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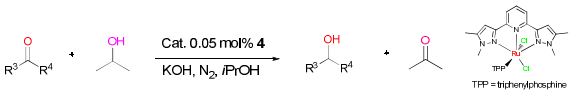
A graphical and textual abstract for the contents pages



Four new ruthenium(II) complexes (**1**, **2**, **3**, **4**) exhibited good to excellent catalytic activity, under the high substrate to catalyst ratio (2000:1).

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Construction of Pincer-Type symmetrical Ruthenium(II) complexes bearing a Pyridyl-2,6-Pyrazolyl Arms: Catalytic Behavior in Transfer Hydrogenation of Ketones

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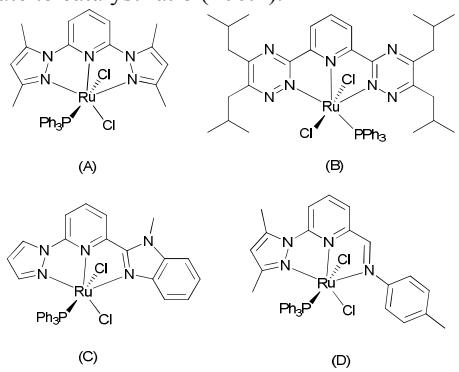
Convenient synthesis of four new distorted octahedral ruthenium(II) complexes (**1**, **2**, **3**, **4**) having general molecular formula [$RuCl_2$**L**PAr_3] (**L** = pyridine-based tridentate ligands not containing N-H bond) has been described. Their composition and structure have been determined by elemental analysis and NMR spectra, and complexes **2**, **4** were also identified by X-ray single crystal diffraction. All ruthenium(II) complexes exhibited good to excellent catalytic activity in the transfer hydrogenation of ketones. Among them, complex **4** achieved the highest final TOF value of 51600 h^{-1} under the high molar ration of substrate to catalyst (2000:1).

Introduction

Catalytic transfer hydrogenation of unsaturated organic compounds has become reliable synthetic protocols beyond conventional reduction reactions,[1] not only because it meets the increasing demand for clean and environmentally benign processes in chemistry, but it is also considered relatively low cost and easy operation. More recently, there is rapid growth in the various transition metal complexes like cobalt,[2] nickel,[3] palladium,[4a] iron,[4b-4c] rhodium,[5a] iridium[5b-5d] employed for the transfer hydrogenation of ketones, and particular attention has been devoted to ruthenium-based[6] complexes.

In the meanwhile, varying levels of catalytic efficiency were observed for this transformation in the presence of ruthenium complexes containing Schiff base,[7] tripodal phosphine [$MeC(CH_2PPh_2)_3$],[8] arene,[9] *N*-heterocyclic carbene,[10] amine-based ligands,[11] and pincer ligands.[12] In particular, pincer type tridentate pyridine-based framework (L_1-Py-L_2) has recently been proven to be the convenient and attractive ligands because of their tunable properties and potential application. Thus, much effort has been devoted to the preparation of tridentate pyridine-based analogues PNP,[13] PNN[14] and CNN.[15]

There be recently reported highly active ruthenium(II) NNN phosphine complex[16] for transfer hydrogenation of ketones. An acceleration effect is shown by the N-H functionality in the pyrazolyl arms. However, several symmetrical and unsymmetrical Ru(II) catalysts featuring no N-H functionality have also been documented for TH of ketones: complex (A),[17a] (B),[17b] (C),[17c] (D)[17d] (Scheme 1). Among both of unsymmetrical Ru(II) complexes, (C) exhibited poor catalytic activity in the presence of 0.3 mol% catalyst with final TOF values of 1960 h^{-1} and (D) reached 5940 h^{-1} at S:C/200:1. Symmetrical (A) (6000 h^{-1}) exhibited higher reactive activity than (B) (1080 h^{-1}) under the substrate to catalyst ratio (200:1).



