Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Accepted Article

Title: Air-stable Ru(II)-NNN Pincer Complexes for Efficient Coupling of Aromatic Diamines and Alcohols to 1H-benzo[d]imidazoles with liberation of H2

Authors: Lin Li, Qi Luo, Huahua Cui, Renjie Li, Jing Zhang, and Tianyou Peng

To be cited as: *ChemCatChem* 10.1002/cctc.201800017

Link to VoR: http://dx.doi.org/10.1002/cctc.201800017

A Journal of
ChemPubSoc Europe

WILEY-VCH

www.chemcatchem.org

Air-stable Ru(II)-NNN Pincer Complexes for Efficient Coupling of Aromatic Diamines and Alcohols to 1*H*-benzo[*d*]imidazoles with liberation of H_2

Lin Li, Qi Luo, Huahua Cui, Renjie Li, Jing Zhang* and Tianyou Peng*

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, P. R. China

Abstract: Two new phosphine-free Ru(II)-NNN pincer complexes ([RuCl(**L1**)$(CH_3CN)_2$]Cl (**1**) and [RuCl(**L2**)$(CH_3CN)_2$]Cl (**2**), **L1** = 2,6-bis(1*H*-imidazole-2-yl)pyridine, **L2** = 2,6-bis(1-hexyl-1*H*-imidazole-2-yl)pyridine) were synthesized for homogeneously catalyzing the condensation of benzyl alcohol and benzene-1,2-diamine to 2-pheny-1*H*-benzo[*d*]imidazole and H_2. It was found that the reactivity with an order of **1 > 2** is lower than that of the phosphine-containing Ru(II)-NNN pincer complex [$RuCl_2$(**L1**)$(PPh_3)_3$] (**3**), and thus a homogeneous system containing complex **1**, 1 equiv. of 1,2-bis(diphenyl-phosphanyl)ethane (dppe), and 10 equiv. of $NaBPh_4$ was developed to improve the catalytic efficiency for the condensation of primary alcohols and benzene-1,2-diamine (or its derivatives) to 2-substituted 1*H*-benzo[*d*]imidazoles in excellent yields (up to 97%) and turnover number (TONs ~ 388). The present system realizes facile one-step synthesis of 1*H*-benzo[*d*]imidazole derivatives from alcohols without using the oxidant and/or the stoichiometric amount of inorganic bases that is usually necessary in homogeneous systems reported previously.

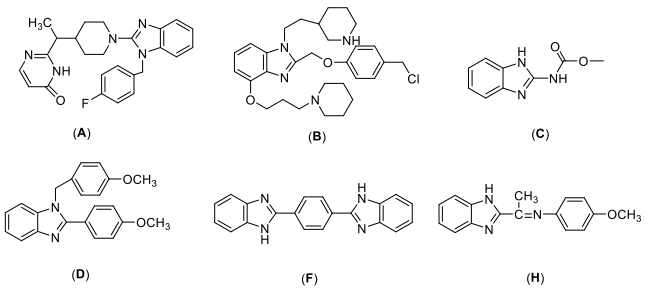
Introduction

Acceptorless dehydrogenative coupling (ADC) of alcohols with amines, as an atom-economical and environmentally friendly method for the construction of new C-N bond, has recently emerged as an important process to afford many useful organic compounds such as imines,[1] amides,[2] amines,[3] or nitrogen-containing heterocyclic compounds.[4] Pioneered by Milstein and co-workers, who reported a Ru-PNN complex as an efficient catalyst for coupling primary alcohols and amines to amides,[2d,5] several precious metal pincer complexes have been developed for these conversion, in which the pincer ligand is usually constructed by at least one strong electron-rich donor (such as phosphine or N-heterocyclic carbene moiety).[5a-c] From the view of normally relative comprehensive synthetic process and the air- or moisture-sensitive nature of phosphine or N-heterocycle carbene ligand, it is worthy to develop new pincer system containing alternative donors such as N or O atoms instead.

1*H*-benzo[*d*]imidazole and its derivatives are essential components of biologically active molecules, which have led to extensive applications in pharmaceutical,[6] agrochemicals,[7] and functional materials (Scheme 1),[8] and therefore much attention has been devoted to the synthesis of 1*H*-benzo[*d*]imidazole derivatives using various protocols. Among which, one-pot synthesis of 1*H*-benzo[*d*]imidazole derivatives through the ADC process of alcohols and aromatic diamines by using well-defined transition metal complexes as catalyst is much attractive since its by-products are water and H_2 that can be used elsewhere.[9] Although several heterogeneous systems developed are capable of this conversion,[10] only one homogeneous system was reported by Kepe and co-workers in 2014,[9a] in which a Ir(I) pincer complex [Ir(cod)2,6-DiAmPy(iPr)$_2$] achieved the catalytic acceptorless condensation of primary alcohols and benzene-1,2-diamine to 2-functionalized 1*H*-benzo[*d*]imidazole derivatives with yields of 56-96% in the presence of 1.4 mol% catalyst and 1 equiv. of KOH (relative to the substrate).[9a]

Based on our previous reports on Ru(II) and Ni(II) complexes bearing pyridine-based NNN pincer ligands, which show high reactivity for acceptorless dehydrogenation of primary alcohols to carboxylic acid and hydrogenation of CO_2 to formic acid in the homogeneous system,[11,12] here we illustrate a new homogeneous system consisting of Ru(II)-NNN (NNN = 2,6-bis(1*H*-imidazol-2-yl)pyridine) and 1,2-bis(diphenylphosphanyl) ethane (dppe) to efficiently catalyze the condensation of various primary alcohols and benzene-1,2-diamine to 2-substituted 1*H*-benzo[*d*]imidazole derivatives with excellent yields (up to 97%) and high turnover number (TON) of ~388. This system just need 2.5 mol% $NaBPh_4$ (relative to the substrate) as an additive, and avoids the utilization of the oxidant and/or the stoichiometric

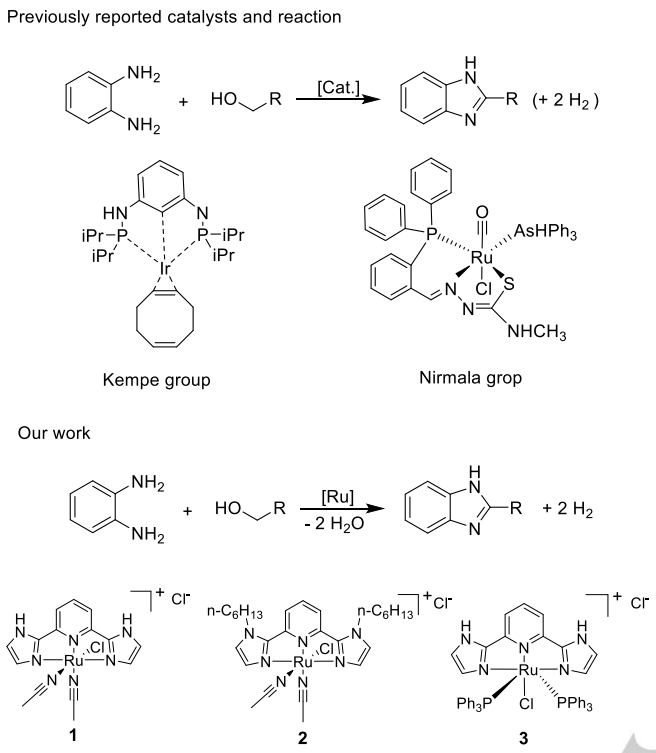
Scheme 1. Examples of important molecules containing 1*H*-benzo[*d*]imidazole moiety.



