Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2016, **45**, 17843

Diruthenium(II)–NNN pincer complex catalysts for transfer hydrogenation of ketones†

Huining Chai,[a] Qingfu Wang,[a] Tingting Liu[a] and Zhengkun Yu*[a,b]

Received 18th September 2016,
Accepted 10th October 2016

DOI: 10.1039/c6dt03620a

www.rsc.org/dalton

Dinuclear ruthenium(II)–NNN pincer complexes bearing a π linker-supported bis(pyrazolyl-imidazolyl-pyridine) ligand were synthesized and structurally characterized, and they exhibited excellent catalytic activity for the transfer hydrogenation of ketones in refluxing isopropanol, reaching TOF values up to 1.3 × 10^6 h^{-1}. Compared with the corresponding mononuclear Ru(II)–NNN pincer complexes, the bimetallic complexes could be applied at concentrations as low as 0.03 mol% Ru and demonstrated remarkably enhanced catalytic activity in the transfer hydrogenation reactions of ketones. The high catalytic activity of the diruthenium(II) complexes is attributed to the excellent stability and possible cooperativity of the two coordinated Ru(II) metal centers through the π linker. The present synthetic methodology has established an applicable strategy to construct highly active bimetallic NNN pincer complex catalysts.

Introduction

The construction of highly active metal complex catalysts has been a challenging task in homogeneous catalysis and organic synthesis.[1] Organometallic complexes that incorporate more than one metal center may exhibit unusual reactivity and/or catalytic activity due to the cooperative electronic and steric effects from the ligand and metal centers.[2] Particularly, bimetallic complexes have been paid much attention due to their potential to effect efficient catalysis.[3] In this context, an array of bimetallic complex catalysts have recently been documented. Diruthenium complexes for selective intramolecular allylic C–H amination[4a] and 1,3-insertion of carbenes into N–H and O–H bonds[4b] were reported. Dinuclear Au(II) complexes acted as the key intermediates for gold-catalyzed heteroarylation.[4c] Bimetallic boryl-cobalt (or nickel) complexes catalyzed olefin hydrogenation.[4d] Both dinuclear cobalt and ruthenium N-heterocyclic complexes promoted the oxidation of water.[4e,f] Oxo-bridged bimetallic titanium(salen) complexes exhibited high catalytic activity in the enantioselective cyanation of aldehydes,[4g] and bimetallic oxovanadium complexes effected the enantioselective oxidative coupling of 2-naphthols.[4h] The cooperativity effects of zirconium-based bimetallic complexes played a key role in the olefin polymerization catalysis.[4i] Heterobimetallic Ru–Cu complexes facilitated the E-selective semi-hydrogenation of alkynes.[4j]

Transition metal-catalyzed transfer hydrogenation has been well explored as a potentially useful method for the reduction of ketones to alcohols.[5] Mononuclear transition metal complex catalysts have usually been employed for this purpose,[6–9] whereas only a few less efficient bimetallic transition metal complex catalysts have been reported in this area to date.[10] We recently established a strategy for constructing highly active mononuclear ruthenium(II)–NNN pincer complex catalysts for the transfer hydrogenation of ketones.[11,12] In this regard, unsymmetrical tridentate pyrazolyl-imidazolyl-pyridines and pyrazolyl-NH-pyrazolyl-pyridine were used as ligands to synthesize the corresponding Ru(II)–NNN pincer complex catalysts.[11] At the outset of our investigations, we envisioned that the same strategy might be applied for the construction of bimetallic Ru(II)–NNN pincer complex catalysts by linking two such NNN coordinating functionalities with a π-electronic platform. Herein, we disclose the synthesis and catalytic activity of diruthenium(II) bis(pyrazolyl-imidazolyl-pyridine) complexes for the transfer hydrogenation of ketones (Scheme 1).

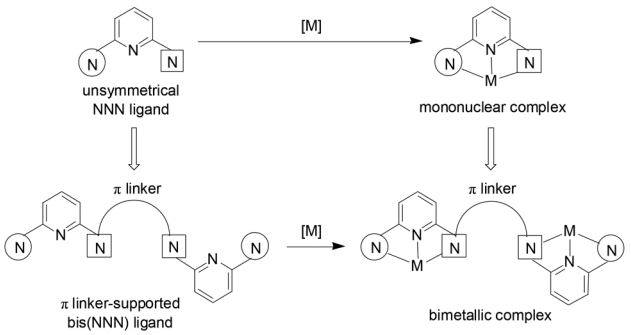
Results and discussion

Bis(pyrazolyl-imidazolyl-pyridine) ligand **5** was synthesized by a multistep synthetic procedure as shown in Scheme 2. The condensation of 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinimidate (**1**)[12d] with *N*,*N*′-(4,5-diamino-1,2-phenylene)bis(4-methylbenzenesulfonamide) (**2**)[13,14] by a modified literature

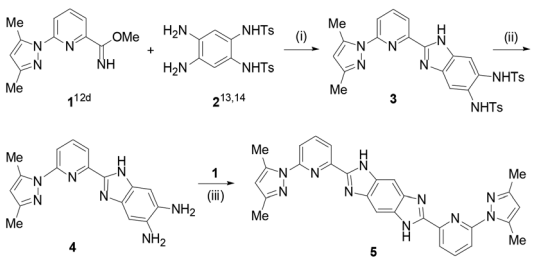
[a]*Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, P. R. China. E-mail: zkyu@dicp.ac.cn; Fax: +86-411-84379227; Tel: +86-411-84379227*

[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China*

† Electronic supplementary information (ESI) available: Experimental details and NMR spectra. CCDC 1053207 and 1002186. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt03620a



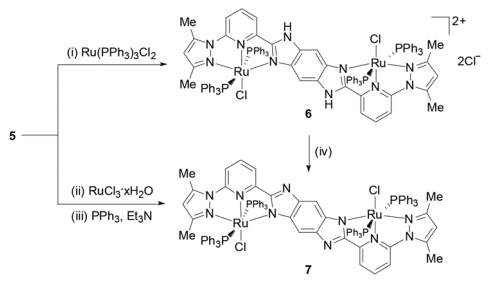
Scheme 1 The design strategy of highly active bimetallic NNN pincer complex catalysts.



