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Review article

Mono- and multinuclear pincer-type Ru(II) complex catalysts and their catalytic applications

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Dedicated to Prof. Howard Alper

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ABSTRACT

Various pincer-type ruthenium(II) complexes were developed from our laboratories and herein the relevant advance is summarized from a viewpoint of their synthesis and organic synthetic applications as homogeneous catalysts. The investigated Ru(II)–NNN and Ru(II)–NNNN-type complexes exhibited highly catalytic activities in the transfer hydrogenation of ketones, C–C bond formation from alcohols and ketones, and dehydrogenation. RuH complexes were identified or considered as the catalytically active intermediates for these transformations. This review deals with the following subjects: (i) mononuclear ruthenium(II) pincer complexes with high catalytic activity in (asymmetric) transfer hydrogenation of ketones; (ii) multinuclear ruthenium(II) complexes for transfer hydrogenation of ketones; (iii) mononuclear ruthenium(II) complexes for other reactions such as Oppenauer-type oxidation, β-alkylation of secondary alcohols, synthesis of multisubstituted heterocycles, acceptorless dehydrogenation of *N*-heterocycles and secondary alcohols.

1. Introduction

Ruthenium complexes have been extensively applied as homogeneous catalysts and are of great importance in organic synthesis due to their specific characteristics including low redox potentials, high coordination capacity to heteroatoms, high electron transfer ability and Lewis acid activity [1,2]. The unique reactivity of the metal species and intermediates such as carbene complexes, metallacycles, and oxo-metals made them diversely used in homogeneous catalysis [3]. In the presence of ruthenium complex catalysts, a lot of organic compounds such as alcohols, imines, amines, pyridines, pyrroles, and acetals, as well as carboxylic acid derivatives, esters and amides can be accessed [4]. Consequently, ruthenium catalysis has become an important catalytic tool in organic synthesis [5]. Pincer-type ruthenium(II) complexes often offer higher efficiency, selectivity and functional group tolerance compared to traditional ruthenium(II) catalysts [6]. It has been well known that the molecular structures of ligands are crucial for fine tuning the stereoselectivity and catalytic performances of metal complexes. In general, the catalytic activity of a homogenous transition metal catalyst can be enhanced with its stability decreased. A pincer ligand coordinates to the metal center and thus leads to the formation of two stable rings which could be five- or six-membered (Scheme 1), or a hybrid of both rings that exhibit an exceptional balance of stability versus reactivity [7]. In this regard, pincer ligands are crucial for the construction of our pincer-type ruthenium(II) complex catalysts. Herein, we summarize the strategies for the construction of Ru(II)–NNN and Ru(II)–NNNN-type complex catalysts and their catalytic applications in Yu group over the period of 2005–2022.

2. Synthesis of pincer-type ligands

Pincer-type ligands have played a very important role in coordination and catalytic chemistry since the pioneering work [8] in the 1970 s, which was focused on NCN, CNC, NNN, PCP and PNP-type pincer ligands [9,10]. With the vast array of NCN and CNC pincer ligand types, synthesis of the ligand systems cannot be generalized owing to the

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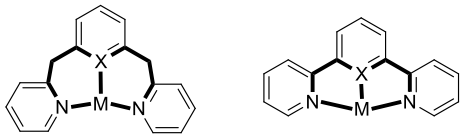
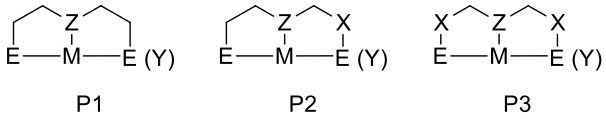
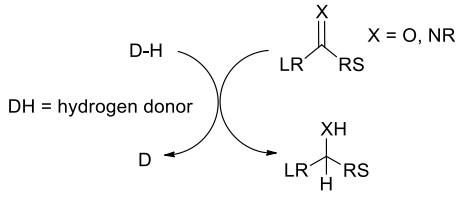


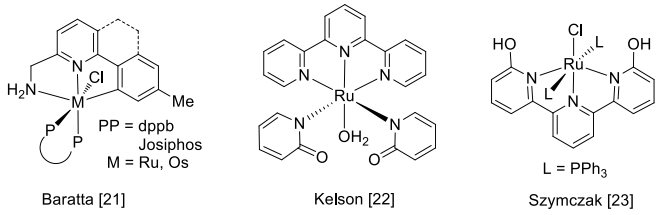
Scheme 1. Typical coordinating moieties in pincer ligands.



Scheme 2. Typical pincer complex architectures.



Scheme 3. Transfer hydrogenation reactions.



Scheme 4. Catalysts for Transfer hydrogenation reactions.

variation in compositions and architectures. To construct diverse NCN and CNC-type ligand systems several moieties/fragments have been employed such as chiral bis(oxazolinyl)phenyl (phebox) [9a], chiral pyrroloimidazolone [9b], and *N*-heterocyclic carbenes (NHCs) [9c,9d]. NHC ligands facilitate wide variations in structures and properties of the complexes which combine the strong electron-donating properties with their steric and electronic tunability. NNN-type pincer ligands are mainly based on bis(imino)pyridines [10a], bis(pyridylimino)isoindoles [10b], the 2,6-bis-amido-pyridine backbone [10c], and 2,6-bis(5-*tert*-buthyl-1H-pyrazol-3-yl)pyridine [10d]. The bridging groups on the backbone of the pincer system allow for different conformations which impact the coordination geometry of the complexes and the metal–ligand interaction. Depending on the spacer between the central aromatic ring and phosphines, different synthetic strategies have been developed for the synthesis of PCP and PNP-type pincer ligands. PNP and PCP ligands with methylene-spacers were prepared from 2,6-bis (bromomethyl)pyridine or 1,3-bis(bromomethyl)benzene by treatment with lithium phosphides [11]. Starting with a 2,6-diaminopyridine or 1,3 diaminobenzene derivative is a simpler method for the preparation of PXP ligands through further interaction with chlorophosphines. However, well defined and tunable ligand systems are usually required for the development of new more efficient catalysis systems to overcome the bottleneck in modern chemistry.

By means of tuning the central moiety of a pincer ligand the tuned electronic/steric properties of the donor sites could modify the coordination capability of the ligand, which can be accomplished in diverse ways. Changing the ring nature (aromatic versus aliphatic), ring itself (benzene, pyridine, acridine, etc.), ring size (five-, six- or seven-membered), or eliminating the ring itself to build an acyclic pincer ligand is the most common means to modify the central group. The pincer complexes are stabilized by the side arms of the ligands which can also be varied to tune the ligands with certain electronic and steric properties. An *N*-heterocyclic carbene, a heteroatom or part of a heterocyclic moiety could be the arm donor site (E) in a pincer ligand (Scheme 2). A symmetrical pincer (EZE) ligand features two same arm donor sites, a unsymmetrical pincer (EZY) have two different arm donor sites (E and Y). The spacer (X) variation can generate chiral pincers, thus altering the spacers controls the enantioselectivity of the pincer-based catalyst. The spacer length impacts on the coordination pocket of the pincer ligand directly. It is usually difficult to design a pincer ligand with well defined backbone, donor sites, and spacers to make the pincer metal complex with excellent catalytic activity in confined reactions.

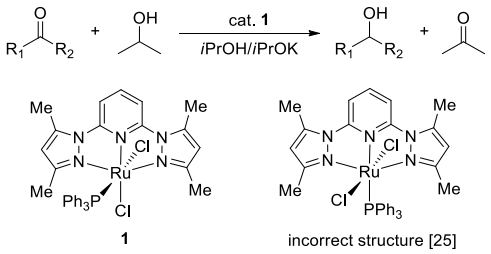
3. Mononuclear ruthenium(II) complexes for transfer hydrogenation of ketones

Transition-metal-catalyzed transfer hydrogenation (TH) reactions refer to shuttle of the hydrogen atom between hydrogen donors and hydrogen acceptors through a catalyst, usually accompanying with the reduction of unsaturated bonds (Scheme 3) [12]. The most frequently employed hydrogen donors are 2-propanol and formic acid, and sodium formate is usually used in aqueous reactions. Ketones and imines are the general hydrogen acceptors for the TH reactions. Aldehydes [13], alkynes [14], nitro and cyano-based compounds [15,16] can also be used as the hydrogen acceptors under certain conditions. Platinum group metal catalysts such as ruthenium, rhodium, iridium and palladium have achieved outstanding performances in such TH reactions [17].

Transfer hydrogenation is an important reductive reaction, which may be employed in industrial applications [18]. Compared to direct hydrogenation reaction, transfer hydrogenation reaction has owned several advantages: (i) it avoids using of dangerous H_2 and pressured vessels, which reduces potential safety issues and simplifies technical procedures; (ii) it is a real homogeneous reaction with simple kinetic data while hydrogenation is a two-phase heterogeneous reaction which requires sophisticated design for gas supplying lines on a large scale; (iii) it exhibits unique properties and selectivity [19]. Therefore, it could be considered as ideal complementary and emergent alternative when H_2 and pressured vessels are unavailable. Ruthenium(II) complexes have usually been represented the most extensively investigated catalysts for transfer hydrogenation of ketones [20].

