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New Type of 2,6-Bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine-Based Ruthenium Complexes: Active Catalysts for Transfer Hydrogenation of Ketones

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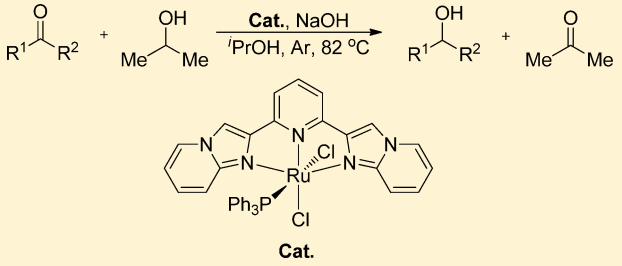
Supporting Information

ABSTRACT: Neutral and cationic ruthenium(II) complexes bearing a symmetrical 2,6-bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine were synthesized and structurally characterized by NMR analysis and X-ray crystallographic determinations. These complexes have exhibited good catalytic activity in the transfer hydrogenation of ketones. In refluxing isopropyl alcohol, the conversion of the substrates reached up to 99%, and a TOF value of 356 400 h^{-1} with 0.1 mol % catalyst was achieved.



INTRODUCTION

Transfer hydrogenation (TH) of carbonyl compounds catalyzed by transition metal complexes has been well explored and applied as the most useful catalytic method of hydrogenation of ketones for the production of alcohols due to the easy manipulations, high reactivities, and wide substrate scope.[1] Ruthenium(II) complexes have represented the most extensively investigated catalysts.[2] In this area, Ru(II) complexes containing *N*-tosylethylenediamine or *β*-amino alcohol ligands developed by Noyori and co-workers have exhibited efficient catalytic activity in the transfer hydrogenation of ketones and imines.[3] Baratta et al. have documented that cyclometalated Ru(II) complexes containing 2-(aminomethyl)pyridine ligands can be used as powerful catalysts for the transfer hydrogenation of ketones.[4] Yu's group has also reported versatile pyridyl-based pseudo-N_3 ligands and their active Ru(II) complexes for the transfer hydrogenation of ketones.[5] Although various types of ligands and their transition metal complexes have been developed for transfer hydrogenation, 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 application, and the most common phosphine-free ligands are those with tridentate pyridyl-based N_3 or pseudo-N_3 ligands where the N donors are pyridines, amines, oxazoline, imidazolines, benzimidazole, pyrazole, or other N-containing heterocycles, which have been well documented and successfully employed in organic synthesis, homogeneous catalysis, and fabrication of functional materials.[6] Substituted imidazo[1,2-*a*]pyridine compounds attracted great attention recently owing to their applications for pharmaceutical[7] and organic light-emitting diodes (OLEDs).[8] To the best of our knowledge, imidazo[1,2-*a*]pyridine itself has seldom been used as a coordinating functionality in a polydentate ligand for homogeneous catalysis.

We have recently worked on symmetrical 1,3-bis(2′-imidazolinyl)benzene (Phebim) and 1,3-bis(benzimidazol-2′-yl)benzene (Bzimb) and unsymmetrical 2-aryl-6-(oxazolinyl)-pyridine, N-substituted-2-aminomethyl-6-phenylpyridine, and oxazolinyl-pyrazolyl- or oxazolinyl-diethylamino benzene ligands to construct metal complex catalysts.[9] The Pt-, Pd-, Ni-, Rh-, Ir-, and Ru-ligand complexes were prepared successfully, and some of them exhibited high efficiency and selectivity in many catalytic reactions such as Friedel–Crafts alkylation,[9i,l] alkynylation of trifluoropyruvates with terminal alkynes,[9f] allylation of aldehydes,[9j] carbonyl-ene reaction of trifluoropyruvates,[9c,h] enantioselective hydrophosphination of enones with diphenylphosphine,[9g] and asymmetric Michael addition.[9k] The Pt-Phebim[9m] and Pt-Bzimb[9d,e] complexes were found to be luminescent in solution at room temperature. As a continuation of our work, herein we report in detail our studies on the synthesis of the neutral and cationic ruthenium(II) complexes bearing a symmetrical 2,6-bis(imidazo[1,2-*a*]pyridin-2-yl)-pyridine. Investigations on their application to the transfer hydrogenation of ketones are also presented.

RESULTS AND DISCUSSION

Synthesis of Ligand and the Ru(II) Complexes. Reaction of pyridine-2,6-dicarboxylic acid with ethanol in toluene, containing a few drops of H_2SO_4 as catalyst, afforded pyridine-2,6-dicarboxylate (**1**) in 88% yield. The 2,6-diacetylpyridine (**2**) was obtained from the reaction of **1** with ethyl acetate and metallic sodium followed by treatment with 20% aqueous HCl. Bromination of **2** with *N*-bromosuccinimide

