Ruthenium Complex Catalysts Supported by a Bis(trifluoromethyl)pyrazolyl–Pyridyl-Based NNN Ligand for Transfer Hydrogenation of Ketones

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ABSTRACT: Ru(III) and Ru(II) complexes bearing a tridentate 2-(3′,5′-dimethylpyrazol-1″-yl)-6-(3′,5′-bis(trifluoromethyl)pyrazol-1″-yl)pyridine or 2-(benzimidazol-2″-yl)-6-(3′,5′-bis(trifluoromethyl)pyrazol-1″-yl)pyridine ligand were synthesized and applied to the transfer hydrogenation of ketones. The Ru(II) complex was structurally confirmed by the X-ray crystallographic analysis and achieved up to 2150 turnover numbers and final TOFs up to 29700 h⁻¹ in the transfer hydrogenation of ketones. The benzimidazolyl moiety with an unprotected NH functionality in the ligand exhibited an enhancement effect on the catalytic activity of its RuCl₃-bis(trifluoromethyl)pyrazol-1″-yl)pyridine complex in the ketone reduction reactions, reaching a final TOF value up to 35640 h⁻¹. The controlled experiments have revealed that the compatibility of the trifluoromethylated pyrazolyl and unprotected benzimidazolyl is crucial for the establishment of the highly active catalytic system.

Transition-metal-catalyzed transfer hydrogenation (TH) of unsaturated substrates has attracted much attention in recent years, not only because it provides reliable reduction methods under mild conditions with simple procedures but also because it is considered as a promising alternative for direct hydrogenation reactions. N-Tosylphenylethylene and the Ru(II) complexes developed by Noyori et al. have been demonstrated as the most powerful catalysts in the asymmetric transfer hydrogenation of ketones and imines. Other types of ligands and their transition-metal complex catalysts have also been studied to achieve broader substrate scopes and improve reaction efficiency. Among the above established catalytic systems, Ru(II) complexes have represented the most extensively investigated catalysts, while their Ru(III) analogues have been seldom explored in the transfer hydrogenation of ketones.

Trifluoromethylated molecules have been demonstrated to have versatile applications in various areas due to the inherent properties of CF₃ groups such as high electronic negativity, lipophilicity, H-bonding formation, etc. The electronic properties of a pyrazolyl moiety could be substantially modified by incorporating a CF₃ group into its backbone, which thus dramatically alters both the physical and chemical properties of its metal complexes.

3,5-Bis(trifluoromethyl)pyrazolyl was used to build scorpionate ligands and bidentate (3,5-bis(trifluoromethyl)pyrazolyl)-methane. Dias and others have revealed that fluoro substituents on the pyrazolyl rings can exert a significant effect on the metal centers of their complexes. The relevant metal complexes usually exhibited unique properties such as great stabilities toward air and thermal conditions, and some structurally unique and unstable complexes could be stabilized by these ligands. Although 3,5-bis(trifluoromethyl)pyrazolyl has been employed as a unique functionality, it has seldom been used for fabricating transition-metal complex catalysts.

We have recently worked on unsymmetrical pyrazolyl–pyridyl-based NNN ligands to construct highly active ruthenium(II) complex catalysts for the transfer hydrogenation of ketones (Scheme 1). Highly active Ru(II) complex catalysts bearing a pyrazolyl–(1H-imidazolyl) pyridine (B and C) or pyrazolyl–(1H-pyryl) pyridine (D) NNN ligand were synthesized. With these results in hand, we reasonably envisioned that combination of the distinctive 3,5-bis(trifluoromethyl)pyrazolyl functionality with unprotected benzimidazolyl or electron-rich pyrazolyl may lead to tridentate NNN ligands with unique properties suitable for constructing transition-metal complex catalysts. Herein, we report the synthesis of two bis(trifluoromethyl)pyrazolyl–pyridyl-based NNN ligands and their application in ruthenium-catalyzed TH reactions of ketones.

