Journal of Organometallic Chemistry 694 (2009) 3068–3075

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Ruthenium(II) complex catalysts bearing a pyridyl-supported pyrazolyl-imine ligand for transfer hydrogenation of ketones

Miao Zhao [a,b], Zhengkun Yu [b,*], Shenggang Yan [c], Yang Li [a]

[a] Department of Polymer Materials, College of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning 116012, PR China
[b] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China
[c] Electromechanics and Materials Engineering College, Dalian Maritime University, Dalian, Liaoning 116026, PR China

ARTICLE INFO

Article history:
Received 20 March 2009
Received in revised form 18 May 2009
Accepted 21 May 2009
Available online 27 May 2009

Keywords:
Arylimino
Pyrazolylpyridine
Ruthenium
Transfer hydrogenation
Ketones

ABSTRACT

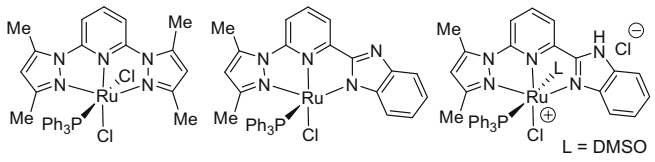
A new class of hemilabile unsymmetrical 2-(1-arylimino)-6-(pyzazol-1-yl)pyridine ligands and their ruthenium(II) and nickel(II) NNN complexes were synthesized. The Ru(II) complex catalysts have been fully characterized and exhibited good to excellent catalytic activity in the transfer hydrogenation (TH) of ketones in refluxing 2-propanol. These results have demonstrated rare examples of active ruthenium(II) NNN complex catalysts that do not feature a N–H functionality for TH of ketones.

1. Introduction

Transfer hydrogenation (TH) with 2-propanol as the hydrogen source is the most promising alternative method to replace hydrogenation for reduction of ketones to alcohols [1]. Ruthenium(II) complexes have proven to be the efficient catalysts for this purpose. Among the most efficient catalyst systems are the Ru(II) complexes bearing a monotosylated 1,2-diamine or aminoalcohol ligand discovered by Noyori and co-workers, which can offer high catalytic activity and selectivity due to a N–H effect [2]. Following their pioneering work, a lot of related ligands and transition metal complexes have been reported in this area [3,4]. Baratta et al. recently reported highly active ruthenium(II) 2-(aminomethyl)pyridine (ampy) phosphane complex catalysts for TH of ketones which have shown an acceleration effect by the N–H functionality in the ampy ligand [5–8]. Several Ru(II) complex catalysts featuring no N–H functionality have also been documented for TH of ketones [9–12]. In order to construct highly active transition metal complex catalysts, development of versatile ligands has been strongly desired. Nitrogen-containing heterocyclic ligands have been paid more and more attention in the fields of coordination chemistry, homogeneous catalysis and organic synthesis because organometallic complexes bearing nitrogen donor ligands usually exhibit high reactivities. Planar tridentate NNN ligands have recently been paid much attention due to their potential applications in homogeneous catalysis, organic synthesis, materials and physical chemistry [13–15]. However, examples of unsymmetrical planar tridentate NNN ligands and their transition metal complexes have only been scattered [16–20]. Recently, we found that phosphine-free unsymmetrical pyridyl-supported 2,6-(mixed *N*-heterocycles) ligands can demonstrate a dynamic "on and off" chelating effect for the metal center during catalysis, and their transition metal complexes usually exhibit enhanced catalytic activity and selectivity [21–26]. In our complex catalysts, although pyrazolyls themselves are poor ligands to late transition metals, they can exhibit both suitable electron-donating ability (coordination ability) to stabilize the metal center and hemilability to enhance the catalytic activity of the complex catalysts bearing a planar pyrazoly-containing NNN ligand. Highly active Ru(II) complex catalysts such as **1**–**3** have been developed from our laboratories (Chart 1). During the course to extend the generality of our protocol to construct highly active Ru(II) NNN complex catalysts, imino was applied to act as a coordinating arm in the unsymmetrical planar pyridyl-supported pyrazolyl-*N*-moiety ligands. Bis(imino)pyridines have been well known to construct complex catalysts for olefin polymerization and organic synthesis [27]. In other cases, an imino functionality is usually used to construct a bidentate ligand [28], although rare examples of planar NNX ligands containing an imino functionality have also been documented [29]. Herein, we report synthesis of ruthenium(II) complexes bearing a unsymmetrical 2-(1-arylimino)-6-(pyzazol-1-yl)pyridine ligand and their catalytic activity in transfer hydrogenation of ketones.

* Corresponding author. Tel./fax: +86 411 8437 9227.
E-mail address: zkyu@dicp.ac.cn (Z. Yu).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.05.028



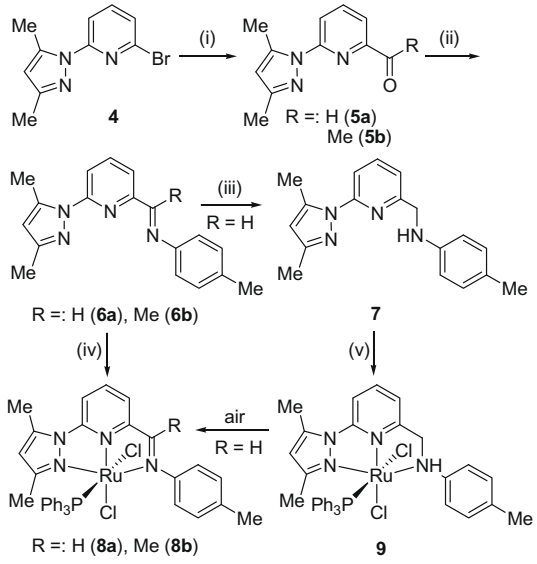
1 [23] **2** [24] **3** [26]

Chart 1.