Baratta and co-workers reported the synthesis and catalytic activity of 2-(aminomethyl)pyridine-based bidentate and tridentate ligands and their ruthenium(II) and osmium(II) complexes (Scheme 4) [21]. These complexes exhibited excellent catalytic activity and chirality-inducing ability in (asymmetric) transfer hydrogenation of ketones. The outstanding catalytic performance is rationalized by hydrogen bonding between the N—H functionality in the amino group with the solvents and substrates through an inner-sphere mechanism. Transfer hydrogenation of ketones by tpy ligand-supported Ru(II) complexes was investigated by Kelson, et al. [22]. In this case, the Ru(II) complex catalyst achieved > 95% yields and > 1000 TON (turnover numbers) by using 2-propanol as both the solvent and reducing agent, and bulky ketones, e.g., adamantan-2-one, could also be reduced with little or no indication of catalyst degradation. This catalyst exhibited good chemoselectivity: the C═C bonds of alkenes, for example, cyclohexene or styrene, were remained untouched during the TH reaction, which suggests that this Ru (II) complex catalyst is promising for selective carbonyl reduction. Szymczak, et al. reported a Ru(II) complex bearing a dihydroxylterpyridine ligand to mediate the proton transfer reaction [23]. The two hydroxyl groups can act as hydrogen donors at normal state; but it may undergo isomerization to the ketone forms to become a hydrogen acceptor under basic conditions, which thus activates 2-propanol. Under the optimal conditions, acetophenone was reduced with 98% conversion within 2 h in the presence of 0.5 mol % catalyst.

In 2005, we firstly reported the catalytic synthesis of 2,6-bis(3,5-dimethyl- pyrazol-1-yl)pyridine (Me_4BPPy) and its application for the construction of air-stable complex $RuCl_2(PPh_3)(Me_4$-BPPy) (**1**) [24]



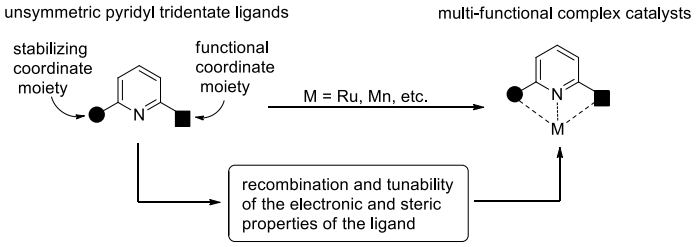
Scheme 5. Transfer hydrogenation of ketones catalyzed by complex **1**.

(Scheme 5). Fortunately, we structurally characterized complex **1** as shown in Scheme 5 by the X-ray crystallographic analysis and corrected its structural assignment reported in reference [25]. We found that complex **1** exhibit a high catalytic activity in the TH reaction of ketones in refluxing 2-propanol [24]. After a mixture of a ketone substrate and complex **1** was refluxed in 2-propanol (82 °C) for 10 min, an *i*PrOK/*i*PrOH solution was introduced to initiate the reaction. In the presence of 0.2 mol % complex **1** as the catalyst, most of the investigated acetophenones and cyclohexanone were nearly quantitatively converted to the corresponding alcohols over a period of 5 min.

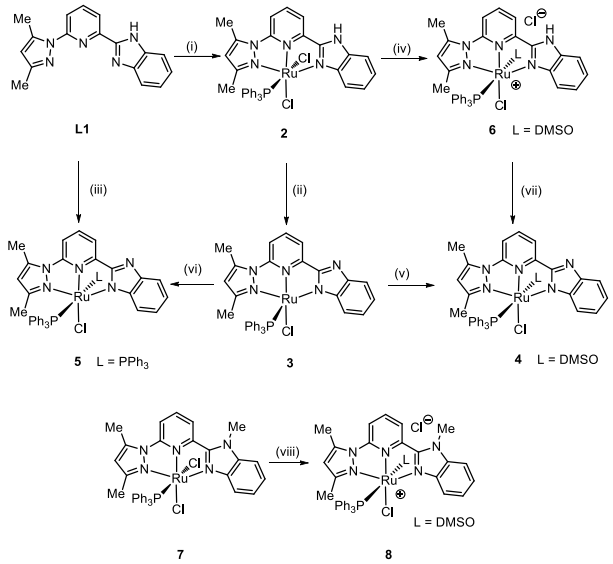
The catalytic activity of complex **1** for the TH reaction of ketones was thoroughly investigated which was very difficult to improve its catalytic performance by varying the reaction conditions. After the catalytic activities of the Ru(II) complexes developed by Baratta [21], Kelson [22], Szymczak [23] and others were comparatively studied, we found that the symmetry property of pyridine-based symmetrical NNN ligands is not beneficial to improve their Ru(II) complexes catalytic activities. Thus, exploration of new unsymmetrical NNN ligands for the construction of highly active Ru(II) complex catalysts for transfer hydrogenation has become one of the motivations in our work [26-28].

A construction concept to synthesis unsymmetrical pyridyl-based tridentate ligands and their complexes was then proposed in Scheme 6 [26a]. Unsymmetrical pyridyl-based NNN ligands could be accessed and readily tuned by the electronic and steric properties of the coordinating moieties introduced to the 2- and 6-positions of the pyridyl backbone, and cooperation of the two functional coordinating arm moieties might result in a synergic effect on the catalytic activity of the resultant Ru(II) complex catalysts.

In our first trial, a pyrazol-1-yl and N—H unprotected benzimidazol-2-yl were introduced to the 2- and 6-positions of a pyridyl, respectively, forming ligand **L1**, which was then reacted with $RuCl_2(PPh_3)_3$ in refluxing toluene to efficiently generate complex **2** (Scheme 7). Complex



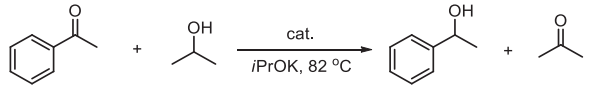
Scheme 6. Construction of unsymmetrical pyridyl-based tridentate complexes.



Conditions: (i) $RuCl_2(PPh_3)_3$, PhMe, 110 °C, 2 h, 91%. (ii) $NaHCO_3$, CH_2Cl_2/MeOH (v/v, 5:1), r.t., 5 h, 96%. (iii) $RuCl_2(PPh_3)_3$, Et_3N, PhMe, 110 °C, 2 h, 65%. (iv) DMSO/DMF (v/v, 5:1), 100 °C, 15 min, 77%. (v) DMSO/DMF (v/v, 5:1), 100 °C, 15 min, 60%. (vi) PPh_3, $CDCl_3$, r.t. (vii) $NaHCO_3$, CH_2Cl_2/MeOH (v/v, 5:1), r.t., 15 h, 96%. (viii) DMSO/DMF (v/v, 5:1), 100 °C, 15 min, 86%.

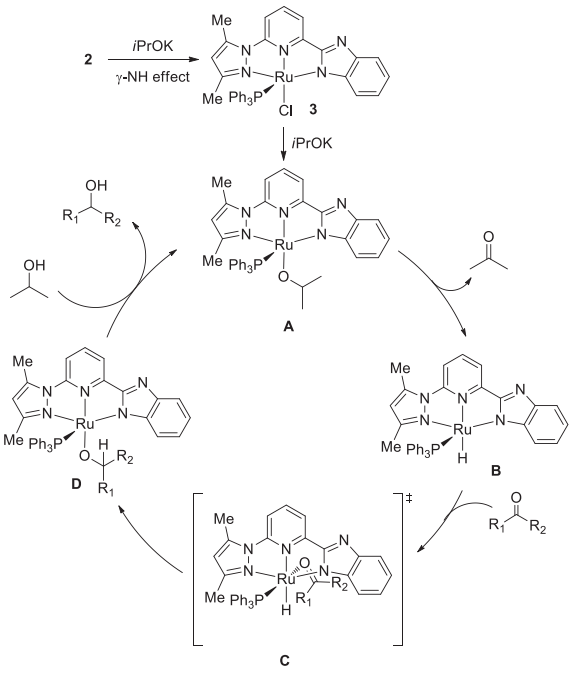
Scheme 7. Synthesis of mononuclear ruthenium(II)–NNN catalysts. Conditions: (i) $RuCl_2(PPh_3)_3$, PhMe, 110 °C, 2 h, 91%. (ii) $NaHCO_3$, CH_2Cl_2/MeOH (v/v, 5:1), r.t., 5 h, 96%. (iii) $RuCl_2(PPh_3)_3$, Et_3N, PhMe, 110 °C, 2 h, 65%. (iv) DMSO/DMF (v/v, 5:1), 100 °C, 15 min, 77%. (v) DMSO/DMF (v/v, 5:1), 100 °C, 15 min, 60%. (vi) PPh_3, $CDCl_3$, r.t. (vii) $NaHCO_3$, CH_2Cl_2/MeOH (v/v, 5:1), r.t., 15 h, 96%. (viii) DMSO/DMF (v/v, 5:1), 100 °C, 15 min, 86%.

Table 1
Comparison of the catalytic activity for complexes **2**–**8** in the transfer hydrogenation of acetophenone. [a]



entry	cat. (mol %)	time (min)	yield (%)[b]	final TOF (h^{-1})
1	**2** (0.05)	1/6	98	705,600
2	**3** (0.05)	1/6	98	705,600
3	**4** (0.05)	1	98	117,600
4	**5** (0.1)	15	97	3880
5	**6** (0.05)	1	98	117,600
6	**7** (0.3)	10	98	1960
7	**8** (0.1)	5	98	11,760

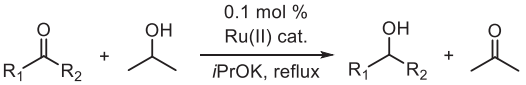
[a] Conditions: acetophenone, 2.0 mmol (in 20 mL *i*PrOH); *i*PrOK/cat. = 20/1; 0.1 MPa, 82 °C
[b] Determined by GC analysis.