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Initially, we tried to introduce a 3,5-bis(trifluoromethyl)pyrazolyl functionality to a pyridyl backbone by the palladium- or copper-catalyzed cross-coupling reaction of 2-bromopyridine with 3,5-bis(trifluoromethyl)pyrazole in a fashion similar to that for the preparation of 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine. Unfortunately, the reaction did not occur regardless of using palladium and copper catalysts or changing to harsh conditions. This consequence may be attributed to the highly electron-deficient properties of 3,5-bis(trifluoromethyl)pyrazole. An indirect procedure was then developed to synthesize the target bis(trifluoromethyl)pyrazolyl−pyridyl-based NNN ligand 4 (Scheme 2). Starting from the nucleophilic substitution reaction of 2-bromo-6-(3′,5′-dimethylpyrazolyl)pyridine (1) with hydrazine hydrate in butanol on heating, pyridyl hydrazine 2 was obtained in 65% yield. Cyclization of 2 with 1,1,1,5,5,5-hexafluoropentane-2,4-dione in refluxing THF afforded the intermediate product 3 (95%), which was efficiently dehydrated to give the desired ligand 4 (90%) in the presence of concentrated H$_2$SO$_4$. Treatment of 4 with an equivalent amount of RuCl$_3$·xH$_2$O in refluxing ethanol formed Ru(III) complex 5 (85%). The reaction of 5 with an equivalent amount of PPh$_3$ and triethylamine in ethanol gave Ru(II) complex 6 (55%). In a fashion similar to the preparation of 3, compound 9 was obtained from the reaction of 2,6-dibromopyridine with hydrazine hydrate followed by cyclization with 1,1,1,5,5,5-hexafluoropentane-2,4-dione (Scheme 3). Dehydration of 9 under the acidic conditions gave 2-bromo-6-((3′,5′)-bis(trifluoromethyl)pyrazolyl)pyridine (10). Formylation of 10 with DMF in THF produced 11 (60%), which was condensed with 1,2-phenylenediamine to produce the desired ligand 12 (55%). Methylation of 12 by methyl iodide formed its derivative: that is, ligand 13. In a manner similar to the synthesis of complexes 5 and 6, we failed to obtain the desired Ru(III) complex product from the reaction of ligand 12 or 13 with RuCl$_3$·xH$_2$O, and in the presence of PPh$_3$ and Et$_3$N the corresponding Ru(II) complex product was not successfully collected either. In all our attempts to isolate the desired Ru(III) and Ru(II) complexes bearing ligands 12 and 13, only a mixture of complexes and no pure complex products 14−17 could be obtained. This result is presumably attributed to the highly electron-deficient properties of the 3,5-bis(trifluoromethyl)pyrazolyl functionality, which may not be very compatible with the benzimidazolyl moiety in the ligand as compared with that in ligand 4, resulting in variable Ru(III) species under the reaction conditions.

All the intermediate compounds, ligands, and complex 6 were characterized by $^1$H, $^{13}$C($^1$H), $^{31}$P($^1$H), and $^{19}$F($^1$H) (if any) NMR and HRMS techniques or elemental analysis. Ru(III) complex 5 is paramagnetic, and its NMR spectra could
not be successfully collected. The HRMS (ESI-TOF) analysis of complex 5 revealed two peaks featuring values of 546.9343 ([M – Cl]) and 604.8874 ([M + Na]+), which are consistent with the calculated values: i.e., 546.9339 and 604.8925, respectively. The elemental analysis suggests its composition as expected. The molecular structure of complex 6 was further confirmed by the X-ray crystallographic determination (Figure 1). In the solid state, the six-coordinated metal center is surrounded by ligand 4, two chlorides, and one PPh3 ligand in a distorted-bipyramidal environment, which is similar to that of our previously reported Ru(II) complex bearing a 2,6-bis(3′,5′-dimethylpyrazol-1-′-yl)pyridine ligand. The Cl(1) – Ru – Cl(2) angle is 85.72(3)°, suggesting that the two Cl atoms are cis positioned. The P–Ru–N(1), P–Ru–N(3), and P–Ru–N(5) angles are 92.74(8), 93.03(8), and 92.83(8)°, respectively, indicating that the PPh3 ligand is nearly vertically situated above the planar ligand. The N(3) – Ru – Cl(2) angle is 170.39(8)°, revealing that Cl(2) is positioned trans to the pyridyl nitrogen atom. The Ru–P bond length is 2.3237(9) Å, which is longer than that (2.2927(14) Å) in the aforementioned complex, suggesting that the ruthenium metal center in 5 is situated in a more loose environment as compared with that in the Ru(II) complex bearing a 2,6-bis(3′,5′-dimethylpyrazol-1-′-yl)pyridine ligand. Such a structural element usually enhances the catalytic activity of a metal complex catalyst.

