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Two *pseudo*-N_3 ligands and the catalytic activity of their ruthenium(II) complexes in transfer hydrogenation and hydrogenation of ketones

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Abstract

Complex $RuCl_2(PPh_3)$(*i*Bu-BTP) (**5**) was synthesized by the reaction of 2,6-bis(5,6-bis(*iso*-butyl)-1,2,4-triazin-3-yl)pyridine (*i*Bu-BTP) and $RuCl_2(PPh_3)_3$ in refluxing toluene, and its molecular structure was confirmed by X-ray crystallographic determination. Complex **5** was applied as a catalyst for transfer hydrogenation of ketones and exhibited catalytic activity comparable to $RuCl_2(PPh_3)(Me_4BPPy)$ (**1**) (Me_4BPPy = bis(3,5-dimethylpyrazol-1-yl)pyridine) in some cases. The difference between the catalytic activity of **5** and **1** is attributed to the significantly different arrangement and positions of the PPh_3 and chlorides and also to the different electron density on the *N*-heterocycles. Complex **1** exhibited good to excellent catalytic activity in hydrogenation of ketones under mild conditions. These results have suggested new applications of *i*Bu-BTP and Me_4BPPy as promising planar tridentate *pseudo*-N_3 ligands to construct highly active transition-metal catalysts.

Keywords: N_3 Ligands; Ruthenium; Transfer hydrogenation; Hydrogenation; Ketones

1. Introduction

Nitrogen-containing ligands have been extensively studied in coordination chemistry, and have been shown important applications in the fields of homogeneous catalysis and organic synthesis due to the easy manipulations and high reactivities of their transition metal complexes [1]. Recently, planar tridentate nitrogen donor (N_3) ligands 2,2′:6′,2″-terpyridines (**A**, terpy) [2], 2,6-bis(imino)pyridines (**B**) [3], and 2,6-bis(oxazolinyl)pyridines (**C**, Pybox) [4] (Chart 1) have been paid much attention. Non-planar *pseudo*-N_3 ligands hydridotris(pyrazol-1-yl)borates (**D**, Tp) have also been employed to build transition metal catalysts [5]. Planar N_3 ligand 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine (**E**, BMTZP) was used to synthesize lanthanide complexes [6]. Very recently, bis(pyrazol-1-yl)pyridines (**F**) were reported to construct rare transition metal catalysts from our laboratories [7a,7b] and Karam's group [7c], respectively. In our previous communication [7b], complex $RuCl_2(PPh_3)(Me_4BPPy)$ (**1**) (Me_4BPPy = a ligand of **F** type, i.e., bis(3,5-dimethylpyrazol-1-yl)pyridine) was synthesized and used as an efficient catalyst for transfer hydrogenation of ketones. Fe(II) and Co(II) complexes of ligands of type **F**, i.e., $\mathbf{F}\cdot FeCl_2$ and $\mathbf{F}\cdot CoCl_2$, were prepared and applied for ethylene polymerization [7c]. However, other types of N_3 and *pseudo*-N_3 ligands have seldom reported to construct late transition metal catalysts. Encouraged by the excellent catalytic activity of complex **1** in transfer hydrogenation of ketones [7b], we further investigated

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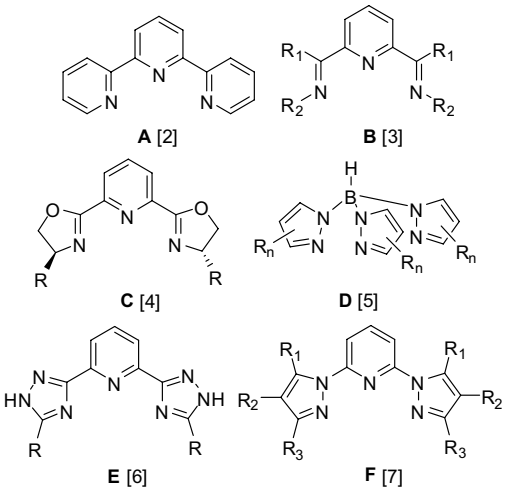


Chart 1. N_3 and *pseudo*-N_3 ligands.