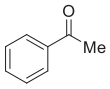
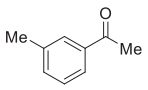
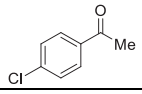


Scheme 8. A proposed inner-sphere mechanism for transfer hydrogenation of ketones.

2 (0.05 mol %) was applied in the transfer hydrogenation of ketones in refluxing 2-propanol, reaching a final TOF (turnover frequency) value of up to 720000 h^{-1} and 99% yield within 10 s, demonstrating a remarkable N—H accelerating effect [26a,26b]. With 0.1 mol % loading of complex **2**, the TH reaction of ketones could show a final TOF value of 55800 h^{-1} at room-temperature [26c]. Based on complex **2** the 16-electron Ru(II) complex **3** and 18-electron Ru(II) complexes **4**–**8** were also synthesized and investigated their catalytic activity in TH reaction of ketones under the same condition. Complex **3** exhibited the same catalytic activity as complex **2**, whereas complexes **4**–**8** showed lower catalytic activity than both complexes **2** and **3**. The comparison of complexes **2**-**8**′s catalytic activity was conducted in the TH reaciton of acetophenone (Table 1). With a 0.05–0.3 mol % catalyst loading, 0.1 M solution of acetophenone in refluxing 2-propanol, and freshly prepared *i*PrOK as the base, acetophenone was efficiently reduced to 1-phenylethanol. Complexes **2** and **3** exhibited exceptionally high catalytic activity and completed the TH reaction in 98% yield within 10 s, reaching a final TOF value of 705 600 h^{-1} (Table 1, entries 1 and 2). Under the basic conditions cationic complex **6** could be transformed to neutral

Table 2
The catalytic activity of complexes **9** for transfer hydrogenation of ketones.[a]



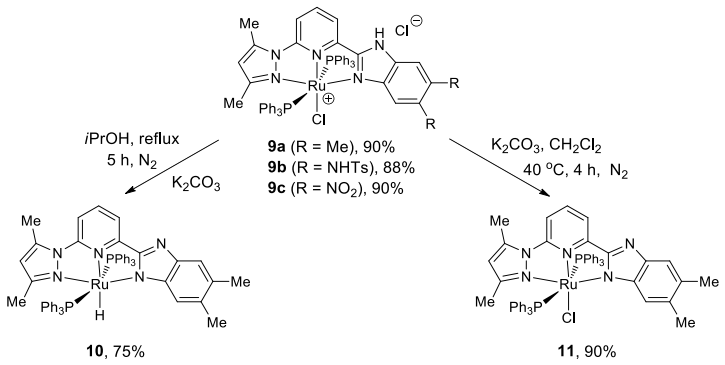
entry	Ru(II) cat.	ketone	time (min)	conversion[b] (%)	final TOF (h^{-1})
1	**9a**		10	97	5820
	9b		1/2	97	116,400
	9c		60	92	920
2	**9a**		60	95	950
	9b		20	95	2850
	9c		240	77	193
3	**9a**		1/2	100	120,000
	9b		1/3	99	178,200
	9c		5	96	11,520

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst, 0.1 mol %; ketone/*i*PrOK/Ru(II) cat. = 1000:20:1; 0.1 MPa N_2, 82 °C.
[b] Determined by GC analysis.

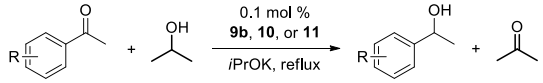
complex **4**, thus complex **4** and its precursor complex **6** demonstrated the same high catalytic activity, giving 98% yield and a final TOF of 117 600 h^{-1} within one minute (Table 1, entries 3 and 5). For the complex bearing two PPh_3 ligands and those featuring no N—H effect, that is, complexes **5**, **7** and **8** only showed a moderate catalytic activity even with a higher loading such as 0.1 mol % or 0.3 mol % complex catalyst, yielding the reduction product in 97–98% yields.

The TH reaction of ketones may follow an inner-sphere mechanism as proposed in Scheme 8. Coordinatively unsaturated complex **3** is resulted directly from **2** by extrusion of one equivalent of hydrogen chloride with the assistance of *i*PrOK base. Then the TH reaction is initiated and complex **3** interacts with the base to generate Ru(II)-alkoxide **A**. β-H elimination of species **A** results in Ru-H intermediate **B** which is then coordinated by a ketone substrate to produce species **C**. Ru(II)-alkoxide **D** is formed by insertion of the coordinated ketone carbonyl into the Ru-H bond which then regenerates species **A** and affords the alcohol product when reacting with 2-propanol. Although Ru(II) hydride **B** was not successfully prepared or isolated, it is presumably considered as the catalytically active species [26d,26e]. It is obvious that unsymmetrical structure of ligand **L1** is crucial for the exceptionally high catalytic activity of complexes **2** and **3** as well as the coordinatively unsaturated 16-electron environment around the ruthenium(II) center [26a,26b].

To tune the catalytic activity, different substituents on the imidazolyl moiety of the investigated NNN ligand were introduced in complexes **9a**-**9c** [27a]. Their catalytic activity for the TH reaction of ketones follows the order NHTs (**9b**) > Me (**9a**) > NO_2 (**9c**) (Table 2), suggesting that the substituents exhibit a remarkable impact on the catalytic activity of the resulting Ru(II) complexes. Among these catalysts, the Ru(II)-NHTs-substituted NNN complex achieved the highest final TOF value of 345600 h^{-1} by means of 0.05 mol % catalyst loading [27a]. By means of weak K_2CO_3 as base, cationic complex **9a** was transformed to the corresponding neutral RuH complex **10** in refluxing 2-propanol, while in dichloromethane neutral complex **11** was obtained through extrusion of one molecule of HCl from **9a** (Scheme 9). The catalytic behaviors of complexes **9b**, **10**, and **11** were comparatively tested in the TH reaction of acetophenone, 2′-chloroacetophenone and 2′-methyl acetophenone to investigate the reaction mechanism (Scheme 10). These three complexes exhibited almost the same catalytic activity for the TH reactions of the investigated acetophenones under the standard conditions.



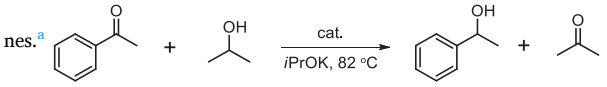
Scheme 9. Mononuclear ruthenium(II) complex catalysts **9**–**11**.



	time (min)	conversion of ketone (%) using **9b**	using **10**	using **11**
R = H	10	97	97	97
R = *o*-Cl	1/2	100	98	100
R = *o*-Me	60	94	93	94

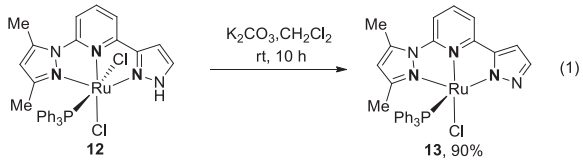
Scheme 10. Comparative experiments.

Table 3
The catalytic activity of complexes **12**–**18** for transfer hydrogenation of ketones.[a]



entry	cat. (mol %)	time (min)	yield (%)[b]
1	**12** (0.05)	1	95
2	**13** (0.05)	1	95
3	**14a** (0.1)	5	97
4	**14b** (0.1)	120	96
5	**15** (0.1)	5	98
6	**16** (0.1)	5	97
7	**17a** (0.2)	60	96
8	**17b** (0.2)	60	90
9	**18** (0.2)	60	93

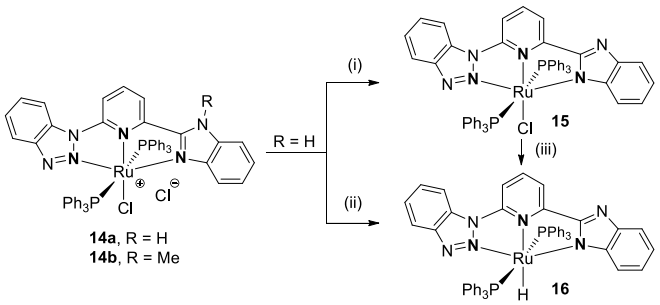
[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst, 0.1 mol %; *i*PrOK/Ru(II) cat. = 20:1; 0.1 MPa N_2, 82 °C.
[b] Determined by GC analysis.



(1)

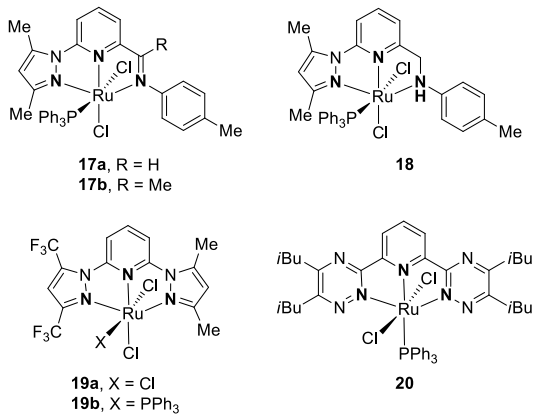
The *β*-NH functionality of a coordinating pyrazole moiety was then explored and pyrazol-1-yl-pyridyl-3-pyrazole based ruthenium(II) complex **12** was synthesized [27b]. Complex **12** demonstrated a remarkable acceleration effect on the TH reaction of ketones and exhibited exceptionally high catalytic activity. With a 0.05 mol % catalyst loading, complex **12** reached up a final TOF of 720000 h^{-1} in refluxing 2-propanol. Such a high catalytic activity is attributed to the presence of a convertible N—H group in the coordinating pyrazole arm. By dehydrochlorination under the basic conditions complex **12** was readily converted to complex **13** (eq.1), and thus both complexes **12** and **13** exhibited the same catalytic activity for the ketone substrates. In most cases, the TH reaction reaching > 95% yields within 1 min (Table 3, entries 1 and 2).

