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Ruthenium (II) complexes of benzimidazole derivatives: synthesis, characterization, and catalytic properties in the hydrogenation of ketones

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Stable complexes with ruthenium are formed by benzimidazole derivative ligands. Here, 2-aryl-1H-benzimidazole (L1-3) and 1-benzyl-2-aryl-1H-benzimidazole (L4-6) were prepared. Heteroleptic arene [RuIICl2(L1-6)] (K1-6) complexes were synthesized from the reaction of [RuCl2(p-cymene)]2 with the synthesized benzimidazole derivatives. Various methods were used for the characterization of all synthesized compounds. The catalyst in the transfer hydrogenation reactions of acetophenone derivatives was K1-6. Good catalytic activity was found in the synthesized complexes.

Keywords: *Benzimidazole, Transfer hydrogenation, heteroleptic Ru(II) complexes*

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1. Introduction

Benzimidazole derivatives are found in a variety of natural products and pharmaceuticals [1]. Benzimidazole derivative molecules demonstrate efficacy in various biological activities, including anticancer, antiallergic, antioxidant, antihistamine, and antimicrobial responses. Benzimidazole structures with different substituted groups are present in many drugs [2, 3]. Benzimidazole derivative compounds can quickly coordinate with metals through the pyridine-type nitrogen atoms they contain in their structures. Organic compounds containing nitrogen and their metal complexes have various biological applications, including antibacterial, antitumor, antiviral, and antifungal properties.

Transition metal complexes serve as catalysts in the manufacture of chemically essential organic compounds [4, 5]. These catalysts have practical applications in various fields such as polymers, pharmaceuticals, and cosmetics [6, 7].

Hydrogenation reactions are a critical technique used in organic molecule synthesis. Hydrogenation reactions employ metal complexes containing benzimidazole and its derivatives, including Ru (II), Rh (I), and Ir (I) [8-10].

Hydrogen transfer reactions are of significant interest in synthetic chemistry due to their high selectivity and ease of handling. Asymmetric reduction of unsaturated compounds is a viable method for the introduction of new functional groups into organic compound structures. Thus, this approach has become one of the most common methods in asymmetric synthesis and is presently utilized for preparing biologically active organic compounds that contain diverse functional groups [11].

Transfer hydrogenation is also considered crucial because of the straightforward nature of the approach, its eco-friendliness, and the mild reaction conditions that are easy to apply [12]. In both homogeneous and heterogeneous catalysis media, transfer hydrogenation allows for the application of a vast range of substrates. For instance, ketones, α,β-unsaturated carbonyl compounds, α,β-unsaturated acids and ethers, imine, and nitro compounds are among the substrates used in this process [13].

The pharmaceutical industry places a significant emphasis on secondary alcohols, which can be easily synthesized through the transfer hydrogenation of ketones [14]. Ruthenium complexes serve as the most effective catalysts in the transfer hydrogenation of ketones [15]. The ligands that are present in the complex structure have a significant impact on the catalysts' activity. Recent research has focused on the potential application of metal complexes containing benzimidazole derivatives in the transfer hydrogenation of ketones [16]. In their study [17], Özdemir et al. synthesized six [RuCl$_2$(1-alkylbenzimidazole)(*p*-cymene)] derivative complexes and demonstrated their effectiveness as active catalysts in the transfer hydrogenation reactions of ketones.

The study synthesized a series of benzimidazole (L1-6) derivatives. The ligands were reacted with [RuCl$_2$(*p*-cymene)]$_2$ to synthesize [RuCl$_2$(*p*-cymene)(L1-6)] (K1-6)-type complexes. Different characterization techniques were used to elucidate the structures of all synthesized compounds. K1-6 complexes were used as catalysts in the transfer hydrogenation of derivatives of acetophenone. Under transfer hydrogenation conditions, K1-6 complexes were found to be efficient in hydrogenating aryl ketones.