Complex 5 was then applied as the catalyst for transfer hydrogenation of ketones (Table 1). Under the standard conditions, a wide range of acetophenones, aliphatic cyclic and acyclic ketones were reduced to their corresponding alcohols using 1 mol % 5 as the precatalyst in refluxing 2-propanol under a nitrogen atmosphere. Most of the substrates reached ≥97% conversions and TOF values of ca. 100 within 30 min. In particular, both 2′-chloroacetophenone and 2′,4′-dichloroacetophenone were reduced to the corresponding alcohols in 99% yields within 1 min, achieving the highest final TOF value of 5940 h⁻¹ (Table 1, entries 3 and 6), demonstrating a rare and highly efficient example of Ru(III)-catalyzed transfer hydrogenation of ketones. Various substituents were tolerated, and electron-withdrawing groups such as chloro, bromo, and fluoro usually facilitated the reaction, whereas an o-trifluoromethyl group deteriorated the reaction efficiency (Table 1, entry 13). Electron-donating substituents, that is, methyl and methoxy, made the ketone substrates more electron rich and thus reacted less efficiently than their electron withdrawing group(s) bearing analogues. Increasing the steric hindrance of the ketones required longer time and/or a higher catalyst loading for the reaction to reach satisfactory yields (Table 1, entries 19–21). It was observed that acetophenones bearing an ortho substituent usually reacted more quickly than those bearing meta or para substituent(s) (Table 1, entries 3 vs 4 and 5, 7 vs 8 and 9, 10 vs 11 and 12, and 16 vs 17 and 18), except for the case of using the ketone bearing a sterically hindered o-CF3 substituent (Table 1, entry 13). Aliphatic ketones were also reduced to the corresponding alcohols, and the cyclic substrates cyclohexanone and cyclohexanone exhibited much higher reactivity than their acyclic analogues: i.e., 2-heptanone (Table 1, entries 22–24). On the basis of the observations we reasonably propose that during the TH reaction Ru(III) complex 5 is initially reduced to a Ru(II) species which subsequently interacts with the alkoxy (e.g., iPrOK) to form a catalytically active RuH species to initiate the TH reaction.

The reduction of ketones was also performed by using 0.2 mol % of complex 6 as catalyst. As shown in Table 1, complex 6 exhibited a much higher catalytic activity than its Ru(III) analogue 5, reaching 99% yield and a final TOF value of up to 29700 h⁻¹ within 1 min (Table 1, entry 4). Similar electronic and steric effects of the substituents from the ketone substrates were observed (Table 1). In particular, complex 6 was catalytically superior to our previously reported Ru(II) complex A bearing a 2,6-bis(3′,5′-dimethylpyrazol-1-′-yl)pyridine ligand. Under the same conditions with 0.2 mol % A as catalyst, the TH reaction of ketones only formed the corresponding alcohols in up to 99% yield with the highest final TOF (5940 h⁻¹) over a period of 5 min. These results suggest that the hemilability of unsymmetrical ligands is crucial for their transition-metal complexes to exhibit high catalytic activity. The TON values ranged between 450 and 495 in the cases of using 0.2 mol % 6 as catalysts, which are higher than those achieved by using 1 mol % complex 5. However, on a 10 mmol scale of the ketone in the presence of 0.04 mol % 6 as catalyst, the TON reached 2150 (Table 1, entry 4). The modest TON values are presumably attributed to the fact that 3,5-bis(trifluoromethyl)pyrazolyl is a relatively weak coordinating group, and complexes 5 and 6 bearing a ligand containing such a coordinating functionality could not be stabilized enough and were gradually decomposed to deactivation during the reaction.