With these highly active Ru(II) − NNN complex catalysts in hand, we envisioned that benzotriazolyl might be a promising coordinating *N*-heterocyclic moiety in the construction of pyridyl-based NNN ligands (Scheme 11) [28a]. Thus, unsymmetrical 2-(benzimidazol-2-yl)-6-(benzotriazol-1-yl)pyridine and its *N*-methyl analog and the corresponding air- and moisture-stable ruthenium(II) complexes **14** were synthesized. In the TH reaction of ketones cationic complex **14a** and its neutral Ru-Cl (**15**) and Ru-H (**16**) complexes exhibited excellent catalytic activity (Table 3, entries 3, 5 and 6), reaching final TOFs up to 176400 h^{-1} in refluxing 2-propanol. Under the stated reaction conditions, complex **14a** could be readily converted to neutral Ru-Cl complex **15** and Ru-H complex **16** which exhibited the same high catalytic activity in the TH reaction. However, complex **14b** bearing no convertible

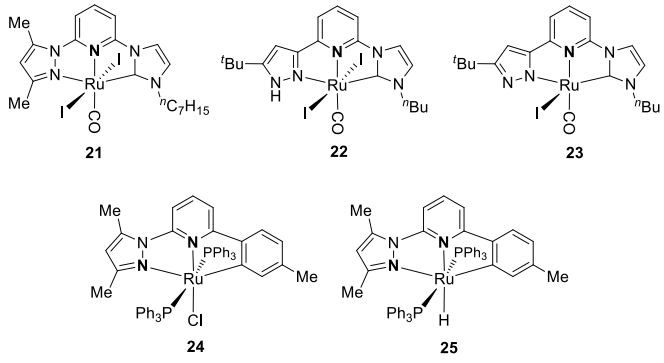


Conditions: (i) K_2CO_3, CH_2Cl_2, 39 °C, 5 h, 91%; (ii) K_2CO_3, 2-propanol, 82 °C, 3 h, 72%; (iii) K_2CO_3, 2-propanol, 82 °C, 3 h, 75%.

Scheme 11. Mononuclear ruthenium(II) complex catalysts **14**–**16**.

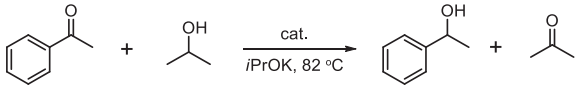


Scheme 12. Mononuclear ruthenium(II) complex catalysts **17**–**20.**



Scheme 13. Mononuclear ruthenium(II) complex catalysts **21**–**25**.

Table 4
The catalytic activity of complexes **21**–**25** for transfer hydrogenation of ketones.[a]

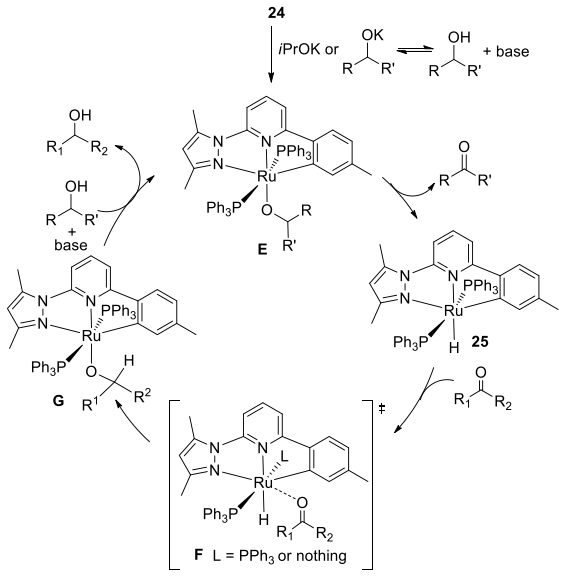


entry	cat. (mol %)	time (min)	yield (%)[b]
1	**21** (0.2)	240	98
2	**22** (0.2)	120	98
3	**23** (0.2)	120	97
4	**24** (0.1)	1	98
5	**25** (0.1)	1	97
6[c]	**25** (0.1)	720	95

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst, 0.1 mol %; *i*PrOK/Ru(II) cat. = 20:1; 0.1 MPa N2, 82 °C.
[b] Determined by GC analysis.
[c] Without base.

N—H functionality only exhibited a low catalytic activity (Table 3, entry 4). The controlled experiments have revealed that the catalytically active species is the corresponding isolated and structurally characterized RuH complex **16** (Scheme 11). The hemilabile unsymmetrical coordination environment around the metal center and presence of a convertible benzimidazolyl N—H functionality leads to the high catalytic activity of the resultant Ru(II) complex catalysts (Table 3).

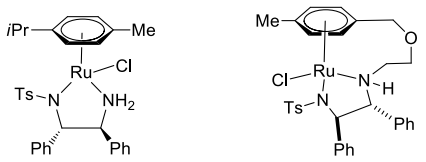
Based on hemilabile unsymmetrical 2-(1-arylimino)-6-(pyzazol-1-yl) pyridine ligand, imino-functionalized ruthenium(II)–NNN complexes **17** and **18** were synthesized (Scheme 12). Though complex **17** features no N—H functionality, it exhibited good to excellent catalytic activity in the TH reaction of ketones in refluxing 2-propanol, achieving up to 99% yields and final TOF values up to 5940 h^{-1} (Table 3, entries 7 and 8) [28b]. In this case, acetophenone was smoothly reduced to 1-phenylethanol in 90–96% yields by means of 0.2 mol % complex catalysts **17** and **18** in the presence of *i*PrOK base over a period of 1 h, demonstrating a catalytic activity order for the TH reaction of acetophenone: **17a** > **18** > **17b**.



Scheme 14. A proposed inner-sphere mechanism.

Trifluoromethyl-functionalized pyrazolyl was introduced to the pyridyl backbone to test the electronic impact of the coordination arm on the catalytic activity of the Ru(II)–NNN complex catalysts (Scheme 12) [28c]. Ru(III) and Ru(II) complexes (**19a** and **19b**) bearing a tridentate 2-(3′,5′-dimethylpyrazol-1′-yl)-6-(3″,5″-bis(trifluoro- methyl) pyrazol-1″-yl)pyridine ligand were synthesized and applied in the TH reaction of ketones, achieving up to 2150 TON and final TOFs up to 29700 h^{-1} (Scheme 12). The controlled experiments have revealed that this highly active catalytic system is attributed to the compatibility of the trifluoromethylated pyrazolyl and dimethylated pyrazol coordinating arms. Complex **20** was found to exhibit a comparable catalytic activity with complex **1** for the transfer hydrogenation of ketones in a few cases (Scheme 12) [29]. The molecular structure of complex **20** was confirmed by the X-ray crystallographic analysis, revealing the *trans*-positioning of PPh_3 ligand and the pyridyl nitrogen atom. In most cases, complex **1** showed much higher catalytic activity than complex **20**, which is presumably attributed to not only the significantly different arrangements of the PPh_3 ligand and the two chloride atoms around the metal centers, but also the various electronic properties of the pyridyl-supported *N*-heterocycles. The pyrazolyl moieties in complex **1** may help to form a relatively electron-rich ruthenium center, suggesting that they are stronger σ-donors than 1,2,4-triazin-3-yls in complex **20** and can stabilize the catalytically active species more during the reaction. These results have demonstrated that arrangement of the PPh_3 and chloride moieties in complex **20** may not be favorable to stabilize the catalytically active species and thus resulted in a lower catalytic activity.

N-heterocyclic carbenes (NHCs) are a useful class of ligands and have been extensively applied in homogeneous catalysis, organic synthesis over the decades [30,31]. Unsymmetrical NHC-functionalized "pincer"-type pyridyl-based (pyrazol-3-yl)-*N*-heterocyclic carbene (NNC) ligands and their ruthenium(II)–NNC complexes **21**–**23** were synthesized (Scheme 13) [31a]. In the presence of 0.2 mol % of complex **22**, 4-bromoacetophenone was reduced to the corresponding alcohol within 15 min with a final TOF up to 1940 h^{-1}. Complexes **22** and **23** exhibited nearly the same catalytic activity which is presumably due to the instant transformation of 18-electron complex **22** to 16-electron species **23** under the reaction conditions. The coordinatively unsaturated Ru(II) center in complex **23** may be coordinated by the ketone substrate via an



Scheme 15. Ruthenium(II) complex catalysts for ATH reaction.

inner-sphere TH mechanism and then accelerates the reduction of ketone. Both complexes **22** and **23** exhibited a higher catalytic acvtivity than the coordinatively saturated complex **21** (Table 4, entries 1–3).