2. Results and discussion

2.1. Synthesis of ligands 6 and 7, complexes 8 and 9

Aldehyde **5a** and ketone **5b** were synthesized by reaction of 2-bromo-6-(3,5-dimethylpyrazol-1-yl)pyridine [26] with *n*-BuLi in THF followed by treatment with *N*,*N*-dimethylformamide (DMF) or *N*,*N*-dimethylacetamide (DMA). Condensation of **5** with 4-toluidine in the presence of *p*-TsOH and 4A molecular sieves in refluxing toluene afforded 2-(1-tolylimino)-6-(3,5-dimethylpyrazol-1-yl)pyridines **6** in 83–90% yields. Reduction of **6a** with $NaBH_4$ in methanol produced 2-(aminomethyl)-6-(3,5-dimethylpyrazol-1-yl)pyridine **7** (Scheme 1). Reactions of ligands **6** and **7** with $RuCl_2(PPh_3)_3$ in refluxing toluene gave complexes **8** and **9**, respectively. Complex **8b** was only isolated in 20% yield presumably due to the introduction of a methyl group to the imino moiety which affects the coplanarity of the NNN ligand **6b** in the complex. Complexes **8** are purple and **9** is yellow in the solid state and solution. Exposure of a yellow solution of **9** in CH_2Cl_2 to air with stirring at room temperature for 2 h led to a purple solution containing **8a**. During the purification of **9** by flash silica gel column chromatography in air, transformation of yellow **9** to purple **8a** was always accompanied that pure complex **9** could not be obtained. It has been known that cationic and pincer-type Ru(II) amine complexes can be oxidized to Ru(II) imino complexes by oxygen [30,31]. Complex **8a** is bestowed with a poor solubility in organic solvents and its satisfied $^{13}C\{^1H\}$ NMR spectrum was not successfully collected. The $^{31}P\{^1H\}$ NMR signal of **8a** in CD_3OD appeared at 50.3 ppm. For complex **8b,** it showed a much better solubility in $CDCl_3$ than **8a** due to introduction of a methyl group to the imino moiety and its $^{31}P\{^1H\}$ NMR signal was shown at 42.7 ppm. Although pure ligand **7** was obtained, its pure Ru(II) complex **9** could not be successfully isolated because it was easily oxidized to **8a** by air in solution. Thus, complex **9** was always obtained as a mixture containing **8a**.



R =: H (**6a**), Me (**6b**) **4** R =: H (**5a**) Me (**5b**) **7** R =: H (**8a**), Me (**8b**) **9**

Conditions: (i) *n*-BuLi, THF -78 – 0 °C, DMF for **5a** (48%), DMA for **5b** (50%). (ii) 4-toluidine, *p*-TsOH, 4A MS, toluene, reflux, 48 h, 90% for **6a**, 83% for **6b**. (iii) $NaBH_4$, MeOH, r.t. to reflux, 54%. (iv) 1.0 equiv $RuCl_2(PPh_3)_3$, toluene, N_2, 110 °C, 2 h, 80% for **8a**; 24 h, 20% for **8b**. (v) $RuCl_2(PPh_3)_3$, toluene, N_2, 110 °C, 2 h, 72%.

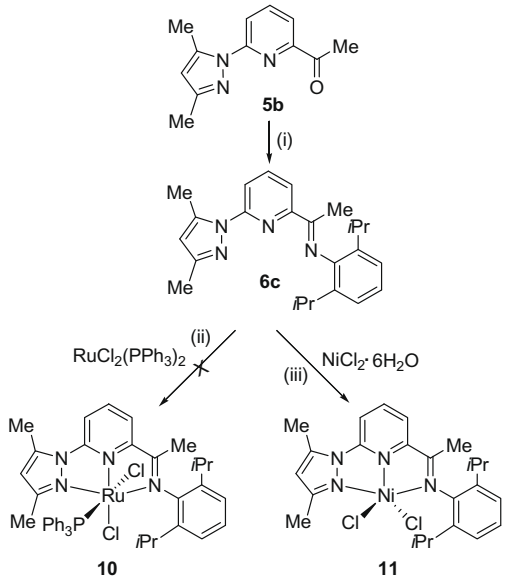
Scheme 1. Synthesis of ligands **6a**, **b** and **7**, complexes **8** and **9**.

2.2. Synthesis of ligand 6c and complex 11

In a fashion similar to the synthesis of ligands **6a** and **6b**, relatively bulky ligand **6c** was prepared in 72% yield by condensation of **5b** with 2,6-diisopropylaniline (Scheme 2). Unexpectedly, under the same conditions employed for synthesis of complexes **8** and **9**, ligand **6c** did not react with $RuCl_2(PPh_3)_3$ to form the desired complex **10**, which is attributed to the steric hindrance from the methyl group on the imino group and the two isopropyls on the aryl moiety. However, treatment of **6c** with $NiCl_2{\cdot}6H_2O$ in THF afforded Ni(II) complex **11** in 90% yield. The NMR spectra of **11** in solution could not be obtained due to its paramagnetic property. The IR stretching vibrations of the C=N bonds in the imino, pyrazolyl and pyridyl moieties and the aromatic C=C bonds in complex **11** varied from 12 to 100 cm^{-1} as compared with those of the free ligand **6c**. The red shift phenomena of the C=N bonds suggest coordination of the three *N*-donor atoms to the metal center. An analogous complex of **11** was also obtained from the 1:1 molar ratio reaction of **6a** and $NiCl_2{\cdot}6H_2O$ in THF, but its X-ray single crystal structure was not successfully determined. The stretching vibration of the C=N bond in this complex appeared at 1578 cm^{-1}, red-shifted by 15 cm^{-1} as compared with that of **11**.

2.3. X-ray crystallographic studies

It was very difficult to obtain single crystals of complex **8a**. Eventually, its single crystals suitable for the X-ray single crystal structure determination was grown by vapor diffusion of diethyl ether into a saturated solution of **8a** in CH_3CN at ambient temperature. The single crystals of complex **11** were collected by vapor



5b **6c** **10** **11**

Conditions: (i) 2,6-diisopropylaniline, *p*-TsOH, 4A MS, toluene, reflux, 48 h, 72%. (ii) $RuCl_2(PPh_3)_3$, 1.0 equiv.; toluene, N_2, 110 °C, 2 h. (iii) $NiCl_2{\cdot}6H_2O$, 1.0 equiv.; THF, r.t., 4 h, 90%.

Scheme 2. Synthesis of ligand **6c** and complex **11**.

Table 1
Crystallographic date and refinement details for **8a** and **11**.