[a] L. Li, Q. Luo, H. Cui, Prof. R. J. Li, Prof. J. Zhang, Prof. T. Y. Peng
College of Chemistry & Molecular Sciences
Wuhan University
Wuhan 430072, P. R. China
E-mail: jzhang03@whu.edu.cn (J. Zhang); typeng@whu.edu.cn (T. Peng)

Supporting information for this article is given via a link at the end of the document.

Scheme 2. Representative examples for 1*H*-benzo[*d*]imidazole synthesis from alcohol.



amount of strong base (KO^{t}Bu or KOH) that is normally necessary in the previously reported homogeneous systems as shown in Scheme 2.[13,14]

Results and Discussion

Synthesis of 2,6-bis(1-hexyl-1H-imidazol-2-yl)pyridine (L2) and Ru(II) complexes 1~3.

The pincer ligand 2,6-bis(1*H*-imidazol-2-yl)pyridine (**L1**) was prepared from pyridine-2,6-dicarbonitrile according to the reported procedure.[15] By refluxing **L1** and 2 equiv. of 1-bromohexane in acetone for 24 h in the presence of 2 equiv. of KO^{t}Bu, 2,6-bis(1-hexyl-1*H*-imidazol-2-yl)pyridine (**L2**) was obtained in good yield as a yellow oil (80%). There is no signal observed in the region of 9~14 ppm in ^{1}H NMR, indicating the two imidazolyl groups of **L2** are alkylated (Supporting Information, Figure S1). While a triplet peak at 4.42 ppm with integration of four protons can be assigned to the two N-CH_2-C_5H_{11} groups of **L2**. Upon refluxing the acetonitrile solution containing **L1** or **L2** with 0.5 equiv. of $[RuCl_2(p\text{-cymene})]_2$ for 12 h under N_2 flow, [RuCl(**L1**)$(CH_3CN)_2$]Cl (**1**) and {RuCl(**L2**)$(CH_3CN)_2$}Cl (**2**) can be obtained in 88% and 85% (Scheme 3), respectively. The ^{1}H NMR spectrum of complex **1** shows two singlet peaks with integration of three protons each at 2.19 and 2.89 ppm, respectively, which are assigned to the CH_3 groups of two acetonitrile ligands (Supporting Information, Figure S3). This observation is consistent with the two acetonitrile ligands coordinated to the Ru(II) center in axial and meridional position,[16] respectively and similar to that observed in our previous reported complexes.[11b,12]

The ^{1}H NMR spectrum of complex **2** exhibits one triplet peak with integration of four protons at 4.61 ppm, which is assigned to the N-CH_2- groups of **L2**, representing a downfield of 0.19 ppm compared to that of the free ligand **L2** (Supporting Information, Figure S5). There also exist two singlet peaks at 2.16 and 2.87 ppm assigned to the two coordinated acetonitrile ligands, indicating complexes **1** and **2** have the same coordination geometry around the Ru(II) center. When ligand **L1** and 1 equiv. of $[RuCl_2(PPh_3)_3]$ were refluxed in anhydrous ethanol for 6 h under N_2 flow, complex [RuCl(**L1**)$(PPh_3)_2$]Cl (**3**) was obtained as a yellow solid in 86% yield (Scheme 3). Due to its very poor solubility in normal organic solvents ($CHCl_3$, CH_2Cl_2, THF, toluene, acetone, DMSO, *etc.*), there is no ^{1}HNMR or ^{13}C NMR spectra of complex **3** was recorded. The FT-IR spectrum (Supporting Information, Figure S11) of **3** shows a strong peak at 3059 cm^{-1} assigned to the imidazolyl NH of **L1**, while the ESI-MS exhibits the isotopic peaks (M/z) at 871.8 and 610.0 which can be assigned to [RuCl(**L1**)$(PPh_3)_2]^+$ and [RuCl(**L1**)$(PPh_3)]^+$, respectively (Supporting Information, Figure S12). The elemental analysis result (*ref.* Experimental Section) of complex **3** also confirm its structure.

Catalytic condensation of alcohol and benzene-1,2-diamine to 1*H*-benzo[*d*]imidazole derivatives and H_2.

In the preliminary studies, benzyl alcohol and benzene-1,2-diamine were selected as the substrates. A typical experiment was carried out by using complex **1** (6.25 μmol) and benzene-1,2-diamine (2.5 mmol) with additive (62.5 μmol) in an excess amount of benzyl alcohol (7.5 mmol) at 165°C (oil bath) under nitrogen atmosphere for 24 h. When using the neutral salt $NaBPh_4$ as an additive, 2-phenyl-1*H*-benzo[*d*]imidazole can be produced in a yield of 31%, higher than that using strong bases (KO^{t}Bu, KOH, Cs_2CO_3) as an additive (Table 1, entries 1-4). The unreacted starting materials can be recovered (for example, 65% for benzene-1,2-diamine).

Scheme 3. Synthesis of complexes **1-3**.

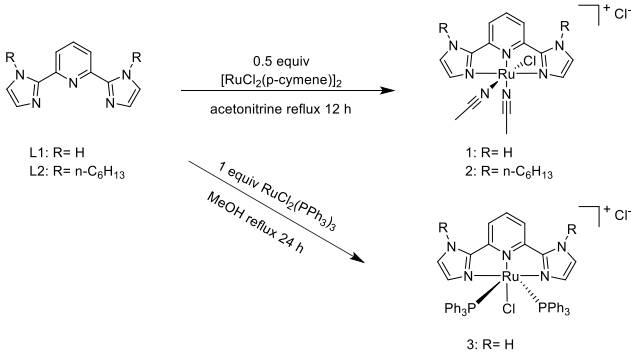
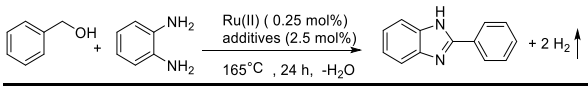


Table 1. Optimization of Catalytic Condition for the 2-phenyl-1*H*-benzo[*d*]imidazole Synthesis.[a]