The strong σ-donor property of a carbene ligand may decrease the catalytic activity of its transition-metal complexes. Then, we explored a carbanion to replace the carbene coordinating arm in the pyridyl-based NNC ligand and synthesized NNC-based Ru(II)–NNC complex **24** as well as its corresponding hydride complex **25** [31b] (Scheme 13). Complex **24** exhibited a high catalytic activity for both the TH reation of ketones and Oppenauer-type oxidation of alcohols. By using K_2CO_3 as base, Ru-H complex **25** was synthesized from complex **24**. Under the same conditions for the transfer hydrogenation of ketones, complex **25** exhibited a catalytic activity similar to that of complex **24**, acetophenone could be transformed to the corresponding alcohol in 97% yield within 1 min (Table 4, entries 4 and 5). A plausible inner-sphere mechanism is proposed for both the transfer hydrogenation and dehydrogenative oxidation pathways in Scheme 14. In this case, 2-propanol was the solvent and hydrogen donor for transfer hydrogenation of ketones, whereas acetone was the solvent and hydrogen acceptor for the Oppenauer-type oxidation. Both of the pathways involve four steps: (i) Ru(II)-alkoxide **E** is produced from complex **24** and *i*PrOK and undergoes a *β*-H elimination to afford Ru-H intermediate **25**; (ii) intermediate **25** is coordinated by a ketone substrate (or acetone) to generate species **F**; (iii) Ru(II)-alkoxide **G** is formed via the insertion of the coordinated ketone carbonyl into the Ru-H bond; and (iv) metathesis of species **G** with an alcohol gives the new alcohol product and regenerates species **E**, closing a catalytic cycle. This mechanism revealed that Ru-H complex **25** is the catalytically active species. And it is reasonable to propose that under basic conditions exchanging of the alkoxide product with another alcohol is facilitated, which may provide an explanation for the inferior catalytic activity of **25** in the absence of a base (Table 4, entry 6).

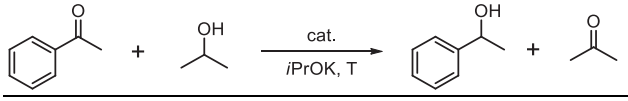
4. Mononuclear ruthenium(II) complexes for asymmetric transfer hydrogenation of ketones

N-Monotosylethylenediamine (Ts-DPEN) and *β*-amine alcohols developed by Noyori, et al. [32] were powerful ligands in ruthenium-catalyzed asymmetric transfer hydrogenation (ATH) of ketones and imines (Scheme 15). The N—H functionality in the amine ligands is crucial for the catalytic performance. Detailed investigation has revealed that the ligand and the ruthenium center work cooperatively as a bifunctional catalyst, and an outer-sphere mechanism based on the concerted transfer of both the Ru-H and the N—H to the substrate has been established. Due to Noyori's pioneering work, many outstanding ligands and Ru(II) complexes have been documented [33], in which NH moieties in the organometallic catalysts can serve as coordinating groups, hydrogen bonding donors, hydrogen bonding acceptors, and/or proton sources. These functions can be utilized to achieve metal–ligand multifunctional catalysis [34].

Wills [35] and Ikariya [36] have developed a family of tether catalysts (Scheme 15) in which the tosylated amide is linked to the aromatic ring. Such a strategy makes the Ru(II) complexes highly stable with enhanced catalytic activity and enantioselectivity, and suitable for broad substrate scopes. Aqueous ATH reactions of ketones and heterocycles [37] have also been realized by Xiao [37a,37b], Deng [37c,37d] and other research groups [37e,37f] through derivation of Ts-DPEN ligands under the modified conditions. ATH has also been extended as a crucial chirality-producing step in other reactions [38]. Johnson, et al. reported dynamic kinetic resolution reactions of α-ketoester substrates using Ru(II) complex catalysts bearing a chiral diamine ligand [38a–38c], and isomerization of allylic alcohols for the production of chiral carbonyl products [38d–38f].

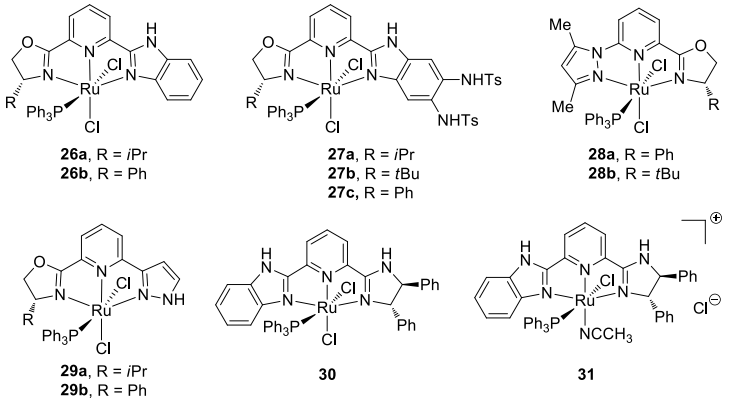
Ruthenium(II) complexes have been attractive catalysts for asymmetric transfer hydrogenation of ketones to form chiral alcohols [39–41]. In our laboratories, chiral ruthenium(II)–NNN complexes

Table 5
The ATH reaction of acetophenone.[a,b]

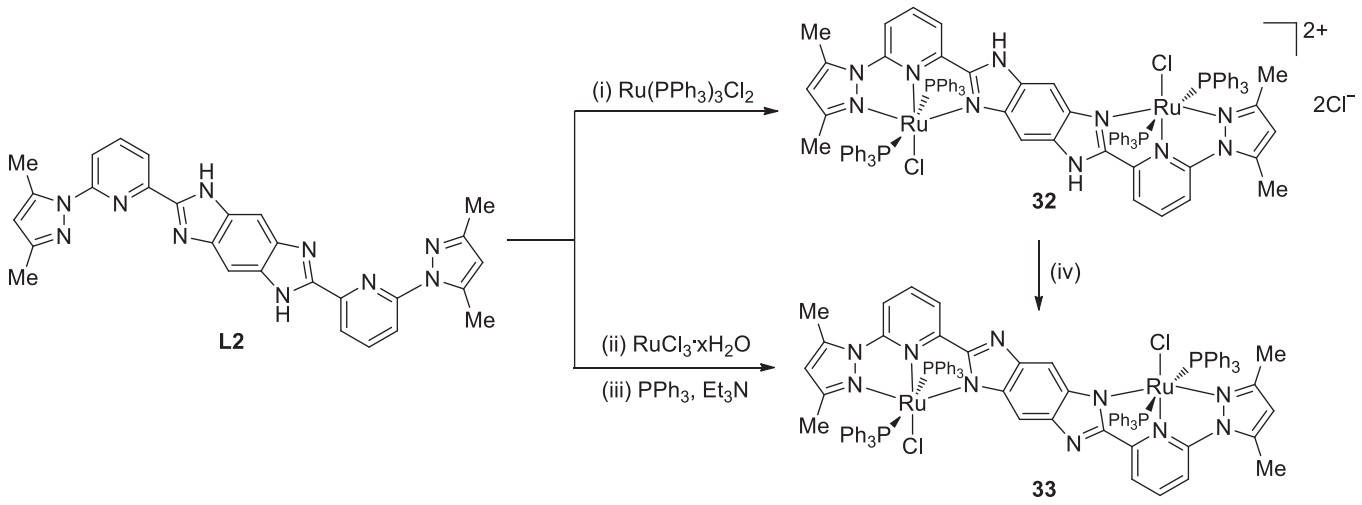


entry	cat. (mol %)	temp (°C)	time (min)	yield (%)[b]	*ee* (%)[b]
1	**26a** (0.1)[c]	28	3	96	56 (*S*)
2	**26b** (0.1)[c]	28	4	96	79 (*R*)
3	**27a** (0.1)	28	4	97	98 (*S*)
4	**27b** (0.1)	28	4	10	88 (*R*)
5	**27c** (0.1)	28	4	82	38 (*S*)
6	**28a** (0.5)	40	60	98	36 (*R*)
7	**28b** (1.0)	40	120	94	27 (*R*)
8	**29a** (0.4)	30	10	93	90 (*S*)
9	**29b** (0.4)	40	15	97	23 (*R*)
10	**30** (0.2)[c]	28	5	95	90 (*S*)
11	**31** (0.2)	28	5	96	85 (*S*)

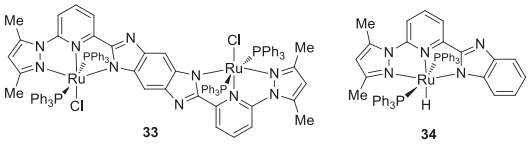
[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); *i*PrOK/catalyst = 20/1; 0.1 MPa N2.
[b] Determined by GC analysis on a chiral column β DEX 225.
[c] iPrOK/ catalyst = 10/1.



Scheme 16. Chiral ruthenium(II)–NNN complex catalysts for ATH of ketones.

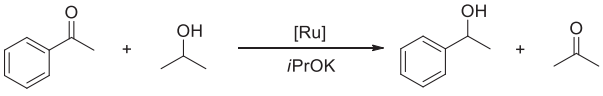


Reagents and conditions: (i) $RuCl_2(PPh_3)_3$, *i*PrOH, reflux, 0.1 MPa N_2, 6 h, 92%. (ii) $RuCl_3{\cdot}xH_2O$, EtOH, reflux, 0.1 MPa N_2, 5 h, 85%. (iii) PPh_3, Et_3N, EtOH, reflux, 0.1 MPa N_2, 6 h, 80%. (iv) K_2CO_3, CH_2Cl_2, reflux, 0.1 MPa N_2, 5 h, 80%.



