Exceptionally Efficient Unsymmetrical Ruthenium(II) NNN Complex Catalysts Bearing a Pyridyl-Based Pyrazolyl−Imidazolyl Ligand for Transfer Hydrogenation of Ketones

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Summary: Rare ruthenium(II) complexes bearing a pyridyl-based pyrazolyl−imidazolyl ligand were synthesized and exhibited exceptionally high catalytic activity in the transfer hydrogenation of ketones in 2-propanol at 82 °C or room temperature, reaching 100% conversion of the substrates and final TOFs up to 7.2 × 10^5 h^{-1} with 0.05 mol % catalyst at 82 °C and 55 800 h^{-1} with 0.1 mol % catalyst at room temperature.

Transfer hydrogenation (TH) in 2-propanol has emerged as an efficient alternative to hydrogenation of ketones for the production of alcohols.[1] Ruthenium(II) complexes have usually been applied as the most useful catalysts for this purpose, and those bearing ligands featuring an ancillary N−H functionality generally offer high catalytic activity and selectivity.[1−5] Among the well-documented Ru(II) catalysts are Ru(II) *N*-tosylethylenediamine complexes developed by Noyori et al.,[2] their recent versions,[3] and Ru(II) β-amino alcohol complexes.[4] However, it is often structurally prerequisite for an active Ru(II) complex catalyst that its ancillary ligand features a N−H functionality: i.e., forming XRu−NHR in the complex. Baratta et al. reported Ru(II) 2-(aminomethyl)pyridine complex catalysts for the TH of ketones which have demonstrated a remarkable acceleration effect by the NH-containing moiety of the ligand.[5] Although a few active Ru(II) complex catalysts which do not feature an ancillary N−H functionality have also been documented for the TH of ketones,[6] the need to develop new efficient catalysts is still strongly desired in this area. Recently, non-phosphorus planar tridentate NNN ligands such as 2,2′:6′,2″-terpyridines (terpy),[7] 2,6-bis(imino)pyridines,[8] and 2,6-bis(oxazolinyl)pyridines (Pybox)[9] have been successfully developed and explored, but little attention has been paid to unsymmetrical planar tridentate ligands, due to complicated synthetic schemes. Very recently, our group[10a,b] and Karam et al.[11] reported a new class of NNN ligands, i.e., symmetrical 2,6-bis(pyrazol-1-yl)pyridines, which have been successfully employed to construct effective transition-metal catalysts. In our case,[10a] a 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine-supported Ru(II) complex can efficiently catalyze the TH reactions of ketones in 2-propanol, achieving a final TOF value of 6000 h^{-1} at 82 °C. During our ongoing investigation on new polydentate N-heterocyclic ligands,[10] we have become interested in the construction of unsymmetrical planar pyridyl-based 2,6-(mixed N-heterocycle) ligands in which the mixed N-heterocycles themselves are usually bestowed with poor capability to coordinate late transition metals and the tridentate ligand often exhibits some hemilability to the metal center of the complex, resulting in a highly active transition-metal complex catalyst. Herein, we report the synthesis of a new class of pyridyl-based pyrazolyl−imidazolyl ligands and

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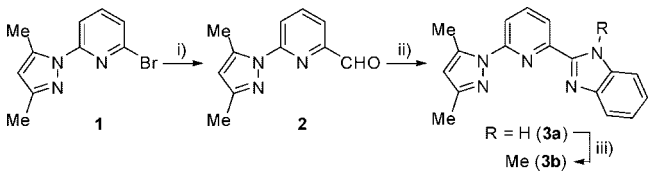
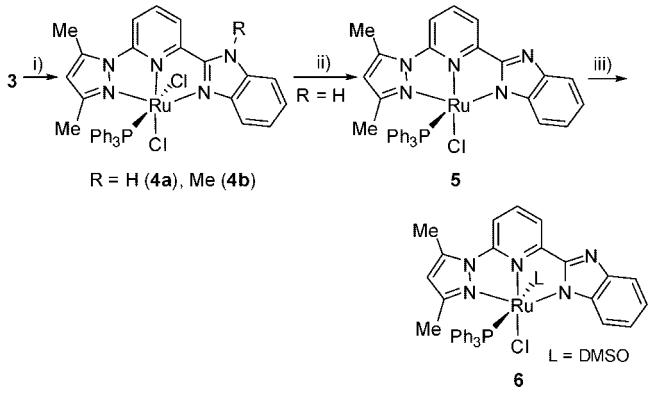
Scheme 1. Synthesis of Ligand 3[a,12]



[a] Legend: (i) *n*-BuLi, −78 °C, DMF, 48%; (ii) 1,2-phenylenediamine, nitrobenzene, 150 °C, 5 h, 71%; (iii) MeI, Cs_2CO_3, DMSO, room temperature, 3.5 h, 99%.