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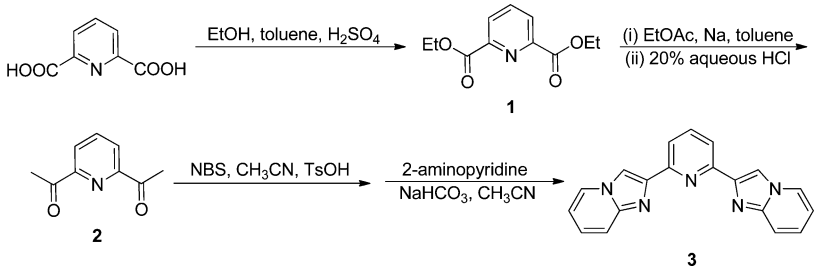
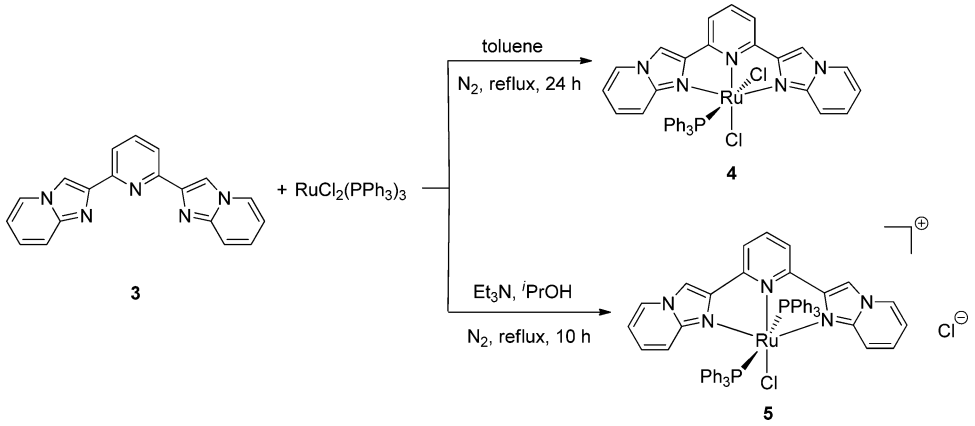
Scheme 1. Synthesis of Ligand 3



Scheme 2. Synthesis of Ru(II) Complexes 4 and 5



(NBS) as brominating agent in the presence of *p*-toluenesulfonic acid monohydrate afforded the intermediate *α,α′*-dibromo-2,6-diacetylpyridine, which was refluxed with 2-aminopyridine and sodium hydrogen carbonate in acetonitrile for 7 h to produce the desired ligand **3** (Scheme 1).

Neutral and cationic ruthenium(II) complexes **4** and **5** were obtained in 86% and 64% yields, respectively, by reacting an equimolar amount of ligand **3** with $RuCl_2(PPh_3)_3$ in refluxing toluene or isopropyl alcohol and NEt_3 (Scheme 2). Both complexes were stable in air.

Characterization of Ru(II) Complexes 4 and 5. The NMR analyses of the complexes are in agreement with their compositions. The ^{1}H NMR signals of the imidazo[1,2-*a*]pyridin-CH in ligand **3** appear at 8.64, 8.61, 7.64, 7.31, and 6.96 ppm, and those of the Ru(II) complex **4** are shifted downfield to 8.87, 8.66, 8.14, 7.62, and 7.14 ppm, revealing that the imidazo[1,2-*a*]pyridine is coordinated to the metal center. The ^{31}P NMR signal of complex **4** in DMSO-d_6 appeared at 34.0 ppm, suggesting no obvious alteration of the environment around the PPh_3 ligand, and that of complex **5** in CD_2Cl_2 appeared at 24.5 ppm, revealing the presence of two identical PPh_3 ligands. The single-crystal structures of complexes **4** and **5** were further confirmed by X-ray crystallographic determination (Figures 1 and 2).

In the solid state, the six-coordinated Ru(II) center is in a distorted pseudo-octahedral coordination environment in each case. In the molecular structure of **4** (Figure 1), the Ru−N distances are significantly shorter for the central N(3) (1.996(4) Å) than for the terminal N(1) and N(4) atoms (2.101(4) and 2.106(4) Å, respectively). The bulky PPh_3 ligand has its plane oriented normal to the central chelate ligand plane. Consequently, the PPh_3 ligand adopts a position *cis* to the nitrogen atoms from the N_3-pincer ligand and leads to a *cis* orientation of the chlorido ligand Cl(1). The P(1)−Ru−Cl(2)

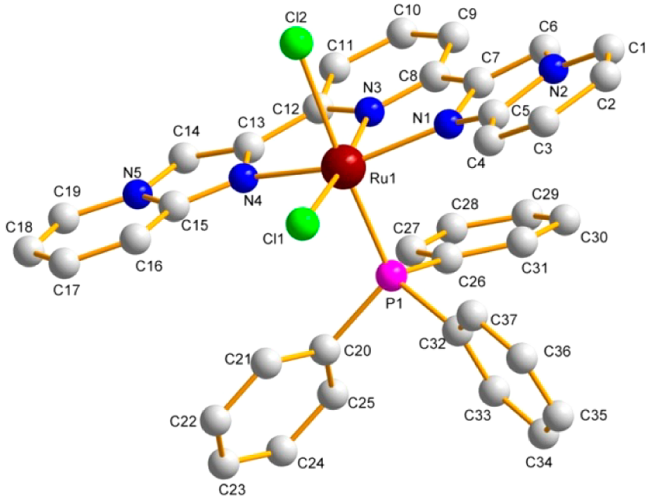


Figure 1. Molecular structure of complex **4** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−N(1), 2.101(4); Ru(1)−N(3), 1.996(4); Ru(1)−N(4), 2.106(4); Ru(1)−Cl(1), 2.4675(12); Ru(1)−Cl(2), 2.5135(11); Ru(1)−P(1), 2.2805(11); N(3)−Ru(1)−N(1), 79.38(15); P(1)−Ru(1)−Cl(1), 94.13(4); P(1)−Ru(1)−Cl(2), 176.68(5); Cl(1)−Ru(1)−Cl(2), 88.64(4); N(3)−Ru(1)−P(1), 91.68(10); N(3)−Ru(1)−Cl(1), 174.00(10).