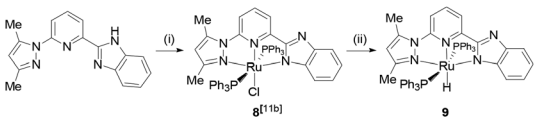
Scheme 2 Synthesis of π linker-supported bis(NNN) ligand **5**. Conditions: (i) AcOH, 118 °C, 4 h, 86%. (ii) Conc. H_2SO_4, 100 °C, 4 h, then Na_2CO_3, 39%. (iii) AcOH, 118 °C, 4 h, 96%.

method[15] afforded tosyl-protected NNN compound **3** in 86% yield. Deprotection of **3** with concentrated sulfuric acid[16] gave diamino-substituted NNN compound **4** (39%). Further condensation of **4** with **1** in glacial acetic acid followed by neutralization with aqueous ammonia yielded the target π linker-supported bis(NNN) ligand **5** (96%) (see the ESI† for details).

Treatment of ligand **5** with $RuCl_2(PPh_3)_3$ in a 1 : 2 molar ratio in refluxing isopropanol formed the cationic diruthenium(II)–NNN pincer complex **6** (92%) (Scheme 3). Alternatively, reacting ligand **5** with 2 equiv. of $RuCl_3{\cdot}xH_2O$ in refluxing ethanol afforded a paramagnetic ruthenium complex in 85% yield, which was then reduced to give the neutral diruthenium(II)–NNN pincer complex **7** (80%) in the presence



Scheme 3 Synthesis of diruthenium(II) complexes **6** and **7**. Conditions: (i) $RuCl_2(PPh_3)_3$, iPrOH, reflux, 0.1 MPa N_2, 6 h, 92%. (ii) $RuCl_3{\cdot}xH_2O$, EtOH, reflux, 0.1 MPa N_2, 5 h, 85%. (iii) PPh_3, Et_3N, EtOH, reflux, 0.1 MPa N_2, 6 h, 80%. (iv) K_2CO_3, CH_2Cl_2, reflux, 0.1 MPa N_2, 5 h, 80%.



Scheme 4 Synthesis of Ru(II) complexes **8** and **9**. Conditions: (i) $Ru(PPh_3)_3Cl_2$, Et_3N, toluene, 110 °C, 0.1 MPa N_2, 2 h, 85%; (ii) K_2CO_3, iPrOH, 82 °C, 0.1 MPa N_2, 6 h, 61%.

of the PPh_3 ligand and Et_3N base. Complex **6** treated with an excessive amount of K_2CO_3 base by extrusion of two molecules of HCl also afforded complex **7** (80%). In order to compare the catalytic properties of the bimetallic complexes with their corresponding mononuclear NNN pincer complexes complex **8** was prepared by our previously reported procedure,[11b,c] which was reduced to its corresponding hydride complex, that is RuH–NNN pincer complex **9**, in refluxing isopropanol under basic conditions (Scheme 4).

The NMR analyses of new complexes **6**, **7**, and **9** are consistent with their compositions, and **6** and **7** showed very similar resonance signals in their ^1H NMR spectra. The NH resonance signal in **6** was absent because of the H–D exchange in CD_3OD. The $^{31}P\{^1H\}$ NMR signals of **6** and **7** appeared at 21.4 and 26.6 ppm as singlets, respectively, suggesting a different electronic impact from the metal centers and equivalence of the PPh_3 ligands in the two PPh_3 pairs which are positioned *trans* to each other in the bimetallic complexes. Due to the poor solubility of **6** and **7** their $^{13}C\{^1H\}$ NMR spectra were not successfully collected. Complex **9** features a Ru–H bond which was signaled as a triplet at −6.7 ppm in the ^1H NMR spectrum, and in its $^{31}P\{^1H\}$ NMR spectrum a doublet split by the Ru–H hydrogen appeared at 48.5 ppm for the two *trans*-PPh_3 ligands.

The molecular structures of complexes **7** and **9** were further confirmed by the X-ray single crystal structural determinations (see the ESI† for details). In the solid state, bimetallic complex **7** exhibits a centrosymmetrical pattern and the two metal centers are positioned in a distorted octahedral environment established by the tridentate NNN coordinating functionality, two *trans*-PPh_3 ligands, and one chloride, respectively (Fig. 1). The P–Ru–P angle in **7** is 177.4°, which is close to that of 178.8° in the mononuclear complex **8**.[11b] The average Ru–P

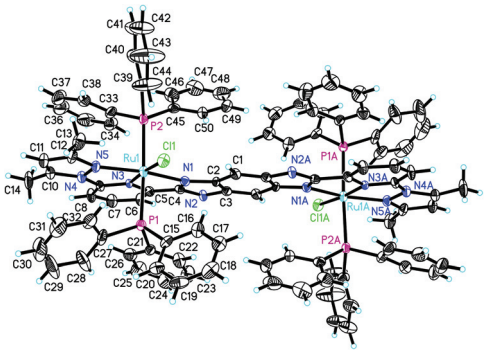


Fig. 1 Molecular structure of diruthenium(II)–NNN pincer complex **7**.

