph

Scheme 3. Synthesis of bis(carbene)-Pd complexes via carbene transfer reaction.



3: R=CH$_3$, X=I, PF$_6$
4: R=2-CN-Ph, X=Br, PF$_6$

5: R=CH$_3$
6: R=2-CN-Ph

Scheme 4. Catalytic oxidation of 1-octene by Pd(II)-NHC complexes **5** and **6** in the presence of hydrogen peroxide.

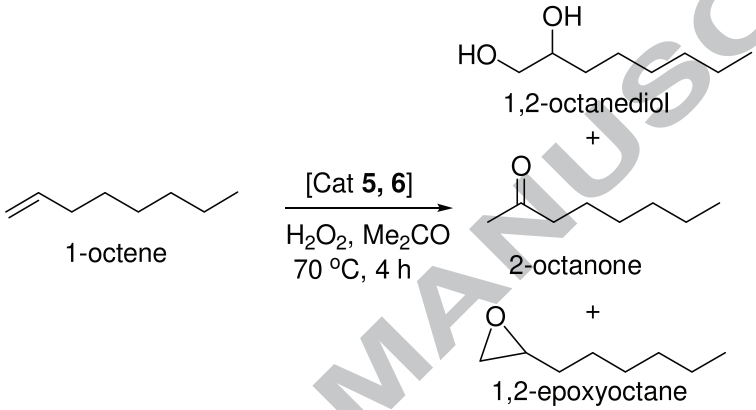


Figure 1. Percentage conversion of 1-octene and the formation of 1,2-octanediol and 2-octanone from epoxidation using aqueous hydrogen peroxide at 70 ^{o}C catalyzed palladium complex **5**.

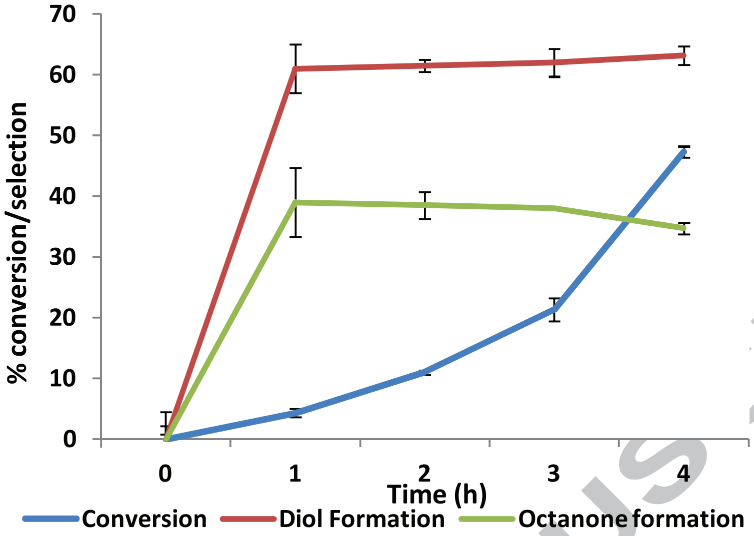


Figure 2. Percentage conversion of 1-octene and the formation of 1,2-octanediol and 2-octanone from epoxidation using aqueous hydrogen peroxide at 70 ^{o}C catalyzed palladium complex **6**.

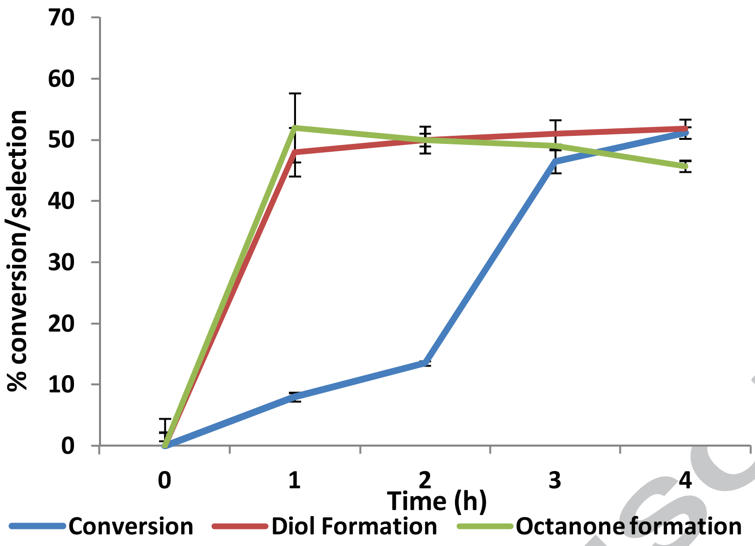

70
60
50
40
30
20
10
0
% conversion/selection
0
1
2
3
4
Time (h)
Conversion
Diol Formation
Octanone formation

Figure 3. Energy of the molecular orbitals for HOMO-2 through to LUMO+2 and band gaps for the cis and trans conformations for the complexes **5** and **6**.