angle is 176.68(5)°, revealing that Cl(2) is positioned *trans* to the P atom. The PPh_3 ligand exerts a notable *trans* effect, which results in a relatively longer Ru−Cl(2) bond distance of 2.5135(11) Å versus that of Ru−Cl(1) (2.4675(12) Å). Complex **5** features a molecular structure similar to that of **4** (Figure 2). The remaining chloride ligand resides at a *trans* coordination site relative to the central pyridine nitrogen atom, forming a parallelogram skeleton with good planarity. The two

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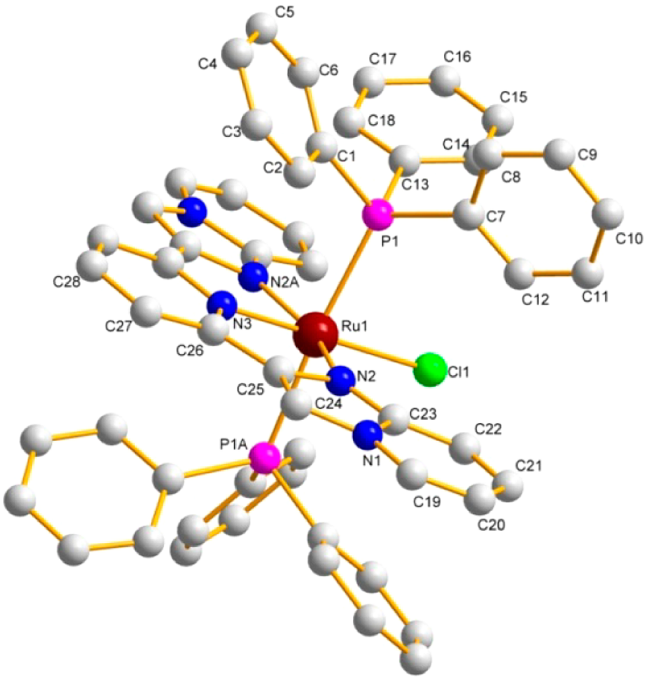
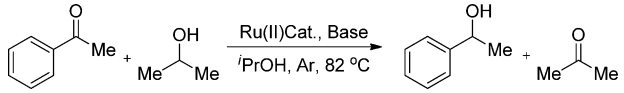


Figure 2. Molecular structure of complex **5** with hydrogen atoms and a chloride anion omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−N(3), 1.993(4); Ru(1)−N(2), 2.095(3); Ru(1)−Cl(1), 2.4334(10); Ru(1)−P(1), 2.4152(8); N(3)−Ru(1)−N(2), 78.98(9); N(3)−Ru(1)−P(1), 92.90(2); N(3)−Ru(1)−Cl(1), 180; N(2)−Ru(1)−Cl(1), 101.02(9); P(1)−Ru(1)−Cl(1), 87.10(2); N(2)−Ru(1)−N(2A), 157.95(17); P(1)−Ru(1)−P(1A), 174.21(4).

bulky PPh_3 ligands are in a *trans* arrangement at the axial positions, implying that the ruthenium metal center can be effectively protected by the phenyl rings. The Ru−P bond lengths in **5** (2.4152(8) and 2.4153(8) Å) are longer than that in **4** (2.2805(11) Å), suggesting that the two PPh_3 ligands in **5** have great *trans* influences on each other. The results suggest that the ruthenium metal center in **4** is situated in a more loose environment as compared with that in the Ru(II) complex **5**, bearing two PPh_3 ligands. Such a structural element usually enhances the catalytic activity of a metal complex catalyst.

Transfer Hydrogenation of Ketones by Ruthenium Complexes. Complexes **4** and **5** were tested as the catalysts for the transfer hydrogenation of acetophenone in refluxing isopropyl alcohol (Table 1). The reaction was performed with a molar ratio of 2000/20/1 for ketone/base/catalyst using 0.05 mol % of ruthenium complex as the catalyst in the presence of *i*PrOK as base under an argon atmosphere. It can be seen from the initial results in Table 1 (entries 1 and 2) that the ruthenium complex **4** gave the best results, with a 94% yield within 10 min. For comparison, *i*PrOK, *t*BuOK, *t*BuONa, KOH, and NaOH were tested as the bases. Over a period of 1 min, the corresponding alcohol product from acetophenone reached 79%, 68%, 76%, 96%, and 96% yields by GC analysis in the reactions using *i*PrOK, *t*BuOK, *t*BuONa, KOH, and NaOH as the base, respectively (Table 1, entries 3−7). NaOH was selected as the reaction promoter for its fast dissolution and high efficiency, although KOH also worked well as a base in the reactions. On increasing the catalyst loading, the reaction was accelerated. For example, with 0.1 mol % **4**, acetophenone reached a complete conversion to form the alcohol product within 10 s (Table 1, entry 9).

Table 1. Optimization of Reaction Conditions for the Transfer Hydrogenation of Acetophenone Catalyzed by Ru(II) Complexes 4 and 5[a]



entry	cat.	base	time (min)	yield (%)[b]
1	**4**	*i*PrOK	10	94
2	**5**	*i*PrOK	10	70
3	**4**	*i*PrOK	1	79
4	**4**	*t*BuOK	1	68
5	**4**	*t*BuONa	1	76
6	**4**	KOH	1	96
7	**4**	NaOH	1	96
8	**4**	NaOH	1/6	89
9[c]	**4**	NaOH	1/6	96
10[d]	**4**	NaOH	10	48
11		NaOH	10	NR
12	**4**		10	NR

[a]Reaction conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); ketone/base/cat. = 2000/20/1; Ar (0.1 MPa); 82 °C. [b]GC yield. [c]Ketone/base/cat. = 1000/10/1. [d]Reaction was carried out under an air atmosphere.