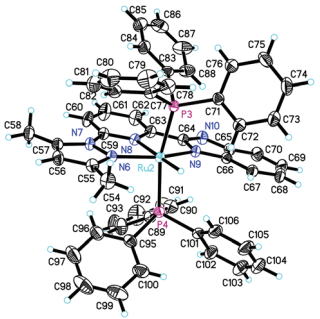
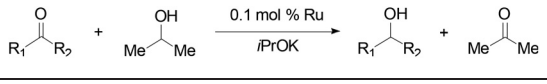


Fig. 2 Molecular structure of RuH NNN pincer complex **9**.

bond length in complex **7** is 2.426 Å, longer than that (2.391 Å) in **8**,[11b] revealing that the metal centers in **7** are in a much more loose environment than the mononuclear metal center in **8**. These data suggest that the bimetallic complex **7** may act as a more catalytically active catalyst than the mononuclear complex **8**. The mononuclear RuH complex **9** presents a coordination pattern similar to that in complexes **6**, **7**, and **8**,[11b] and its P–Ru–P angle and Ru–H bond are 169.6° and 1.52 Å (Fig. 2), respectively. It is noteworthy that in the X-ray crystallographic molecular structures of complexes **7** and **9**, the unit cells include a region of disordered solvent molecules, which could not be modeled as discrete atomic sites. PLATON/SQUEEZE was used to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities. The SQUEEZE calculations showed the residual electron density amounted to 30 electrons per unit cell of complex **7** and 52 electrons per unit cell of complex **9**, corresponding to three molecules of water in complex **7** and one molecule of toluene in complex **9**.

Next, the catalytic activities of complexes **6–9** were comparatively investigated. Under the typical conditions for transfer hydrogenation of ketones,[11–13] these four Ru(II) NNN pincer complexes were tested as catalysts by using the same loading of the metal content, that is 0.1 mol% Ru, for the transfer hydrogenation reactions of acetophenone, 3′-methyl-acetophenone, 2′-chloroacetophenone, 2-acetylnaphthalene, and 2-octone in refluxing isopropanol, respectively. In all the cases the reactions reached 95–99% yields, exclusively forming the corresponding alcohol products (see Table S1 in the ESI† for details). It was found that the bimetallic complex pair **6** and **7**, and the mononuclear complex pair **8** and **9**, exhibited identical catalytic activities, respectively, and complexes **6** and **7** were much more catalytically active than complexes **8** and **9**, demonstrating a catalytic activity order **6** = **7** ≫ **8** = **9**. Thus, the comparative investigation was extended to more ketone substrates by merely employing complexes **7** and **8** as catalysts (Table 1). It should be noted that complexes **6** and **7** could be stored at room temperature over half a year and did not lose their catalytic activity. Using the bimetallic complex catalyst **7** all the substituted acetophenones, 2-acetylnaphthalene, and 2-octone underwent the reactions to exclusively yield the corresponding alcohol products over a period of

Table 1 Comparison of the catalytic activity of complexes **7** and **8** [a]



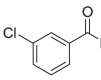
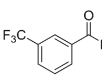
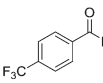
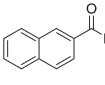
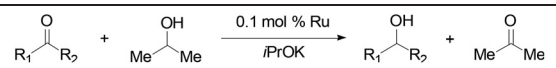
Entry	Cat.	Ketone	Time [min]	Yield[b] [%]
1	7		1 (90)[c]	98 (82)[c]
	8		15 (120)[c]	97[d] (80)[c]
2	7		3	97
	8		60	98[d]
3	7		0.5 (15)[f]	99 (99)[f]
	8		120	98[d]
4	7		1 (40)[c]	97 (80)[c]
	8		5 (60)[c]	98[d] (80)[c]
5	7		0.5	98
	8		10	98[d]
6	7		1	98
	8		20	95
7	7		3	97
	8		10	95
8	7		3	97
	8		5	95
9	7		3	96
	8		40	96
10	7		1	99
	8		30	95
11	7		3	98
	8		30	96
12	7		3	98
	8		120	96[d]
13	7		0.5	100
	8		120	94
14	7		3	97
	8		10	96
15	7		0.5	100
	8		60	37
16	7		10	99
	8		60	95[d]
17	7		5	98
	8		180	95
18	7		2	96
	8		15	95
19	7		10	99
	8		15	99[d]
20	7		7	96
	8		10	96[d]

Table 1 *(Contd.)*



Entry	Cat.	Ketone	Time [min]	Yield[b] [%]
21	7		10	99
	8		240	94[d,e]

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL iPrOH); catalyst, 0.1 mol% Ru (ketone/iPrOK/Ru = 1000 : 20 : 1); 0.1 MPa N_2, 82 °C. [b] Average value from three parallel experiments by GC analysis. [c] Result from the reaction at 40 °C given in parentheses. [d] From ref. 11*b*. [e] Using 0.2 mol% Ru. [f] Scale-up reaction conditions: ketone, 20.0 mmol (1.0 M in 20 mL iPrOH); catalyst 7 (0.005 mol%), 0.01 mol% Ru (ketone/iPrOK/Ru = 10 000 : 20 : 1); 0.1 MPa N_2, 82 °C.

0.5–10 minutes, while the mononuclear complex catalyst **8** exhibited a much lower catalytic activity, rendering the same reactions close to completion within 5–240 minutes (Table 1). For example, complex 7 catalyzed the reactions of acetophenone, 2′-chloroacetophenone, 2′-fluoroacetophenone, and 4-(trifluoromethyl)acetophenone to completion at 1, 0.5, 3, and 0.5 minutes, while the same reactions were finished at 15, 120, 40, and 60 minutes by using complex **8** as the catalyst, respectively (Table 1, entries 1, 3, 9, and 14). Complex 7 exhibited a remarkable enhancement of catalytic activity, which is presumably attributed to its high stability and the possible cooperativity of the two coexisting metal centers in the complex.[2,3] However, the reactions underwent slowly at 40 °C (Table 1, entries 1 and 4).

