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Cooperative N–H and CH_2 Skeleton Effects on the Catalytic Activities of Bimetallic Ru(II)–NNN Complexes: Experimental and Theoretical Study

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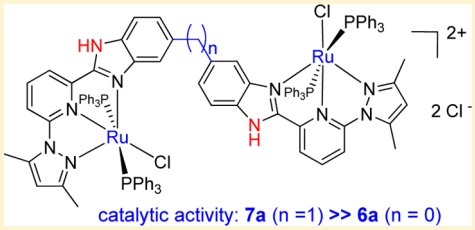
Supporting Information

ABSTRACT: Bimetallic ruthenium(II) complexes bearing a bis(pyrazolyl-imidazolylpyridine) ligand bridged by a rotatable single C–C bond or methylene linker were synthesized, structurally characterized, and exhibited diverse catalytic activities for the transfer hydrogenation (TH) reactions of ketones in refluxing isopropyl alcohol. Both the unprotected NH functionality and bridging methylene moiety demonstrated an acceleration effect on such TH reactions. Combination of the NH and CH_2 skeleton functionalities into the bimetallic Ru(II)–NNN complexes remarkably enhanced the catalytic activities of the complex catalysts. Density functional theory calculations have suggested that the difference in the catalytic activities of these Ru(II)–NNN complexes is attributed to the inherent nucleophilic character of the coordinative nitrogen atoms in the bis(NNN) ligand, and the metal–metal interaction resulted from the number of net natural bond orbital charges on these nitrogen atoms.

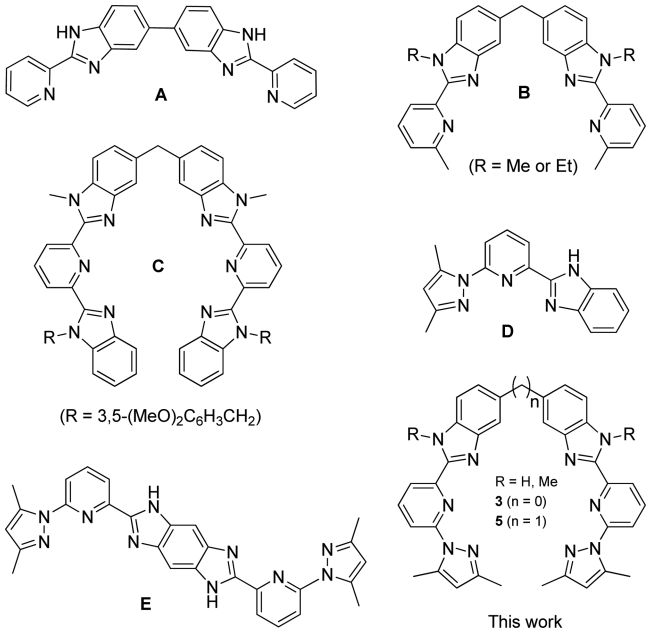


INTRODUCTION

It has been widely recognized that organometallic complexes that incorporate more than one reactive metal center may supply a class of catalytic species with unusual reactivity patterns derived from both the intramolecular electron transfer process between the metal centers and steric effect.[1] Recently, bimetallic complexes have attracted more and more attention for their potentials to act as effective catalysts.[2] Basset's group reported a bimetallic W/Ti precatalyst anchored on a single silica surface for metathesis of propane.[3a] The bimetallic Ni/Zn catalyst could promote production of a polymer with significantly high M_n value.[3b] Musaev et al. found that the palladium acetate dimer was more stable than the monomer due to the interactions between the paddle wheel ligands and the palladium centers.[3c] Uyeda and co-workers documented the dinuclear nickel catalyst, which was significantly more active than its mononuclear counterpart in alkyne hydrosilylations.[3d] Dinuclear indium catalysts exhibited high catalytic activity for the ring-opening polymerization of lactide to form poly(lactic acid) at room temperature.[3e] Bimetallic Ir(III) complexes with bridging ligands achieved highly efficient piezochromic and aggregation-induced emission phosphorescence behaviors.[3f] Coates et al. synthesized a highly active and enantioselective bimetallic cobalt(III) complex catalyst for the polymerization of monosubstituted epoxides.[3g]

Poly(*N*-heterocycle) ligands have usually been employed to construct bimetallic complex catalysts (Scheme 1).[4,5] A dinuclear ruthenium(II) complex bearing a polypyridyl ligand bridged by a

Scheme 1. Poly(*N*-heterocycle) Ligands



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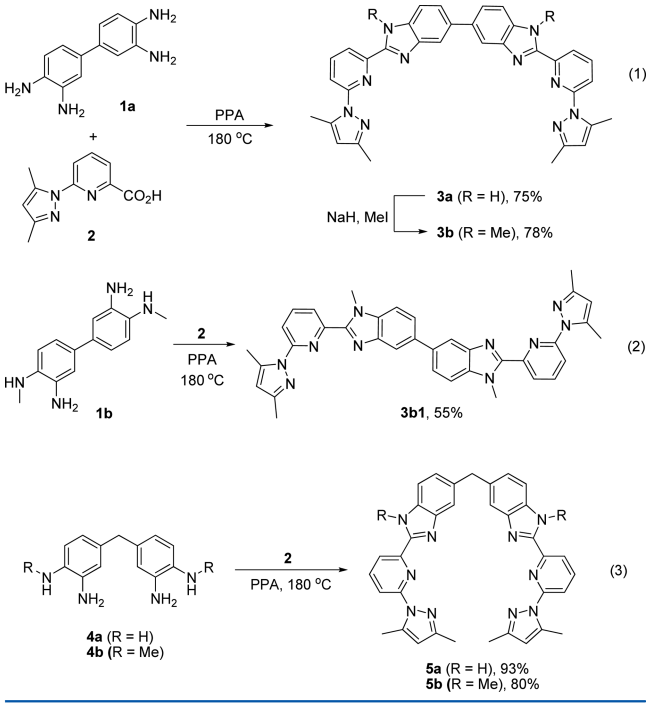
flexible methylene chain ($(CH_2)_n$ skeleton) selectively targeted polysomes in vivo.[6] Dinuclear ruthenium and osmium complexes supported by a 2,2′-bis(2-pyridyl)dibenzimidazole ligand (**A**) were successfully utilized as the proton-induced switching for metal−metal interaction.[4] Proton transfer in the ligand can be applied as a trigger signal to change the metal−metal interaction or structures of the complexes.[4c] Moreover, ligand **A** can be used to construct photoexcited Ru(II)−Rh(III) dinuclear complexes that exhibit intramolecular electron transfer.[4b]

Bis(bidentate) ligands **B**[5a,b,e] and bis(tridentate) ligand **C**[5c,d] containing a flexible bridging methylene reacted with the metal ions to form dinuclear metal complexes that could self-assemble into triple-helical structures with specific properties. These complexes have demonstrated an important theoretical interest, that is, metal-to-metal energy transfer restricted to an intramolecular process, which can be applied to test the validity of the dipole−dipolar mechanism.[5d]