2. Experimental

The chemicals were acquired from commercial sources without any further purification. Fourier transform infrared (FT-IR) spectra were recorded using the Perkin-Elmer Spectrum One FTIR system and an attenuated total reflection (ATR) sampling accessory within the range of 4000-550 cm^{-1}. Nuclear magnetic resonance (NMR) spectra were taken at 297 K using a Bruker 300 MHz Ultrashield TM NMR spectrometer with a frequency of 300 MHz (1H), 75.48 MHz (13C), or at 297 K using a Varian Mercury AS 400 NMR spectrometer with a frequency of 400 MHz (^{1}H), 100.56 MHz (^{13}C). Analysis of carbon, hydrogen, and nitrogen was done with CHNS-932 (LECO). The melting point was determined using a digital Stuart SMP10 melting point apparatus with capillary tubes. Analysis by gas chromatography was carried out using a Younglin Acme 6100 GC with a flame ionization detector and an Optima 5 MS capillary column.

2.1. General Synthesis of L1-3

The L1-3 were synthesized by making slight modifications to the literature method [18]. *o*-phenylenediamine (4.6 mmol) and its corresponding benzaldehyde (4.6 mmol) were refluxed in 10 ml of distilled water under a refluxer for 12 hours. After 12 hours, the solution was distilled until dryness. The solid was purified through recrystallization in ethanol. Data were given in the “Results” part.

2.2. General Synthesis of L4-6

L1-3 (2.18 mmol) and KOH (2.18 mmol) were refluxed in 5 ml of THF for 4 hours. After the solution was brought to room temperature, benzyl chloride (2.18 mmol) was added, and the mixture was refluxed for 24 hours. The solvent was removed under vacuum, and the remaining material was washed with water and filtered. Recrystallization was carried out using ethanol. Data were given in the “Results” part.

2.3. General Synthesis of K1-6

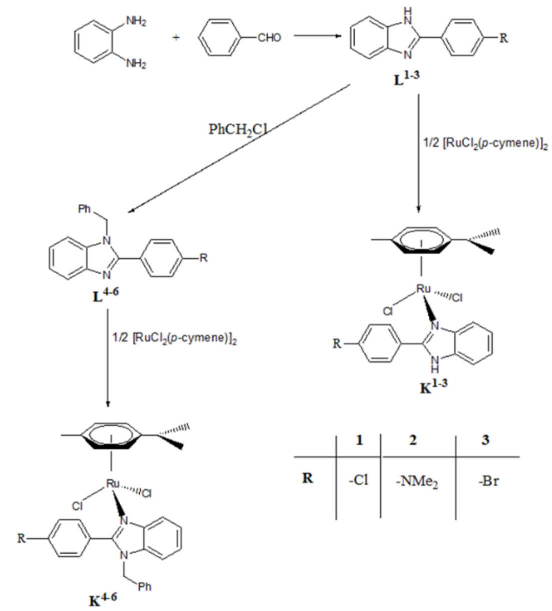
0.16 mmol of [RuCl$_2$(*p*-cymene)]$_2$ and 0.32 mmol of L1-6 were refluxed in 10 ml of methanol for 24 hours. After the given time, the solution was concentrated, and diethyl ether was added to induce precipitation of the complex. The mixture was then filtered. The residue was washed twice (2 x 10 ml) with diethyl ether. Lastly, the compound was dried under vacuum. Data were given in the “Results” part.

2.4. Transfer Hydrogenation Reactions

Under an argon atmosphere, 0.01 mmol of catalysts (K1-6), 1.00 mmol of substrate, and 2 ml of 2-propanol were stirred at 82°C. 0.1 mmol of KOH was added after 5 minutes. The reaction mixture was sampled at specific times and analyzed via GC.

3. Results

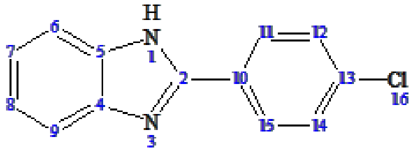
There has been an increasing interest in synthesizing compounds containing the imidazole ring because of their chemical and physical properties. Benzimidazoles and their derivatives are of significant interest in coordination chemistry as ligands. Compounds that contain benzimidazole have both pyrrole-type and pyridine-type nitrogen in their structures. While pyridine-type nitrogen can readily form coordination compounds with transition metals, pyrrole-type nitrogen can alter the steric and electronic properties of the metal through N-alkylation. This study describes the synthesis of 2-Aryl-1H-benzimidazoles (L1-3) through refluxing o-phenylenediamine with suitable aldehydes in an aqueous medium. Refluxing the L1-3 ligands with KOH and benzyl chloride in THF solvent led to the synthesis of 1-benzyl-2-aryl-1H-benzimidazoles (L4-6). The heteroleptic arene-Ru (II) complexes (K1-6) were prepared by reacting the synthesized benzimidazole derivatives (L1-6) with [RuCl2(p-cymene]2. Using the synthesized Ru (II) complexes (K1-6), the study enabled the catalysis of the transfer hydrogenation of acetophenone derivatives. All synthesized compounds were characterized using appropriate methods. Synthesis diagrams of the prepared compounds are shown in Scheme 1.