On the basis of the above results, the molar ratio of 1000/10/1 for ketone/base/catalyst, 0.1 mol % of complex **4** in refluxing isopropyl alcohol, and NaOH as the base under an argon atmosphere were considered as the optimized reaction conditions. The reaction was extended to other ketones in the transfer hydrogenation under the optimized conditions to evaluate the scope of the system (Table 2). Thus, the reduction of a variety of acetophenones, aryl alkyl ketones, and aliphatic cyclic ketones was efficiently performed. In most of the cases shown in Table 2, the transfer hydrogenation reactions obtained 93−99% yields within 10−120 s, reaching final TOFs of up to 356 400 h^{-1} (Table 2, entries 1−3, 5, 6, 11−16, and 23). The reduction yields of 4′-*tert*-butylacetophenone, 3′-methoxyacetophenone, and 4′-methoxyacetophenone furnished 90−99% yields over a period of 30 min (Table 2, entries 7, 18, and 19). By using 0.5 mol % of catalyst **4**, the reaction of 2′-methoxyacetophenone, 3′-methoxyacetophenone, and 4′-methoxyacetophenone gave the product in 99% yield within 1 min (Table 2, entries 17−19). The transfer hydrogenations of fluoro-substituted acetophenones were also accomplished, but only achieved moderate yields within 10−120 s (85−90% yields, Table 2, entries 8−10). Benzophenone, 1-acetonaphthone, and 2-acetonaphthone reacted smoothly to give the desired product in 97−99% yields within 10 min (Table 2, entries 20−22). Aliphatic ketones showed moderate reactivity (Table 2, entries 24 and 25), but cyclohexanone exhibited high reactivity (Table 2, entry 23).

Transfer Hydrogenation Mechanism. The transfer hydrogenation mechanism is unclear at present, although Ru(II)-catalyzed transfer hydrogenation reactions have been investigated with a Ru(II)-H complex as the catalytically active species.[1h,4g,10] Ligand dissociation is a common initiation step for most Ru-based *inner-sphere* hydrogenation catalysts.[10b,11] Thus, we examined whether exogenous PPh_3 hindered catalytic transfer hydrogenation mediated by **4**. When an excess of PPh_3 was added to the reaction mixture, the rate of transfer hydrogenation catalyzed by the **4**/NaOH system was significantly affected (Figure 3). This result suggests that the

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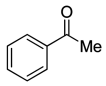
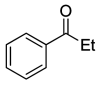
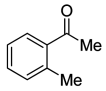
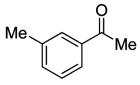
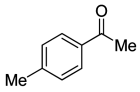
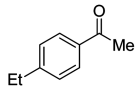
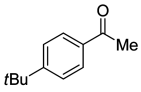
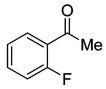
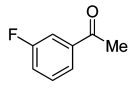
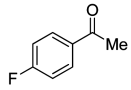
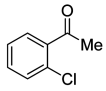
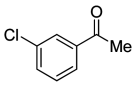
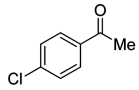
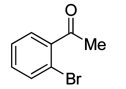
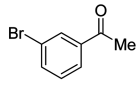
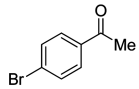
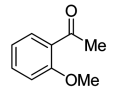
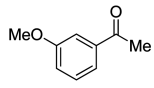
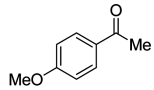
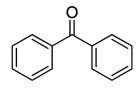
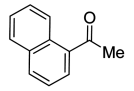
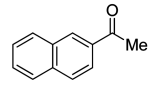
Table 2. Transfer Hydrogenation of Ketones Catalyzed by Complex 4[a]

entry	ketone	time (min)	yield (%)[b]	final TOF (h^{-1})
1		1	99	59400
2		1/6	93	334800
3		1/6	99	356400
4		30	71	1420
5		2	93	27900
6		2	93	27900
7		30	91	1820
8		1/6	85	306000
9		1	86	51600
10		2	90	27000
11		1/6	98	352800
12		1/2	99	118800
13		1/2	99	118800
14		1/6	99	356400
15		1/2	99	118800
16		1/6	96	345600
17		30 1	70 99[c]	1400 11880
18		30 1	99 99[c]	1980 11880
19		30 1	90 99[c]	1800 11880
20		10	97	5820
21		10	98	5880
22		10	99	5940
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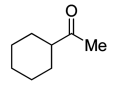
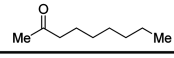
24		30 30	72[d] 97[c,d]	1440 388
25		30 30	6[d] 96[c,d]	140 384

[a]Reaction conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); ketone/base/cat. = 1000/10/1; Ar (0.1 MPa); 82 °C. [b]Isolated yield. [c]0.5 mol % **4** was used. [d]GC yield.

present transfer hydrogenation reactions may follow an inner-sphere mechanism.[5i−k,10a]

According to the related reported literature,[5a−c,10a,12] we were encouraged to propose the plausible mechanism in Scheme 3, even though the Ru−H active specics of complex **4** was not isolated successfully. The transfer hydrogenation of a ketone is initiated from complex **4**. It interacts with the base and isopropyl alcohol to form a Ru(II)-alkoxide **A**, which undergoes β-H elimination to form a Ru−H species **B** and releases of acetone. Intermediate **B** is presumably considered as the catalytically active species, although it was not successfully isolated by reacting complex **4** with NaOH or *i*PrOK in refluxing isopropyl alcohol. The formation of Ru−H complexes from Ru−Cl precursors has been documented,[13] and such in situ formed Ru−H species have been well-known to act as the active catalysts for the transfer hydrogenation of ketones.[10a,14] Coordination to the metal center and insertion to the Ru−H bond in **B** by the carbonyl of a ketone substrate yields Ru(II)-alkoxide **D**. Lastly, base-mediated alcohol metathesis with **D** regenerates species **A** to furnish the desired product and complete the catalytic cycle.

