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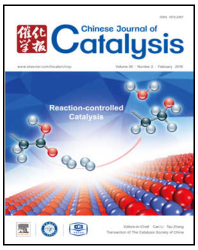

Article

Ruthenium(II) complex catalysts bearing a 2,6-bis(tetrazolyl)pyridine ligand for the transfer hydrogenation of ketones

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ABSTRACT

Three ruthenium(II) complex catalysts bearing 2,6-bis(tetrazolyl)pyridine were synthesized, structurally characterized, and applied in the transfer hydrogenation of ketones. Their different catalytic activities were attributed to the different phosphine ligands on the 4-chloro-2,6-bis(1-(*p*-tolyl)-1*H*-tetrazol-5-yl)pyridine ruthenium(II) complexes, with that based on 1,4-bis(diphenylphosphino)butane exhibiting better catalytic activity. A variety of ketones were reduced to their corresponding alcohols with >95% conversion.

1. Introduction

Nitrogen-containing ligands have been widely used in coordination chemistry and homogeneous catalysis owing to ease of manipulation and the high catalytic activity of their transition metal complexes [1–5]. Many pyridyl-based symmetric ligands, such as 2,2':6',2''-terpyridines [6–10], 2,6-bis(oxazolinyl)pyridines [11–15], 2,6-bis(imino)pyridines [16–20], and 2,6-bis(pyrazoyl) pyridines [21–25] have been reported and applied in organic synthesis and homogeneous catalysis.

2,6-Bis(tetrazolyl)pyridines are pyridyl-based multidentate chelating agents containing nine N atoms, and their metal complexes have been applied in functional materials fabrication, coordination chemistry, and catalysis. These ligands can be used in the synthesis of luminescent materials using a self-assembly strategy. Both visible and near-infrared (IR) luminescence emissions of lanthanide cations (Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb) can be efficiently sensitized using 2,6-bis(tetrazole)pyridine [26,27]. Furthermore, platinum(II) complexes bearing 2,6-bis(tetrazole)pyridine can be used as luminescent films, dopants for OLEDs, and to form supramolecular polymeric nanofibers [28–31]. Ruthenium complexes based on mixed ligands 2,2':6',2''-terpyridine and 2,6-bis(tetrazole)pyridine have been reported and used in dye-sensitized solar cells to afford novel ruthenium dyes [32–34]. These ligands can also be coordinated with other metals, such as a reported series of homoleptic complexes of 2,6-bis(tetrazole)pyridine with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} [35]. Furthermore, 2,6-bis(tetrazolyl)pyridine ligands can recover trivalent minor actinides effectively and selectively from HNO_3 media, while exhibiting weak or almost no extraction of trivalent lanthanides with similar chemical properties [36,37]. However, 2,6-bis(tetrazolyl)pyridine ligands have rarely been applied in catalytic reactions. In 2016, zinc polymers based on

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2,6-bis(tetrazole)pyridine with different morphologies and particle sizes were obtained and used in the cyclization of aromatic dinitriles with *β*-aminoalcohols as heterogeneous catalysts [38].

The transfer hydrogenation (TH) of unsaturated substrates catalyzed by transition metal complexes has attracted much attention owing to its capacity for reliable reduction using simple procedures with mild conditions and is considered a prospective alternative to direct hydrogenation [39–43]. Versatile ruthenium(II) 2-aminomethylpyridine (ampy) complexes have been reported by Baratta et al. [44–49] and demonstrated very high catalytic activity in the TH and asymmetric TH (ATH) of ketones. Moreover, Noyori ruthenium(II) complexes, containing *N*-sulfonylated 1,2-diamines as chiral ligands, have been used as efficient catalysts for the ATH of ketones and imines [50–55]. Furthermore, transition-metal complexes bearing a ligand with NH functionality also exhibit high catalytic activity in transfer hydrogenation reactions [56–59]. Although various ligands and their transition-metal complexes have been synthesized for TH, the development of efficient catalytic systems is still needed. We have been interested in developing *N*-heterocyclic ligands and the corresponding highly effective catalyst system for application in homogeneous catalysis. Various pyridyl-based *N*-containing ligands and their ruthenium(II) complexes have been reported and applied to the TH of ketones [60–65]. Herein, we describe the synthesis and structural characterization of ruthenium(II) complexes of 4-chloro-2,6-bis(1-(*p*-tolyl)-1*H*-tetrazol-5-yl)pyridine with different phosphorus ligands and their catalytic behavior in TH reactions of ketones.

2. Experimental

2.1. General considerations

All manipulation of air- and moisture-sensitive compounds was carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use according to literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX-400 spectrometer (Bruker, Germany) and all chemical shift values are referenced to $\delta_{\rm TMS}$ = 0.00 ppm or $CDCl_3$ (δ(^{1}H), 7.26 ppm and δ(^{13}C), 77.16 ppm). HRMS analysis was performed by the Analysis Center, Dalian University of Technology. All melting points are uncorrected. Thin-layer chromatography (TLC) analysis was performed using glass-backed plates coated with silica gel (0.2 mm). Flash column chromatography was performed on silica gel (200–300 mesh). All chemical reagents were purchased from commercial suppliers and used as received unless otherwise indicated.