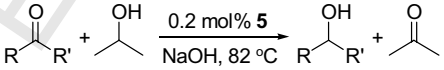
hydrogenation of ketones catalyzed by $RuCl_2(PPh_3)(Me_4BPPy)$ (**1**). As a comparison study, ligand 2,6-bis(5,6-bis(*iso*-butyl)-1,2,4-triazin-3-yl)pyridine (*i*Bu-BTP) (**4**) and complex $RuCl_2(PPh_3)$(*i*Bu-BTP) (**5**) were synthesized. Herein, we report synthesis and X-ray crystal structure of complex **5** and the catalytic activity of complexes **5** and **1** in transfer hydrogenation and hydrogenation of ketones under mild conditions (see Chart 2).

2. Results and discussion

2.1. Synthesis and X-ray crystal structure of complex 5

Ligand **4** was prepared by means of a modified literature procedure (Chart 3) [6,8]. Condensation of pyridine-2,6-dicarbohydrazide imide (**2**) with 1,2-diketone (**3**) at heating afforded 2,6-bis(5,6-bis(*iso*-butyl)-1,2,4-triazin-3-yl)pyridine (*i*Bu-BTP) (**4**). Compound **4** is usually hydrated with one molecule of water after isolation from flash silica gel column chromatography. Although **4** is a *poly*-heterocyclic compound, it is bestowed with very good solubility in organic solvents including petroleum ether due to introduction of four *iso*-butyl side chains to the two triazinyl rings. Reaction of ligand **4** with 1.0 equiv of $RuCl_2(PPh_3)_3$ [9] in refluxing toluene afforded complex $RuCl_2(PPh_3)$(*i*Bu-BTP) (**5**) in 86% yield (Chart 3). Complex **5** is air- and moisture-stable and its single crystals suitable for X-ray crystallographic study were obtained from recrystallization in CH_2Cl_2/hexane (v/v, 1/4) at −20 °C. The NMR spectra of **5** reveals **4** to be a coordinating ligand in **5**. The chemical shifts of the pyridyl CH hydrogen atoms in complex **5** are shifted upfield by 0.2–0.3 ppm in the proton NMR spectrum as compared with those of the free ligand **4**.

In the solid state, complex **5** exhibits a neutral molecular structure in which **4** acts as a planar *pseudo*-N_3 ligand, and the metal center is six-coordinated with the tridentate *pseudo*-N_3 ligand, two chlorides, and one PPh_3 ligand (Fig. 1). The three Ru–N, two Ru–Cl and Ru–P bond distances are 1.982(3), 2.032(3), 2.058(3), 2.3919(13), 2.4110(13), and 2.3631(11) Å, respectively (Table 2). The Ru–N bond distances in **5** are very close to their analogues in **1** [7b], but the Ru–Cl and Ru–P bonds in **5** are shorter than those in **1**. The significant structural difference between complexes **5** and **1** is that the two chlorides in **5** are closely linear to each other (Cl(1)–Ru–Cl(2), 174.91(3)°) and positioned on the two sides of the *pseudo*-N_3 ligand plane, while the two chloride atoms in **1** are nearly perpendicular to each other. The pyridyl nitrogen atom is positioned *trans* to the PPh_3 ligand in **5** (N(1)–Ru–P, 175.80(8)°) (Fig. 1), while the PPh_3 ligand in **1** is arranged *trans* to one chloride and they are situated on the two sides of the ligand plane, respectively [7b]. The molecular structure of **5** demonstrates a rare example of transition metal complexes of a new pyridyl-based *pseudo*-N_3 ligand which has been structurally characterized.



(1)

2.2. Transfer hydrogenation of ketones catalyzed by complex 5

Ruthenium(II) complexes have been used as the most potential catalysts for transfer hydrogenation of ketones

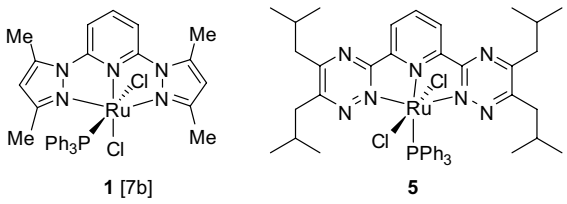


Chart 2. Ru(II) complexes **1** and **5**.

