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FULL PAPER

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Half-sandwich ruthenium complexes with Schiff base ligands bearing a hydroxyl group: Preparation, characterization and catalytic activities

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Three half-sandwich ruthenium(II) complexes with hydroxyl group functionalized Schiff-base ligands [Ru(*p*-cymene)LCl] (**2a-2c**) have been synthesized and characterized. All ruthenium complexes were fully characterized by ^{1}H and ^{13}C NMR spectra, mass spectrometry and infrared spectrometry. The molecular structure of ruthenium complex **2c** was confirmed by single-crystal X-ray diffraction methods. Furthermore, these half-sandwich ruthenium complexes were found to exhibit high catalytic activity for nitro compounds reduction using $NaBH_4$ reducing agent in the presence of cetyltrimethylammonium bromide (CTAB) in water at room temperature.

KEYWORDS
nitro compound, reduction, ruthenium, Schiff-base, structure

1 | INTRODUCTION

Metal and ligand synergistic effect is an important catalysts design concept, many efficient catalysts were applied in a wide variety of chemical transformations.[1–8] The complexes containing functional ligands with two or more distinct states can adjust the electronic configuration of the metal center, accept or donate proton, and induce reversible structural changes in the processes of substrate activation and product formation. The complexes based on "synergistic" ligands have exhibited remarkable catalytic activity.[9,10] During the past decades, half-sandwich metal (M = Rh, Ir and Ru) complexes were widely used as powerful catalysts in organic transformation and anticancer reagent.[11–17] The half-sandwich metal (M = Rh, Ir and Ru) complexes coordinated by the hydroxyl group functionalized bipyridine ligands show unique catalytic properties, such as transfer hydrogenation reaction, CO_2 hydrogenation and formic acid decomposition.[18–20] The hydroxyl group functionalized bipyridine reversibly generates hydroxyl, keto, and oxyanion structure, which will significantly improve water-soluble and the hydrogenation ability of half-sandwich metal complex under basic conditions.[21]

Chen and co-worker found that the ruthenium complexes with unsymmetrical NNN ligands with 2-hydroxypyridyl fragment showed high catalytic activity for β-alkylation of secondary alcohols with primary alcohols.[22] Himeda and co-worker discovered an efficient proton-responsive and water-soluble half-sandwich iridium complex bearing one or more hydroxyl groups functionalized bipyridine ligands for highly CO_2

hydrogenation and formic acid decomposition under mild conditions.[23,24] They found that the catalysts bearing hydroxyl group act as cooperating ligands would reversibly deprotonated to generate an oxyanion (O^-) to enhance the catalytic efficiency.[25] Zhang and co-worker reported Cp*Ir complexes with ortho-hydroxyl group functionalized bipyridine ligands exhibit remarkably high catalytic activity for hydrogenation of 5-hydroxymethylfurfural in acidic water.[26] The catalytic efficiencies of Cp*Ir complex with four hydroxyl groups functionalized pyrimidine ligands were promoting further for hydrogenation of CO_2.[27]

Water is readily available, inexpensive, nontoxic and environmentally benign solvent in nature, and has gained immense attention in transfer hydrogenation reaction.[28–31] Thus, efforts towards hydrogenations of unsaturated compounds with new water-soluble transition metal complexes with functional synergistic ligands are required. We previously reported the synthesis and catalytic activity of a series of half-sandwich ruthenium complexes containing [N,O] ligand such as benzo oxazoline and Schiff-base.[32–36] These complexes catalyze nitro compounds reduction using $NaBH_4$ reducing agent under basic conditions. Moreover, we demonstrated that the active species during catalysis is Ru-H intermediate. With respect to the development of our target catalyst, the necessary feature is water solubility with no additives.