Transfer hydrogenation of ketones catalyzed by transition-metal catalysts has been well explored as an efficient reduction method to access alcohols.[7] Our group has also paid much attention to this area.[8] Diruthenium(II) complexes assembled by the monoruthenium(II) complex of ligand **D** with 4,4′-bipyridines[9a] and those bearing a π linker-supported bis(pyrazolylimidazolylpyridine) ligand **E**[9b] have recently been reported for this purpose. Cooperativity effects of the metal centers in these bimetallic Ru(II)−NNN complexes are remarkable on the enhancement of the catalytic activities as compared to the corresponding mononuclear Ru(II)−NNN complexes. It has been known that transition-metal complexes bearing a polydentate ligand with an unprotected NH functionality usually exhibit high catalytic activity in the transfer hydrogenation reactions.[7d−h,10] Such a "NH effect" strategy has been utilized in the design of Ru(II)−diphosphine diamine complexes by Noyori and co-workers,[11] transition-metal complex catalysts bearing a NNP ligand by Beller,[12] or a NPP ligand by Kempe et al.[13] Intrigued by the literature work and our interest in highly active transition-metal complexes for catalytic transformations, herein, we report construction of imidazolyl-pyrazolylpyridine-based bis(NNN) ligands **3** and **5** and their diruthenium(II) complex catalysts for transfer hydrogenation of ketones as well as the relevant theoretical study.

RESULTS AND DISCUSSION

Ligand Synthesis and Characterization. Condensation of tetraaminobiphenyl **1a**[14] with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl) picolinic acid (**2**) in the presence of polyphosphoric acid (PPA) afforded bis(NNN) ligand **3a** in 75% yield. Methylation of **3a** with iodomethane gave *N*-methylated ligand **3b** (78%) (eq 1). In order to attain the specific isomers, an alternative approach was used to synthesize one of the geometrical isomers of ligand **3b**, that is, **3b1**, from the reaction of *N*-methylated tetraaminobiphenyl **1b**[15] with **2** (eq 2). By a literature method,[5b] *o*-nitroaniline was reacted with paraformaldehyde to give 4,4′-methylene-bis(2-nitroaniline), which was reduced with hydrazine hydrate to form tetraamino compound **4a**. In a fashion similar to the synthesis of **3a** and **3b**, condensation of **4a** with **2** yielded *N*-unprotected ligand **5a**. The *N*-methylated derivative of **4a**, that is, **4b**,[5e] reacted with **2** to form **5b** (eq 3) (see the Supporting Information (SI) for details). Due to the free rotation around the C−C and C−N single bonds, ligands **3** and **5** have three possible geometrical isomers which can be bonded with metals (Figure 1). In the ^{1}H and ^{13}C NMR spectra of **3a** in trifluoroacetic acid-*d* (TFA-*d*), only one group of signals



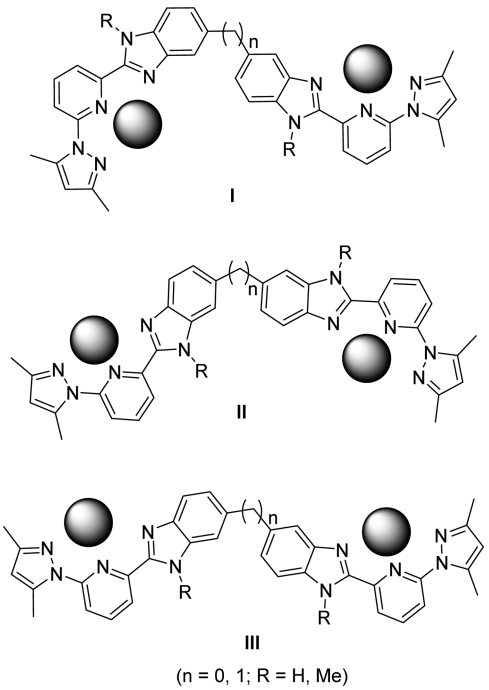


Figure 1. Possible geometrical isomers of ligands **3** and **5** with the coordination shown by a shadow ball.

were observed due to the rapid proton exchange between the imidazolyl NH and C═N functionalities, and the same phenomenon was shown in the NMR spectra determined in DMSO-d_6. Four distinct proton NMR signals of the *N*-methyl groups of **3b** were observed in the ^{1}H NMR spectrum, revealing the existence of three geometrical isomers of ligand **3b** in solution: 4.17 ppm (type **I**), 4.19 and 4.20 ppm (type **III**), and 4.21 ppm (type **II**) (Figure 1; also see the ^{1}H NMR spectrum of **3b** in the SI), which were structurally distinguished from these ^{1}H NMR signals by comparison with those reported in the literature[4b,16] (see the SI for details). The proton resonance signal of the *N*-methyl in **3b1** appeared at 4.18 ppm,

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suggesting its type **I** conformation. One group of ^{1}H and ^{13}C resonance signals was shown in the NMR spectra determined in TFA-*d* for ligand **5a**, while the bridging CH_2 functionality exhibited three proton resonance signals at 4.24, 4.22, and 4.20 ppm in the ^{1}H NMR spectrum determined in DMSO-d_6, revealing the presence of three types of geometrical isomers in DMSO-d_6 solution for ligand **5a**. Ligand **5b** was only shown with one conformation by its ^{1}H and ^{13}C NMR spectra in $CDCl_3$. The single crystal structure of **5b** is presented in Figure 2,

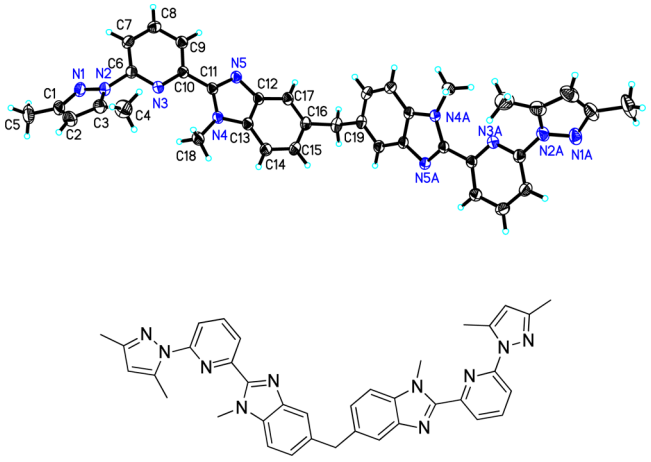
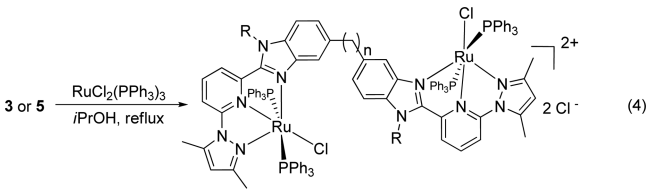


Figure 2. Molecular structure of ligand **5b**.

which adopts type **I** conformation, as shown in Figure 1, revealing that the 3,5-dimethyl-1*H*-pyrazolyl moieties could freely rotate around the C−N single bonds, but the methylene-bridged aromatic blocks could not, presenting a 113.2° angle of C16−C19−C16A (see the SI for details).

