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# Substituent Effect on the Catalytic Activity of Ruthenium(II) Complexes Bearing a Pyridyl-Supported Pyrazolyl-Imidazolyl Ligand for Transfer Hydrogenation of Ketones

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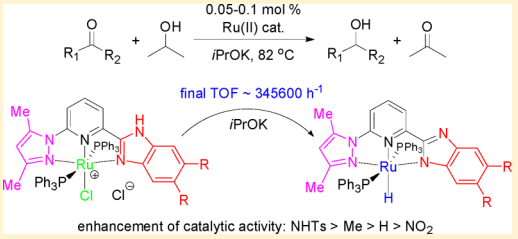
Supporting Information

**ABSTRACT:** Air- and moisture-stable ruthenium(II) complexes bearing a multisubstituted pyrazolyl-imidazolyl-pyridine ligand were synthesized and structurally characterized by NMR and X-ray single-crystal crystallographic analyses. The substituents on the imidazolyl moiety of the NNN ligand exhibited a remarkable impact on the catalytic activity of the corresponding Ru(II) complexes for transfer hydrogenation of ketones in refluxing 2-propanol, following the order NHTs > Me > H > $NO_2$, to tune the catalytic activity. The highest final TOF value of 345 600 $h^{-1}$ was reached by means of 0.05 mol % of the Ru(II)-NHTs-substituted NNN complex as the catalyst. The corresponding structurally confirmed RuH complexes are proposed as the catalytically active species.




## INTRODUCTION

Transition-metal-catalyzed transfer hydrogenation (TH)[1] of unsaturated C═O and C═N bonds using 2-propanol or formic acid as the hydrogen source has been well explored as a robust protocol.[2] The Noyori Ru(II) complexes containing a monotosylated 1,2-diamine[3] or amino alcohol[4] ligand have been used as the most powerful catalysts in the asymmetric transfer hydrogenation of ketones and imines. Baratta et al. reported the versatile ruthenium(II) 2-aminomethylpyridine (ampy) complexes, which had demonstrated efficient catalytic activity in (asymmetric) transfer hydrogenation of ketones.[5] The complexes bearing a ligand with an NH functionality usually exhibit high catalytic activity in the transfer hydrogenation reactions.[6] Although various types of ligands and their transition-metal complexes featuring no NH functionality have also been developed for the same purpose,[7] development of highly active catalytic systems is still strongly desired. Recently, polydentate nitrogen-containing ligands such as 2,6-bis(immino)pyridines,[8a−c] 2,2′:6′,2″-terpyridines (terpy),[8d−f] and 2,6-bis(oxazolinyl)pyridines (pybox)[8g,h] have attracted more and more attention for their tunable properties and potential applications in homogeneous catalysis and organic synthesis. These kinds of ligands usually feature two symmetrical coordinating arms. However, unsymmetrical polydentate ligands have also been applied due to the higher catalytic activity of their transition-metal complexes attributed to the hemilabile properties of the ligands.[9] In general, NNN ligands can be conveniently prepared and structurally modified, and their corresponding transition-metal complexes are usually reactive and air- and moisture-stable, suggesting that they might be used as efficient homogeneous catalysts.

During our ongoing study on Ru(II)-NNN complex catalysts for transfer hydrogenation of ketones, we have found that Ru(II) complex catalysts bearing an unsymmetrical pyridyl-based NNN ligand can exhibit very high catalytic activity.[9e,f,10] Ru(II) complexes bearing a symmetrical 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine ligand (**A**)[11] or a unsymmetrical bis(trifluoromethyl)pyrazolyl-pyridyl-based ligand (**B**)[10b] were synthesized and showed good catalytic activity in the transfer hydrogenation of ketones in refluxing 2-propanol, and the latter performed more efficiently than the former. Both cationic and neutral Ru(II) complexes **C** and **D** demonstrated very good catalytic activity for transfer hydrogenation of ketones under the same conditions.[9f] Intrigued by the catalytic activity difference between complexes **A** and **B** and the structural features of complexes **C** and **D**, we reasonably envisioned that tuning the electronic property of the ligand in complexes of type **C** or **D** may alter the catalytic activity of the corresponding complexes for transfer hydrogenation of ketones (Chart 1). Herein, we report the synthesis of Ru(II) complexes **4**−**6** bearing a pyridyl-based NNN ligand containing a coordinative disubstituted imidazolyl moiety and their catalytic behaviors in the TH reactions of ketones.