Encouraged by these results and in our continuing interest in the nitro compounds reduction, herein we preparation a general and effective half-sandwich ruthenium complexes with hydroxyl group incorporate in Schiff bass ligands that efficiently catalyzes the nitro compounds reduction in water using $NaBH_4$ as the reductant. Such Schiff-base ligands bearing OH unit are consider as "proton-responsive ligands". This property makes them pH-switchable and enables modification of the polarity and electron-donating ability of the ligand, thus tuning the catalytic activity and water-solubility of the complexes.[23–25]

2 | EXPERIMENTAL SECTION

2.1 | Materials and measurements

Commercial reagents were analytical grade and used as received. All the operations were carried out under a pure nitrogen atmosphere using standard Schlenk techniques. All solvents were purified and degassed by standard procedures. The Schiff base compounds (**1a**–**1c**) and [Ru(*p*-cymene)(μ-Cl)Cl]$_2$ were synthesized according to procedures described in the previous literature.[37–41] ^{1}H and ^{13}C NMR were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to internal TMS and are internally referenced to residual ^{1}H and ^{13}C solvent resonances. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Elemental analyses were performed on a PerkinElmer 2400 CHN analyzer. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen, Germany) spectrometers.

2.2 | Synthesis

2.2.1 | Synthesis of the Schiff-Base ligand 1a-1c

2-hydroxy-1-naphthaldehyde (516.6 mg, 3.0 mmol) and corresponding 2-amino-4-substitute phenol (3.0 mmol) were stirred in MeOH (15 ml) and were heated to 75 °C for three hours in the presence of catalytic amount of acetic acid. The obtained yellow solids were filtered off, washed with EtOH for three times (1 ml) and dried under the vacuum in an oven (80 °C) overnight.

1a: Yield: (760.6 mg, 96%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 15.70 (d, J = 9.0Hz, 1H), 10.31 (s, 1H), 9.48 (d, J = 9.0Hz, 1H), 8.37 (d, J = 9.0Hz, 1H), 7.92 (d, J = 9.0Hz, 1H), 7.78 (d, J = 9.0Hz, 1H), 7.65 (d, J = 6.0Hz, 1H), 7.46 (t, J = 6.0Hz, 1H), 7.24 (t, J = 6.0Hz, 1H), 7.09 (t, J = 6.0Hz, 1H), 7.00-6.90 (m, 2H), 6.77 (d, J = 9.0Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 178.1, 149.9, 148.9, 138.4, 134.4, 129.1, 129.0, 128.6, 127.2, 126.3, 125.6, 123.5, 120.3, 120.2, 118.0, 116.4, 108.2. IR (KBr cm^{-1}): 3483 (s), 3033 (m), 1632 (s), 1585 (m), 1549 (s), 1514 (s), 1459 (s), 1360 (s), 1140 (s), 745 (s).

1b: Yield: (793.0 mg, 95%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 15.67 (d, J = 9.0Hz, 1H), 10.05 (s, 1H), 9.45 (d, J = 9.0 Hz, 1H), 8.37 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 6.0 Hz, 2H), 7.65 (d, J = 9.0 Hz, 1H), 7.46 (t, J = 6.0 Hz, 1H), 7.24 (t, J = 6.0 Hz, 1H), 6.87 (s, 2H), 6.76 (d, J = 12.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 128.3, 149.4, 146.6, 138.4, 134.4, 129.4, 129.3, 128.5, 127.6, 126.3, 125.7, 123.4, 120.1, 118.1, 118.1, 116.3, 108.1, 20.8. IR (KBr cm^{-1}) : 3445 (m), 3022 (m), 2923 (m), 1621 (vs), 1593 (s), 1544 (s), 1516 (s), 1459 (m), 1352 (vs), 1140 (s), 887 (m), 813 (s), 750 (s).

1c: Yield: (860.6 mg, 96%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 15.63 (d, J = 9.0Hz, 1H), 10.54 (s, 1H), 9.51 (d, J = 9.0Hz, 1H), 8.45 (d, J = 9.0 Hz, 1H), 8.10 (s, 1H), 7.81 (d, J = 9.0Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.47 (t, J = 9.0Hz, 1H), 7.26 (t, J = 9.0 Hz, 1H), 7.10 (d, J = 9.0 Hz, 1H), 6.96 (d, J = 6.0Hz, 1H), 6.79 (d, J=9.0Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 177.5, 150.7, 147.9, 138.6, 134.2, 130.7, 129.4, 128.6, 126.5, 126.5, 125.1, 124.1, 123.8, 120.7, 117.7, 117.5, 108.6. IR (KBr cm^{-1}) : 3439 (w), 3060 (m), 1632 (vs),

1582 (m), 1546 (s), 1505 (m), 1489 (m), 1349 (m), 1146 (s), 882 (m), 833 (s), 800 (m), 745 (s).