Scheme 1. Synthesis of the compounds

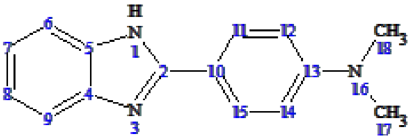
Characterization of ligands and complexes

The characterization of the L1 ligand



In the ^{1}H-NMR spectrum of ligand L1, $-H_{6\text{-}9}$ protons were observed as a double peak corresponding to two protons at 8.18 ppm, $-H_{7\text{-}8}$ protons were observed as a multiple peak corresponding to two protons between 7.22 and 7.26 ppm, and $-H_{11\text{-}15}$ protons were observed as a multiple peak corresponding to four protons between 7.60 and 7.65 ppm. Following are the ^{13}C-NMR peaks that belong to aromatic carbons in L1: 114.8, 116.1, 117.0, 127.9, 128.1, 128.8, 130.1, 134.7, 135.4, 135.4, 144.1, 150.1, and 154.8 ppm. The infrared (IR) spectra of L1 reveals that the frequency range for aromatic C-H stretching is observed to be within the range of 3089 - 2662 cm^{-1}. The C=N stretching vibration is also part of this spectrum at 1623 cm^{-1}.

The characterization of the L2 ligand

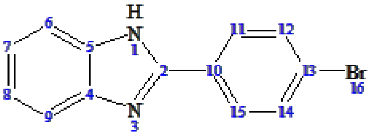


The L2 ligand's ^{1}H-NMR spectrum displayed the $-H_{7}$ proton as a triple peak at 7.83 ppm, the $-H_{6}$ proton as a double peak at 7.64 ppm, and the $-H_{9}$ proton as a double peak at 7.03 ppm. Other Ar-CH protons were seen as multiple peaks that were equivalent to three protons between 6.69 and 6.77 ppm and as multiple peaks that were equivalent to two protons between 7.21 and 7.32 ppm. The compound's $-H_{17\text{-}18}$ protons displayed two single peaks that were equivalent to six protons at 2.96 and 3.20 ppm.

When the ^{13}C-NMR spectrum of L2 was examined, the peak of $-N(CH_3)_2$ was observed at 40.2 ppm, while peaks of 11 aromatic carbons were observed at 112.0, 114.8, 116.8, 117.2, 124.9, 126.8, 130.6, 137.0, 143.8, 152.6, and 156.9 ppm.

In the IR spectrum of L2, the aromatic CH stretching vibration was observed at 3051 cm^{-1}, while the C=N stretching vibration was observed at 1609 cm^{-1}.

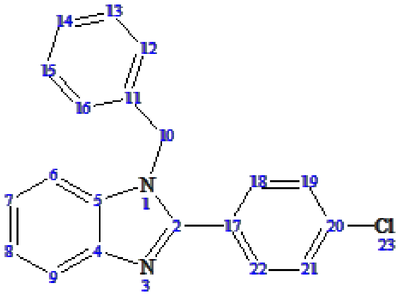
The characterization of the L3 ligand



When analyzing the ^{1}H-NMR spectrum of the L3 ligand, a double peak equivalent to two protons at 8.11 ppm was observed for $-H_{6\text{-}9}$ protons. The remaining Ar-Hs were observed as double peaks equivalent to two protons at 7.22-7.26 ppm, 7.60-7.66 ppm, and 7.71-7.78 ppm, respectively. The ^{13}C-NMR spectrum of L3 shows 13 aromatic carbon peaks at 115.2, 117.8, 119.4, 120.4, 122.4, 123.3, 128.4, 129.2, 131.0, 131.7, 131.9, 132.0, and 150.2 ppm.

The IR spectrum of L3 shows an aromatic CH stretching at 3052 cm^{-1} and a C=N stretching vibration at 1609 cm^{-1}.