CONCLUSION

In summary, ruthenium(II) complexes bearing a symmetrical 2,6-bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine have been successfully synthesized and exhibited exceptionally high catalytic activity in the transfer hydrogenation of ketones. In refluxing isopropyl alcohol, a 99% conversion of the substrates and a TOF value of 356 400 h^{-1} with 0.1 mol % catalyst loading can be achieved.

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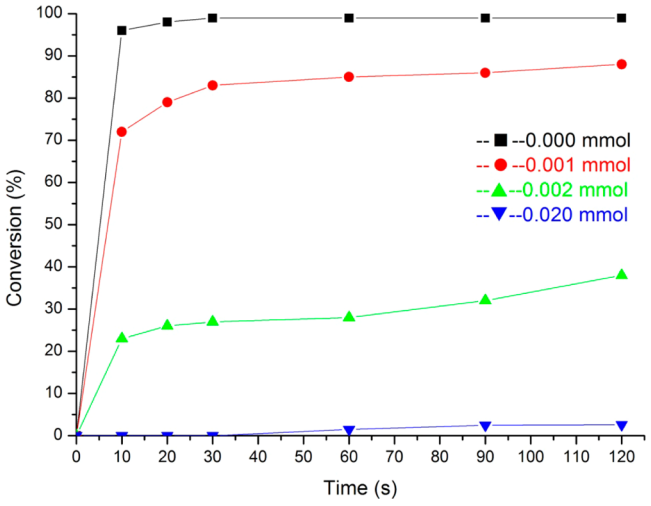
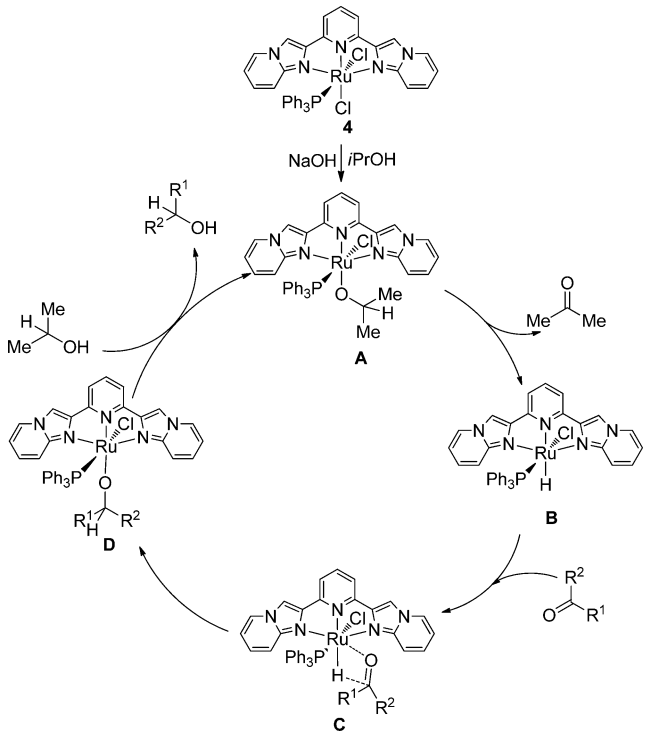


Figure 3. Product distribution during the transfer hydrogenation of acetophenone using **4** with PPh_3. Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); ketone/base/cat. = 1000/10/1; Ar (0.1 MPa); 82 °C.

Scheme 3. Proposed Mechanism



EXPERIMENTAL SECTION

General Considerations. Solvents were dried with standard methods and freshly distilled prior to use if needed. Unless otherwise noted, all the starting materials were commercially available and used without further purification. Reactions for the preparation of Ru(II) complexes as well as all the catalytic reactions were carried out under an argon atmosphere. Melting points were measured on a melting point apparatus and are uncorrected. Infrared spectra were obtained by a spectrophotometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were all recorded using TMS as an internal standard. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = single, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants in hertz (Hz). HRMS were determined on a Q-Tof Micro MS/MS System ESI spectrometer. Flash column chromatography was performed on silica gel (200−300 mesh).

Synthesis of 2,6-Diacetylpyridine (2). To a solution of pyridine-2,6-dicarboxylic acid (1.67 g, 0.01 mmol) in ethanol (14 mL) and toluene (8 mL) was added three drops of concentrated sulfuric acid. The mixture was heated to reflux and water removed by a Dean−Stark trap for 12 h. The reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue was dissolved in water (20 mL) and neutralized by solid Na_2CO_3. The aqueous solution was extracted with ether three times, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated to dryness to give diethylpyridine-2,6-dicarboxylate (**1**) (1.98 g, 89%) as a colorless solid. Mp: 41−42 °C (literature: 42−43 °C).[15]

Sodium (2.30 g, 0.1 mol) was added portionwise to a stirred solution of **1** (4.46 g, 0.02 mol) in toluene (80 mL) and ethyl acetate (50 mL) under argon, and the reaction mixture was refluxed at 120 °C (oil bath) for 9 h. The mixture was cooled to room temperature and stirred rapidly and continuously during the slow addition of the 20% aqueous HCl (25 mL). The reaction mixture was then refluxed for 5 h. After cooling to room temperature, it was neutralized by solid Na_2CO_3. The aqueous solution was extracted with ether three times, and the organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether (2/1) as eluent, providing 2,6-diacetylpyridine (**2**) (2.10 g, 64%) as a white solid.. Mp: 81−83 °C (literature: 79−80 °C).[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22 (d, J = 8.0 Hz, 2H), 8.00 (t, J = 8.0 Hz, 1H), 2.80 (s, 6H).