2.2.2 | Synthesis of half-Sandwich ruthenium complexes with naphthalene-based Schiff Base ligands 2a-2c

A solution of [Ru(*p*-cymene)(μ-Cl)Cl]$_2$ (122.4 mg, 0.20 mmol), schiff base (0.50 mmol), and K_2CO_3 (69.0 mg, 0.50 mmol) in MeOH (15 ml) was purged with N_2 and then stirred for 4 hr at room temperature. The reaction mixture was separated from insoluble salts by filtration and dried in vacuo. The crude material was subjected to silica gel chromatography with ethyl acetate and petroleum ether (2 : 1) to give dark red half-sandwich ruthenium complexes.

2a: Yield (145.2 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (s,1H), 8.35 (s,1H), 7.64 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 6.0 Hz, 1H), 7.33-7.26 (m, 2H), 7.17-6.98 (m, 5H), 5.45 (s, 2H), 4.95 (d, J = 6.0 Hz, 1H), 4.19 (d, J = 3.0 Hz, 1H), 2.76-2.67 (m, 1H), 2.18 (s, 3H), 1.24 (d, J = 6.0 Hz, 3H), 1.14 (d, J = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2, 159.6, 151.4, 146.1, 137.1, 135.1, 129.3, 128.83, 128.0, 127.0, 125.2, 124.5, 122.7, 119.8, 119.4, 118.0, 109.0, 101.2, 99.2, 88.5, 85.2, 83.9, 81.2, 30.9, 23.4, 21.7, 18.8. Anal. Calcd. for $C_{27}H_{26}NO_2RuCl$: C 60.84, H 4.92, N 2.63 Found: C 60.88, H 4.87, N 2.73. MS (MALDI-TOF): calcd. for $C_{27}H_{26}NO_2Ru^+$ [M-Cl]$^+$ 498.1007, found 498.0990. IR (KBr cm^{-1}) : 3458 (m), 3059 (m), 2961 (s), 2926 (s), 2853 (m), 1614 (s), 1599 (s), 1576 (s), 1535 (vs), 1465(vs), 1423 (s), 1381(s), 1354 (s), 1328(s), 1282(s), 1190(s), 1160 (s), 1093 (m), 985(w), 820 (s), 746 (vs), 671(s), 557 (w).

2b: Yield (142.5 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s,1H), 8.16 (s,1H), 7.64 (t, J = 9.0 Hz, 2H), 7.55 (d, J = 9.0 Hz, 1H), 7.31 (t, J = 6.0 Hz, 1H), 7.15-6.97 (m, 4H), 6.84 (s,1H), 5.45 (d, J = 3.0 Hz, 2H), 4.96 (d, J = 6.0 Hz, 1H), 4.22 (d, J = 6.0 Hz, 1H), 2.76-2.67 (m, 1H), 2.38 (s, 3H), 2.18 (s, 3H), 1.25 (d, J = 9.0 Hz, 3H), 1.15 (d, J = 9.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1, 159.5, 149.0, 145.8, 136.9, 135.2, 129.3, 129.2, 129.2, 128.0, 127.0, 125.3, 124.8, 122.7, 119.5, 117.7, 109.0, 101.2, 99.1, 88.5, 85.3, 84.1, 81.2, 30.9, 23.4, 21.7, 21.0, 19.8. Anal. Calcd. for $C_{28}H_{28}NO_2RuCl$: C 61.48, H 5.16, N 2.56 Found: C 61.56, H 5.22, N 2.45. MS (MALDI-TOF): calcd. for $C_{28}H_{28}NO_2Ru^+$ [M-Cl]$^+$ 512.1164, found 512.1151. IR (KBr cm^{-1}): 3456 (s), 3060 (w), 2967 (w), 2873 (w), 1615 (s), 1599 (s), 1579 (m), 1535(s), 1503 (m), 1464 (vs), 1428(m), 1371 (m), 1286(m), 1190 (w), 983(w), 830 (s), 750 (s), 671 (m), 580 (w).

