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Oxidant-free Synthesis of Benzimidazoles from Alcohols and Aromatic Diamines Catalysed by New Ru(II)-PNS(O) Pincer Complexes

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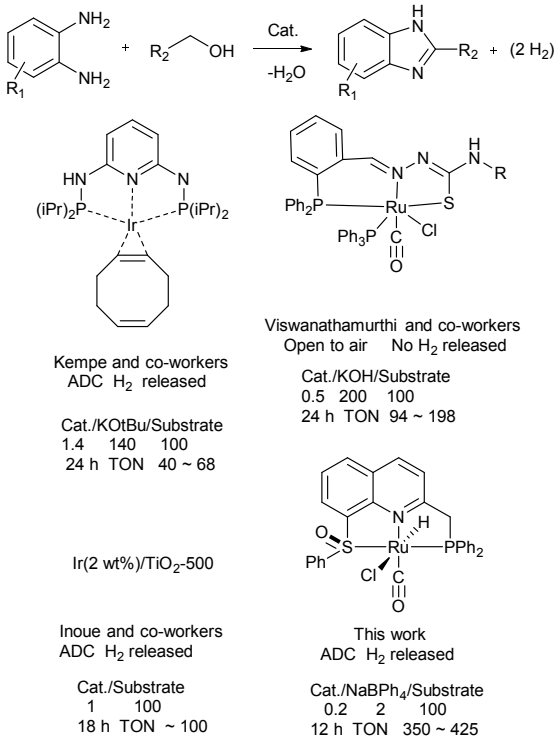
Benzimidazoles are chemically and pharmaceutically important, and an environmentally benign synthetic method based on acceptorless dehydrogenative condensation of primary alcohols and benzene-1,2-diamine is developed in this work. Three Ru(II) hydride complexes [RuHCl(CO)(**PNS(O)**)] (containing two isomers **1a** and **1b**) and [RuHCl(CO)(PPh_3)(**SNC^{NHC}**)]PF_6 (**2**) based on two new quinoline-based ligands 2-(diphenylphosphanylmethyl)-8-phenylsulfinylquinoline (**PNS(O)**) and 1-mesityl-3-(8-phenylthioquinolyl-2-methyl)-2-imidazole carbene (**SNC^{NHC}**) are prepared and fully characterized. These complexes catalyse the condensation of benzyl alcohol and benzene-1,2-diamine to 2-phenylbenzimidazole with the liberation of H_2, and the catalytic activity follows the order: **1a** ≈ **1b** > **2**. When 0.2 mol% **1a** and 2 mol% of $NaBPh_4$ were used, various 2-functionalized benzimidazoles were obtained in good yields (70 – 85%) and high turnover numbers (TONs ~ 425). This homogeneous system does not need oxidants or stoichiometric strong base (KOH or KO^{t}Bu, etc.) that are normally used in the reported homogeneous systems, and thus is a greener process.

Introduction

Various methodologies have been developed to prepare benzimidazole derivatives for their important applications in pharmaceutical industry,[1] PEM fuel cells,[2] textile and dyestuff industry,[3] in which the heterogeneous[4] or homogeneous catalysis[5] was used to make the progress much easier and more alternative. The acceptorless dehydrogenative condensation (ADC) of alcohol and benzene-1,2-diamine catalysed by transition metal complexes is one of the 'green' procedures as the by-products are only water and hydrogen (Scheme 1).[4d, 6] However, homogeneous systems capable of the conversion are scarce, and a stoichiometric amount of strong base (KO^{t}Bu, KOH *etc.*) is usually needed in reported systems, which essentially produces equivalent amount of inorganic salts. For instance, Kempe and co-workers[6] used a Ir(I)-PNP pincer complex [Ir(cod)2,6-DiAmPy(^{i}Pr)$_2$] to catalyse the condensation of primary alcohols and benzene-1,2-diamine to the 2-functionalized benzimidazoles in 56 – 96% yields with the catalyst loading of 1.4 mol%. Nevertheless, one equiv. of KO^{t}Bu relative to the alcohol was still necessary in this system. Therefore, developing new catalytic system for oxidant-free synthesis of benzimidazole from alcohol and amine without the use of stoichiometric amount of strong base is still necessary.

Scheme 1 Catalytic systems for synthesizing benzimidazoles through condensation of primary alcohols and aromatic diamines.



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Transition metal complexes based on electron-rich, 'bulky' pincer ligands have attracted much interest due to their outstanding catalytic performance in organic synthesis, medicinal and material chemistry.[7] Adjustable ligands bearing groups such as pyridine-,[8] dialkylamine-[9] or aryl-centred[10] frameworks, and an alterable metal centre make the pincer complexes versatile in some important catalytic reactions: the hydrogenation of carboxylic acid derivatives[8b,11] or CO_2,[12] the acceptorless alcohol dehydrogenation (AAD),[13] the Heck reaction and Suzuki-Miyaura coupling reaction.[14] Compared with pyridine-based pincer ligand, quinoline-based ligands have a larger framework with more substitutable sites, which may display more variable catalytic properties upon coordinated to the metal centre. However, transition metal complex based on the quinoline-centred pincer ligand is rarely reported to the best of our knowledge.[15]

Usually, C, N and P are common donors of a pincer ligand, whereas S donors (normally functionalized as sulfide or sulfoxide moiety) are rarely used. Milstein and co-workers[16,17] reported several metals (Ir, Rh, Ru) complexes based on pyridine-based PNS (sulfide) and NNS(O)) (sulfoxide) pincer ligands, in which [RuHCl(CO)(PNS)] (PNS = 2-((*tert*-butylthio)methyl)-6-((di-*tert*-butylphosphanyl)methyl) pyridine) was applied to the dehydrogenative coupling of 1-hexanol and benzylamine to form a mixture of hexyl hexanoate and N-benzylhexanamide in a neutral system.[16] In 2013, Gusev and co-workers[18] demonstrated a Ru(II)-SNS type complex [RuCl(PPh_3)(SNS)] (SNS = bis(2-(ethylthio)ethyl)-amine) as an efficient catalyst for the hydrogenation of esters and imine. Meanwhile, several Ru(II) complexes based on other tridentate[19] or bidentate[20] ligand containing sulfide or sulfoxide groups were also structurally characterized.

Herein, we illustrate a new homogeneous system with Ru(II) hydride complexes bearing new quinoline-based pincer ligand 2-(diphenylphosphino)methyl-8-phenylsulfinyl-quinoline (PNS(O)). This system efficiently catalyses the condensation of primary alcohols and aromatic diamines to 2-substituted benzimidazoles and H_2 with a low catalyst loading (0.2 mol%) in the presence of a catalytic amount of $NaBPh_4$ (2 mol% to the substrate). Although Viswanathamurthi and co-workers reported Ru(II)-PNS (thiosemicarbazones) complexes for the condensation of alcohols and benzene-1,2-diamine to 2-substituted benzimidazoles in 2014 (Scheme 1), KOH (two equiv. relative to the alcohol) accompanied with O_2 as the oxidant was used.[5b] The present homogeneous system need neither oxidants nor stoichiometric strong base (KOH or KO^tBu, etc.) to promote the reaction, and thus is a more 'green' process.