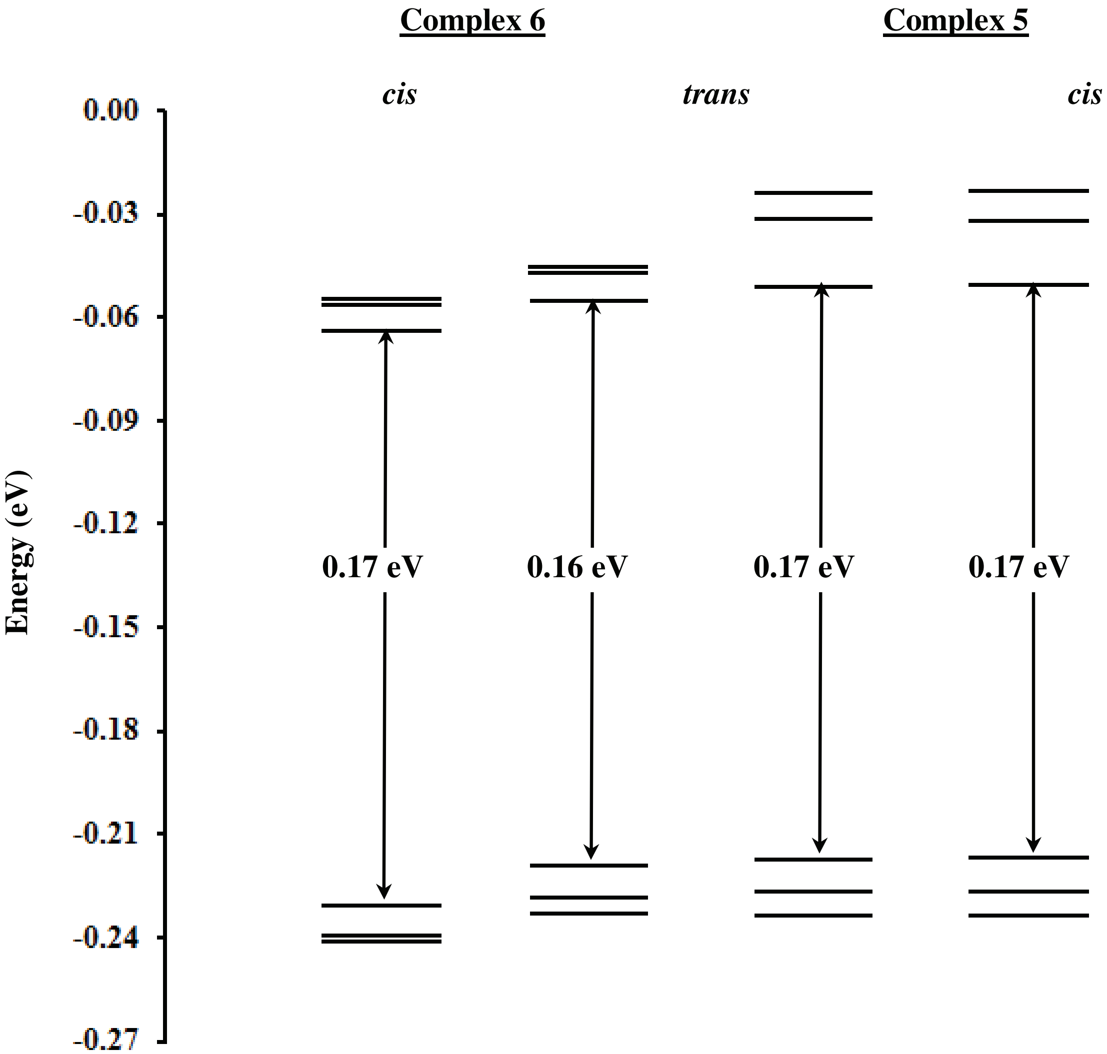


Figure 4. Density distribution for the HOMO and LUMO molecular orbitals for the complex **5**.