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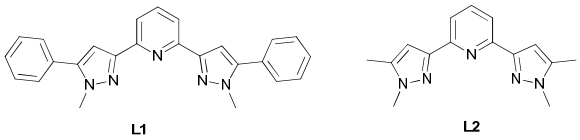
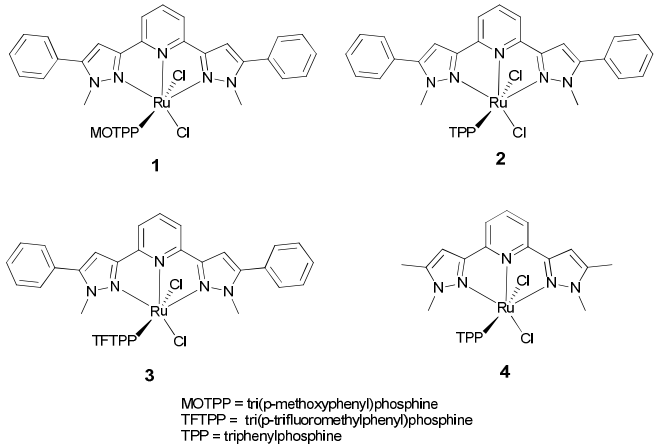
Scheme 1. Ru(II) complexes (A), (B), (C), and (D)

Previously, our research group had reported the synthesis of symmetrical pincer type tridentate pyridine-bridged framework NNN ligands, not incorporating NH group (Scheme 2).[18a] Based on this result, we intend to synthesize symmetrical ruthenium(II) complexes featuring no N-H functionality which can catalyze the hydrogenation of ketones in the low catalyst loading (Scheme 3).



Scheme 2. Ligands **L1** and **L2**

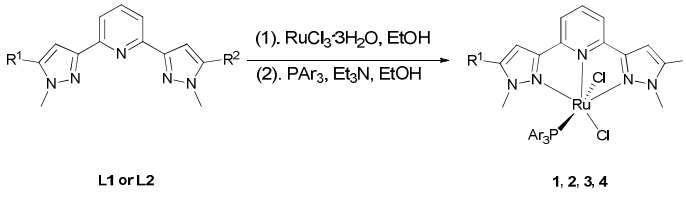


Scheme 3. Ru(II) complexes **1**, **2**, **3** and **4**

Results and discussion

Preparation and Characterization of Ru(II) complexes 1-4

Reacting **L1** or **L2** with an equivalent amount of $RuCl_3 \cdot 3H_2O$, PAr_3 (1 equiv) and triethylamine (1 mL) in ethanol afforded the ruthenium compound **1-4** in red solid state by the similar means of literature procedure (Scheme 4)[18b].



Scheme 4. Preparation of compound **1-4**

These target ruthenium complexes **1-4** were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR or elemental analysis (see Supporting Information). The ^{31}P NMR of **1-4** showed a singlet at δ = 39.9, 43.9, 45.8 and 44.1 ppm respectively. In the ^{1}H NMR spectra of compound **1**, **2** and **3**, the resonances of -NCH_3 and -CH_2 of pyrazolyl, due to the coordination of **L1** with ruthenium metal, have a slight shift compared to that of **L1** [**1-3**: δ (-NCH_3) = 4.17, 4.16, 4.19 ppm, δ(-CH_2) = 6.85, 6.84, 6.86 ppm; **L1**: δ (-NCH_3) = 3.98 ppm, δ(-CH_2) = 7.14 ppm]. Similarly, there is the same phenomenon in the ^{1}H NMR spectra of compound **4**.

By slow diffusion of diethyl ether into a CH_2Cl_2 solution of complexes, single crystals of **2** and **4** were obtained (Figure 1, 2). Attempts to obtain the single crystals of **1** and **3** were not successful. The crystal structures of **2** and **4** were consistent with the results of NMR and elemental analysis (See Electronic Supplementary Information).