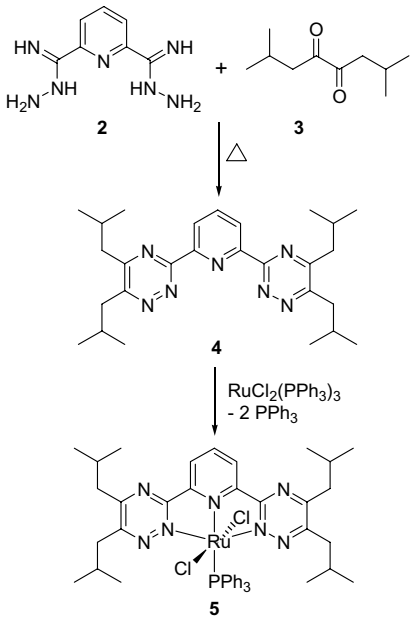


Chart 3. Synthesis of ligand **4** and complex **5**.

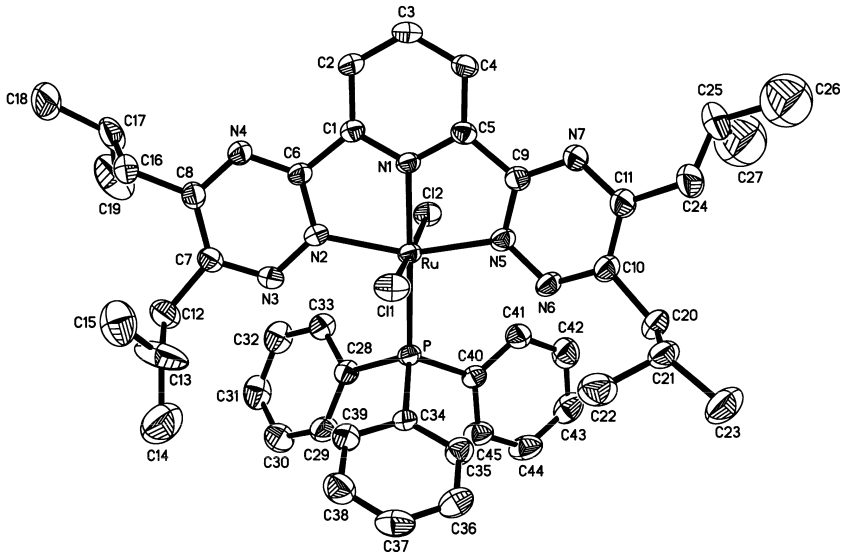


Fig. 1. Perspective view of complex **5**.

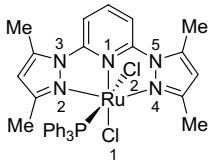
[10] and are also becoming very promising catalysts for hydrogenation of ketones [11,12]. Complex **1** has showed excellent catalytic activity to transfer hydrogenation of ketones in 2-propanol, achieving a final TOF value as high as 6000 h^{-1} [7b]. That is, 2 mmol of acetophenones were completely transformed to the corresponding alcohols within 5 min in refluxing 2-propanol using 0.2 mol% **1** as the catalyst and KO^{i}Pr as the base. In a similar fashion complex **5** was applied in the catalytic transfer hydrogenation of ketones (Table 3). Using 0.2 mol% **5** as the catalyst with a molar ratio of 500/25/1 for ketone/base/catalyst, transfer hydrogenation of acetophenone was carried out in 2-propanol at 82 °C (Eq. 1). K_2CO_3, KO^{i}Pr, KOH, and NaOH were tested as the bases to optimize the reaction conditions. Over a period of 4 h, the corresponding alcohol product from acetophenone reached 98%, 96%, 97%, and 46% yields by GC analysis in the reactions using NaOH, KOH, KO^{i}Pr, and K_2CO_3 as the base, respectively. Thus, NaOH was selected as the reaction promoter although both KOH and KO^{i}Pr also worked well as a base in the

