



Half-sandwich ruthenium complexes with oxygen–nitrogen mixed ligands as efficient catalysts for nitrile hydration reaction



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ABSTRACT

Three ruthenium(II) *p*-cymene complexes containing oxygen–nitrogen mixed ligands [Ru(*p*-cymene)LCI] [HL = 2-(4,5-dihydrooxazol-2-yl)phenol (**2a**); HL = 2-(4,5-dihydrothiazol-2-yl)phenol (**2b**); HL = 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol (**2c**)] have been synthesized and characterized. All half-sandwich ruthenium complexes were fully characterized by ¹H and ¹³C NMR spectra, elemental analyses and infrared spectrometry. The molecular structure of ruthenium complex **2c** was further confirmed by single-crystal X-ray diffraction methods. Furthermore, these half-sandwich ruthenium complexes are active catalysts for the hydration of nitriles to amides in the presence of sodium hydroxide in isopropanol.

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1. Introduction

Half-sandwich ruthenium complexes are useful organometallics compounds which are widely used as organic transformation catalysts in construction C–C and C–heteroatom bond through the direct C–H bond activation [1], C–N bonds formation from alcohols and amines [2], transfer hydrogenation of ketones [3], nitroarene reduction [4] and water oxidation [5]. Many efficient ruthenium complexes have been synthesized and applied to various organic transformations. Phenolate-oxazoline compounds are oxygen–nitrogen mixed ligands that are readily modifiable through changing the starting amino alcohol to allow fine tuning of steric and electronic properties of the transition metal complexes [6]. Exploring the catalytic activities of half-sandwich ruthenium complexes with oxygen–nitrogen mixed ligands would be interesting.

Amides are important building block in the preparation of polymers, agrochemicals and pharmaceuticals [7]. The most widely used method for the synthesis of amides is the hydration of nitriles with transition metal catalysts, which is an ideal atom economical reaction and sustainable method for the preparation of amides [8]. Ruthenium-based complexes are all good catalysts for the hydration of nitriles due to their high catalytic activity [9,10].

Herein, we have synthesized three half-sandwich ruthenium complexes with oxygen–nitrogen mixed ligands [Ru(*p*-cymene)LCI] [HL = 2-(4,5-dihydrooxazol-2-yl)phenol (**2a**); HL = 2-(4,5-

dihydrothiazol-2-yl)phenol (**2b**); HL = 2-(5,6-dihydro-4H-1,3-oxazin-2-yl)phenol (**2c**)] and explored their catalytic activities for the hydration of nitriles to aromatic amides. The half-sandwich ruthenium complex catalysts allowed the hydration of nitriles to proceed in the presence of sodium hydroxide with high yields in isopropanol as solvent. This catalytic system was found to be efficient toward the reduction of various nitriles substrates. Moreover, the solid-state structure of complex **2c** was confirmed by single-crystal X-ray crystallography and the resolved structures reveal that the complex adopt the three-legged piano-stool conformation with a six-membered metallocycle formed by coordination of the oxygen–nitrogen mixed ligands to the metal centers.

2. Experimental

2.1. Materials and physical measurements

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 starting materials [Ru(*p*-cymene)(μ -Cl)Cl]₂ [11] and oxygen–nitrogen mixed ligands **1a** [12], **1b** [13] and **1c** [14] were synthesized according to procedures described in the previous literature. ¹H and ¹³C 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 ¹H and ¹³C solvent resonances. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. Elemental analyses were performed on a PerkinElmer 2400 CHN analyzer.

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2.2. Synthesis of half-sandwich ruthenium complexes **2a–2c**

A solution of [Ru(*p*-cymene)(μ -Cl)Cl]₂ (153.0 mg, 0.25 mmol), oxygen–nitrogen mixed ligand (0.60 mmol), and K₂CO₃ (96.5 mg, 0.60 mmol) in CH₃CN (15 mL) was purged with N₂ and then stirred at 353 K for 3 h. The crude reaction mixture was loaded onto a column of silica gel and purified by column chromatography to give the reddish brown half-sandwich ruthenium complex.