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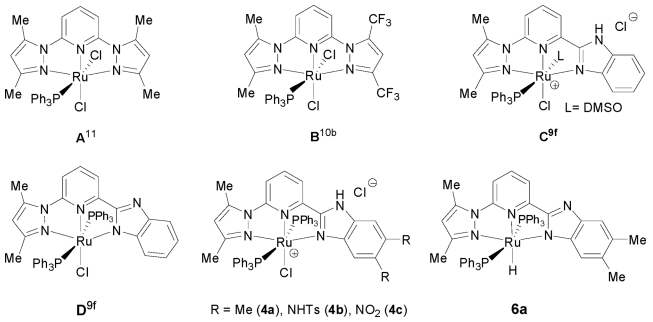
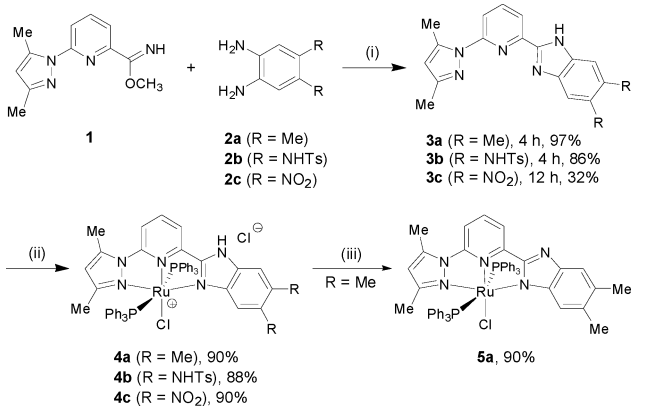
**Chart 1. Ruthenium(II)-NNN Complex Catalysts**




## RESULTS AND DISCUSSION

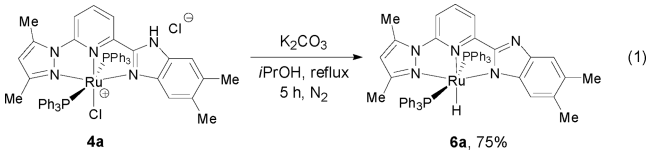
**Synthesis of Ligands and Their Ru(II) Complexes.** Condensation of 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-picolinimidate (**1**)[10d] with 4,5-dimethylbenzene-1,2-diamine (**2a**), *N*,*N*′-(4,5-diamino-1,2-phenylene)bis(4-methylbenzene-sulfonamide) (**2b**),[12] and 4,5-dinitrobenzene-1,2-diamine (**2c**)[12a,13] in the presence of glacial acetic acid afforded **3a** (97%), **3b** (86%), and **3c** (32%), respectively. Ligands **3a** and **3b** were efficiently prepared, but **3c** was obtained in only a low yield by extending the reaction time. Reacting equimolar amounts of ligand **3** with $RuCl_2(PPh_3)_3$ in refluxing 2-propanol gave Ru(II) complexes **4a**–**c** in 88–90% yields. Ionic complex **4a** was further converted to the corresponding neutral complex, that is, complex **5a**, by means of $K_2CO_3$ base to remove one molecule of HCl from **4a** (Scheme 1). Treatment of **4a** with

**Scheme 1. Synthesis of Ligands and Complexes 4 and 5a**[a]




[a]Legend: (i) HOAc, 118 °C, 4–12 h, 0.1 MPa $N_2$; (ii) $Ru(PPh_3)_3Cl_2$, *i*PrOH, 82 °C, 4 h, 0.1 MPa $N_2$; (iii) $K_2CO_3$, $CH_2Cl_2$, 40 °C, 4 h, 0.1 MPa $N_2$.

$K_2CO_3$ in 2-propanol afforded RuH complex **6a** in 75% yield, suggesting that consecutive dehydrochlorination/reduction occurred (eq 1). It is noted that, starting from **5a** under the same conditions, complex **6a** was also obtained in a similar yield.




(1)

**Characterization of Ru(II) Complexes 4–6.** The NMR analyses of complexes **4**–**6** are consistent with their compositions. In the $^1H$ NMR spectra, the proton resonances of the NH functionality in ligand **3a** and its Ru(II) complex **4a** were shown as singlets at 12.31 and 15.20 ppm, respectively, while these signals disappeared in those of neutral complexes **5a** and **6a**, revealing formation of a Ru–N bond in the complexes under basic conditions. The $^{31}P$ NMR resonances of complexes **4a**–**c** and **5a** appeared at 20.4, 23.5, 19.0, and 22.4 ppm, respectively, suggesting the presence of two equivalent $PPh_3$ ligands positioned *trans* to each other in the complexes. Complex **5a** showed a 2.0 ppm increment in its $^{31}P$ NMR spectrum as compared to that of **4a**, which is in accordance with our previous observation[9f,10] and suggests a change of the coordination pattern of the benzimidazolyl nitrogen atom in **5a** through extrusion of HCl from **4a**. The $^1H$ and $^{31}P$ NMR spectra of **6a** exhibited a triplet at −6.84 ppm for Ru–H and a doublet at 43.3 ppm for its two $PPh_3$ ligands, respectively.