Entry	Catalyst	PPh_3 (mol %)	Base	Yield[b]
1	1	None	KO^{t}Bu	12
2	1	None	KOH	11
3	1	None	$CeCO_3$	11
4	1	None	$NaBPh_4$	31
5	1	0.25	$NaBPh_4$	82
6	1	0.50	$NaBPh_4$	88(82[c])
7	1	0.75	$NaBPh_4$	78
8	1	0.50	$NaBPh_4$	70[d]
9	1	0.50	$NaBPh_4$	51[e]
10	2	0.50	$NaBPh_4$	48
11	3	None	$NaBPh_4$	84
12	4[f]	0.50	$NaBPh_4$	34
13	1	0.25[g] (dppe)	$NaBPh_4$	92[h](87[i])
14	$RuCl_2(PPh_3)_3$	None	$NaBPh_4$	33[j]
15	$RuCl_2(PPh_3)_3$	0.50	$NaBPh_4$	35[k]
16	None	None	$NaBPh_4$	0.0
17	1	0.50	none	0.0

[a] Reaction conditions: benzene-1,2-diamine (2.5 mmol), benzyl alcohol (7.5 mmol), base (2.5 mol%), catalyst loading (0.25 mol%), heated at 165°C for 24 h under nitrogen; [b] isolated yield; [c] yield of H_2 = 100% × $n(H_2)/(2\times n(\text{diamine})$; [d] Catalyst (0.25 mol%) in 1 mL of mesitylene at 165°C. [e] Catalyst (0.25 mol%) in 1 mL of *p*-xylene at 150°C. [f] complex **4**, $[Ru(Cl(\mathbf{L_3})(CH_3CN)_2)Cl$, **L3** = 2,6-bis(benzimidazole-2-yl)-4-hydroxypyridine;[12] [g] Using dppe instead of PPh_3, heated at 165°C for 12 h; [h] The reaction hour is 6 h; [i] yield of H_2= 100% × $n(H_2)/(2\times n(\text{diamine})$; [j], [k] yield of 1-benzyl-2-phenyl-1*H*-benzo-[*d*]imidazole as the main by-product in 37% and 36%, respectively.

To our delighted, when PPh_3 was loaded with $NaBPh_4$ under the same condition, 2-phenyl-1*H*-benzo[*d*]imidazole was obtained in good yields (Table 1, entries 5-7), in which the use of 2 equiv. of PPh_3 (relative to complex **1**) gave the best yield (88%). A hydrogen production test exhibited the H_2 was obtained in 82% (Table 1, entry 6 and Supporting Information, Table S1). It was well consistent with the production of 2-phenyl-1*H*-benzo[*d*]imidazole, indicating the oxidant or hydrogen acceptor is not necessary in our catalytic system.

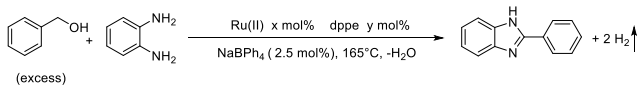
Upon using the mesitylene or *p*-xylene as solvent, the yields of 2-phenyl-1*H*-benzo[*d*]imidazole dropped to 70% or 51% (Table 1, entries 8 and 9), respectively. The use of complex **2** instead of **1** resulted in the formation of 2-phenyl-1*H*-benzo[*d*]imidazole in 48% under the same condition, indicating the imidazolyl N-H groups of complex **1** play an important role in the catalytic cycle (Table 1, entry 10). Complex **3** gave almost the same yield (84%) as complex **1** (accompanied by 2 equiv. of PPh_3), indicating that the coordination of phosphorus donor to the Ru center increases the catalytic reactivity (Table 1, entry 11). It is noted that the use of 1,2-bis(diphenylphosphanyl)ethane (dppe, 1 equiv. relative to complex **1**) afforded the excellent yield (92%) in a shorter time (6 h), which was also confirmed by the hydrogen production (87% in 4 h) (Table 1, entry 13, and Supporting Information, Table S2 and Figure S13). These results again suggest that the more electron-rich Ru center (upon chelated by dppe) exhibit a higher catalytic reactivity. Using the $RuCl_2(PPh_3)_3$ instead of complex **1** as the catalyst under the same condition, 2-phenyl-1*H*-benzo[*d*]imidazole was isolated in 33% yield accompanied by the formation of N-benzyl-2-phenyl-1H-benzo[d]imidazole in 37% (Table 1, entry 14), while addition of PPh_3 (2 equiv. relative to Ru(II) precursor) did not improve the yield (Table 1, entries 14 and 15). Although the system containing $RuCl_2(PPh_3)_3$ /dppe (1:1 mol) afforded the 2-phenyl-1*H*-benzo[*d*]imidazole in good yield (70%), it is not efficient for conversion of benzene-1,2-diamine with aliphatic alcohols. For instance, 2-cyclohexyl-1*H*-benzo[*d*]imidazole was obtained in low yield (22%) (Table 2, **3j** and Supporting Information, Table S4), while the diamine was recovered in ~ 70%. These results indicated that the coordination of NNN pincer ligand to the Ru(II) center led to the higher yield and higher selectivity for 2-substituted 1*H*-benzo[*d*]imidazole with a broader substrate scope. As expected, there was almost no product observed without the use of Ru(II) complex or $NaB(Ph)_4$ (Table 1, entries 16, 17).

Using the optimized reaction conditions (165°C, 0.25 mol% complex **1**, 0.25 mol% dppe, 2.5 mol% $NaBPh_4$), the substrate scope of the reaction was then examined, and results are listed in Table 2. Both aromatic alcohols and aliphatic alcohols can be dehydrogenative coupled with benzene-1,2-diamine to corresponding 2-substituted 1*H*-benzo[*d*]imidazole in excellent yields (up to 97%). Aromatic alcohols functionalized by both electron-donating groups (methyl, methoxy) and weak electron-withdrawing groups (Cl, Br) afforded the 2-substituted 1*H*-benzo[*d*]imidazoles in 90-96% yields (Table 2, 3**d**, 3**e**, 3**g**, 3**i**). It is noted that both (2-chlorophenyl)methanol and (4-chlorophenyl)methanol gave the corresponding products in almost the same yields (96%, Table 2, 3**f** and 3**g**). The excellent yields for products with the halogen substitution on the aromatic ring of alcohol or diamine indicate the halogens (F, Cl, Br) are tolerant to the catalytic reaction condition (Table 2, 3**c**, 3**f**-3**i**, 3**s**). When aliphatic alcohol with high boiling point (>135°C) was used, the corresponding 2-alkyl-1*H*-benzo[*d*]imidazole was obtained in almost quantitative isolated yield (95%) (Table 2, 3**j**-3**l**, 3**r**). But the 1-butanol (bp ~110°C) gave 2-propyl-1*H*-benzo[*d*]imidazole in a relative lower yield (75%) even though the mesitylene was used as the solvent. Unfortunately, 2-*tert*-butyl-1*H*-benzo[*d*]imidazole was obtained in very low yield (18%) when 2,2-dimethyl-1-propanol was loaded, probably due to the steric reason (Table 2, 3**n**). As expected, 1,4-bis(1*H*-benzo[*d*]imidazol-2-yl)benzene was formed in good yield (87%, Table 2, 3**t**) when 1,4-phenylenedimethanol was coupled with benzene-1,2-diamine.