2a, Yield: (160.0 mg, 74%). ¹H NMR (300 MHz, CDCl₃) δ 7.42 (d, *J* = 7.5 Hz, 1H), 7.15 (t, 1H), 6.96 (d, *J* = 6.3 Hz, 1H), 6.40 (t, 1H), 5.50 (d, *J* = 4.5 Hz, 1H), 5.46 (d, *J* = 4.5 Hz, 2H), 5.37 (d, *J* = 4.5 Hz, 1H), 4.56 (t, 2H), 4.44 (t, 2H), 2.86 (m, 1H), 2.21 (s, 3H), 1.31 (d, *J* = 5.0 Hz, 3H), 1.26 (d, *J* = 4.9 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.91, 164.43, 134.39, 129.31, 123.55, 114.11, 109.67, 101.99, 97.13, 83.26, 82.48, 81.70, 81.06, 67.43, 59.30, 31.18, 22.67, 22.55, 18.77; *Anal. Calc.* for C₁₉H₂₂NO₂RuCl: C, 52.71; H, 5.12; N, 3.24. Found: C, 52.70; H, 5.16; N, 3.27. IR (KBr, cm⁻¹): 2968 (m) 1629 (vs), 1544 (m), 1473 (s), 1441(s), 1391 (m), 1345 (s), 1244 (s), 1154 (w), 1074 (s), 927 (m), 854 (m), 755 (s), 680 (w), 571 (w).

2b, Yield: (161.4 mg, 72%). ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 6.0 Hz, 1H), 7.14 (d, *J* = 6.0 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 6.42 (d, *J* = 6.0 Hz, 1H), 5.39 (m, 3H), 5.19 (d, *J* = 10.0 Hz, 1H), 4.73 (m, 2H), 3.41 (m, 2H), 2.75 (m, 1H), 2.14 (s, 3H), 1.21 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 169.85, 166.77, 134.33, 132.06, 124.06, 118.56, 114.98, 102.50, 97.44, 83.17, 82.47, 81.80, 81.00, 70.48, 31.19, 30.53, 23.14, 22.18, 18.98. *Anal. Calc.* for C₁₉H₂₂ClNO₂RuS: C, 50.83; H, 4.94; N, 3.12. Found: C, 50.250; H, 5.10; N, 3.22. IR (KBr cm⁻¹): 3003 (m), 1628 (vs), 1542 (m), 1470 (s), 1441 (s), 1360 (m), 1242 (s), 1155 (s), 1050 (w), 853 (m), 751 (s), 686 (m), 571 (w).

2c, Yield: (145.1 mg, 65%). ¹H NMR (300 MHz, CDCl₃) δ 7.43 (d, *J* = 6.0 Hz, 1H), 7.11 (t, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.43 (t, 1H), 5.47 (d, *J* = 6.0 Hz, 1H), 5.26 (s, 2H), 5.13 (d, *J* = 6.0 Hz, 1H), 5.26 (m, 4H), 4.44 (s, 2H), 4.38 (s, 1H), 4.70 (t, 1H), 2.74 (t, 1H), 2.06 (s, 3H), 1.86 (s, 2H), 1.16 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 170.26, 158.90, 133.11, 128.81, 123.71, 119.67, 114.75, 102.93, 96.58, 82.09, 81.99, 81.83, 80.56, 66.30, 52.23, 31.10, 23.53, 23.25, 22.00, 18.87; *Anal. Calc.* for C₂₀H₂₄ClNO₂Ru C₁₉H₂₂NO₂RuCl: C, 53.75; H, 5.41; N, 3.13. Found: C, 53.66; H, 5.20; N, 3.19. IR (KBr cm⁻¹): 2956 (m), 1622 (vs), 1542 (m), 1465 (s), 1441 (s), 1366 (m), 1334 (m), 1242 (s), 1160 (s), 1102 (s), 1022 (w), 858 (m), 751 (s), 686 (m), 571 (w).