	8a·0.5OEt_2	**11**·H_2O
Empirical formula	$C_{38}H_{38}Cl_2N_4O_{0.50}PRu$	$C_{24}H_{32}Cl_2N_4NiO$
Formula weight	761.66	522.15
T (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
a (Å)	15.5402(11)	9.5307(17)
b (Å)	31.771(2)	13.585(3)
c (Å)	14.6564(10)	10.2132(19)
α (°)	90	90
β (°)	105.545(2)	103.712(3)
γ (°)	90	90
V (Å^3)	6971.6(9)	1284.7(4)
Z	8	2
D_c (g cm^{-3})	1.451	1.350
μ (mm^{-1})	0.684	0.986
F (0 0 0)	3128	548
Crystal size (mm^3)	0.48 × 0.28 × 0.06	0.51 × 0.42 × 0.06
θ Limits (°)	1.81–25.50	2.05–27.00
Number of data collected	36 583	7373
Number of unique data	12 945	4893
R_{int}	0.1433	0.0847
Number of data observed with $I > 2\sigma(I)$	5481	3927
Number of refined parameters	822	303
Goodness-of-fit (GOF) on F^2	0.850	0.968
R (all data/observed data)	0.1575/0.0968	0.0685/0.0572
wR_2 (ll data/observed data)	0.2544/0.2156	0.1433/0.1378
Residual ρ_{max} (e Å^{-3})	1.802 (−1.632)	0.591 (−0.514)

Table 2
Selected bond distances (Å) and angles (°) for **8a** and **11**.

*Complex **8a***					
Ru(1)–N(1)	1.937(7)	Ru(1)–N(2)	2.126(7)	Ru(1)–N(3)	2.063(8)
Ru(1)–P(1)	2.295(3)	Ru(1)–Cl(2)	2.438(3)	N(2)–N(6)	1.335(12)
N(1)–Ru(1)–Cl(2)	179.0(2)	N(2)–Ru(1)–N(3)	155.3(3)		
P(1)–Ru(1)–Cl(1)	176.10(10)	Cl(1)–Ru(1)–Cl(2)	88.86(10)		
N(1)–Ru(1)–Cl(1)	90.2(2)	P(1)–Ru(1)–N(1)	92.7(2)		
*Complex **11***					
Ni–N(1)	1.992(4)	Ni–N(2)	2.174(4)	Ni–N(3)	2.107(5)
Ni–Cl(2)	2.248(2)	C(2)–N(6)	1.280(7)		
N(1)–Ni–N(2)	152.50(13)	N(2)–Ni–N(3)	151.60(17)		
N(1)–Ni–Cl(1)	94.98(13)	Cl(1)–Ni–Cl(2)	112.51(7)		

diffusion of diethyl ether into a saturated solution of **11** in methanol at ambient temperature. A non-coordinate Et_2O molecule was incorporated in the single crystals of **8a** that its highly satisfied crystallographic date could not be collected (Table 1). In the unit cell, two differently oriented molecules of **8a** shared a diethyl ether molecule (Fig. 1). **6a** acts as a planar tridentate NNN ligand in complex **8a**, and the ruthenium atom is situated in a distorted octahedral environment with the PPh_3 ligand and one chloride *trans* to each other on the two sides of the ligand plane, which is crucial to provide the complex with high catalytic activity for TH of ketones in our cases [8b-f]. The unsymmetrical "pincer"-type NNN ligand occupies the three meridional sites with the two *N*-heterocycles and the imino moiety in a *quasi*-planar disposition, and the second chloride is arranged *trans* to the pyridyl nitrogen atom. The distances between the metal center and the pyridyl nitrogen, pyrazolyl nitrogen, and imino nitrogen in **8a** are 1.94, 2.13, and 2.06 Å, respectively, indicating that these *N*-donor atoms are not equally coordinated to the metal (Table 2). The pyridyl nitrogen, Ru(1) and Cl(2) atoms are nearly linearly positioned (N(1)–Ru(1)–Cl(2), 179.0°) and the N(2)–Ru(1)–N(3) angle is 155.3°. The nickel atom in complex **11** is in a distorted pyramidal environment and also coordinated by the three σ-donor nitrogen atoms (Fig. 2). The three Ni–N bonds are longer than those corresponding Ru–N bonds in **8a** (Table 2), suggesting that structure of **11** is more loose than that of **8a**.

2.4. Catalytic transfer hydrogenation (TH) of ketones

TH of acetophenone to 1-phenylethanol by 2-propanol was tested with complexes **8** and **9** as the catalysts (Table 3). In a 0.1 M solution in refluxing 2-propanol, reduction of acetophenone smoothly proceeded to form 1-phenylethanol as the only product by means of 0.2 mol% complex catalyst in the presence of *i*PrOK base. Over a period of 1 h, conversion of acetophenone was reached 96%, 90%, and 93%, respectively, revealing an order of the catalytic activity for TH of acetophenone: **8a** > **9** > **8b**. Next, the reduction of a variety of ketones was carried out by using **8a** or **9** as the catalyst, producing the desired alcohol products in decent yields within 5 min – 5 h, reaching up to 99% conversion for the substrates with final TOF values up to 5940 h^{-1} (Table 4, entries 4–5, and 23–24). Pyridyl ketones showed relatively low reactivity (Table 4, entries

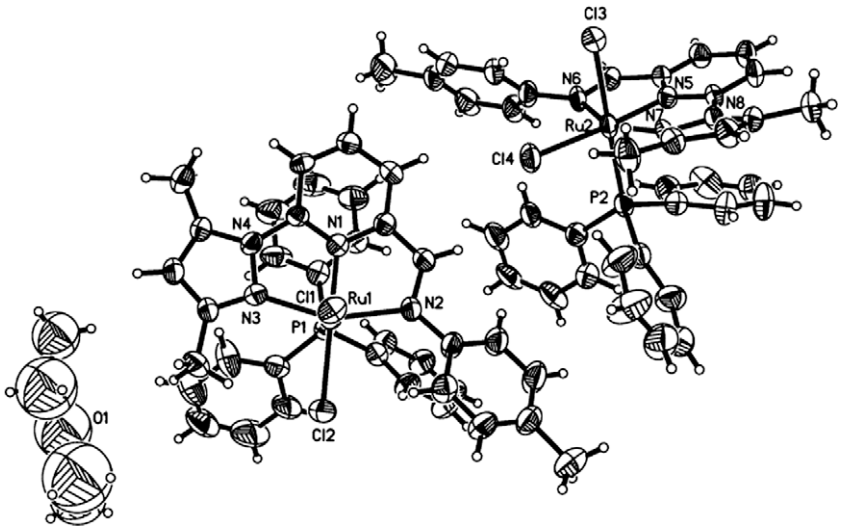


Fig. 1. Molecular structure of **8a** incorporated with an Et_2O molecule.

