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Ruthenium(II) Complex Catalysts Bearing a Pyridyl-Based Benzimidazolyl−Benzotriazolyl Ligand for Transfer Hydrogenation of Ketones

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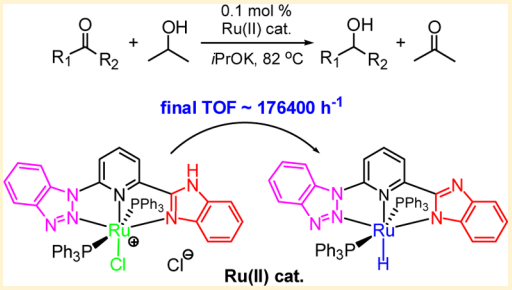
Supporting Information

ABSTRACT: Air- and moisture-stable ruthenium(II) complexes bearing a unsymmetrical 2-(benzimidazol-2-yl)-6-(benzotriazol-1-yl)pyridine ligand were synthesized and structurally characterized by NMR analysis and X-ray crystallographic determinations. These complexes have exhibited excellent catalytic activity in the transfer hydrogenation of ketones in refluxing 2-propanol, reaching final TOFs up to 176400 h^{-1}. The corresponding RuH complex was isolated and is proposed as the catalytically active species by controlled experiments. The high catalytic activity of the Ru(II) the complex catalysts is attributed to the hemilabile unsymmetrical coordinating environment around the central metal atom in the complexes and presence of a convertible benzimidazolyl NH functionality in the ligand.



INTRODUCTION

Transfer hydrogenation (TH) of unsaturated C═O and C═N bonds has been well explored[1] as a promising reduction strategy and is considered as good complement to hydrogenation reactions.[2] In this area, Noyori et al. have documented that *N*-tosylethylenediamine Ru(II) complexes[3] and their later versions, i.e., *β*-amino alcohol Ru(II) complexes,[4] can be used as powerful catalysts for asymmetric transfer hydrogenation (ATH) of ketones and imines, and cyclometalated Ru(II) and Os(II) complexes containing 2-(aminomethyl)pyridine ligands developed by Baratta and co-workers[5] have also exhibited efficient catalytic activity in the (asymmetric) transfer hydrogenation of ketones. Tetradentate chiral NNPP ligands and their iron(II) complexes usually demonstrate moderate catalytic activity for the same reactions under mild conditions.[6] Although various types of ligands and their transition-metal complexes have been developed for TH or ATH reactions,[7] highly active catalytic systems are still strongly desired to extend the substrate scope and enhance the reaction efficiency. Recently, non-phosphorus ligands have attracted more and more attention for their versatile applications,[8] and polydentate ligands such as 2,2′:6′,2″-terpyridines (terpy),[9] 2,6-bis(imino)-pyridines,[10] and 2,6-bis(oxazolinyl)pyridines (Pybox)[11] have been well documented and successfully employed in organic synthesis, homogeneous catalysis, and fabrication of functional materials. Among the aforementioned cases, most of the reported complex catalysts bear ligands containing two symmetrical coordinating arms, while the complex catalysts supported by a polydentate ligand containing two unsymmetrical coordinating arms usually exhibit much higher catalytic activity due to the hemilabile electronic and steric properties of the ligand. Unfortunately, such highly active complex catalysts have less been investigated.[12] Benzotriazole has been widely used as a synthetic auxiliary in organic synthesis, and some of its derivatives can be utilized as important UV photostabilizers. Due to the three adjacent nitrogen donors, benzotriazole can also act as a versatile ligand in coordination chemistry for the preparation of supramolecular complexes and functional materials.[13] However, benzotriazole itself has seldom been used as a coordinating functionality in a polydentate ligand for homogeneous catalysis.

During our ongoing exploration of highly active transition-metal complex catalysts for homogeneous catalysis,[14] we have disclosed that both benzimidazolyl and pyrazolyl NH functionalities in a Ru(II) complex catalyst can show a remarkable acceleration effect on the TH or ATH reactions of ketones.[15] Such an acceleration effect is attributed to easy deprotonation of the unprotected NH functionalities of the ligands in the complex catalysts under basic conditions by releasing one HCl molecule and simultaneously forming catalytically active species for TH or ATH reactions of ketones (Scheme 1).[14−16] With a successful strategy to construct highly active Ru^{II}−NNN and −NNC complex catalysts in hand, we envisioned that benzotriazolyl might be utilized as a coordinating moiety to establish pyridyl-based NNN ligands.

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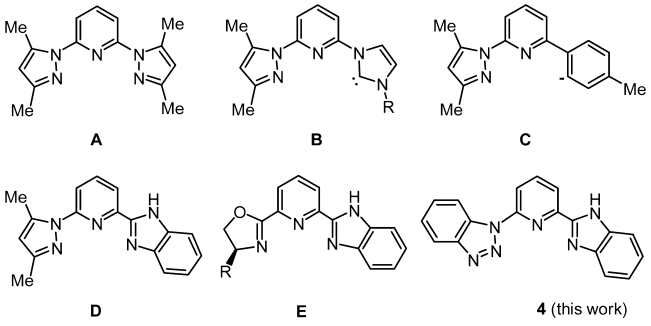
Scheme 1. NNN and NNC Ligands Developed in Our Laboratories

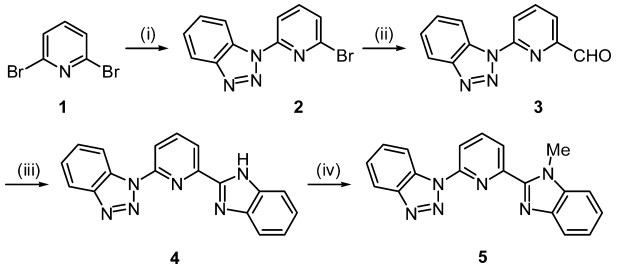


Herein, we report the synthesis of Ru(II) complexes bearing a pyridyl-based benzimidazolyl−benzotriazolyl NNN ligand and their catalytic behaviors in the TH of ketones.

RESULTS AND DISCUSSION

Synthesis of Ligands and Their Ru(II) Complexes. Reaction of 2,6-dibromopyridine (**1**) with benzotriazole under solvent-free conditions afforded **2** in 72% yield. Aldehyde **3** was obtained from the reaction of **2** with *n*BuLi followed by treatment with DMF. Condensation of **3** with 1,2-phenylenediamine gave ligand **4** in nitrobenzene upon heating at 150 °C. The *N*-methyl derivative of **4**, i.e., ligand **5**, was readily prepared from methylation of **4** by MeI in the presence of NaH (Scheme 2).

