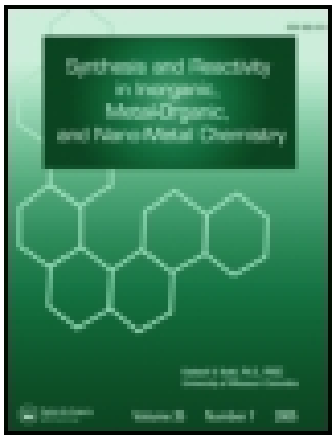

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Synthesis and characterization of Ruthenium(II) complexes bearing benzimidazole ligands: for transfer hydrogenation catalysis

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Synthesis and characterization of Ruthenium(II) complexes bearing benzimidazole ligands: for transfer hydrogenation catalysis

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Abstracts

Ru(II) complexes with the general formula [$RuCl_2$(*p*-cymene)(**L1-3**)], **K1-3**, (**L1-3**: monodentate benzimidazole ligands), [$RuCl_2$(**L5-6**)(**S**)], **K4-7**, (**L5-6**: tridentate benzimidazole ligands, S: Solvents (methanol or acetonitrile)) and [$RuCl_2$(**L5**)(**L1-2**)], **K8-9**, were synthesized from [$RuCl_2$(*p*–cymene)]$_2$ dimer and mono- and tridentate benzimidazole ligands. The compounds were characterized by elemental analysis, IR, UV-Vis, and NMR. The synthesized Ru(II) complexes (**K1–9**) were tested as catalysts for the transfer hydrogenation (TH) of acetophenone to secondary alcohols in the presence of KOH using 2–propanol as a hydrogen source at 82 °C. All complexes were active catalysts for TH of acetophenone with good yields under mild conditions (after 60 minutes, yields of up to 97%).

Keywords: Ru(II) complexes, transfer hydrogenation, benzimidazoles, acetophenone

1. Introduction

Transition metal complexes of benzimidazole ligands have been frequently utilized for their unique properties such as biological activity, high thermal stability and good catalytic performance [1-4]. Because of the outstanding properties of these ligands in many applications, there is increased interest in synthesis of their derivatives. Benzimidazole and their derivatives can be easily modified due to its pyrol type nitrogen. Thus, steric and electronic parameters on the metal center bearing benzimidazole derivatives can be tunable, and the complex, with best properties, can be synthesized [5-16].

In particular, recent studies have shown that the transition metal complexes (such as Cu, Pd) of 2,6-bis(benzimidazol-2-yl)pyridines (a tridentate benzimidazole ligand) are especially good catalyst for different catalytic reactions [1-2, 17].

The reduction of C=Y (Y=N or O) bonds via catalytic transfer hydrogenation using Ru(II) catalyst is very attractive because of its simplicity and safety. Thus, studies in this area have been continuing with increasing interest in the synthesis of the best catalyst. Notably, when Noyori's Ru(II) catalysts, containing N-Donor ligands, provided good performance, scientists focused on N-donor ligands [18-19]. In particular, several studies indicate that Ru complexes containing 2,6-bis(benzimidazol-2-yl)pyridine ligands are good catalysts for the transfer hydrogenation of ketones [4, 20-21].

In this study, Ru(II) complexes containing benzimidazole ligands (monodentate and tridentate) have been synthesized and characterized using different spectroscopic techniques. In

addition, their catalytic performance for transfer hydrogenation of acetophenone was investigated.

2. Experimental

The reactions were performed in air, unless otherwise stated. The reagents and solvents were obtained from commercial suppliers and used without further purification. **L1** [22], **L2-L3** [23], **L4** [24]; **L5-L6** [4]; $[RuCl_2(p\text{-cymene})]_2$ [25]; and $[RuCl_2(DMSO)_4]$ [26] were synthesized by modification of the method in the published procedure. All ligands were obtained in good yields (Supporting Information).

NMR spectra were recorded at 297 K on a Bruker 300 MHz Ultrashield TM NMR spectrometer at 300 MHz (^{1}H), 75.48 MHz (^{13}C). Chemical shifts (δ) are given in parts per million. Infrared spectra were measured with a Perkin Elmer Spectrum One FTIR system and recorded using a universal ATR sampling accessory within the range 550–4000 cm^{-1}. UV-Vis spectra were measured with a Perkin Elmer Lambda 25 system. The C, H and N analyses were performed using a CHNS–932 (LECO) instrument. Melting points were determined in open capillary tubes on a digital Stuart SMP10 melting point apparatus. GC measurements for catalytic experiments were performed using a Younglin Acme 6100 GC instrument with a flame ionization detector and an Optima 5MS capillary column. (The GC parameters were as follows: Oven: 80 °C (isothermal); Carrier gas: H_2 (Split ratio 15:1); Flow rate: 4 mL/min.; Injector port temperature: 220 °C; Detector temperature: 280 °C; Injection volume: 6.0 μL.)

2.1. *Synthesis of Compounds*

***[RuCl$_2$(p-cymene)(L1)],* (K1): L1** (0.0385 g, 0.326 mmol) and $[RuCl_2(p\text{-cymene})]_2$ dimer (0.1 g, 0.163 mmol) were placed in the same Schlenk tube and methanol (10 mL) as solvent was

added. Then the mixture was stirred under reflux for 1 day. At the end of this time, the mixture was concentrated to 3 mL, precipitated by addition of diethyl ether, and filtered off. The residue was crystallized from MeOH/Et_2O.