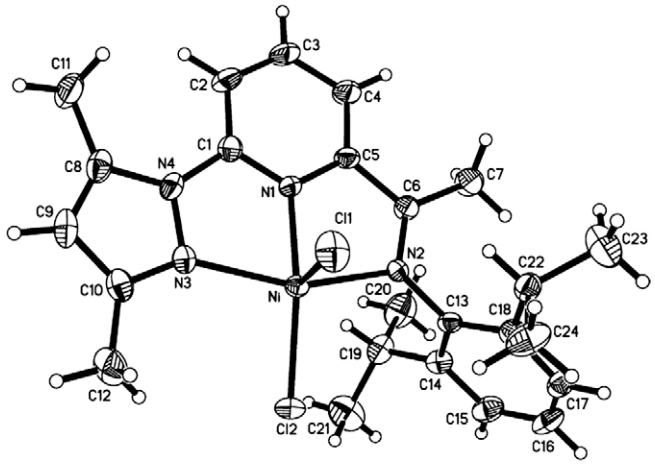
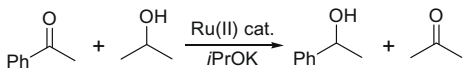
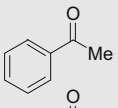
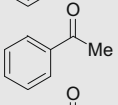
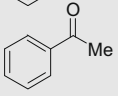


Fig. 2. Molecular structure of **11**.

21–22), presumably due to the competing coordination of the *N*-donor atoms in the substrates to the Ru(II) metal center which thus decreased the catalyst activity. Basically, complex **8a** exhibited an excellent catalytic activity comparable to that of complex **1** for TH of ketones in refluxing 2-propanol [23]. However, **8a** only demonstrated a catalytic activity much lower than complex catalysts **2** and **3** in TH of ketones [24,26] because no 16-electron Ru(II) species could be formed during the catalytic reactions for **8a** and the less efficient coplanarity of the pyrazolyl-imino-pyridine ligands of type **6** than pyrazolyl-imidazolyl-pyridine ligands in **2** and **3**. The catalytic activity of complex **8a** was also explored at room temperature (Table 5). With 0.2 mol% **8a** as the catalyst, TH of acetophenone at 28 °C under nitrogen atmosphere reached 87% conversion for the substrate within 7 h, while the conversion was obviously improved by increasing the catalyst loading to 0.5 mol% (Table 5, entry 1). Thus, TH of chloroacetophenones, cyclohexanone and 2-heptanone was carried out at room temperature for 4–5 h, forming the corresponding alcohol products in 89–95% yields and revealing a moderate catalytic activity for complex **8a** at room temperature (Table 5). As shown in Table 6, complex **9** demonstrated a catalytic activity lower than **8a** in most cases, showing no N–H effect of the ligand during the reaction. It is plausible that ligand **7** may not exist as a planar NNN ligand in complex **9**, resulting in steric/electronic effects which lessen the catalyst activity. However, complexes **8a** and **9** showed no catalytic

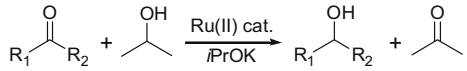
Table 3
Screening of catalysts for TH of acetophenone.



Entry	Ketone	Cat.	Time (h)	Yield[a] (%)
1		**8a**	1	96
2		**8b**	1	90
3		**9**	1	93

Reaction conditions: ketone/cat./*i*PrOK = 500/1/25. Ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.1 MPa, 82 °C.
[a] GC yield of the corresponding alcohol.

Table 4
TH of ketones catalyzed by complex **8a**.



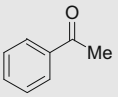
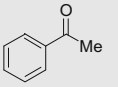
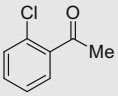
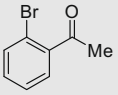
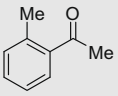
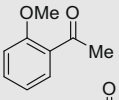
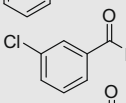
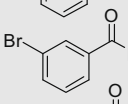
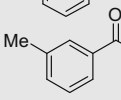
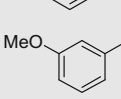
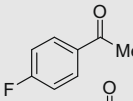
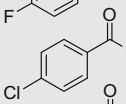
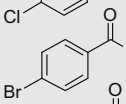
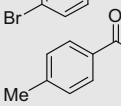
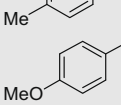
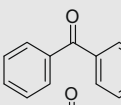
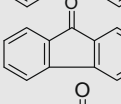
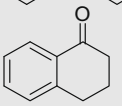
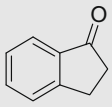
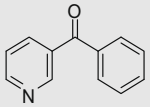
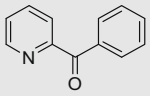
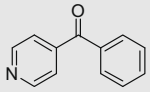
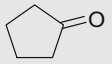
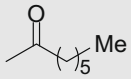
Entry	Ketone	Time (h)	Yield[a] (%)	Final TOF (h^{-1})
1		1	96	480
2		1	96	480
3		1/2	99	990
4		1/12	99	5940
5		1/12	99	5940
6		1/6	97	2910
7		1/2	98	980
8		1/2	98	980
9		1	97	485
10		2	90[b]	225
11		1/2	98	980
12		1	98	490
13		1	97	485
14		1/2	94	940
15		2	98	245
16		3	96[b]	160
17		5	99[b,c]	99
18		5	60[c]	60

Table 4 (*continued*)

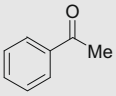
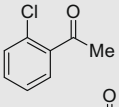
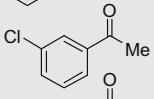
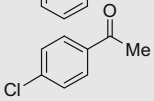
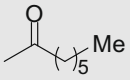
Entry	Ketone	Time (h)	Yield[a] (%)	Final TOF (h^{-1})
19		1	67[c]	335
20		1/2	95	950
21		24	65	14
22		24	70	15
23		1/12	99	5940
24		1/12	99	5940
25		1	99	495

Reaction conditions: ketone/cat./*i*PrOK = 500/1/25. Ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.1 MPa, 82 °C.
[a] GC yield of the corresponding alcohol.
[b] Isolated yields.
[c] cat. = 0.5 mol%.

activity for the TH of ketimines such as butylimine and phenylimine of acetophenone under the conditions shown in Tables 4 and 6.

Although no catalytically active species has been isolated, a possible mechanism is proposed to explain the TH of ketones catalyzed by **8** and **9**. The present TH reactions may follow an inner-sphere mechanism [26,32]. Thus, TH of a ketone is initiated by the reaction of **8** with *i*PrOK base to form a Ru(II)–alkoxide species which then undergoes β-H elimination to form a RuH species and acetone. Such a RuH species is presumably considered as the catalytically active species although it was not successfully isolated by reacting **8** or **9** with EtONa or *i*PrOK in refluxing ethanol or 2-propanol. Formation of RuH complexes from Ru–Cl precursors has been reported [33], and the *in situ* generated RuH species have been known to act as the active catalysts for TH of ketones [34,35]. The ketone substrate is then reduced to alcohol on the RuH species.