Synthesis of 2,6-Bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine (3). To a solution of 2,6-diacetylpyridine (163 mg, 1.0 mmol) and *p*-toluenesulfonic acid monohydrate (571 mg, 3.0 mmol) in acetonitrile (5 mL) was added NBS (445 g, 2.5 mmol). The reaction was refluxed for 16 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated to afford a crude product, which was filtered by a short silica gel chromatography column with CH_2Cl_2 as eluent to give α,α'-dibromo-2,6-diacetylpyridine (white solid). Then the obtained α,α'-dibromo-2,6-diacetylpyridine reacted with 2-aminopyridine (235 mg, 2.5 mmol) and sodium hydrogen carbonate (252 mg, 3.0 mmol) in acetonitrile (5 mL) at reflux for 7 h. After cooling and filtration, the solvent was evaporated in vacuo, and purification by column chromatography on silica gel with ethyl acetate as eluent gave 2,6-bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine (**3**) (75 mg, 24%) as a yellow solid. Mp: 220−223 °C. IR (KBr pellet): ν 3167, 3069, 3032, 1631, 1604, 1571, 1497, 1402, 1365, 1327, 1254, 1206, 1081, 931, 830, 739 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.64 (d, J = 6.8 Hz, 2H), 8.61 (s, 2H), 8.04 (d, J = 7.2 Hz, 2H), 7.97 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 9.2 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 6.96 (t, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.4, 144.8, 144.5, 137.8, 127.3, 125.4, 118.8, 116.9, 112.7, 111.5. HRMS (positive ESI, m/z): $[M + H]^+$ calcd for $C_{19}H_{14}N_5$ 312.1249, found 312.1244.

Synthesis of Neutral Ruthenium Complex 4. A mixture of $RuCl_2(PPh_3)_3$ (96 mg, 0.1 mmol) and compound **3** (31 mg, 0.1 mmol) in toluene (10 mL) was refluxed for 24 h under an argon atmosphere. The mixture was cooled to ambient temperature to precipitate a red-brown microcrystalline solid. The solid was filtered off, washed with diethyl ether (3 × 10 mL), and dried under reduced pressure to afford complex **4** (64 mg, 86%) as a red-brown crystalline solid. Mp: >300 °C. IR (KBr pellet): ν 3125, 1637, 1506, 1475, 1401, 1295, 1092, 751, 697 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.87 (s, 2H), 8.66 (d, J = 6.8 Hz, 2H), 8.14 (d, J = 9.2 Hz, 2H), 7.86−7.76 (m, 3H), 7.62 (t, J = 8.0 Hz, 2H), 7.20−7.08 (m, 11H), 7.01 (t, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.7, 146.6, 145.5, 134.9, 132.7, 132.6, 131.2, 130.8, 129.4, 129.3, 128.7, 127.8, 127.7, 119.5, 116.2, 114.8, 114.3. ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6): δ 34.0 (s, PPh_3). HRMS (positive ESI, m/z): $[M - Cl]^+$ calcd for $C_{37}H_{28}ClN_5PRu$ 710.0814, found 710.0818.

Synthesis of Cationic Ruthenium Complex 5. Under an argon atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (96 mg, 0.1 mmol), compound **3** (31 mg, 0.1 mmol), 2-propanol (10 mL), and NEt_3 (70 μL, 0.5 mmol) was refluxed with stirring for 10 h. After cooling to ambient temperature, the solvent was evaporated in vacuo, and

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purification by column chromatography on Al_2O_3 with CH_2Cl_2/MeOH (10/1) as eluent gave complex **5** (64 mg, 64%) as red-brown crystals. Mp: disintegrated at 230 °C. IR (KBr pellet): ν 3334, 1636, 1612, 1574, 1504, 1477, 1432, 1400, 1296, 1089, 747, 697 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.57 (s, 2H), 8.39 (d, J = 6.8 Hz, 2H), 8.18 (d, J = 9.2 Hz, 2H), 7.35 (s, 3H), 7.21 (dd, J = 6.8, 8.4 Hz, 2H), 7.14−7.09 (m, 18H), 6.93 (dd, J = 7.2, 8.4 Hz, 12H), 6.86 (dt, J = 0.8, 6.8 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 154.6, 147.8, 146.5, 133.83, 133.78, 133.73, 132.8, 132.7, 132.5, 132.4, 129.6, 128.6, 128.2, 128.14, 128.09, 126.9, 120.0, 119.1, 114.5, 114.0. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 24.5 (s, PPh_3). HRMS (positive ESI, m/z): $[M - Cl - PPh_3]^+$ calcd for $C_{37}H_{28}ClN_5PRu$ 710.0814, found 710.0816.