The kinetic profiles of acetophenone, 4′-fluoroacetophenone, and 3-methylacetophenone catalyzed by complexes 7 and **8** also revealed a remarkable enhancement of the catalytic activity of the bimetallic complex (Fig. 3). Additionally, complex **8** could not promote the reactions to completion or just made the reactions cease at an incomplete conversion of the ketone substrates when a catalyst loading of <0.1 mol% Ru was applied (see Table S2 in the ESI†). These results have revealed that the complex catalysts have a concentration limit applicable for the transfer hydrogenation reactions, suggesting that bimetallic complex 7 is more stable than mononuclear complex **8** under the stated reaction conditions, and can be applied at a lower concentration than complex **8**. Moreover, based on the kinetic profiles obtained from the reaction of 3-methylacetophenone (Table 1, entry 17, and Fig. 3), the cooperativity of the two coordinated Ru(II) metal centers through the π linker is possibly present to enhance the catalytic activity of the diruthenium(II)–NNN pincer complex. Furthermore, the reaction was scaled up to 10 000 : 1 of ketone/Ru by using 20 mmol of 2′-chloroacetophenone and 0.005 mol% complex 7, and the corresponding alcohol product was obtained in 99% yield within 15 minutes (Table 1, entry 3).

Then, the catalytic activity of bimetallic complex 7 was further explored at a lower catalyst loading (0.025 mol% 7), that is 0.05 mol% Ru, for the transfer hydrogenation of ketones (Table 2). At such a low catalyst concentration, the reaction of acetophenone became relatively slow to be complete within 20 minutes, achieving a TOF value of 1.5×10^5 h^{-1} at 50% conversation of the ketone substrate (Table 2, entry 1). The chloro and bromo substituents on the phenyl ring of the substituted acetophenones exhibited an acceleration effect on

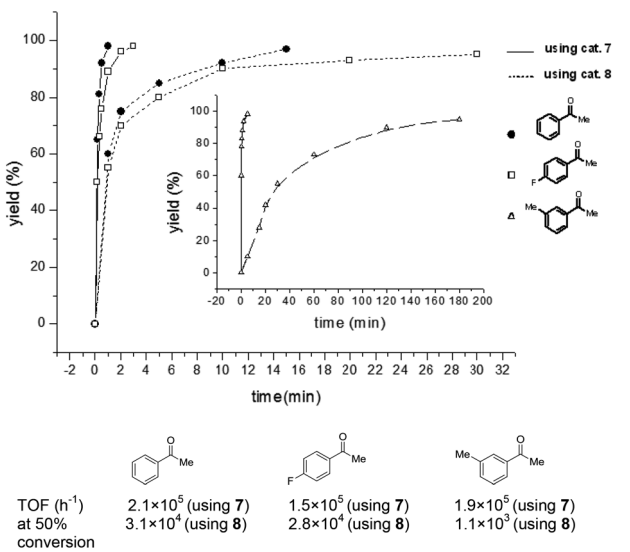
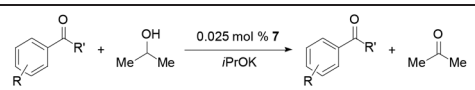
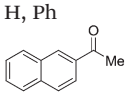
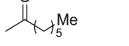


Fig. 3 Representative kinetic profiles using 0.1 mol% Ru under the conditions shown in Table 1.

Table 2 Transfer hydrogenation catalyzed by complex 7[a]



Entry	R, R′	Time [min]	Yield[b] [%]	TOF[c] [h^{-1}]
1	H, Me	20	98	1.5×10^5
2	H, Et	20	95	4.7×10^4
3[d]	*o*-Cl, Me	2	98	8.1×10^5
4[d]	*m*-Cl, Me	3	98	4.7×10^5
5[d]	*p*-Cl, Me	2	98	1.3×10^6
6	*o*-Br, Me	5	97	1.4×10^5
7	*m*-Br, Me	15	98	2.2×10^4
8	*p*-Br, Me	5	97	3.0×10^5
9	*o*-F, Me	20	96	3.8×10^4
10	*m*-F, Me	20	98	3.9×10^4
11	*p*-F, Me	25	95	4.0×10^5
12	*o*-CF_3, Me	0.5	100	1.1×10^6
13	*m*-CF_3, Me	10	97	3.2×10^4
14[e]	*o*-Me, Me	30	96	3.7×10^4
15[e]	*m*-Me, Me	15	98	2.1×10^5
16[e]	*p*-Me, Me	10	96	2.3×10^5
17[f]	*m*-OMe, Me	20	98	1.1×10^5
18	H, Ph	30	98	1.5×10^5
19		20	96	4.2×10^5
20[f]		15	98	1.2×10^4

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL iPrOH); catalyst 7, 0.025 mol% (ketone/iPrOK/Ru = 2000 : 20 : 1); 0.1 MPa N_2, 82 °C. [b] Average value from three parallel experiments by GC analysis. [c] Turnover frequency (moles of ketone converted per mol of Ru per hour) at 50% conversion of the ketone. [d] 0.015 mol% 7 (0.03 mol% Ru). [e] 0.03 mol% 7. [f] 0.04 mol% 7.