The solid-state molecular structures of complexes **4b** and **6a** were confirmed by X-ray crystallographic studies (Figures 1 and

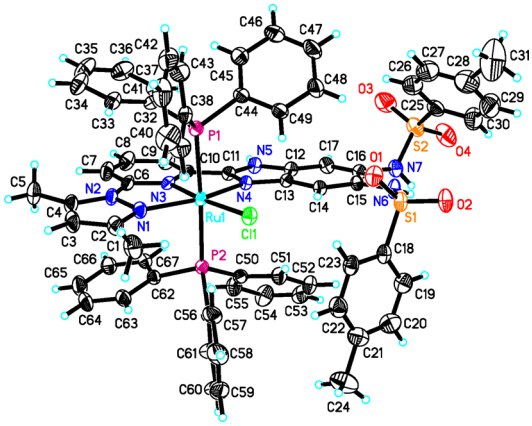


**Figure 1.** Molecular structure of complex **4b**. Thermal ellipsoids are set at 30% probability. Two chloroform molecules are omitted for clarity.

2). In the solid state, the central ruthenium atom of complex **4b** is situated in a distorted octahedral environment surrounded by tridentate NNN ligand **3b**, two *trans* $PPh_3$, and a chloro ligand

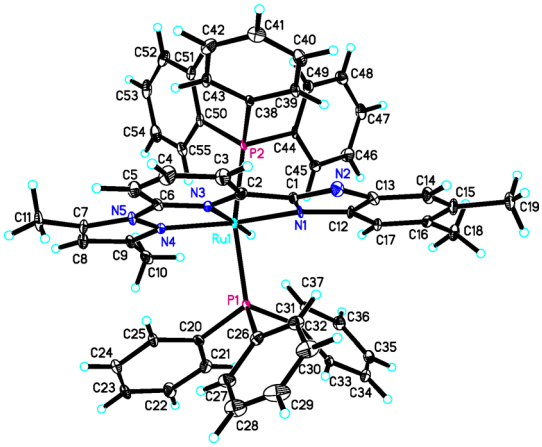


**Figure 2.** Molecular structure of complex **6a**. Thermal ellipsoids are set at 30% probability.



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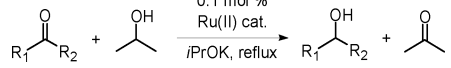
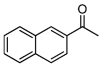
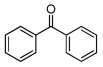
positioned *trans* to the pyridyl nitrogen atom, with another dissociated chloride anion nearby (Figure 1). The P–Ru–P angle in **4b** is 177.3°, revealing that the two $PPh_3$ ligands are almost vertically situated at the two sides of the ligand plane. The molecular structure of complex **6a** is similar to that of **4b**, but with a discrete Ru–H bond (1.28 Å). Such a Ru–H bond is shorter than those reported (~1.53 Å).[9e,10b] The P–Ru–N (85.65–102.68°), P(1)–Ru–P(2) (159.73°), and N(3)–Ru–H (176.10°) angles, two Ru–P bonds (2.316 and 2.318 Å), and three Ru–N bonds (2.067–2.109 Å) also reveal a distorted six-coordinated metal center in complex **6a**. It is noteworthy that the average Ru–P bond length in complex **4b** (2.399 Å) is a little bit longer than that in complex **D** (2.391 Å),[9f] suggesting that the Ru(II) center of complex **4b** is in a more loose environment than that in complex **D**, and complex **4b** may be more catalytically active than complex **D**.