Yield: 83%, 0.063 g. m.p.: 264 °C. *Anal*. Calcd. for $C_{17}H_{23}Cl_2N_2Ru$: C: 48.12; H: 4.75; N: 6.60 %; found**:** C: 47.89; H: 5.12; N: 6,55 %. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.09-1.22 (m, 6H, -H_t), 1.91-2.20 (s, 3H, -H_p), 2.67-2.88 (m, 1H, -H_s), 5.47-6.24 (m, 4H, -$H_{q,r}$), 7.04-7.38 (m, 4H, -$H_{b,c,d,e}$), 8.57 (s, 1H, -H_a), 13.39-13.82 (br, 1H, -NH). ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): 18.4 (aliph. –CH), 22.0 (aliph. –CH), 22.5 (aliph. –CH), 30.5 (aliph. –CH), 80.7 (arom. –CH), 83.4 (arom. –CH), 86.0 (arom. –CH), 86.9 (arom. –CH), 97.6 (arom. –CH), 101.0 (arom. –CH), 101.4 (arom. –CH), 106.8 (arom. –CH), 115.6 (arom. –CH), 122.8 (arom. –CH), 133.1 (arom. –CH), 140.9 (arom. –CH), 146.3. IR (cm^{-1}): 3142, 3110, 3091, 2970, 2912, 2872, 1622, 1595, 1489, 1414, 1383, 1304, 1245, 1160, 1133, 1108, 1057, 1008, 965, 951, 891, 871, 804, 776, 741, 696, 676. UV(nm): 216, 274, 325, 404.

***[RuCl$_2$(p-cymene) (L2)],* (K2): K2** was synthesized according to the synthesis method of **K1** using **L2** (0.0679 g, 0.326 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ dimer (0.1 g, 0.163 mmol).

Yield: 84%, 0.115 g. m.p.: 248 °C. *Anal*. Calcd. for $C_{24}H_{26}Cl_2N_2Ru$: C: 56.03; H: 5.09; N: 5.45 %; found**:** C: 55.75; H: 5.21; N: 5.82 %. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.19-1.21 (m, 6H, -H_t), 2.09 (s, 3H, -H_p), 2.80-2.89 (m, 1H, -H_s), 5.49-5.84 (m, 6H, -$H_{f,q,r}$), 7.19-7.37 (m, 9H, -$H_{b,c,d,e,g,h,i}$), 8.43 (s, 1H, -H_a). ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): 18.4 (aliph. –CH), 22.0 (aliph. –CH), 22.5 (aliph. –CH), 48.1 (aliph. –CH), 86.0 (arom. –CH), 86.9 (arom. –CH), 97.8 (arom. –CH), 100.6 (arom. –CH), 106.8 (arom. –CH), 110.2 (arom. –CH), 120.0 (arom. –CH), 122.1 (arom. –CH), 122.9 (arom. –CH), 127.9 (arom. –CH), 129.2 (arom. –CH), 133.7 (arom. –CH),

137.5 (arom. –CH), 142,2 (arom. –CH), 142.7 (arom. –CH), 144.7 (arom. –CH). IR (cm^{-1}): 3133, 3120, 3062 ; 3041, 2977, 2960, 2925, 2867, 1614, 1588, 1512, 1461, 1448, 1392, 1362, 1291, 1258, 1208, 1184, 1160, 1118, 1080, 1056, 1012, 1004, 952, 866, 802, 774, 741, 726, 698, 663. UV(nm): 211, 268, 324, 403.

[RuCl$_2$(p-cymene)(L3)], **(K3): K3** was synthesized according to the synthesis method of **K1** using **L3** (0.0862 g, 0.326 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ dimer (0.1 g, 0.163 mmol).

Yield: 92%, 0.158 g. m.p.: 225 °C. *Anal*. Calcd. for $C_{28}H_{34}Cl_2N_2Ru$: C: 58.94; H: 6.01; N: 4.91%; found**:** C: 58.78; H: 6.25; N: 4.83%. ^{1}H-NMR ($CDCl_3$, δ ppm): 1.01-2.23 (m, 21H, –$H_{g,h,p,t}$), 2.79-2.88 (m, 1H, -H_s), 5.40-6.03 (m, 6H, -$H_{f,q,r}$), 7.00-8.00 (m, 6H, -$H_{a,b,c,d,e,i}$). ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): 15.4 (aliph. –CH), 15.8 (aliph. –CH), 20.7 (aliph. –CH), 22.0 (aliph. –CH), 30.5 (aliph. –CH), 43.9 (aliph. –CH), 80.6 (arom. –CH), 83.2 (arom. –CH), 86.0 (arom. –CH), 86.9 (arom. –CH), 98.2 (arom. –CH), 100.6 (arom. –CH), 100.9 (arom. –CH), 106.8 (arom. –CH), 111.0 (arom. –CH), 120.0 (arom. –CH), 122.1 (arom. –CH), 122.9 (arom. –CH), 127.9 (arom. –CH), 129,2 (arom. –CH), 133.7 (arom. –CH), 137.5 (arom. –CH), 142.2 (arom. –CH), 142.7 (arom. –CH), 144.7 (arom. –CH). IR (cm^{-1}): 3154, 3071, 3004, 2970, 2965, 2866, 1611, 1515, 1460, 1402, 1348, 1325, 1255, 1204, 1057, 1025, 1011, 947, 903, 875, 851, 803, 770, 756, 685, 655. UV(nm): 210, 269, 324, 398.