The NH functionality of benzimidazolyl has been proven as a great accelerating element in the ruthenium(II) complex catalysts developed by our group, and such complexes can be efficiently applied in the TH reactions of ketones. Because pure Ru(III) and Ru(II) complexes 14–17 could not be successfully prepared, a combination of RuCl3·H2O and ligand 12 or 13 in a 1/1 molar ratio was used as the catalyst for the TH reaction of ketones under the standard conditions. By means of a loading of 0.5 mol % RuCl3·H2O and 0.5 mol % of 12 in refluxing 2-propanol, the TH reaction of ketones was efficiently realized (Table 2). In most cases, >97% yields were obtained within 10 min, and the reaction of 2’-chloroacetophenone reached 99% yield with a final TOF value of 35640.
h−1 over a period of 20 s (Table 2, entry 3), demonstrating one of the best results in Ru(III)-catalyzed TH reactions of ketones under phosphine-free conditions to date.6 The TON values were around 200 in the cases of using 0.5 mol % RuCl₃·xH₂O as catalyst, which could be increased to 720 on a 10 mmol scale of the ketone in the presence of 0.1 mol % RuCl₃·xH₂O (Table 2, entry 3). The modest TON values are also presumably attributed to the fact that 3,5-bis(trifluoromethyl)-pyrazolyl is a relatively weakly coordinating functionality which could not effectively stabilize the central metal of the complex catalyst during the reaction.

The interaction of RuCl₃·xH₂O with ligand 12 possibly generated variable Ru(III) complex 14, which was readily transformed to 14' by extrusion of one molecule of HCl in the presence of a base and then reduced to Ru(II) species E under the reaction conditions. During the reaction species E may be stabilized by the solvent, ketone substrate, and/or alcohol product, and it may also coexist with its dimer. The precatalyst E reacted with iPrOK base to initiate the catalytic cycle, as we

Table 1. Transfer Hydrogenation of Ketones Catalyzed by 5 or 6

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Determined by GC analysis. aData given in parentheses for the cases of using 6 as catalyst. bThe reaction was conducted on a scale of 10 mmol of ketone with 0.04 mol % of 6 in 100 mL of iPrOH. cUsing 2 mol % of 5. dConditions: ketone, 2.0 mmol (0.1 M in 20 mL of iPrOH); complex 5 (1 mol %), ketone/iPrOK/cat. 5 = 100/15/1, or complex 6 (0.2 mol %), ketone/iPrOK/cat. 6 = 500/15/1; 0.1 MPa of N₂; 82 °C.

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previously reported. Although most of the substrates could be efficiently reduced to their corresponding alcohols, the reaction of some electron-rich and sterically hindered ketones required a longer time to achieve satisfactory yields. To our delight, the reaction efficiency of these relatively stubborn ketones was obviously improved by adding 0.5 mol % of PPh₃ to the catalytic system (Table 2, entries 19 − 21 and 23). Such an acceleration effect is ascribed to the coordination of PPh₃ ligand to the ruthenium center, which stabilizes the catalytically active species during the reaction. After all the volatiles were evaporated under reduced pressure, the reaction residue was analyzed by ⁳¹P{¹H} NMR determination to reveal a singlet at 29.4 ppm for a PPh₃ ligand coordinated to the ruthenium atom.¹⁴