Table 1
Crystal data and refinement details for complex **5**

Empirical formula	$C_{45}H_{54}C_{12}N_7PRu$
Formula weight	895.89
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2(1)/c$
Unit cell dimensions	
a (Å)	11.286(5)
b (Å)	11.148(5)
c (Å)	35.528(15)
α (°)	90
β (°)	97.230(8)
γ (°)	90
V (Å^3)	4435(3)
Z, D_c (g cm^{-3})	4, 1.342
μ (mm^{-1})	0.550
$F(000)$	1864
Crystal size (mm^3)	$0.503 \times 0.458 \times 0.367$
θ Limit (°)	1.82–27.00
Reflections collected/unique	25260/9612 [$R_{int} = 0.0882$]
Completeness to $\theta = 27.00$	99.2%
Data/restraints/parameters	9612/2/508
No. of data observed with $I > 2\sigma(I)$	6414
Goodness-of-fit on F^2	0.933
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0486$, $wR_2 = 0.1112$
R indices (all data)	$R_1 = 0.0720$, $wR_2 = 0.1182$
Largest difference peak and hole (e Å^{-3})	0.822 and −0.472

Table 2
Selected bond distances (Å) and angles (°) for complexes **5** and **1**

Complex **5**			
Ru–N(1)	1.982(3)	Ru–N(2)	2.032(3)
Ru–N(5)	2.058(3)	Ru–P	2.3631(11)
Ru–Cl(1)	2.3919(13)	Ru–Cl(2)	2.4110(13)
N(5)–N(6)	1.341(4)		
Cl(1)–Ru–Cl(2)	174.91(3)	N(1)–Ru–N(2)	78.85(12)
N(1)–Ru–N(5)	78.67(12)	N(2)–Ru–N(5)	156.03(12)
N(1)–Ru–P	175.80(8)	N(1)–Ru–Cl(1)	90.05(8)
N(1)–Ru–Cl(2)	84.96(8)	N(2)–Ru–Cl(2)	93.88(8)
P–Ru–Cl(1)	93.83(4)	N(2)–Ru–P	99.77(9)
P–Ru–Cl(2)	91.20(4)	N(5)–Ru–P	103.23(9)
Complex **1** [7b]			



Ru–N(1)	1.955(3)	Ru–N(2)	2.078(4)
Ru–N(4)	2.051(4)	Ru–P	2.2927(14)
Ru–Cl(1)	2.4546(12)	Ru–Cl(2)	2.4771(13)
N(1)–Ru–Cl(1)	176.97(12)	P–Ru–N(1)	94.87(11)
Cl(1)–Ru–Cl(2)	91.56(4)	P–Ru–Cl(1)	88.09(5)
P–Ru–Cl(2)	176.06(5)	N(2)–Ru–N(4)	156.97(15)

Table 3
Transfer hydrogenation of ketones catalyzed by **5**[a]

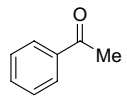
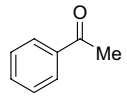
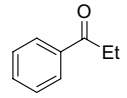
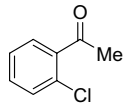
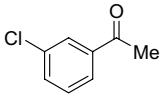
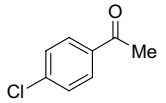
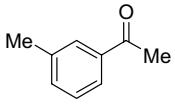
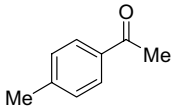
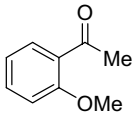
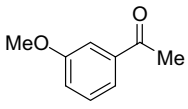
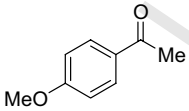
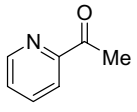
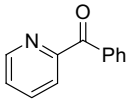
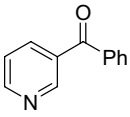
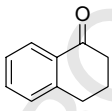
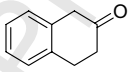
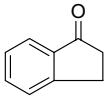
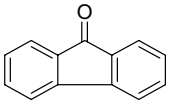
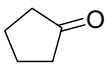
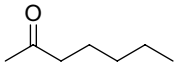
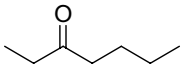
Entry	Ketone	Time (h)	Yield[b] (%)	TOF[c] (h^{-1})
1		4	98 (36)	1080
2[d]		2.5	100 (45)	900
3[e]		4	100 (9)	180
4		30	60 (35)	1050
5		24	96 (35)	1050
6		30	89 (32)	960
7		7	100 (10)	300
8		10	99 (19)	570
9		8	100 (20)	600
10		8	85[f]	53[g]
11		6	98 (31)	930
12		24	63 (1)	30