**Transfer Hydrogenation of Ketones.** Under the typical conditions for transfer hydrogenation of ketones (82 °C, 0.1 M ketone in 2-propanol), the TH reactions of various ketones was conducted by means of complexes **4a–c** as the catalysts (Table 1). Alcohols were produced as the sole products in the presence of *i*PrOK base and 0.1 mol % of the complex catalyst in refluxing 2-propanol under a nitrogen atmosphere. Due to the substituent effect from the functional groups on the imidazolyl moiety of the NNN ligand, complexes **4a–c** demonstrated various catalytic activity different from that of complex **D**. Among all the explored complexes, that is, **4a–c** and **D**, complex **4b**, bearing two NHT substituents on the imidazoly moiety of its ligand, exhibited the highest catalytic activity, **4a**, containing an NNN ligand with a $Me_2$-imidazolyl functionality, showed a catalytic activity lower than **4b**, but higher than complex **D**, bearing a unsubstituted imidazolyl-containing NNN ligand, whereas complex **4c**, bearing an $(NO_2)_2$-imidazoly pyridyl-pyrazolyl ligand, that is, ligand **3c**, exhibited the lowest catalytic activity (Table 1). A remarkable substituent effect was thus observed. The stronger electron-donating capability of NHT functionalities than that of methyl groups renders complex **4b** more catalytically active than complex **4a**,[14] while introduction of electron-withdrawing $NO_2$ groups to ligand **3c** deteriorates the catalytic activity of complex **4c**. The capability for these substituents to enhance the catalytic activity of the Ru(II)-NNN complexes is consistent with the electron-donating property of the substituents, following the order NHTs > Me > H > $NO_2$. The catalytic activity order of the complexes is **4b** > **4a** > **D** > **4c**, revealing that introduction of electron-donating substituents onto the coordinative imidazolyl arm of the NNN ligands of type **3** enhances the catalytic activity of complexes **4**.

Due to the highest catalytic activity of complex **4b**, it was applied as the catalyst to explore the substrate scope in the transfer hydrogenation of ketones (Table 2). Under the stated conditions, acetophenone was converted to the corresponding alcohol within 30 s, reaching a final TOF value of 116 400 $h^{-1}$ (Table 1, entry 1), while propiophenone exhibited a lower reactivity (Table 2, entry 1). A variety of substituted acetophenones, aryl alkyl ketones, and aliphatic ketones were also reacted to give the alcohol products. In most of the cases, the reactions reached ≥96% conversions for the ketones over a period of 20 s to 15 min. Substituents such as chloro, bromo, fluoro, trifluoromethyl, methyl, and methoxy were tolerated on the aryl groups of the ketone substrates, and they demonstrated various electronic and steric effects (Tables 1 and 2). Lowering the catalyst loading to 0.05 mol % still rendered the TH

**Table 1. Catalytic Activity of Complexes 4 and D for Transfer Hydrogenation of Ketones[a]**




| entry | Ru(II) cat. | ketone | time (min) | conversion[b] (%) | final TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 | **4a** |  | 10 | 97 | 5820 |
| | **4b** | | 1/2 | 97 | 116400 |
| | **4c** | | 60 | 92 | 920 |
| | **D** | | 15[c] | 97[c] | 3880[c] |
| 2 | **4a** |  | 60 | 95 | 950 |
| | **4b** | | 20 | 95 | 2850 |
| | **4c** | | 240 | 77 | 193 |
| | **D** | | 180[c] | 95[c] | 317[c] |
| 3 | **4a** |  | 1/2 | 100 | 120000 |
| | **4b** | | 1/3 | 99 | 178200 |
| | **4c** | | 5 | 96 | 11520 |
| | **D** | | 3 | 96 | 19200 |
| 4 | **4a** |  | 5 | 96 | 11520 |
| | **4b** | | 3 | 96 | 19200 |
| | **4c** | | 10 | 94 | 5640 |
| | **D** | | 10[c] | 96[c] | 5760[c] |
| 5 | **4a** |  | 5 | 98 | 11760 |
| | **4b** | | 1 | 98 | 58800 |
| | **4c** | | 60 | 94 | 940 |
| | **D** | | 15[c] | 99[c] | 3960[c] |
| 6 | **4a** |  | 3 | 98 | 19600 |
| | **4b** | | 2 | 98 | 29400 |
| | **4c** | | 120 | 84 | 420 |
| | **D** | | 5[c] | 98[c] | 11760[c] |
| 7 | **4a** |  | 120 | 94 | 470 |
| | **4b** | | 5 | 98 | 11760 |
| | **4c** | | 240 | 59 | 148 |
| | **D** | | 240[c,d] | 94[c,d] | 118[c,d] |

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); catalyst, 0.1 mol %; ketone/*i*PrOK/Ru(II) cat. = 1000:20:1; 0.1 MPa $N_2$, 82 °C. [b]Determined by GC analysis. [c]Cited from ref 9f. [d]Using 0.2 mol % catalyst.

reactions of *p*-, *m*-, and *o*-chloroacetophenones to efficiently form the target alcohol products, reaching the highest final TOF value of 345 600 $h^{-1}$ (Table 2, entries 2–4). Coordinatively saturated complex **4b** is a highly active Ru(II) complex catalyst for TH of ketones,[5,9,10] but it is noted that the related unsaturated Ru(II) complex reached a final TOF value of 720 000 $h^{-1}$ under the same conditions.[10h]