the reactions (Table 1, entries 3–8). Surprisingly, in the cases of chloro-substituted acetophenones the applicable catalyst loading was as low as 0.015 mol% **7** (0.03 mol% Ru), and the reactions were complete within 2–3 minutes, reaching a maximum TOF value of 1.3×10^6 h^{-1} (Table 2, entries 3–5). The substituent effect from electron-withdrawing fluoro, and trifluoromethyl, and electron-donating methyl and methoxy varied, rendering the reactions to be complete over a period of 0.5–30 minutes, achieving TOF values in the region of 3.2×10^4–1.1×10^6 h^{-1} (Table 2, entries 9–16). It should be noted that the *o*-trifluoromethyl substituent exhibited a remarkable acceleration effect: the reaction was finished within 0.5 minutes, achieving 100% conversion and a TOF value of 1.1×10^6 h^{-1} (Table 2, entry 12). Unexpectedly, sterically hindered benzophenone and 2-acetylnaphthalene smoothly underwent the reaction to produce the corresponding alcohol products in 96–98% yields (Table 2, entries 18 and 19). Using a higher catalyst loading (0.04 mol%) 2-octone also efficiently reacted to form the target product (Table 2, entry 20). These results have illustrated a rare efficient catalyst system for the transfer hydrogenation of ketones at a low catalyst loading.[8,11–13] It is noteworthy that one of Baratta's Ru(II)–NNC complexes could reach a TOF value of 3.8×10^6 h^{-1} with 99% conversion within 0.5 minutes at 0.005 mol% catalyst loading in the transfer hydrogenation of 3′-bromoacetophenone.[8d]

Based on the comparative investigation of the catalytic activity of complexes **8** and **9** (see Table S1 in the ESI†) we can reasonably conclude that Ru(II) hydride may act as the catalytically active species for the transfer hydrogenation of ketones.[17] The Ru(II) hydride species is initially generated *in situ* from the Ru(II)–Cl precatalyst by interaction with potassium alkoxide under the stated reaction conditions. Then, the *in situ* generated RuH species catalyzes the reduction of ketone *via* a possible inner-sphere pathway[18] (see Scheme S1 in the ESI†).

Conclusions

In summary, diruthenium(II) bis(pyrazolyl-imidazolyl-pyridine) pincer complexes have been successfully synthesized, and they exhibited very high catalytic activity for the transfer hydrogenation of ketones at low catalyst loadings. The present protocol provides an applicable route to highly active bimetallic NNN pincer complex catalysts for homogeneous catalysis and organic synthesis.

Experimental

General considerations

All the manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using the standard Schlenk techniques. The solvents were dried and distilled prior to use by the literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ (δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm) and DMSO-d_6 (δ(^{1}H), 2.50 ppm; δ(^{13}C), 39.52 ppm). Elemental and HRMS analyses were performed by the Analysis Center, Dalian University of Technology and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. All the melting points were uncorrected. TLC analysis was performed by using glass-backed plates coated with 0.2 mm silica gel. Flash column chromatography was performed on silica gel (200–300 meshes). All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

Synthesis of ligands and complexes

Synthesis of compound 4. A mixture of compound **3** (628 mg, 1.0 mmol) and 5 mL concentrated sulfuric acid was heated at 100 °C for 4 h. The resulting dark violet mixture was carefully poured into 50 mL ice water. Treatment of the resultant mixture with saturated aqueous Na_2CO_3 was performed until the solution became basic (pH > 8), forming a clear green solution. The green solution was then extracted with dichloromethane (3 × 60 mL). The combined organic phase was dried over $MgSO_4$, and filtered. Removal of all the volatiles under reduced pressure gave the product as a green solid (130 mg, 39% yield). Mp: 198–201 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.74 (s, 1 H, NH), 8.04 and 7.66 (d each, J = 7.7 and 7.8 Hz, 1 : 1 H, 3-H and 5-H), 7.99 (t, J = 7.8 Hz, 1 H, 4-H), 6.83 and 6.74 (s each, 1 : 1 H, 8″-H and 5″-H), 6.16 (s, 1 H, 4′-H), 4.68 and 4.37 (s each, 2 : 2 H, 5″-NH_2 and 8″-NH_2), 2.71 (s, 3 H, C3′-CH_3), 2.23 (s, 3 H, C5′-CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 152.4 and 148.9 (s and Cq each, C2 and C6), 147.7 and 141.1 (s and Cq each, C3′ and C5′), δ 145.9 (s and Cq, C2″), 139.5 and 135.5 (s and Cq each, C4″ and C9″), 137.4 (s, C4), 133.3 and 129.0 (s and Cq each, C7″ and C6″), 117.6 and 115.1 (s each, C8″ and C5″), 108.6 and 102.9 (s each, C3 and C5), 95.4 (s, C4′), 13.9 (s, C3′-CH_3), 13.4 (s, C5′-CH_3). HRMS: calcd for $C_{17}H_{17}N_7$ 319.1545, found 319.1556.

Synthesis of compound 5. A mixture of methyl 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-picolinimidate (**1**) (80 mg, 0.3 mmol) and compound **4** (115 mg, 0.3 mmol) in 10 mL glacial acetic acid was stirred at reflux under a nitrogen atmosphere for 4 h. The resultant mixture was cooled to ambient temperature, followed by addition of 30 mL water and neutralization with aqueous ammonia (25%, 5 mL). The precipitate was collected by filtration and dried under reduced pressure. Further purification by silica gel column chromatography (CH_2Cl_2/CH_3OH, 20 : 1, v/v) afforded the target product as a light yellow solid (150 mg, 96% yield). Mp: >300 °C dec. ^{1}H NMR (TFA-*d*, 400 MHz): δ 8.20 (m, 4 H, 3-H and 5-H), 8.08 (t, J = 7.7 Hz, 2 H, 4-H), 7.67 and 7.65 (s each, 1 : 1 H, 6″-H), 6.21 (s, 2 H, 4′-H), 2.33 (s, 6 H, C3′-CH_3), 2.20 (s, 6 H, C5′-CH_3). ^{13}C{^{1}H} NMR (TFA-*d*, 100 MHz) δ 149.8 (s and Cq, C6), 148.4 (s and Cq, C3′), 147.1 (s and Cq, C2), 145.9 (s, C4), 142.8 (s and Cq, C5′), 139.2 and 130.3 (s and Cq each, C5″ and C4″), 124.2 and 120.1 (s each, C3 and C5), 111.0 (s, C4′), 100.5 (s C6″). IR (KBr pellets, cm^{-1}): 3402, 2926, 1634, 1596, 1580, 1483, 1464, 1440, 1408, 1384, 1364, 1289, 1246, 971, 815, 775, 724, 656. HRMS: calcd for $C_{28}H_{24}N_{10}$ 500.2185, found 500.2187.