Scheme 17. Dinuclear ruthenium(II) complex catalysts **32**–**34**. Reagents and conditions: (i) $RuCl_2(PPh_3)_3$, *i*PrOH, 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%.

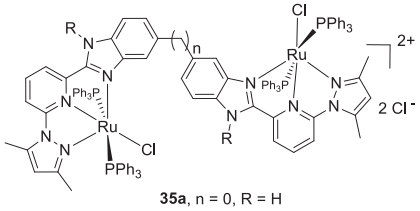
Table 6
Transfer hydrogenation of ketones catalyzed by complexes **5** and **32**–**35**.[a]



entry	cat. (mol % Ru)	time (min)	yield[b] (%)
1	**32** (0.1)	1	98
2	**33** (0.1)	1	98
3	**5** (0.1)	15	97
4	**34** (0.1)	15	97
5	**35a** (0.05)	30	93
6	**35b** (0.05)	2	98
7	**35c** (0.05)	120	90

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); ketone/iPrOK/Ru = 1000:20:1; 0.1 MPa N2, 82 °C.
[b] Determined by GC analysis.

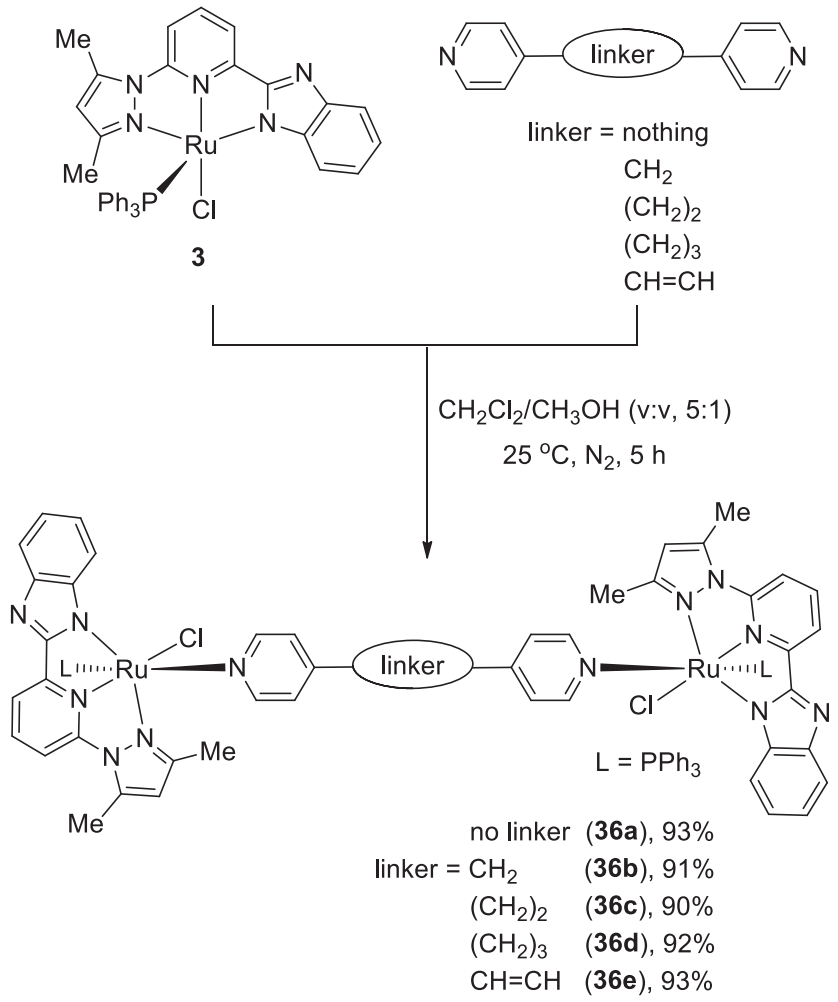
26–**31** were synthesized by featuring the ligands with an N—H functionality and were efficiently used in the ATH reaction of ketones (Scheme 16). Complex **26** bearing a chiral pyridyl-benzimidazolyl-based NNN ligand exhibited high catalytic activity in the ATH reaction of ketones [39a]. At 28 °C, 0.1 mol % complex **26a** catalyzed the ATH of acetophenone to afford the target alcohol product in 96% yield with 56% *ee*, whereas **26b** gave the product in a better enantioselectivity (79% *ee*) (Table 5, entries 1 and 2). These results have revealed that the enantioselectivity of the target product was obviously affected by the



Scheme 18. Dinuclear ruthenium(II) complex catalysts **35**.

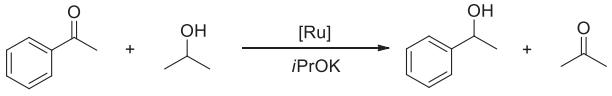
steric effect from the chiral oxazolyl moiety. However, the enantioselectivity was remarkably improved to 98% *ee* by using $(NHTs)_2$-functionalized Ru(II) complex **27a** as the catalysts (Table 5, entry 3) [39b]. A remarkable NH-Ts effect was observed and the catalytic activity order for complexes **27** for the TH reaction of acetophenone was observed as **27a** > **27c** > **27b** (Table 5, entries 3–5).

Ruthenium(II) NNN complexes bearing a chiral pyridyl–pyrazolyl–oxazolinyl ligand (**28**) and pyridyl-based 1*H*-pyrazolyl–oxazolinyl ligand (**29**) were also synthesized and applied as the catalysts for ATH of ketones [40]. Due to the acceleration effect from the pyrazolyl N—H functionality, the following catalytic activity order for the ATH reaction of acetophenone was established: **29a** > **29b** > **28a** > **28b** (Table 5, entries 6–9). In a similar fashion, chiral Ru(II) complexes **30** and **31** bearing benzimidazolyl and imidazolinyl moieties were synthesized and exhibited high catalytic activity in the ATH reaction of



Scheme 19. Synthesis of dinuclear ruthenium(II) complex catalysts **36**.

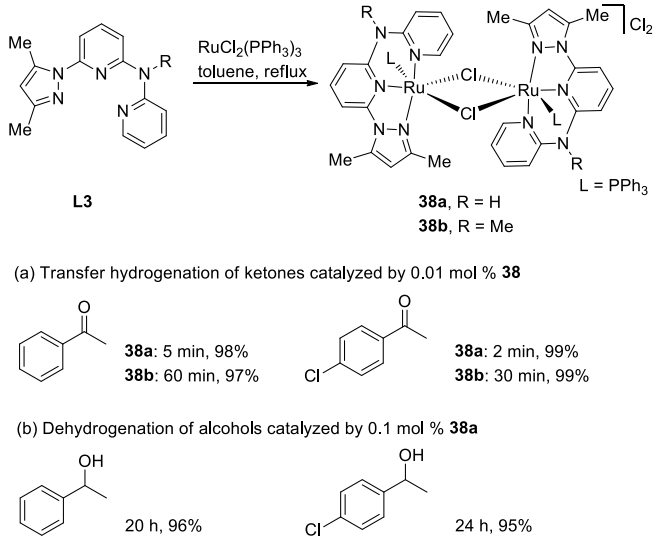
Table 7
The TH reaction of acetophenone catalyzed by complexes **36** and **37**.[a]



entry	cat.	time (min)	yield[b] (%)	TOF[c] (h^{-1})
1	**36a**	1	98	3.3×10^6
2	**36b**	1	98	4.4×10^6
3	**36c**	2	98	2.5×10^6
4	**36d**	1	99	6.3×10^6
5	**36e**	1	97	3.9×10^6
6	**37**	1	98	5.0×10^6

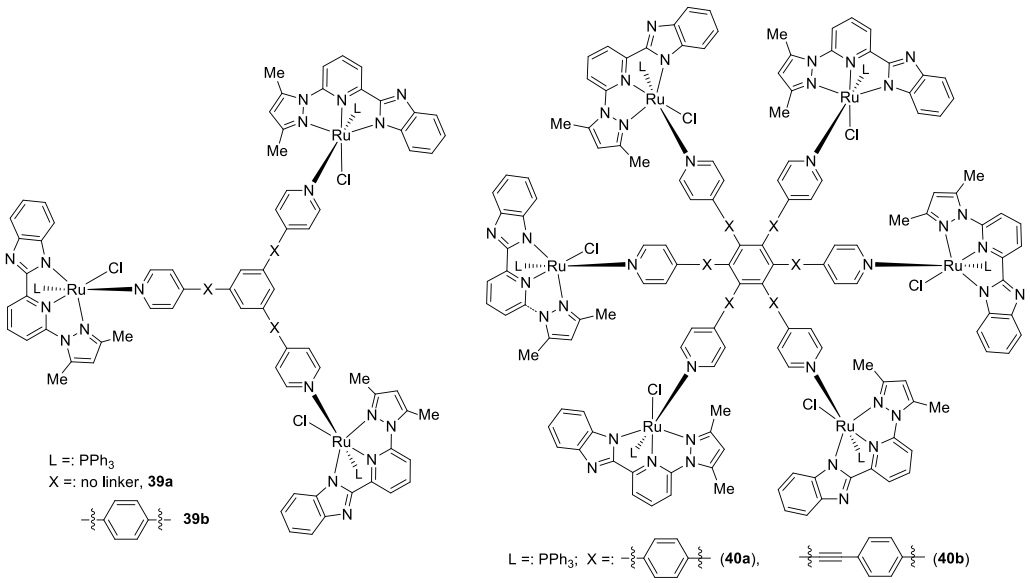
[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); complex catalyst 36 or 37, 0.0125 mol % Ru (iPrOK/Ru = 20:1); 0.1 MPa N2, 82 °C.
[b] Determined by GC analysis.
[c] Turnover frequency (moles of ketone converted per mole of Ru per hour) at 50% conversion of the ketone substrate.