**Reaction Mechanism.** In order to investigate the reaction mechanism, the catalytic behaviors of complexes **4a**, **5a**, and **6a** were comparatively tested in the TH reactions of acetophenone, 2′-chloroacetophenone, and 2′-methyl acetophenone (Scheme 2), respectively. Under the standard conditions as shown in Table 2, the three complexes almost exhibited the same catalytic activity. On the basis of the present experimental results and those previously observed,[9e,f,10b] RuH complexes of type **6** are proposed as the catalytically active species[15] for the



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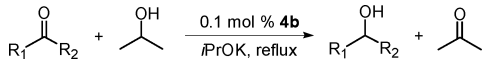
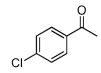
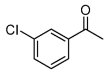
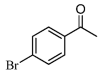
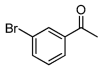
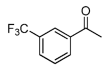
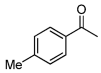
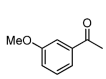
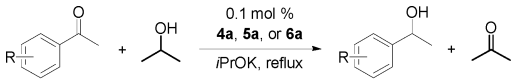
**Table 2. Transfer Hydrogenation of Ketones Catalyzed by 4b**[a]




| entry | ketone | time (min) | conversion[b] (%) | final TOF ($h^{-1}$) |
|---|---|---|---|---|
| 1 |  | 3 | 99 | 19800 |
| 2 |  | 1/2[c] | 98[c] | 235200[c] |
| 3 |  | 1/3 (15)[c] | 100 (95)[c] | 180000 (7600)[c] |
| 4 |  | 1/3 (1/3)[c] | 100 (96)[c] | 180000 (345600)[c] |
| 5 |  | 30 | 95 | 1900 |
| 6 |  | 5 | 97 | 11640 |
| 7 |  | 15 | 96 | 3840 |
| 8 |  | 15 | 96 | 3840 |
| 9 |  | 2 | 99 | 29700 |
| 10 |  | 10 | 95 | 5700 |
| 11 |  | 15 | 97 | 3880 |
| 12 |  | 20 | 95 | 2850 |
| 13 |  | 5 | 97 | 11640 |
| 14 |  | 30 | 97 | 1940 |
| 15 |  | 15 | 95 | 3800 |
| 16 |  | 10 | 95 | 5700 |

[a]Conditions: ketone, 2.0 mmol (0.1 M in 20 mL of *i*PrOH); cat. **4b**, 0.1 mol %; ketone/*i*PrOK/**4b** = 1000:20:1; 0.1 MPa $N_2$, 82 °C. [b]Determined by GC analysis. [c]Using 0.05 mol % catalyst.

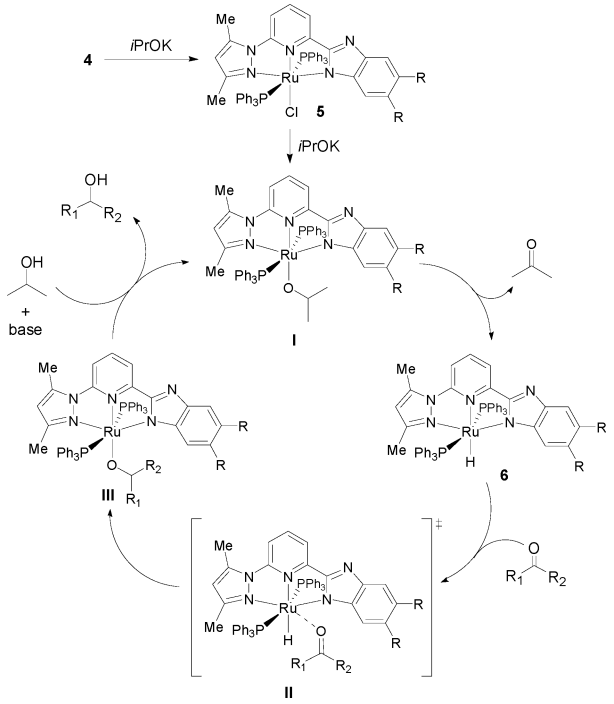
**Scheme 2. Comparative Experiments**




| | time (min) | conversion of ketone (%) using 4a | using 5a | using 6a |
|---|---|---|---|---|
| R = H | 10 | 97 | 97 | 97 |
| R = *o*-Cl | 1/2 | 100 | 100 | 98 |
| R = *o*-Me | 60 | 94 | 94 | 93 |

TH reactions, involving a plausible inner-sphere pathway.[16] The TH reaction initially starts from the dehydrochlorination of complex **4** by *i*PrOK base, forming complex **5**. The potassium alkoxide reacts with complex **5** to give an R(II)-alkoxide intermediate species of type **I**, which undergoes $\beta$-H elimination to generate the RuH complex. Complex **6** acts as the catalytically active species to catalyze the reduction of ketone via an inner-sphere pathway.