Synthesis of complex 6. Under a nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (96 mg, 0.10 mmol) and ligand **5** (25 mg, 0.05 mmol) in 2-propanol (10 mL) was stirred at reflux for 6 h. The resulting mixture was cooled to ambient temperature and the resultant red precipitate was filtered off, rinsed with diethyl ether (4 × 6 mL), and dried under reduced pressure to afford the target complex product as a red-brown crystalline solid (90 mg, 92% yield). Mp: >300 °C dec. ^{1}H NMR ($CDCl_3$/CD_3OD, 400 MHz): δ 8.52 (s, 2 H, 6″-H), 7.59 (m, 2H, 4-H), 7.41 and 7.33 (d each, J = 8.6 Hz and J = 7.7 Hz, 2 : 2 H, 3-H and 5-H), 7.17, 7.10 and 7.00 (m each, 24 : 12 : 24 H, 4 × PPh_3), 6.17 (s, 2 H, 4′-H), 2.77 and 2.18 (s each, 6 : 6 H, methyl of pyrazolyl). Due to poor solubility, the $^{13}C\{^1H\}$ NMR is not available. $^{31}P\{^1H\}$ NMR ($CDCl_3$/CD_3OD, 162 MHz): δ 21.6 (s, 4 × PPh_3). IR (KBr pellets, cm^{-1}): 3417, 3051, 1610, 1556, 1482, 1432, 1412, 1307, 1092, 741, 698, 521. Anal. Calcd for $C_{101}H_{87}Cl_4N_{10}P_4Ru_2$: C, 63.56; H, 4.59; N, 7.34. Found: C, 63.15; H, 4.61; N, 7.32.

Synthesis of complex 7. Under a nitrogen atmosphere a mixture of $RuCl_3{\cdot}xH_2O$ (26 mg, 0.10 mmol) and ligand **5** (25 mg, 0.05 mmol) in ethanol (20 mL) was stirred at reflux for 5 h. After the mixture was cooled to ambient temperature, the resultant precipitate was filtered off, rinsed with diethyl ether (3 × 5 mL), and dried under reduced pressure to afford a brown powder (38 mg, 0.04 mmol). The brown powder was then reacted with PPh_3 (43 mg, 0.16 mmol) and triethylamine (1.0 mL) in EtOH (5 mL) at reflux for 6 h under a nitrogen atmosphere. After the mixture was cooled to ambient temperature, the resultant precipitate was filtered off, rinsed with diethyl ether (3 × 5 mL), and dried under reduced pressure to give the complex product as a red powder (60 mg, 80% yield). Single crystals suitable for X-ray crystallographic determination were grown from the recrystallization of **7** in $CHCl_3$/CH_3OH/*n*-hexane (20 : 1 : 60, v/v/v) at 25 °C.

Mp: >300 °C dec. ^{1}H NMR ($CDCl_3$/CD_3OD, 400 MHz): δ 8.49 (s, 2 H, 6″-H), 7.54 (t, J = 8.1, 2 H, 4-H), 7.34 and 7.30 (d each, J = 8.0 Hz and J = 8.4 Hz, 2 : 2 H, 3-H and 5-H), 7.14, 7.07 and 6.97 (m each, 24 : 12 : 24 H, 4 × PPh_3), 6.11 (s, 2 H, 4′-H), 2.73 and 2.19 (s each, 6 : 6 H, methyl of pyrazolyl). Due to poor solubility, the $^{13}C\{^1H\}$ NMR is not available. $^{31}P\{^1H\}$ NMR ($CDCl_3$/CD_3OD, 162 MHz): δ 26.6 (s, 4 × PPh_3). IR (KBr pellets, cm^{-1}): 3420, 3035, 1608, 1553, 1519, 1482, 1465, 1438, 1318, 1091, 744, 696, 516. Anal. Calcd for $C_{101}H_{85}Cl_2N_{10}P_4Ru_2$: C, 66.08; H, 4.67; N, 7.63. Found: C, 66.15; H, 4.61; N, 7.54.

Synthesis of complex 7 from complex 6. Under a nitrogen atmosphere, a mixture of complex **6** (98 mg, 0.05 mmol) and K_2CO_3 (69 mg, 0.50 mmol) in dichloromethane (6 mL) was stirred at reflux for 5 h. The resultant mixture was filtered through a short pad of Celite, and the Celite was rinsed with 5 mL dichloromethane. The combined filtrate was evaporated to remove all the volatiles under reduced pressure to afford complex **7** (75 mg, 80% yield).