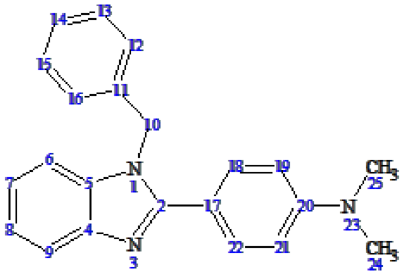
The characterization of the L4 ligand



When the ^{1}H-NMR spectrum of ligand L4 was analyzed, it was found that $-H_{10}$ hydrogens appeared as a single peak representing two protons at 5.40 ppm, $-H_{6}$ proton appeared as a double peak representing one proton at 7.85 ppm, and $-H_{19,21}$ protons appeared as a double peak representing two protons at 7.60 ppm. In addition, $-H_{18,22}$ protons were observed as a double peak with two proton equivalences at 7.39 ppm; $-H_{12,16}$ protons were observed as a double peak with two proton equivalences at 7.06 ppm; and the remaining aromatic -Hs were recorded as multiple peaks with six proton equivalences in the range of 7.19-7.33 ppm. During the analysis of the ^{13}C-NMR spectrum of ligand L4, the $-CH_2-$ carbon peak was detected at 48.3 ppm, and the other 15 aromatic carbon peaks were detected at 110.4, 120.0, 122.8, 123.2, 123.5, 125.8, 127.8, 128.5, 129.0, 129.1, 130.4, 131.6, 136.1, 143.1, and 152.9 ppm.

The IR spectrum of the L4 ligand also revealed aromatic CH stretching at 3085 cm-1 and C=N stretching at 1601 cm^{-1}.

The characterization of the L5 ligand

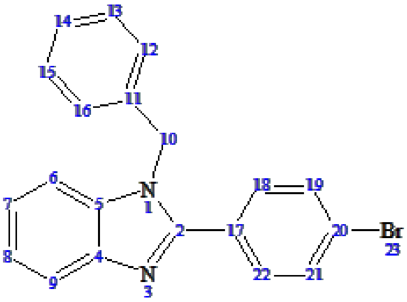


Analyzing the ^{1}H-NMR spectra of ligand L5, we detected the -$H_{24,25}$ hydrogens as a single peak at 2.93 ppm, which corresponds to six protons. We also found the -$H_{18,22}$ hydrogens as a double peak, corresponding to two protons, at 6.76 ppm. Moreover, two protons were observed as a double peak at 7.01 ppm for -$H_{19,21}$ hydrogens, whereas other aromatic -Hs exhibited a multiple peak with seven protons between 7.12-7.35 ppm and a multiple peak with two protons between 7.54-7.67 ppm.

The ^{13}C-NMR spectrum of the L5 ligand exhibited a peak at 40.2 ppm corresponding to the -$N(CH_3)_2$- carbon, a peak at 48.0 ppm for the -CH_2- carbon, and peaks for the remaining aromatic carbons at 111.1; 112.2; 117.2; 119.2; 122.3; 122.4; 126.4; 127.9; 129.3; 130.3; 136.6; 137.8; 143.4; 151.5; and 154.5 ppm.

The IR spectrum of the L5 ligand demonstrated an aromatic CH stretching vibration at 3049 cm^{-1} and a C=N stretching vibration at 1609 cm^{-1}.

The characterization of the L6 ligand

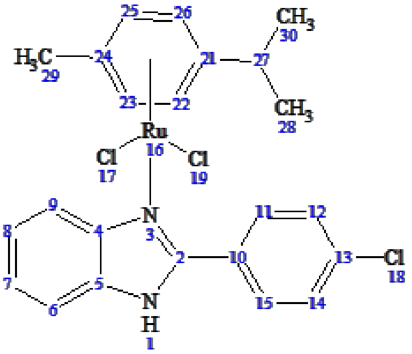


Upon examination of the ^{1}H-NMR spectrum of the L6 ligand, it was determined that the -H_{10} hydrogens presented as a single peak, equivalent to two protons at 5.45 ppm. The -H_6 hydrogen appeared as a double peak, equivalent to one proton at 7.89 ppm. Two protons were observed at 7.64 ppm as a double peak for the -$H_{19,21}$ hydrogens. Additionally, a double peak consisting of two protons equivalent to -$H_{18,22}$ hydrogens was observed at 7.43 ppm, along with another double peak consisting of two protons equivalent to -$H_{12,16}$ hydrogens at 7.08 ppm. The range of 7.24-7.37 ppm showed multiple peaks, indicating the presence of seven aromatic protons.