**Scheme 3. Proposed Mechanism**




## CONCLUSIONS

In summary, Ru(II) complexes bearing an unsymmetrical pyrazolyl-substituted imidazolyl-pyridine ligand have exhibited different catalytic activity in the TH reactions of ketones. The substituent effect from the functional groups on the imidazolyl moiety of the ligand follows the order NHTs > Me > H > $NO_2$. Introduction of electron-donating NHTs and Me groups onto the coordinative imidazolyl arm of the ligand remarkably enhances the catalytic activity of the corresponding Ru(II) complex catalysts. The structurally characterized RuH complex is proposed to be the catalytically active species.

## EXPERIMENTAL SECTION

**General Considerations.** The solvents were dried and distilled prior to use by the literature methods. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker DRX-400 spectrometer, and all chemical shift values refer to $\delta_{TMS}$ = 0.00 ppm, $CDCl_3$ ($\delta$($^1$H), 7.26 ppm; $\delta$($^{13}$C), 77.16 ppm) and DMSO-$d_6$ ($\delta$($^1$H), 2.50 ppm; $\delta$($^{13}$C), 39.52 ppm). Elemental and HRMS analysis were achieved by the Analysis Center, Dalian University of Technology and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. All 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. All chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

**X-ray Crystallographic Studies.** The X-ray single-crystal structures of complexes **4b** and **6a** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Cell parameters were obtained by global refinement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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 1003352 for **4b** and CCDC 1003351 for **6a**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

*General Procedure for the Synthesis of Ligands **3**: Synthesis of **3a***. A solution of methyl 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-picolinimidate (**1**) (230 mg, 1.0 mmol) and 4,5-dimethylbenzene-1,2-diamine (**2a**) (136 mg, 1.0 mmol) in 10 mL of glacial acetic acid was refluxed under a nitrogen atmosphere for 4 h. The cooled solution was diluted with water and neutralized with concentrated aqueous ammonia (25%, 5 mL). The precipitate was collected and dried under vacuum to afford **3a** as a brown solid (310 mg, 97% yield). Mp: 199−200 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 12.31 (s, 1 H, NH), 8.19 and 7.80 (d each, $J$ = 7.2 and 7.6 Hz, 1:1 H, 3-H and 5-H), 8.05 (t, $J$ = 7.8 Hz, 1 H, 4-H), 7.49 and 7.39 (s each, 1:1 H, 8″-H and 5″-H), 6.14 (s, 1 H, 4′-H), 2.73 (s, 3 H, C3′-$CH_3$), 2.22 (s, 3 H, C5′-$CH_3$), 2.33 (s, 6 H, C6″-$CH_3$ and C7″-$CH_3$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$, 100 MHz): $\delta$ 152.5 and 149.1 (Cq each, C2 and C6), 147.1 and 141.2 (Cq each, C3′ and C5′), 142.5 and 133.5 (Cq each, C4″ and C9″), 139.8 (C4), 132.1 and 130.5 (Cq each, C7″ and C6″), 119.3 and 112.2 (C8″ and C5″), 118.6 and 116.4 (C3 and C5), 108.8 (C4′), 20.1(C7″-$CH_3$), 20.0 (C6″-$CH_3$) 14.0 (C3′-$CH_3$), 13.3 (C5′-$CH_3$). HRMS: calcd for $C_{19}H_{19}N_5$ 317.1640, found 317.1638.

*Synthesis of **3b***. In a fashion similar to the synthesis of **3a**, **1** (377 mg, 1.6 mmol) reacted with *N*,*N*′-(4,5-diamino-1,2-phenylene)bis(4-methylbenzenesulfonamide) (**2b**) (730 mg, 1.6 mmol) to form **3b** as a brown solid (890 mg, 86% yield). Mp: 168−169 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 12.48 (s, 1 H, NH), $\delta$ 9.21 (br, 2 H, 6″-NH and 7″-NH), 8.11 and 7.81 (d each, $J$ = 7.0 and 8.0 Hz, 1:1 H, 3-H and 5-H), 8.04 (t, $J$ = 7.9 Hz, 1 H, 4-H), 7.39 and 7.19 (s each, 1:1 H, 8″-H and 5″-H), 7.62 (m, 4 H, 4‴-H), 7.34 (d, $J$ = 8.2 Hz, 4 H, 5‴-H), 6.14 (s, 1 H, 4′-H), 2.68 (s, 3 H, C3′-$CH_3$), 2.21 (s, 3 H, C5′-$CH_3$), 2.33 (s, 6 H, C6‴-$CH_3$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$, 100 MHz): $\delta$ 152.6 and 151.4 (Cq each, C2 and C6), 149.3 and 141.2 (Cq each, C3′ and C5′), 146.1 (Cq, C2″), 143.6 and 135.9 (Cq each, C4″ and C9″), 140.0 (C4), 135.6 and 125.2 (Cq each, C7″ and C6″), 133.0 (Cq, C3‴), 127.7 (Cq, C6‴), 129.7 (C4‴), 127.1 (C5‴), 118.9 and 117.1 (C3 and C5), 115.4 and 107.1 (C8″ and C5″), 109.0 (C4′), 20.1 (C6‴-$CH_3$), 14.0 (C3′-$CH_3$), 13.3 (C5′-$CH_3$). HRMS: calcd for $C_{31}H_{29}N_7O_4S_2$ 627.1722, found 627.1708.