In order to make comparison with ligand 12, ligand 13 with an N-methyl benzimidazolyl moiety was applied in the catalytic system for the TH reaction of ketones. It was found that the combination of RuCl₃·xH₂O and 13 could only exhibit a modest catalytic activity under the same conditions. For the five tested ketone substrates, a much longer time (30 − 120 min) was required to get acceptable yields (Table 3) in comparison with those cases (3 − 20 min) using the RuCl₃·xH₂O/12 catalyst system (Table 2). For example, 4′-bromoacetophenone was converted to the corresponding alcohol in 97% yield within 3 min by using the RuCl₃·xH₂O/12 catalyst system, reaching a final TOF value of 3880 h⁻¹ (Table 2, entry 9), whereas the same reaction only achieved 84% yield within 1 h by means of RuCl₃·xH₂O/13 as catalyst, exhibiting a final TOF value of 168

### Table 2. Transfer Hydrogenation of Ketones Catalyzed by RuCl₃·xH₂O/12

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¹⁴ Determined by GC analysis. ¹⁵ The reaction was conducted on a 10 mmol scale of ketone with 0.1 mol % RuCl₃·xH₂O/ligand 12 as catalyst in 100 mL of iPrOH. ¹⁶ Data given in parentheses for the cases of adding 0.5 mol % PPh₃. ¹⁷ Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of iPrOH); RuCl₃·xH₂O, 0.5 mol % ligand 12, 0.5 mol % iPrOK, 7.5 mol %; 0.1 MPa of N₂; 82 °C.
h−1 (Table 3, entry 3). These results suggest that the unprotected NH functionality in the benzimidazolyl moiety is a key factor for constructing highly active transition-metal complex catalysts for TH reactions of ketones.

The TH mechanism is unclear at present, although Ru(II)-catalyzed TH reactions have been investigated15 with a Ru(II)−H complex as the catalytically active species.16 In our cases of using the Ru(III) precatalysts, reduction of Ru(III) to Ru(II) may occur first.17 The 1H NMR analysis of the residue from the in situ reduction of complex 5 reveals unambiguous 1H NMR signals (see the Supporting Information), suggesting transformation of the Ru(III) species, i.e., 5, to some Ru(II) species because Ru(III) complex 5 is paramagnetic and its 1H and 13C NMR signals could not be collected. In addition, the Ru(III) precatalyst could be unambiguously reduced to the Ru(II) species containing a Ru(II)−PPh3 bond in the presence of PPh3.18 In the absence of a phosphine ligand, the Ru(II) species generated from the in situ reduction of the Ru(III) precatalyst may not be effectively stabilized by the ligand, so that performance of the Ru(III) complex catalyst was inferior to that of its corresponding Ru(II) analogue bearing a PPh3 ligand. Thus, we reasonably proposed an in situ formed Ru(II) hydride as the catalytically active species to promote the TH reaction via an inner-sphere pathway.

The mechanism is depicted by means of complex 5 as the precatalyst (Scheme 5). Ru(III) complex 5 is initially reduced to Ru(II) species E in situ. A subsequent ligand substitution with iPrOK forms Ru(II)−alkoxide F, and the subsequent β-H elimination from F generates Ru(II)−H intermediate G with release of acetone. Coordination to the metal center and insertion to the Ru−H bond in G by the carbonyl of a ketone substrate yields Ru(II)−alkoxide I, which undergoes alcohol metathesis to furnish the desired product and complete the catalytic cycle.

In summary, we have successfully synthesized pyridyl-supported NNN ligands bearing a 3,5-bis(trifluoromethyl)-pyrazolyl moiety and their Ru(III) and Ru(II) complexes. These complexes and the combination of the NNN ligands with RuCl3·xH2O exhibited very high catalytic activity in the TH reaction of ketones, demonstrating one of the most efficient Ru(III) catalysts for TH reactions of ketones.