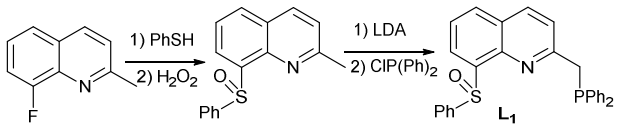
Results and discussion

Synthesis of Pincer Ligands PNS(O) (L1) and SNC(^{NHC}) (L2)

The starting material 8-fluoro-2-methylquinoline was synthesized according to the reported method.[21] When 8-fluoro-2-methylquinoline and two equivalents of thiophenol were heated in dry DMF at 150°C for 12 h in the presence of NaH (excess), 2-methyl-8-phenylthioquinoline was obtained in good yield (80%). The sulfide moiety of this compound could be easily oxidized by an excess amount of H_2O_2 to form 2-methyl-8-phenylsulfinylquinoline in almost quantitative yield. The methyl group of this intermediate was deprotonated with LDA (lithium di-*iso*-propylamide) and then reacted with 1 equiv. of chlorodiphenylphosphine to form the new ligand 2-(diphenyl-phosphanylmethyl)-8-phenylsulfinylquinoline (PNS(O), **L1**) in 81% isolated yield (Scheme **2**) as a white solid. The $^{31}P\{^1H\}$ NMR spectrum of **L1** shows a singlet at -12.04 ppm, which is much different to those of other reported ligands 2,6-bis(diphenylphosphanylmethyl)pyridine (37.8 ppm)[22] or bis(2-(diphenylphosphanyl)ethyl)amine (-20.5 ppm),[23a] and is similar to that of 4,5-bis(diphenylphosphanyl)acridine (-14.7 ppm).[23b] In the ^1H NMR spectrum, one singlet peak with integration of two protons appears at 3.83 ppm, which can be assigned to the methylene group of **L1**. Moreover, a doublet at 39.60 ppm with the coupling constants J_{PC} = 18.2 Hz was observed in its ^{13}C NMR spectrum, indicating the methylene group is attached to the phosphorus atom of **L1**.

Using 8-fluoro-2-methylquinoline as the starting material, the imidazolium salt 1-mesityl-3-(8-phenylthioquinolyl-2-methyl)imidazolium bromide (H**L2**Br) was synthesized through the procedure depicted in Scheme **3**. Refluxing 8-fluoro-2-methylquinoline with 1.2 equivalents of SeO_2 in dry pyridine resulted in the formation of 8-fluoroquinoline-2-carboxylic acid, in which the fluoride group could be easily substituted by the phenylthiol to form 8-phenylthio-quinoline-2-carboxylic acid. This compound was esterified with ethanol and then reduced by an excess amount of $NaBH_4$ to form 2-hydroxymethyl-8- phenylthioquinoline in excellent yield (93% for two steps). After this intermediate was reacted with conc. HBr/AcOH and then treated with 1-mesityl-imidazole, the N-heterocycle carbene precursor H**L2**Br was obtained in good yield (80% for two steps). An alternative procedure involving the direct bromination of 2-methyl-8-phenylthioquinoline with N-bromosuccinimide to form the 2-bromomethyl-8-phenylthioquinoline was unsuccessful, resulting in a mixture of *muti*-brominated products and no desired product was isolated from the mixture. In the ^1H NMR spectrum of H**L2**Br, one singlet peak with integration of two protons appears at 6.45 ppm, which can be assigned to the methylene group of H**L2**Br. Moreover, a characteristic singlet at 10.22 ppm in its ^1HNMR spectrum, associated with the imidazolium proton that is deprotonated upon the formation of the free NHC. These observations are very similar to those of a pyridine-NHC pincer ligand reported by Milstein and co-workers.[24]

Scheme 2 Synthesis of **L1**



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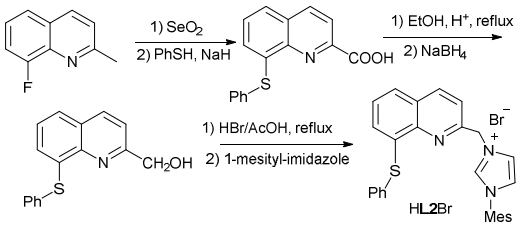
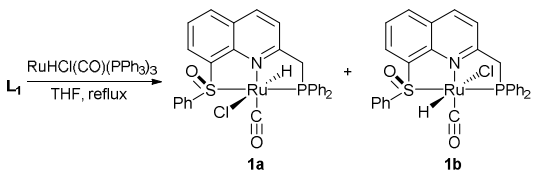
Scheme 3 Synthesis of NHC Precursor H**L2**Br(SNC(^{NHC}))



Synthesis and Characterization of Ru(II) Complexes.

When a THF solution of **L1** and 1 equiv. of [RuHCl(CO)(PPh_3)$_3$] was refluxed for 3 h under a nitrogen atmosphere, a yellow solid of [RuHCl(CO)(**L1**)] (containing the mixture isomers of **1a** and **1b**, 1:1 mol/mol) was precipitated (determined by ^{1}H NMR and ^{31}P{^{1}H} NMR). The pure complexes **1a** and **1b** were isolated by the flash column chromatography in 40% and 45% yields, respectively (Scheme **4**). The IR spectrum of **1a** exhibits a strong absorption at 1940 cm^{-1} assigned to the coordinated CO. The ^{31}P{^{1}H} NMR spectrum exhibits a singlet peak at 55.47 ppm, representing a downfield of 67.5 ppm compared to the free ligand **L1**. The presence of the hydride coordinated to the Ru(II) centre is confirmed by the ^{1}H NMR spectrum, which shows a doublet peak at -13.07 ppm with J_{PH} = 22.8 Hz. Furthermore, the ^{1}H NMR of complex **1a** shows the methylene group as two doublets of doublets at 4.80 and 5.08 ppm, indicating the lack of a symmetry plane involving the P, N, S atoms. Similarly, the ^{31}P{^{1}H} NMR spectrum of complex **1b** shows a singlet peak at 58.14 ppm, which represents a downfield of 70.2 ppm compared to the free ligand **L1**. The ^{1}H NMR of complex **1b** shows the hydride ligand as a doublet peak at -12.90 ppm with J_{PH} = 21.6 Hz and the two magnetic nonequivalent protons of methylene moiety as two groups of double doublet peaks at 4.73 and 5.15 ppm. The chemical shifts of the hydride ligand in **1a** (-13.07 ppm) and **1b** (-12.90 ppm) indicate the hydride is located *trans* to the chloride or to the pyridine nitrogen atom rather than to CO. This observation is consistent to other reported PNP-Ru(II) and PNN-Ru(II) hydride complexes.[25] The ^{1}H NMR and ^{13}C NMR spectra of complex **1a** are similar to these of complex **1b**, indicating they are stereoisomers. Both complexes **1a** and complex **1b** can be kept in air for weeks at room temperature in the solid state without obviously decomposition.

Scheme 4 Preparation of Complexes **1a** and **1b**



For further characterization of complex **1a**, single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of the diethyl ether to a concentrated CH_2Cl_2 solution of complex **1a**. The structure of **1a** is shown in Fig. **1** and the selected bond distances and bond angles are listed in Table **1**.

The crystal structure of complex **1a** displays a distorted octahedral geometry around the metal centre. The CO ligand is bound to the Ru(II) centre *trans* to the nitrogen atom of **L1** while the hydride is located *trans* to the chloride ligand. Looking from the top of H(hydride)-Ru-Cl axis, the coordinated atoms of S, N, P, C (carbonyl) are sequentially anti-clockwise arranged (Fig. **2**, left). The bond distance of Ru1-S1 (2.2782(6) Å) is slightly shorter than that of Ru1-P1 (2.2883(7) Å) while the bond distance of Ru1-N1(quinolyl) (2.123(2) Å) is longer than the reported Ru-N(pyridyl) complexes [RuCl(H)(CO)(PNN)] (2.103(2) Å) and [RuCl(H)(CO)(PNP)] (2.087(2) Å).[25] Due to the meridional coordination geometry of the **L1** framework and the lack of a plane of symmetry involving the P, N, S atoms, the two protons of the methylene group are inequivalent.

With the similar method to that for complex **1a**, bright yellow single crystals of complex **1b** suitable for the X-ray diffraction analysis were obtained by slow diffusion of the diethyl ether to a concentrated CH_2Cl_2 solution of **1b**. The structure of **1b** is shown in Figure **1** while the selected bond distances and bond angles are listed in Table **1**. The crystal structure of **1b** displays the Ru(II) centre adopts a distorted octahedral geometry with the CO ligand is bound to the metal centre *trans* to the nitrogen atom of **L1** while the hydride is located *trans* to the chloride ligand. Different to that of complex **1a**, the coordinated atoms of S, N, P, C (carbonyl) are sequentially clockwise arranged (**Fig**. **2**, right, looking from the top of H(hydride)-Ru-Cl axis).