Upon lowering the catalyst loading to 0.025 mol%, 2-phenyl-1*H*-benzo[*d*]imidazole was obtained in yield of 90% with TONs of ~3600 when the reaction was carried out for 24 h (Scheme 4). A higher TONs (6000) was obtained when 0.01 mol% complex **1**

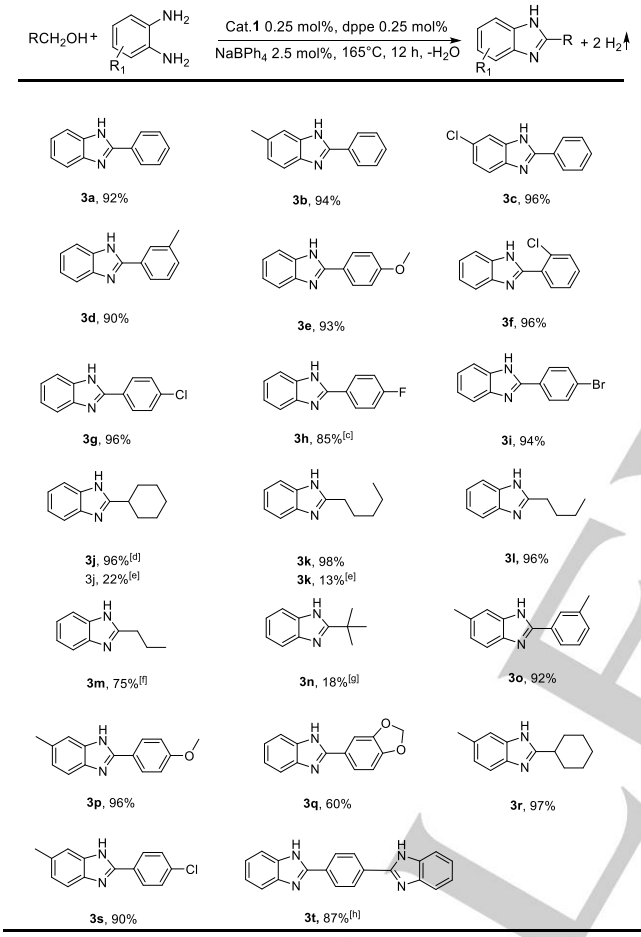
10.1002/cctc.201800017

Scheme 4. The synthesis of 2-phenyl-1*H*-benzo[*d*]imidazole with lower catalyst loading.



Ru(II) x mol%	dppe y mol%	Time/h	Yield (%)
0.25	0.25	12	92
0.025	0.025	24	90
0.01	0.01	48	60

Table 2. Acceptoless Dehydrogenative Condensation of Primary Alcohols and Functionalized benzene-1,2-diamine.[a],[b]

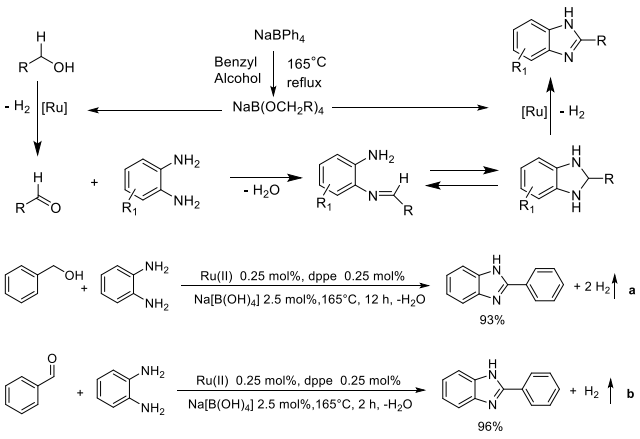


[a] Reaction conditions: benzene-1,2-diamine derivatives (2.5 mmol), alcohol (7.5 mmol), complex **1** (0.25 mol%), dppe (0.25 mol%), $NaBPh_4$ (2.5 mol%), at 165°C for 12 h; [b] Isolated yield; [c], [d] The reaction time is 6 h; [e], $RuCl_2(PPh_3)_3$ (0.25 mol%) was used instead of complex **1**; [f], [g] Catalyst (0.25 mol%) in 1 mL of mesitylene at 150°C; [g] The reaction hour is 24 h; [h] benzene-1,2-diamine (2.5 mmol), benzene-1,4-dimethanol (1 mmol), 1 mL mesitylene.

was used with longer reaction time (48 h). These results indicate that complex 1 is an excellent catalyst precursor for acceptorless dehydrogenative coupling of alcohol and diamine to 2-substituted 1*H*-benzo[*d*]imidazole (Scheme 4).

Heating 0.25 mol% complex **1** and 2.5 mol% $NaBPh_4$ in benzyl alcohol at 165°C for 12 h under nitrogen atmosphere, benzaldehyde was obtained in yield of 6% (based on the alcohol) accompanied by the liberation of hydrogen (confirmed by the GC), indicating the benzaldehyde is probably the first intermediate in the catalytic cycle. A possible mechanism to rationalize this transformation is illustrated in Scheme 5. Initially, complex **1** catalyzes the dehydrogenation of primary alcohol promoted by the borate salts, leading to the formation of aldehyde and H_2. The aldehyde subsequently reacts with benzene-1,2-diamine to generate the imine intermediate, which can be in equilibrium with dihydrobenzimidazole. The dihydrobenzimidazole is then dehydrogenated to form the final product and liberate the second H_2 catalyzed by the Ru(II) complex and borate salts.[9f,10a] Since the $NaBPh_4$ is necessary in the catalytic reaction (Table 1, entry 15), it is worthy to illustrate the role of $NaBPh_4$ in the catalytic cycle. We initially think the excess amount of $NaBPh_4$ relative to Ru(II) complex just help to remove the two chloride ligands from the Ru(II) center. However, upon using the complex $[Ru(\mathbf{L1})(MeCN)_2(solvent)](BPh_4)_2$ [17] with dppe as the catalyst precursor (both 0.25 mol% relative to the diamine), 2-phenyl-1*H*-benzo[*d*]imidazole was obtained in only 8% yield when the reaction was carried out at 165°C for 12 h under N_2 flow. However, the yield dramatically increased to 93% when 2 mol% $NaBPh_4$ was added to this system under the same condition (Supporting Information, Figure S14). After the catalytic reaction was complete, the borate was collected and determined by the ^{11}B NMR spectrum, which exhibits only one broad singlet peak at 2.93 ppm (Supporting Information, Figure S10). This signal is located at the region of $B(OR_4)^-$ anion and is very different to that of $B(Ph_4)^-$ anion (-6.62 ppm, Supporting Information, Figure S8).[18] This observation indicates that $NaB(Ph)_4$ is probably decomposed to $NaB(OR)_4$ during the catalytic cycle. When $B(OH)_3$ and 1 equiv. of NaOH were heated in benzyl alcohol at 165°C for 2 h, the ^{11}B NMR spectrum shows only one broad singlet signal at 3.18 ppm (Supporting Information, Figure S9), which is similar to that observed in our catalytic cycle, again suggesting the decomposition of $NaB(Ph)_4$ to $NaB(OR)_4$ (R = alkyl or H). Since the $B(OH)_3$ was reported as an efficient dehydration catalyst for coupling the carboxylic acid and amine (or alcohol) to form the amide (or ester),[19] the formation of $B(OR)_4^-$ anion would also help the dehydrogenation or dehydration during the catalytic cycle because it can easily bind to protonic H of alcohol, aldehyde or dihydrobenzimidazole through hydrogen bond. Furthermore, when $NaB(OH)_4$ (formed