The ^{13}C-NMR analysis of ligand L6 revealed an identifiable -CH_2- carbon peak at 48.4 ppm, as well as other detected aromatic carbons at the chemical shifts: 110.6, 119.5, 123.2, 123.6, 125.8, 128.0, 129.1, 129.7, 130.5, 135.7, 136.5, 141.7, and 152.4 ppm.

Moreover, observations from the IR spectrum of L6 indicated the presence of an aromatic CH stretching vibration at 3085 cm^{-1} and a C=N stretching vibration at 1611 cm^{-1}.

The characterization of the K1 complex

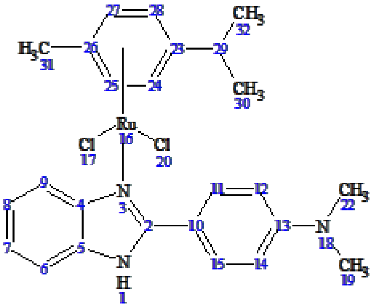


Upon examination of the ^{1}H-NMR spectrum of the K1 complex, it was found that -$H_{28,30}$ hydrogens presented as a double peak, equivalent to six protons, at 1.17 ppm. Likewise, -H_{29} hydrogens displayed as a single peak, equivalent to three protons, at 2.07 ppm, and -H_{27} hydrogen was observed as a multiple peak, equivalent to one proton in the range of 2.77-2.86 ppm. Hydrogens -$H_{22,23,25,26}$ were detected as multiple peaks equivalent to four protons at 5.75-5.82 ppm, while hydrogen -H_7 appeared as a triple peak equivalent to one proton at 7.35 ppm, and hydrogens -$H_{12,14}$ as a double peak equivalent to two protons at 8.34 ppm. Furthermore, other aromatic hydrogens associated with the imidazole skeleton were observed as two proton-equivalent multiple peaks between 7.50-7.57 ppm and four proton-equivalent multiple peaks between 7.75-7.82 ppm, respectively.

During analysis of the ^{13}C-NMR spectrum of the K1 complex, the -C29 carbon peak was observed at 18.4 ppm, while the -C28,30 carbons peak was observed at 22.0 ppm, and the -C27 carbon peak was observed at 30.5 ppm. Other aromatic carbon peaks were also detected at 86.0, 86.9, 100.6, 106.8, 114.7, 126.0, 130.2, 133.2, 133.6, 134.3, 138.1, 140.5, 142.3, 148.6, and 159.0 ppm.

When analyzing the IR spectrum of the K1 complex, it was observed that there was an NH stretching vibration at 3328 cm^{-1}, a CH stretching vibration at 3040 cm^{-1}, and a C=N stretching vibration at 1603 cm^{-1}.

The characterization of the K2 complex

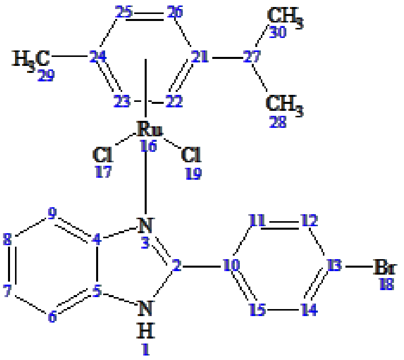


When the ^{1}H-NMR spectrum of the K2 compound was evaluated, a double peak was identified at 1.89 ppm corresponding to six protons, which can be attributed to -$H_{30,32}$ hydrogens. A single peak at 2.1 ppm with three protons was assigned to -H_{31} hydrogens. Furthermore, a multiple peak was detected for the -H_{29} hydrogen, which was equivalent to only one proton and observed between 2.79 and 2.90 ppm. Additionally, six protons were observed for -$H_{19,22}$ hydrogens at 3.06 ppm as a singlet peak. Several peaks equal to four protons were detected for -$H_{24,25,27,28}$ hydrogens at 5.78-5.84 ppm. A double peak corresponding to two protons was recorded for -$H_{11,15}$ hydrogens at 6.91 ppm and for -$H_{12,14}$ hydrogens at 8.14 ppm. Additionally, multiple peaks of two protons each were observed in the range of 7.32-7.36 ppm and 7.63-7.67 ppm for the remaining aromatic hydrogens.