The bond angle of Ru1-S1-O1 (119.48 (6)°) of **1b** is smaller than that of complex **1a** (124.20 (7)°), while the bond angle of S1-Ru1-Cl1 (93.69 (2)°) of **1a** is smaller than that of complex **1b** (99.64 (2)°). Furthermore, the bond distances of Ru1-S (2.2850 (5) Å) and Ru1-N(quinolyl) (2.136(2) Å) in **1b** are slightly longer than those in complex **1a** (2.2782(6) Å) and (2.123(2) Å, respectively).

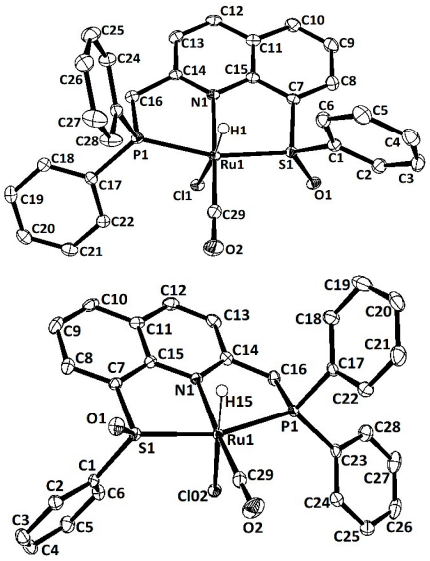


Fig. 1 The structures of complexes **1a** (top) and **1b** (bottom) with thermal ellipsoids drawn at the 30% level. All hydrogen atoms excepting Ru-H and the solvent are omitted for clarity.

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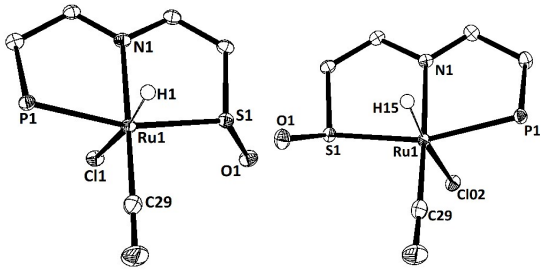
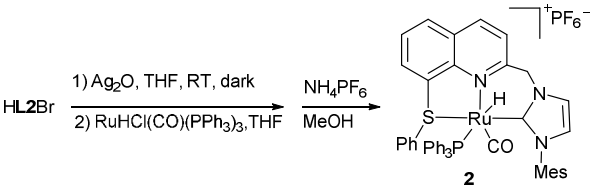


Fig. 2 The coordination geometries of complexes **1a** (left) and **1b** (right)

Metal complexes bearing NHC ligands were typically prepared from imidazolium salts *via* the silver carbene transfer reaction,[26] or the free carbene route.[27] In the former method, the carbenic proton of an imidazolium salt was deprotonated by Ag_2O followed by the transmetallation of the metal precursor with the Ag(I)-NHC intermediate; while the latter method involves in the use of a strong base for the acidic proton abstraction and the free carbene generated then being trapped, after isolation or *in situ*, by a metal precursors. In this work, the Ru(II)-**L2** hydride complexes was synthesized by the former method (Scheme **5**). The intermediate silver(I)-NHC (Ag-**L2**^{NHC}) was obtained as a pale yellow solid by the reaction of the imidazolium salt (H**L2**Br) with Ag_2O in CH_2Cl_2 at room temperature. The absence of imidazolium (NC*H*N) resonance at 10.40 ppm in the ^{1}H NMR spectrum indicates the formation of the Ag(I)-C(NHC) bond. When a THF solution containing the *in situ* formed Ag-NHC intermediate and 1 equiv. of [RuHCl(CO)(PPh_3)$_3$] was refluxed for 12 h, followed by the extraction of the halogen ligand from the Ru(II)-NHC complex with an excess amount of NH_4PF_6 in methanol, the pure complex [RuHCl(CO)(PPh_3)(**L2**)](PF_6) (**2**) was obtained in 41% isolated yield as a yellow microcrystals. Complex **2** is stable in air for weeks at room temperature in the solid state.

The fully characterized complex **2** gives rise to a doublet peak at -7.26 ppm with J_{PH} = 107.4 Hz in the ^{1}H NMR spectrum. This large coupling constant clearly indicates the hydride is coordinated to the Ru(II) centre *trans* to the P atom of triphenylphosphine ligand, which is consistent to other reported Ru(II) complexes.[28] In the ^{13}C{^{1}H} NMR spectrum the carbonyl ligand gives rise to a broad singlet at 203.26 ppm, and the NHC carbon appears at 184.45 ppm as a broad singlet. The ^{31}P{^{1}H} NMR exhibits a singlet at 23.7 ppm for the coordinated PPh_3 ligand, which is similar to that of the reported complex [RuHCl(CO)(PPh_3)(NNC^{NHC})] (24.03 ppm).[24]

Scheme 5. Synthesis of Complex **2**



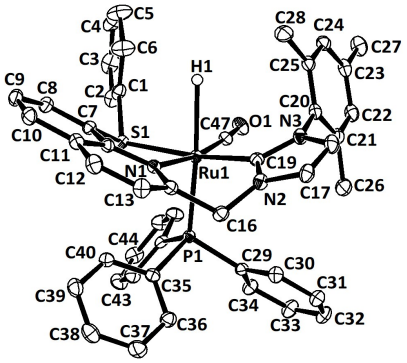


Fig. 3 The structure of complex **2** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms excepting Ru-H1 and PF_6^- anion are omitted for clarity.

The bright yellow single crystals suitable for the X-ray diffraction analysis were obtained by the slow diffusion of the diethyl ether to a concentrated CH_2Cl_2 solution of complex **2**. The structure of **2** is shown in Figure **3** while the selected bond distances and bond angles are listed in Table **1.** The structure of complex **2** exhibits the CO ligand is coordinated to the Ru(II) centre *trans* to the N atom of the pincer system while the location of the hydride is *trans* to the phosphine. The bond distance of Ru1-C19 (NHC) (2.034(2) Å) is slightly longer than that in the reported Ru-NHC complexes containing a bipyridine nitrogen *trans* to the NHC ligand (1.995 ~ 2.014Å).[24] The bond distance of Ru1-P1 (2.4402(6) Å) is significantly longer than those in complexes **1a** (2.2883(7) Å) and **1b** (2.3070(5) Å), as a result of the strong *trans* effect of the hydride ligand. The bond distance of Ru1-S1 in complex **2** (2.3698(6) Å) is also longer than those in complexes **1a** (2.2782(6) Å) and **1b** (2.2850(5) Å). This observation is also consistent to the strong *trans* effect of NHC carbene relative to the phosphine ligand.

Table 1 Selected Bond Lengths (Å) and Angles (deg) of Complexes **1a**, **1b** and **2**

Selected bond lengths (Å) and angles (deg) of complex **1a**			
Ru1-N1	2.123(2)	Ru1-S1	2.2782(6)
Ru1-P1	2.2883(7)	Ru1-Cl1	2.5189(6)
Ru1-C29	1.861(3)	Ru1-H1	1.58(3)
P1-Ru1-S1	164.25(2)	N1-Ru1-C29	175.42(9)
N1-Ru1-P1	81.72 (6)	N1-Ru1-S1	83.89(6)
P1-Ru1-Cl1	90.99(2)	S1-Ru1-Cl1	93.69(2)
H1-Ru1-Cl1	171.3(11)	O1-S1-Ru1	124.20(7)
C1-S1-Ru1	116.87(8)	Cl1-Ru1-S1-O1	-31.42

Selected bond lengths (Å) and angles (deg) of complex **1b**			
Ru1-N1	2.136(2)	Ru1-S1	2.2850(5)
Ru1-P1	2.3070(5)	Ru1-Cl02	2.5003(5)
Ru1-C29	1.852(2)	Ru1-H15	1.56(3)
P1-Ru1-S1	162.99(2)	N1-Ru1-C29	171.35(7)
N1-Ru1-P1	81.44 (4)	N1-Ru1-S1	83.69(4)
P1-Ru1-Cl02	88.62(2)	S1-Ru1-Cl02	99.64(2)
H15-Ru1-Cl02	172.4(10)	O1-S1-Ru1	119.48(6)
C1-S1-Ru1	121.85(6)	Cl02-Ru1-S1-O1	-39.45