General Procedure for the Catalytic Transfer Hygrogenation of Ketones. The catalyst solution was prepared by dissolving complex **4** (14.9 mg, 0.02 mmol) in 2-propanol (10.0 mL). Under an argon atmosphere, the mixture of a ketone (2.0 mmol), 1.0 mL of the catalyst solution (0.002 mmol), and 2-propanol (18.0 mL) was stirred at 82 °C for 10 min. Then 1.0 mL of a 0.02 M NaOH (0.02 mmol) solution in 2-propanol was introduced to initiate the reaction. The reaction was monitored by GC analysis. After the reaction was complete, the reaction mixture was evaporated and the residue was purified by TLC on silica gel plates to afford the alcohol product. The purified products were identified by ^1H NMR spectra, and their analytical data are given in the Supporting Information.

X-ray Diffraction Studies. Crystals of **4** and **5** (CCDC file numbers 1027736 and 1027735) were obtained by recrystallization from CH_2Cl_2/MeOH at ambient temperature. The data were collected on an Oxford Diffraction Gemini E diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.541 84 Å for complex **4**) and Mo Kα radiation (λ = 0.7107 Å for complex **5**) at ambient temperature. The structures were solved by direct methods using the SHELXS-97 program, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique, which used the SHELXL-97 crystallographic software package.[17] The hydrogen atoms were included but not refined. Details of the crystal structure determination are summarized in Table S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A table giving crystallographic details for the Ru(II) complexes **4** and **5**, figures giving NMR spectra of the new compounds **3**−**5** and NMR spectra of the catalysis products, text giving characterization data of the known catalysis products, and CIF files giving crystallographic data for complexes **4** and **5**. 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.

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■ REFERENCES

(1) For selected reviews, see: (a) Simon, M.-O.; 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, R.; 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.; Xiao, J. *Chem. Asian. J.* **2008**, *3*, 1750−1770. (g) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300−1308. (h) Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 235−248.

(2) (a) Everaere, K.; Mortreux, A.; Carpentier, J.-F. *Adv. Synth. Catal.* **2003**, *345*, 67−77. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102.

(3) (a) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931−7944. (b) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466−1478. (c) Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1703−1707. (d) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285−288. (e) Gao, J.-X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087−1089. (f) Takehara, J.; Hashiguchi, S.; Fujii, A.; Inoue, S.-i.; Ikariya, T.; Noyori, R. *Chem. Commun.* **1996**, 233−234. (g) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521−2522.

(4) (a) Putignano, E.; Bossi, G.; Rigo, P.; Baratta, W. *Organometallics* **2012**, *31*, 1133−1442. (b) Baratta, W.; Bossi, G.; Putignano, E.; Rigo, P. *Chem.—Eur. J.* **2011**, *17*, 3474−3481. (c) Baratta, W.; Benedetti, F.; Zotto, A. D.; Fanfoni, L.; Felluga, F.; Magnolia, S.; Putignano, E.; Rigo, P. *Organometallics* **2010**, *29*, 3563−3575. (d) Baratta, W.; Barbato, C.; Magnolia, S.; Siega, K.; Rigo, P. *Chem.—Eur. J.* **2010**, *16*, 3201−3206. (e) Baratta, W.; Chelucci, G.; Magnolia, S.; Siega, K.; Rigo, P. *Chem.—Eur. J.* **2009**, *15*, 726−732. (f) Baratta, W.; Rigo, P. *Eur. J. Inorg. Chem.* **2008**, 4041−4053. (g) Baratta, W.; Ballico, M.; Esposito, G.; Rigo, P. *Chem.—Eur. J.* **2008**, *14*, 5588−5595. (h) Baratta, W.; Ballico, M.; Chelucci, G.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4362−4365. (i) Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Magnolia, S.; Rigo, P. *Chem.—Eur. J.* **2008**, *14*, 9148−9160. (j) Zotto, A. D.; Baratta, W.; Ballico, M.; Herdtweck, E.; Rigo, P. *Organometallics* **2007**, *26*, 5636−5642. (k) Baratta, W.; Siega, K.; Rigo, P. *Chem.—Eur. J.* **2007**, *13*, 7479−7986. (l) Baratta, W.; Siega, K.; Rigo, P. *Adv. Synth. Catal.* **2007**, *349*, 1633−1636. (m) Baratta, W.; Bosco, M.; Chelucci, G.; Zotto, A. D.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. *Organometallics* **2006**, *25*, 4611−4620. (n) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214−6219.

(5) (a) Du, W.; Wang, Q.; Wang, L.; Yu, Z. *Organometallics* **2014**, *33*, 974−982. (b) Wang, Q.; Du, W.; Liu, T.; Chai, H.; Yu, Z. *Tetrahedron Lett.* **2014**, *55*, 1585−1588. (c) Du, W.; Wu, P.; Wang, Q.; Yu, Z. *Organometallics* **2013**, *32*, 3083−3890. (d) Ye, W.; Zhao, M.; Yu, Z. *Chem.—Eur. J.* **2012**, *18*, 10843−10846. (e) Jin, W.; Wang, L.; Yu, Z. *Organometallics* **2012**, *31*, 5664−5667. (f) Du, W.; Wang, L.; Wu, P.; Yu, Z. *Chem.—Eur. J.* **2012**, *18*, 11550−11554. (g) Ye, W.; Zhao, M.; Du, W.; Jiang, Q.; Wu, K.; Wu, P.; Yu, Z. *Chem.—Eur. J.* **2011**, *17*, 4737−4741. (h) Zhao, M.; Yu, Z.; Yan, S.; Li, Y. *Tetrahedron Lett.* **2009**, *50*, 4624−5628. (i) Zeng, F.; Yu, Z. *Organometallics* **2009**, *28*, 1855−1862. (j) Zeng, F.; Yu, Z. *Organometallics* **2008**, *27*, 2898−2901. (k) Zeng, F.; Yu, Z. *Organometallics* **2008**, *27*, 6025−6028. (l) 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. (m) Deng, H.; Yu, Z.; Dong, J.; Wu, S. *Organometallics* **2005**, *24*, 4110−4112.