Scheme 2. Synthesis of Ru(II) Complexes 4−6[a,13]



[a] Legend: (i) $RuCl_2(PPh_3)_3$, PhMe, 110 °C, 2 h, 91% (**4a**), 92% (**4b**); (ii) $NaHCO_3$, CH_2Cl_2/MeOH (5/1 v/v), room temperature, 5 h, 96%; (iii) DMSO/DMF (5/1 v/v), 100 °C, 15 min, 60%.

the exceptionally high catalytic activity of their Ru(II) complexes in the TH of ketones.

Aldehyde **2** was prepared from the reaction of 2-bromo-6-(3,5-dimethylpyrazol-1-yl)pyridine[10b] and DMF in the presence of *n*-BuLi. Oxidative condensation of **2** with 1,2-phenylenediamine afforded the pyrazolyl−imidazolyl pyridine **3a**,[12] which was easily converted to its *N*-methyl analogue **3b** (Scheme 1). Reactions of **3** with 1.0 equiv of $RuCl_2(PPh_3)_3$ in refluxing toluene produced Ru(II) complexes **4** in 91−92% yields.[13] **4a** was further transformed to the 16-electron complex **5** by treatment with $NaHCO_3$ (Scheme 2). Complex **6** was obtained by reacting **5** with DMSO. All the complexes are stable in air at ambient temperature. The ^{1}H NMR signals of the NH in **4a** and pyrazolyl CH in the complexes are shifted downfield by about 3.0 and 0.2−0.3 ppm as compared to those in the free ligands **3**, respectively, suggesting that both the imidazolyl and pyrazolyl groups in the complexes are coordinated to the metal center. The ^{31}P NMR signals of complexes **4a**,**b** in DMSO-d_6 appear at 31.5 and 31.9 ppm, respectively, and those of **5** and **6** are shown at the same position (33.8 ppm). In $CDCl_3$, the ^{31}P

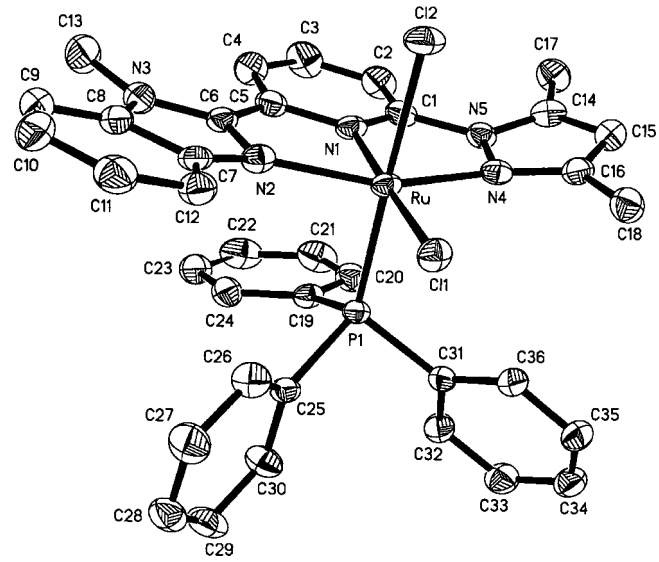


Figure 1. Perspective view of **4b** with the methanol molecule omitted for clarity.