2.2. Preparation of ligand and ruthenium complexes

4-Chloro-2,6-bis(1-(*p*-tolyl)-1*H*-tetrazol-5-yl)pyridine (**2**). A mixture of N^2,N^6-di-*p*-tolylpyridine-2,6-dicarboxamide (**1**) (20.0 g, 58 mmol), PCl_5 (24.2 g, 116 mmol), and $SOCl_2$ (120 mL) were heated at 80 °C for 3 h. Excess $SOCl_2$ was removed under reduced pressure and the resulting imidoyl chloride was dissolved in CH_2Cl_2 (100 mL). This solution was then added dropwise to a stirred suspension of NaN_3 (13.6 g, 209 mmol) in DMF (100 mL). After addition was completed, stirring was continued for 16 h at room temperature. The reaction mixture was then treated with water, the organic layer was separated and washed with water (3×200 mL), and all volatiles were removed under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60–90 °C)/CH_2Cl_2 = 2:1, *v/v*) to afford **2** as a white solid (8.7 g, 35%). m.p. 247–248 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 8.28 (s, 2 H, pyridyl CH), 7.11 (d, 4 H, J = 8.2 Hz) and 6.92 (d, 4 H, J = 8.3 Hz) (both *p*-tolyl CH), 2.38 (s, 6 H, *p*-tolyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 150.7, 147.1, 145.8, 140.6, 131.8, 129.8, 127.2, 124.8, 21.4. HRMS Calcd. for $C_{21}H_{16}ClN_9$: 429.1217; Found: 429.1212.

Ruthenium complex **3a**. Under a nitrogen atmosphere, a mixture of 4-chloro-2,6-bis(1-(*p*-tolyl)-1*H*-tetrazol-5-yl)pyridine **2** (215 mg, 0.5 mmol), $RuCl_2(PPh_3)_3$ (480 mg, 0.5 mmol), and CH_2Cl_2 (40 mL) was stirred at 40 °C for 4 h. After cooling to ambient temperature, all volatiles were evaporated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel (eluent: CH_2Cl_2/CH_3OH = 10:1, *v/v*). Recrystallization in hexane–CH_2Cl_2 (3:1, *v/v*) at room temperature gave ruthenium(II) complex **3a** as a reddish brown solid (479 mg, 85%). m.p. >155 °C dec. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.56, 7.40, 7.33, 7.27, 7.13, and 6.72 (each m, 10:9:3:6:6:6 H, aromatic CH), 2.56 (s, 6 H, *p*-tolyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 153.25, 153.22, 146.8, 145.1, 144.2, 134.8, 134.7, 134.2, 133.7, 133.3, 133.2, 131.6, 130.8, 129.9, 129.8, 129.3, 128.7, 128.6, 128.5, 127.8, 127.7, 125.5, 125.3, 21.5. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 25 °C) δ 40.4, 35.0.

Ruthenium complex **3b**. Under a nitrogen atmosphere, a mixture of 1,4-bis(diphenylphosphino)butane (512 mg, 1.2 mmol), $RuCl_2(PPh_3)_3$ (959 mg, 1.0 mmol), and CH_2Cl_2 (50 mL) was stirred at room temperature for 2 h. Then, 4-chloro-2,6-bis(1-(*p*-tolyl)-1*H*-tetrazol-5-yl)pyridine **2** (429 mg, 1.0 mmol) was added and the mixture was stirred at 40 °C for 4 h. After cooling to ambient temperature, all volatiles were evaporated under reduced pressure. The resultant residue was purified by flash chromatography on silica gel (eluent: AcOEt/CH_3OH = 5:1, *v/v*). Recrystallization in hexane–CH_2Cl_2 (3:1, *v/v*) at room temperature gave ruthenium(II) complex **3b** as a reddish brown solid (754 mg, 71%). m.p. >180 °C dec. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.95, 7.62, 7.45, 7.36, 7.28, 7.07 and 6.86 (each m, 4:8:6:2:4:2:4 H, aromatic CH), 2.83, 2.37, 2.11 and 1.79 (each m, 4×CH_2), 2.57 (s, 6 H, *p*-tolyl CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 25 °C) δ 153.2, 145.7, 144.8, 144.4, 136.4, 136.0, 134.0, 133.9, 132.7, 132.2, 131.8, 131.6, 131.5, 131.0, 130.2, 129.3, 129.2, 129.1, 128.1, 128.0, 125.6, 124.3, 33.0, 32.7, 29.3, 29.1, 26.1, 21.7, 20.1. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 25 °C) δ 40.4, 33.9.

Ruthenium complex **3c**. Under a nitrogen atmosphere, a mixture of 1,5-bis(diphenylphosphino)pentane (106 mg, 0.24 mmol), $RuCl_2(PPh_3)_3$ (193 mg, 0.2 mmol), and CH_2Cl_2 (10 mL) was stirred at room temperature for 2 h. Then 4-chloro-2,6-bis(1-(*p*-tolyl)-1*H*-tetrazol-5-yl)pyridine **2** (86 mg, 0.2 mmol) was added and the mixture was stirred at 40 °C for 4 h. After