[RuCl$_2$(L5)(CH$_3$OH)], **(K4): L5** (0.150 g, 0.305 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ (0.0931 g, 0.152 mmol) were placed in the same Schlenk tube and methanol (10 mL) was added. The mixture was stirred under reflux for 1 day. At the end of time, the reaction mixture was concentrated to 3 mL, precipitated by addition of Et_2O, and filtered off.

Yield: 80%, 0.17g. m.p.: >280 °C. *Anal*. Calcd. for $C_{34}H_{29}Cl_2N_5ORu$: C: 58.71; H: 4.20; N: 10.07%; found**:** C: 58.39; H: 4.12; N: 11.21%. ^{1}H-NMR ($CDCl_3$, δ ppm): 3.17 (d, 3H, *CH*$_3$OH), 4.13-4.18 (m, 1H, –*OH*), 6.35 (s, 4H, -H_f), 7.11-7.32 (m, 10H, -$H_{g,h,i}$), 7.63-8.09 (m, 8H, -$H_{l,m,n,o}$), 8,32 (d, 2H, –H_k), 8,47 (t, 1H, -H_j). ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): 48.6 (aliph. –CH), 49.1 (aliph. –CH), 112.2 (arom. –CH), 113.2 (arom. –CH), 119.1 (arom. –CH), 122.8 (arom. –CH), 124.4 (arom. –CH), 126.3 (arom. –CH), 126.6 (arom. –CH), 127.0 (arom. –CH), 128.4 (arom. –CH), 129.5 (arom. –CH), 135.7 (arom. –CH), 136.3 (arom. –CH), 136.9 (arom. –CH), 137.4 (arom. –CH), 141.5 (arom. –CH), 142.1 (arom. –CH), 152.2 (arom. –CH), 152.5 (arom. –CH), 153.8 (arom. –CH). IR (cm^{-1}): 3486, 3231, 3059, 3026, 2970, 2895, 2877, 2847, 2776, 1596, 1519, 1499, 1485, 1471, 1454, 1438, 1414, 1360, 1333, 1310, 1297, 1282, 1256, 1191, 1180, 1155, 1121, 1095, 1081, 1026, 1002, 944, 916, 877, 861, 814, 789, 761, 752, 742, 734, 699, 684. UV (nm): 205, 318, 360, 444.

***[RuCl$_2$(L5)(CH$_3$CN)],* (K5): L5** (0.150 g, 0.305 mmol) and [$RuCl_2$(*p*-cymene)]$_2$ (0.0931 g, 0.152 mmol) were placed in the same Schlenk tube and acetonitrile (10 mL) was added. The reaction mixture was stirred under reflux for 1 day. At the end of this time, the mixture was concentrated to 3 mL, precipitated by addition of Et_2O, and filtered off.

Yield: 98%, 0.21g. m.p.: >280 °C. *Anal*. Calcd. for $C_{35}H_{28}Cl_2N_6Ru$: C: 59.66; H: 4.01; N: 11.93%; found**:** C: 60.18; H: 3.85; N: 12.35%. ^{1}H-NMR ($CDCl_3$, δ ppm): 2.09 (s, 3H, C*H*$_3$CN), 6.34 (s, 4H, -H_f), 7.15-7.32 (m, 10H, -$H_{g,h,i}$), 7.63-8.07 (m, 8H, -$H_{l,m,n,o}$), 8.31 (d, 2H, –H_k), 8.46 (t, 1H, -H_j). ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): 1.7 (aliph. –CH), 48.5 (aliph. –CH), 113.9 (arom. –CH), 119.1 (arom. –CH), 124.4 (arom. –CH), 126.2 (arom. –CH), 126.6 (arom. –CH), 127.0 (arom. –CH), 128.4 (arom. –CH), 129.5 (arom. –CH), 135.7 (arom. –CH), 136.9 (arom. –CH),

137.3 (arom. –CH), 141.4 (arom. –CH), 152.2 (arom. –CH), 152.5 (arom. –CH). IR (cm-1): 3488, 3102, 3061, 3027, 1657, 1619, 1599, 1498, 1483, 1454, 1439, 1362, 1334, 1301, 1260, 1202, 1177, 1156, 1120, 1094, 1077, 1029, 1001, 989, 947, 902, 862, 842, 816, 781, 765, 752, 726, 691, 679. UV (nm): 209, 317, 345, 361, 499.

***[RuCl$_2$(L6)(CH$_3$OH)],* (K6): K6** was synthesized according to the synthesis method of **K4** using **L6** (0.12 g, 0.199 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ dimer (0.061 g, 0.0995 mmol).