Table 5
TH of ketones catalyzed by complex **8a** at room temperature.

Entry	Ketone	Time (h)	Yield[a] (%)
1		5	93 (94)[b]
2		4	92
3		4	93
4		4	91
5		4	95
6		4	89

Reaction conditions: ketone/cat./*i*PrOK = 200/1/25. Ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.1 MPa, 28 °C.
[a] GC yield of the corresponding alcohol.
[b] 7 h.

3. Summary

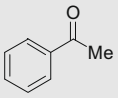
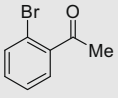
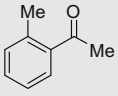
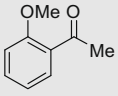
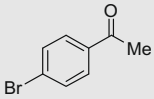
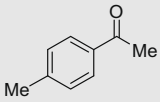
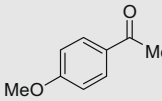
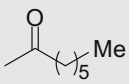
In summary, ruthenium(II) NNN complexes bearing a unsymmetrical pyrazolyl-imino-pyridine ligand have been synthesized and exhibited good to excellent catalytic activity in transfer hydrogenation of ketones in refluxing 2-propanol. These results have demonstrated rare examples of active ruthenium(II) NNN complex catalysts that do not feature a N–H functionality for efficient TH of ketones.

4. Experimental

4.1. General considerations

Unless otherwise noted, all the starting materials were commercially available and used without further purification. The catalytic reactions were carried out under a nitrogen atmosphere. All

Table 6
TH of ketones catalyzed by complex **9**.

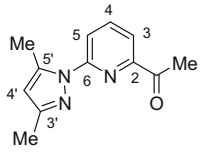
Entry	Ketone	Time (h)	Yield[a] (%)	Final TOF (h^{-1})
1		1	93	465
2		1/12	98	5880
3		1/12	98	5880
4		1/3	99	1485
5		1/3	96	1440
6		2	97	243
7		1	92	460
8		1	95	475

Reaction conditions: ketone/cat./*i*PrOK = 500/1/25. Ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.1 MPa, 82 °C.
[a] GC yield of the corresponding alcohol.

the solvents were dried prior to use according to the standard procedures. Ligand **5a** was synthesized according to the literature procedure [24]. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$NMR spectra were obtained with a 400 MHz NMR spectrometer.

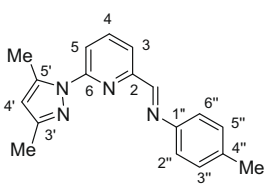
4.2. X-ray crystallographic studies

Single crystal X-ray crystallographic studies for compounds **8a** and **11** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic data and refinement details are listed in Table 1 and the selected bond lengths and angles are given in Table 2.



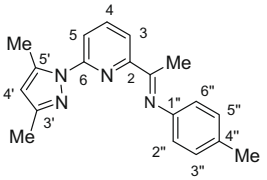
4.3. Synthesis of 6-(3,5-dimethylpyrazol-1-yl)-2-acetylpyridine (**5b**)

To a stirred mixture of 4.0 mL *n*-BuLi (2.5 M in hexanes, 10.0 mmol) and 30 mL THF was added dropwise a solution of 2-bromo-6-(3,5-dimethylpyrazol-1-yl)pyridine (2.51 g, 10.0 mmol) in 20 mL THF at −78 °C over a period of 30 min. After the mixture was further stirred at −78 °C for 30 min, anhydrous DMA (0.87 g, 10.0 mmol) was added. The mixture was allowed to warm up to 0 °C within one hour and the reaction was then quenched with saturated aqueous NH_4Cl (20 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered. All the volatiles were removed under reduced pressure and the resultant residue was subject to purification by flash silica gel column chromatography (petroleum ether (60–90 °C)/ethyl acetate, v/v = 100:1), affording compound **5b** as a white solid (1.07 g, 50%). M.p.: 104–106 °C. ^{1}H NMR ($CDCl_3$, 23 °C) δ 8.12 and 7.91 (d each, $J = 7.6$ and 7.8 Hz, 1:1 H, 3-H and 5-H), 7.87 (t, $J = 7.6$ Hz, 1 H, 4-H), 6.03 (s, 1 H, 4′-H), 2.74, 2.69, and 2.30 (s each, 3:3:3 H, $3 \times CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 23 °C) δ 199.6 (Cq, C=O), 152.9 and 141.7 (Cq each, C2 and C6), 151.3 and 150.5 (Cq each, C3′ and C5′), 139.3 (C4), 119.0 and 118.4 (C3 and C5), 109.9 (C4′), 26.4 (*C*H$_3$CO), 15.4 and 13.8 (C3′–*C*H$_3$ and C5′–*C*H$_3$). HRMS (EI) Anal. Calc. for $C_{12}H_{13}N_3O$: 215.1059. Found: 215.1062.



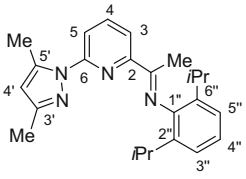
4.4. Synthesis of {6-[(3,5-dimethyl-pyrazol-1-yl)pyridin-2-yl]methylene}-p-tolyl-amine (**6a**)

A mixture of 6-(3,5-dimethylpyrazol-1-yl)pyridine-2-carbaldehyde (**5a**) (0.40 g, 2.0 mmol), *p*-methylaniline (0.22 g, 2.0 mmol), *p*-toluenesulfonic acid (0.02 g, 0.1 mmol), and 4A MS (3.00 g) in 30 mL toluene was refluxed with stirring under N_2 atmosphere for 2 days. After filtered, the volatiles were removed under reduced pressure and the resultant residue was recrystallized from methanol at −20 °C to give **6a** as a yellow solid (0.52 g. 90%). M.p.: 111–112 °C. ^{1}H NMR ($CDCl_3$, 23 °C) δ 8.55 (s, 1 H, CH=N), 8.07 and 7.94 (d each, $J = 7.4$ and 7.9 Hz, 1:1 H, 3-H and 5-H), 7.88 (t, $J = 7.6$ Hz, 1 H, 4-H), 7.23 (s, 4 H, C_6H_4), 6.02 (s, 1 H, 4′-H), 2.71, 2.39, and 2.32 (s each, 3:3:3 H, $3 \times CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 23 °C) δ 159.5 (Cq, C=NAr), 153.5 and 148.4 (Cq each, C2 and C6), 153.0 and 150.2 (Cq each, C3′ and C5′), 141.8 and 136.9 (Cq each, C1″ and C4″, C_6H_4), 138.9 (C4), 130.0 and 121.2 (C3″ and C2″), 118.1 and 117.0 (C3 and C5), 109.4 (C4′), 21.2 (C4″–*C*H$_3$), 14.9 and 13.8 (C3′–*C*H$_3$ and C5′–*C*H$_3$). HRMS (EI) Anal. Calc. for $C_{18}H_{18}N_4$: 290.1531. Found: 290.1525.