acetophenones (Scheme 16) (Table 5, entries 10 and 11) [41a]. Both electron-withdrawing and electron-donating group-substituted acetophenones could be efficiently reduced to the corresponding chiral alcohol products in up to 99% yields and 97% *ee* values. We have shown that complexes **2**, **26,** and **27** with a benzimidazolyl N—H functionality can accelerate the TH and ATH reactions of ketones, and imidazolinyl N—H functionality could also improve the enantioselectivity in ATH of



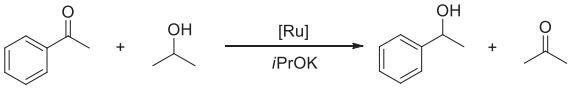
Scheme 20. Dinuclear ruthenium(II) complex catalysts **38**.

ketones [41b]. Combination of the two N—H functionalities in complexes **30** and **31** bestows them with high catalytic activity and good enantioselectivity for ATH of ketones under mild conditions.



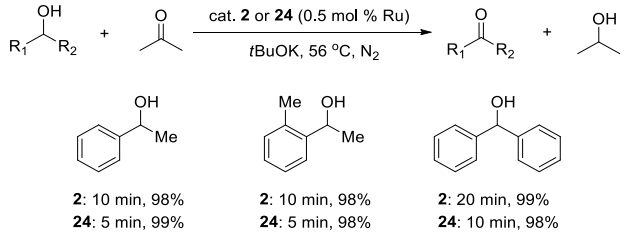
Scheme 21. Multinuclear ruthenium(II) complex catalysts **39** and **40**.

Table 8
The TH reaction of acetophenone catalyzed by complexes **39–41**.[a]



entry	cat.	time (min)	yield[b] (%)	TOF[c] (h^{-1})
1	**39a**	1	96	1.6×10^6
2	**39b**	1	98	2.4×10^6
3	**40a**	2	96	5.6×10^5
4	**40b**	30	90	6.7×10^5
5	**41**	30	85	3.4×10^5

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); 0.025 mol % Ru (*i*PrOK/Ru = 20:1); 0.1 MPa N2, 82 °C.
[b] Determined by GC analysis.
[c] Turnover frequency (moles of ketone converted per mole of Ru per hour) at 50% conversion.



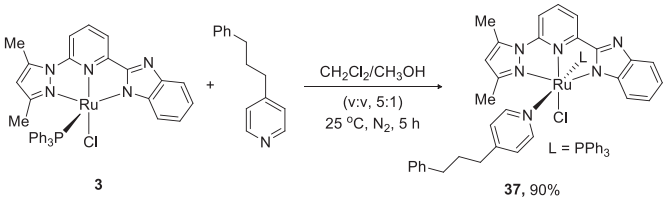
Scheme 22. Oppenauer-type oxidation of secondary alcohols catalyzed by complexes **2** and **24**.

5. Dinuclear and polynuclear ruthenium complexes for transfer hydrogenation of ketones

Dinuclear complex catalysts have been paid considerable attention and applied in homogeneous catalysis due to the possible cooperative electronic and steric effects from the metal centers and ligands, which may result in unusual reactivity and/or catalytic activity [42]. To make the metal centers in a cooperative manner the choice of the stereo-electronic property and flexibility of the ligands is crucial to determine the suitability of a multinuclear complex for a specific catalytic reaction [43-45].

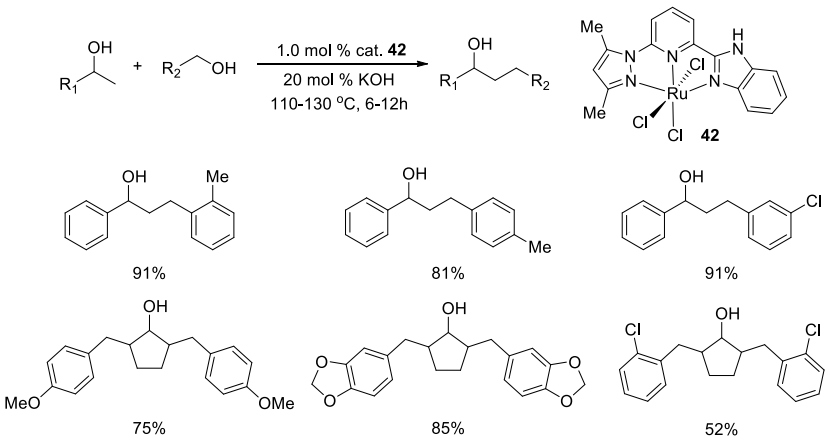
Bis-(tridentate NNN) ligand **L2** was successfully prepared and used to synthesize dinuclear Ru(II)–NNN complex **33** (Scheme 17) [44a]. Compared with the corresponding mononuclear Ru(II)–NNN pincer complexes, the resultant π linker-supported dinuclear ruthenium(II)–NNN pincer complexes **33** could be applied at a very low catalyst loading such as 0.03 mol % Ru in the TH reactions of ketones and reached a maximum TOF value of $1.3 \times 10^6 h^{-1}$, which is presumably attributed to the possible metal − metal interaction through the π linker that enhances the catalytic activity. Compared with mononuclear Ru(II) complex **5** and its corresponding Ru-H complex **34**, the π linker-supported dinuclear complex **33** exhibited much higher catalytic activity (Table 6, entries 1–4). Bimetallic ruthenium(II) complexes **35** bridged by a rotatable single C — C bond or methylene linker were synthesized and tested as the TH catalysts of ketones in refluxing 2-propanol (Scheme 18) [44b]. It was found that the TH acceleration effect was not only enhanced by the unprotected N—H functionality but also by the bridging methylene moiety in the ligands. The catalytic activity order was observed as follows: **35b** > **35a** > **35c** (Table 6, entries 5–7). Density functional theory calculations have revealed that the nucleophilic character of the nitrogen atoms and the metal − metal interaction result in the different catalytic activities of the bimetallic complexes.

By means of coordinatively unsaturated mononuclear ruthenium(II) complex **3** as a building block and 4,4′-linked bipyridines as the ligands, dinuclear ruthenium(II)–NNNN complexes **36** were efficiently assembled (Scheme 19) [45a]. For comparison, mononuclear complex **37** was also synthesized from the 1:1 M ratio reaction of complex **3** and 4-(3-phenylpropyl)pyridine (eq. (2). Among the investigated complex catalysts complex **36d** exhibited the best catalytic activity (Table 7). In the TH reaction of 4′-bromoacetophenone in refluxing 2-propanol complex **36d** reached a TOF value of $1.4 \times 10^7 h^{-1}$. The linker 4,4′-$(CH_2)_3$-bipyridine bestows the two metal centers with the most flexible situation and makes them

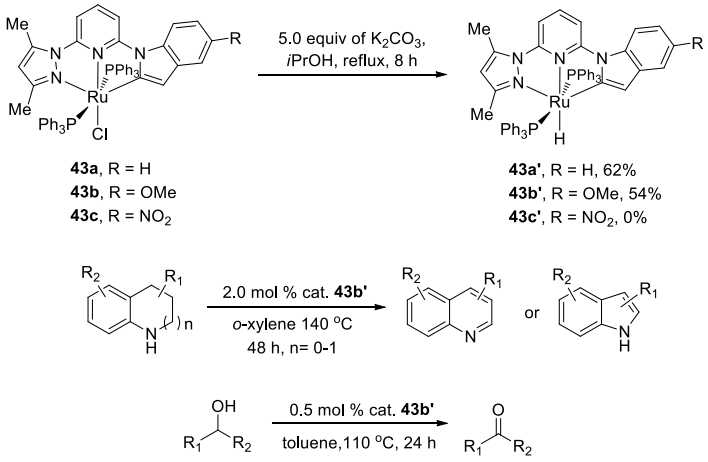


(2)

cooperatively interact in the confined environment of the molecular structure, which thus enhances the catalytic activity of complex **36d**. A

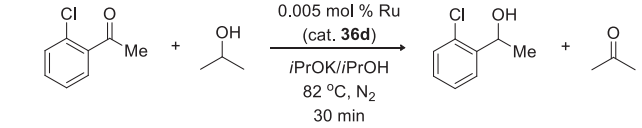


Scheme 23. Ruthenium(II)–NNN complex-catalyzed *β*-alkylation of secondary alcohols.



Scheme 24. Ruthenium(II) complex catalysts for acceptorless dehydrogenation.

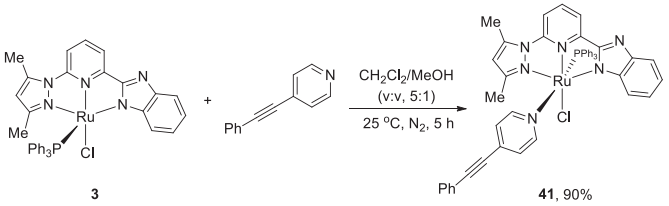
scale-up TH reaction of 20 mmol 2′-chloroacetophenone was conducted in the presence of 0.005 mol % Ru loading of complex **36d**, giving the target alcohol product in 96% yield within 0.5 h, and reached a TON value of 1.9×10^4 (eq. (3)).