Yield: 80%, 0.128 g. m.p.: >280 °C. *Anal*. Calcd. for $C_{42}H_{45}Cl_2N_5ORu$: C: 62.45; H: 5.61; N: 8.67%; found**:** C: 61.48; H: 5.86; N: 8.42%. ^{1}H-NMR ($CDCl_3$, δ ppm): 2.11-2.24 (d, 24H, -$H_{g,h}$), 3.17 (d, 3H, CH_3OH), 4.15-4.20 (m, –*OH*), 6.36 (s, 4H, -H_f), 6.54 (d, 2H, -H_l), 7.17 (s, 2H, -H_i), 7.25 (t, 2H, –H_m), 7.45 (t, 2H, –H_n), 8.28 (t, 1H, -H_j), 8.42 (d, 2H, -H_k), 8,92 (d, 2H, -H_o). ^{13}C{^{1}H}-NMR ($CDCl_3$, ppm): 16.0 (aliph. –CH), 20.7 (aliph. –CH), 48.9 (aliph. –CH), 49.1 (aliph. –CH), 113.7 (arom. –CH), 119.2 (arom. –CH), 125.7 (arom. –CH), 126.2 (arom. –CH), 130.5 (arom. –CH), 131.0 (arom. –CH), 133.0 (arom. –CH), 134.5 (arom. –CH), 135.8 (arom. –CH), 136.1 (arom. –CH), 137.1 (arom. –CH), 141.9 (arom. –CH), 142.6 (arom. –CH), 152.9 (arom. –CH), 153.5 (arom. –CH). 154.6 (arom. –CH). IR (cm^{-1}): 3575, 3049, 2994, 2970, 2917, 2894, 2863, 2787, 1612, 1599, 1499, 1459, 1447, 1430, 1389, 1372, 1345, 1329, 1308, 1289, 1276, 1237, 1203, 1186, 1154, 1113, 1087, 1056, 1039, 1012, 927, 902, 876, 859, 839, 820, 802, 756, 740, 696, 683, 664. UV(nm): 214, 318, 357, 368, 441.

***[RuCl$_2$(L6)(CH$_3$CN)],* (K7): K7** was synthesized according to the synthesis method of **K5** using **L6** (0.15 g, 0.248 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ dimer (0.076 g, 0.124 mmol).

Yield: 95%, 0.20 g. m.p.: >280 °C. *Anal*. Calcd. for $C_{43}H_{44}Cl_2N_6Ru$: C: 63.23; H: 5.43; N: 10.29%; found**:** C: 62.96; H: 5.62; N: 9.58%. ^{1}H-NMR ($CDCl_3$, δ ppm): 2.06-2.12 (m, 24H, -

$H_{g,h}$), 2.24 (s, 3H, CH_3CN), 6.33 (s, 4H, -H_f), 6.48 (d, 2H, -H_l), 7.16-8.84 (m, 11H, -$H_{arom.}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, ppm): 1.2 (aliph. –CH), 15.4 (aliph. –CH), 20.1 (aliph. –CH), 48.2 (aliph. –CH), 106.2 (arom. –CH), 114.2 (arom. –CH), 117.7 (arom. –CH), 118.7 (arom. –CH), 122.3 (arom. –CH), 125.1 (arom. –CH), 125.6 (arom. –CH), 130.0 (arom. –CH), 132.5 (arom. –CH), 134.1 (arom. –CH), 134.9 (arom. –CH), 135.5 (arom. –CH), 142.0 (arom. –CH), 151.6 (arom. –CH), 152.9 (arom. –CH). IR (cm^{-1}): 3383, 3060, 2969, 2916, 2868, 1606, 1591, 1571, 1528, 1509, 1459, 1450, 1031, 1383, 1355, 1325, 1294, 1253, 1233, 1205, 1171, 1121, 1085, 1031, 1008, 994, 950, 911, 880, 851, 824, 804, 764, 743, 683. UV(nm): 315, 341, 356, 490.

[RuCl$_2$(L5)(L1)] **(K8): L5** (0.157 g, 0.32 mmol) and [$RuCl_2(DMSO)_4$] (0.155 g, 0.32 mmol) were placed in the same Schlenk tube and ethanol (15 mL) was added. The mixture was heated under reflux for 1 day. Then, **L1** (0.038 g, 0.32 mmol) was added to the reaction mixture and reflux process continued for 1 day more. At the end of this time, the mixture was concentrated to 3 mL, precipitated by addition of Et_2O, and filtered off.

Yield: 80%, 0.2 g. m.p.: >280 °C. *Anal*. Calcd. for $C_{40}H_{31}Cl_2N_7Ru$: C: 61.46; H: 4.00; N: 12.54%; found**:** C: 61.83; H: 4.23; N: 11.96%. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.33 (d, 4H, –H_f), 6.89-8.71 (m, 26H, -$H_{arom.}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): $^{13}C\{^1H\}$-NMR spectrum of **K8** could not be recorded because of its low solubility. IR(cm^{-1}): 3098, 3058, 3025, 2971, 1620, 1597, 1507, 1498, 1486, 1459, 1439, 1357, 1333, 1304, 1260, 1230, 1217, 1204, 1154, 1088, 1030, 1012, 965, 915, 860, 814, 786, 755, 743, 693, 678. UV(nm): 214, 318, 343, 357, 434.

[RuCl$_2$(L5)(L2)], **(K9): K9** was synthesized according to the synthesis method for **K8** using **L5** (0.165g, 0.32 mmol), [$RuCl_2(DMSO)_4$] (0.155 g, 0.32 mmol) and **L2** (0.038 g, 0.32 mmol).