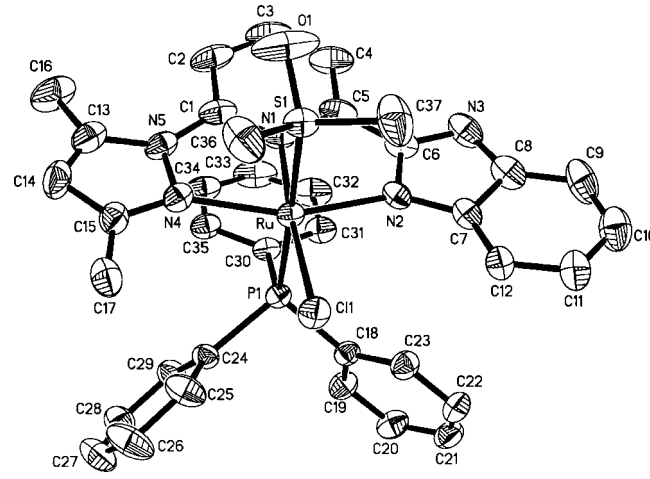


Figure 2. Perspective view of complex **6**.

resonance signals of **5** and **6** appear at 59.3 and 32.7 ppm, respectively, while that of **5** is shifted upfield to 32.7 ppm after DMSO is added to the sample solution, revealing that **5** is easily converted to **6** in the presence of DMSO. The molecular structures of **4b** and **6** were determined by X-ray crystallographic studies (Figures 1 and 2).[14] Coordination of a DMSO molecule to the Ru(II) center through its sulfur atom in complex **6** is indicated by the ^{13}C NMR signal of the coordinated $(CH_3)_2SO$ at ca. 40.4 ppm and further confirmed by the X-ray single-crystal structure of **6** (Figure 2). Thus, compounds **3** act as tridentate planar NNN ligands in complexes **4**−**6** in which one chloride is positioned trans to the pyridyl nitrogen atom and other ligands are arranged at the two sides of the NNN plane.

Transfer hydrogenation of acetophenone in 2-propanol was chosen as the model reaction to test the catalytic activity of

(12) A typical procedure is given for ligand preparation. Synthesis of **3a**: a mixture of aldehyde **2** (4.70 g, 23.36 mmol) and 1,2-phenylenediamine (2.53 g, 23.36 mmol) in nitrobenzene (250 mL) was stirred at 150 °C for 5 h. All the volatiles were removed under reduced pressure, and the resultant residue was subject to purification by flash silica gel column chromatography (CH_2Cl_2/ethyl acetate, 3/1 v/v), affording compound **3a** as a pale yellow solid (4.80 g, 71%) (see the Supporting Information).

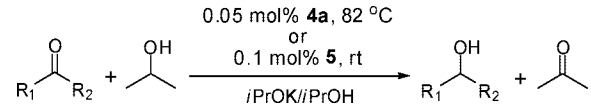
(13) A typical procedure is given for complex preparation. Synthesis of **4a**: under a nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (0.48 g, 0.50 mmol) and benzoimidazole **3a** (0.15 g, 0.50 mmol) in toluene (40 mL) was refluxed for 2 h, giving a red-brown microcrystalline solid. The mixture was cooled to ambient temperature, and the solid was filtered off, washed with diethyl ether (3 × 50 mL), and dried under vacuum to afford complex **4a** (0.33 g, 91%) as a red-brown crystalline solid (see the Supporting Information).

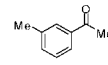
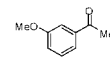
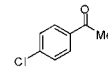
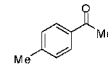
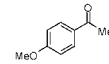
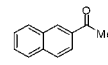
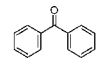
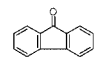
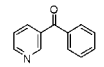
(14) Crystal data for **4b**·CH_3OH: $C_{37}H_{36}Cl_2N_5POPRu$, monoclinic, *Cc*, $a = 14.5821(12)$ Å, $b = 15.1108(12)$ Å, $c = 15.6511(13)$ Å, $\alpha = \gamma = 90°$, $\beta = 104.7770(10)°$, $V = 3334.6(5)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_{calcd} = 1.533$ g cm^{-3}, $R(F) = 5.06\%$ for 4726 observed reflections ($2.96 \le 2\theta \le 54.00°$). Crystal data for **6**: $C_{37}H_{35}ClN_5OPRuS$, monoclinic, $P2_1/n$, $a = 16.3548(12)$ Å, $b = 11.1683(8)$ Å, $c = 19.8291(14)$ Å, $\alpha = \gamma = 90°$, $\beta = 107.6350(10)°$, $V = 3451.7(4)$ Å^3, $Z = 4$, $T = 293(2)$ K, $D_{calcd} = 1.473$ g cm^{-3}, $R(F) = 4.60\%$ for 7506 observed reflections ($2.86 \le 2\theta \le 54.00°$).

