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Highly Active Ruthenium(II) Complex Catalysts Bearing an Unsymmetrical NNN Ligand in the (Asymmetric) Transfer Hydrogenation of Ketones

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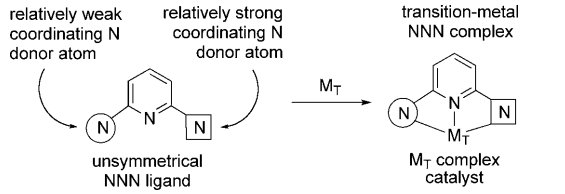
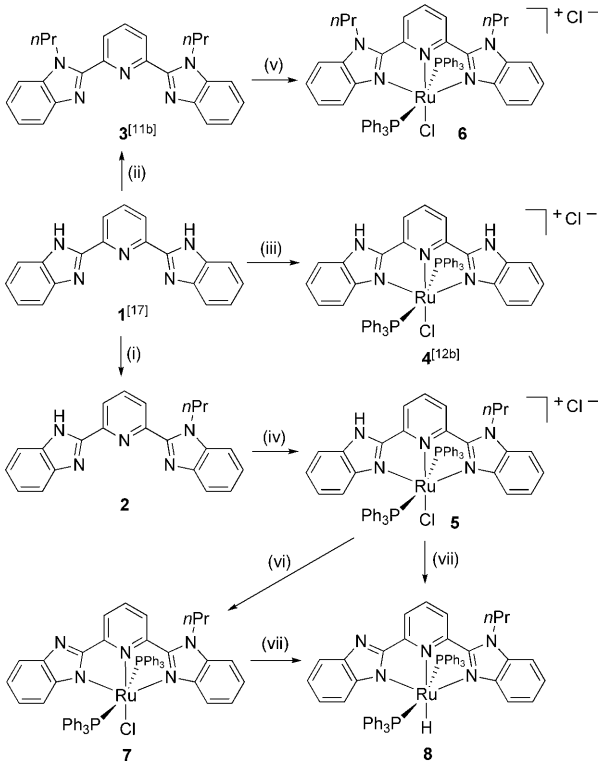
N-Heterocylic ligands have recently become more and more attractive in homogeneous catalysis and organic synthesis because their organometallic complexes usually exhibit higher reactivity and better stability than those with phosphine ligands.[1] Tridentate NNN ligands such as Pybox,[2] 2,6-bis(imino)pyridines,[3] terpyridines,[4] and other symmetrical NNN ligands[5] have demonstrated their potential applications. However, examples of unsymmetrical tridentate NNN ligands and their transition-metal complexes are scarce.[6,7] Transition-metal complexes bearing an unsymmetrical polydentate ligand are usually bestowed with good catalytic activity.[7–10] Thus, unsymmetrical pyridyl-based NNN ligands are strongly desired for the construction of highly active transition-metal complex catalysts. Functional metal complexes[11] were obtained with symmetrical bis(benzimidazol-2-yl)pyridines and bis(*N*-alkylbenzimidazol-2-yl)pyridines, and the electronic properties of the respective ruthenium complexes have been described.[12] However, only a few of them have been applied as catalysts.[13] We recently synthesized very efficient Ru^{II} pyridyl–pyrazolyl-based NNN complex catalysts for transfer hydrogenation of ketones.[7] Ru^{II}-catalyzed transfer hydrogenation reactions with 2-propanol as the hydrogen source have been extensively studied by Noyori et al.[14,15] Baratta's group recently reported highly active Ru^{II} 2-(aminomethyl)pyridinylphosphane complex catalysts for the transfer hydrogenation of ketones.[10] A few Ru^{II} complex catalysts featuring no N–H functionality have also been documented for the same purpose.[16] Herein, we report the construction of unsymmetrical (chiral) pyridyl–benzimidazolyl-based NNN ligands and their Ru^{II} complex catalysts for the (asymmetric) transfer hydrogenation of ketones by following the strategy shown in Scheme 1.