Yield: 77%, 0.2 g. m.p.: >280 °C. *Anal*. Calcd. for $C_{47}H_{37}Cl_2N_7Ru$: C: 64.75; H: 4.28; N: 11.25%; found**:** C: 64.28; H: 4.65; N: 10.89%. ^{1}H-NMR ($CDCl_3$, δ ppm): 5.56 (s, 2H, $-H_f$), 6.33 (s, 4H, $-H_f$), 7.14-8.74 (m, 31H, $-H_{arom}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): $^{13}C\{^1H\}$-NMR spectrum of **K9** could not be recorded because of its low solubility. IR(cm^{-1}) : 3635, 3465, 3103, 3085, 3059, 3023, 2971, 2922, 1629, 1599, 1507, 1497, 1486, 1460, 1456, 1438, 1355, 1332, 1308, 1260, 1198, 1156, 1121, 1085, 1053, 1030, 1002, 957, 916, 860, 812, 786, 756, 730, 697, 677. UV(nm): 317, 343, 358, 433.

2.2. *Transfer hydrogenation of acetophenone using Ru(II) complexes as catalysts:*

In a typical catalytic reaction, a Ru(II) complex (0.0085 mmol) and acetophenone (0.849 mmol) was dissolved in isopropyl alcohol (4 mL). This mixture was stirred at 82 °C for 10 minutes. After cooling to room temperature, KOH (0.849 mmol) was introduced and the mixture was stirred at 82 °C. Reactions were monitored by GC.

3. Result and discussion

In this study, Ru(II) complexes (**K1-9**) containing monodentate-, tridentate- and monodentate+tridentate-benzimidazole ligands were synthesized, characterized and their catalytic application for transfer hydrogenation of acetophenone was investigated. For this purpose, benzimidazole (**L1),** in the form of light yellow crystals, was prepared in good yield using *o*-phenylene diamine and formic acid in hot water. **L2** and **L3** were synthesized in good yield by the reaction of **L1**, KOH and RX (RX= $C_6H_5CH_2Cl$ and 2,3,5,6-$(CH_3)_4$-C_6HCH_2Cl, respectively) in refluxing acetone. Similarly, **L4** as a cream solid was prepared in good yield using pyridine-2,6-dicarboxylic acid and o-phenylene diamine in polyphosphoric acid at 190 °C. Finally, **L5** and **L6,** in the form of yellow solids, were synthesized in good yield by the reaction

of **L4**, KOH and RX (RX= $C_6H_5CH_2Cl$ and 2,3,5,6-$(CH_3)_4$-$C_6H_1CH_2Cl$, respectively) (Scheme 1). **L1-6** were soluble in most organic solvents such as THF, MeOH, DMF, DMSO, $CHCl_3$ and CH_2Cl_2, and spectral properties and melting points of these compounds are compatible with the literature (Supporting Information).

Six-coordinate ruthenium complexes, **K1-9**, were synthesized by the appropriate use of these ligands. Heteroleptic [$RuCl_2$(*p*-cymene)(**L1-3**)], (**K1-3**) type complexes which contain monodenate benzimidazole ligands were synthesized by the reaction of [$RuCl_2$(*p*-cymene)]$_2$ and **L1-3** in MeOH at room temperature as yellow-orange solids. **K1-3** complexes are soluble in chlorinated solvents such as $CHCl_3$ and CH_2Cl_2. **K4-7**, [Ru(**L5-6**)(Solvent)Cl_2], type complexes containing tridentate benzimidazole ligands were synthesized by the reaction of [(*p*-cymene)$RuCl_2$]$_2$ and **L5** or **L6** in solvent (Solvent=CH_3OH for **K4** and **K6**; Solvent=CH_3CN for **K5** and **K7**) at room temperature as purple-brown solids. Finally, [Ru(**L5**)(**L1-2**)Cl_2] type complexes which contain tridentate and monodentate benzimidazole ligands at the same time were synthesized by the reaction of [Ru(DMSO)$_4Cl_2$], **L5** and **L1** or **L2** in ethanol under reflux conditions as brown solids (Scheme 2).

All complexes gave ^{1}H– and ^{13}C{^{1}H}-NMR spectra corresponding to the proposed formulations. From ^{1}H-NMR spectra of heteroleptic aren-Ru(II) complexes containing monodentate benzimidazole ligands (**K1-3**), the characteristic peaks belonging to $–H_q$ and $–H_r$ protons were observed in the range 5.40-6.24 ppm. For **K2** and **K3**, the peaks belonging to $-H_f$ protons were observed in the range 5.40-6.03 ppm together with $–H_q$ and $–H_r$ protons as