Scheme 2. Synthesis of Ligands 4 and 5[a]

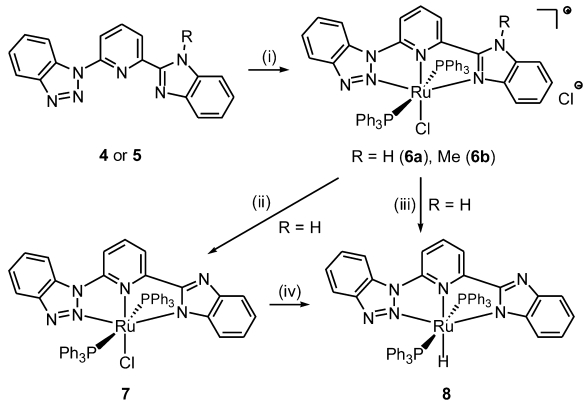


[a]Legend: (i) benzotriazole, 180 °C, 3 h, 72%; (ii) *n*BuLi, −78 °C, DMF, 62%; (iii) 1,2-phenylenediamine, 150 °C, 6 h, 65%; (iv) MeI, NaH, THF, 65 °C, 3 h, 92%.

Ru(II) complexes **6a**,**b** were obtained in 83% and 86% yields, respectively, by reacting equimolar amount of ligand **4** or **5** with $RuCl_2(PPh_3)_3$ in refluxing 2-propanol (Scheme 3). The ionic complex **6a** was further converted to neutral complex **7** by K_2CO_3 base in refluxing CH_2Cl_2 through releasing 1 equiv of HCl. RuH complex **8** was isolated in 72% yield from the reaction of **6a** in basic 2-propanol, and it could also be prepared by reacting complex **7** with K_2CO_3 in 2-propanol, which reveals that β-H elimination was involved in the transformations.

Characterization of Ru(II) Complexes 6−8. The NMR analyses of the complexes are in agreement with their compositions. In the ^{1}H NMR spectra, the NH protons in ligand **4** and its Ru(II) complex **6a** exhibited singlets at 12.94 and 15.65 ppm, respectively, and their resonance signals disappeared in complexes **7** and **8**, suggesting the formation of Ru−N bonds in the complexes under basic conditions. In the ^{31}P{^{1}H} NMR spectra of complexes **6a**,**b** and **7**, the resonance signals appeared at 22.2, 22.0, and 22.7 ppm, respectively,

Scheme 3. Synthesis of Complexes 6−8[a]



[a]Legend: (i) $RuCl_2(PPh_3)_3$, 2-propanol, 82 °C, 3 h, 83% (**6a**), 86% (**6b**); (ii) K_2CO_3, CH_2Cl_2, 39 °C, 5 h, 91%; (iii) K_2CO_3, 2-propanol, 82 °C, 3 h, 72%; (iv) K_2CO_3, 2-propanol, 82 °C, 3 h, 75%.

revealing the presence of two identical PPh_3 ligands in each complex. Complex **7** showed a 0.5 ppm shift in the ^{31}P{^{1}H} NMR spectrum as compared with that of **6a**, which is in accordance with our previous observation,[15] suggesting that the coordination pattern of the coordinating benzimidazolyl nitrogen atom in **7** was changed by means of extrusion of HCl from **6a**. Complex **8** features a Ru−H bond. Its ^{1}H and ^{31}P{^{1}H} NMR spectra showed a triplet at −6.17 ppm for Ru−H and a doublet at 46.5 ppm for the two *trans*-PPh_3 ligands, respectively. The single-crystal structures of complexes **6a** and **8** were further confirmed by X-ray crystallographic determinations (Figures 1 and 2).

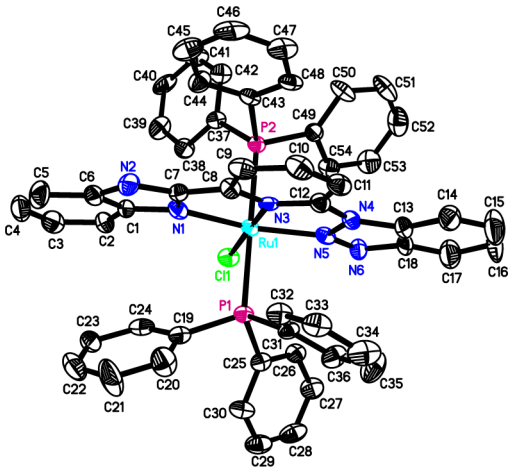


Figure 1. Molecular structure of complex **6a** with hydrogen atoms and a chloride anion omitted for clarity.

In the solid state, the cationic metal center of complex **6a** is surrounded by the tridentate NNN ligand **4**, two PPh_3 ligands, and a chloride anion in a distorted-bipyramidal environment, with another dissociated chloride anion in the vicinity (Figure 1). The P−Ru−P angle in **6a** is 178.37(7)°, suggesting that the two PPh_3 ligands are almost linearly positioned (Table 1). Complex **8** features a molecular structure similar to that of **6a**, but with a discrete Ru−H bond (1.55(4) Å). Such a Ru−H bond length is in the region of those reported (~1.53 Å).[16b,17] The presence of two Ru−P bonds (2.340(14) and 2.3197(14)

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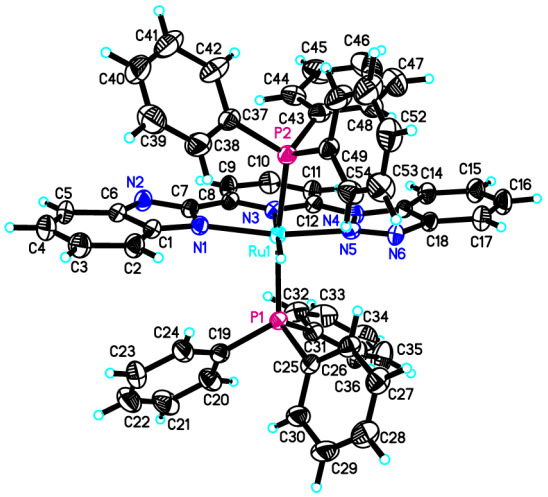
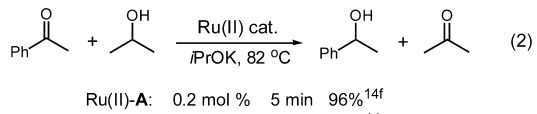


Figure 2. Molecular structure of complex **8**.

Å), three Ru–N bonds (2.030(4), 2.048(4), and 2.105(4) Å), P–Ru–N angles (88.13(11)–98.16(11)°), and P(1)–Ru–P(2) and N(3)–Ru–H angles (163.19(5) and 177.3(14)°) reveals a six-coordinated metal center of complex **8** in a distorted-bipyrimidal environment with the hydride *trans* to the N(3) atom of the pyridyl backbone. Unlike our previously prepared RuH complex supported by a tridentate NNC ligand,[14a] which easily decomposes upon exposure to air, complex **8** can be kept in air at ambient temperature for 5 months without any decomposition. Such excellent stability is partially attributed to the stabilized coordinating environment from the pyridyl–benzimidazolyl–benzotriazolyl NNN ligand.