The mono-*N*-alkyl derivative of bis(benzimidazol-2-yl)pyridine (**1**),[17] that is, **2**, and bis(*N*-propylbenzimidazol-2-yl)pyridine (**3**)[11b] were obtained by reacting **1** with 1-bromopropane in the presence of NaH (Scheme 2). Reactions of ligands **1**–**3** with one equivalent of $[Ru(PPh)_3Cl_2]$ in refluxing methanol afforded Ru^{II} complexes **4**–**6** in 76–91% yields. Treatment of **5** with K_2CO_3 base in CH_2Cl_2 formed



Scheme 1. The strategy for constructing highly active transition-metal complex catalysts bearing a unsymmetrical NNN ligand.



Scheme 2. Synthesis of NNN ligands and their Ru^{II} complexes **4**–**8**. i) NaH, 1.0 equiv *n*PrBr, DMF, 80 °C, 3 h, 38%; ii) NaH, 2.0 equiv *n*PrBr, DMF, 80 °C, 3 h, 47%; iii) $[Ru(PPh_3)_3Cl_2]$, MeOH, 65 °C, 2.5 h, 87%; iv) $[Ru(PPh_3)_3Cl_2]$, MeOH, 65 °C, 3 h, 76%; v) $[Ru(PPh_3)_3Cl_2]$, MeOH, 65 °C, 3 h, 91%; vi) K_2CO_3, CH_2Cl_2, reflux, 48 h, 92%; vii) *i*PrOK/*i*PrOH, toluene, 60 °C, 24 h, 50%.

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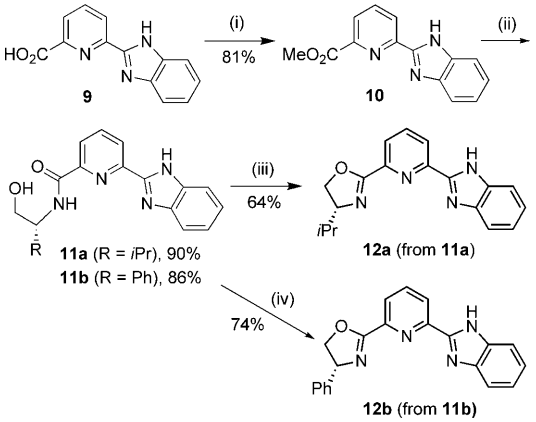
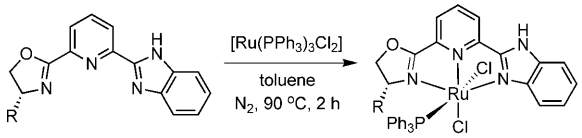
neutral Ru^{II} complex **7**. Heating a mixture of **5** or **7** with *i*PrOK/*i*PrOH in toluene generated Ru^{II} hydride **8** (50%). Starting from compound **9**, chiral pyridyl-based benzimidazolyl–oxazolyl NNN ligands **12** were prepared in 64–74% yields (Scheme 3). Treatment of **12** with one equivalent of



Scheme 3. Synthesis of chiral NNN ligands **12**. i) MeOH, H_2SO_4, reflux, 12 h. ii) 1,2-amino alcohol, 70°C, 2 h for **11a**; 90°C, 4 h for **11b**. iii) a) $SOCl_2$, $ClCH_2CH_2Cl$, 70°C, 4 h; b) NaOH, EtOH, reflux, 12 h. iv) $BF_3{\cdot}Et_2O$, 120°C, 6 h.

$[Ru(PPh_3)_3Cl_2]$ in toluene at 90°C produced the chiral Ru^{II} complexes **13** in 86–89% yields [Eq. (1)], respectively.The molecular structures of complexes **5** and **8** were confirmed by X-ray crystallographic studies (Figure 1 and 2).