*Synthesis of **3c***. In a fashion similar to the synthesis of **3a**, **1** (285 mg, 1.2 mmol) reacted with 4,5-dinitrobenzene-1,2-diamine (**2c**) (245 mg, 1.2 mmol) to give a brown solid, which was subject to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/ethyl acetate: 1:20, v/v), affording **3c** as a yellow solid (150 mg, 32% yield). Mp: 251−252 °C. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 13.60 (s, 1 H, NH), 8.48 (s, 1:1 H, 5″-H and 8″-H), 8.30 and 7.96 (d each, $J$ = 7.6 and 8.1 Hz, 1:1 H, 3-H and 5-H), 8.20 (t, $J$ = 7.9 Hz, 1 H, 4-H), 6.20 (s, 1 H, 4′-H), 2.73 (s, 3 H, C3′-$CH_3$), 2.24 (s, 3 H, C5′-$CH_3$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$, 100 MHz): $\delta$ 156.5 and 152.6 (Cq each, C2 and C6), 149.3 and 141.1 (Cq each, C3′ and C5′), 144.7 and 144.7 (Cq each, C4″ and C9″), 140.1 (C4), 138.4 and 138.4 (Cq each, C7″ and C6″), 118.3 and 118.3 (C8″ and C5″), 119.8 and 113.5 (C3 and C5), 108.8 (C4′), 13.5 (C3′-$CH_3$), 13.0 (C5′-$CH_3$). HRMS: calcd for $C_{17}H_{13}N_7O_4$ 379.1029, found 379.1020.

*General Procedure for the Synthesis of **4**: Synthesis of **4a***. Under a nitrogen atmosphere, a mixture of $RuCl_2(PPh_3)_3$ (437 mg, 0.5 mmol) and **3a** (145 mg, 0.5 mmol) in 2-propanol (10 mL) was refluxed for 3 h, forming a red-brown microcrystalline solid. After cooling to ambient temperature, the precipitate was filtered off, washed with diethyl ether (3 × 10 mL), and dried under vacuum to afford **4a** as a red-brown crystalline solid (423 mg, 90% yield). Mp: >320 °C dec. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 15.20 (s, 1 H, NH), 8.62 and 6.64 (d each, $J$ = 7.8 and 8.3 Hz, 1:1 H, 3-H and 5-H), 8.08 and 7.39 (s each, 1:1 H, 8″-H and 5″-H), 7.29 (m, 1 H, 4-H), 7.18, 7.10, and 6.93 (m each, 12:6:12 H, 2 × $PPh_3$), 5.98 (s, 1 H, 4′-H), 2.47 and 2.44 (s each, 3:3 H, C7″-$CH_3$ and C6″-$CH_3$) 2.39 (s, 3 H, C3′-$CH_3$), 2.31 (s, 3 H, C5′-$CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz): $\delta$ 157.8 and 151.7 (Cq each, C2 and C6), 151.1 and 143.4 (Cq each, C3′ and C5′), 148.9 and 134.7 (Cq each, C4″ and C9″), 141.3 (C4), 133.6 and 132.5 (Cq each, C7″ and C6″), 132.0 (Cq, 2 × $PPh_3$), 133.3, 129.2, and 127.7 (CH of 2 × $PPh_3$), 120.5 and 113.0 (C8″ and C5″), 120.0 and 113.6 (C3 and C5), 108.3 (C4′), 20.5 (C7″-$CH_3$), 20.3 (C6″-$CH_3$) 15.3 (C3′-$CH_3$), 15.2 (C5′-$CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz): $\delta$ 20.4 ($PPh_3$). IR (KBr pellets, cm$^{-1}$): $\nu$ 3418, 3052, 1609, 1556, 1481, 1466, 1414, 1385, 1326, 1282, 1188, 1159, 1091, 1029, 999, 855, 791, 745, 619. Anal. Calcd for $C_{55}H_{49}Cl_2N_5P_2Ru{\cdot}2/3C_6H_{14}$: C, 66.14; H, 5.48; N, 6.54. Found: C, 65.94; H, 5.38; N, 6.60.