multiplets. For these type complexes, the protons belonging to the benzimidazole fragment were monitored above 7.00 ppm as various peaks. For **K1**, -N*H* proton was shown in the range 13.39-13.82 ppm as a broad peak. From ^{1}H-NMR spectra of [Ru(Cl)$_2$(**L5-6**)(S)] type complexes (**K4-7**), characteristic -H_k and -H_j protons were observed at 8.32 and 8.47 ppm for **K4**, at 8.31 and 8.46 ppm for **K5**, and at 8.42 and 8.28 ppm for **K6**. These -H_k and -H_j protons of **K7** were monitored in the range 7.16-8.84 ppm as multiples together with other aromatic peaks. From ^{1}H-NMR spectra of [Ru(Cl)$_2$(**L5**)(**L1-2**)] type complexes (**K8-9**), the –H_f proton was observed at 6.33 ppm for **K8**, and at 5.56 and 6.33 ppm for **K9**. Other peaks for **K8-9** were monitored in the aromatic region as various multiplets with appropriate integral values. The total count of carbon peaks for all complexes matched well with the composition of the complexes except for **K8-9** in ^{13}C{^{1}H}-NMR spectra. ^{13}C{^{1}H}-NMR spectrum of **K8-9** could not be recorded because of its very low solubility. However, satisfactory elemental analyses were obtained for all complexes.

The characteristic C=N stretching vibration of the benzimidazole ring of **L1-3** are observed at 1620, 1613 and 1612 cm^{-1}, respectively. Similarly, the C=C stretching vibration of **L1-3**, another characteristic peak for benzimidazole derivatives, was observed at 1588, 1584 and 1586 cm^{-1}, respectively. Upon coordination of Ru(II), **K1-3**, the C=N stretching vibration of the benzimidazole ring slightly shifted to 1622, 1614 and 1611 cm^{-1}. For 2,6-bis(benzimidazolyl)pyridine derivatives (**L4-6**), the strong peaks at 1622, 1614 and 1611 cm^{-1} are attributed to the C=N stretching vibration of the benzimidazole ring. In the IR spectra of **K4** and **K6**, which are derivatives of **L5**, C=N stretching vibration of the benzimidazole ring is monitored at 1596 and 1612 cm^{-1}, respectively. For **K5** and **K7**, the peaks at 1619 and 1612 cm^{-1} are attributed to C=N stretching vibration of the benzimidazole ring, respectively. In the IR

spectra of Ru(II) complexes bearing monodentate and tridentate benzimidazole ligands at the same time, **K8-9**, C=N stretching vibration belonging to benzimidazole rings are monitored at 1620 and 1597 cm^{-1} for **K8** and at 1629 and 1599 cm^{-1} for **K9**.

The UV-Vis absorption spectra were recorded in CH_3OH at room temperature (Supporting Information, Figure S1). The normalized UV-Vis absorption spectra of **L1-3** and their heteroleptic arene-Ru(II) complexes (**K1-3**) are shown in Figure S1a and b, respectively. The **L1-3** have three absorption bands in the range of 208-273 nm, which can be assigned to $\pi\rightarrow\pi^*$ transitions. The heteroleptic **K1-3** complexes show two absorption bands in the range of 210-275 nm, which can be assigned to intra ligand $\pi\rightarrow\pi^*$ transitions and another two absorption bands in the range of 324-404 nm, which can be assigned to the spin-allowed metal to ligand charge transfer transitions (MLCT). The normalized UV-Vis absorption spectra of **L4-6** and their Ru(II) complexes (**K4-7**) are shown in Figure S1c and d respectively. The **L4-6** have two absorption bands in the range of 215-316 nm, which can be assigned to intra molecular $\pi\rightarrow\pi^*$ transitions. The K**4-7** complexes show three absorption bands in the range of 205-368 nm, which can be assigned to intra ligand $\pi\rightarrow\pi^*$ transitions and another one absorption band in the range of 441-499 nm, which can be assigned to the metal to ligand charge transfer transition (MLCT). The UV-vis spectra of [Ru(**L4-6**)(S)Cl_2] type complexes are very interesting. If S=CH_3CN, the maxima of the MLCT band are red shifted by approximately 50 nm compared to S=MeOH analogues. The UV-Vis spectra of **K8-9** are shown in Figure S1. The **K8-9** complexes show four absorption bands in the range of 214-358 nm, which can be assigned to intra ligand $\pi\rightarrow\pi^*$ transitions. The MLCT bands of **K8-9** are very broad in the range of approximately 400-650 nm with wavelength maxima at 434 and 433 nm.

3.1. *Catalytic Studies*

Transfer hydrogenation reactions catalyzed by transition metal complexes (especially Ru(II) complexes) has attracted attention in both academic and industrial fields because multiple bonds can be easily reduced under mild conditions. Due to this, new catalysts have been continuously synthesized. In this study, the synthesized Ru(II) complexes (**K1-9**) were employed as catalyst for transfer hydrogenation of acetophenone as model substrate of aryl ketones.

Catalytic reactions were performed under identical conditions to allow comparison of results and optimization reactions were carried out using **K7**. First, catalytic reactions under inert atmosphere were compared with open air. Results show that catalytic yields are good under inert atmosphere. Second, a significant increase in the yield of the catalytic reaction was observed by increasing the amount of base. Third, according to base survey results, the best catalytic yield was provided by KOH. Finally, lowering the temperature of the catalytic reaction caused a significant decrease in catalytic yield. Under thus optimized conditions, all Ru(II) complexes were employed as catalyst for catalytic transfer hydrogenation of acetophenone. Results are given in Table 1.