4.5. Synthesis of {1-[6-(3,5-dimethyl-pyrazol-1-yl)pyridin-2-yl]ethylidene}-p-tolylamine (**6b**)

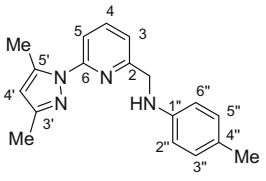
In a fashion similar to the synthesis of **6a**, reaction of **5b** (1.08 g, 5.0 mmol) and *p*-methylaniline (0.52 g, 5.0 mmol) in refluxing toluene (40 mL) afforded **6b** as a yellow solid (1.26 g, 83%). M.p.: 89–91 °C. ^{1}H NMR ($CDCl_3$, 23 °C) δ 8.13 and 7.98 (d each, $J = 7.6$ and 8.0 Hz, 1:1 H, 3-H and 5-H), 7.87 (t, $J = 7.6$ Hz, 1 H, 4-H), 7.19 and 6.75 (d each, $J = 7.8$ Hz, 2:2 H, C_6H_4), 6.03 (s, 1 H, 4′-H), 2.73 (s, 3 H, C4″–CH$_3$), 2.37 (s, 3 H, C3′–CH$_3$), 2.34 (s, 3 H, N=CC*H*$_3$), 2.33 (s, 3 H, C5′–CH$_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 23 °C) δ 166.9 (Cq, C=NAr), 154.9 and 150.1 (Cq each, C2 and C6), 152.6 and 148.6 (Cq each, C3′ and C5′), 141.5 and 133.2 (Cq each, C_6H_4), 138.8 (C4), 129.7 and 119.4 (2:2 CH, C_6H_4), 118.1 and 116.5 (C3 and C5), 109.4 (C4′), 21.0 (C4″–*C*H$_3$), 16.7 (N=CC*H*$_3$), 15.2 and 13.8 (C3′–*C*H$_3$ and C5′–*C*H$_3$). HRMS (EI) Anal. Calc. for $C_{19}H_{20}N_4$: 304.1688. Found: 304.1689.



4.6. Synthesis of (2,6-Diisopropylphenyl)-{1-[6-(3,5-dimethyl-pyrazol-1-yl)pyridin-2-yl]ethylidene} amine (**6c**)

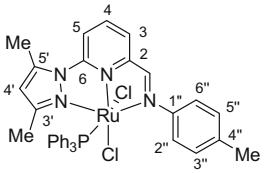
In a fashion similar to the synthesis of **6a**, reaction of **5b** (0.86 g, 4.0 mmol) and 2,6-diisopropylaniline (0.71 g, 4.0 mmol) in refluxing toluene (30 mL) afforded **6c** as a yellow solid (1.08 g, 72%) after purification by flash silica gel column chromatography (petroleum ether (60–90 °C)/ethyl acetate, v/v = 100:1). M.p.: 151–152 °C. ^{1}H NMR ($CDCl_3$, 23 °C) δ 8.26 and 8.05 (d each, $J = 7.6$ and 8.1 Hz, 1:1 H, 3-H and 5-H), 7.91 (t, $J = 8.1$ Hz, 1 H, 4-H), 7.21 (d, $J = 7.3$ Hz, 2 H, 3″-H and 5″-H), 7.14 (t, $J = 6.8$ Hz, 1 H, 4″-H), 6.06 (s, 1 H, 4′-H), 2.79 (m, 2 H, $2 \times CH(CH_3)_2$), 2.78 (s, 3 H, N=CCH$_3$), 2.36 (s, 3 H, C3′–CH$_3$), 2.23 (s, 3 H, C5′–CH$_3$), 1.20 and 1.19 (d each, $J = 6.8$ Hz, 12 H, $4 \times CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 23 °C) δ 166.6 (Cq, C=NAr), 154.3 and 150.0 (Cq each, C2 and C6), 152.8 and 146.3 (Cq each, C3′ and C5′), 141.4 (Cq, C1″), 138.9 (C4), 135.9 (Cq, C2″

and C6″), 123.8 (C4″), 123.1 (C3″ and C5″), 118.0 and 116.5 (C3 and C5), 109.4 (C4′), 28.4 (*C*(CH_3)$_2$), 23.3 and 23.0 (CH_3 of C(*C*H_3)$_2$), 17.7 (*C*H_3C=NAr), 15.2 and 13.8 (C3′–CH_3 and C5′–CH_3). HRMS (EI) Anal. Calc. for $C_{24}H_{30}N_4$: 374.2470. Found: 374.2480.



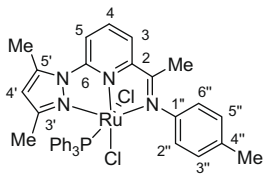
*4.7. Synthesis of [6-(3,5-dimethyl-pyrazol-1-yl)pyridin-2-ylmethyl]-p-tolylamine (**7**)*

To a stirred solution of **6a** (1.17 g, 4 mmol) in 40 mL anhydrous methanol was added $NaBH_4$ (0.45 g, 12 mmol) in several portions at 0–5 °C within 0.5 h. After the addition, the mixture was further stirred for 1 h at room temperature and then refluxed for 2 h. The mixture was cooled to ambient temperature and the reaction was quenched with 10 mL aqueous 10% NH_4Cl solution. Most of the methanol was removed under reduced pressure and the resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried over anhydrous sodium sulfate, and filtered. All the volatiles were removed under reduced pressure and the resultant residue was subject to purification by flash silica gel column chromatography (petroleum ether (60–90 °C)/ethyl acetate = 50:1), affording compound **7** as a white solid (0.61 g, 54%). M.p.: 72–74 °C. ^{1}H NMR ($CDCl_3$, 23 °C) δ 7.72 (d, J = 4.3 Hz, 2 H, 3-H and 5-H), 7.18 (t, J = 7.9 Hz, 1 H, 4-H), 7.00 and 6.59 (d each, J = 8.0 Hz, 2:2 H, C_6H_4), 6.01 (s, 1 H, 4′-H), 4.59 (s and br, 1 H, NH), 4.43 (s, 2 H, CH_2NH), 2.67 (s, 3 H, C4″–CH_3), 2.31 (s, 3 H, C3′–CH_3), 2.24 (s, 3 H, C5′–CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 157.2 and 150.0 (Cq each, C2 and C6), 153.2 and 145.7 (Cq each, C3′ and C5′), 141.5 and 127.0 (Cq each, C_6H_4), 139.0 (C4), 129.9 and 113.3 (2:2 CH, C_6H_4), 118.4 and 114.0 (C3 and C5), 109.2 (C4′), 49.4 (NHCH_2), 20.5 (C4″–CH_3), 14.9 and 13.8 (C3′–CH_3 and C5′–CH_3). HRMS (EI) Anal. Calc. for $C_{18}H_{20}N_4$: 292.1688. Found: 292.1682.