Complexes **4**–**7** were treated with a solution containing EtONa/EtOH, *i*PrOK/*i*PrOH, or *i*PrOK/*i*PrOH in toluene under heating. Only in the cases of **5** and **7**, was the Ru^{II} hydride **8** successfully isolated and structurally characterized.



(1)

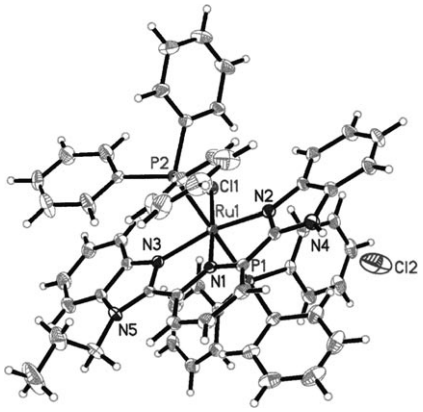


Figure 1. The molecular structure of complex **5**. The chloride anion was omitted for clarity.

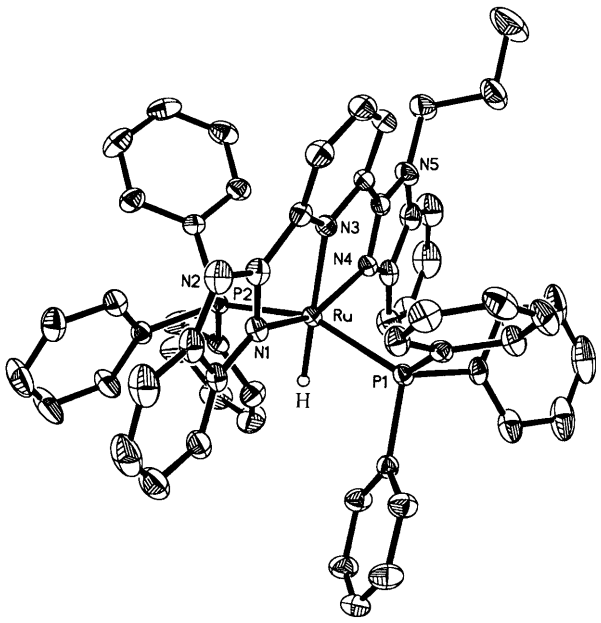
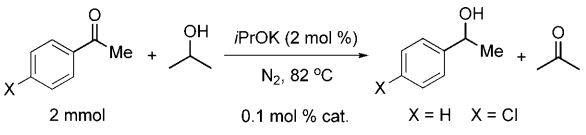


Figure 2. The molecular structure of complex **8**.

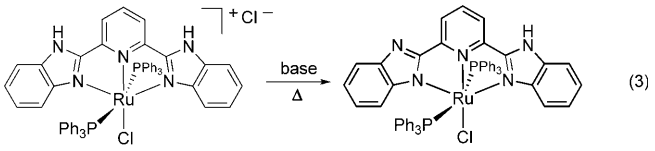
Its ^1H and $^{31}P\{^1H\}$ NMR spectra in $CDCl_3$ revealed a triplet at $\delta = -5.79$ ppm for Ru–H and a doublet at $\delta = 49.6$ ppm for its *trans*-PPh_3 ligands. The Ru–H bond length is 1.53 Å, indicative of an isolated Ru–H bond (Figure 2).[20] The Ru–P bond lengths are 2.3419 and 2.3190 Å, and Ru–N1, Ru–N3, and Ru–N4 bond lengths are 2.079, 2.046, and 2.085 Å, respectively, demonstrating a Ru^{II} core surrounded by two nonequivalent PPh_3 ligands and three nonequivalent nitrogen donor atoms in a distorted bipyrimidal environment.