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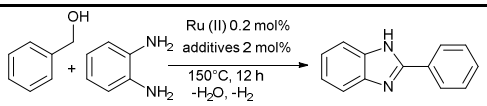
Selected bond lengths (Å) and angles (deg) of complex **2**			
Ru1-N1	2.164(2)	Ru1-C19	2.034(2)
Ru1-C47	1.850(2)	Ru1-S1	2.3698(6)
Ru1-P1	2.4402(6)	Ru1-H1	
S1-Ru1-C19	165.77(7)	N1-Ru1-C47	170.25(9)
N1-Ru1-P1	94.41(5)	S1-Ru1-P1	89.15(2)
C19-Ru1-C47	94.7(1)	S1-Ru1-C47	94.36(7)
N1-Ru1-C19	87.84(8)	C19-Ru1-P1	101.03(7)

Catalytic dehydrogenative condensation of alcohol and benzene-1,2diamine.

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 **1a** (5 µmol) and benzene-1,2-diamine (2.5 mmol) with Cs_2CO_3 (50 µmol) in an excess amount of benzyl alcohol (7.5 mmol) at 150°C (oil bath) under nitrogen atmosphere for 12 h. The 2-phenyl-benzimidazole was obtained in 78% isolated yield (Table 2, entry 1). Upon using complexes **1b** or **2** under the same condition, the desired product of 2-phenyl-benzimidazole was obtained in 77% and 53% yields, respectively (Table 2, entries 2 and 3). These results indicate the catalytic activity follows the order: **1a** ≈ **1b** > **2**. With complex **1a** as the catalyst, using the strong base (KO^tBu or CsOH) resulted in the formation of 2-phenylbenzimidazole in relatively lower yields (62% and 60%, respectively) accompanied by the formation of several kinds of N-alkylation products. An alternative procedure involving the use of the stoichiometric amount of CsOH or KO^tBu according to the reported literature[20] was much less successful, giving a mixture contains a number of N-alkylation products and the 2-phenyl-benzimidazole was obtained in low yield (~ 15%). It is noted that the high yield (80%) of 2-phenyl-benzimidazole was obtained when a catalytic amount of the neutral salt $NaBPh_4$ (10 equivalents relative to complex **1a**) was used as the additive under the same condition, while the $NaPF_6$ or $NaBF_4$ gave almost no product (Table 2, entries 10, 11). Interestingly, there is only 33% yield of desired product obtained when the precursor $RuHCl(CO)(PPh_3)_3$ was used (Table 2, entry 16), which clearly indicates that the coordination of the pincer ligand to the Ru(II) centre greatly improve the catalytic reaction. As expected, there is no 2-phenyl-benzimidazole obtained in the absence of complex **1a** or additives (Table 2, entries 12, 13). Increasing the reaction temperature to 165°C (oil bath) afforded the 2-phenyl-benzimidazole in 85% yield (Table 2, entry 14), which is consistent to the hydrogen gas production (82%, seeing the supporting information, **S4-5**). The hydrogen gas is double mole relative to the 2-phenylbenzimidazole, which clearly indicates the hydrogen acceptor is not necessary in our catalytic system.

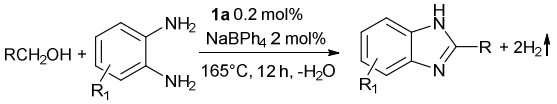
Table 2 Optimization of Catalytic Condition for the Benzimidazole Synthesis.

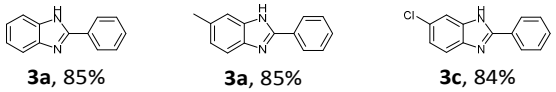


Entry	Catalyst	Additive	Yield(%)[a,b]
1	1a	Cs_2CO_3	78
2	1b	Cs_2CO_3	77
3	2	Cs_2CO_3	53
4	1a	KO^tBu	62
5	1a	$CsOH·H_2O$	60
6	1a	K_2CO_3	50
7	1a	DBU[d]	37
8	1a	$NaBPh_4$	80
9	1a	$CsBPh_4$[e]	64
10	1a	$NaBF_4$	2
11	1a	$NaPF_6$	2
12	1a	none	0
13	none	$NaBPh_4$	2
14[c]	1a	$NaBPh_4$	85(82[f])
15[g]	1a	$KOBu^t$	21
16	$RuHCl(CO)(PPh_3)_3$	$NaBPh_4$	33

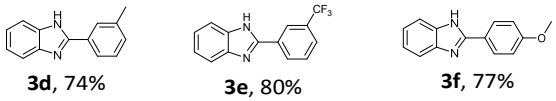
[a] Reaction conditions: benzene-1,2-diamine (2.5 mmol), benzyl alcohol (7.5 mmol), additive (0.05 mmol), catalyst loading (0.005 mmol), 150°C, 12 h. [b] Isolated yield. [c] The reaction temperature is 165°C. [d] DBU = 1,8-diazabicyclo [5.4.0] undec-7-ene. [e] Prepared by the reaction of $NaBPh_4$ and $CsOH·H_2O$ in EtOH. [f] Yield of H_2. [g] 0.005 mmol $KOBu^t$ (1 equiv. to 1a) was used

Table 3 Acceptorless Dehydrogenative Condensation of Primary Alcohols and Functionalized benzene-1,2-diamine. [a, b]

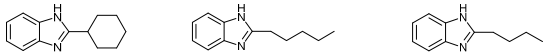




3a, 85% **3a**, 85% **3c**, 84%



3d, 74% **3e**, 80% **3f**, 77%



3g, 70% **3h**, 79% (64%)[c] **3i**, 83%

[a] Reaction condition: benzene-1,2-diamine derivatives (2.5 mmol), alcohol (7.5 mmol), complex **1a** (0.2 mol%), $NaBPh_4$ (2 mol%), 165°C, 12 h. [b] Isolated yield. [c] Cs_2CO_3 was used.

With the optimized reaction condition in hand, we next examined the substrate scopes of the reaction, the results are listed in Table 3. Both aromatic alcohols and aliphatic alcohols can be dehydrogenative coupled with benzene-1,2-diamine to corresponding 2-substituted benzimidazoles in good yields (70 – 85%). It is noted that the electronic effect of aromatic alcohol gives very little difference between the strong

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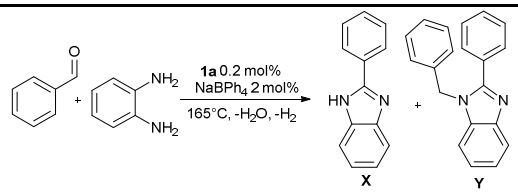
electron-withdrawing group and the strong electron-donating group for the desired coupling products. For instance, when 3-trifluoromethylbenzylic alcohol was used, the product **3e** was obtained in 80% yield while the 4-methyloxybenzyl alcohol gave the corresponding coupling product in 77% yield (Table 3, **3e**, **3f**). Although the use of Cs_2CO_3 instead of $NaBPh_4$ resulted in a similar yield (78%) when benzyl alcohol was used (table 1, entry 1), a lower yield of 2-pentyl-benzimidazole was obtained (64%) while the $NaBPh_4$ gave 79% yield under the same condition (Table 3, **3h**).

Traditionally, the plausible mechanism for the synthesis of 2-substituted benzimidazoles from benzene-1,2-diamine and alcohols involves the *in situ* alcohol dehydrogenation to aldehyde catalysed by a Ru(II) hydride complex with (or without) a hydrogen acceptor, followed by the condensation of the aldehyde with benzene-1,2-diamine to generate the imine/2,3-dihydro-benzimidazole, this intermediate is further dehydrogenated to form the 2-substituted benzimidazole with (or without) the Ru(II) catalyst.[29] In order to study the mechanism of this catalytic system, the controlled experiments were carried out without the complex **1a** or $NaBPh_4$, which resulted in almost no desired product formation (Table 2, entries 12, 13), indicating both the Ru(II) hydride complex and $NaBPh_4$ are necessary for the catalytic reaction.