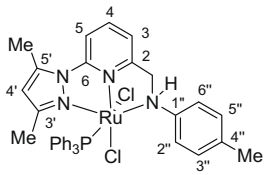
*4.8. Synthesis of complex **8a***

Under nitrogen atmosphere a mixture of **6a** (0.32 g, 1.1 mmol) and $RuCl_2(PPh_3)_3$ (1.05 g, 1.1 mmol) in 20 mL toluene was refluxed for 2 h. After cooling to ambient temperature, 15 mL diethyl ether was added to precipitate the crude product. The solid was filtered off, washed with diethyl ether and dried in vacuo, affording **8a** as a purple solid (0.70 g, 80%). Single crystals suitable for X-ray crystallographic study were obtained by diffusion of diethyl ether vapor into a saturated solution of **8a** in CH_3CN at ambient temperature. M.p.: >300 °C, dec. ^{1}H NMR (CD_3OD, 23 °C) δ 8.47 (s,1 H, CH=NAr), 7.79 (t, J = 7.6 Hz, 1 H, 4-H), 7.75 and 7.69 (d each, J = 8.2 and 7.4 Hz, 1:1 H, 3-H and 5-H), 7.48 and 7.24 (d each, J = 8.0 Hz, 2:2 H, C_6H4), 7.25, 7.14 and 7.04 (m each, 3:6:6 H, PPh_3), 6.31 (s, 1 H, 4′-H), 2.83 (s, 3 H, C4″–CH_3), 2.63 (s, 3 H, C3′–CH_3), 2.48 (s, 3 H, C5′–CH_3). ^{31}P{^{1}H} NMR (CD_3OD, 23 °C) δ 50.4 (s, PPh_3). Anal. Calc. for $C_{36}H_{33}Cl_2N_4PRu{\cdot}0.5O(C_2H_5)_2$: C, 59.92; H, 5.03; N, 7.36. Found: C, 59.66; H, 5.00; N, 7.40%.



*4.9. Synthesis of complex **8b***

In a fashion similar to the synthesis of **8a**, reaction of **6b** (0.20 g, 0.66 mmol) and $RuCl_2(PPh_3)_3$ (0.63 g, 0.66 mmol) in refluxing toluene (40 mL) for 24 h afforded complex **8b** as a purple solid (0.10 g, 20%) after purification by flash silica gel column chromatography (CH_2Cl_2/MeOH, v/v = 30:1). M.p.: >300 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C) δ 8.25, 6.83 and 6.05 (br each, 1:1:1 H, 4-H, 3-H and 5-H), 7.43 and 7.39 (d each, J = 8.0 Hz, 1:1 H), and 7.31 and 7.28 (d each, J = 8.0 and 7.8 Hz, 1:1 H) (aromatic CH of C_6H_4), 5.98 (s, 1 H, 4′-H), 2.68 (s, 3 H, C4″–CH_3), 2.64 (s, 3 H, C3′–CH_3), 2.42 (s, 3 H, CH_3C=NAr), 2.30 (s, 3 H, C5′–CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 170.0 (Cq, *C*=NAr), 162.4 and 154.2 (Cq each, C2 and C6), 157.5 and 145.1 (Cq each, C3′ and C5′), 143.0 (Cq, C1″), 136.6 (C4"), 133.3, 129.0 and 127.7 (s each, CH of 3 × Ph), 133.2 and 127.6 (2:2 CH of C_6H_4), 132.7 and 132.2 (Cq and d, PPh_3), 130.5 (C4), 121.5 and 113.5 (C3 and C5), 107.9 (C4′), 21.4 (C4″–*C*H_3), 18.4 (*C*H_3C=NAr), 15.2 and 14.7. (C3′–*C*H_3 and C5′–*C*H_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C) δ 42.7 (s, PPh_3). Anal. Calc. for $C_{37}H_{35}Cl_2N_4PRu$: C, 60.16; H, 4.78; N, 7.59. Found: C, 59.60; H, 4.82; N, 7.54%.



*4.10. Synthesis of complex **9***

In a fashion similar to the synthesis of complex **8a**, reaction of **7** (0.15 g, 0.5 mmol) and $Ru(PPh_3)_3Cl_2$ (0.48 g, 0.5 mmol) in refluxing toluene (30 mL) for 2 h afforded complex **9** as a yellow solid (0.26 g, 72%). Complex **9** always coexisted with **8a** due to the easy oxidation of **9** to **8a** in solution by air during the work-up process. M.p.: >260 °C, dec. ^{1}H NMR ($CDCl_3$, 23 °C) δ 8.02 (d, J = 20.1 Hz, 1 H, 3-H), 7.82 and 7.67 (m each, 1:1 H, 5-H and 4-H), 7.42 and 6.86 (d each, J = 7.4 Hz, 2:2 H, C_6H_4), 7.25–7.12 and 7.05–6.93 (m each, 9:6 H, 3 × Ph), 5.89 (s, 1 H, 4′-H), 4.02 (d, J = 15.0 Hz) and 3.72 (t, J = 13.0 Hz) (1:1 H, CH_2NH), 2.82, 2.72 and 2.29 (s each, 3:3:3 H, 3 × CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C) δ 53.0 (s, PPh_3).