Transfer Hydrogenation of Ketones. In a fashion similar to our previously reported procedures for TH or ATH reactions of ketones,[14–16] complex **6a** was applied as a catalyst for the transfer hydrogenation of ketones (Table 2). Alcohols were produced as the sole products by means of 0.1 mol % catalyst in refluxing 2-propanol under a nitrogen atmosphere. The reaction of acetophenone was nearly complete within 5 min, reaching 97% yield for the alcohol product with a final TOF value of 11640 h^{-1} (entry 1, Table 2). In comparison with our previously reported Ru^{II}–NNN or –NNC catalyst systems, complex **6a** exhibited an excellent catalytic activity for the TH of ketones (eq 2).[14] Thus, the reduction of a variety of acetophenones, aryl alkyl ketones, and aliphatic cyclic and acyclic ketones was efficiently performed. In most of the cases shown in Table 2, the TH reactions reached ≥97% yields within 2–10 min, achieving up to 99% conversions for the ketone substrates and final TOF values up to 176400 h^{-1} (entry 20, Table 2). The electronic and steric effects were obvious, in

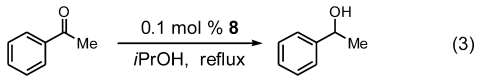


Ru(II)-**A**: 0.2 mol % 5 min 96%[14f]
Ru(II)-**B**: 0.2 mol % 4 h 98%[14c]
Ru(II)-**C**: 0.1 mol % 1 min 98%[14a]
Ru(II)-**D**: 0.05 mol % 10 s 98%[14d]

that electron-withdrawing substituents such as chloro, bromo, fluoro, and trifluoromethyl usually facilitated the TH reactions (entries 3–12 and 20, Table 2), while acetophenones bearing an electron-donating 3′-methyl or 3′- or 4′-methoxy substituent required a longer reaction time to reach high conversions (entries 14–16, Table 2). Unexpectedly, 2′-methylacetophenone reacted quickly to achieve 97% conversion over a period of 10 min (entry 13, Table 2).

Under the same conditions, complex **6b** was also employed as the catalyst for TH of ketones. Selected examples are presented in Table 3. In comparison with **6a**, complex **6b** had a much lower catalytic activity for the TH of ketones. All the tested ketone substrates reached 95–98% conversions within 3 h, with 980 h^{-1} as the highest final TOF value (entry 3, Table 3). However, in the case of 4′-chloroacetophenone reduction, complex **6a** promoted the reaction to completion in 97% yield with a final TOF value of 29100 h^{-1} within 2 min (entry 5, Table 2). These results suggest that the NH functionality in a coordinating benzimidazolyl moiety plays a crucial role in enhancing the TH reaction rate of ketones.

TH Reaction Mechanism. The catalytic behaviors of complexes **6a**, **7**, and **8** were comparatively explored in the TH reactions of acetophenone, propiophenone, 2′-fluoroacetophenone, and cyclohexanone, respectively (Table 4). All three complexes almost exhibited the same catalytic activity under the stated conditions, suggesting that complex **8** may be the catalytically active species for the TH reactions. Under the controlled conditions, complex **8** was further tested to catalyze the TH reaction of acetophenone in the absence of a base, resulting in the desired product in 96% yield over a period of 20 h (eq 3); neither **6a** nor **7** could catalyze the same reaction



without *i*PrOK: 20 h, 96%
with *i*PrOK: 5 min, 97%

under base-free conditions. These results suggest that both **6a** and **7** act as the precatalysts for the TH reactions of ketones, because they could be readily converted to RuH complex **8** under basic conditions (Scheme 2), and **8** behaved as the catalytically active species. This transformation can be initiated

Table 1. Selected Bond Distances (Å) and Angles (deg) for 6a and 8

Complex **6a**					
Ru–N(1)	2.086(5)	Ru–N(3)	2.086(5)	Ru–N(5)	2.019(5)
Ru–P(1)	2.3930(19)	Ru–P(2)	2.4298(18)	Ru–Cl(1)	2.4405(17)
N(1)–Ru–N(5)	157.7(2)	P(1)–Ru–P(2)	178.37(7)	N(3)–Ru–Cl(1)	177.68(15)
P(2)–Ru–Cl(1)	91.88(6)	N(3)–Ru–P(1)	91.19(14)	N(5)–Ru–P(1)	88.52(16)
Complex **8**					
Ru(1)–N(3)	2.030(4)	Ru(1)–N(5)	2.048(4)	Ru(1)–N(1)	2.105(4)
Ru(1)–P(1)	2.3404(14)	Ru(1)–P(2)	2.3197(14)	Ru(1)–H(1)	1.55(4)
N(1)–Ru–P(2)	93.39(11)	N(5)–Ru–P(2)	89.52(10)	N(3)–Ru–H	177.3(14)
N(3)–Ru–P(1)	98.16(11)	N(1)–Ru–P(1)	95.67(11)	P(2)–Ru–Cl(1)	163.19(5)

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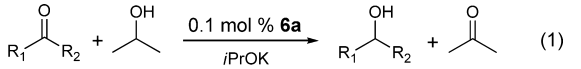
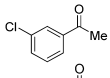
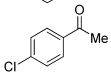
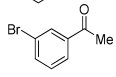
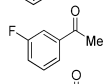
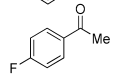
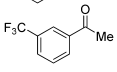
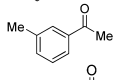
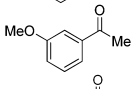
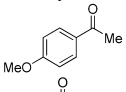
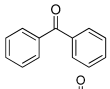
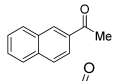
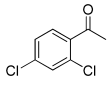
Table 2. Transfer Hydrogenation of Ketones Catalyzed by 6a[b]

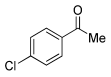
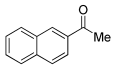


(1)

entry	ketone	time (min)	yield[a] (%)	final TOF (h^{-1})
1		5	97	11640
2		10	97	5820
3		2	99	29700
4		2	98	29400
5		2	97	29100
6		2	97	29100
7		2	97	29100
8		5	99	11880
9		5	98	11760
10		10	98	5880
11		10	97	5820
12		2	98	29400
13		10	97	5820
14		60	98	980
15		20	94	2820
16		120	85	425
17		10	90	5400
18		5	98	11760
19		240	82	205
20		1/3	98	176400
21		5	97	11640
22		10	99	5880

[a]Determined by GC analysis. [b]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); complex **6a**, 0.1 mol %; ketone/*i*PrOK/cat.= 1000:20:1; 0.1 MPa; 82 °C.

Table 3. Transfer Hydrogenation of Ketones Catalyzed by 6b[b]

entry	ketone	time (min)	yield[a] (%)	final TOF (h^{-1})
1		120	96	480
2		180	95	317
3		60	98	980
4		120	97	485
5		90	97	640
6		120	95	475

[a]Determined by GC analysis. [b]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); complex **6b**, 0.1 mol %; ketone/*i*PrOK/cat. = 1000:20:1; 0.1 MPa; 82 °C.