Table 4 Condensation of benzaldehyde and benzene-1,2-diamine catalysed by 1a. [a]

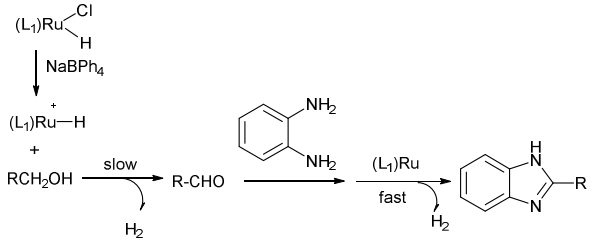


Entry	**1a** (mol%)	$NaBPh_4$ (mol%)	**X** (%)	**Y** (%)
1	0	0	21	19
2	0	2	41	<5
3	0.2	2	70	<5
4	0.2	0	95	trace
5[b]	0.2	0	90(86[c])	trace

[a] Reaction condition: benzene-1,2-diamine (3.0 mmol), benzaldehyde (2.5 mmol), $NaBPh_4$ (0.05 mmol), **1a** (0.005 mmol), mesitylene (1 mL), 165°C, 12 h, N_2 atmosphere. [b] The reaction time is 1 h. [c] Yields of H_2.

Heating 0.2 mol% complex **1a** and 2 mol% $NaBPh_4$ in benzyl alcohol at 150°C for 12 h under a nitrogen atmosphere only afforded a small amount of benzaldehyde (4% based on the alcohol) accompanied by the liberation of hydrogen (confirmed by the GC), indicating the benzaldehyde is probably the intermediate and the formation of benzaldehyde from alcohol is slower than the dehydrogenative condensation of aldehyde with aromatic diamines. When complex **1a** and 1 equiv. of KO^tBu were heated in a mixture of benzyl alcohol and benzene-1,2-diamine (1:3 mol/mol) at 150°C for 12 h under nitrogen atmosphere, the 2-phenylbenzimidazole was obtained in 21% (table 2, entry 15), indicating a slightly excess of additive (10 equiv. to **1a**) favour to formation of the desired product (table 2, entry 4). Heating **1a** and 1 equiv. of KO^tBu in DMSO-d_6 at 80°C for 2 h resulted in the formation of the dearomatic species (confirmed by ^1H NMR, **S6–7**) which is similar to other reported Ru(II)-PNN[25] or Ru(II)-PNP[30] complexes. The aromatization-dearomatization is a commonly process in bond activation and the detail was fully studied by Milstein and co-workers.[31] Further experiments were carried out by using benzaldehyde and benzene-1,2-diamine with/without complex **1a** or $NaBPh_4$ at 165°C under nitrogen. The results are listed in Table 4. When benzaldehyde and 1 equiv. of benzene-1,2-diamine were heated at 165°C for 12 h, 2-phenylbenzimidazole was obtained in 21% yield accompanied by the formation of 1-benzyl-2-phenylbenzimidazole in 19% (Table 4, entry 1). Interestingly, the loading of $NaBPh_4$ (2 mol%) give a higher selectivity for the 2-phenylbenzimidazole (41%) relative to the 1-benzyl-2-phenylbenzimidazole (5%) (Table 4, entry 2). It is noted that complex **1a** can efficiently catalyse the acceptorless condensation of benzaldehyde and benzene-1,2-diamine to 2-phenylbenzimidazole in excellent yield (95%) with high selectivity (Table 4, entry 4). A hydrogen production test exhibits the hydrogen was obtained in 86% yield (based on the benzaldehyde, supporting information, **S4-5**) when the reaction was carried out at 165°C for 1 h, which is well consistent to the formation of 2-phenylbenzimidazole (90%). These results confirm the condensation of aldehyde and benzene-1,2-diamine is much faster than the dehydrogenation of alcohol to the aldehyde. The formation of the stoichiometric amounts of hydrogen (two equivalents to the desired product) also supports the plausible mechanism shown in Scheme **6**. The investigation of the detail catalytic mechanism involving the isolation of the active Ru intermediates from the system is currently underway.

Scheme 6 The plausible mechanism of catalytic dehydrogenative condensation of benzene-1,2-diamine with primary alcohol to 2-substituted benzimidazole



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. Compound 8-fluoro-2-

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methylquinoline[21] was prepared according to the reported method. The NMR spectra were received using a Mercury 300 and 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. The ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. *J* values are given in Hz. All spectra were recorded at room temperature unless otherwise noted. Elemental analysis was performed by the Test Centre of Wuhan University. Ru(II) precursor $[RuHCl(CO)(PPh_3)_3]$[32] was prepared according to the reported literature.

Synthesis of 2-methyl-8-phenylthioquinoline. To a solution of 8-fluoro-2-methylquinoline (6.00 g, 37 mmol) in dry DMF (80 mL) was added NaH (1.80 g, 74 mmol) and Ph-SH (8.10 g, 74 mmol), and the mixture was stirred and heated at 150°C for 12 h. The solvent was removed under vacuum and the residue was dispersed in 400 mL water. The solution was adjusted to pH ~ 2 by using HCl (6 M) and the product was extracted with ethyl acetate (3 × 100 mL). The combined organic solution was dried over Na_2SO_4 and then evaporated under vacuum. The residue was passed through the column chromatography on silica gel (eluent: ethyl acetate/pentane: 1/9) to give a yellow solid of product (7.4 g, 80%).
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 2.79 (s, 3H, CH_3), 6.92 (d, *J*=7.2 Hz, 1H), 7.20 (t, *J*=7.8 Hz, 1H), 7.29 (d, *J*=8.7 Hz, 1H), 7.43-7.47 (m, 4H), 7.60-7.68 (m, 2H), 7.97 (d, *J*=8.1 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 25.41, 122.63, 123.90, 124.75, 125.64, 126.20, 128.85, 129.60, 131.96, 135.83, 136.17, 139.39, 144.12, 158.38. Found: C, 76.55; H, 5.07; N, 5.72. Calc. for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57.

Synthesis of 2-methyl-8-phenylsulfinylquinoline. To a solution of 2-methyl-8-phenylthioquinoline (2.51 g, 10 mmol) in CH_3COOH (50 mL) was added H_2O_2 (1.13 g, 30 wt% in water, 15 mmol) dropwisely, and then heated at 50°C for 2 h. After cooling to the room temperature, 200 mL water was added to the mixture and the solution was then neutralized by Na_2CO_3. The white precipitate was collected by filtration, washed with water, and then dried under vacuum overnight at 50°C. The crude product was recrystallized from a CH_2Cl_2/hexane solution to give colourless crystals of 2-methyl-8-phenylsulfinylquinoline (2.60 g, 97%).
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 2.72 (s, 3H, CH_3), 7.24-7.32 (m, 4H), 7.63 (t, *J*=7.2 Hz, 1H), 7.78 (d, *J*=7.2 Hz, 1H), 7.96-7.98 (m, 3H), 8.37 (d, *J*=6.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 25.02, 122.75, 124.63, 125.69, 126.29, 128.52, 129.86, 130.43, 135.91, 142.50, 143.54, 146.08, 159.01; Found: C, 69.61; H, 5.04; N, 5.23. Calc. for $C_{16}H_{13}NOS{\cdot}0.5H_2O$: C, 69.54; H, 5.10; N, 5.07.