In the NMR spectrum of the K2 compound, carbon -C_{31} exhibited a peak at 17.9 ppm, while carbons -$C_{30,32}$ and -$C_{19,22}$ displayed peaks at 21.5 ppm and 24.0 ppm, respectively. Moreover, the peak for -C_{29} appeared at 30.0 ppm. The peaks for aromatic carbons were found at 85.5, 86.4, 94.7, 100.1, 106.3, 111.8, 113.6, 123.6, 126.1, 126.6, 128.7, 134.8, 150.6, and 152.4 ppm.

The infrared spectrum of the K2 complex displayed an aromatic CH stretching vibration at 3051 cm-1 and a C=N stretching vibration at 1607 cm-1.

The characterization of the K3 complex

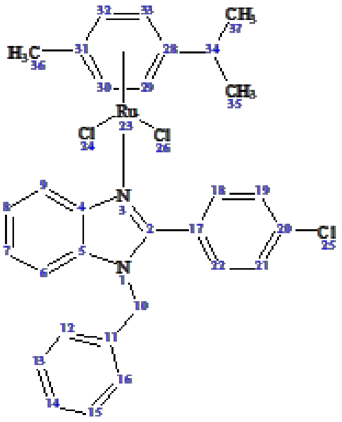


Upon examining the ^{1}H-NMR spectrum of the K3 complex, it was observed that the -$H_{28,30}$ hydrogens appeared as a double peak, equivalent to six protons, at 1.17 ppm. The -H_{29} hydrogens were observed as a single peak, equivalent to three protons, at 2.07 ppm. In contrast, the -H_{27} hydrogen was observed as a multiple peak, equivalent to one proton, at 2.77-2.86 ppm. Furthermore, the -$H_{22,23,25,26}$ hydrogens were observed as a multiple peak, equivalent to four protons, at 5.75-5.82 ppm. Hydrogens of the imidazole structure were detected as two proton equivalent multiple peaks within the range of 7.31-7.34 ppm, three proton equivalent multiple peaks within the range of 7.66-7.70 ppm, one proton equivalent double peak at 7.82 ppm, one proton equivalent double peak at 8.18 ppm, and one proton equivalent double peak at 8.26 ppm, respectively.

It was seen that the -C_{29} carbon peak appeared at 17.7 ppm in the ^{13}C-NMR spectrum of the K3 complex, while the -C_{28} and -C_{30} carbon peaks appeared at 21.5 ppm. Furthermore, the peak of the -C27 carbon appeared at 30.0 ppm, along with other aromatic peaks observed at 85.5, 86.3, 100.0, 106.3, 114.8, 123.5, 124.6, 126.1, 128.7, 128.9, 129.3, 129.6, 131.1, 132.2, 149.3, and 149.4 ppm.

Upon examination of the IR spectrum of the K3 compound, the stretching vibration of the aromatic CH was observed to occur at 3469 cm^{-1}, while the stretching vibration of C=N appeared at 1625 cm^{-1}.

The characterization of the K4 complex

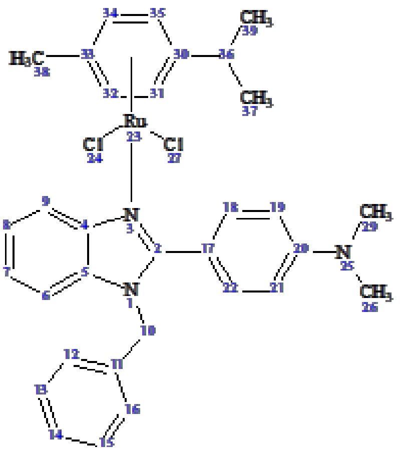


Upon analysis of the ^{1}H-NMR spectrum of the K4 complex, it was noted that the -$H_{35,37}$ hydrogens appeared as a double peak, representing six hydrogens, at a chemical shift of 1.28 ppm. Additionally, the -H_{36} hydrogen appeared as a single peak, equivalent to three protons, at a chemical shift of 2.15 ppm. In a similar manner, the presence of -H_{34} hydrogen was detected within the chemical shift range of 2.22-2.29 ppm. Additionally, -$H_{29, 30, 32, 33, 10}$ hydrogens were identified as multiple peaks, collectively representing a total of six protons, within the chemical shift range of 5.32-5.68 ppm. Multiple peaks corresponding to twelve protons are detected within the chemical shift range of 6.84–8.26 ppm for additional aromatic hydrogens.