Table 4. Transfer Hydrogenation of Ketones Catalyzed by Ru(II) Complexes[b]

entry	ketone	yield[a] (%)		
		using **6a**	using **7**	using **8**
1		97	98	97
2		95	94	94
3		99	98	99
4		97	97	96

[a]GC yields of alcohols at 5 min by using the complex catalysts. [b]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst, 0.1 mol %; ketone/*i*PrOK/catalyst = 1000:20:1; 0.1 MPa; 82 °C.

in situ by deprotonating the NH fuctionality of the coordinating benzimidazolyl moiety in **6a** to generate complex **7** and then forming **8** to trigger the TH reaction.[14a,16b] Thus, a plausible inner-sphere pathway[18] involving a RuH intermediate as the catalytically active species[19] is proposed (Scheme 4). The reaction can directly start from complex **7** or from in situ generated **7** by extrusion of HCl from the precursor complex **6a** with a base such as K_2CO_3 or *i*PrOK. The ruthenium(II) hydride complex **8** is then formed by releasing one molecule of acetone through β-H elimination from Ru(II) alkoxide **F**. Coordination of a ketone substrate to **8** generates intermediate **G**, followed by insertion of the ketone carbonyl into the Ru−H bond to produce Ru(II) alkoxide **H**. The metathesis of **H** by 2-propanol yields the desired alcohol product. Extrusion of an

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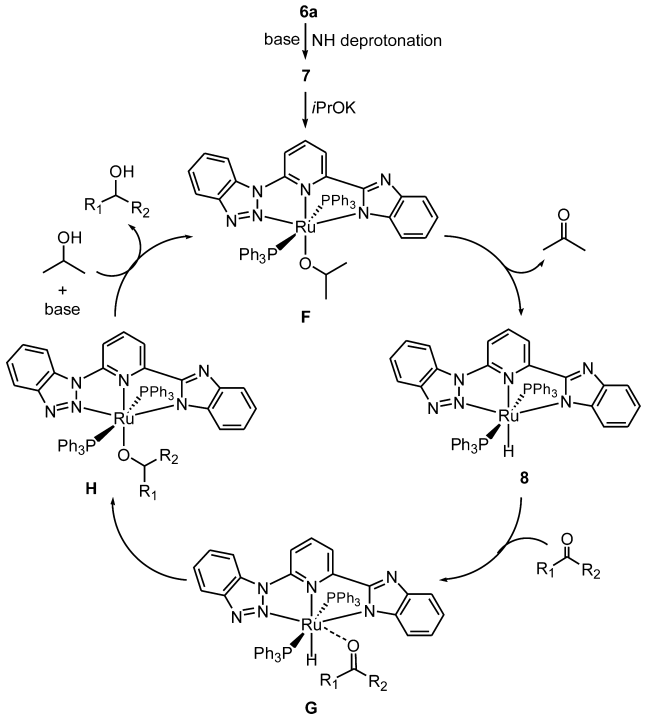
Scheme 4. Proposed Mechanism



alkoxide anion by an alcohol in the final step can be facilitated by a base, which rationalizes the inferior catalytic activity of **8** under base-free conditions.

CONCLUSION

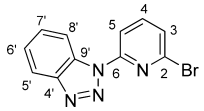
In summary, Ru(II) complexes bearing a unsymmetrical pyridyl-based benzimidazolyl−benzotrizolyl NNN ligand have exhibited excellent catalytic activity in the TH of ketones. The structurally characterized RuH complex is proposed to be the catalytically active species. The combination of readily coordinating benzotriazolyl and NH-benzimidazolyl in a unsymmetrical 2,6-pyridyl-supported ligand provides a route to construct highly active transition-metal complex catalysts.

EXPERIMENTAL SECTION

General Considerations. All the manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using the standard Schlenk techniques. The solvents were dried and distilled prior to use by literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer, and all chemical shift values refer to δ_{TMS} 0.00 ppm, $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm), CD_2Cl_2 ($\delta(^{1}H)$, 5.32 ppm; $\delta(^{13}C)$, 53.84 ppm), and DMSO-d_6 ($\delta(^{1}H)$, 2.50 ppm; $\delta(^{13}C)$, 39.52 ppm). Elemental and HRMS analyses were achieved by the Analysis Center, Dalian University of Technology. All the melting points were uncorrected. TLC analysis was performed by using glass-backed plates coated with 0.2 mm silica gel. Flash column chromatography was performed on silica gel (200−300 mesh). All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

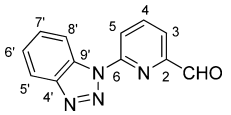
X-ray Crystallographic Studies. The X-ray single-crystal structure studies of compounds **6a** and **8** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. 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 by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 927801 for **6a** and CCDC 927800 for **8**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk). X-ray crystallographic data and refinement details for **6a** and **8** are given in the Supporting Information, and selected bond lengths and angles are given in Table 1.

Synthesis of Compound 2.



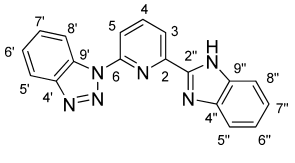
Under a nitrogen atmosphere, a mixture of 2,6-dibromopyridine (4.74 g, 20.0 mmol) and benzotrizole (3.57 g, 30.0 mmol) was stirred at 180 °C for 3 h. After the reaction mixture was cooled to ambient temperature, 100 mL of dichloromethane was added and the solution was filtered to separate the insoluble substances; all the volatiles were removed under reduced pressure to give a crude product which was subjected to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/ethyl acetate: 20/1, v/v) to afford the desired product as a white solid (3.96 g, 72% yield). Mp: 80−82 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, J = 8.3 and 8.0 Hz, 1 H, 5-H), 8.20 and 8.07 (d each, J = 8.0 and 8.2 Hz, 1:1 H, 5′-H and 8′-H), 7.73 and 7.58 (m, 2 H, 4-H and 3-H), 7.43 (m, 2 H, 6′-H and 7′-H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 151.0 and 146.7 (C_q each, C2 and C6), 140.0 and 131.2 (C_q each, C4′ and C9′), 140.8, 125.3, and 119.9 (pyridyl CH), 129.3, 126.1, 114.7, and 112.5 (aromatic CH of benzotriazolyl). HRMS: calcd for $C_{11}H_7BrN_4$ 273.9854, found 273.9865.

Synthesis of Compound 3.



To a stirred mixture of 6.8 mL of *n*BuLi (1.6 M in hexanes, 10.8 mmol) and THF (40 mL) was added dropwise a solution of **2** (2.45 g, 9.0 mmol) in THF (40 mL) at −78 °C over a period of 30 min. After the mixture was further stirred at −78 °C for another 30 min, anhydrous DMF (1.4 mL, 18.0 mmol) was added. The mixture was warmed to 0 °C within 1 h, and the reaction was then quenched with methanol (10 mL). Saturated aqueous NH_4Cl (150 mL) was added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. All the volatiles were removed under reduced pressure, and the resultant residue was subjected to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/diethyl ether: 8/1, v/v) to afford the desired product as a white solid (1.25 g, 62% yield). Mp: 132−133 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.18 (s, 1 H, CHO), 8.74 and 8.56 (d each, J = 8.4 and 8.2 Hz, 1:1 H, 3-H and 5-H), 8.13 (m, 2 H, 4-H and 5′-H), 7.96 (d, J = 7.5 Hz, 1 H, 8′-H), 7.65 and 7.49 (m, 2 H, 6′-H and 7′-H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.8 (CHO), 152.0 and 151.3 (C_q each, C2 and C6), 146.9 and 131.4 (C_q each, C4′ and C9′), 140.1, 120.0, and 118.7 (pyridyl CH), 129.3, 125.4, 120.1, and 114.8 (aromatic CH of benzotriazolyl). HRMS: calcd for $C_{12}H_8N_4O$ 224.0698, found 224.0698.