Synthesis of complex 9. Complex **8** (403 mg, 0.42 mmol) was reacted with K_2CO_3 (138 mg, 1.0 mmol) in 10 mL refluxing iPrOH for 6 h under a nitrogen atmosphere. After cooling to ambient temperature all the volatiles were removed under reduced pressure, and 5 mL toluene was introduced to dissolve the crude product, followed by filtration to separate the inorganic salts. The filtrate was condensed to 1/3 volume under reduced pressure and then recrystallized in toluene/*n*-hexane (1 : 2, v/v) at ambient temperature to give the target complex product as red-brown crystals (238 mg, 61% yield). Mp: >300 °C dec. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 7.7 Hz, 1 H, 3-H), 7.41 (m, 2 H, 4-H and 5-H), 7.18 (s, 1 H, phenyl CH), 6.99, 6.91 and 6.85 (m each, 6 : 12 : 12 H, 2 × PPh_3), 6.74 and 6.49 (t each, J = 7.2 Hz and J = 7.3 Hz, 6″-H and 7″-H), 6.65 (d, J = 8.0 Hz, 1 H, phenyl CH), 5.60 (s, 1 H, 4′-H), 2.52 (s, 3 H, C3′-CH_3), 1.17 (s, 3 H, C5′-CH_3), −6.71 (t, J = 25.6 Hz, Ru–H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.0 and 153.1 (Cq each, C2 and C6), 152.8 and 145.8 (Cq each, C3′ and C5′), 148.9, 147.3, 132.0 (Cq each, C2″, C4″ and C9″), 140.9 (s, C4), 132.0 (Cq, 2 × PPh_3), 133.1, 128.2 and 127.3 (CH of 2 × PPh_3), 119.4, 119.2, 116.0, 110.8 (s each, phenyl CH), 118.2 and 117.6 (s each, C3 and C5), 105.3 (s, C4′), 16.1 (s, C3′-CH_3), 15.3 (s, C5′-CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 48.5 (d, J(P,H) = 25.0 Hz, 2 × PPh_3). IR (KBr pellets, cm^{-1}): 3438, 3042, 1840, 1600, 1553, 1497, 1478, 1456, 1434, 1408, 1391, 1351, 1321, 1088, 743, 698, 518. Anal. Calcd for $C_{53}H_{45}N_5P_2Ru$: C, 69.57; H, 4.96; N, 7.65. Found: C, 69.51; H, 4.90; N, 7.64.

X-Ray crystallographic studies

Single crystal X-ray diffraction studies for complexes **7** and **9** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 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 the calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1053207 for **7** and CCDC 1002186 for **9**.

A typical procedure for the transfer hydrogenation reactions of ketones

A catalyst solution was prepared by dissolving complex **7** (11.3 mg, 0.006 mmol) in 2-propanol (60 mL). Under a nitrogen atmosphere, a mixture of ketone (2.0 mmol), 10 mL of the catalyst solution (0.001 mmol), and 2-propanol (9.6 mL) was stirred at 82 °C for 5–10 minutes. Then, 0.4 mL of 0.1 M iPrOK (0.04 mmol) solution in 2-propanol was introduced to initiate the reaction. At the stated time, 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of 2-propanol pre-cooled at 0 °C, and filtered through a short pad of Celite to remove the complex catalyst to quench the reaction. The resultant filtrate was used for GC analysis. After the reaction was complete, the reaction mixture was quickly cooled to ambient temperature, filtered through Celite, condensed under reduced pressure, and then subjected to purification by

silica gel column chromatography to afford the corresponding alcohol product which was identified by comparison with the authentic sample through NMR and GC analysis.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (21672209) for financial support of this research.

Notes and references

1 C. Gunanathan and D. Milstein, *Science*, 2013, **341**, 249.

2 For selected recent reviews, see: (*a*) P. Buchwalter, J. Rosś and P. Braunstein, *Chem. Rev.*, 2015, **115**, 28; (*b*) J. A. Meta, F. E. Hahn and E. Peris, *Chem. Sci.*, 2014, **5**, 1723; (*c*) S. Matsunaga and M. Shibasaki, *Chem. Commun.*, 2014, **50**, 1044.

3 For selected recent reports on bimetallic catalysis, see: (*a*) D. L. J. Broere, L. L. Metz, B. de Bruin, J. N. H. Reek, M. A. Siegler and J. I. Vander Vlugt, *Angew. Chem., Int. Ed.*, 2015, **54**, 1516; (*b*) G. Yin, I. Kalvet and F. Schoenebeck, *Angew. Chem., Int. Ed.*, 2015, **54**, 6809; (*c*) W. J. Wolf, M. S. Winston and F. D. Toste, *Nat. Chem.*, 2014, **6**, 159; (*d*) R. J. Burford, W. E. Piers, D. H. Ess and M. Parvez, *J. Am. Chem. Soc.*, 2014, **136**, 3256.

4 For selected recently reported bimetallic complex catalysts, see: (*a*) M. E. Harvey, D. G. Musaev and J. Du Bois, *J. Am. Chem. Soc.*, 2011, **133**, 17207; (*b*) S. Chuprakov, B. T. Worrell, N. Selander, R. K. Sit and V. V. Fokin, *J. Am. Chem. Soc.*, 2014, **13**, 195; (*c*) E. Tkatchouk and N. P. Mankad, *J. Am. Chem. Soc.*, 2011, **133**, 14293; (*d*) T.-P. Lin and J. C. Peters, *J. Am. Chem. Soc.*, 2014, **136**, 13672; (*e*) H.-Y. Wang, E. Mijangos, S. Ott and A. Thapper, *Angew. Chem., Int. Ed.*, 2014, **53**, 14499; (*f*) Y. Jiang, F. Li, B. B. Zhang, X. N. Li, X. H. Wang, F. Huang and L. C. Sun, *Angew. Chem., Int. Ed.*, 2013, **52**, 3398; (*g*) Z. Zhang, Z. Wang, R. Zhang and K. L. Ding, *Angew. Chem., Int. Ed.*, 2010, **38**, 6746; (*h*) Q.-X. Guo, Z.-J. Wu, Z.-B. Luo, Q.-Z. Liu, J.-L. Ye, S.-W. Luo, L.-F. Cun and L.-Z. Gong, *J. Am. Chem. Soc.*, 2007, **129**, 13927; (*i*) J. P. McInnis, M. Delferro and T. J. Marks, *Acc. Chem. Res.*, 2014, **47**, 2545; (*j*) M. K. Karunananda and N. P. Mankad, *J. Am. Chem. Soc.*, 2015, **137**, 14598.