The perspective view of **2** is shown in Figure 1, a distorted octahedral geometry around the ruthenium center was observed, with the two *cis* Cl atoms and the phosphorus located in the apical position. The bond angles of Cl(1)-Ru-Cl(2), P-Ru-Cl(1), P-Ru-N(3) and N(3)-Ru-Cl(2) are 87.55(3)°, 87.15(3)°, 94.31(9)° and 91.00(9)° and the bond lengths of Ru-Cl(1), Ru-Cl(2), Ru-P, Ru-N(2), Ru-N(3), Ru-N(4) are 2.4558 Å, 2.4681 Å, 2.2958 Å, 2.117 Å, 1.989 Å, 2.081 Å.

The structural assignment of **4** is similar to complex **2** (Figure 2): The bond angles of Cl(1)-Ru-Cl(2), P-Ru-Cl(2), P-Ru-N(1) and N(1)-Ru-Cl(1) are 87.72(6)°, 93.19(6)°, 93.88(16)° and 85.18(16)° respectively. The bond angle of P1-Ru1-Cl1 [178.28(6)°] is obviously larger than that [171.77(4)°] of P1-Ru1-Cl2 in compound **2**. The Ru-Cl(1) (2.4646 Å) bond length is longer than Ru-Cl(2) (2.4550 Å), maybe because the phosphine ligand is in the *trans*-position of Cl(1). The average bond length (2.063 Å) of Ru-N is little longer than that (2.028 Å) [$RuCl_2(PPh_3)(Me_4BPPy)$] (A)[17a] and (2.053 Å) as the reported analogous complex [$RuCl_2(PPh_3)$(NNN)](NNN: tridentate dipyrazolpyridines).[19]

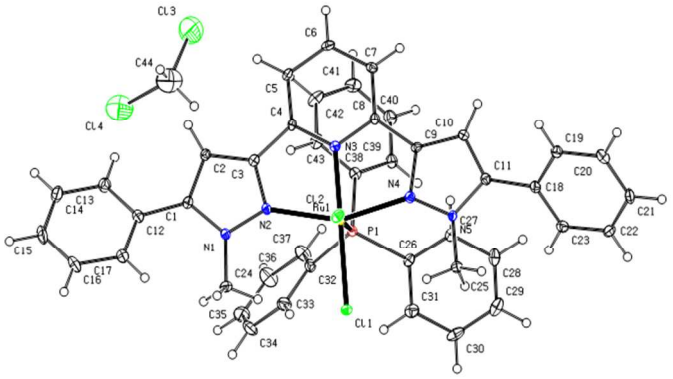


Figure 1. The molecular structure of complex **2**. Selected bond lengths [Å]: Ru1-Cl1 = 2.4558(9), Ru1-Cl2 = 2.4681(10), Ru1-P1 = 2.2958(11), Ru1-N2 = 2.117(3), Ru1-N3 = 1.989(3), Ru1-N4 = 2.081(3); angles [°]: Cl1-Ru1-Cl2 = 87.55(3), P1-Ru1-Cl1 = 87.15(3), P1-Ru1-Cl2 = 171.77(4), N3-Ru1-Cl1 = 178.53(10), N3-Ru1-P1 = 94.31(9), N4-Ru1-N2 = 153.96(12), N3-Ru1-Cl2 = 91.00(9).

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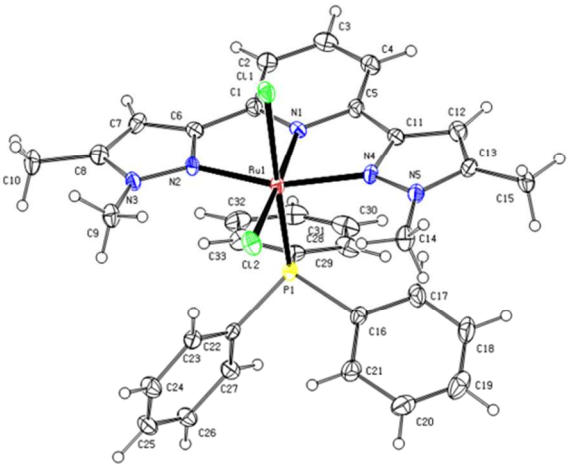
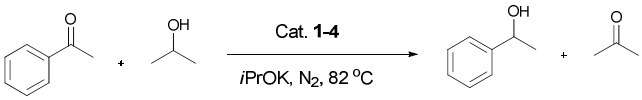