Synthesis of Compound 4.



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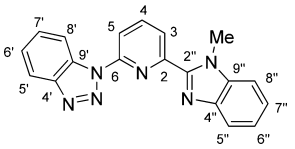
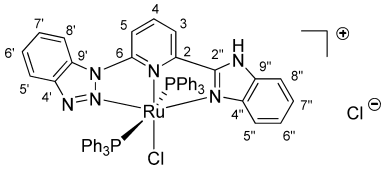
A mixture of **3** (1.12 g, 5.0 mmol) and 1,2-phenylenediamine (545 mg, 5.0 mmol) in nitrobenzene (30 mL) was stirred at 150 °C for 6 h. All the volatiles were removed under reduced pressure at 80−100 °C, and the resultant residue was subject to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/ethyl acetate/triethylamine: 50/20/1, v/v/v) to afford the desired product as a white solid (1.02 g, 65% yield). Mp: 258−259 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.94 (s, 1H, NH), 8.82 and 8.22 (d each, J = 8.4 and 8.3 Hz, 1:1 H, 3-H and 5-H), 8.41 and 8.31 (m each, 1:2 H, 5′-H, 6′-H and 7′-H), 7.79 (m, 2 H, 5″-H and 8″-H), 7.69 (d, J = 7.8 Hz, 8′-H), 7.60 (t, J = 8.4 and 8.2 Hz, 1 H, 4-H), 7.29 (m, 2 H, 6″-H and 7″-H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz): δ 151.0 and 150.0 (C_q each, C2 and C6), 148.3, 146.5, and 135.5 (C_q each, C2″, C4″, and C9″), 144.1 and 131.3 (C_q each, C4′ and C9′), 141.6, 121.5, and 119.9 (pyridyl CH), 130.0, 126.0, 119.9, and 115.3 (aromatic CH of benzotriazolyl), 124.2, 122.9, 116.2, and 113.0 (aromatic CH of benzimidazlyl). HRMS: calcd for $C_{18}H_{12}N_6$ 312.1123, found 312.1129.

Synthesis of Compound 5.



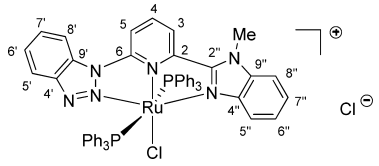
A mixture of **4** (156 mg, 0.5 mmol) and NaH (160 mg, 60% in mineral oil, 4.0 mmol) in 10 mL of THF was stirred at ambient temperature for 30 min. Iodomethane (1.42 g, 1.0 mmol) was added, and the reaction mixture was heated to reflux for 3 h. After the mixture was cooled to ambient temperature, methanol (5 mL) was added to quench the reaction. All the volatiles were evaporated under reduced pressure, and the resultant residue was subjected to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/ethyl acetate: 4/1, v/v) to afford the desired product as a white solid (150 mg, 92% yield). Mp: 197−198 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.47 and 7.86 (d each, J = 8.3 and 7.5 Hz, 1:1 H, 3-H and 5-H), 8.32 and 8.12 (m each, 2:2 H, aromatic CH of benzotriazolyl), 7.58(t, J = 8.3 and 7.5 Hz, 1 H, 4-H), 7.46 and 7.36 (m each, 2:2 H, aromatic CH of benzimidazolyl), 4.22 (s, 3 H, M-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.3 and 149.4 (C_q each, C2 and C6), 149.0, 146.7, and 137.0 (C_q each, C2″, C4″, and C9″), 142.3 and 131.2 (C_q each, C4′ and C9′), 139.9, 124.9, and 122.9 (pyridyl CH), 128.8, 120.1, 120.0, and 113.5 (aromatic CH of benzotriazolyl), 123.7, 123.6, 115.2, and 109.9 (aromatic CH of benzimidazolyl), 32.4 (N−CH_3). HRMS: calcd for $C_{19}H_{14}N_6$ 326.1280, found 326.1284.

Synthesis of Complex 6a.



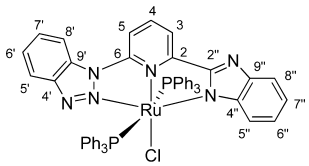
Under a nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (480 mg, 0.5 mmol) and **4** (156 mg, 0.5 mmol) in 2-propanol (10 mL) was refluxed for 3 h, forming a red-brown microcrystalline solid. The mixture was cooled to ambient temperature, and the solid was filtered off, washed with diethyl ether (3 × 10 mL), and dried under vacuum to afford the desired product as a red-brown crystalline solid (418 mg, 83% yield). Single crystals suitable for X-ray crystallographic determination were grown from the recrystallization of **6a** in $CHCl_3$/n-hexane (1/3, v/v) at 25 °C. Mp: >300 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 15.65 (s, 1 H, NH), 8.33 and 8.08 (d each, J = 8.2 and 7.8 Hz, 1:1 H, 3-H and 5-H), 7.65 and 7.26 (m each, 2:2 H, aromatic CH of benzimidazolyl), 7.53 (m, 4 H, aromatic CH of benzotriazolyl), 7.39 (br, 1 H, 4-H), 7.18, 7.11, and 6.92 (m each, 12:6:12 H, 2 × PPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 150.0 and 149.2 (C_q each, C2 and C6), 148.9, 146.3, and 134.9 (C_q each, C2″, C4″, and C9″), 141.9 and 131.3 (C_q each, C4′ and C9′), 134.7, 123.3, and 121.6 (pyridyl CH), 133.2, 129.6, and 127.9 (CH of 2 × PPh_3), 129.8 (C_q, 2 × PPh_3), 130.0, 129.5, 108.7, and 108.3 (aromatic CH of benzotriazolyl), 126.0, 125.2, 119.2, and 113.5 (aromatic CH of benzimidazolyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 22.2 (s, 2 × PPh_3). Anal. Calcd for $C_{54}H_{42}Cl_2N_6P_2Ru$: C, 64.29; H, 4.20; N, 8.33. Found: C, 64.30; H, 4.22; N, 8.35.

Synthesis of Complex 6b.