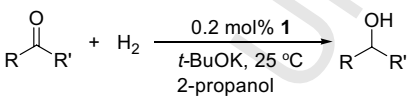
Table 3 (*continued*)

Entry	Ketone	Time (h)	Yield[b] (%)	TOF[c] (h^{-1})
13		24	78 (2)	60
14		8	34 (<1)	<30
15		24	80 (8)	240
16		24	0	0
17		24	96 (16)	480
18		9	97 (19)[h]	570
19		4.5	98 (39)	1170
20[e]		2.5	100 (64)	1280
21[e]		4	100 (33)	660
22		26	3 (3)	90

[a] Reaction conditions: ketone/base/**5** = 500/25/1. Ketone, 2 mmol; catalyst **5**, 3.6 mg (0.2 mol%); NaOH, 0.1 mmol; 2-propanol, 20 mL; 0.1 MPa, 82 °C.
[b] GC yield of the alcohol product. Data in parentheses are the GC yields after 10 min.
[c] TOF after 10 min.
[d] 0.3 mol% **5**.
[e] 0.3 mol% **5**, and KOH as the base.
[f] Isolated yield.
[g] Final TOF.
[h] HPLC yield.

reactions. Increasing the catalyst loading, the reaction was accelerated. For example, with 0.3 mol% **5**, acetophenone was reached a complete conversion to form the alcohol product within 2.5 h (Entry 2, Table 3). Because a comparison study was intended between complexes **5** and **1**, 0.2 mol% catalyst loading was used in the typical reactions (Table 3).

For most of the acetophenone substrates, their initial reaction rates were fast within the first 10 min within the first 10 min and then became smooth, or even very slow (Entries 1–11, Table 3). For example, acetophenone, substituted chloroacetophenones, and *p*-methylacetophenone reached 36–45%, 32–35%, and 31% conversions within the first 10 min (Entries 1, 2, 4–6, and 11, Table 3). For propiophenone, its initial reaction rate was not fast, but its reaction proceeded at a very constant rate, achieving a complete conversion within 4 h (Entry 3, Table 3). Pyridyl ketones slowly underwent the reactions and could not reach a high conversion within 24 h (Entries 12–14, Table 3), neither did α-tetralone show a high reactivity (Entry 15, Table 3). Internal ketones, i.e., β-tetralone and 3-heptanone hardly reacted over a period of 24 h (Entries 16 and 22, Table 3). However, 1-indanone and 9-fluorenone reached >96% conversions within 9–24 h (Entries 17 and 18, Table 3). Catalyst **5** exhibited excellent catalytic activity to cyclohexanone, cyclopentanone, and 2-heptanone (Entries 19–21, Table 3). It should be noted that the catalytic activity of complex **5** is comparable to that of complex **1** in the reactions of propiophenone, 4-methoxyacetophenone, 2-benzopyridine, α-tetralone, 1-indanone, 9-fluorenone, and the aliphatic ketones (Entries 3, 11, 13, 15, and 17–21) under the stated conditions, and in other cases complex **1** showed much higher catalytic activity than **5** [7b]. The difference between the catalytic activity of complexes **1** and **5** in transfer hydrogenation of ketones is presumably attributed to the significantly different arrangements of the PPh_3 ligand and the two chloride atoms around the metal centers and also to the various electronic properties of the pyridyl-supported *N*-heterocycles. That pyrazolyls in **1** are stronger σ-donor ligands than 1,2,4-triazin-3-yls in **5** may help to form a relatively electron-rich ruthenium center, thus stabilizing the active catalytic species. These results suggest that the arrangement of the PPh_3 and chloride moieties in **1** may be more favorable to stabilize the active catalytic species.