Then, complexes **4**–**7** were tested as the catalysts for the transfer hydrogenation of acetophenone and 4′-chloroacetophenone in the presence of *i*PrOK in refluxing 2-propanol under a nitrogen atmosphere [Eq. (2)]. With 0.1 mol% loading, their catalytic activities were exhibited as **5**=**7** ≥ **4** > **6**. Complex **4** showed a catalytic activity comparable to those of **5** and **7** in the transfer hydrogenation reactions of relatively active ketones (see the Supporting Information), presumably due to the interconversion of the symmetrical ligand **1** in complex **4** to unsymmetrical ligand **1'** in the neutral complex **4'** through a γ-H effect [Eq. (3)]. Under the reaction conditions given, complex **5** can be instantly converted to **7**; TLC monitoring indicated that both **5** and **7** exhibited the same catalytic activity. Introduction of an *n*-propyl group to one of the 2,6-benzimidazolyl moieties broke the symmetry of the ligands in **5** and **7**, enhancing the electron-donating ability of the ligand.



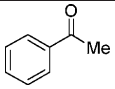
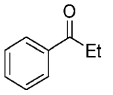
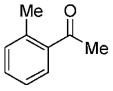
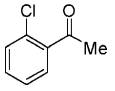
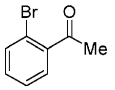
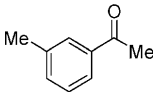
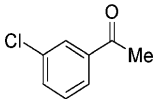
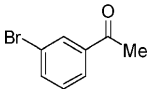
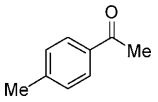
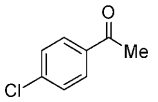
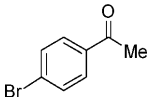
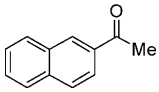
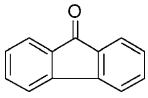
(2)

0.1 mol % cat.		X = H	X = Cl
4	20-30 s	95%	98%
5	**20 s**	**98%**	**98%**
6	120 min	55%	50%
7	**20 s**	**98%**	**98%**



4 4' (3)

Table 1. Transfer hydrogenation of ketones catalyzed by complex **5**.[a]

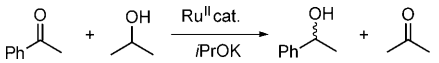
Entry	Ketone	Time	Yield[b] [%]	final TOF [h^{-1}]
1		20 s	98	176400
2		20 s	80	144000
		10 min	98	5880
3		20 s	99	178200
4		30 min	95	1900
		60 min	97	970
5		20 s	>99	178200
6		20 s	87	156600
		5 min	95	11400
7		20 s	99	178200
8		20 s	100	180000
9		20 s	96	172800
10		20 s	98	176400
11		20 s	97	174600
12		1 min	96	57600
13		1 min	97[c]	58200
14		20 s	98	176400
15		20 s	>99	178200

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst **5**, 0.1 mol%, ketone/*i*PrOK/**5** = 1000:20:1; 0.1 MPa, 82 °C. [b] By GC analysis. [c] By ^{1}H NMR analysis.

In a similar fashion, transfer hydrogenation reactions of a variety of ketones were explored by using 0.1 mol% **5** as the catalyst (Table 1). Alcohols were produced as the only products, and the reactions reached up to 100% conversion for the ketone substrates and final TOFs up to 180000 h^{-1} (Table 1, entry 8). In most cases, the reactions ended within 20 s, forming the corresponding alcohol products in $\geq$96% yields. As compared with Ru^{II} complexes bearing symmetrical unconvertible ligands such as 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine[8c] and **3**, the remarkable enhancement of the catalytic activities of complexes **5** and **7** for the transfer hydrogenation of ketones is presumably attributed to the establishment of an unsymmetrical environment around the Ru^{II} metal center by means of two different coordinating donor arms at 2,6-positions of the pyridyl backbone.