### 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 the literature methods. 1H and 13C(1H) NMR spectra were recorded on a Bruker DRX-400.
spectrometer, and all chemical shift values refer to δTMS: 0.00 ppm, CDCl₃ (δ(1H), 7.26 ppm; δ(13C), 77.16 ppm), CD₂Cl₂ (δ(1H), 5.32 ppm; δ(13C), 33.84 ppm), and acetone-d₆ (δ(1H), 2.05 ppm; δ(13C), 29.84 and 206.26 ppm). HRMS and elemental analysis were carried out by the Analysis Center, Dalinan University of Technology, and the HRMS data given for compounds 8–10 refer to the 19Br isotope. All of the resulting residues were uncorrected for Lorentz and polarization effects. All hydrogen atoms were placed in calculated positions and refined anisotropically. All hydrogen atoms were placed in calculated positions.

X-ray Crystallographic Studies. Red-brown single crystals of complex 6 suitable for an X-ray structural determination were obtained by recrystallization in CHCl₃/cyclohexane (1/3 v/v) at −20 °C. The X-ray single-crystal structure of compound 6 was determined 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 corrections were applied by full-matrix least squares on F². 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 data and refinement details for 6 are given in the Supporting Information.

Synthesis of Compound 2. Under an nitrogen atmosphere, a mixture of (1.402 g, 16.0 mmol) and 10 mL of hydrazine hydrate in 10 mL of nBuOH was stirred at 120 °C for 20 h. After the mixture was cooled to ambient temperature, all of the volatiles were removed under reduced pressure. Purification of the resultant residue by silica gel column chromatography (eluent petroleum ether (60–90 °C)/ethyl acetate, 5/1 v/v) afforded the desired product 2 as a brown solid (2.09 g, 55% yield). Mp: >300 °C dec. Anal. Calcd for C₉H₆Cl,F₆N₂: C, 27.67; H, 1.58; N, 12.09. Found: C, 27.64; H, 1.47; N, 12.10. HRMS (ESI-TOF): calcd for C₉H₆Cl,F₆N₂, [M + H]+ 323.0655, found 323.0661.

Synthesis of Compound 3. Under a nitrogen atmosphere, a mixture of (1.27 g, 10.8 mmol), 1,1,1,5,5,5-hexafluoro-2,4-dione (1.87 g, 9.0 mmol), and CF₃COOH (75 μL, 5 mol %) in 50 mL of THF was stirred under reflux for 12 h. After the mixture was cooled to ambient temperature, all of the volatiles were removed under reduced pressure. Purification of the resultant residue by silica gel column chromatography (eluent petroleum ether (60–90 °C)/ethyl acetate, 10/1 v/v) afforded the desired product 3 as a white solid (3.36 g, 95% yield). Mp: 160–162 °C. 1H NMR (CDCl₃, 400 MHz): δ 73.48 (t, J = 8.2 Hz and J = 7.9 Hz, 1 H, 4-H), 7.06 and 6.43 (each, J = 8.2 Hz and J = 7.7 Hz, 1:1 H, 3-H and 5-H), 6.24 (s, 1 H, 1-H), 5.92 (s, 1 H, 4-H), 3.90 (s, 2 H, 2-H′), 2.53 and 2.24 (each, 3:3 H, methyl of pyrazolyl). 13C{1H} NMR (CDCl₃, 100 MHz): δ 136.9 and 151.8 (Cq each, C2 and C6), 149.5 and 140.9 (Cq each, C3 and C5′), 139.5, 108.6, and 105.6 (pyridyl CH), 103.7 (Ct), 14.5 and 13.6 (methyl of pyrazolyl). HRMS: calcd for C₃H₆Cl,F₆N₂, 2013.2011, found 2013.2074.