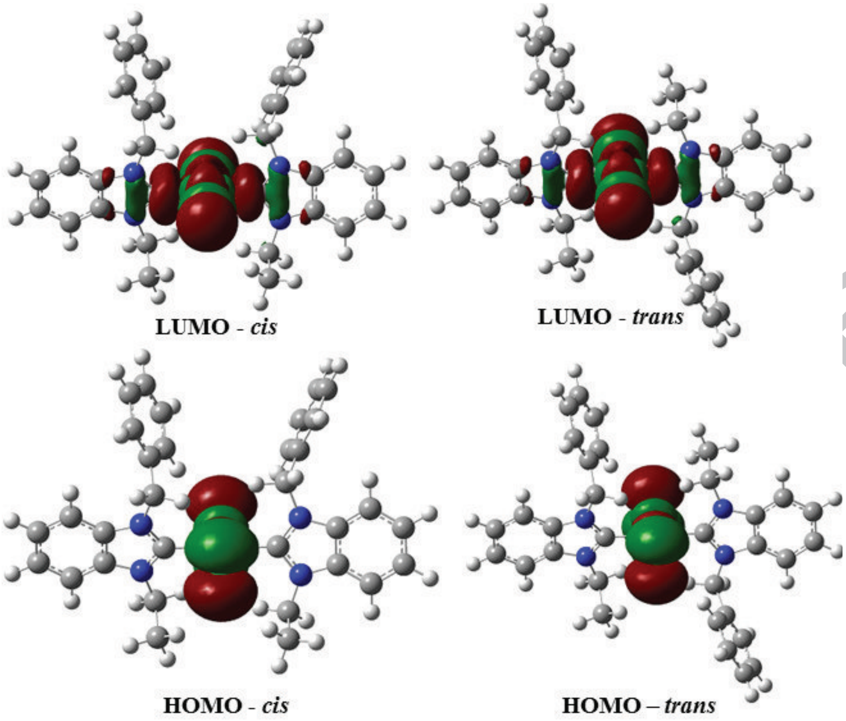


Figure 5. Density distribution for the HOMO and LUMO molecular orbitals for the complex **6**.

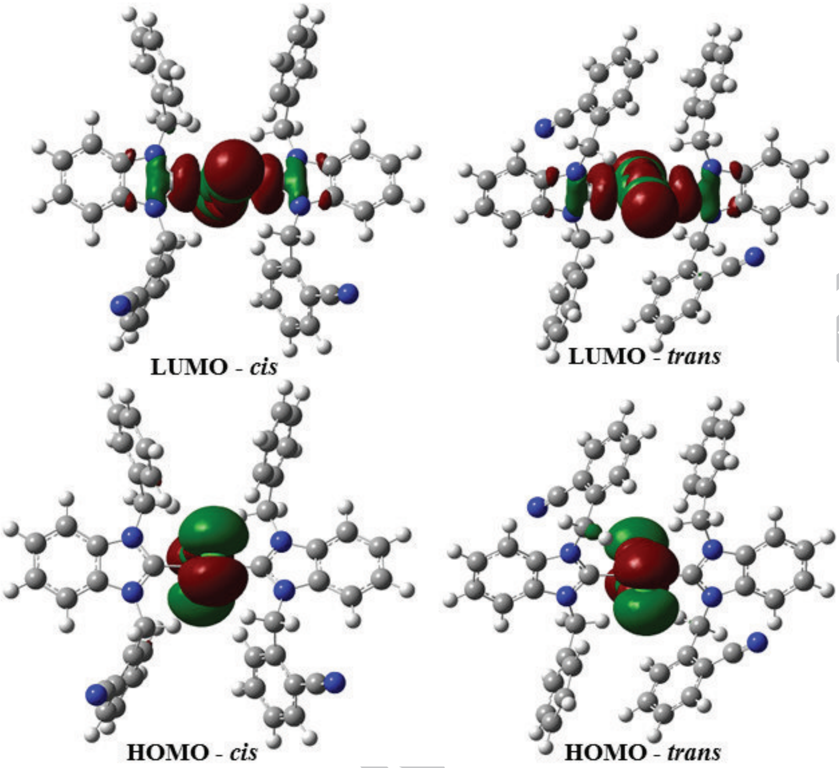


Table Captions

Table 1: Catalytic performance of the palladium complexes **5** and **6** in 1-octene oxidation.

Table 2: Bond distances and angles for the optimized complexes **5** and **6** in comparison with the crystal structure of complex *trans*-bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]dibromopalladium(II) [18].

Table 3: Electronic energies and relative energy for the complexes **5** and **6** according to the density functional theory.

Figure Captions

Chart 1. Catalytically active benzimidazole-derived Pd(II)-NHC complexes.

Scheme 1. Synthesis of benzimidazol-2-ylidenes.

Scheme 2. Synthesis of bis(carbene)-Ag complexes.

Scheme 3. Synthesis of bis(carbene)-Pd complexes via carbene transfer reaction.

Scheme 4. Catalytic oxidation of 1-octene by Pd(II)-NHC complexes **5** and **6** with hydrogen peroxide.

Figure 1. Percentage conversion of 1-octene and the formation of 1,2-octanediol and 2-octanone from epoxidation using aqueous hydrogen peroxide at 70 °C catalyzed palladium complex **5**.