In short, the results show that **K1-9** complexes are active catalysts under these conditions for transfer hydrogenation of acetophenone. However, **K4** and **K5** are much more efficient catalysts than the others. For [$RuCl_2$(**L5-6**)(S)] type complexes, the complexes containing acetonitrile ligand (**K5** and **K7**) are slightly better catalysts than methanol containing analogues (**K4** and **K6**). [$RuCl_2$(*p*-cymene)(**L1-3**)] type complexes showed relatively low catalytic activity

compared to the complexes containing tridentate benzimidazole ligands except for **K9**. Lower catalytic activity of **K9** may be related to the low solubility of this complex.

4. Conclusions

In this work, Ru(II) complexes (**K1-9**) containing mono- and tri-dentate benzimidazole ligands were synthesized, characterized and their catalytic efficiency for transfer hydrogenation of acetophenone was investigated. All complexes are active catalysts under working conditions, and the sequence of catalytic activity is **K5>K4>K7>K6>K8>K1>K3=K9>K2.** As expected, the Ru(II) complexes containing tridentate benzimidazole ligands (**K4-K7**) are more active than their arene containing analogues (**K1-3**).

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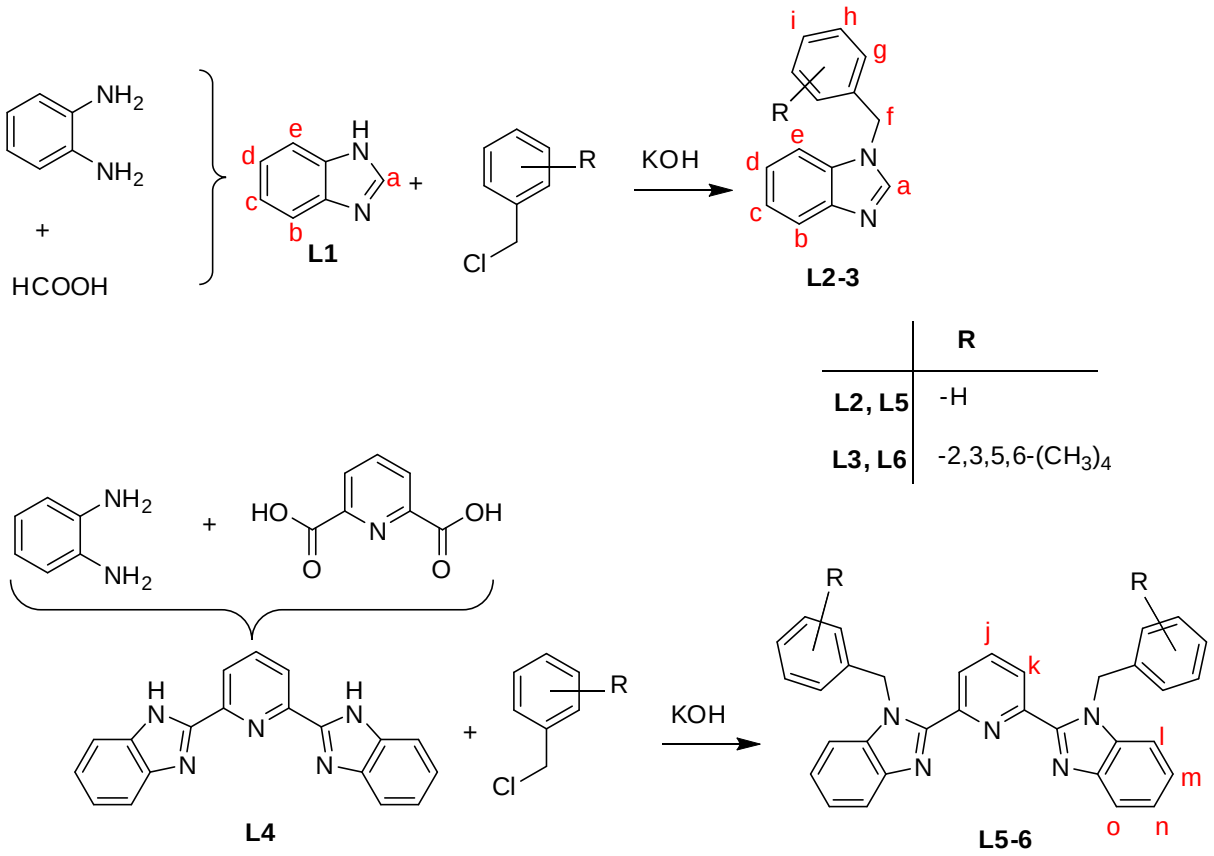
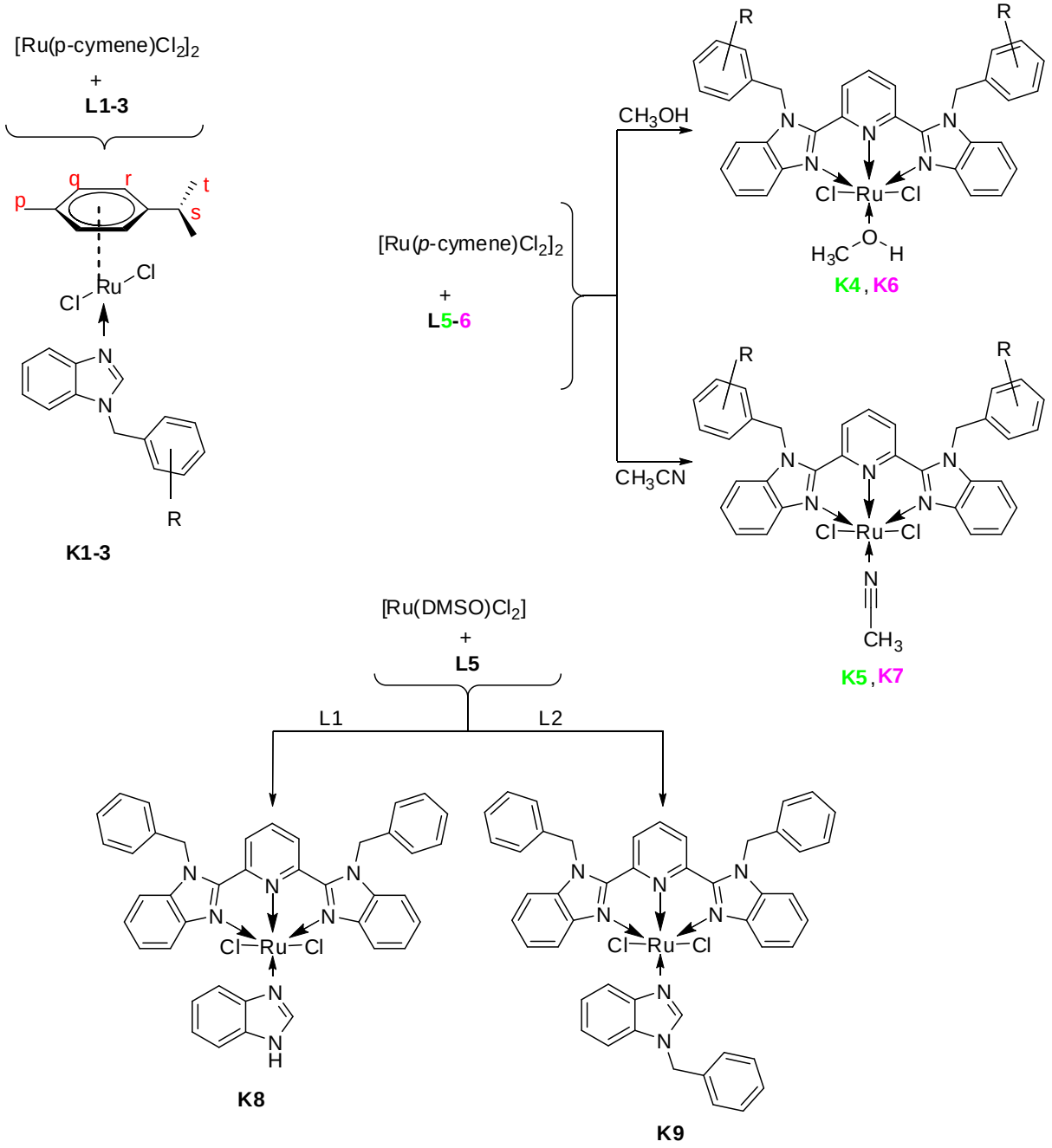
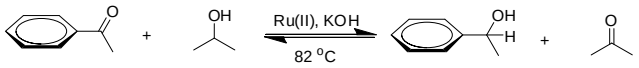