Next, the asymmetric transfer hydrogenation of acetophenone was investigated (Table 2). At ambient temperature (ca. 28 °C), acetophenone was converted to form the alcohol in 96% yield and 56% *ee* by using 0.1 mol% **13a** as the catalyst (Table 2, entry 1), whereas **13b** gave a much better enantioselectivity (79% *ee*) of the target product (Table 2, entry 2). These results suggest that the steric effect of the substituent on the chiral oxazolyl moiety clearly affected the enantioselectivity of the product. Complex **13b** was thus employed as the catalyst to screen the asymmetric transfer hydrogenation conditions. Using 0.05–0.1 mol% catalyst at 40–60 °C, the asymmetric transfer hydrogenation reaction also took place efficiently without loss of the enantioselectivity of the product (Table 2, entries 4–6), whereas the reaction proceeded rapidly in refluxing 2-propanol to produce the product with a lower enantioselectivity (72% *ee*; Table 2, entry 7).

Table 2. Asymmetric transfer hydrogenation of acetophenone catalyzed by complexes **13**.[a]

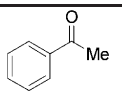
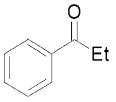
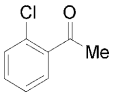
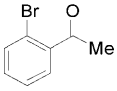
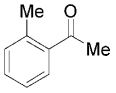
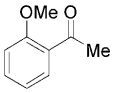
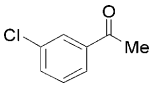
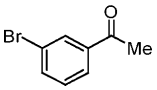
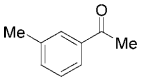
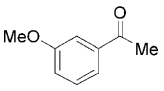
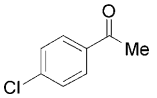
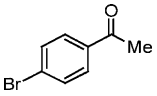


Entry	Cat.	Temp. [°C]	Time [min]	Yield[b] [%]	*ee*[b] [%]	Final TOF [h^{-1}]
1	**13a**	rt	3	96	56 (*S*)	19200
2	**13b**	rt	4	96	79 (*R*)	14400
3	**13b**	rt	6[c]	95	79 (*R*)	9500
4	**13b**	40	1	96	79 (*R*)	57600
5	**13b**[d]	40	10	96	79 (*R*)	11520
6	**13b**[d]	60	1	95	79 (*R*)	114000
7	**13b**[e]	82	1	96	72 (*R*)	288000

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst **13**, 0.1 mol%, ketone/*i*PrOK/**13** = 1000:10:1; 0.1 MPa, about 28 °C. [b] Determined by GC analysis (column: HP-Chiral B233). The absolute configuration of the alcohol product was obtained by comparing its optical rotation with the literature data. [c] *i*PrOK/cat. = 5:1. [d] 0.05 mol% cat. [e] 0.02 mol% cat.

Under the optimized conditions, asymmetric transfer hydrogenation reactions of various aromatic ketones were explored with 0.1 mol% **13b** as the catalyst at ambient tem-

Table 3. Asymmetric transfer hydrogenation of ketones catalyzed by complex **13b**.[a]

Entry	Ketone	Time [min]	Yield[b] [%]	*ee*[b] [%]	Final TOF [h^{-1}]
1		4	96	79	14400
2		45[c]	95	90	633
3		45	>99	97	1320
4		30	>99	97	1980
5		30	94	89	1960
6		20[c]	98	94	1470
7		4	99	95	14850
8		5	99	96	11880
9		10	93	92	5580
10		5[c]	95	92	5700
11		5	98	86	11760
12		5	98	89	11760

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.1 mol% **13b**, ketone/*i*PrOK/**13b** = 1000:10:1; 0.1 MPa, about 28 °C. [b] Determined by GC analysis (column: HP-Chiral B233). All the major alcohol products had an *R* configuration by comparing their optical rotations with the literature data. [c] 0.2 mol% catalyst.