(6) (a) Moore, C. M.; Szymczak, N. K. *Chem. Commun.* **2013**, *49*, 400−402. (b) Ito, J.-i.; Ujiie, S.; Nishiyama, H. *Organometallics* **2009**, *28*, 630−638. (c) Beach, N. J.; Spivak, G. J. *Inorg. Chim. Acta* **2003**, *343*, 244−252.

(7) (a) Koubachi, J.; Kazzouli, S. E.; Bousmina, M.; Guillaumet, G. *Eur. J. Org. Chem.* **2014**, 5119−5238. (b) Wang, S.; Liu, W.; Cen, J.; Liao, J.; Huang, J.; Zhan, H. *Tetrahedron Lett.* **2014**, *55*, 1589−1592. (c) Gudmundsson, K. S.; Johns, B. A. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 2735−2739.

(8) (a) Stasyuk, A. J.; Banasiewicz, M.; Cyrański, M. K.; Gryko, D. T. *J. Org. Chem.* **2012**, *77*, 5552−5558. (b) Shono, H.; Ohkawa, T.; Tomoda, H.; Mutai, T.; Araki, K. *ACS Appl. Mater. Interfaces* **2011**, *3*,

DOI: 10.1021/om501119x
Organometallics XXXX, XXX, XXX−XXX

654−657. (c) Takizawa, S.-y.; Nishida, J.-i.; Tsuzuki, T.; Tokito, S.; Yamashita, Y. *Inorg. Chem.* **2007**, *46*, 4308−4319.
(9) (a) Niu, J.-L.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. *Dalton Trans.* **2011**, *40*, 5135−5150. (b) Hao, X.-Q.; Niu, J.-L.; Zhao, X.-M.; Gong, J.-F.; Song, M.-P. *Chin. J. Org. Chem.* **2013**, *33*, 663−674. (c) Wang, T.; Hao, X.-Q.; Huang, J.-J.; Wang, K.; Gong, J.-F.; Song, M.-P. *Organometallics* **2014**, *33*, 194−205. (d) Wang, Z.; Niu, J.-L.; Zhang, L.-Z.; Guo, J.-W.; Hao, X.-Q.; Song, M.-P. *Tetrahedron* **2014**, *70*, 7496−7504. (e) Wang, Z.; Sun, Z.; Hao, X.-Q.; Niu, J.-L.; Wei, D.; Tu, T.; Gong, J.-F.; Song, M.-P. *Organometallics* **2014**, *33*, 1563−1573. (f) Wang, T.; Niu, J.-L.; Liu, S.-L.; Huang, J.-J.; Gong, J.-F.; Song, M.-P. *Adv. Synth. Catal.* **2013**, *355*, 927−937. (g) Hao, X.-Q.; Zhao, Y.-W.; Yang, J.-J.; Niu, J.-L.; Gong, J.-F.; Song, M.-P. *Organometallics* **2014**, *33*, 1801−1811. (h) Wang, T.; Hao, X.-Q.; Huang, J.-J.; Niu, J.-L.; Gong, J.-F.; Song, M.-P. *J. Org. Chem.* **2013**, *78*, 8712−8721. (i) Hao, X.-Q.; Xu, Y.-X.; Yang, M.-J.; Wang, L.; Niu, J.-L.; Gong, J.-F.; Song, M.-P. *Organometallics* **2012**, *31*, 835−846. (j) Wang, T.; Hao, X.-Q.; Zhang, X.-X.; Gong, J.-F.; Song, M.-P. *Dalton Trans.* **2011**, *40*, 8964−8976. (k) Shao, D.-D.; Niu, J.-L.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. *Dalton Trans.* **2011**, *40*, 9012−9019. (l) Wu, L.-Y.; Hao, X.-Q.; Xu, Y.-X.; Jia, M.-Q.; Wang, Y.-N.; Gong, J.-F.; Song, M.-P. *Organometallics* **2009**, *28*, 3369−3380. (m) Hao, X.-Q.; Gong, J.-F.; Du, C.-X.; Wu, L.-Y.; Wu, Y.-J.; Song, M.-P. *Tetrahedron Lett.* **2006**, *47*, 5033−5036.
(10) (a) Comas-Vives, A.; Ujaque, G.; Lledós, A. *Organometallics* **2007**, *26*, 4135−4144. (b) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201−2237.
(11) Moore, C. M.; Szymczak, N. K. *Chem. Commun.* **2013**, *49*, 400−402.
(12) Zhu, Z.; Zhang, J.; Fu, H.; Yuan, M.; Zheng, X.; Chen, H.; Li, R. *RSC Adv.* **2014**, *4*, 52734−52739.
(13) Li, T.; Churlaud, R.; Lough, A. J.; Abdur-Rashid, K.; Morris, R. H. *Organometallics* **2004**, *23*, 6239−6247.
(14) (a) Casey, C. P.; Clark, T. B.; Guzei, I. A. *J. Am. Chem. Soc.* **2007**, *129*, 11821−11827. (b) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805−7814.
(15) Singer, A. W.; Mcelvain, S. M. *J. Am. Chem. Soc.* **1935**, *57*, 1135−1137.
(16) Zhang, D.-f.; Xie, G.-y. *Huaxue Shiji* **2008**, *30*, 49−50.
(17) (a) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

DOI: 10.1021/om501119x
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