Upon analysis of the ^{13}C-NMR spectra of the K4 complex, it was noted that the -C_{36} carbon exhibited a peak at 18.9 ppm, the -C_{35} and -C_{37} carbons exhibited peaks at 22.0 ppm, the -C_{34} carbon exhibited a peak at 30.5 ppm, and the -C_{10} carbon exhibited a peak at 48.2 ppm. Additional aromatic peaks were found at various chemical shifts, specifically at 80.4, 81.2, 82.6, 89.2, 96.6, 101.1, 102.4, 110.2, 111.7, 117.0, 122.7, 123.6, 124.8, 125.9, 127.9, 128.6, 129.0, 129.4, 129.8, 131.6, 134.4, 136.0, 139.4, and 141.2 ppm.

Upon analysis of the IR spectrum of the K4 complex, it was revealed that the aromatic CH stretching occurred at a frequency of 3089 cm^{-1}, whereas the C=N stretching vibration was detected at 1600 cm^{-1}.

The characterization of the K5 complex

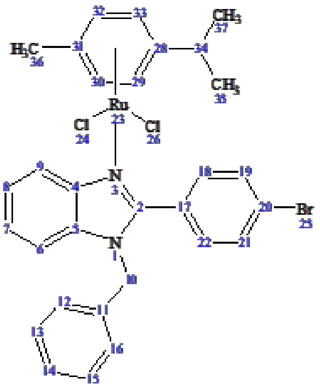


Upon examination of the ^{1}H-NMR spectra of the K5 complex, it was seen that the -$H_{37,39}$ hydrogens exhibited a double peak, corresponding to a total of six protons at a chemical shift of 1.19 ppm. Furthermore, the -H_{38} hydrogens were observed as a singular peak, indicating the presence of three protons at a chemical shift of 2.09 ppm. In a similar manner, the -H_{36} proton exhibited chemical shift values ranging from 2.79 to 2.89 ppm. The hydrogens -$H_{28,\ 29}$ exhibited a singular peak with an intensity equivalent to that of three hydrogens, which were detected at a chemical shift of 3.04 ppm. Multiple peaks were observed in the range of 5.78–5.84 ppm for the hydrogens labeled as -$H_{31,32,34,35,10}$. Additionally, aromatic hydrogens were detected within the range of 6.88–7.87 ppm.

In the analysis of the ^{13}C-NMR spectrum pertaining to the K5 complex, several carbon peaks were identified. Specifically, the -C_{38} carbon peak was discovered at a chemical shift of 17.9 ppm, the -C_{37} and -C_{39} carbon peaks were detected at 21.5 ppm, the -C_{26} and -C_{29} carbon peaks were found at 24.0 ppm, and the -C_{10} carbon peak was recorded at 48.5 ppm. Aromatic carbon peaks were detected at several chemical shifts, specifically at 85.5, 86.3, 100.0, 106.3, 111.7, 112.7, 125.1, 125.6, 126.0, 126.2, 128.0, 128.6, 128.8, 129.0, 130.8, 133.1, 135.1, 151.4, and 152.6 ppm.

Upon analysis of the IR spectrum of the K5 complex, it was seen that the aromatic CH stretching occurred at a frequency of 3054 cm^{-1}, whereas the C=N stretching vibration was detected at 1604 cm^{-1}.

The characterization of the K6 complex



When the ^{1}H-NMR spectrum of the K6 complex was analyzed, -H_{35} and -H_{37} hydrogens were observed as a single peak equivalent to six protons at 1.28 ppm, -H_{36} hydrogen was observed as a single peak equivalent to three protons at 2.15 ppm, and -H_{34} hydrogen was observed as a broad peak equivalent to one proton at 2.29 ppm. Also, -$H_{29,\ 30,\ 32,\ 33}$ hydrogens were observed as multiple peaks equivalent to six protons at 5.20–5.65 ppm, and other aromatic hydrogens were observed as multiple peaks equivalent to 13 protons at 6.85–8.26 ppm.