*4.11. Synthesis of complex **11***

A mixture of ligand **6c** (0.19 g, 0.5 mmol) and $NiCl_2{\cdot}6H_2O$ (0.118 g, 0.5 mmol) in 10 mL THF was stirred at room temperature for 4 h. The resultant precipitate was filtered off, washed with diethyl ether (3 × 15 mL) and dried in vacuo to give **11** as a brown powder (0.227 g, 90%). Single crystals suitable for X-ray crystallographic study were grown by diffusion of diethyl ether vapor into a saturated solution of the complex in MeOH at ambient temperature. M.p.: >300 °C, dec. IR (KBr, cm^{-1}) ν 3442 (H_2O), 3128 (aromatic CH), 2961 and 2871 (aliphatic C–H), 1593 (C=N), 1476, 1374, 1318, 1263, 1198, 1041, 988, 808. Anal. Calc. for $C_{24}H_{30}Cl_2N_4Ni{\cdot}H_2O$: C, 55.21; H, 6.18; N, 10.73. Found: C, 55.11; H, 6.15; N, 10.78%.

4.12. A general procedure for catalytic transfer hydrogenation of ketones

Under nitrogen atmosphere, a mixture of ketone (2.0 mmol), 2-propanol (19 mL), and the catalyst (0.004 mmol) was stirred at 82 °C for 10 min. About 1.0 mL of 0.1 M *i*PrOK solution in 2-propanol was then introduced to initiate the TH reaction. At the stated time, 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.2 mL of 2-propanol for GC analysis. After the reaction was complete, the reaction mixture was evaporated all the volatiles under reduced pressure and subject to purification by flash silica gel column chromatography to afford the alcohol product. The alcohol products were identified by comparison of their GC traces with the authentic samples and/or by proton NMR measurements.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (20772124) and the National Basic Research Program of China (2009CB825300) for support of this research.

Appendix A. Supplementary material

CCDC 724507 and 724506 contain the supplementary crystallographic data for **8a** and **11**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.028.

References

[1] T. Ikariya, A.J. Blacker, Acc. Chem. Res. 40 (2007) 1300.
[2] T. Ohkuma, N. Utsumi, K. Tsutsumi, C. Sandoval, R. Noyori, J. Am. Chem. Soc. 128 (2006) 8724.
[3] A. Schlattera, W.-D. Woggon, Adv. Synth. Catal. 350 (2008) 995.
[4] F.K. Cheung, C.X. Lin, F. Minissi, A.L. Criville, M.A. Graham, D.J. Fox, M. Wills, Org. Lett. 9 (2007) 4659.
[5] W. Baratta, M. Ballico, G. Esposito, P. Rigo, Chem. Eur. J. 14 (2008) 5588.
[6] W. Baratta, G. Chelucci, E. Herdtweck, S. Magnolia, K. Siega, P. Rigo, Angew. Chem., Int. Ed. 46 (2007) 7651.
[7] W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zanette, E. Zangrando, P. Rigo, Angew. Chem., Int. Ed. 44 (2005) 6214.
[8] W. Baratta, P. Da Ros, A. Del Zotto, A. Sechi, E. Zangrando, P. Rigo, Angew. Chem., Int. Ed. 43 (2004) 3584.
[9] D.L. Liu, F. Xie, X.H. Zhao, W.B. Zhang, Tetrahedron 64 (2008) 3561.
[10] R.J. Lundgren, M.A. Rankin, R. McDonald, G. Schatte, M. Stradiotto, Angew. Chem., Int. Ed. 46 (2007) 4732.
[11] M.T. Reetz, X.G. Li, J. Am. Chem. Soc. 128 (2006) 1044.
[12] K. Leijondahl, A.-B.L. Fransson, J.-E. Bäckvall, J. Org. Chem. 71 (2006) 8622.
[13] G. Lu, H. Morimoto, S. Matsunaga, M. Shibasaki, Angew. Chem., Int. Ed. 47 (2008) 6847.
[14] S.W. Smith, G.C. Fu, J. Am. Chem. Soc. 130 (2008) 12645.
[15] V.C. Gibson, C. Redshaw, G.A. Solan, Chem. Rev. 107 (2007) 1745.
[16] Y.J. Chen, P. Hao, W.W. Zuo, K. Gao, W.-H. Sun, J. Organomet. Chem. 693 (2008) 1829.
[17] L.W. Xiao, S.Y. Jie, Y.X. Song, X.P. Gao, W.-H. Sun, J. Organomet. Chem. 693 (2008) 3858.
[18] V.A. Brunet, D. O'Hagan, Angew. Chem., Int. Ed. 47 (2008) 1179.
[19] A.T. Vallina, H. Stoeckli-Evans, A. Neels, J. Ensling, S. Decurtins, Inorg. Chem. 42 (2003) 3374.
[20] C. Mazet, L.H. Gade, Organometallics 20 (2001) 4144.
[21] F.L. Zeng, Z.K. Yu, J. Org. Chem. 71 (2006) 5274.
[22] X.J. Sun, Z.K. Yu, S.Z. Wu, W.-J. Xiao, Organometallics 24 (2005) 2959.
[23] H.X. Deng, Z.K. Yu, J.H. Dong, S.Z. Wu, Organometallics 24 (2005) 4110.
[24] F.L. Zeng, Z.K. Yu, Organometallics 27 (2008) 2898.
[25] F.L. Zeng, Z.K. Yu, Organometallics 27 (2008) 6025.
[26] F.L. Zeng, Z.K. Yu, Organometallics 28 (2009) 1855.
[27] S.K. Russell, E. Lobkovsky, P.J. Chirik, J. Am. Chem. Soc. 131 (2009) 36.
[28] N. Marquet, E. Kirillov, T. Roisnel, A. Razavi, J.-F. Carpentier, Organometallics 28 (2009) 606.
[29] W.-H. Sun, X.B. Tang, T.L. Gao, B. Wu, W.J. Zhang, H.W. Ma, Organometallics 23 (2004) 5037.
[30] J. Gmez, G. Garca-Herbosa, J.V. Cuevas, A. Arniz, A. Carbayo, A. Muoz, L. Falvello, P.E. Fanwick, Inorg. Chem. 45 (2006) 2483.
[31] C. Gemel, K. Folting, K.G. Caulton, Inorg. Chem. 39 (2000) 1593.
[32] S. Enthaler, B. Hagemann, S. Bhor, G. Anilkumar, M.K. Tse, B. Bitterlich, K. Junge, G. Erre, M. Beller, Adv. Synth. Catal. 349 (2007) 853.
[33] T. Li, R. Churlaud, A.J. Lough, K. Abdur-Rashid, R.H. Morris, Organometallics 23 (2004) 6239.
[34] A. Comas-Vives, G. Ujaque, A. Lledós, Organometallics 26 (2007) 4135.
[35] C.P. Casey, T.B. Clark, I.A. Guzei, J. Am. Chem. Soc. 129 (2007) 11821.