Figure 2. The molecular structure of complex **4**. Selected bond lengths [Å]: Ru1-Cl1 = 2.4646(17), Ru1-Cl2 = 2.4550(17), Ru1-P1 = 2.2760(17), Ru1-N1 = 1.999(5), Ru1-N2 = 2.106(5), Ru1-N4 = 2.085(5); angles [°]: Cl1-Ru1-Cl2 = 87.72(6), P1-Ru1-Cl1 = 178.28(6), P1-Ru1-Cl2 = 93.19(6), N1-Ru1-Cl2 = 172.87(16), N1-Ru1-P1 = 93.88(16), N4-Ru1-N2 = 154.9 (2), N1-Ru1-Cl1 = 85.18(16).

Hydrogenation of ketones catalyzed by complexes 1-4

Complexes **1**-**4**, were employed as the catalysts for transfer hydrogenation of acetophenone in low catalyst loading of 0.1 mol%, full details of which are provided in Table 1. From the entries 1-3 in Table 1, it can be seen that the catalyst **2** containing triphenylphosphine is a judicious choice for this transformation. Over a period of 1 h, conversion of acetophenone was reached 64%, 82%, and 59% respectively, revealing in an order of the catalytic activity for TH of ketones: **2**>**1**>**3**, under the precise control of tridentate NNN ligand's electronic and geometric properties. Compared with the **L1** ligand, complex **4** bearing **L2** ligand was also applied in the catalytic system for the TH reaction of ketones and it exhibited the highest catalytic activity under the same conditions (Table 1, entries 4 vs 2). So complex **4** was chosen as the catalyst in the following investigation.

Table 1. Screening the catalytic activity of various complexes[a]



Entry	Catalyst	Base	Conv. (%)[b]			
			10 min	60 min	120 min	240 min
1	**1**	*i*PrOK	43	64	69	75
2	**2**	*i*PrOK	55	82	89	90
3	**3**	*i*PrOK	18	59	76	80
4	**4**	*i*PrOK	76	88	90	91

[a] Reaction conditions: acetophenone (3.2 mmol), catalysts **1-4** (0.1 mol%) and base (2 mol%) dissolved in *i*PrOH 4 mL. [b] Conversion determined by GC.

After examining the effects of various bases in the presence of catalyst **4**, we found only a trace amount of desired product was detected in the absence of base, indicating presence of a base is essential for the reaction to proceed efficiently (Table 2, entry 10). Strong bases showed a better promotional role than the weak ones (Table 2, entries 1-9). KOH was selected as the reaction promoter although *i*PrOK, *i*PrONa, *i*PrOLi also worked well in reaction.

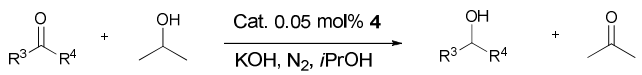
Table 2. Optimizing condition of base for TH of ketones[a].

Entry	Base	Conv. (%)[b]			
		10 min	60 min	120 min	240 min
1	*t*BuOK	61	87	88	90
2	*i*PrOK	76	88	90	91
3	*i*PrONa	75	89	90	90
4	*i*PrOLi	75	89	90	91
5	KOH	85	90	90	91
6	K_3PO_4	67	83	84	85
7	K_2CO_3	35	50	58	68
8	$NaHCO_3$	56	76	80	85
9	CH_3COOK	--	--	--	--
10	--	--	--	--	--

a Reaction conditions: acetophenone (3.2 mmol), catalyst 4 (0.1 mol%) and base (2 mol%) dissolved in *i*PrOH 4 mL. b Conversion determined by GC.

After attempts to scope optimizing control of reaction condition, we found the transformation was smoothly performed in the presence of KOH with the substrate to catalyst ratio (2000:1), using *i*PrOH as hydrogen source. Next, the complex **4** catalytic behavior has been explored with aryl-substituted acetophenone derivatives and additional ketones as substrates (Table 3).