Synthesis of Complex 6. Under a nitrogen atmosphere, a mixture of (410 mg, 0.77 mmol), PPh₃ (184 mg, 0.77 mmol), and triethylamine (1.7 mL in EtOH (15 mL) was stirred at 60 °C for 3 h. After the mixture was cooled to ambient temperature, all of the volatiles were removed under reduced pressure. Purification of the resultant residue by silica gel column chromatography (eluent dichloromethane/methanol, 40/1 v/v) afforded crude 6, which was further purified by recrystallization in CHCl₃/n-hexane (1/3 v/v) at −20 °C to give 6 as a deep red-brown solid (312 mg, 55% yield). Mp: >300 °C dec. 1H NMR (CDCl₃, 400 MHz): δ 77.71 (m, 1 H, 4-H), 7.56 and 7.47 (d each, J = 7.7 Hz and J = 7.3 Hz, 1:1 H, 3-H and 5-H), 7.32 (s, 1 H, 1-H), 7.50–7.30 (3 m, 10 H), 2.83 and 2.60 (each, 3:3 H, methyl of pyrazolyl). 13C{1H} NMR (CDCl₃, 100 MHz): δ 160.3 and 155.0 (Cq each, C2 and C6), 153.1 and 146.4 (Cq each, C3 and C5), 148.5 and 136.0 (q and Cq each, C3 and C5′), 137.1, 116.6, and 118.5 (pyridyl CH), 135.0 (C4′), 134.9, 131.4, and 129.7 (CH of PPh₃), 134.6 (Cq, PPh₃), 120.5 and 120.0 (and Cq, J = 270.8 Hz and J = 266.8 Hz, C4′), 110.4 (C4′), 169 (s) and 16.2 (s) (methyl of pyrazolyl). 19P{1H} NMR (CDCl₃, 400 MHz): δ −58.40 and −58.42 (each, Cq, C3′). 31P{1H} NMR (CDCl₃, 162 MHz): δ 38.9 (s, PPh₃). Anal. Calcd for C₉H₆Cl,F₆N₂PPh₃: C, 31.10; H, 2.02; N, 12.18. Found: C, 31.06; H, 2.07; N, 12.31.

Synthesis of Compound 8. Under a nitrogen atmosphere, a mixture of 2,6-dibromopyrididine (7; 23.70 g, 100.0 mmol) and 25 mL of hydrazine hydrate in 25 mL of nBuOH was stirred at 120 °C for 12 h. After the mixture was cooled to ambient temperature, all of the volatiles were removed under reduced pressure to give a crude product which was subject to recrystallization in EtOAc/methanol (5/1 v/v) at −4 °C to afford 8 as a brown solid (12.53 g, 67% yield). Mp: 109–111 °C. 1H NMR (CDCl₃, 400 MHz): δ 8.63 (s, 1 H, 1′-H), 7.44 (t, 1 H, J = 8.3 Hz and J = 7.4 Hz, 4-H), 7.09 and 6.83 (each, J = 8.3 Hz and J = 7.4 Hz, 1:1 H, 3-H and 5-H), 4.05 (s, 2 H, 2′-H). 13C{1H} NMR (CDCl₃, 100 MHz): δ 158.2 and 139.1 (Cq each, C2 and C6), 140.2 (C4′), 117.4 and 105.3 (C3 and C5). HRMS: calcd for C₃H₆Cl₂F₆N₄, 186.9745, found 186.9749.

Synthesis of Compound 9. Under a nitrogen atmosphere, a mixture of (8; 8.98 g, 40.0 mmol), 1,1,1,5,5,5-hexafluoro-2,4-dione (8.08 g, 40.0 mmol), and CF₃COOH (0.3 mL, 5 mol %) in 100 mL of THF was stirred under reflux for 12 h. After the mixture was cooled to ambient temperature, all of the volatiles were removed under reduced pressure. Purification of the resultant residue by silica gel column chromatography (eluent petroleum ether (60–90 °C)/diethyl ether, 50/1 v/v) afforded 9 as a white solid (14.63 g, 97% yield). Mp: 32–33 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.74 (t, J = 9.6 Hz and J = 8.0 Hz, 1 H, 4-H), 7.40 and 7.27 (each, J = 9.6 Hz and J = 7.7 Hz, 1:1 H, 3-H and 5-H), 3.89 and 3.58 (each, J = 19.6 Hz, 1 H, 4-H), 3.12 (s, 1 H, OH). 13C{1H} NMR (CDCl₃, 100 MHz): δ 154.5 and 137.8 (Cq each, C2 and C6), 141.2 and 94.3 (q
and Cq each, J = 7.7 Hz and J = 7.7 Hz, 1 H, 4-H), 7.98 and 7.79 (d each, J = 8.0 Hz and J = 7.7 Hz, 1 H, 4-H), 7.92 and 7.69 (d each, J = 7.4 Hz and J = 8.1 Hz, 1 H, 3-H and 5-H).$^{13}$C{1H} NMR (CD3COCD3, 100 MHz): $\delta$ 149.9 and 139.0 (Cq each, C2 and C6), 143.1 and 134.0 (q and Cq each, J = 39.8 Hz and J = 42.2 Hz, C3′ and C3′), 142.2, 128.8, and 115.5 (pyridyl CH), 120.4 and 119.1 (q and Cq, J = 267.0 Hz and J = 267.0 Hz, CF3), 109.9 (C4′).$^{19}$F{1H} NMR (CD3COCD3, 400 MHz) $\delta$ −59.4 and −64.0 (s each, CF3). HRMS: calculated for C6H5BrF6N3=0.0921.