5 D. Wang and D. Astruc, *Chem. Rev.*, 2015, **115**, 6621.

6 R. Noyori and T. Ohkuma, *Angew. Chem., Int. Ed.*, 2001, **40**, 40.

7 (*a*) J. M. Zimbron, M. Dauphinais and A. B. Charette, *Green Chem.*, 2015, **17**, 3255; (*b*) M. Coll, K. Ahlford, O. Pàmies, H. Adolfsson and M. Diéguez, *Adv. Synth. Catal.*, 2012, **354**, 415.

8 For selected recent reports on transfer hydrogenation from the Baratta group, see: (*a*) G. Chelucci, S. Baldino and W. Baratta, *Acc. Chem. Res.*, 2015, **48**, 363; (*b*) G. Chelucci, S. Baldino and W. Baratta, *Coord. Chem. Rev.*, 2015, **300**, 29; (*c*) W. Baratta, C. Barbato, S. Magnolia, K. Siega and P. Rigo, *Chem. – Eur. J.*, 2010, **16**, 3201; (*d*) W. Baratta, M. Ballico, A. Del Zotto, E. Herdtweck, S. Magnolia, R. Peloso, K. Siega, M. Toniutti, E. Zangrando and P. Rigo, *Organometallics*, 2009, **28**, 4421; (*e*) W. Baratta, M. Ballico, G. Chelucci, K. Siega and P. Rigo, *Angew. Chem., Int. Ed.*, 2008, **47**, 4362.

9 (*a*) W. W. Zuo and R. H. Morris, *Nat. Protoc.*, 2015, **10**, 241; (*b*) W. W. Zuo, A. J. Lough, Y. F. Li and R. H. Morris, *Science*, 2013, **342**, 1080.

10 (*a*) Q. Fu, T. Yi, M. J. Zou, X. Y. Wang, H. Y. Fu, R. X. Li and H. Chen, *Inorg. Chem. Commun.*, 2013, **38**, 28; (*b*) M. Aydemir, N. Meric and A. Baysal, *J. Organomet. Chem.*, 2012, **720**, 38; (*c*) L. Wang, Q. Yang, H. Chen and R. X. Li, *Inorg. Chem. Commun.*, 2011, **14**, 1884; (*d*) M. Ito, A. Watanabe, Y. Shibata and T. Ikariya, *Organometallics*, 2010, **29**, 4584; (*e*) M. Aydemir, F. Durap, A. Baysal, N. Meric, A. Buldağ, B. Gümgüm, S. Özkar and L. T. Yıldırım, *J. Mol. Catal. A: Chem.*, 2010, **326**, 75; (*f*) C. Ganesamoorthy, M. S. Balakrishna and J. T. Mague, *J. Organomet. Chem.*, 2009, **694**, 3390; (*g*) M. Aydemir, A. Baysal, N. Meric and B. Gümgüm, *J. Organomet. Chem.*, 2009, **694**, 2488; (*h*) B. Therrien, G. S-Fink, P. Govindaswamy and C. S-Mohamed, *Polyhedron*, 2007, **26**, 4065.

11 (*a*) W. W. Jin, L. D. Wang and Z. K. Yu, *Organometallics*, 2012, **31**, 5664; (*b*) F. L. Zeng and Z. K. Yu, *Organometallics*, 2009, **28**, 1855; (*c*) F. L. Zeng and Z. K. Yu, *Organometallics*, 2008, **27**, 2898.

12 (*a*) W. M. Du, Q. F. Wang, L. D. Wang and Z. K. Yu, *Organometallics*, 2014, **33**, 974; (*b*) W. M. Du, P. Wu, Q. F. Wang and Z. K. Yu, *Organometallics*, 2013, **32**, 3083; (*c*) W. M. Du, L. D. Wang, P. Wu and Z. K. Yu, *Chem. – Eur. J.*, 2012, **18**, 11550; (*d*) W. J. Ye, M. Zhao and Z. K. Yu, *Chem. – Eur. J.*, 2012, **18**, 10843; (*e*) W. J. Ye, M. Zhao, W. M. Du, Q. B. Jiang, K. K. Wu, P. Wu and Z. K. Yu, *Chem. – Eur. J.*, 2011, **17**, 4737.

13 H. N. Chai, T. T. Liu, Q. F. Wang and Z. K. Yu, *Organometallics*, 2015, **34**, 5278.

14 F. E. Arnold, *J. Polym. Sci., Polym. Chem. Ed.*, 1970, **8**, 2079.

15 X. W. Liu, Y. D. Chen, L. Li, J. L. Lu and D. S. Zhang, *Spectrochim. Acta, Part A*, 2012, **86**, 554.

16 A. Kleineweischede and J. Mattay, *Eur. J. Org. Chem.*, 2006, 947.

17 (*a*) R. H. Perry, K. R. Brownell, K. Chingin, T. J. Cahill III, R. M. Waymouth and R. N. Zare, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 2246; (*b*) F. E. Fernández, M. C. Puerta and P. Valerga, *Organometallics*, 2012, **31**, 6868.

18 (*a*) J. Bosson, A. Poater, L. Cavallo and S. P. Nolan, *J. Am. Chem. Soc.*, 2010, **132**, 13146; (*b*) Ó. Pablo, D. Guijarro, G. Kovács, A. Lledós, G. Ujaque and M. Yus, *Chem. – Eur. J.*, 2012, **18**, 1969; (*c*) S. Enthaler, B. Hagemann, S. Bhor, G. Anilkumar, M. K. Tse, B. Bitterlich, K. Junge, G. Erre and M. Beller, *Adv. Synth. Catal.*, 2007, **349**, 853.