Complex Synthesis and Characterization. Treatment of ligands **3** or **5** with $RuCl_2(PPh_3)_3$ in a 1:2 molar ratio in refluxing isopropyl alcohol formed the cationic diruthenium(II) complexes **6a** (83%), **7a** (85%), and **7b** (81%) (eq 4). Unexpectedly, ligand **3b1** could not react with $RuCl_2(PPh_3)_3$ to



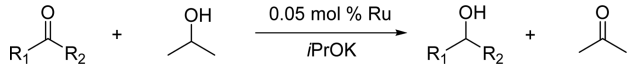
(4)

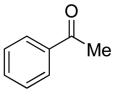
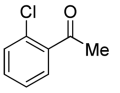
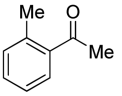
n	R
0	H (**6a**), 83% Me (**6b**), 0%
1	H (**7a**), 85% Me (**7b**), 81%

give the target complex product **6b** under the same conditions. In a similar fashion, compound **3b** was reacted with $RuCl_2(PPh_3)_3$, yielding no desired complex product either. The ligand of complex **6a**, that is, compound **3a**, features the same bis(imidazolylpyidine) backbone as 2,2′-bis(2-pyridyl)-6,6′-dibenzimidazole. The latter exhibits three types of coordination modes in the corresponding ruthenium(II)−PPh_3 complex.[16] However, the ^{31}P NMR spectrum of complex **6a** in $CDCl_3$ only exhibited two singlets at 19.7 and 19.3 ppm. The three intrinsic ^{31}P resonance signals for type **I**−**III** isomers of complex **6a** may coalesce to show only two signals at ambient temperature. The ^{1}H NMR spectrum of complex **7a** in $CDCl_3$ showed three types of bridging CH_2 proton resonances at 4.16, 4.12, and 4.11 ppm, and its ^{31}P NMR spectrum also exhibited two singlets at 19.8 and 19.5 ppm as did complex **6a**. The ^{1}H resonance signal of the bridging CH_2 in complex **7b** appeared at 4.41 ppm as a singlet, and the ^{31}P NMR signal was shown at 20.8 ppm. These results have suggested that complex **7b** exists as a single isomer. Many attempts were made to obtain single crystals of the bimetallic complexes for the X-ray structural analysis, but no success has been achieved.

Transfer Hydrogenation of Ketones. To investigate the N−H effect on the catalytic activities of the bimetallic ruthenium(II)−NNN complexes, **7a** and **7b**, differentiated by the imidazolyl NH and NCH_3 functionalities, were tested as the catalysts for the transfer hydrogenation reactions of acetophenone, 2′-chloroacetophenone, and 2′-methyl-acetophenone in refluxing isopropyl alcohol (Table 1). It was found that

Table 1. Comparison of the Catalytic Activities of Complexes 7a and 7b[a]



Entry	Catalyst	Ketone	Time (min)	Yield[b] (%)	TOF[c] (h^{-1})
1	**7a**		2	98	5.0×10^5
	7b		120	90	7.1×10^3
2	**7a**[d]		3	98	4.4×10^6
	7b[d]		60	91	2.5×10^4
3	**7a**		1	98	6.4×10^5
	7b		120	96	7.9×10^3

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); catalyst, 0.025 mol % (0.05 mol % of Ru) (ketone/*i*PrOK/Ru = 2000:20:1); 0.1 MPa N_2, 82 °C. [b]Average value from three parallel experiments by GC analysis. [c]Turnover frequency (moles of ketone converted per mol of Ru per hour) at 50% conversion of the ketone. [d]0.01 mol % catalyst (0.02 mol % of Ru).

complex **7a** exhibited catalytic activity much higher than that of complex **7b**, reaching 98% yield and TOF values of 5.0×10^5 to 4.4×10^6 h^{-1} within 1−3 min, whereas **7b** only promoted the same TH reactions to achieve 90−96% yields with TOF values of 7.1×10^3 to 2.5×10^4 h^{-1} within 1−2 h. These results have revealed that the N−H effect of the ligand was remarkable on the enhancement of the catalytic activity of the resultant transition-metal complexes.

Then, the catalytic behaviors of complexes **6a** and **7a** bearing the *N*-unprotected bis(NNN) ligands **3a** and **5a** were investigated using 0.025 mol % of catalyst (0.05 mol % of Ru). It was found that bimetallic complex **7a** bearing the *N*-unprotected bis(NNN) ligand bridged by a CH_2 functionality was much more catalytically active than complex **6a** supported by the *N*-unprotected bis(NNN) ligand bridged directly through the biphenyl backbone for the TH reactions of all the substituted

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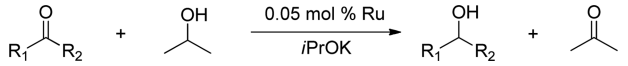
Table 2. Catalysis by Complexes 6a and 7a[a]



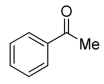
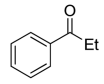
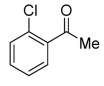
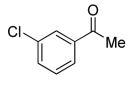
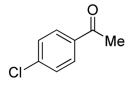
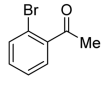
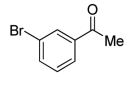
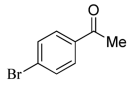
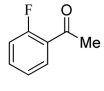
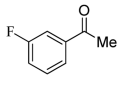
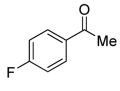
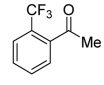
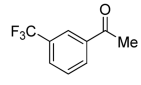
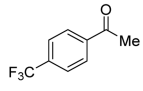
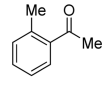
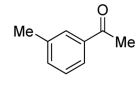
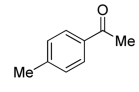
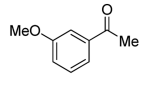
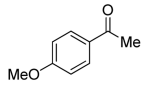
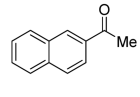
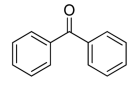
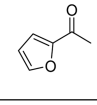
Entry	Catalyst	Ketone	Time (min)	Yield[b] (%)	TOF[c] (h^{-1})
1	**6a**		30	93	3.2×10^5
	7a		2	98	5.0×10^5
2	**6a**		30	93	2.7×10^4
	7a		5	99	7.0×10^4
3	**6a**[d]		15	92	2.7×10^6
	7a[d]		3	98	4.4×10^6
4	**6a**[d]		15	81	3.9×10^5
	7a[d]		2	98	3.7×10^6
5	**6a**[d]		15	83	3.1×10^5
	7a[d]		2	99	4.3×10^6
6	**6a**		15	91	2.2×10^5
	7a		1	100	1.7×10^6
7	**6a**		10	96	2.6×10^5
	7a		1	100	1.7×10^6
8	**6a**		15	95	7.6×10^4
	7a		2	99	6.2×10^5
9	**6a**		15	94	1.4×10^5
	7a		1	100	2.2×10^6
10	**6a**		5	96	4.3×10^5
	7a		1	100	6.5×10^5
11	**6a**		6	97	4.7×10^5
	7a		5	99	7.6×10^5
12	**6a**		15	76	1.3×10^5
	7a		2	100	6.4×10^5
13	**6a**		3	99	2.0×10^5
	7a		2	99	4.3×10^5
14	**6a**		3	100	3.5×10^5
	7a		2	100	1.3×10^6
15	**6a**		10	97	2.2×10^5
	7a		1	98	6.4×10^5
16	**6a**		15	88	2.2×10^5
	7a		5	98	6.0×10^5
17	**6a**		10	92	2.7×10^5
	7a		2	96	9.5×10^5
18	**6a**		2	98	4.7×10^5
	7a		1	98	1.1×10^6
19	**6a**		20	87	1.4×10^5
	7a		15	95	2.2×10^5
20	**6a**[d]		15	96	8.0×10^5
	7a[d]		1	98	2.0×10^6
21	**6a**[d]		3	97	1.2×10^6
	7a[d]		2	97	1.6×10^6
22	**6a**[e]		10	95	6.4×10^4
	7a[e]		2	97	1.9×10^5