complexes **4**−**6**.[15] With an optimized loading of the catalyst, i.e., 0.05 mol %, and using *i*PrOK as the base, complexes **4a** and **5** exhibited the same catalytic activities in the reaction (2 mmol of ketone, 0.1 M) at 82 °C, reaching a final TOF value of 705 600 h^{-1} for the catalyst and 98% conversion for the substrate within 10 s, while the same reaction only reached 94% and 98% conversion for the substrate by means of 0.2 mol % of **4b** and 0.05 mol % of **6** as the catalyst over a period of 5 h and 1 min, respectively. Presumably due to the instant transformation of **4a** to **5** under the basic conditions, they exhibited the same catalytic activity. It should be noted that 1-phenylethanol was the only product and the substrate could not be reduced to the alcohol product within the first 5−10 min in the absence of a base. Under the same conditions, the TH of various ketones was carried out by using **4a** and **5** as the catalysts. Because **4a** and **5** exhibited the same catalytic activity, only the data using **4a** are given in Table 1. For most of the substrates, the reactions were very fast, achieving >97% conversion within 10 s. In particular, 2-methylacetophenone and cyclohexanone were quantitatively reduced to their corresponding alcohols within 10 s and the catalyst reached the highest final TOF value of 7.2×10^5 h^{-1} (entries 4 and 17). To date, the highest TOF value in the TH of ketones, i.e., 2.5×10^6 h^{-1} (at 50% conversion of the ketone, 82 °C), has been reported in the TH of 3-chloroacetophenone by using 0.005 mol % of Baratta's Ru(II) CNN catalyst featuring a N−H functionality.[5b] Stradiotto's cationic Ru(II) catalyst featuring no N−H functionality has also shown high catalytic activity in the TH of ketones by means of 0.05 mol % catalyst (TOFs up to 2.2×10^5 h^{-1}).[6a] In our cases using **4a** or **5** as the catalyst, 98−100% conversion was obtained within 10 s for most of the ketones and the catalysts achieved final TOFs of ca. 7.0×10^5 h^{-1}.

Intrigued by the high catalytic activity of **4a** and **5** in refluxing 2-propanol, we carried out the room-temperature TH of ketones with these as the catalysts. Surprisingly, **4a** and **5** also exhibited extremely high catalytic activity, achieving TOFs up to 55 800 h^{-1} by using 0.1 mol % of the catalyst (Table 1, entry 10). Because **4a** and **5** also demonstrated the same catalytic activity in room-temperature TH, only the data using **5** are given in Table 1. For most of the ketones, their TH reactions at room temperature were finished within 15 min and the catalyst usually exhibited final TOFs higher than 10 000 h^{-1} with >96% conversion of the substrates. To date, the known transition-metal catalysts for TH and/or hydrogenation of ketones near room temperature have only shown the highest TOFs in the range 100−4000 h^{-1}.[16] In our cases, if low loading of a catalyst such as 0.05 mol % of **5** was used, the room-temperature TH of ketones proceeded slowly. For example, the TH reactions of acetophenone, propiophenone, and 2′-chloroacetophenone catalyzed by 0.05 mol % of **5** only achieved ca. 90% conversion within 1 h. With 0.01 mol % of **5** as the catalyst, the same reactions only reached <5% conversion for the substrates within 30 min, suggesting that a ketone substrate in a dilute sample cannot be obviously reduced to alcohol during the sampling process. It should be noted that in order to reduce the analysis error resulted from sampling and sample making, at the stated time 0.05−0.1 mL of the reaction mixture was immediately withdrawn and diluted with 0.5 mL of room-temperature 2-propanol, followed by immediate GC analysis. As discussed above, the transfer hydrogenation of a ketone substrate proceeded very slowly at room temperature with a low catalyst loading, i.e., 0.01 mol %. Thus, after the sample of a TH reaction