Table 3. Transfer hydrogenation of various ketones[a]



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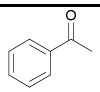
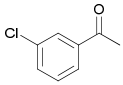
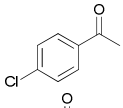
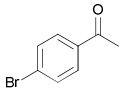
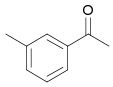
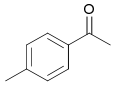
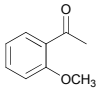
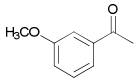
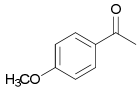
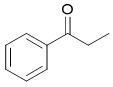
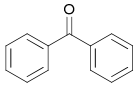
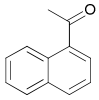
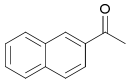
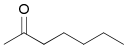
Entry	Ketones	Time(min)	Conv.(%)[b]	TOF(h^{-1})[c]
1		10	97(73)	43800
2		30	98(50)	30000
3		5	98(83)	49800
4		5	96(82)	49200
5		60	96(40)	24000
6		10	94(76)	45600
7		10	98(86)	51600
8		900	93[d](35)	10500
9		30	91(76)	45600
10		60	92(27)	16200
11		120	93(28)	16800
12		900	71[d](18)	5400
13		60	92(38)	22800
14		30	98(42)	25200
15		120	97[d](48)	14400
16		30	93(61)	36600
17		1200	53[e](27)	4050
18		120	90(26)	15600
19		30	99(63)	37800
20		60	92(46)	27600
21		60	90(30)	18000

[a] Reaction conditions: acetophenone (3.2 mmol), catalyst **4** (0.05 mol%) , KOH (2.0 mol%), *i*PrOH 4 mL.

[b] Conversion determined by GC. Data in parentheses are the GC yields after 2 min.

[c] TOF in 2 min.

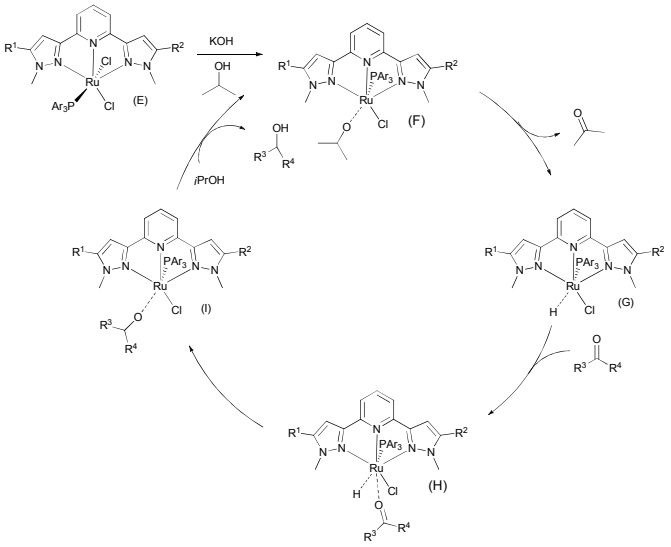
[d] 0.1 mol % **4** was used.

[e] 0.2 mol % **4** was used.

As seen in Table 3, most of the substrates could be converted in good to excellent yields (≥ 90 %) and TOF value of 12000-51600 h^{-1} as initial reaction. Favorable yields were expected for the relatively weaker electron-deficient substrates (Table 3, entries 2-6, 14) as the strong electron withdrawing group CF_3 in the substrate reduced the electron density in the ketone group and deteriorated the catalytic efficiency (Table 3, entry 15). It should be noted that the electron-donating substituents, that is, methyl and methoxyl, made the ketone substrates more electron-rich and thus reacted less efficiently than their analogues bearing electron-deficient moiety (Table 3, entries 3 vs 8, 11 and 4, 6 vs 9, 12 and 2, 5 vs 10) except 2'-chloroacetophenone (Table 3, entry 7).

As anticipated, increasing the steric hindrance of substrates retarded the reaction. But attempt to prolong reaction time or enlarge catalyst loading, it provided satisfactory yields (Table 3, entries 16-19). Surprisingly, although acetophenone bearing an *ortho*-Cl, Br substituent reacted slower than those bearing *meta* or *para* substituents, a contradictory result was observed for the *ortho*-methyl, methoxyl substrates (Table 3, entries 2 vs 3, 4 and 5 vs 6 and 7 vs 8, 9 and 10 vs 11, 12).