2c: Yield (145.4 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (s, 1H), 7.65 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 6.0 Hz, 1H), 7.36-7.23 (m, 2H), 7.19-7.11(m, 2H), 7.04 (d, J = 6.0 Hz, 2H), 5.47 (d, J = 3.0 Hz, 2H), 5.00 (d, J = 6.0 Hz, 1H), 4.24 (d, J = 6.0 Hz, 1H), 2.76-2.67 (m, 1H), 2.18 (s, 3H), 1.25 (d, J = 6.0 Hz, 3H), 1.16 (d, J = 9.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.7, 159.6, 150.4, 146.4, 137.5, 135.0, 129.3, 128.6, 128.2, 127.1, 125.2, 124.3, 124.2, 123.0, 119.4, 119.1, 108.9, 101.6, 99.2, 88.5, 85.2, 83.8, 80.9, 30.9, 23.4, 21.8, 18.8. Anal. Calcd. for $C_{27}H_{25}NO_2RuCl_2$: C 57.15, H 4.44, N 2.47 Found: C 57.24, H 4.47, N 2.53. MS (MALDI-TOF): calcd. for $C_{27}H_{25}NO_2RuCl^+$ [M-Cl]$^+$ 532.0617, found 532.0598. IR (KBr cm^{-1}) : 3447 (m), 3059 (m), 2926 (m), 2926 (m), 2849 (m), 1617 (s), 1599 (s), 1576 (s), 1532 (vs), 1466 (vs), 1328 (s), 1282 (s), 1190 (s), 904 (w), 827 (s), 746 (s), 672 (s), 555(m)

2.2.3 | General procedure for the reduction of nitro compounds with ruthenium catalysts

Ruthenium complex (0.003 mmol, 0.01 equiv) was dissolved in solvent (2.0 ml), then appropriate nitro compounds (0.3 mmol, 1.0 equiv) CTAB (0.2 mmol) and $NaBH_4$ (45.4 mg, 1.2 mmol, 4.0 equiv) was added. Subsequently, the resulting mixture was stirred at room temperature in closed vessel. After completion of the reaction (monitored by TLC), the crude reaction mixture was extraction with ether (3×2 ml). After solvents were removed in vacao from combined organic extracts, the crude products loaded directly onto a column of silica gel and purified by column chromatography petrol ether and ethyl acetate (1 : 3) to get the corresponding products.[34,42]

2.3 | X-ray structure determination

Diffraction data of **2c** were collected on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Mo Kα radiation (λ = 0.71073 Å). All the data were collected at 298 K and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL),[43] SADABS absorption corrections were applied to the data,[44] all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculation was performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information are given in Table S1, selected bond angles and distances are given in Table S2.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of Schiff Base compounds and half-Sandwich ruthenium complexes

The naphthalene-based Schiff base compounds **1a-1c** were prepared by condensation of 2-hydroxy-1-naphthaldehyde with different 2-amino-4-substitute phenol in high yields in methanol solvent according to the published method.[37–40] A few drops of CH_3COOH were added to the mixture to accelerate the condensation reaction. The dark red half-sandwich complexes [(*p*-cymene)LRuCl] (**2a-2c**) were obtained by treatment of 2 equiv of the schiff base (**1a-1c**) with $[(p\text{-cymene})Ru(\mu\text{-}Cl)Cl]_2$ in the presence of K_2CO_3 in MeOH at room temperature (Scheme 1). The pure half-sandwich ruthenium complexes (**2a-2c**) were achieved by column chromatography on silica gel using ethyl acetate/petroleum ether (2:1, v:v). All complexes have been characterized by a combination of NMR spectroscopy, mass spectrometry, and X-ray crystallography. The half-sandwich ruthenium complexes are air and moisture stable, soluble in chlorohydrocarbon, alcohol, acetonitrile solvents but slightly soluble in water. But the ruthenium complexes are insoluble in non-polar solvents such as diethyl ether and hexane. Aqueous solutions of the ruthenium complexes remain unchanged for at least ten days with no sign of decomposition.