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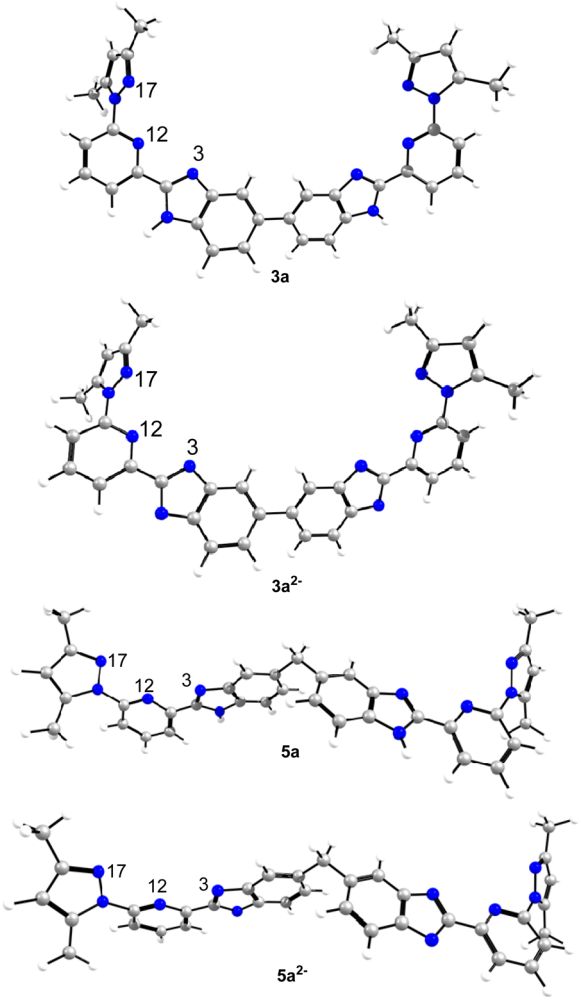
Table 2. continued

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); catalyst, 0.025 mol % (0.05 mol % of Ru) (ketone/*i*PrOK/Ru = 2000:20:1); 0.1 MPa N_2, 82 °C. [b]Average value from three parallel experiments by GC analysis. [c]Turnover frequency (moles of ketone converted per mol of Ru per hour) at 50% conversion of the ketone. [d]Using 0.01 mol % of catalyst (0.02 mol % of Ru). [e]Using 0.05 mol % of catalyst (0.1 mol % of Ru).

acetophenones, 2-acetylnaphthalene, and benzophenone (Table 2). With **6a** as the catalyst, acetophenone was converted to 1-phenylethanol in 93% yield over a period of 30 min, while the same reaction was complete within 2 min using **7a** as the catalyst (Table 2, entries 1 and 2). Similar results were obtained in the case of propiophenone (Table 2, entry 3). The chloro substituent exhibited an acceleration impact on the reaction rates of chloro-substituted acetophenones that they could be transformed to the corresponding alcohols in 98−99% yields within 2−3 min by means of a lower catalyst loading, that is, 0.01 mol % of **7a** as the catalyst, reaching the highest TOF value of 4.4×10^6 h^{-1} (Table 2, entries 3−5). The bromo-acetophenones also underwent the TH reactions very efficiently with **7a** as the catalyst, whereas the same reactions could only achieve 91−95% yields within 10−15 min by means of **6a** as the catalyst (Table 2, entries 6−8). The fluoro-acetophenones reacted more efficiently than the corresponding bromo-acetophenones (Table 2, entries 9−11). For the electron-withdrawing CF_3-substituted acetophenone substrates, only 2′-CF_3-acetophenone reacted inefficiently to reach a 76% yield within 15 min in the case of using **6a** as the catalyst, whereas 3′- and 4′-CF_3-acetophenones reacted well to give the corresponding alcohols in 99−100% yields within 2−3 min using either **6a** or **7a** as the catalyst (Table 2, entries 12−14). In the cases of using electron-donating methyl or methoxy-substituted ketone substrates, complex **6a** could not efficiently promote the TH reactions of 3′- and 4′-Me-acetophenones and 4′-MeO-acetophenone, only reaching 87−92% yields within 10−20 min (Table 2, entries 16, 17, and 19), whereas complex **7a** efficiently catalyzed the TH reactions of all the Me- and MeO-substituted acetophenones to form the target products (Table 2, entries 15−19).

Unexpectedly, both complexes **6a** and **7a** exhibited excellent catalytic activities to the bulky 2-acetylnaphthalene and benzophenone, and their TH reactions efficiently occurred to reach 96−98% yields within 1−15 min using 0.01 mol % of the complex catalysts (Table 2, entries 20 and 21). By increasing the catalyst loading to 0.05 mol % (0.1 mol % of Ru), hetero-aromatic ketone 2-acetylfuran was reacted to form the corresponding alcohol in 95% yield within 10 min by means of complex **6a** as the catalyst, and complex **7a** promoted the same reaction more efficiently to yield the target product (97%) within 2 min (Table 2, entry 22). However, 2-acetylpyridine did not react under the same conditions, presumably due to the strong binding of the pyridyl nitrogen atom to the catalytic metal center. Additionally, the catalytic behaviors of complex **6a** and its monometallic counterpart, that is, complex **8**,[21a] were also comparatively investigated with 0.1 mol % of Ru loading, and complex **6a** exhibited a catalytic activity much higher than that of complex **8** (see Table S1 in the SI).