According to the related reported literature[16b-16d, 20], we were encouraged to propose the plausible mechanism in Scheme 5, even though the Ru-H active species of complex **4** was not isolated successfully. Ru(II) species (E) forms Ru(II)-alkoxide (F) under the presence of KOH and *i*PrOH, then the subsequent *β*-H elimination from (F) generates Ru(II)-H intermediate (G) with release of acetone. Coordination to the metal center and insertion to the Ru-H bond in (G) by the carbonyl of a ketone substrate yields Ru(II)-alkoxide (I), which undergoes alcohol metathesis to give the desired product and complete the catalytic cycle.



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Scheme 5. The plausible catalytic cycle

Experimental Section

General considerations

Unless otherwise noted, all the starting materials were purchased from commercial sources and used as received. The solvents were dried with the standard procedures prior to use. All the preparation and purification of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using the standard Schlenk techniques. Ligands **L1** and **L2** were prepared by means of literature procedure.[18a] ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded using a Bruker Advance II-400 MHz spectrometer. The chemical shifts of ^{31}P{^{1}H} NMR were relative to 85% H_3PO_4 as external standard, and ^{1}H NMR relative to TMS as internal standard. Elemental analysis was carried out on an Italy CARLO ERBA 1106 Elemental analyzer. Mass Spectra (MS) was performed on an Agilent LCMS-IT-TOF Premier mass spectrometer. Single crystals of **2** and **4** were measured on a Xcalibur, Eos diffractometer using graphite monochromated Mo Kα radiation (λ = 0.7107 Å) at 142.95(10) K and 140.00(10) K, respectively. Using Olex2, the structure was solved with the Superflip structure solution program using Charge Flipping and refined with the **ShelXL-2012** refinement package using Least Squares minimisation. The chromatographic analyses (GC) were performed with an
GC Agilent 6890N instrument equipped with an FID detector and EC- WAX capillary column (30 m×0.25 mm, 0.25 μm film) was used to detect the reaction products.

Synthesis of Ru(II) complexes 1-4

Under nitrogen atmosphere, a mixture of $RuCl_3 \cdot 3H_2O$ (143 mg, 0.55 mmol) and **L1** or **L2** (215/146 mg, 0.55 mmol) in EtOH (30 mL) was refluxed for 5 h. The color of the solution changed from black brown to red-brown slowly and further generated the red-brown precipitates. After being cooled to room temperature, the precipitates were filtered, washed with EtOH and Et_2O, and dried under vacuum. Without purification, this compound was slurried in the EtOH solution (15 mL) of MOTPP/TPP/TFTPP (194/144/256 mg, 0.55 mmol) and was treated with excess Et_3N (1 mL). The solid substance slowly dissolved and the colour of the solution changed to red-orange. After refluxed 6 h, the red-orange solution was cooled to room temperature and the solvent was removed under vacuum to give a solid red substance.