The ^1H NMR spectra of complexes **2a-2c** display a distinct resonance shift of the Schiff base ligands protons in comparison with the equivalent protons in the free compounds. The proton signal at 15.6 ppm corresponds to the OH group of the free ligand disappear in complexes due to the coordination effect of the ligand with the ruthenium metal. And proton singal appear at $\delta = 8.5$ ppm, which indicates the presence of free hydroxyl group in the complexes. It was observed that the broad and intense band at approximately 3450 cm^{-1} due to the stretching vibration of hydroxyl group in infrared spectroscopy, which also confirmed the hydroxyl group existence in the complexes. The main peaks owing to the $[M\text{-}Cl]^+$ fragments of the complexes was also confirmed by positive-mode electrospray ionization mass spectrometry (ESI-MS) (Figures S14-S16, supporting information).

X-ray diffraction of single crystals for complex **2c** was obtained. The crystal was grown by slow diffusion of diethyl ether into a concentrated solution of the complex in methanol solution. The molecular structure of **2c** is shown in Figure 1. The crystal was solved with and monoclinic $P2_1/c$ space groups. As shown in Figure 1, each ruthenium atom is coordinated by *p*-cymene, one nitrogen atom and one oxygen atom of Schiff base ligand and one chlorine atom adopted typical piano-stool configuration. The Ru-O distances (2.0673(10)) and Ru-N distances (2.0909(13)) are consistent with Ru-N/Ru-O bond length values reported for those of half-sandwich ruthenium complexes.[45–48] The dihedral angle between naphthalene group and phenyl moiety is 82.37°, which is

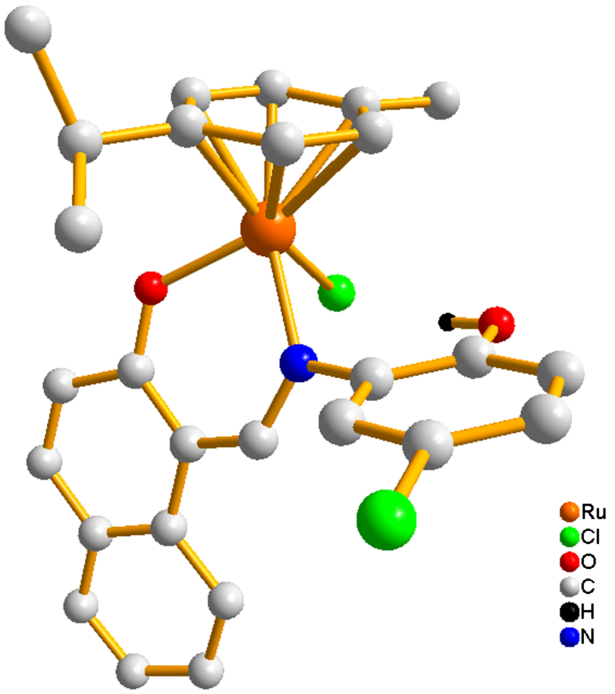
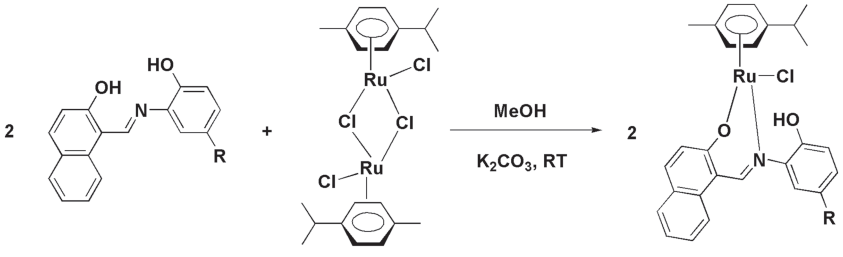


FIGURE 1 Molecular structure of **2c**, some hydrogen atoms are omitted for clarity 158 × 171 mm (96 × 96 DPI)



1a R = H
1b R = CH_3
1c R = Cl

2a R = H
2b R = CH_3
2c R = Cl

SCHEME 1 Synthesis of half-sandwich ruthenium complexes (**2a-2c**) 162 × 68mm (300 × 300 DPI)