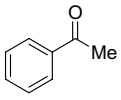
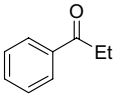
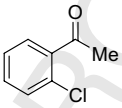
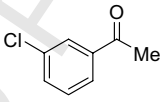
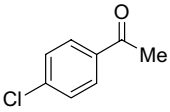
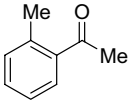
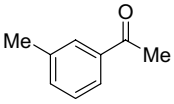
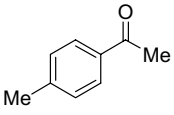
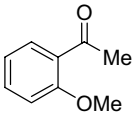
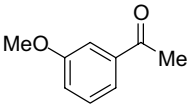


(2)

2.3. Hydrogenation of ketones catalyzed by complex 1

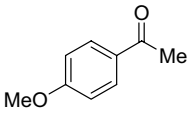
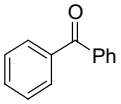
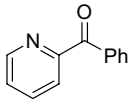
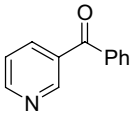
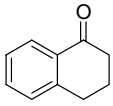
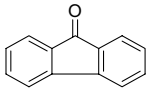
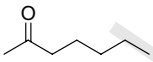
Complex **1** exhibited excellent catalytic activity for transfer hydrogenation of ketones [7b], which led us to investigate its catalytic activity for hydrogenation of ketones. It was found that complex **1** can also exhibit high catalytic activity in hydrogenation of ketones under mild

Table 4
Hydrogenation of ketones catalyzed by **1**[a]

Entry	Ketone	Time (h)	$P(H_2)$ (atm)	Yield[b] (%)
1		4	20	96
2		4	20	94
3		4	20	>99
4		4	20	43 (96)[c]
5		4	20	97
6		4	20	>99
7		4	20	98
8		4	20	96
9		8	50	99[d]
10		4	20	98

(*continued on next page*)

Table 4 (*continued*)

Entry	Ketone	Time (h)	$P(H_2)$ (atm)	Yield[b] (%)
11		4	20	96
12		4	20	83[e]
13		8	50	1.8[d]
14		8	50	23
15		4	20	5
		6	30	97[c]
16		4	20	22
		8	50	27[d]
17		4	20	92[f]
18		4	20	99
19		4	20	79 (97[c])
20		4	20	>99

[a] Reaction conditions: ketone/*t*-BuOK/catalyst = 500:10:1. Ketone, 1.5 mmol; catalyst **1**, 2 mg (0.2 mol%); KO^{t}Bu, 3.4 mg (2 mol%); 2-propanol, 3 mL; 25 °C.
[b] GC yield.
[c] Catalyst, 0.5 mol%.
[d] Catalyst, 2 mol%.
[e] Isolated yield.
[f] HPLC yield.

conditions (Eq. 2, Table 4). With a molar ratio of 500/20/1 for ketone/base/catalyst, the catalyst system with a combination of 2-propanol as the reaction medium and KO^{t}Bu as the base promoter showed the best efficiency for hydrogenation of ketones. With 0.2 mol% **1** as the catalyst, hydrogenation of ketones was carried out in 2-propanol at 25 °C under a hydrogen atmosphere (20 atm). Over a period of 4 h, acetophenones and aliphatic ketones were reduced to the corresponding alcohols in excellent yields (Entries 1–11, 15, and 18–20). For benzophenone and 9-fluorenone, their corresponding alcohol products were formed in 83–92% yields (Entries 12 and 17, Table 4), while pyridyl ketones and 1-indanone were stubborn to be reduced under the stated conditions (Entries 13, 14, and 16, Table 4). It is noteworthy that by-products were not detected in the reaction mixtures. This protocol has demonstrated a promising catalyst system for hydrogenation of ketones under mild conditions.