Density Functional Theory (DFT) Calculations. In order to explain the catalytic activity differences between complexes **6** and **7**, the electronic structures of their corresponding ligands, **3a** and **5a**, and their corresponding conjugate bases, $\mathbf{3a}^{2-}$ ([**3a**-2H]) and $\mathbf{5a}^{2-}$ ([**5a**-2H]), were computed by means of Becke's three-parameter hybrid exchange functional with Lee−Yang−Parr gradient-corrected correlation (B3LYP functional)[17] with the Gaussian 09 program.[18] The optimization of the geometries and calculations of natural bond orbital (NBO) charges were performed with 6-31g(d) basis sets.[19] Figure 3 depicts



	3a	3a^{2-}	5a	5a^{2-}
N3	-0.49583	-0.58039	-0.49748	-0.58079
N12	-0.44509	-0.46913	-0.4457	-0.47001
N17	-0.32105	-0.32392	-0.32153	-0.32454
N3+N12+N17	-1.26197	-1.37344	-1.26471	-1.37534

Figure 3. DFT-optimized geometries of ligands **3a**, **5a**, and their deprotonated anions. In the geometry determination, no assumption such as the planarity of benzene and pyridine rings was made. Data in this figure represent anionic net NBO charges on the coordinative nitrogen atoms 3, 12, and 17.

their optimized geometries. According to the calculations, the number of net NBO charges on the coordinative nitrogen atoms are $\mathbf{3a}^{2-}$ > **3a**, $\mathbf{5a}^{2-}$ > **5a**, and **5a** > **3a**. The anionic nature

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of the nitrogen atoms is strengthened by double deprotonation of the NH functionalities or adding a bridging methylene functionality in the ligand backbone. These effects lead to obviously enhanced electron-donating ability of the anionic nitrogen atoms compared to those of the neutral nitrogen atoms and stronger metal−ligand electrostatic attraction in the complexes. It is noteworthy that during the TH reaction under the basic conditions, a hydrochloride molecule is initially removed from the cationic complex **6a** or **7a** to form a neutral precatalyst bearing the anionic *N*-coordinating ligand $\mathbf{3a}^{2-}$ or $\mathbf{5a}^{2-}$. In fact, it is the precatalysts that demonstrated catalytic activities much higher than those of complexes **6b** and **7b** bearing a ligand with all neutral *N*-coordinating moieties. The enhanced metal coordination effect can be well transmitted to the bimetallic partner metal via the least skeleton route as previously reported,[4c] and thus the metal−metal interaction is enhanced. For clarity, monometallic complex **8** was employed as the precatalyst to depict the reaction mechanism instead of using the bimetallic complex as the precatalyst (Figure 4). Based on a similar inner-sphere pathway as

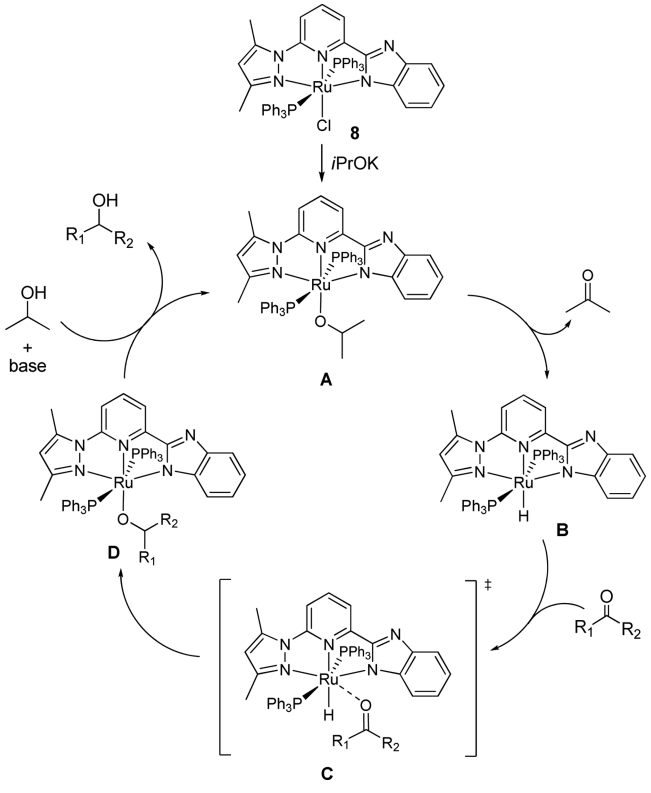


Figure 4. Proposed mechanism for the inner-sphere pathway mechanism represented using mononuclear complex **8** as the precatalyst.

shown,[8a,9b,20,21b] a plausible explanation of the catalytic activity difference between complexes **7a** and **7b** was made. Complex **7a** is initially deprotonated by the imidazolyl NH functionalities of the coordinating benzimidazolyl moieties to generate a neutral complex (the "precatalyst") that can exhibit stronger metal−metal interaction, whereas complex **7b** containing two imidazolyl *N*-Me functionalities could not undergo such a transformation to show the N−H acceleration effect.[21] The strengthened metal−metal interaction in complex **7a** is partially attributed to the higher net NBO charges of the anionic *N*-containing ligand in its precatalyst form. In addition, the different nucleophilic characters of the coordinating nitrogen atoms derived from their net charges may justify the diverse reactivities of the complexes.[8a,9b]

CONCLUSIONS

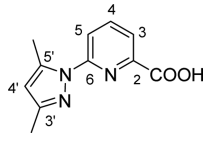
In conclusion, pincer-type bimetallic ruthenium(II)−NNN complex catalysts have been successfully synthesized and showed excellent catalytic activity for the transfer hydrogenation of ketones. The complexes bearing a bis(NNN) ligand with unprotected imidazolyl NH functionalities were much more catalytically active than those supported by the corresponding *N*-protected bis(NNN) ligand. The bimetallic complexes bearing a *N*-unprotected bis(NNN) ligand bridged by a methylene functionality exhibited catalytic activity higher than those supported by a *N*-unprotected bis(NNN) ligand connected directly through a biphenyl unit. Combination of such N−H and CH_2 skeleton effects has demonstrated a cooperativity to remarkably enhance the catalytic activity of the resultant bimetallic complex catalysts. The nucleophilic character of the coordinating nitrogen atoms and the degree of metal−metal interaction can justify the different catalytic activities of the bimetallic complexes in the transfer hydrogenation of ketones.

EXPERIMENTAL SECTION

General Considerations. All the manipulations of air- and/or moisture-sensitive compounds were carried out under nitrogen atmosphere using the standard Schlenk techniques. The solvents were dried and distilled prior to use by the literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a 400 MHz spectrometer, and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ (δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm), DMSO-d_6 (δ(^{1}H), 2.50 ppm; δ(^{13}C), 39.52 ppm), and TFA-*d* (δ(^{1}H), 11.50 ppm; δ(^{13}C), 164.2, 116.6 ppm). Elemental and HRMS analysis were achieved by the Analysis Center, Dalian University of Technology and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for compound **5b** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition number CCDC 1522009. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Synthesis of Compound 2.