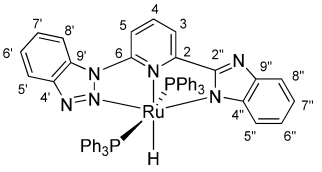
Under a nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (576 mg, 0.6 mmol) and **5** (196 mg, 0.6 mmol) in 2-propanol (10 mL) was refluxed for 3 h, forming a red-brown microcrystalline solid. The mixture was cooled to ambient temperature, and the solid was filtered off, washed with diethyl ether (4 × 6 mL), and dried under vacuum to afford the desired product as a red-brown crystalline solid (527 mg, 86% yield). Mp: >300 °C dec. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 and 7.98 (d each, J = 7.8 and 7.3 Hz, 1:1 H, 3-H and 5-H), 8.37 (br, 1 H, 4-H), 7.68, 7.54, and 7.44 (br each, 1:1:2 H, aromatic CH of benzotriazolyl), 7.31 and 7.23 (m each, 2:2 H, aromatic CH of benzimidazolyl), 7.10 and 6.90 (m each, 18:12 H, 2 × PPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 149.5 and 149.1 (C_q each, C2 and C6), 148.5, 146.2, and 136.0 (C_q each, C2″, C4″ and C9″), 141.2 and 131.4 (C_q each, C4′ and C9′), 133.2, 130.0, and 128.3 (CH of 2 × PPh_3), 132.0, 122.6, and 119.0 (pyridyl CH), 129.5 (C_q of 2 × PPh_3), 125.9, 125.8, 122.2, and 122.0 (aromatic CH of benzotriazolyl), 125.4, 123.8, 111.9, and 110.7 (aromatic CH of benzimidazolyl), 65.8 (N−CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 22.0 (s, 2 × PPh_3). Anal. Calcd for $C_{55}H_{44}Cl_2N_6P_2Ru$: C, 64.58; H, 4.34; N, 8.22. Found: C, 64.56; H, 4.37; N, 8.24.

Synthesis of Complex 7.



Under a nitrogen atmosphere, a mixture of complex **6a** (504 mg, 0.5 mmol) and K_2CO_3 (690 mg, 5.0 mmol) in 10 mL of dichloromethane was refluxed for 5 h. After it was cooled to ambient temperature, the reaction mixture was passed through a short pad of Celite which was rinsed with 5 mL of dichloromethane. The filtrate was collected, and all the volatiles were removed under reduced pressure to afford the desired product (443 mg, 91% yield) as a red solid. Mp: >300 °C dec. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.39 (d, J = 6.6, 5′-H), 8.21 and 8.06 (d each, J = 7.3 and 7.4 Hz, 1:1 H, 3-H and 5-H), 7.50 (m, 4 H, 6′-H, 7′-H, 8′-H, and 4-H), 7.38 and 6.89 (d each, J = 7.8 and 8.2 Hz, 1:1 H, 5″-H and 8″-H), 7.30 and 6.98 (m each, 6″-H and 7″-H), 7.19, 7.10, and 6.97 (m each, 12:6:12 H, 2 × PPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 152.7 and 148.8 (C_q each, C2 and C6), 146.4, 132.7, and 132.6 (C_q each, C2″, C4″, and C9″), 143.8 and 131.3 (C_q each, C4′ and C9′), 134.1, 122.0, and 120.8 (pyridyl CH), 133.4, 129.3, and 127.7 (CH of 2 × PPh_3), 130.2 (C_q, 2 × PPh_3), 129.0, 125.7, 108.0, and 107.0 (aromatic CH of benzotriazolyl), 122.8, 119.0, 118.8, and 115.7 (aromatic CH of benzimidazolyl). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 22.7 (s, 2 × PPh_3). Anal. Calcd for $C_{54}H_{41}ClN_6P_2Ru$: C, 66.70; H, 4.25; N, 8.64. Found: C, 66.76; H, 4.22; N, 8.61.

Synthesis of Complex 8.



Under a nitrogen atmosphere, a mixture of complex **6a** (605 mg, 0.60 mmol) or complex 7 (583 mg, 0.60 mmol) and K_2CO_3 (828 mg, 6.0 mmol) in 15 mL of 2-propanol was refluxed for 3 h. After the mixture

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was cooled to ambient temperature, all the volatiles were removed under reduced pressure. An 8 mL portion of toluene was then added to dissolve the crude product, followed by filtration to separate the inorganic salts. The filtrate was condensed under reduced pressure and then recrystallized in toluene/*n*-hexane (1/2, v/v) at −20 °C to give the desired product as red-brown crystals (405 mg, 72% yield from **6a**; 422 mg, 75% yield from **7**). Mp: >300 °C dec. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01, 7.65, and 7.46 (m each, 1:3:3 H, pyridyl CH and aromatic CH of benzotriazolyl), 7.33, 7.24, and 6.64 (m each, 1:2:1 H, aromatic CH of benzimidazolyl), 7.13, 6.99, and 6.86 (m each, 12:6:12 H, 2 × PPh_3), −6.17 (t, J = 23.9, Ru−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.1 and 152.1 (C_q each, C2 and C6), 147.0, 145.9, 132.1 (C_q each, C2″, C4″, and C9″), 144.6 and 131.2 (C_q each, C4′ and C9′), 133.7 (C_q, 2 × PPh_3), 133.0, 128.4, and 127.3 (CH of 2 × PPh_3), 132.7, 120.0, and 119.4 (pyridyl CH), 126.5, 124.3, 107.3, and 103.9 (aromatic CH of benzotriazolyl), 118.1, 118.0, 117.7, 115.9 (aromatic CH of benzimidazolyl). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 46.5 (d, J(P,H) = 22.7 Hz, 2 × PPh_3). Anal. Calcd for $C_{54}H_{42}N_6P_2Ru$: C, 69.15; H, 4.51; N, 8.69. Found: C, 69.19; H, 4.57; N, 8.64.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones. The catalyst solution was prepared by dissolving complex **6a** (20.2 mg, 0.02 mmol) in 2-propanol (20.0 mL). Under a nitrogen atmosphere, a mixture of the ketone (2.0 mmol), 2.0 mL of the catalyst solution (0.002 mmol), and 2-propanol (17.6 mL) was stirred at 82 °C for 10 min. Then, 0.4 mL of an 0.1 M *i*PrOK (0.04 mmol) solution in 2-propanol was introduced to initiate the reaction. At the stated time, 0.1 mL of the reaction mixture was sampled and immediately diluted with 0.5 mL of 2-propanol precooled to 0 °C for GC analysis. After the reaction was complete, the reaction mixture was condensed under reduced pressure and subjected to purification by flash 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

Figures, tables, and CIF files giving NMR spectra of the new compounds and X-ray crystallographic data for **6a** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