Ruthenium hydride species generated from complexes **1** and **5** were presumably considered as the catalytically active species in transfer hydrogenation and hydrogenation of ketones. Thus, reduction of complexes **1** and **5** was carried out in methanol with $NaBH_4$ or dihydrogen under pressure and heating in order to isolate the ruthenium hydride complexes. Unfortunately, no success has been achieved. Ligands **4** and Me_4BPPy did not react with $RuH(Cl)(PPh_3)_3$ in CH_2Cl_2 or toluene at ambient temperature or heating to form the desired complexes $RuH(Cl)(L)(PPh_3)$ which might be generated *in situ* to promote the catalytic transfer hydrogenation and hydrogenation of ketones. For the present transfer hydrogenation of ketones catalyzed by complex **5**, no obvious reaction undergo at ambient temperature in most cases, suggesting that heating is necessary to promote formation of the catalytically active species. In the hydrogenation of ketones using complex **1** as the catalyst, the reaction was negligible under a nitrogen atmosphere without dihydrogen, indicating that dihydrogen under pressure was involved in the reaction to promote formation of the catalytically active species at ambient temperature.

3. Summary

In summary, complex $RuCl_2(PPh_3)$(*i*Bu-BTP) (**5**) has exhibited moderate to good and excellent catalytic efficiency in the transfer hydrogenation of ketones, and its catalytic activity is comparable to that of complex $RuCl_2(PPh_3)(Me_4BPPy)$ (**1**) in some cases. In most cases, complex **5** showed lower catalytic activity than **1**, which is presumably attributed to the significant structural difference between **5** and **1** and also to the various electronic properties of the pyridyl-supported *N*-heterocyclic rings. That the PPh_3 ligand and one chloride are linearly arranged and positioned on the two sides of the *pseudo*-N_3 ligand plane may lead to high catalytic activity for complexes of type $RuCl_2(PPh_3)L$ (L = a planar tridentate ligand). The structural confirmation of complex **5** by X-

ray crystallography and its catalytic activity have revealed promising applications of the new family of planar tridentate *pseudo*-N_3 ligands, i.e., 2,6-bis(1,2,4-triazin-3-yl)pyridines, in transition metal-promoted catalysis. Complex $RuCl_2(PPh_3)(Me_4BPPy)$ (**1**) exhibited good to excellent catalytic activity in hydrogenation of ketones under relatively mild conditions, suggesting that Me_4BPPy is a promising planar tridentate *pseudo*-N_3 ligand to construct highly active transition-metal catalysts.

4. Experimental section

4.1. General considerations

All the reactions were carried out under a nitrogen atmosphere with a drybox and standard Schlenk techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer. Chemicals were used as received.

4.2. Preparation of the ligand iBu-BTP (4)

Under nitrogen atmosphere, a mixture of pyridine-2,6-dicarbohydrazide imide **2** (9.66 g, 50 mmol) and 1,2-diketone **3** (17.02 g, 100 mmol) was stirred at 160 °C for 7 h. After cooled to ambient temperature, the resultant residue was purified by flash silica gel column chromatography with petroleum ether (30–60 °C) as the eluent. Further recrystallization from petroleum ether (30–60 °C) at −20 °C afforded yellow crystalline solid **4** (11.00 g, 45.9%). M.p.: 61–63 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.73 (d, $J = 5.82$ Hz, 2H) and 8.10 (t, 1H) (pyridyl CH), 3.55 (br, 2H, H_2O), 2.96 (d, 4H, $J = 5.37$ Hz, $2 \times CH_2$), 2.83 (d, 4H, $J = 5.31$ Hz, $2 \times CH_2$), 2.43 and 2.29 (m each, 2:2H, $4 \times CH$), 1.03 (d, $J = 4.89$ Hz, $4 \times CH_3$), 1.01 (d, $J = 4.92$ Hz, $4 \times CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.75, 161.09, 159.63, and 154.07 (Cq each, C–N), 138.16 and 125.16 (1:2, aromatic CH), 42.49 and 41.25 (2:2, $4 \times CH_2$), 28.53 and 28.04 (2:2, $4 \times CH$), 22.77 and 22.63 (4:4, $8 \times CH_3$). Anal. Calc. for $C_{27}H_{39}N_7 \cdot H_2O$: C, 67.61; H, 8.62; N, 20.44. Found: C, 67.64; H, 8.51; N, 20.95%.