Scheme 5. The plausible mechanism of catalytic dehydrogenative condensation of benzene-1,2-diamine with alcohol.



in situ from $B(OH)_3$ (2.5 mol%) and NaOH (2.5 mol%)) was used as additives instead of $NaBPh_4$ under the same condition listed in Table 2 (3**a**), 2-phenyl-1*H*-benzo[*d*]omidazole was obtained in 93%, indicating the $Na[B(OR)_4]$ is probably the real additive which play an important role in the catalytic cycle (Scheme 5, a).

Further experiment was carried out by using benzaldehyde and benzene-1,2-diamine with complex **1** (0.25 mol%) and 2.5 mol% $Na[B(OH)_4]$ at 165°C under nitrogen for 2 h (Scheme 5, b). 2-phenyl-1*H*-benzo[*d*]imidazole was obtained in excellent yield (96%) while H_2 was obtained in 94% (based on benzaldehyde, Supporting Information, Table S3). This observation again supports the plausible mechanism shown in Scheme 5.

Conclusions

In conclusion, we have illustrated two fully characterized Ru(II)-NNN complexes as the catalyst precursor for dehydrogenative condensation of primary alcohol and aromatic diamine to the 2-substituted 1*H*-benzo[*d*]imidazole and H_2 in the presence of catalytic amount of $NaBPh_4$. The catalytic reactivity follows the order: **1** > **2**. The coordination of strong electron-donating ligand dppe to the Ru center greatly improved the catalytic reactivity. Decomposition of $NaB(Ph)_4$ to $NaB(OR)_4$ play an important role during the catalytic cycle. Examination of substrate scope indicates that the electron-donating groups or weak electron-withdrawing groups on alcohols or diamines gave the excellent yield (~ 97%). A high turnover numbers (~ 6000) was achieved with lower catalyst loadings and longer reaction time. This homogeneous system is a good example for one-step synthesis of 1*H*-benzo[*d*]imidazole derivatives from alcohols using neither the oxidant nor the stoichiometric amount of inorganic bases, thus is a greener method compared with other reported homogeneous system.

Experimental Section

General Information.

All experiments were carried out under an atmosphere of purified nitrogen except other noted. All solvents were purified with the standard procedure. Commercially available reagents were used as received. The NMR spectra were received using Bruker Avance II HD 400 MHz spectrometer. The ^{1}H NMR chemical shifts are referenced to the residual hydrogen signals of the deuterated solvent or TMS, the ^{13}C NMR chemical shifts are referenced to the ^{13}C signals of the deuterated solvent, and the Boron trifluoride diethyl etherate is used as an external reference for ^{11}B NMR. All spectra were recorded at room temperature unless otherwise noted. Elemental analysis and ESI-Ms was performed by the Test Centre of Wuhan University. Fourier transform infrared (FTIR) spectrum was recorded by using a Nicolet iS10 spectrometer (Thermo Electron). Ligand 2,6-bis(1*H*-imidazol-2-yl)pyridine (**L1**),[15] Ru(II) precursors $[RuCl_2(PPh_3)_3]$,[20] and $[RuCl_2(p\text{-cymene})]_2$[21] were prepared according to the reported literature. Ligand 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridine-4-ol (**L3**) and complex $[RuCl(CH_3CN)_2$(**L3**)]Cl were synthesized with the method reported by our group previously.[12]

Synthesis and characterization of 2,6-bis(1-hexyl-1*H*-imidazole-2-yl)pyridine (L2) and Ru(II) complexes 1-3.

Synthesis of 2,6-bis(1-hexyl-1H-imidazol-2-yl) pyridine (L2)

A solution of 2,6-bis(1H-imidazol-2-yl)pyridine (0.211 g, 1 mmol) and KO^{t}Bu (0.224 g, 2 mmol) in acetone (50 mL) was stirred at room temperature for 2 h. Then the 1-bromohexane (0.330 g, 2 mmol) was added and the mixture was refluxed for 24 h. Upon cooling to the room temperature, the solvent was removed in vacuum and the residue was extracted with a mixed solvent of CH_2Cl_2 / CH_3OH (10:1, V: V, 3×50 mL). The combined organic solution was evaporated under reduced pressure and the crude product of was further purified by the column chromatography using silica gel (elute: CH_2Cl_2/ethyl acetate, 1/1 (v/v)) to obtain the pure ligand **L2** as a yellow oil. Yield: 0.304 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, *J*=8.0 Hz, 2H), 7.87 (t, *J*=8.0 Hz, 1H), 7.14 (d, *J*=1.2 Hz, 2H), 7.04 (d, *J*=1.2 Hz, 2H), 4.48 (t, *J*=7.4 Hz 4H), 1.67(m, 4H), 1.13 (m, 12H), 0.77(t, *J*=8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.92 (s), 22.45 (s), 26.14 (s), 31.23 (s), 47.54 (s), 122.48 (s), 122.91 (s), 128.51 (s), 137.66 (d), 144.99 (s), 149.71 (s). Elemental Anal. Calcd for $C_{23}H_{33}N_5$ (%): C, 72.78; H, 8.76; N, 18.45. Found: C, 72.73; H, 8.64; N 18.63.