Synthesis of 2-(diphenylphosphinomethyl)-8-phenylsulfinyl-quinoline (PNS(O)) (L1). To an oven-dried, nitrogen flashed, 3-neck round bottom flask was charged with 2-methyl-8-phenylsulfinylquinoline (0.53 g, 2.0 mmol) in 10 mL dry THF. The solution was cooled to -78°C and LDA (1.2 mL, 2 M in THF, 2.4 mmol) was slowly added with a syringe. The mixture was stirred for 5 h at -78°C and a solution of chlorodiphenylphosphine (0.44 g, 2.0 mmol) in 10 mL dry THF was added. The mixture was allowed slowly to warm up to room temperature and stirred overnight. To this reaction mixture was added 10 mL of degassed water and the organic phase was washed with degassed brine (3 × 10 mL) under N_2 atmosphere. The THF phase was separated and dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum. The residue was purified through the column chromatography using silica gel with ethyl acetate/hexane (9/1) as eluent, **L1** (0.73 g, 81%) was obtained as a white solid.
$^{31}P\{^{1}H\}$ NMR (DMSO-D_6) δ (ppm): -12.04 (s). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ: 3.81 (s, 2H, CH_2), 7.15 (d, *J*=8.1 Hz, 1H), 7.32 (s, 9H), 7.47-7.51 (m, 4H), 7.60 (t, *J*=7.8 Hz, 1H), 7.74 (d, *J*=8.1 Hz, 1H), 7.90 (d, *J*=8.7 Hz, 1H), 7.96 (m, 2H), 8.35 (d, *J*=7.5 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 39.60 (d, CH_2, *J*=18.2 Hz), 122.73-122.85 (m), 124.73 (d, *J*=9.1 Hz), 125.55, 125.71, 125.92, 126.44, 128.39-128.51 (m), 128.62-128.74 (m), 128.91 (d, *J*=8.4 Hz), 129.80, 130.35 (d, *J*=8.3 Hz), 130.62 (d, *J*=11.1 Hz), 132.39-132.57 (m), 133.10 (d, *J*=19.5 Hz), 135.93 (d, *J*=5.6 Hz), 137.42 (d, *J*=15.4 Hz), 138.23 (d, *J*=15.4 Hz), 143.00, 143.61, 146.10, 159.03 (d, *J*=7.0 Hz). Found: C, 74.21; H, 4.68; N, 3.02. Calc. for $C_{28}H_{22}NOPS$: C, 74.48; H, 4.91; N, 3.10.

Synthesis of complexes [RuHCl(CO)(L1)] (1a) and (1b). To a suspension of $RuHCl(CO)(PPh_3)_3$ (0.19 g, 0.2 mmol) in THF (5 mL) was added **L1** (90 mg, 0.2 mmol), and the mixture was heated at 70°C for 12 h, and cooled to room temperature. The yellow solid thus obtained was filtered, washed with ether (3 × 3 mL), and then dried under vacuum (89 mg in total, 85%). The isomers of complexes **1a** and **1b** were separated by column chromatography on silica gel with CH_2Cl_2/MeOH (1/1) as eluent. The complex **1a** (42 mg, 40%) was obtained as a pale yellow solid while complex **1b** (47 mg, 45%) was a yellow solid.
Complex 1a: $^{31}P\{^{1}H\}$ NMR (DMSO-D_6) δ (ppm): 55.47 (s). ^{1}H NMR (300 MHz, DMSO-D_6, 298 K) δ: 4.80 (dd, *J*=17.1, 10.8 Hz, 1H, CH_2), 5.08 (dd, *J*=17.1, 10.8 Hz, 1H, CH_2), 7.44 (s, 3H), 7.54-7.66 (m, 7H), 7.78-8.00 (m, 6H), 8.07 (d, *J*=8.4 Hz, 1H)), 8.34 (d, *J*=7.5 Hz, 1H), 8.75 (d, *J*=9.1 Hz, 1H), -13.07 (d, J_{PH}=22.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-D_6, 298 K) δ (ppm): 44.84 (d, *J*=28.0 Hz, CH_2), 123.23 (d, *J*=9.9 Hz), 125.94, 127.30, 128.47, 128.89 (d, *J*=10.7 Hz), 129.20 (d, *J*=9.9 Hz), 129.52, 130.86, 131.22, 131.70-131.94 (m), 132.16, 133.23, 133.52 (d, *J*=10.7 Hz), 137.01, 137.76, 139.32, 143.64, 149.35, 150.36, 164.84 (d, *J*=7.4 Hz), 205.30 (d, *J*=13.2 Hz, CO). IR (KBr pellets): 1940 cm^{-1} (CO). Found: C, 51.53; H, 3.59; N, 2.12. Calc. for $C_{29}H_{24}ClNO_2PRuS{\cdot}CH_2Cl_2$: C, 51.25; H, 3.73; N, 1.99;

Complex 1b: $^{31}P\{^{1}H\}$ (DMSO-D_6) δ (ppm): 58.14 (s). ^{1}H NMR (300 MHz, DMSO-D_6, 298 K) δ (ppm): 4.73 (dd, *J*=17.1, 11.1Hz, 1H, CH_2), 5.15 (dd, *J*=17.1, 10.8 Hz, 1H, CH_2), 7.43 (s, 3H), 7.53 (s, 6H), 7.65 (s, 2H), 7.83-7.89 (m, 5H), 8.06-8.11 (m, 1H)), 8.36 (d, *J*=7.2 Hz, 1H), 8.75 (d, *J*=8.7 Hz, 1H), -12.90 (d, J_{PH}=21.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-D_6, 298 K) δ (ppm): 44.42 (d, J=28.0 Hz, CH_2), 123.31 (d, J=10.7 Hz), 127.00, 127.28, 128.56, 128.74, 128.91-129.20 (m), 130.81, 131.39, 131.66 (d, *J*=11.5 Hz), 131.88 (d, *J*=5 Hz), 133.52, 133.62, 137.39, 137.87, 139.56, 144.34, 145.80 (d, *J*=7.4 Hz), 149.67, 164.86 (d, *J*=2.7

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Hz), 205.55 (d, *J*=13.2 Hz, CO). IR: 1945 cm^{-1} (CO). Found: C, 51.48; H, 3.52; N, 2.05. Calc. for $C_{29}H_{24}ClNO_2PRuS{\cdot}CH_2Cl_2$: C, 51.25; H, 3.73; N, 1.99.

Synthesis of 8-fluoroquinoline-2-carboxylic acid. To a solution of 8-fluoro-2-methylquinoline (10 g, 62 mmol) in pyridine (100 mL) was added SeO_2 (8.35 g, 75 mmol) and the solution was refluxed at 120°C for 12 h. After cooling to the room temperature, the precipitate was filtrated off, and the solution was taken to dryness under vacuum and the residue was dispersed in 50 mL water, which was adjusted to the pH ~ 12 by using NaOH and then extracted with $CHCl_3$ (3 × 20 mL). The aqueous phase was acidized by HCl (6 M) under stirring to precipitate a brown solid, which was dried under vacuum to give 8-fluoroquinoline-2-carboxylic acid (8.20 g, 70%).
^{1}H NMR (400 MHz, DMSO-D_6, 298 K) δ (ppm): 7.66-7.74 (m, 2H), 7.91 (d, *J*=8.0 Hz, 1H), 8.18 (d, *J*=8.0 Hz, 1H), 8.62 (d, *J*=8.0 Hz, 1H), 13.61 (s, 1H, -COOH). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-D_6, 298 K) δ (ppm):144.58 (d, *J*=18.2 Hz), 121.95, 124.07, 128.73, 130.40, 136.97 (d, *J*=12.0 Hz), 136.67, 149.02, 157.62 (d, J_{CF}=255.6 Hz), 166.15. Found: C, 2.94; H, 3.04; N, 7.48. Calc. for $C_{10}H_6FNO_2$: C, 62.83; H, 3.16; N, 7.33.