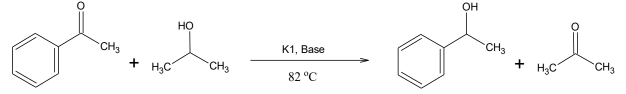
The ^{13}C-NMR spectrum of the K6 complex shows that the -C_{36} carbon peak is at 19.2 ppm, the -C_{35} and -C_{37} carbon peaks are at 22.4 ppm, the -C_{34} carbon peak is at 30.9 ppm, and the -C_{10} carbon peak is at 49.8 ppm. Other aromatic carbon peaks were seen at 80.8, 81.6, 83.1, 89.6, 97.0, 101.5, 110.7, 111.8, 119.0, 123.2, 124.1, 125.4, 126.2, 128.7, 129.9, 131.7, and 134.9 ppm.

When the IR spectrum of the K6 complex was examined, the aromatic CH stretching vibration was observed at 3055 cm^{-1}, while the C=N stretching vibration was observed at 1601 cm^{-1}.

Transfer Hydrogenation of Ketones

Initially, the experimental conditions were tuned for the transfer hydrogenation of acetophenone. This was achieved by systematically adjusting the catalyst quantity, 2-propanol quantity, base concentration, and temperature parameters.

Table 1. Optimizing the transfer hydrogenation of acetophenone with the K1 catalyst under varying conditions

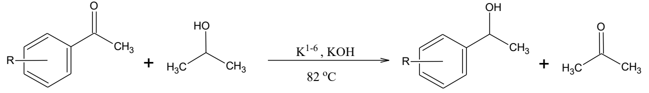


Entry	Amount of K1 (mmol)	Amount of 2-propanol (ml)	Base	Convers.(%)
1	0.01	2	KOH	94; 0[a]
2	0.01	4	KOH	85
3	0.01	6	KOH	82
4	0.005	2	KOH	14
5	0.02	2	KOH	100
6	0.01	2	Cs_2CO_3	40
7	0.01	2	K_2CO_3	66
8	0.01	2	Na_2CO_3	44
9	0.01	2	$NaHCO_3$	34
10	0.01	2	NaOH	75

[a] the reaction was achieved at 25 °C.

The optimal experimental settings were determined based on our findings, which indicated that the parameters employed in experiment 1, as outlined in Table 1, were most effective. Later, the catalysts synthesized in this study were tested as catalysts in the presence of KOH in the transfer hydrogenation reaction of different acetophenone derivatives under these conditions. The results are presented in Table 2.

Table 2. Transfer hydrogenation of acetophenone derivatives using K1-6 catalysts in the presence of KOH in 2-propanol at 82 °C.



Entry	Catalyst	R	Conversation (%)
1	K1	H	94
2	K2		40
3	K3		41
4	K4		73
5	K5		68
6	K6		90
7	K1	4-Br	56
8	K2		64
9	K3		70
10	K4		55
11	K5		75
12	K6		20
13	K1	4-Cl	45
14	K2		59
15	K3		43
16	K4		56
17	K5		63
18	K6		85
19	K1	4- OCH_3	50
20	K2		58
21	K3		31
22	K4		29
23	K5		48
24	K6		39
25	K1	2,4,6-$(CH_3)_3$	6
26	K2		9
27	K3		4
28	K4		14
29	K5		17
30	K6		9

Cat.:Base:Substrate=0.01:0.1:1 mmol, 2 ml 2-propanol

4. Conclusion

Transfer hydrogenation reactions of ketones are extensively applied in both industrial and academic settings due to their ease of use, non-hazardous nature, and low cost. Selective catalysts in these reactions often involve N-coordinated metal compounds. Six benzimidazole ligands, designated as L1-6, were synthesized through reaction with $[RuCl_2(p\text{-cymene})]_2$, producing six complexes of the type $[Ru^{II}Cl_2(K1\text{-}6)]$. Structural identification was performed utilizing spectroscopic techniques. Subsequently, the catalytic efficacy of the Ru(II) complexes (K1-6) in transfer hydrogenation reactions of acetophenone-derived ketones was explored, with products generated in good yields after reactions carried out under an argon atmosphere. The $[Ru^{II}Cl_2(K1\text{-}6)]$ complexes synthesized using ligands of benzimidazole derivatives demonstrated effective catalytic properties in the transfer hydrogenation reactions of ketones.

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