Synthesis of $[RuCl(L1)(MeCN)_2]Cl$ (1) and $[RuCl(L2)(MeCN)_2]Cl$ (2)

Ligand **L1** (0.422 g, 2 mmol) and $[RuCl_2$ (p-cymene)$]_2$ (0.616 g, 1 mmol) were dissolved in acetonitrile (20 mL) and the solution was refluxed for 12 h under a nitrogen atmosphere. After cooling to room temperature, the red-brown precipitate was filtered, washed with diethyl ether (3 × 10 mL) and then dried under vacuum for 12 h. Complex **1** was obtained as a red-brown power (0.82 g, 88%). ^{1}H NMR (400 MHz, [D_6]DMSO) δ (ppm): 2.17 (s, 3H); 2.86 (s, 3H); 7.42(d, *J* = 1.2 Hz, 2H); 7.69 (d, *J* = 1.2 Hz, 2H); 7.89 (t, *J* = 8.0 Hz, 1H); 8.21 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 3.70; 4.51; 117.02; 120.43; 122.20; 127.31; 131.12; 136.73; 147.30; 152.59. ESI-MS (M/z): 429.7 ($[RuCl(C_{11}N_5H_9)(CNCH_3)_2]^+$), 352.9 ($[RuCl(C_{11}N_5H_8)(CH_3CN)]^+$); Elemental Anal. Calcd. for $C_{15}H_{15}N_7Cl_2Ru$ (%): C, 38.72; H, 3.24; N, 21.07. Found: C, 38.59; H, 3.32; N, 21.12.

The same procedure was used for the synthesis of complex **2** as a yellowish - brown solid (1.07 g, 85%). ^{1}H NMR (400 MHz, [D_6]DMSO) δ (ppm): 0.83 (s, 6H); 1.28 (m, 12H); 1.82 (m, 4H); 2.13 (s, 3H); 2.83 (s, 3H); 4.60 (t, *J* = 8.0 Hz, 4H); 7.43 (d, *J* = 7.3 Hz, 2H); 7.76 (t, *J* = 8.0 Hz, 2H); 7.97 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 3.86; 4.71; 114.07; 118.64; 121.62; 122.44; 125.04; 126.11; 129.95; 134.57; 136.09; 143.29; 152.61; 153.45. Elemental Anal. Calcd. for $C_{27}H_{39}N_7Cl_2Ru$ (%): C, 51.18; H, 6.20; N, 15.47. Found: C, 51.26, H, 6.03, 15.59.

Synthesis of $[RuCl(L1)(PPh_3)_2]Cl$ (3)

Ligand **L1** (0.211 g, 1 mmol) and $[RuCl_2(PPh_3)]$ (0.958 g, 1 mmol) were dissolved in anhydrous ethanol (30 mL) and the solution was refluxed for 6 h under a nitrogen atmosphere. After cooling to room temperature, the yellow precipitate was filtered, washed with diethyl ether (3 × 10 mL) and then dried under vacuum for 12 h to obtain pure complex **3** as a yellow power (1.0 g, 88%). FT-IR (KBr pellet): 3059 cm^{-1}; ESI-MS (M/z): 871.8 ($[RuCl(L1)(PPh_3)_2]^+$), 610.0 ($[RuCl($**L1**$)(PPh_3)]^+$); Elemental Anal. Calcd. for $C_{47}H_{39}N_5Cl_2P_2Ru$ (%): C, 62.19; H, 4.33; N, 7.71 Found: C, 62.03, H, 4.18, N 7.80.

General procedure for catalytic reactions.

Method A: Benzyl alcohol (0.81 g, 7.5 mmol), benzene-1,2-diamine (0.27 g, 2.5 mmol), Ru(II) complex **1**, **2**, **3** or **4** (6.25 μmol, 0.25 mol%), phosphine (0 ~ 18.75 μmol), and additive (62.5 μmol, 2.5 mol%) were mixed in a 25 mL schlenk tube and the reaction mixture was heated at 165°C (oil bath) for 12 h in an open system under purified nitrogen. After cooling to the room temperature, the unreacted alcohol was removed under vacuum and the residue was purified by column chromatography on silica gel with ethyl acetate/pentane (1/4, v/v) as eluent to yield pure 2-phenyl-benzimidazole as a white solid, which is characterized by ^{1}H NMR and ^{13}C NMR in comparison with the standard sample.

Method B: Alcohol (7.5 mmol), benzene-1,2-diamine derivatives (2.5 mmol), complex **1** (6.25 μmol, 0.25 mol%), dppe (6.25 μmol, 0.25 mol%), and $NaBPh_4$ (62.5 μmol, 2.5 mol%) were mixed in a 25 mL schlenk tube and the reaction mixture was heated at 165 °C for 12 h in an open system under purified nitrogen. After cooling to the room temperature, the unreacted alcohol was removed under vacuum and the residue was purified by column chromatography on silica gel with ethyl acetate/pentane (1/4, v/v) as eluent to yield pure 2-substituted-benzimidazole as a white solid, which is characterized by ^{1}H NMR and ^{13}C NMR in comparison with the standard sample.

Method C: Benzyl alcohol (8.1 g, 75 mmol), benzene-1,2-diamine (2.7g, 25 mmol), complex **1** (6.25 μmol 0.025 mol%), dppe (6.25 μmol, 0.025 mol%), and $NaBPh_4$ (625 μmol, 2.5 mol%) were mixed in a 100 mL schlenk tube and the reaction mixture was heated at 165 °C for 24 h in an open system under purified nitrogen. After cooling to the room temperature, the unreacted alcohol was removed under vacuum and the residue was purified by column chromatography on silica gel with ethyl acetate/pentane (1/4, v/v) as eluent to yield pure 2-substituted-benzimidazole as a white solid, which is characterized by ^{1}H NMR and ^{13}C NMR in comparison with the standard sample.

Method D: Benzyl alcohol (9.7 g, 90 mmol), benzene-1,2-diamine (3.24 g, 30 mmol), complex **1** (3 μmol, 0.01 mol%), dppe (3 μmol, 0.01 mol%), and $NaBPh_4$ (600 μmol, 2 mol%) were mixed in a 100 mL schlenk tube and the reaction mixture was heated at 165 °C for 48 h in an open system under purified nitrogen. After cooling to the room temperature, the unreacted alcohol was removed under vacuum and the residue was purified by column chromatography on silica gel with ethyl acetate/pentane (1/4, v/v) as eluent to yield pure 2-substituted-benzimidazole as a white solid, which is characterized by ^{1}H NMR and ^{13}C NMR in comparison with the standard sample.

Procedure for H_2 gas production.

Under a nitrogen atmosphere, benzene-1,2-diamine (0.54 g, 5.0 mmol), benzyl alcohol (1.62 g, 15 mmol), phosphine (25 μmol, 0.50 mol%) or dppe (12.5 μmol, 0.25 mol%), $NaBPh_4$ (125 μmol, 2.5 mol%), and complex **1** (12.5 μmol, 0.25 mol%) were added to a 100 mL schlenk tube which is connected with a gas collection instrument through gravity drainage method. The reaction mixture was heated at 165°C (oil bath). Over a period of time, the volume of the gas was recorded (Supporting Information Table S1, S2). The hydrogen was confirmed by the GC. After cooling to the room temperature, the mixture was treated with the same procedure according to the Method A. A blank experiment without catalyst was taken at the same condition.