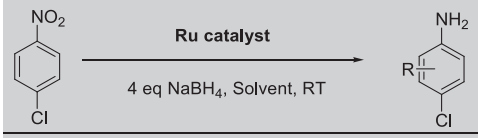
bigger than that of half-sandwich ruthenium complexes with naphthalene-based Schiff base ligands.[49] It is indicated that the hydroxyl group on phenyl ring has important spatial effects intramolecular structure. Furthermore, the dihedral angle between half-sandwich moiety and phenyl moiety is 14.83°. Non-covalent intermolecular interactions of C-H···X in the crystal packing structure of the complex are not observed.

3.2 | The nitro compounds reduction catalyzed by ruthenium complexes

Aromatic anilines are quintessential blocks in the synthesis of dyes, agrochemicals, pharmaceuticals, and pigments.[50] The typical method for the synthesis of aromatic anilines is the reduction of nitro compounds using $NaBH_4$.[51,52] We and others have reported the highly efficient nitro compounds reduction with half-sandwich ruthenium complexes catalysts.[31,45] With the ruthenium complexes with hydroxyl group incorporate in Schiff bass ligands in hand, the catalytic reactivity for nitro compounds reduction with these ruthenium complexes was investigated in the presence of $NaBH_4$ reducing agent.

And the optimized reaction conditions were screened using 1-chloro-4-nitrobenzene as the standard substrate, the results were summerized in Table 1. The ruthenium complexes (**2a-2c**) catalysts were screened with 1 mol% and 4.0 equiv of $NaBH_4$ in 2 ml ethanol at room temperature for 0.5 hr. As shown in Table 1, the half-sandwich ruthenium complex **2c** was the best catalyst toward the nitro compounds reduction (Table 1, entries 1–3). When the catalyst amount decreased, the high conversion was needed with longer reaction time (Table 1, entries 4–6). Then, the complex **2c** was chosen as the optimal catalyst to screen the various solvents (Table 1, entries 7–10). The yield was inferior when MeOH, CH_3CN or CH_2Cl_2 was used as the solvent. And 30% desired products were detected in water (Table 1, entry 10). To our delight, the yield was increased to 60% when 0.2 mmol CTAB was added the reaction for 4 hr. The yield could be increased to 95% by prolonging the reaction time to 7 hr (Table 1, entries 11–14). The micellar formation with the help of CTAB helps to overcome the phase-transfer limitations for water-organic catalytic system and increase the desired product yield in water.[53–58] A control

TABLE 1 Optimization of the reaction conditions for 1-chloro-4-nitrobenzene reduction using ruthenium complexes[a]