Compound methyl 6-(3,5-dimethyl-1*H*-pyrazol-1- yl)picolinate (1.0 g, 4.30 mmol) was dissolved in methanolic solution of sodium hydroxide (6 mL, 1 mol L^{-1}) and refluxed for 6 h. The solvent of the cooled solution was removed under reduced pressure, and the residue was dissolved in water. The obtained solution was added dropwise to

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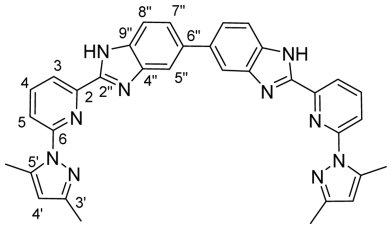
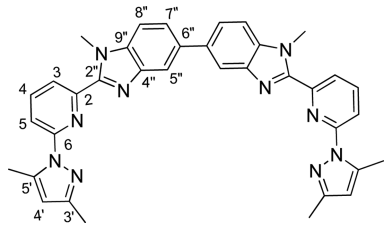
5% HCl, then a white solid separated out and was dried under reduced pressure to afford a white solid (800.0 mg, 85%): mp 158−161 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.07 (t, J = 7.8 Hz, 1 H, 4-H), 8.00 and 7.91 (d each, J = 8.2 and 7.3 Hz, 1:1 H, 5-H and 3-H), 6.13 (s, 1 H, 4′-H), 2.67 (s, 3 H, C5′-CH_3), 2.20 (s, 3 H, C3′-CH_3); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 165.8, 152.6, 146.5, 149.4, 140.1, 141.4, 121.7, 118.0, 109.5, 14.4, 13.4; HRMS calcd for $C_{11}H_{11}N_3O_2$ 217.0851, found 217.0849.

Synthesis of Compound 3a.



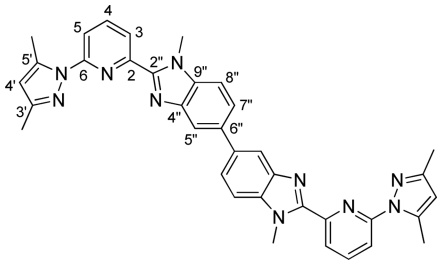
[1,1′-Biphenyl]-3,3′,4,4′-tetraamine **1a** (147.9 mg, 0.69 mmol) and 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid **2** (300.1 mg, 1.38 mmol) were dissolved in concentrated phosphoric acid (85%, 10 mL), slowly heated to 180 °C, and maintained at this temperature for 5 h. After being cooled, the mixture was poured into water (50 mL) and neutralized to pH 6.0−7.0 with concentrated aqueous ammonia (25%). The precipitate was filtered, washed with water (20 mL), and dried under vacuum to give a brown solid which was subjected to purification by silica gel column chromatography (eluent dichloromethane/methanol: 40/1, v/v), affording **3a** as a yellow solid (300.0 mg, 75%): mp 191−193 °C; ^{1}H NMR (TFA-d, 400 MHz) δ 8.54 (d, J = 7.6 Hz, 2 H, 3-H), 8.44 (t, J = 7.9 Hz, 2 H, 4-H), 8.13(s, 2 H, 5-H), 8.00−7.98 (m, 6 H, 5″-H, 7″-H, 8″-H), 6.60 (s, 2 H, 4′-H), 2.72 (s, 6 H, C3′-CH_3), 2.59(s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR (TFA-d, 100 MHz) δ 149.3, 146.7, 145.5, 144.5, 142.3, 139.9, 139.6, 130.7, 130.0, 127.7, 123.2, 119.1, 114.2, 110.5, 103.4, 10.7, 8.7; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.67 and 12.65 (s each, 2 H, NH), 8.27 (d, J = 7.5 Hz, 2 H, 3-H), 8.13 (t, J = 7.9 Hz, 2 H, 4-H), 8.04 (d, J = 9.4 Hz, 1 H, 7″-H), 7.90−7.82 (m, 4 H, 5-H and 5″-H), 7.74−7.61 (m, 3 H, 7″-H and 8″-H), 6.19 (s, 2 H, 4′-H), 2.77 (s, 6 H, C3′-CH_3), 2.24 (s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 153.1, 151.2, 151.1, 150.9, 149.8, 147.2, 147.2, 145.3, 145.1, 143.8, 143.6, 141.8, 141.8, 140.6, 137.2, 136.2, 136.2, 134.8, 134.7, 123.8, 122.6, 122.5, 120.2, 120.1, 119.5, 117.8, 117.4, 113.2, 113.1, 110.8, 109.5, 14.5, 13.9; HRMS calcd for $C_{34}H_{28}N_{10}$ 576.2498, found 576.2507.

Synthesis of Compound 3b.



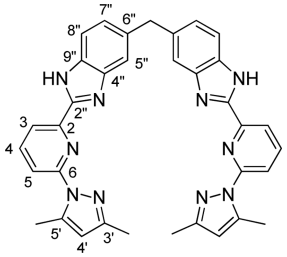
A mixture of ligand **3a** (100.0 mg, 0.17 mmol), NaH (20.9 mg, 0.51 mmol), and iodomethane (72.4 mg, 0.51 mmol) in 20 mL of THF was stirred at 66 °C for 5 h; then the solvent was removed under reduced pressure, and the resulting crude solid was purified by silica gel column chromatography (eluent dichloromethane/methanol: 50/1, v/v), affording **3b** as a yellow solid (80.0 mg, 78%): mp 102−104 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19−8.16 (m, 2 H, 3-H), 8.06 (d, J = 6.0 Hz, 1 H, 7″-H), 7.93−7.84 (m, 5 H, 7″-H, 5″-H and -5H), 7.65−7.59 (m, 3 H, 4-H and 8″-H), 7.45 (d, J = 8.4 Hz, 1 H, 8″-H), 5.98 (s, 2 H, 4′-H), 4.21, 4.20, 4.19, and 4.17 (s each, 6 H, N-CH_3), 2.59 (s, 6 H, C3′-CH_3), 2.26 (s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 152.7, 150.9, 150.4, 148.4, 143.2, 141.2, 139.5, 137.9, 137.3, 124.0, 123.4, 122.5, 120.4, 118.8, 117.1, 110.3, 109.4, 108.8, 108.7, 32.8, 32.8, 32.7, 32.7, 14.4, 13.8; HRMS calcd for $C_{36}H_{32}N_{10}$ 604.2811, found 604.2814.

Synthesis of Compound 3b1.