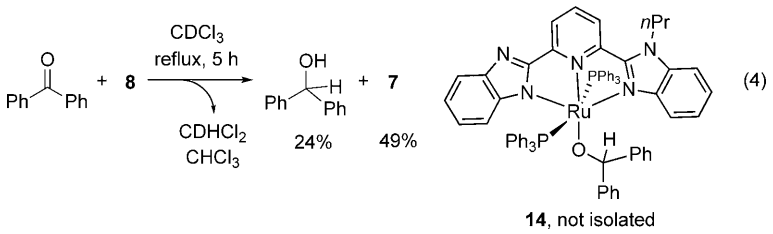
perature (Table 3). The target alcohol products from the reactions of acetophenone, propiophenone, 2′-chloroacetophenone, and 2′-bromoacetophenone were obtained in 90–97% *ee* (Table 3, entries 2–4). Other *ortho*- and *meta*-substituted aromatic ketones reached 93–99% conversion within 4–30 min, forming the products in 89–96% *ee* (Table 3, entries 5–10). For *para*-substituted acetophenones, their asymmetric transfer hydrogenation reactions proceeded rapidly to afford less enantioselective alcohols (86–89% *ee*, Table 3, entries 11 and 12). All the major alcohol products had an *R* configuration, the highest final TOF value was 14850 h^{-1} (Table 3, entry 7). Notably, Ru^{II} complexes bearing a Ph-Pybox[18] or a chiral bis(2-imidazolyl)pyridine ligand[19] exhibited much lower catalytic efficiency than **13b** in the asymmetric transfer hydrogenation of aromatic ketones.

The 1:1 molar ratio reaction of **8** with benzophenone in $CDCl_3$ was monitored by NMR measurements, which revealed a slow reaction at room temperature; after heating for 5 h the Ru–H triplet of **8** disappeared. The ^1H NMR spectrum showed a singlet at $\delta = 5.84$ ppm for Ph_2CHOH (24%), the ^{13}C NMR spectrum showed a signal at $\delta =$ 77.37 ppm for $CHCl_3$, and the ^{31}P NMR spectrum showed a signal at $\delta = 22.39$ ppm for the PPh_3 ligands of complex **7** (49% isolated yield) [Eq. (4)], demonstrating H–D/H–Cl exchanges between **8** and $CDCl_3$. Within 2.5 h the same reaction in refluxing *i*PrOH afforded Ph_2CHOH in 89% isolated yield. Addition of the PPh_3 ligand ([PPh_3]/**5** = 1–5) to the reaction system decreased the conversion of acetophenone to 56–20% under the same conditions (Table 1). Complex **8** exhibited the same catalytic activity as **5** and **7** did in the transfer hydrogenation reaction of acetophenone, suggesting that **8** may be the catalytically active species.[10c,f,21]

In conclusion, we have developed a strategy to construct highly active Ru^{II} NNN complex catalysts for the (asymmetric) transfer hydrogenation of ketones. Novel Ru^{II} complexes bearing a (chiral) unsymmetrical pyridyl–benzimidazolyl-based NNN ligand were synthesized and found to exhibit high catalytic activity in transfer hydrogenation and asymmetric transfer hydrogenation of ketones. These complexes are thus rare examples of exceptionally active Ru^{II} NNN complex catalysts that do not feature an ancillary N–H functionality.

Experimental Section

A general procedure for the catalytic transfer hydrogenation of ketones: Under a N_2 atmosphere, the mixture of a ketone (2 mmol), *i*PrOH (9.8 mL), and a catalyst solution (10 mL) containing the Ru^{II} complex (2 μmmol) in *i*PrOH was stirred at the stated temperature for 5 min.



(4)

Then 0.2 mL of a 0.1 M *i*PrOK solution in *i*PrOH was added to initiate the reaction. Thereafter, 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5–1.0 mL *i*PrOH precooled at 0 °C for GC analysis. After the reaction was complete, the reaction mixture was con-

densed under reduced pressure and purified by silica gel column chromatography to afford the alcohol product, which was identified by comparison with the authentic sample by ^{1}H NMR and GC analysis.

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