(1) For selected recent reviews, see: (a) Simon, M.; Li, C. J. *Chem. Soc. Rev.* **2012**, *41*, 1415−1427. (b) Alonso, F.; Riente, P.; Yus, M. *Acc. Chem. Res.* **2011**, *44*, 379−391. (c) Malacea, E.; Poli, R.; Manoury, E. *Coord. Chem. Rev.* **2010**, *254*, 729−752. (d) Bartók, M. *Chem. Rev.* **2010**, *110*, 1663−1705. (e) Morris, R. H. *Chem. Soc. Rev.* **2009**, *38*, 2282−2291. (f) Wang, C.; Wu, X. F.; Xiao, J. L. *Chem. Asian J.* **2008**, *3*, 1750−1770. (g) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300−1308. (h) Wu, X. F.; Xiao, J. L. *Chem. Commum.* **2007**, 2449−2466. For selected recent examples, see: (i) Moore, C. M.; Szymczak, N. K. *Chem. Commun.* **2013**, *49*, 400−402. (j) Li, J.; Tang, Y.; Wang, Q.; Li, X.; Cun, L.; Zhang, X.; Zhu, J.; Li, L.; Deng, J. G. *J. Am. Chem. Soc.* **2012**, *134*, 18522−18525. (k) Sorribes, I.; Wienhöer, G.; Vicent, C.; Junge, K.; Llusar, R.; Beller, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 7794−7798. (l) Ariger, M. A.; Carreira, E. M. *Org. Lett.* **2012**, *14*, 4522−4524. (m) Steward, K. M.; Gentry, E. C.; Johnson, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 7329−7332. (n) Vázquez-Villa, H.; Reber, S.; Ariger, M. A.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8979−8981. (o) Ghoochany, L. T.; Farsadpour, S.; Sun, Y.; Thiel, W. R. *Eur. J. Inorg. Chem.* **2011**, 3431−3437. (p) Wang, C.; Li, C.; Wu, X.; Pettman, A.; Xiao, J. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 6524−6528.

(2) de Vries, J. G.; Elsevier, C. J. *The Handbook of Homogeneous Hydrogenation*; Wiley-VCH: Weinheim, Germany, 2007.

(3) (a) Touge, T.; Hakamata, T.; Nara, H.; Kobayashi, T.; Sayo, N.; Saito, T.; Kayaki, Y.; Ikariya, T. *J. Am. Chem. Soc.* **2011**, *133*, 14960−14963. (b) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724−8725. (c) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466−1478. (d) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102.

(4) For selected recent examples, see: (a) Coll, M.; Ahlford, K.; Pàmies, O.; Adolfsson, H.; Diéguez, M. *Adv. Synth. Catal.* **2012**, *354*, 415−427. (b) Coll, M.; Pàmies, O.; Adolfsson, H.; Diéguez, M. *Chem. Commun.* **2011**, *47*, 12188−12190. (c) Guijarro, D.; Pablo, Ó.; Yus, M. *Tetrahedron Lett.* **2011**, *52*, 789−791. (d) Deshpande, S. H.; Kelkar, A. A.; Gonnade, R. G.; Shingote, S. K.; Chaudhari, R. V. *Catal. Lett.* **2010**, *138*, 231−238. (e) Quintard, A.; Darbost, U.; Vocanson, F.; Pellet-Rostaing, S.; Lemaire, M. *Tetrahedron: Asymmetry* **2007**, *18*, 1926−1933.

(5) (a) Baratta, W.; Ballico, M.; Esposito, G.; Rigo, P. *Chem. Eur. J.* **2008**, *14*, 5588−5595. (b) Baratta, W.; Ballico, M.; Chelucci, G.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4362−4365. (c) Baratta, W.; Rigo, P. *Eur. J. Inorg. Chem.* **2008**, 4041−4053. (d) Baratta, W.; Chelucci, G.; Herdtweck, E.; Magnolia, S.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7651−7654. (e) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214−6219. (f) Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P. *Organometallics* **2005**, *24*, 1660−1669. (g) Baratta, W.; Ros, P. D.; Zotto, A. D.; Sechi, A.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3584−3588. (h) Putignano, E.; Bossi, G.; Rigo, P.; Baratta, W. *Organometallics* **2012**, *31*, 1133−1142. (i) Baratta, W.; Barbato, C.; Magnolia, S.; Siega, K.; Rigo, P. *Chem. Eur. J.* **2010**, *16*, 3201−3206. (j) Baratta, W.; Chelucci, G.; Magnolia, S.; Siega, K.; Rigo, P. *Chem. Eur. J.* **2009**, *15*, 726−732.

(6) (a) Mikhailine, A. A.; Maishan, M. I.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 12266−12280. (b) Sonnenberg, J. F.; Coombs, N.; Dube, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 5893−5899. (c) Lagaditis, P. O. A.; Lough, J.; Morris, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 9662−9665. (d) Mikhailine, A. A.; Morris, R. H. *Inorg. Chem.* **2010**, *49*, 11039−11044. (e) Lagaditis, P. O.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2010**, *49*, 10057−10066. (f) Mikhailine, A.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 1394−1395.

(7) For selected recent examples, see: (a) Johnson, T. C.; Totty, W. G.; Wills, M. *Org. Lett.* **2012**, *14*, 5230−5233. (b) Soni, R.; Collinson, J.; Clarkson, G. C.; Wills, M. *Org. Lett.* **2011**, *13*, 4304−4307. (c) Díaz-Valenzuela, M. B.; Phillips, S. D.; France, M. B.; Gunn, M. E.; Clarke, M. L. *Chem. Eur. J.* **2009**, *5*, 1227−1232. (d) Clark, M. L.; Díaz-Valenzuela, M. B.; Slawin, A. M. Z. *Organometallics* **2007**, *26*, 16−19. (e) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4732−4735.

(8) For selected recent reviews and examples, see: (a) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. *Chem. Rev.* **2012**, *112*, 1001−1033. (b) Cowan, M. G.; Olguín, J.; Narayanaswamy, S.; Tallon, J. L.; Brooker, S. *J. Am. Chem. Soc.* **2012**, *134*, 2892−2894. (c) Olguín, J.; Brooker, S. *Coord. Chem. Rev.* **2011**, *255*, 203−240. (d) Boča, M.; Jameson, R. F.; Linert, W. *Coord. Chem. Rev.* **2011**, *255*, 290−317. (e) Concepcion, J. J.; Jurss, J. W.; Brennaman, M. K.; Hoertz, P. G.; Patrocinio, A. O. T.; Iha, N. Y. M.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954−1965. (f) van der Vlugt, J. I.; Reek, N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832−8846.

(9) For selected recent reviews and examples, see: (a) Li, S. L.; Xiao, T.; Lin, C.; Wang, L. *Chem. Soc. Rev.* **2012**, *41*, 5950−5968.

(b) Berardi, S.; La Ganga, G.; Natali, M.; Bazzan, I.; Puntoriero, F.; Sartorel, A.; Scandola, F.; Campagna, S.; Bonchio, M. *J. Am. Chem. Soc.* **2012**, *134*, 11104−11107. (c) Kaveevivitchai, N.; Chitta, R.; Zong, R.; Ojaimi, M. E.; Thummel, R. P. *J. Am. Chem. Soc.* **2012**, *134*, 10721−10724. (d) Kotova, O.; Daly, R.; dos Santos, C. M. G.; Boese, M.; Kruger, P. E.; Boland, J. J.; Gunnlaugsson, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 7208−7212. (e) Aribia, K. B.; Moehl, T.; Zakeeruddin, S. M.; Grätzel, M. *Chem. Sci.* **2013**, *4*, 454−459.