(3)

The structurally characterized dimeric pincer-type ruthenium(II)–NNN complexes **38** were accessed for the TH reaction of ketones and acceptorless dehydrogenation of secondary alcohols (Scheme 20) [45b]. In this case pyrazol-2-aminopyridyl-pyridine ligands (**L3**) were applied. With 0.01 mol % complex catalyst **38**, the TH reaction of ketone substrates exclusively gave the corresponding alcohol products in 96–99% yields over a period of 5–90 min. Both the unprotected N—H functionality and hemilabile unsymmetrical coordination environment improved the catalytic activity of complex **38a** which exhibited a much higher catalytic activity than that of complex **38b** and achieved TOF values up to $1.9 \times 10^6 h^{-1}$. Complex **38a** also exhibited a very high catalytic activity for the acceptorless dehydrogenation of secondary alcohols with 0.1 mol % catalyst loading, which avoids use of stoichiometric amounts of oxidants for the target synthesis (Scheme 20).

By means of the similar assembly stategy as shown for the synthesis of dinuclear complexes **36**, multinuclear Ru(II)–NNNN complexes **39** and **40** as well as mononuclear complex **41** (eq. (4)) were synthesized (Scheme 21 and eq. (4)) [46]. The triruthenium(II) – NNNN pincer complex based on 1,3,5-tri(pyridin-4-yl)benzene **39a** exhibited exceptionally high catalytic activity in the TH reaction of 2′-chloroacetophenone, reaching a TOF value of $7.1 \times 10^6 h^{-1}$ at an extremely low catalyst loading (0.008 mol % Ru) in refluxing 2-propanol. The catalytic activity order for the TH reaction of acetophenone is: **39a** ≈ **39b** > **40a** > **40b** > **41** (Table 8).

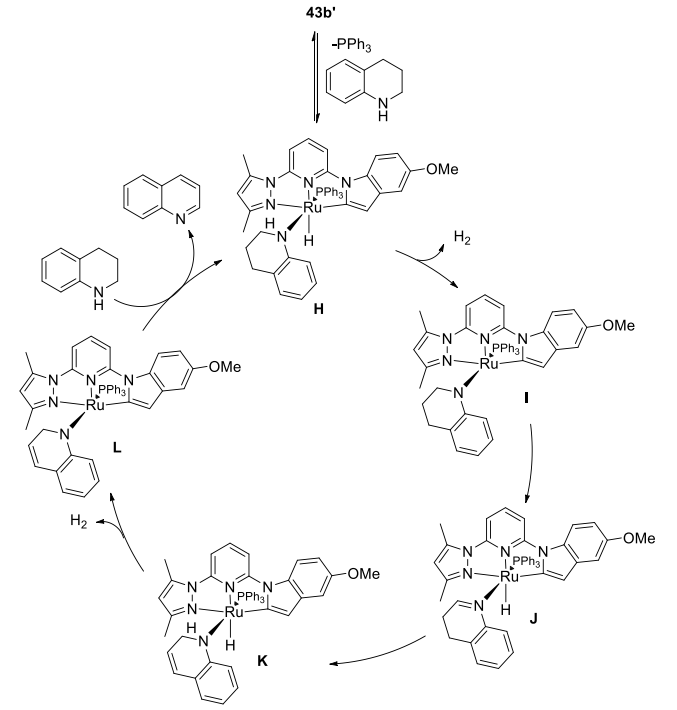


(4)

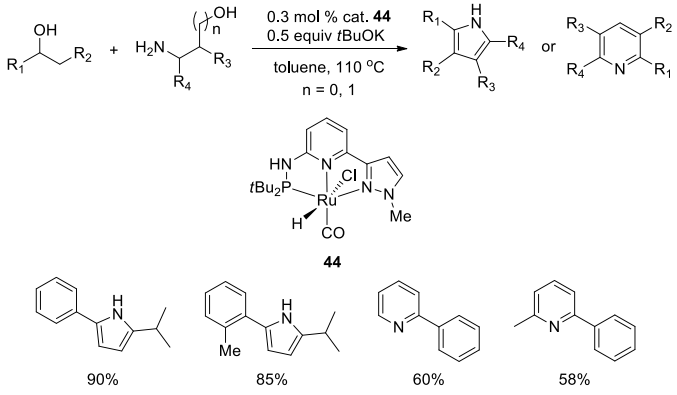
6. Ruthenium complexes for other catalytic reactions

Ruthenium complexes have been used as the homogeneous catalysts not only for transfer hydrogenation of ketones, but also for Oppenauer-type oxidation, *β*-alkylation of secondary alcohols, synthesis of multi-substituted heterocycles, acceptorless dehydrogenation of *N*-heterocycles and secondary alcohols, etc. [1–5].

Complexes **2** and **24** were successfully applied to realize the Oppenauer-type oxidation of secondary alcohols, affording the



Scheme 25. A proposed inner-sphere mechanism for the dehydrogenation of *N*-heterocycles.



Scheme 26. Ruthenium(II)-NNP complex catalysts for multisubstituted pyrrole and pyridine synthesis.

corresponding ketones [31b,47]. Complex **2** were suitable for a wide range of substrates bearing electron-donating substituents such as methyl and methoxyl, and electron-withdrawing groups such as bromo, chloro, fluoro, and trifluoromethyl (Scheme 22).

β-Alkylation of secondary alcohols were also efficiently performed by ruthenium(III) complex **42** through a hydrogen borrowing pathway with water formed as the byproduct (Scheme 23) [48]. Benzylic alcohols bearing electron-deficient substituents (2-, 3-, or 4-chlorobenzyl alcohols) and electron-donating substituents (methyl, methoxy, or 3,4-methylenedioxy) substituents reacted with 1-phenylethanol to form the desired products in 78–91% yields. Dialkylated secondary alcohols were also accessed from the reaction of benzyl alcohols with cyclopentanol. The yields of electron-donating 4-methoxy and 3,4-methylenedioxy substituted benzyl alcohols exhibited a much higher reactivity than those electron-withdrawing chloro-substituted benzyl alcohols.

Ruthenium(II) hydride complexes have been considered as the catalytically active species for the TH reactions of ketones [49]. In our studies, Ru-NNC hydride complexes **43′** were successfully synthesized and applied in the acceptorless dehydrogenation of unsaturated *N*-heterocycles (Scheme 24) [50]. A mixture of the precursor complex **43** and K_2CO_3 base was refluxed in 2-propanol to produce the corresponding Ru (II) hydride complexes **43a'** and **43b'** in 62% and 54% yields, respectively. When a strong electron-withdrawing 4-nitro was located on the benzo ring of the indolyl moiety, the corresponding Ru(II)–NNC hydride complex **43c'** could not be accessed. Ru-H complex **43b'** exhibited a high catalytic activity for the acceptorless dehydrogenation of *N*-heterocycles and secondary alcohols with a good tolerance of the substrates. The plausible mechanism for the dehydrogenation of *N*-heterocycles is proposed in Scheme 25. A coordinately unsaturated ruthenium(II) hydride species is generated from the precatalyst complex **43b'** by dissociation of a PPh_3 ligand, which then coordinates 1,2,3,4-tetrahydroquinoline, forming Ru-H amine complex **H**. By an intramolecular dehydrogenation from the amino hydrogen and Ru-H moiety of complex **H**, a molecule of dihydrogen and coordinately unsaturated complex **I** are formed. Ru-H species **J** is formed via a *β*-H elimination process. Due to the energetically unfavorable dehydrogenation from the C3 − C4 bond, ruthenium(II) hydride immine complex **J** isomerizes to the more stable intermediate complex **K**. A second dehydrogenation and further *β*-H elimination proceeds with liberating dihydrogen and coordination with the *N*-heterocycle substrate, affording the final product quinoline and regenerating Ru-H species **H**, completing the catalytic cycle.

Unsymmetrical Ru(II)-NNP complex **44** based on pyrazolyl-(NH-P*t*Bu$_2$)pyridine ligand was synthesized and efficiently utilized for the synthesis of multisubstituted pyrroles and pyridines from the reactions of secondary alcohols with *β*- or *γ*-amino alcohols through deoxygenation and selective C — N and C — C bond formation (Scheme 26) [51]. In the presence of 0.3 mol % catalyst the cross-coupling reactions took place with a wide range of substrates and tolerated diverse functional groups.

7. Conclusions

Over the last decade significant achievements have been made in the development of pincer-type ruthenium complex catalysts from our laboratories. By tuning the electronic and steric properties of the pincer-type ligands the catalytic behaviors of the resultant ruthenium(II) complexes could be remarkably adjusted. The N—H effect of the coordinating arms, electronic and steric properties of the ligand and linker between polydentate coordination moieties are crucial to the catalytic activity of the resultant mono- and multinuclear Ru(II) complexes. The assembly strategy can also be applied to construct highly active Ru(II) complex catalysts which could be used at a very low loading. The present strategies for complex catalyst construction may be used in homogenous catalysis with other earth-abundant metals such as iron, cobalt, nickel, and manganese, etc.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

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