Catalytic acceptorless dehydrogenation of the benzyl alcohol to benzaldehyde. Benzyl alcohol (2.5 mmol), complex **1** (6.25 μmol 0.25 mol%), $NaBPh_4$ (62.5 μmol 2.5 mol%) were mixed in a 25 mL schlenk tube and the reaction mixture was heated at 165°C for 12 h in an open system under purified nitrogen. After cooling to room temperature, the solution was subjected to GC-MS and ^{1}HNMR analysis. The yield of benzaldehyde was determined by ^{1}HNMR using the dioxane as the inner standard.

Condensation of benzaldehyde and benzene-1,2-diamine. Benzaldehyde (2.5 mmol), benzene-1,2-diamine (3.0 mmol), complex **1** (6.25 μmol 0.25 mol%), dppe (6.25 μmol, 0.25 mol%), $NaB(OH)_4$ (62.5 μmol, 2.5 mol%), and mesitylene (1 mL) were mixed in a 25 mL schlenk tube and the reaction mixture was heated at 165°C for several hours in an open system under purified nitrogen. After cooling to the room temperature, the mixture was treated with the same procedure according to the Method A.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21171134, 21573166), the Natural Science Fund of Hubei Province (2011CDB441), and the Funds for Creative Research Groups of Hubei Province (2014CFA007).

Keywords: dehydrogenative condensation • 1*H*-benzo[*d*]imidazole • homogeneous catalysis • Ru(II)-NNN complex • $NaB(Ph)_4$

[1] a) D. Cho, K. C. Ko, J. Y. Lee, *Organometallics* **2013**, *32*, 4571-4576; b) K. S. Sandhya, C. H. Suresh, *Organometallics* **2013**, *32*, 2926-2933; c) S. Musa, S. Fronton, L. Vaccaro, D. Gelman, *Organometallics* **2013**, *32*, 3069-3073; d) G. Zhang, S. K. Hanson, *Org. Lett.* **2013**, *15*, 650-653. e) J. W. Rigoli, S. A. Moyer, S. D. Pearce, J. M. Schomaker, *Org. Biomol. Chem.* **2012**, *10*, 1746-1749; f) H. Li, X. Wang, M. Wen, Z.-X. Wang, *Eur. J. Inorg. Chem.* **2012**, 5011-5020; g) N. D. Schley, G. E. Dobereiner, R. H. Crabtree, *Organometallics* **2011**, *30*, 4174-4179; h) G. Zeng, S. Li, *Inorg. Chem.* **2011**, *50*, 10572-10580; i) B. Gnanaprakasam, J. Zhang, D. Milstein, *Angew. Chem. Int. Ed.* **2010**, *49*, 1468-1471.

[2] a) D.G. Gusev, *ACS Catal*. **2016**, *6*, 6967-6981; b) N.J. Oldenhuis, V.M. Dong, Z.B. Guan, *Tetrahedron* **2014**, *70*, 4213-4218; c) L.U. Nordstrom, H. Vogt, R. Madsen, *J. Am. Chem. Soc.* **2008**,*130*,17672-17673; d) Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790-792.

[3] a) G. Walther, J. Deutsch; A. Martin, F.-E. Baumann; D. Fridag, R. Franke, A. Köckritz, *ChemSusChem* **2011**, *4*, 1052-1054; b) X. Ye, P. N. Plessow, M. K. Brinks, M. Schelwies, T. Schaub, F. Rominger, R. Paciello, M. Limbach, P. Hofmann, *J. Am. Chem.Soc.* **2014**, *136*, 5923-5929; D. Pingen, C. Müller, D. Vogt, *Angew. Chem., Int. Ed.* **2010**, *49*, 8130-8133; S. Imm, S. Ba.hn, L. Neubert, H. Neumann, M. Beller, *Angew. Chem., Int. Ed.* **2010**, *49*, 8126-8129.

[4] a) N. Deibl, R. Kempe, *Angew. Chem. Int. Ed.* **2017**, *56*, 1663-1666; b) B. Emayavaramban, M. Sen, B. Sundararaju, *Org. Lett.* **2017**, *19*, 6-9; c) M. Kojima, M. Kanai, *Angew. Chem. Int. Ed.* **2016**, *55*, 12224-12227; d) P. Daw, S. Chakraborty, J. A. Garg, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2016**, *55*, 14373-14377; e) S. M. A. H. Siddiki, A. S. Touchy, C. Chaudhari, K. Kon, T. Toyao, K.-i. Shimizu, *Org. Chem. Front.* **2016**, *3*, 846-851; f) K. Iida, T. Miura, J. Ando, S. Saito, *Org. Lett.* **2013**, *15*, 1436-1439; g) D. Srimani, Y. Ben-David, D. Milstein, *Chem. Commun.* **2013**, *49*, 6632-6634; h) D. Srimani, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2013**, *52*, 4012-4015; i) S. Michlik, R. Kempe, *Angew. Chem. Int. Ed.* **2013**, *52*, 6326-6329; j) J. Schranck, A. Tlili, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 7642-7644; k) M. Zhang, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *125*, 625-629.

[5] a) P. Hu, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2016**, *55*, 1061-1064; b) C. Gunanathan, D. Milsten, *Chem. Rev*. **2014**, *114*, 12024-12087; c) C. Gunanathan, D. Milsten, *Scinenc* **2013**, *341*, 1229712; d) B. Gnanaprakasam, E. Balaraman, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.* **2011**, *50*, 12240-12244; e) C. Gunanathan, D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588-602.

[6] a) D. Dai, J. R. Burgeson, D. N. Gharaibeh, A. L. Moore, R. A. Larson, N. R. Cerruti, S. M. Amberg, T. C. Bolken, D. E. Hruby, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 744-749; b) D. A. Horton, G. T. Bourne, M. L. Smythe, *Chem. Rev.* **2003**, *103*, 893-930; c) T. Roth, M. L. Morningstar, P. L. Boyer, S. H. Hughes, R. W. Buckheit, C. J. Michejda, *J. Med. Chem.* **1997**, *40*, 4199-4207. d) J. S. Kim, B. Gatto, C. Yu, A. Liu, L. F. Liu, *J. Med. Chem.* **1996**, *39*, 992-998.

[7] a) J. Dessingou, A. Mitra, K. Tabbasum, G. S. Baghel, C. P. Rao, *J. Org. Chem.* **2012,** *77*, 371-378; b) Z. Guo, N. R. Song, J. H. Moon, M. Kim, E. J. Jun, J. Choi, J. Y. Lee, C. W. Bielawski, J. L. Sessler, J. Yoon, *J. Am. Chem.Soc.* **2012,** *134* , 17846-17849.