4.3. Preparation of complex $RuCl_2(PPh_3)$ (iBu-BTP) (5)

A mixture of ligand *i*Bu-BTP **4** (0.498 g, 1.0 mmol), $RuCl_2(PPh_3)_3$ (0.995 g, 1.0 mmol) in 60 mL of refluxing toluene was stirred until all the ligand was consumed over a period of ca 3 h. The reaction mixture was cooled to ambient temperature, and all the volatiles were removed under reduced pressure, affording a purple residue. The resultant residue was washed with hexane (10×2 mL) until no free ligand was detected from the filtrate by TLC analysis. The resultant material was dissolved in 40 mL toluene at 50 °C and then cooled to ambient temperature. Recrystallization at −20 °C overnight afforded purple crystals. The mother liquor was concentrated under reduced pressure and then subject to flash silica gel column chromatography (diethyl ether/petroleum (30–60 °C), 10/1). Combined the purple solid, a total of 0.80 g (86.0%) **5** was obtained. The single crystals suitable for X-ray crystallographic study were grown in CH_2Cl_2/hexane (v/v, 1/4) at −20 °C. M.p.: 232 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, 2H), 7.90 (m, 7H) and 7.27 (m, 9H) (pyridyl and phenyl CH), 2.70 (d, $J = 5.16$ Hz, 4H, $2 \times CH_2$), 2.41 (d, $J = 5.37$ Hz, 4H, $2 \times CH_2$), 2.35 and 1.63 (m each, 2:2H, $4 \times CH$), 1.06 and 0.79 (d each, $J = 4.95$ Hz, 12:12H, $8 \times CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.72, 159.88, 158.13 and 155.76 (Cq each, C–N), 136.26 (Cq, *i*-C of Ph), 135.87, 135.31, 135.22, 128.53, 127.10, 127.02, and 124.41 (pyridyl and phenyl CH), 41.98 and 40.95 (2:2, $4 \times CH_2$), 27.64 and 27.52 (2:2, $4 \times CH$), 22.88 ($8 \times CH_3$). Anal. Calc. for $C_{45}H_{54}C_{l2}N_7PRu$: C, 59.96; H, 6.10; N, 10.80. Found: C, 60.33; H, 6.08; N, 10.94%.

4.4. General procedure for transfer hydrogenation of ketones catalyzed by 5

Under nitrogen atmosphere, a mixture of ketone (2 mmol), catalyst **5** (3.6 mg, 0.004 mmol), and 2-propanol (19 mL) was stirred at 82 °C for 10 min. 1.0 mL of 0.1 M NaOH solution in 2-propanol was then introduced. The reaction mixture was stirred at the refluxing temperature and samples were taken for GC analysis at 10 min, 1 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, 3.5 h, 4.0 h, 4.5 h, 5.0 h, 24 h, etc. After the reaction was finished, the mixture was condensed under reduced pressure and subject to flash silica gel column chromatography to afford the alcohol product. Acetone and the corresponding alcohols were detected as the products in all the cases. The alcohol products were identified by comparison with the authentic samples and/or by proton NMR measurements.

4.5. Typical procedure for hydrogenation of ketones catalyzed by 1

Under nitrogen atmosphere, complex **1** (2.0 mg, 0.003 mmol), KO^{t}Bu (3.4 mg, 0.03 mmol) and 1 mL of 2-propanol were successively added to a 10-mL vial, and the mixture was stirred at ambient temperature for 5 min. A ketone (1.5 mmol) in 2 mL 2-propanol were added, and the vial was placed in a 200-mL autoclave, and then the autoclave atmosphere was replaced with hydrogen for three times, pressured H_2 to the stated pressure to start the reaction with stirring. After the reaction was finished, the reaction mixture was analyzed or condensed for isolation of the product in the above mentioned procedures.

4.6. X-ray crystallographic studies

Single crystal X-ray diffraction studies for complex **5** was 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. Crystal data and refinement details for these complex **5** are summarized in Table 1.

Acknowledgements

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Appendix A. Supplementary material

CCDC 626622 contains the supplementary crystallographic data for **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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