Figure 2. Percentage conversion of 1-octene and the formation of 1,2-octanediol and 2-octanone from epoxidation using aqueous hydrogen peroxide at 70 °C catalyzed palladium complex **6**.

Figure 3. Energy of the molecular orbitals for HOMO-2 through to LUMO+2 and band gaps for the cis and trans conformations for the complexes **5** and **6**.

Figure 4. Density distribution for the HOMO and LUMO molecular orbitals for the complex **5**.

Figure 5. Density distribution for the HOMO and LUMO molecular orbitals for the complex **6**.

Table 1: Catalytic performance of the palladium complexes **5** and **6** in 1-octene oxidation.

Entry	Catalyst	Time (h)	Oxidant	% conversion	% selectivity		
					1,2-octanediol	2-octanone	1,2-epoxyoctane
1	1	4	H_2O_2	---	---	---	---
2	2	4	H_2O_2	---	---	---	---
3	3a	4	H_2O_2	---	---	---	---
4	4a	4	H_2O_2	1	trace[a]	---	---
5	5	4	---	---	---	---	---
6	6	4	---	---	---	---	---
7	5	1	H_2O_2	4.3	61	39	---
8	5	2	H_2O_2	11.0	61.5	38.5	---
9	5	3	H_2O_2	21.3	62.0	38.0	---
10	5	4	H_2O_2	47.3	63.2	34.7	2.1
11	6	1	H_2O_2	8.0	48	52	---
12	6	2	H_2O_2	13.5	50	50	---
13	6	3	H_2O_2	46.5	51	49	---
14	6	4	H_2O_2	51.2	51.8	45.7	2.5

[a]: Not determined

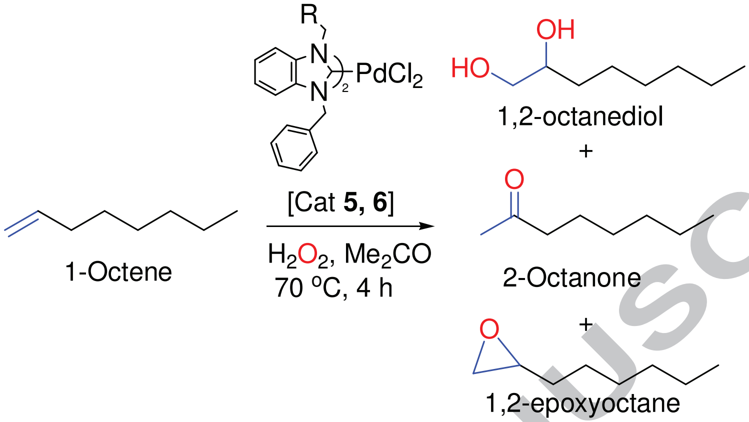
Table 2: Bond distances and angles for the optimized complexes **5** and **6** in comparison with the crystal structure of complex *trans*-bis[1-benzyl-3-(2,3,4,5,6-pentafluorobenzyl)benzimidazol-2-ylidene]dibromopalladium(II) [18].

	complex **6**		complex **5**	
Bond(s)	*cis*	*trans*	*cis*	*trans*
Pd-Cl	2.396	2.395	2.394	2.389
Pd-C:	2.059	2.063	2.054	2.055
C-N (benz.)	1.356	1.362	1.359	1.359
C-N (alph)	1.359	1.462	1.356	1.356
N-CH2 (benz.)	1.467	1.464	1.467	1.466
N-CH2 (alph)	1.463	1.463	1.465	1.466
Cl-Pd-C:	89.7	88.9	89.9	89.9
Pd-C:-N	126.5	125.3	126.8	126.1
Cl-Pd-C:-N	69.5	70.1	70.4	71.3
Dipole Moment (Debye)	7.105	1.050	0.435	0.120
band gab	0.167	0.164	0.166	0.166

Table 3: Electronic energies and relative energy for the complexes **5** and **6** according to the density functional theory.

Name	Energy (Hartree)	Relative energy (Hartree)	Relative energy (kcal/mol)
Complex **5** *cis*	-2504.99171		
Complex **5** *trans*	-2504.992102	0.0004	0.2543
Complex **6** *cis*	-3072.258819		
Complex **6** *trans*	-3072.240715	-0.0181	-11.7676

Graphical abstract (pictogram)



Graphical abstract (synopsis)

Palladium-carbene complexes of benzimidazole based NHCs were prepared *via* transmetallation technique from corresponding silver-carbene complexes. Palladium-NHCs showed comparable activity in the oxidation of olefins viz., 1-octene and styrene.

Research Highlights

- Two Pd-NHC complexes are prepared by carbene transfer method
- Catalytic olefin oxidations are studied
- Functionalized Pd complex evinced moderate activity
- All compounds are methodically characterized