Scheme 1. Synthesis of ligands and numbering scheme for the ligands



Scheme 2. Synthesis of complexes and numbering scheme for the ligands

Table 1. Catalytic activity for transfer hydrogenation of acetophenone catalyzed by Ru(II) complexes [a]



Entries	Catalyst	Yield[a], %
1	**K1**	39
2	**K2**	21
3	**K3**	35
4	**K4**	95
5	**K5**	**97**
6	**K6**	78
7	**K7**	85, 75[b], 24[c], 68[d], 10[e], 17[f], 34[g], 40[h], 82[i]
8	**K8**	68
9	**K9**	35

[a] TH of acetophenone under argon atmosphere. [Ru:KOH:Substrate][1:100:100]; 2–propanol (4 ml); 82 °C, 1h.

[b] TH of acetophenone under argon atmosphere. [Ru:KOH:Substrate][1:10:100]; 2–propanol (4 ml); 82 °C, 2h.

[c] TH of acetophenone under open air. [Ru:KOH:Substrate][1:10:100]; 2–propanol (4 ml); 82 °C, 2 h.

[d] TH of acetophenone. [Ru:KOH:Substrate][1:10:100]; 2–propanol (4 ml); 82 °C, 1h.

[e] TH of acetophenone. [Ru:Na_2CO_3:Substrate][1:100:100]; 2–propanol (4 ml); 82 °C, 1 h.

[f] TH of acetophenone. [Ru:K_2CO_3:Substrate][1:100:100]; 2–propanol (4 ml); 82 °C, 1 h.

[g] TH of acetophenone. [Ru:Cs_2CO_3:Substrate][1:100:100]; 2–propanol (4 ml); 82 °C, 1 h.

[h] TH of acetophenone. [Ru:NaOMe:Substrate][1:100:100]; 2–propanol (4 ml); 82 °C, 1 h.

[i] TH of acetophenone. [Ru:NaOH:Substrate][1:100:100]; 2–propanol (4 ml); 82 °C, 1 h.