[8] a) K. M. Wiggins, R. L. Kerr, Z. Chen, C. W. Bielawski, *J. Mater. Chem.* **2010**, *20*, 5709-5714; b) A. J. Boydston, C. S. Pecinovsky, S. T. Chao, C. W. Bielawski, *J. Am. Chem. Soc.* **2007**, *129*, 14550-14551; c) J. B. Wright, *Chem. Rev.***1951**, *48*, 397-541.

[9] a) T. Hille, T. Irrgang and R. Kempe, *Chem. Eur. J.*, **2014**, *20*, 5569-5572; b) During the preparation of our manuscript, Milstein and co-worker an Co(II)-PNN complex for dehydrogenative coupling alcohol and aromatic diamine to corresponding 2-substituted 1*H*-

benzo[*d*]imidazole with catalyst loading of 5 mol% relative the substrate, while the 4Å molecular sieves was used as additive for absorption of the *in situ* formed water: D. Prosentjit, B. D. Yehoshoa, D. Milstein, *ACS. Catal.* **2017**, *7*, 7456-7460.

[10] a) K. Tateyama, K. Wada, H. Miura, S. Hosokawa, R. Abe, M. Inoue, *Catal. Sci. Technol.* **2016**, *6*, 1677-1684; b) F. Rajabi, S. De, R. Luque, *Catal. Lett.* **2015**, *145*, 1566-1570; c) Z.-g. Wang, X.-h. Cao, Y. Yang, M. Lu, *Synthetic. Commun.* **2015**, *45*, 1476-1483; d) H Wang, J. Zhang, Y.-M. Cui, K.-F. Yang, Z.-J. Zheng, L.-W. Xu, *RSC Adv*. **2014**, *4*, 34681−34686; e) T. B. Nguyen, L. Ermolenko, A. Al-Mourabit, *J. Am. Chem.Soc.* **2013**, *135*, 118-121; f) Y. Shiraishi, Y. Sugano, S. Tanaka, T. Hirai, *Angew. Chem., Int. Ed.* 2010, *49*, 1656−1660.

[11] a) Z. Dai, Q. Luo, H. J. Cong, R. J. Li, J. Zhang, T. Y. Peng, *Catal. Sci. Technol.* **2017**, *7*, 2506-2511; (b) Z. Dai, Q. Luo, X. Meng, R. J. Li, J. Zhang, T. Y. Peng, *J. Organomet. Chem.* **2017**, *830*, 11-18.

[12] Z. Dai, Q. Luo, H. J. Cong, J. Zhang, T. Y. Peng, *New J. Chem*. **2017**, *4*1, 3055-3060.

[13] a). R. Ramachandran, G. Prakash, S. Selvamurugan, P. Viswanathamurthi, J. G. Malecki, V. Ramkumar, *Dalton Trans.* **2014**, *43*, 7889−7902; b) V. R. Ruiz, A. Corma, M. J. Sabater, *Tetrahedron* **2010**, *66*, 730-735; c) Y.M. Rn, C. Cai, *Org. Prep. Proced. Int.* **2008**, *40*, 101-105; d) M. Khodaei, K.Bahrami, I. Kavianinia, *Synthesis* **2007**, 547-550; d) K. J. Lee, K. D. Janda, *Can. J. Chem.* **2001**, *79*, 1556-1561.

[14] a) J. N. Moorthy, I. Neogi, *Tetrahedron. Lett.* **2011**, *52*, 3868-3871; b) G. M. Raghavendra, A. B. Ramesha, C. N. Revanna, K. N. Nandeesh, K. Mantelingu K. S. Rangappa, *Tetrahedron. Lett.* **2011**, *52*, 5571-5574; c) A. J. Blacker, M. M. Farah, M. I. Hall, S. P. Marsden, O. Saidi, J. M. J. Williams, *Org. Lett.* **2009**, *11*, 2039-2042.

[15] B. G. Hashiguchi, K. J. H. Young, M. Yousufuddin, W. A Goddard, R. A. Periana, *J. Am. Chem. Soc.* **2010**, *132*, 12542-12545.

[16] H.-F. Suen, S. W. Wilson, M. Pomerantz and J. L. Walsh, *Inorg. Chem.*, **1989**, *28*, 786–79.

[17] This complex was prepared in situ in alcohol without separation by the halogen extraction from complex **1** with two equiv. of AgOTf, followed by anion exchange with $NaB(Ph)_4$.

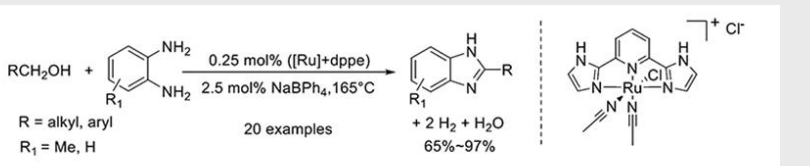
[18] a) H. Noth, H. Vahrenkamp, *Chem. Ber.* **1966**, *99*, 1049; b) W. D. Philips, H. C. Miller, E. L. Mutterties *J. Am. Chem. Soc.* **1959**, *81*, 4496-4500.

[19] a) T. Maki, K. Ishiharaa, H. Yarnarnoto, *Tetrahedron.* **2007**, *63*, 8645; b) T. P. Loh, R. B. Wang, K. Y. Sim, *Tetrahedron Lett.* **1996**, *37*, 2989; c) K. Ishihara, Y. Kuroki, N. Hanakj, S. Ohara, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 1569; d) K. Ishiharaa, Q. Gao, H. Yamamoto, *J. Org. Chem.* **1993**, *58*, 6917.

[20] M. A. Fox, J. E. Harris, S. Heider, V. Pérez-Gregorio, M. E. Zakrzewska, J. D. Farmer, D. S. Yufit, J. A. K. Howard, P. J. Low, *J. Organomet. Chem.* **2009**, *694*, 2350-2358.

[21] M. A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, *Inorg. Synth.* **1982***, 21* 7.

FULL PAPER



We illustrate a homogeneous system with Ru(II)-NNN complex, which efficiently catalyzed the dehydrogenative condensation of primary alcohol with benzene-1,2-diamine to the 2-substituted benzimidazole with the liberation of H_2 in the presence of catalytic amount of $NaBPh_4$. The addition of dppe and the decomposition of $NaBPh_4$ to $NaB(OR)_4$ in the catalytic cycle are favour to this greener process.

Lin Li, Qi, Luo, Huahua Cui, Renjie Li, Jing Zhang and Tianyou Peng**

Page No. – Page No.

Air-stable Ru(II)-NNN Pincer complexes for Efficient Coupling of aromatic diamines and alcohols to 1*H*-benzo[*d*]imidazoles with the liberation of H_2