Complex 1: red solid (306 mg, 61%). ^{1}H NMR (400 MHz, CD_2Cl_2, TMS, 25 ^{o}C, ppm): δ 7.53 (t, ^3J(H,H) = 7.2 Hz, 4H, phenyl), 7.48 (dd, ^3J(H,H) = 11.3, 7.4 Hz, 3H, 4-pyridyl, phenyl), 7.44 (d, ^3J(H,H) = 7.1 Hz, 4H, phenyl), 7.33 (d, ^3J(H,H) = 7.8 Hz, 2H, 3,5-pyridyl), 7.07 (t, ^3J(H,H) = 9.0 Hz, 6H, phenyl), 6.85 (s, 2H, pyrazolyl), 6.67 (d, ^3J(H,H) = 8.0 Hz, 6H, phenyl), 4.17 (s, 6H, NCH_3), 3.75 (s, 9H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, TMS, 25 ^{o}C, ppm): δ 160.0 (phenyl C), 155.9 (pyridyl C), 152.1 (pyrazolyl C), 147.8 (pyridyl CH), 134.7 (phenyl C), 131.7 (pyrazolyl C), 129.3 (phenyl C), 129.2 (phenyl CH), 128.9 (phenyl CH), 125.7 (phenyl CH), 125.2 (pyridyl CH), 116.7 (phenyl CH), 113.1 (phenyl CH), 104.6 (pyrazolyl CH), 55.2 (s, OCH_3), 39.7 (s, NCH_3). ^{31}P NMR (162 MHz, $CDCl_3$, 25 ^{o}C, ppm): δ 39.9. Anal. Calcd for $C_{46}H_{42}Cl_2N_5O_3PRu$ (915.14): C, 60.33; H, 4.62; N, 7.65. Found: C, 60.36; H, 4.58; N, 7.62. HRMS (ESI) m/z: Calcd for $C_{46}H_{42}Cl_2N_5O_3PRuNa$ $[M+Na]^+$: 938.1344. found: 938.1338. $C_{46}H_{42}Cl_2N_5O_3PRu$ (915.1446).

Complex 2: red solid (308 mg, 68%). ^{1}H NMR (400 MHz, CD_2Cl_2, TMS, 25 ^{o}C, ppm): δ 7.54 (d, ^3J(H,H) = 6.6 Hz, 3H, phenyl), 7.50 (d, ^3J(H,H) = 3.9 Hz, 3H, 4-pyridyl, phenyl), 7.48 (s, 1H, phenyl), 7.45–7.41 (m, 6H, phenyl), 7.30 (d, ^3J(H,H) = 7.6 Hz, 4H, phenyl), 7.23 (d, ^3J(H,H) = 7.3 Hz, 2H, 3,5-pyridyl), 7.17 (dd, ^3J(H,H) = 7.5, 3.3 Hz, 9H, phenyl), 6.84 (s, 2H, pyrazolyl), 4.16 (s, 6H, NCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, TMS, 25 ^{o}C, ppm): δ 155.7 (pyridyl C), 152.1 (pyrazolyl C), 147.6 (pyridyl CH), 137.9 (phenyl C), 133.9 (pyrazolyl C), 133.3 (phenyl CH), 132.0 (phenyl CH), 129.3 (phenyl C), 128.9 (phenyl CH), 128.2 (phenyl CH), 127.5 (phenyl CH), 125.3 (pyridyl CH), 116.9(phenyl CH), 104.8 (pyrazolyl CH), 39.7 (s, NCH_3). ^{31}P NMR (162 MHz, $CDCl_3$, 25 ^{o}C, ppm): δ 43.9. Anal. Calcd for $C_{43}H_{36}Cl_2N_5PRu$ (825.11): C, 62.55; H, 4.39; N, 8.48. found: C, 62.47; H, 4.35; N 8.41. HRMS (ESI) m/z: Calcd for $C_{43}H_{36}Cl_2N_5PRuNa$ $[M+Na]^+$: 848.1027. found: 848.1021. $C_{43}H_{36}Cl_2N_5PRu$ (825.1129).