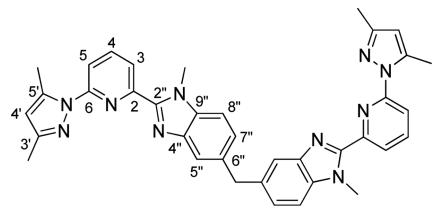
In a fashion similar to the synthesis of **3a**, N^4,$N^{4'}$-dimethyl-[1,1′-biphenyl]-3,3′,4,4′-tetraamine **1b** (36.6 mg, 0.15 mmol) reacted with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid **2** (65.6 mg, 0.30 mmol) to give a yellow solid which was subjected to purification by silica gel column chromatography (eluent dichloromethane/methanol: 50/1, v/v), affording **3b1** as a yellow solid (50.0 mg, 55%): mp 285−287 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J = 7.5 Hz, 2 H, 3-H), 8.06 (s, 2 H, 5″-H), 7.92 and 7.87 (t and d, J = 7.8 and 8.2 Hz, 2:2 H, 4-H and 5-H), 7.65 and 7.46 (d each, J = 8.4 and 8.4 Hz, 2:2 H, 7″ H and 8″-H), 5.99 (s, 2 H, 4′-H), 4.18 (s, 6 H, N-CH_3), 2.59 (s, 6 H, C3′-CH_3), 2.27(s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 152.8, 150.6, 149.9, 146.8, 141.2, 139.8, 137.5, 135.9, 124.5, 123.1, 118.0, 117.8, 110.7, 109.5, 33.0, 14.4, 13.8; HRMS calcd for $C_{36}H_{32}N_{10}$ 604.2811, found 604.2814.

Synthesis of Compound 5a.



In a fashion similar to the synthesis of **3a**, 4,4′-methylenebis(benzene-1,2-diamine) **4a** (157.7 mg, 0.69 mmol) reacted with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid **2** (300.1 mg, 1.38 mmol) to give a white solid (380.0 mg, 93%): mp 208−210 °C; ^{1}H NMR (TFA-d, 400 MHz) δ 8.48 (d, J = 7.7 Hz, 2 H, 3-H), 8.41 (t, J = 7.9 Hz, 2 H, 4-H), 7.96 (d, J = 8.1 Hz, 2 H, 5-H), 7.81 (d, J = 8.5 Hz, 2 H, 7″-H), 7.67 and 7.59 (s and d, J = 8.6 Hz, 2:2 H, 5″-H and 8″-H), 6.58 (s, 2 H, 4′-H), 4.43 (s, 2 H, CH_2), 2.71 (s, 6 H, C3′-CH_3), 2.57(s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR (TFA-d, 100 MHz) δ 149.3, 146.8, 145.6, 143.8, 142.4, 141.1, 139.8, 130.6, 129.3, 129.1, 123.1, 119.0, 113.8, 113.2, 110.7, 40.3, 10.9, 8.8; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 12.52 and 12.42 (s each, 2 H, NH), 8.20 (d, J = 7.3 Hz, 2 H, 3-H), 8.09 (t, J = 7.7 Hz, 2 H, 4-H), 7.82 (d, J = 7.9 Hz, 2 H, 5-H), 7.68−7.64 (m, 2 H, 7″-H), 7.56−7.53 (m, 1 H, 5″-H), 7.44 (s, 1 H, 5″-H), 7.20 (d, J = 8.1 Hz, 2 H, 8″-H), 6.16 (s, 2 H, 4′-H), 4.24, 4.22, and 4.20 (s each, 2 H, CH_2), 2.72 (d, 6 H, C3′-CH_3), 2.22 (s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) δ 152.6, 150.1, 149.9, 149.3, 146.9, 144.2, 142.4, 141.3, 140.1, 137.3, 135.2, 133.4, 123.7, 119.2, 119.1, 118.9, 118.8, 116.8, 116.7, 112.2, 112.1, 111.9, 109.0, 41.6, 14.0, 13.4; HRMS calcd for $C_{35}H_{30}N_{10}$ 590.2655, found 590.2654.

Synthesis of Compound 5b.



In a fashion similar to the synthesis of **3a**, 4,4′-methylenebis(N^1-methylbenzene-1,2-diamine) **4b** (61.5 mg, 0.24 mmol) reacted with 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid **2** (106.8 mg, 0.49 mmol) to give a brown solid which was subjected to purification by silica gel

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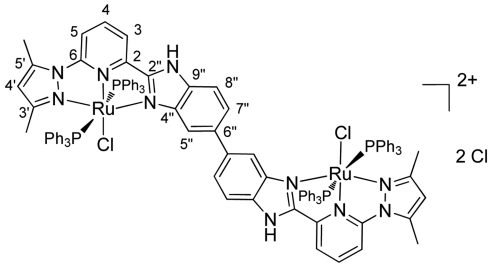
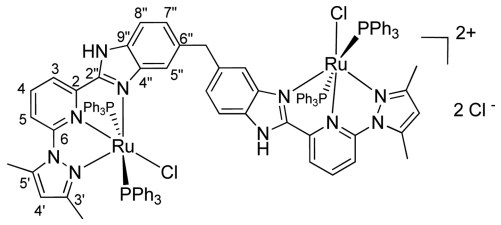
column chromatography (eluent dichloromethane/methanol: 50/1, v/v), affording **5b** as a yellow solid (120.0 mg, 80%): mp 195−197 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J = 7.1 Hz, 2 H, 3-H), 7.95−7.88 (m, 4 H, 4-H and 5-H), 7.71 (s, 2 H, 5″-H), 7.31 and 7.22 (d each, J = 8.4 and 7.6 Hz, 2:2 H, 7″ H and 8″-H), 6.02 (s, 2 H, 4′-H), 4.28 (s, 2 H, CH_2), 4.14 (s, 6 H, N-CH_3), 2.61 (s, 6 H, C3′-CH_3), 2.31(s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 152.5, 150.2, 148.5, 142.9, 141.1, 139.3, 136.7, 135.8, 125.0, 122.3, 120.0, 116.8, 109.9, 109.2, 42.3, 32.5, 14.3, 13.7; HRMS calcd for $C_{37}H_{34}N_{10}$ 618.2968, found 618.2962.

Synthesis of Complex 6a.