Table 1. TH of Ketones Catalyzed (i) by 4a at 82 °C and (ii) by 5 at Room Temperature



entry	ketone	time (min)[a]	conversion (%)[a, b]	final TOF (h^{-1})[a]
1		1/6 (30)	98 (96)	705600 (1920)
2		1/6 (5)	99 (97)	712800 (11640)
3		1/6 (2)	98 (99)	705600 (29700)
4		1/6 (5)	100 (99)	720000 (11880)
5		1/6 (20)	99 (97)	712800 (2910)
6		1/6 (2)	99 (98)	712800 (29400)
7		1/6 (15)	97 (96)	698400 (3840)
8		1/6 (15)	99 (99)[c]	712800 (3960)
9		1/6 (2)	99 (98)	712800 (29400)
10		1/6 (1)	96 (93)	691200 (55800)
11		1/6 (2)	90 (80)	648000 (24000)
12		1/6 (2)	95 (92)	684000 (27600)
13		1/6 (15)	98 (97)[c]	705600 (3880)
14		1/6 (15)	94 (98)[c]	676800 (3920)
15		15 (300)	99 (10)	7920 (20)
16		1/6 (2)	98 (97)	705600 (29100)
17		1/6 (2)	100 (99)	720000 (29700)
18		1/6 (5)	98 (98)	705600 (11760)

[a] Results from room-temperature TH given in parentheses. [b] By GC analysis. [c] By ^{1}H NMR. [d] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); 0.1 MPa. Legend: (i) catalyst, 0.05 mol % of **4a**; ketone/*i*PrOK/**4a** = 2000/20/1; 82 °C; (ii) catalyst, 0.1 mol % of **5**; ketone/*i*PrOK/**5** = 1000/20/1; room temperature (ca. 26 °C).

(15) A typical catalytic procedure is given. Transfer hydrogenation of acetophenone: the catalyst solution **A** was prepared by dissolving complex **4a** (7.2 mg, 10.0 μmol) in 2-propanol (198.0 mL). Under a nitrogen atmosphere, a mixture of acetophenone (0.240 g, 2.0 mmol) and 19.8 mL of the catalyst solution **A** containing 1.0 μmol of complex **4a** was stirred at 82 °C for 5 min. A 0.2 mL portion of 0.1 M *i*PrOK (0.02 mmol) solution in 2-propanol was then introduced to initiate the TH of the ketone. At the stated time, 0.05−0.1 mL of the reaction mixture was immediately sampled and diluted with 0.5 mL of 2-propanol at ambient temperature for GC analysis (see the Supporting Information).

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mixture was diluted with a large amount of 2-propanol at room temperature, the analysis error of a sample can be minimized.

The present TH reactions may follow an inner-sphere mechanism.[17] Thus, the TH of a ketone is initiated directly from **5** or in situ generated **5** by extrusion of 1 equiv of hydrogen chloride from **4a** with *i*PrOK. **5** interacts with the base to form a Ru(II) alkoxide which undergoes β-H elimination to form a RuH species that is presumably considered as the catalytically active species, although it was not successfully isolated by reacting **4a** or **5** with EtONa or *i*PrOK in refluxing ethanol or 2-propanol. The formation of RuH complexes from Ru−Cl precursors has been documented,[18] and such in situ formed RuH species have been well-known to act as the active catalysts for the TH of ketones.[1,6c,17,19]

In summary, unsymmetrical Ru(II) NNN complexes bearing a hemilabile pyridyl-based pyrazolyl−imidazolyl ligand were successfully synthesized and have exhibited exceptionally high catalytic activity in the TH of ketones at 82 °C or room temperature, demonstrating a rare example of highly active Ru(II) NNN complex catalysts that do not feature an ancillary N−H functionality.[20] The hemilability feature of the novel planar tridentate ligand, the formation of a $Ru-N_{imidazolyl}$ bond, and the coordinatively unsaturated (16e) environment around the Ru(II) center in the complex catalyst precursor are attributed to the exceptionally high catalytic activity of these complexes.

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Supporting Information Available: Text, figures, and tables giving experimental procedures, analytical data, and NMR spectra of the compounds prepared in this paper and X-ray crystallographic data for **4b** and **6**; X-ray data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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