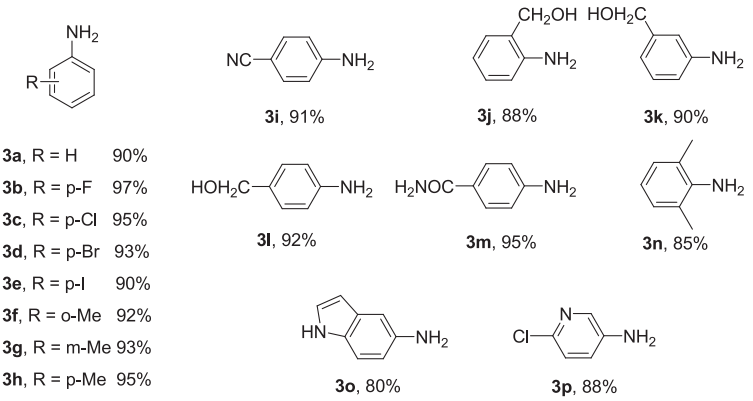


Entry	Catalyst	Loading (mol.%)	Solvent	Additive	Time (h)	TON	TOF (h^{-1})	Yield (%)[b]
1	**2a**	1	EtOH		0.5	92	184	92
2	**2b**	1	EtOH		0.5	85	170	85
3	**2c**	1	EtOH		0.5	95	190	95
4	**2c**	0.5	EtOH		1	180	180	90
5	**2c**	0.25	EtOH		1	340	340	85
6	**2c**	0.1	EtOH		9	880	98	88
7	**2c**	0.1	MeOH		9	750	83	75
8	**2c**	0.1	CH_3CN		9	260	29	26
9	**2c**	0.1	DCM		9	450	50	45
10	**2c**	0.1	H_2O		9	300	33	30
11	**2c**	0.1	H_2O	CTAB	4	600	150	60
12	**2c**	0.1	H_2O	CTAB	5	800	160	80
13	**2c**	0.1	H_2O	CTAB	6	850	142	85
14	**2c**	0.1	H_2O	CTAB	7	950	136	95
15			H_2O	CTAB	24			No reaction
16			H_2O		24			No reaction

[a]Reaction conditions: 1-chloro-4-nitrobenzene (0.3 mmol), $NaBH_4$ (1.2 mmol), Ru catalysts, solvent (2 ml), Additive (0.2 mmol), room temperature.

[b]Isolated yield.

TABLE 2 Screening of substrates for nitro compounds reduction catalyzed by ruthenium complex **2c**[a]



[a]Reaction conditions: nitro compounds (0.3 mmol), $NaBH_4$ (1.2 mmol), Ru catalysts (0.1 mol %), H_2O (2 ml), CTAB (0.2 mmol), 7 hr, room temperature.
[b]Isolated yield.

experiment without the addition of the catalyst or only with CTAB, no desired product was observed for nitro compounds reduction for 24 hr (Table 1, entry 15–16). From these studies, it was confirmed that the optimal conditions for the reduction of nitro compounds were using ruthenium complex **2c** catalyst (0.1 mol %) in the presence of four equivalent $NaBH_4$ and 0.2 mmol CTAB in water at room temperature. And the catalytic efficiency has been improved greatly in comparison with previous reported with half-sandwich ruthenium catalyst for nitro compounds reduction under greener reaction condition.[33] Compared with the previous literature using half-sandwich ruthenium complexes with naphthalene-based Schiff-base ligand catalysts for nitro compounds reduction, the catalytic efficiency have been improved greatly and lower the catalyst loading from 3 mol% to 0.1 mol%, and the solvent changed to water.[49] The hydroxy group introduced to the naphthalene-based Schiff-base ligand have an important effect on the catalytic results with half-sandwich ruthenium complexes for nitro compound reduction in the presence of $NaBH_4$, indeed. The water-solubility of the complexes was also increased when the hydroxy group in introduce to the ligands.

We further evaluated the ruthenium complex catalyzed nitro coumpounds reduction under optimal reaction conditions, and the results are shown in Table 2. As shown in Table 2, many functionalized nitro compounds were investigated. We could see that the reactions worked well, leading to the desired products in good to excellent yield. Both electron-withdrawing and electron-donating substrates were tolerate to the reaction. For 4-nitrobenzaldehyde, the -CHO group was also reduced to $-CH_2OH$ together with the nitro group (Table 2, **3l**). Notably, the nitro group in N-heterocyclic compound and was also suitable for this catalytic system giving the desired product in 80% and 88% yield, respectively.

To understand the mechanism of the ruthenium complex catalyzed nitro compounds reduction further, half-sandwich ruthenium was used to react with $NaBH_4$ under the standard conditions. The half-sandwich ruthenium hydride active species can be confirmed through in stiu NMR studies (δ -10.17 ppm, Figure S13, Supporting information). The possible mechanism of nitro compound reduction is outer-sphere mechanism through Ru-H intermediate as previous reported.[33–35]

4 | CONCLUSION

In conclusion, we have synthesized and characterized three half-sandwich ruthenium complexes with the hydroxyl group functionalized Schiff base ligands and evaluated their catalytic activities for nitro compounds reduction in the presence of $NaBH_4$ in water with the help of CTAB at room temperature. We have shown that the efficiency of the catalytic reaction is improved by introduction of one hydroxy group into Schiff base ligands. The results illustrate that a simple ligand modification imparts dramatic changes to catalysis.

Supplementary Material

CCDC 1946806 contains the supplementary crystallographic data for **2c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

NMR data and spectrum of ruthenium complexes

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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