Synthesis of Compound 10. Under a nitrogen atmosphere, a mixture of 7 (3.4 g, 10.0 mmol) and concentrated H2SO4 (ca. 2 mL) in 40 mL of HOAc was stirred at 120 °C for 5 h. After the mixture was cooled to ambient temperature, all of the volatiles were removed under reduced pressure, and the resultant residue was neutralized by saturated aqueous Na2CO3, washed with 20 mL of water, and extracted with dichloromethane (3 × 15 mL). All of the volatiles were removed under reduced pressure, and the resulting residue was subject to purification by silica gel column chromatography (eluent petroleum ether (60–90 °C)/diethyl ether, 100/1 v/v) to afford 10 as a white solid (7.04 g, 98% yield). Mp: 45-46 °C. $^{1}H$ NMR (CD3COCD3, 400 MHz): $\delta$ 8.06 (t, $J$ = 7.9 Hz and J = 7.7 Hz, 1 H, 4-H), 8.42 (m, 1 H, 3-H), 8.02 and 7.85 (d each, J = 8.0 Hz and J = 8.1 Hz, 1 H, 3-H and 5-H), 7.65 and 7.39 (m each, 2.2 H, aromatic CH of benzimidazolyl), 3.86 (N-Me).$^{13}$C{1H} NMR (CD3COCD3, 100 MHz): $\delta$ 150.8 and 148.6 (Cq each, C2 and C6), 148.6 (C4′), 143.4, 141.4, and 136.0 (Cq each, C2′, C4′ and C9′), 142.3 and 133.3 (q and Cq each, J = 37.9 Hz and J = 40.1 Hz, C3′ and C5′), 139.8, 125.5, and 123.4 (pyridyl CH), 120.4 and 119.1 (q and Cq, J = 268.5 Hz and J = 268.7 Hz, CF3), 122.5, 120.0, 113.8, and 110.4 (aromatic CH of benzimidazolyl), 30.15 (N-Me).$^{19}$F{1H} NMR (CD3COCD3, 400 MHz): $\delta$ −57.6 and −62.0 (s each, CF3).

HRMS: calculated for C21H16F4N3, found 411.0919, found 411.0921.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones. The catalyst solution was prepared by dissolving compound 6 (32.3 mg, 0.044 mmol) in 2-propanol (20.0 mL). Under a nitrogen atmosphere, a mixture of ketone (2.0 mmol), 2.0 mL of the catalyst solution (0.004 mmol), and 2-propanol (17.4 mL) was stirred at 82 °C for 10 min. Then, 0.6 mL of 0.1 M iPrOK (0.06 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 concentrated 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

Text, figures, tables, and a CIF file giving experimental procedures, analytical data, and NMR spectra of the new compounds and X-ray crystallographic data for 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The 31P{1H} NMR spectrum revealed a resonance signal at 28.6 ppm after the complex was reduced in situ in the presence of PPh3, which is deemed as a clue for the formation of the Ru(II)−PPh3 species (see the Supporting Information for details).