Synthesis of 8-phenylthioquinoline-2-carboxylic acid. To a solution of 8-fluoroquinoline-2-carboxylic acid (0.96 g, 5 mmol) in dry DMF (20 mL) was added NaH (0.48 g, 20 mmol) under stirring, then Ph-SH (1.65 g, 15 mmol) were added to the mixture. The mixture was heated at 150°C for 12 h. After removing the solvent under vacuum, the residue was dispersed in 40 mL water, and then was adjusted to pH~2 by using HCl (6 M). The mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue was purified through column chromatography on silica gel with ethyl acetate/pentane (1/4) as eluent, give a yellow solid product (1.20 g, 86%).
^{1}H NMR (300M Hz, $CDCl_3$, 298 K) δ (ppm): 7.18 (d, *J*=7.2 Hz, 1H), 7.47 (s, 4H), 7.59 (s, 2H), 7.68 (d, *J*=8.1 Hz, 1H), 8.26 (d, *J*=8.4 Hz, 1H), 8.37 (d, *J*=8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 119.67, 124.64, 127.70, 129.29, 129.33, 130.00 130.27, 131.13, 139.27, 140.22, 142.33, 144.46, 164.07. Found: C, 64.11; H, 4.45; N, 4.76. Calc. for $C_{16}H_{11}NO_2S{\cdot}H_2O$: C, 64.21; H, 4.38; N, 4.68.

Synthesis of ethyl 8-phenylthioquinoline-2-carboxylate. To a solution of 8-phenylthioquinoline-2-carboxylic acid (1.13 g, 4 mmol) in dry EtOH (25 mL) was added 98% H_2SO_4 (1.8 mL), and the mixture was heated at 90°C for 5 h. After cooling to the room temperature, the solvent was removed under vacuum and the residue was dispersed in 200 mL water, then the solution was adjusted to pH ~ 6 by adding saturated $NaHCO_3$, and the product was extracted with ethyl acetate (3 × 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4. After the solvent was removed under vacuum, the residue was recrystallized by CH_2Cl_2/hexane to give a yellow solid of ethyl 8-phenylthioquinoline-2-carboxylate (1.25 g, 96%).
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 1.50 (t, *J*=7.2 Hz, 3H, CH_3), 4.53 (q, *J*=7.2 Hz, 2H, CH_2), 6.97 (d, *J*=6.9 Hz, 1H), 7.34 (t, *J*=7.5 Hz, 1H), 7.45-7.47 (m, 3H), 7.54 (d, *J*=7.8 Hz, 1H), 7.68-7.71 (m, 2H), 8.19-8.26 (m, 2H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 14.21, 62.01, 121.50, 123.51, 125.15, 128.52, 129.20, 129.73, 131.02, 134.84, 135.99, 137.32, 142.35, 143.68, 146.78, 165.13. Found: C, 70.23; H, 4.78; N, 4.74. Calc. for $C_{18}H_{15}NO_2S$: C, 69.88; H, 4.89; N, 4.53.

Synthesis of (8(phenylthioquinoline-2-yl)-methanol. To a solution of $NaBH_4$ (1.52 g, 40 mmol) in dry EtOH (50 mL) was added a solution of ethyl 8-phenylthioquinoline-2-carboxylate (3.10 g, in 50 mL THF, 10 mmol) slowly, and the mixture was stirred at room temperature for 12 h. After the reaction, the solvent was removed under vacuum and the residue was dispersed in 200 mL water, then the solution was adjusted to pH ~ 6 by adding saturated $NaHCO_3$ solution. And the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic solution was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue was recrystallized from a CH_2Cl_2/hexane solution to give a yellow crystalline solid of (8-(phenylthioquinoline-2-yl)-methanol (1.25 g, 97%).
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 4.53 (t, *J*=4.8Hz, 1H, OH), 4.93 (d, *J*=1.4 Hz, 2H, CH_2), 7.05 (d, *J*=7.8 Hz, 1H), 7.25-7.31 (m, 2H), 7.41-7.43 (m, 3H), 7.53 (d, *J*=8.1 Hz, 1H), 7.59-7.61 (m, 2H), 8.07 (d, *J*=8.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 64.21, 118.93, 124.56, 127.48, 128.84, 129.73, 132.04, 135.19, 137.14, 138.96, 143.02, 158.35. Found: C, 67.20; H, 5.43; N, 5.07. Calc. for $C_{16}H_{13}NO_S{\cdot}H_2O$: C, 67.34; H, 5.30; N, 4.91.

Synthesis of 2-bromomethyl-8-phenylthioquinoline. To a sealed tube charged with (8-phenylthioquinolin-2-yl)-methanol (1.88 g, 7 mmol) and HBr (7 mL, 33% solution in CH_3COOH) were heated under 100°C for 5 h, after cooling to room temperature, the mixture was added to 100 mL ice water and $NaHCO_3$ was added to neutralize the acids. Then the product was extracted with CH_2Cl_2 (3 × 30 mL). The organic solution was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue was purified through the column chromatography on silica gel with EA/PE (1/4, V/V) as eluent to give a yellow solid of 2-bromomethyl- 8-phenylthioquinoline (1.90 g, 80%).
^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 4.76 (s, 2H, CH2), 6.93 (d, J=7.8 Hz, 1H), 7.25 (t, J=7.8 Hz, 1H), 7.43-7.49 (m, 4H), 7.58-7.65 (m, 3H), 8.08 (d, J=8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 34.45 (s, CH_2), 121.92, 123.87, 125.31, 127.20, 129.14, 129.79, 131.43, 140.34, 143.51, 155.98. Found: C, 58.54; H, 3.49; N, 4.46. Calc. for $C_{16}H_{12}BrNS$: C, 58.19; H, 3.66; N, 4.24.

Synthesis of 1-mesityl-3-(8-(phenylthioquinoline-2-yl)methyl) -1H-imidazol-3-ium bromide (HL2Br). A suspension of 2-bromomethyl-8-phenylthioquinoline (3.3 g, 10 mmol) and 1-mesityl-1H-imidazole (2.23 g, 12 mmol) in toluene (55 mL) were heated at 110°C for 20 h. After cooling to room temperature, the precipitate was collected by filtration and washed with Et_2O, and then dried under vacuum at 80°C to give a white solid of H**L2**Br (5.11 g, 98%).

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^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 2.12 (s, 6H, o-CH_3), 2.32 (s, 3H, p-CH_3), 6.45 (s, 2H, CH_2), 6.98 (s, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.44-7.48 (m, 5H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.25 (s, 1H), 10.22 (s, 1H, NHC-H). ^{13}C {^{1}H} NMR (75.5 MHz, $CDCl_3$, 298 K) δ (ppm): 17.68 (s, o-CH_3), 20.96 (s, p-CH_3), 53.61 (s, CH_2), 121.29, 124.60, 127.09, 127.60, 128.69, 129.63, 130.59, 131.62, 134.19, 134.54, 137.73, 137.91, 138.89, 140.97, 143.69, 151.96. Found: C, 58.13; H, 4.52; N, 7.12. Calc. for $C_{28}H_{26}BrN_3S{\cdot}CH_2Cl_2$: C, 57.91; H, 4.69; N, 6.99.

Synthesis of complex [RuH(CO)(L2)](PF$_6$) (2). To a solution of H**L2**Br (0.51 g, 1 mmol) in THF (30 mL) was added Ag_2O (0.14 g, 0.6 mmol), and the mixture was stirred in dark for overnight to afford Ag-NHC intermediate. $RuHCl(CO)(PPh_3)_3$ (0.95 g, 1 mmol) was added to the solution and stirred at room temperature for 1 h, then heated at 65°C for 12 h. After cooling to room temperature, the precipitate was filtered off through a celite pad. The brown filtrate was taken to dryness under vacuum, and then 10 mL MeOH was added. To the solution was added NH_4PF_6 (1.63 g, 10 mmol) and stirred at room temperature for 12 h. The yellow precipitate was collected by the filtration and was recrystallized from a CH_2Cl_2/Et_2O solution to give yellow crystals of complex **2** (0.4 g, 41%).