2.3. General procedure for the nitrile hydration with half-sandwich ruthenium catalysts

To a stirred solution of half-sandwich ruthenium complex (0.25 mol%) in 2.0 mL of isopropanol were added NaOH (0.3 mmol) and benzonitrile (0.3 mmol) followed by stirring for 4 h at 353 K. After completion of the reaction (monitored by TLC), the resulting solution was evaporated to dryness at reduced pressure. The crude products loaded directly onto a column of silica gel and purified by column chromatography to yield the corresponding amides [15].

2.3.1. 4-Fluorobenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.82(t, 2H), 7.12(t, 2H), 5.98(br, 2H).

2.3.2. 4-Chlorobenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.77(d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 5.94(br, 2H).

2.3.3. 4-Bromobenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.70(d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 5.93(br, 2H).

2.3.4. 4-Iodobenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.83(d, *J* = 6.0 Hz, 2H), 7.54 (d, *J* = 6.0 Hz, 2H), 5.86(br, 2H).

2.3.5. 3-Bromobenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.96(s, 1H), 7.74(d, *J* = 9.0 Hz, 1H), 7.67 (d, *J* = 9.0 Hz, 1H), 7.33(t, 1H), 6.01(br, 2H).

2.3.6. Benzamide

¹H NMR (300 MHz, CDCl₃): δ 7.82(d, *J* = 6.0 Hz, 2H), 7.53(d, *J* = 6.0 Hz, 1H), 7.44 (t, 2H), 6.12(br, 2H).

2.3.7. 2-Methylbenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.45(d, *J* = 7.5 Hz, 1H), 7.32 (t, 1H), 7.21(t, 2H), 5.97(br, 2H), 2.49(s, 3H).

2.3.8. 3-Methylbenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.64(s, 1H), 7.58 (s, 1H), 7.33(s, 2H), 6.10(br, 2H), 2.39(s, 3H).

2.3.9. 4-Methylbenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.72(d, *J* = 9.0 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.09(br, 2H), 2.39(s, 3H).

2.3.10. 2-Aminobenzamide

¹H NMR (300 MHz, CDCl₃): δ 7.37(d, *J* = 7.5 Hz, 1H), 7.23(d, *J* = 7.5 Hz, 1H), 6.67 (m, 2H), 5.70(br, 2H).

2.3.11. 4-(Trifluoromethyl)benzamide

¹H NMR (300 MHz, CDCl₃): δ 7.94(d, *J* = 9.0 Hz, 2H), 7.74(d, *J* = 9.0 Hz, 2H), 6.10(br, 2H).

2.4. X-ray crystallography for **2c**

Diffraction data of **2c** were collected on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Mo K α 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) [16], SADABS absorption corrections were applied to the data [17], all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculation was performed using the Bruker Smart program.

3. Result and discussions

The oxygen–nitrogen mixed ligands (**1a–1c**) were synthesized in moderate to good yields according to literature methods. The reddish brown half-sandwich ruthenium complexes (**2a–2c**) were obtained by reaction of [Ru(*p*-Cymene)(μ -Cl)Cl]₂ with two equivalents of the oxygen–nitrogen mixed ligands in the presence of K₂CO₃ in CH₃CN under reflux for 3 h (Scheme 1). Ruthenium complexes were isolated as pure complexes by chromatography on silica gel using EtOAc/petroleum ether as an eluent in yields of 65–74%. All complexes have been characterized by IR, NMR spectroscopy as well as elemental analyses. The proton signals at 7.42, 7.15, 6.96, 6.40, 5.50, 5.46, 5.37, 4.56, 4.44, 2.86, 2.21, 1.31, and 1.26 ppm in the ¹H NMR spectrum can be easily assigned to each of the corresponding hydrogen of **2a**, respectively. The proton signals at 6.40–7.42 ppm are corresponds to the phenyl ring proton of the phenoxide-oxazoline. Two doublets appear at δ = 5.50 and 5.37 ppm with a coupling constant of *J* = 4.50 Hz, respectively, which indicates the presence of cymene ring [18]. Compared with the ligand **1a** infrared spectrum, the O–H stretching vibration of

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