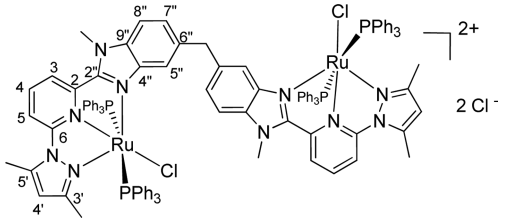
Under a nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (81.4 mg, 0.08 mmol) and **3a** (24.5 mg, 0.04 mmol) in isopropyl alcohol (10 mL) was refluxed for 3 h, forming a red-brown solid. After cooled to ambient temperature, the precipitate was filtered off, washed with diethyl ether (3 × 10 mL), recrystallized from n-hexane/methanol (v/v, 3/1) at ambient temperature, and dried under vacuum to afford **6a** as a red-brown solid (69.0 mg, 83%): mp > 320 °C (decomp); ^{1}H NMR ($CDCl_3$/CD_3OD, 400 MHz) δ 15.64 (br, 2 H, NH), 8.92−8.88 (m, 2 H, 3-H), 8.45−8.41 (m, 2 H, 4-H), 7.74 and 7.68−7.66 (s and m, 1:1 H, 5-H), 7.55−7.52 (m, 1 H, 7″-H), 7.45 (d, J = 8.3 Hz, 2 H, 5″-H), 7.33−7.31 (m, 1:2 H, 7″-H and PPh_3), 7.23−7.22, 7.14−7.11 and 7.01−6.92 (m each, 22:12:24 H, PPh_3), 6.60−6.56 (m, 2 H, 8″-H), 6.02−5.99 (m, 2 H, 4′-H), 2.59−2.46 (m, 12 H, C3′-CH_3 and C5′-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$/CD_3OD, 100 MHz) δ 162.0, 161.7, 155.9, 155.2, 154.7, 148.0, 147.6, 147.6, 146.4, 142.8, 139.9, 137.5, 137.2, 135.8, 133.3, 132.7, 132.5, 131.6, 128.0, 127.2, 125.5, 123.4, 122.7, 118.3, 117.1, 117.0, 115.3, 112.7, 112.5, 19.2, 18.9, 18.9; ^{31}P{^{1}H} NMR ($CDCl_3$/CD_3OD, 162 MHz) δ 19.7, 19.3 (PPh_3); IR (KBr pellets, cm^{-1}) ν 3424, 3039, 2923, 1958, 1604, 1556, 1478, 1461, 1431, 1411, 1319, 1090, 1030, 978, 796, 739, 693, 514, 494. Anal. Calcd for $C_{106}H_{88}Cl_4N_{10}P_4Ru_2{\cdot}C_6H_{14}$: C, 65.43; H, 5.00; N, 6.81. Found: C, 65.79; H, 4.70; N, 6.88.

Synthesis of Complex 7a.



In a fashion similar to the synthesis of **6a**, $RuCl_2(PPh_3)_3$ (95.9 mg, 0.10 mmol) reacted with **5a** (29.5 mg, 0.05 mmol) to afford **7a** as a red-brown solid (84.3 mg, 85%) after recrystallized from n-hexane/methanol (v/v, 3/1) at ambient temperature: mp > 320 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.52−15.46 (m, 2 H, NH), 8.81−8.74 (m, 2 H, 3-H), 8.31−8.23 (m, 2 H, 4-H), 7.57−7.50 (m, 2 H, 5-H), 7.230−7.28 (m, 2 H, 7″-H), 7.17−7.06 and 6.97−6.89 (m each, 36:24 H, 4 × PPh_3), 6.84−6.77 (m, 2 H, 5″-H), 6.69−6.55 (m, 2 H, 8″-H), 6.00−5.96 (m, 2 H, 4′-H), 4.16, 4.12, and 4.11 (s each, 2 H, CH_2), 2.52−2.41 (m, 12 H, C3′-CH_3 and C5′-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 157.7, 157.6, 151.9, 151.8, 150.8, 150.8, 150.1, 149.9, 149.7, 143.7, 143.6, 143.0, 143.0, 141.4, 138.4, 136.6, 136.5, 135.1, 133.6, 133.6, 133.3, 132.0, 129.4, 127.8, 128.7, 128.5, 127.0, 126.3, 125.2, 124.7, 121.3, 121.1, 120.6, 120.4, 120.3, 114.0, 113.6, 113.4, 113.0, 112.9, 108.8, 108.8, 42.4, 42.4, 42.3, 15.7, 15.6, 15.5, 15.5, 15.2; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 19.8, 19.5 (PPh_3); IR (KBr pellets, cm^{-1}) ν 3424, 3050, 2923, 1972, 1958, 1605, 1550, 1483, 1464, 1430, 1412, 1330, 1189, 1159, 1092, 1024, 977, 798, 742, 697, 515, 494. Anal. Calcd for $C_{107}H_{90}Cl_4N_{10}P_4Ru_2{\cdot}C_6H_{14}$: C, 65.57; H, 5.06; N, 6.77. Found: C, 65.91; H, 4.66; N, 6.78.

Synthesis of Complex 7b.



In a fashion similar to the synthesis of **6a**, $RuCl_2(PPh_3)_3$ (52.6 mg, 0.05 mmol) reacted with **5b** (17.0 mg, 0.03 mmol) to afford **7b** as a red-brown solid (45.0 mg, 81%) after recrystallized from n-hexane/methanol (v/v, 3/1) at ambient temperature: mp > 320 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.73 (s, 2 H, 3-H), 8.24 (d, J = 8.0 Hz, 2 H, 5-H), 7.96 (t, J = 8.2 Hz, 2 H, 4-H), 7.32 (s, 2 H, 5″-H), 7.22 (d, J = 8.7 Hz, 4 H, 7″-H and 8″-H), 7.17−7.12 and 7.00−6.96 (m each, 36:24 H, 4 × PPh_3), 5.90 (s, 2 H, 4′-H), 4.41 (s, 2 H, CH_2), 4.17 (s, 6 H, N-CH_3), 2.55 (s, 6 H, C3′-CH_3), 2.46 (s, 6 H, C5′-CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 157.8, 152.5, 150.2, 149.5, 144.4, 142.6, 137.0, 135.8, 135.0, 133.9, 133.3, 131.7, 129.7, 127.9, 128.9, 121.9, 121.4, 113.4, 110.5, 42.1, 33.9, 15.6, 15.1; ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 20.8 (PPh_3); IR (KBr pellets, cm^{-1}) ν 3435, 3057, 2917, 2847, 1726, 1600, 1548, 1510, 1479, 1436, 1339, 1183, 1157, 1093, 1023, 974, 788, 743, 699, 617, 516, 494. Anal. Calcd for $C_{109}H_{94}Cl_4N_{10}P_4Ru_2$: C, 65.07; H, 4.71; N, 6.96. Found: C, 65.46; H, 4.83; N, 6.65.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones. The catalyst solution was prepared by dissolving complex **7a** (19.7 mg, 0.01 mmol) in isopropyl alcohol (100.0 mL). Under a nitrogen atmosphere, a mixture of the ketone (2.0 mmol), 5.0 mL of the catalyst solution (0.0005 mmol), and isopropyl alcohol (14.8 mL) was stirred at 82 °C for 10 min. Then, 0.2 mL of a 0.1 M iPrOK (0.02 mmol) solution in isopropyl alcohol was introduced to initiate the reaction. At the stated time, 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of isopropyl alcohol precooled at 0 °C and filtered through a short pad of Celite to remove the complex catalyst to quench the reaction. The resultant filtrate was used for GC analysis. After the reaction was complete, the reaction mixture was quickly cooled to ambient temperature, filtered through Celite, condensed under reduced pressure, and then subjected to purification by silica gel column chromatography to afford the corresponding alcohol product, which was identified by comparison with the authentic sample through NMR and GC analysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00682.

NMR spectra of the new compounds and X-ray crystallographic data for **5b** (PDF)

Structure of **5b** (XYZ)

Accession Codes

CCDC 1522009 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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