(10) For selected recent reviews and examples, see: (a) Bryliakov, K. P.; Talsi, E. P. *Coord. Chem. Rev.* **2012**, *256*, 2994−3007. (b) Caulton, K. G. *Eur. J. Inorg. Chem.* **2012**, 435−443. (c) Tondreau, A. M.; Stieber, S. C. E.; Milsmann, C.; Lobkovsky, E.; Weyhermüller, T.; Semproni, S. P.; Chirik, P. J. *Inorg. Chem.* **2013**, *52*, 635−646. (d) Darmon, J. M.; Stieber, S. C. E.; Sylvester, K. T.; Fernández, I.; Lobkovsky, E.; Semproni, S. P.; Bill, E.; Wieghardt, K.; De Beer, S.; Chirik, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 17125−17137.

(11) For selected recent reviews and examples, see: (a) Yamashita, Y.; Tsubogo, T.; Kobayashi, S. *Chem. Sci.* **2012**, *3*, 967−975. (b) Das, S.; Join, B.; Junge, K.; Beller, M. *Chem. Commun.* **2012**, *48*, 2683−2685. (c) Dudnik, A. S.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 10693−10697. (d) Desimoni, G.; Faita, G.; Livieri, A.; Mella, M.; Ponta, L.; Boiocchi, M. *Eur. J. Org. Chem.* **2012**, 2916−2928. (e) Harada, T.; Tsumatori, H.; Nishiyama, K.; Yuasa, J.; Hasegawa, Y.; Kawai, T. *Inorg. Chem.* **2012**, *51*, 6476−6485.

(12) Zhang, W.; Chien, S. W.; Hor, T. S. A. *Coord. Chem. Rev.* **2011**, *255*, 1991−2024.

(13) For selected recent reviews and examples, see: (a) Wu, Y. Z.; Zhu, W. H. *Chem. Soc. Rev.* **2013**, *42*, 2039−2058. (b) Aromí, G.; Barrios, L. A.; Roubeau, O.; Gamez, P. *Coord. Chem. Rev.* **2011**, *255*, 485−546. (c) Yang, M.; Chen, X.; Zou, Y.; He, Y. H.; Pan, C. Y.; Xiao, L.; Liu, B. *J. Mater. Sci.* **2013**, *48*, 3177−3184. (d) Kumar, M.; Scobie, M.; Mashuta, M. S.; Hammond, G. B.; Xu, B. *Org. Lett.* **2013**, *15*, 724−727. (e) Verma, A. K.; Jha, R. R.; Chaudhary, R.; Tiwari, R. K.; Danodia, A. K. *Adv. Synth. Catal.* **2013**, *355*, 421−438. (f) Li, C. Y.; Yu, C. J.; Ko, B. T. *Organometallics* **2013**, *32*, 172−180. (g) Srinivas, D.; Ghule, V. D.; Tewari, S. P.; Muralidharan, K. *Chem. Eur. J.* **2012**, *18*, 15031−15037. (h) Tulchinsky, Y.; Iron, M. A.; Botoshansky, M.; Gandelman, M. *Nature Chem.* **2011**, *3*, 525−531.

(14) (a) Du, W. M.; Wang, L. D.; Wu, P.; Yu, Z. K. *Chem. Eur. J.* **2012**, *18*, 11550−11554. (b) Zhao, M.; Yu, Z. K.; Yan, S. G.; Li, Y. *J. Organomet. Chem.* **2009**, *694*, 3068−3075. (c) Zeng, F. L.; Yu, Z. K. *Organometallics* **2008**, *27*, 6025−6028. (d) Yu, Z. K.; Zeng, F. L.; Sun, X. J.; Deng, H. X.; Dong, J. H.; Chen, J. Z.; Wang, H. M.; Pei, C. X. *J. Organomet. Chem.* **2007**, *692*, 2306−2313. (e) Zeng, F. L.; Yu, Z. K. *J. Org. Chem.* **2006**, *71*, 5274−5281. (f) Deng, H. X.; Yu, Z. K.; Dong, J. H.; Wu, S. Z. *Organometallics* **2005**, *24*, 4110−4112. (g) Sun, X. J.; Yu, Z. K.; Wu, S. Z.; Xiao, W. J. *Organometallics* **2005**, *24*, 2959−2963.

(15) (a) Jin, W. W.; Wang, L. D.; Yu, Z. K. *Organometallics* **2012**, *31*, 5664−5667. (b) Zeng, F. L.; Yu, Z. K. *Organometallics* **2009**, *28*, 1855−1862. (c) Zhao, M.; Yu, Z. K.; Yan, S. G.; Li, Y. *Tetrahedron Lett.* **2009**, *50*, 4624−4628. (d) Zeng, F. L.; Yu, Z. K. *Organometallics* **2008**, *27*, 2898−2901.

(16) (a) Ye, W. J.; Zhao, M.; Yu, Z. K. *Chem. Eur. J.* **2012**, *18*, 10843−10846. (b) Ye, W. J.; Zhao, M.; Du, W. M.; Jiang, Q. B.; Wu, K. K.; Wu, P.; Yu, Z. K. *Chem. Eur. J.* **2011**, *17*, 4737−4741.

(17) Wieder, N. L.; Gallagher, M.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2010**, *132*, 4107−4109.

(18) (a) Pablo, Ó.; Guijarro, D.; Kovács, G.; Lledós, A.; Ujaque, G.; Yus, M. *Chem. Eur. J.* **2012**, *18*, 1969−1983. (b) Bosson, J.; Poater, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2010**, *132*, 13146−13149. (c) Casey, C. P.; Clark, T. B.; Guzei, I. A. *J. Am. Chem. Soc.* **2007**, *129*, 11821−11823. (d) Enthaler, S.; Hagemann, B.; Bhor, S.; Anilkumar, G.; Tse, M. K.; Bitterlich, B.; Junge, K.; Erre, G.; Beller, M. *Adv. Synth. Catal.* **2007**, *349*, 853−860. (e) Comas-Vives, A.; Ujaque, G.; Lledós, A. *Organometallics* **2007**, *26*, 4135−4144.

(19) (a) Perry, R. H.; Brownell, K. R.; Chingin, K.; Cahill, T. J., III; Waymouth, R. M.; Zare, R. N. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 2246−2250. (b) Fernández, F. E.; Puerta, M. C.; Valerga, P. *Organometallics* **2012**, *31*, 6868−6879. (c) Jagadeesh, R. V.; Wienhöer, G.; Westerhaus, F. A.; Surkus, A.; Junge, H.; Junge, K.; Beller, M. *Chem. Eur. J.* **2011**, *17*, 14375−14379. (d) Bäckvall, J. E. *J. Organomet. Chem.* **2002**, *652*, 105−111. (e) Jung, H. M.; Shin, S. T.; Kim, Y. H.; Kim, M. J.; Park, J. *Organometallics* **2001**, *20*, 3370−3372. (f) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bäckvall, J. E. *Chem. Commun.* **1999**, 351−352.