^{31}P{^{1}H} (DMSO-D_6) δ (ppm): 23.74 (s), -144.21 (m, PF_6^-). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 1.75 (s, 3H, o-CH_3), 1.91 (s, 3H, o-CH_3), 2.22 (s, 3H, p-CH_3), 4.63 (d, *J* = 15.9 Hz, 1H, C*H*H), 5.57 (d, *J* = 15.9 Hz, 1H, CH*H*), 6.76 (s, 1H), 6.83-6.84 (m, 2H), 6.94-7.00 (m, 6H), 7.13-7.17 (m, 6H), 7.29-7.33 (m, 3H), 7.40-7.42 (m, 3H), 7.55-7.61 (m, 4H), 7.73-7.76 (m, 2H), 7.89 (d, *J* = 3.3 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), -7.26 (d, $^2J_{PH}$ =107.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm): 18.09 (s, o-CH_3), 18.80 (s, o-CH_3), 20.90 (s, p-CH_3), 54.86 (s, CH_2), 122.76, 122.92, 124.19, 127.69, 128.49, 128.58, 128.84, 128.98, 129.62, 130.02, 130.58, 132.12, 132.44, 132.55, 133.41, 133.72, 134.54, 135.05, 135.71, 136.02, 136.35, 139.30, 139.82, 147.53, 157.66, 184.45 (s, NHC), 203.26 (s, CO). IR (KBr pellets): 1953 cm^{-1} (CO). Found: C, 54.73; H, 3.97; N, 4.16. Calc. for $C_{47}H_{41}F_6N_3OP_2RuS{\cdot}CH_2Cl_2$: C, 54.50; H, 4.10; N, 3.97.

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), complex **1a**, **1b** or **2** (0.005 mmol), additive (0.05 mmol) were mixed in a 25 mL schlenk tube and the reaction mixture was heated at 150°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 **1a** (0.005 mmol), $NaBPh_4$ (0.05 mmol) 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.

Procedure for H_2 gas production. Under a nitrogen atmosphere, benzene-1,2-diamine (0.27 g, 2.5 mmol), benzyl alcohol (2.70 g, 25 mmol), $NaBPh_4$ (0.05 mmol), and complex **1a** (0.005 mmol) were added to a 25 mL schlenk tube which is connected with a gas collection instrument through gravity drainage method.[7c] The reaction mixture was heated at 150°C (oil bath). Over a period of time, the volume of the gas was recorded (seeing the supporting information, **S4-5**). 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 (7.5 mmol), complex **1a** (0.005 mmol), $NaBPh_4$ (0.05 mmol) 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.

Condensation of benzaldehyde and benzene-1,2-diamine. Benzaldehyde (3.0 mmol), benzene-1,2-diamine (2.5 mmol), complex **1a** (0.005 mmol), $NaBPh_4$ (0.05 mmol) 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**.

X-ray crystallography. A Bruker KAPPA APEX DUO diffractometer with graphite-monochromated Mo-Kα (λ= 0.71073 Å) was employed to collect the intensity data for the single crystal of complexes **1a**, **1b** and **2**. The data was collected at about 100 K using ω-scan techniques. The structure was solved by direct methods using SHELXL-2014.[33] Multi-scan empirical absorption corrections were applied to the data set using the program SADABS.[34] The structure was refined with SHELXL-2014.[33] Hydrogen atoms bound to carbon were placed at calculated positions and refined using a riding mode. All non-hydrogen atoms were refined by full-matrix least squares on F^2 using the SHELXTL grogram package.[35] Cell refinement, data collection, and reduction were done by Bruker SAINT.[36] The crystallographic data is available in the SI as CIF file.

Complex **1a** + CH_2Cl_2: $C_{30}H_{25}Cl_3NO_2PSRu$, yellow prism, 0.07 x 0.06 x 0.05 mm^3, monoclinic, s.g. $P2_1/n$, a = 12.868 (2) Å, b = 16.395 (3) Å, c = 13.619 (2) Å, β = 93.143 (3)°, V = 2869.9 (6) Å^3, Z = 4, Fw = 701.96, $F(000)$ = 1416, D_c = 1.625 Mg/m^3, μ= 0.985

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mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R_1 = 0.0316 for data with $I>2\sigma$ (I) and wR2 = 0.0763 for all data (7433 reflections) with a goodness-of-fit of 1.015. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H-Ru which was located in the difference map and refined independently. The X-ray crystal structure of complex **1a** is deposited in CCDC number 1524939.

Complex **1b** + CH_2Cl_2: $C_{30}H_{25}Cl_3NO_2PSRu$, colourless prism, 0.08 x 0.07 x 0.06 mm^3, monoclinic, s.g. $P2_1/n$, a= 12.3352 (7) Å, b = 17.842 (1) Å, c = 13.2015 (8) Å, β= 102.1459 (1)°, V = 2837.1 (3) Å^3, Z = 4, Fw = 701.96, $F(000)$ = 1416, D_c = 1.643 Mg/m^3, μ= 0.996 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R_1 = 0.0271 for data with $I>2\sigma$ (I) and wR2 = 0.0658 for all data (7341 reflections) with a goodness-of-fit of 1.038. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H-Ru which was located in the difference map and refined independently. The X-ray crystal structure of complex **1b** is deposited in CCDC number 1525821.

Complex **2** + CH_2Cl_2: $C_{48}H_{43}Cl_2F_6N_3OP_2SRu$, yellow prism, 0.14 x 0.13 x 0.11 mm^3, triclinic, s.g. $P\text{-}1$, a = 11.4078 (6) Å, b = 14.0340 (8) Å, c = 16.4595 (9) Å, α = 73.180 (1)°, β = 71.447 (1)°, γ = 66.832 (1)°, V = 2255.6 (2) Å^3, Z = 2, Fw = 1057.82, $F(000)$ = 1076, D_c = 1.558 Mg/m^3, μ= 0.650 mm^{-1}. The final cycle of refinement based on F^2 gave an agreement factor R_1 = 0.0385 for data with $I>2\sigma$ (I) and wR2 = 0.1054 for all data (11590 reflections) with a goodness-of-fit of 1.039. Idealized hydrogen atoms were placed and refined in the riding mode, with the exception of H-Ru which was located in the difference map and refined independently. The X-ray crystal structure of complex **2** is deposited in CCDC number 1524940.

Conclusions

In summary, we have illustrated three fully characterized Ru(II) hydride complexes bearing new quinoline-based pincer ligands. These complexes catalyse the dehydrogenative condensation of primary alcohol and benzene-1,2-diamine to the 2-substituted benzimidazole and H_2 in the presence of catalytic amount of $NaBPh_4$. The catalytic reactivity follows the order: **1a** ≈ **1b** > **2**. The mechanistic studies demonstrate that the dehydrogenation of alcohol to aldehyde and H_2 is slower than the condensation of aldehyde and diamine. Also, complex **1a** is an efficient catalyst precursor for the condensation of benzaldehyde and benzene-1,2-diamine to 2-phenyl-benzimidazole and H_2 in high yield (95%). The present work demonstrates a more 'green' procedure for the synthesis of 2-substituted benzimidazole from alcohol as compared to the reported homogeneous system in which stoichiometric strong base (KO^tBu, KOH etc.) is usually necessary.

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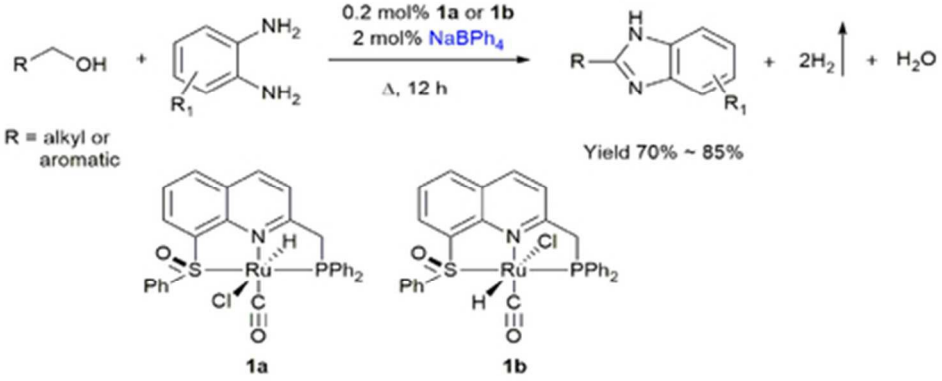

A greener method of synthesizing 2-substituted benzimidazole through the acceptoless dehydrogenative condensation of alcohol and *ortho*-arylenediamine is developed.

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