Complex 3: red solid (413 mg, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2, TMS, 25 ^{o}C, ppm): δ 7.54 (d, ^3J(H,H) = 6.6 Hz, 2H, phenyl), 7.50 (dd, ^3J(H,H) = 14.1, 8.7 Hz, 5H, 4-pyridyl, phenyl), 7.46 (d, ^3J(H,H) = 7.3 Hz, 6H, phenyl), 7.43 (t, ^3J(H,H) = 8.7 Hz, 6H, phenyl), 7.37 (d, ^3J(H,H) = 6.7 Hz, 4H, phenyl), 7.32 (d, ^3J(H,H) = 7.8 Hz, 2H, 3,5-pyridyl), 6.86 (s, 2H, pyrazolyl), 4.19 (s, 6H, NCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, TMS, 25 ^{o}C, ppm): δ 155.3 (pyridyl C), 151.9 (pyrazolyl C), 148.6 (pyridyl CH), 137.7 (pyrazoly C), 137.3 (phenyl C), 133.4 (phenyl CH), 132.8 (phenyl CH), 131.7 (phenyl C), 131.4 (phenyl C), 129.7 (phenyl CH), 129.1 (phenyl CH), 128.7 (phenyl CH), 124.7 (s, CF_3), 117.3 (pyridy CH), 105.1 (pyrazolyl CH), 39.9 (s, NCH_3); ^{31}P NMR (162 MHz, $CDCl_3$, 25 ^{o}C, ppm): δ 45.8. Anal. Calcd for $C_{46}H_{33}Cl_2N_5F_9PRu$ (1029.08): C, 53.65; H, 3.23; N, 6.80. found: C, 53.89; H, 3.29; N 6.81. HRMS (ESI) m/z: Calcd for $C_{46}H_{33}Cl_2N_5F_9PRuNa$ $[M+Na]^+$: 1052.0648. found: 1052.0641. $C_{46}H_{33}Cl_2N_5F_9PRu$ (1029.0750).

Complex 4: red solid (246 mg, 64%). ^{1}H NMR (400 MHz, CD_2Cl_2, TMS, 25 ^{o}C, ppm): δ 7.36 (t, ^3J(H,H) = 7.8 Hz, 1H, 4-pyridyl), 7.26–7.22 (m, 3H, phenyl), 7.17 (d, ^3J(H,H) = 7.8 Hz, 2H, 3,5-pyridyl), 7.09 (dd, ^3J(H,H) = 7.9, 2.8 Hz 12H, phenyl), 6.55 (s, 2H, pyrazolyl), 4.01 (s, 6H, NCH_3), 2.33 (s, 6H, CCH_3). ^{13}C NMR (101 MHz, $CDCl_3$, TMS, 25 ^{o}C, ppm): δ 155.9 (pyridyl C), 151.2 (pyrazolyl C), 142.4 (pyridyl CH), 134.2 (pyrazolyl C), 133.4 (phenyl C), 131.9 (phenyl CH), 128.8 (phenyl CH), 127.4 (phenyl CH), 116.3 (pyridy CH), 104.5 (pyrazolyl CH), 37.3 (s, NCH_3), 12.3 (s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$, 25 ^{o}C, ppm): δ 44.1. Anal. Calcd for $C_{33}H_{32}Cl_2N_5PRu$ (701.08): C, 56.49; H, 4.60; N, 9.98. found: C, 56.38; H, 4.67; N 9.69. HRMS (ESI) m/z: Calcd for $C_{33}H_{32}Cl_2N_5PRuNa$ $[M+Na]^+$: 724.0714. found: 724.0709. $C_{33}H_{32}Cl_2N_5PRu$ (701.0816).

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Typical procedure for the catalytic transfer hydrogenation of ketones

Under nitrogen atmosphere, ketone (3.2 mmol), catalyst (1.6 μmol) and 2-propanol (3 mL) were introduced into a Schlenk tube. The solution was stirred at 82 °C for 10 min. Then 1 mL of 0.064 mmol KOH 2-propanol solution was introduced to initiate the transfer hydrogenation. At the state time, 0.1 mL of the reaction mixture was sampled and diluted with 1 mL of 2-propanol pre-cooled at -10°C for immediate for GC analysis. The conversions are determined by average of two runs of each catalytic reaction. After the reaction was finished, the mixture was purified by flash silica gel column chromatography [petroleum ether (60-90°C)/EtOAc = 50:1] to afford the corresponding alcohol product, which was identified by comparison with the authentic sample through NMR and GC analysis.

Conclusions

Versatile pincer type tridentate pyridine-bridged framework, not incorporating NH group, and their Ru(II) complexes were successfully synthesized and characterized. These ruthenium complexes, featuring no NH functionality, still exhibited very high catalytic activity in the TH reaction of ketones with a high substrate to catalyst ratio (2000:1).

Notes and references

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Electronic supplementary information (ESI) available: Details of the X-ray crystallographic data and refinement of complexes **2** and **4**. CCDC reference numbers 999183 and 999184.

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