*Synthesis of **4b***. In a fashion similar to the synthesis of **4a**, $RuCl_2(PPh_3)_3$ (288 mg, 0.3 mmol) reacted with **3b** (188 mg, 0.3 mmol) to afford **4b** as a brown crystalline solid (350 mg, 88% yield). Single crystals suitable for X-ray crystallographic determination were grown from the recrystallization in $CHCl_3$/*n*-hexane (1:3, v/v) at 25 °C. Mp: >300 °C dec. $^1$H NMR ($CDCl_3$/$CD_3OD$, 400 MHz): $\delta$ 8.37 (s, 1 H, 3-H), 8.22 and 7.50 (d each, $J$ = 8.2 and 8.2 Hz, 2:2 H, 4‴-H), 8.02 (d, $J$ = 7.8 Hz, 1 H, 5-H), 7.41 (t, $J$ = 8.1 Hz, 1 H, 4-H), 7.16 (d, $J$ = 8.1 Hz, 2 H, 5‴-H), 7.03 and 6.83 (m each, 20:12 H, 2 × $PPh_3$ and 5‴-H), 6.64 (d, $J$ = 8.4 Hz, 1 H, 5″-H), 6.58 (s, 1 H, 8″-H), 5.96 (s, 1 H, 4′-H), 2.60 (s, 3 H, C3′-$CH_3$), 2.36 (s, 3 H, C6‴-$CH_3$), 2.26 (s, 3 H, C6‴-$CH_3$), 1.88 (s, 3 H, C5′-$CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$/$CD_3OD$, 100 MHz): $\delta$ 161.5 and 156.1 (Cq each, C2 and C6), 154.9 and 148.3 (Cq each, C3′ and C5′), 153.5 and 148.0 (Cq each, C4″ and C9″), 148.2 (C4), 145.6 and 129.2 (Cq each, C7″ and C6″), 139.8, 138.9, 137.5, 134.6, 134.3, 133.7, 133.5, and 132.5 (phenyl C of NH*Ts*), 135.7 (Cq, 2 × $PPh_3$), 137.0, 133.2, and 131.6 (CH of 2 × $PPh_3$), 123.0 and 117.0 (C3 and C5), 115.1 and 114.2 (C8″ and C5″), 114.8 (C4′), 25.3 and 25.0 (C6‴-$CH_3$), 19.4 (C3′-$CH_3$), 18.6 (C5′-$CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$/$CD_3OD$, 162 MHz): $\delta$ 23.5 ($PPh_3$). IR (KBr pellets, cm$^{-1}$): $\nu$ 3355, 3054, 1607, 1555, 1482, 1435, 1332, 1281, 1185, 1161, 1091, 1031, 975, 936, 811, 747, 698, 665, 547, 517. Anal. Calcd for $C_{67}H_{59}Cl_2N_7O_4P_2S_2Ru{\cdot}2/3C_6H_{14}$: C, 61.72; H, 4.98; N, 7.10. Found: C, 61.46; H, 4.83; N, 7.15.

*Synthesis of **4c***. In a fashion similar to the synthesis of **4a**, $RuCl_2(PPh_3)_3$ (192 mg, 0.2 mmol) reacted with **3c** (76 mg, 0.2 mmol) to afford **4c** as a red-brown crystalline solid (199 mg, 90% yield). Mp: >300 °C dec. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.55 and 8.12 (s, 1:1 H, 5″-H and 8″-H), 7.35 (m, 2 H, 3-H and 4-H), 7.15 and 6.97 (m each, 18:12 H, 2 × $PPh_3$), 6.63 (d, $J$ = 8.3 Hz, 1 H, 5-H), 6.08 (s, 1 H, 4′-H), 2.63 (s, 3 H, C3′-$CH_3$), 2.44 (s, 3 H, C5′-$CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz): $\delta$ 157.8 and 152.3 (Cq each, C2 and C6), 143.8 and 138.4 (Cq each, C3′ and C5′), 139.2 and 139.2 (Cq each, C4″ and C9″), 133.8 (C4), 132.2 (Cq, 2 × $PPh_3$), 133.2, 129.5, and 128.0 (CH of 2 × $PPh_3$), 129.3 and 129.3 (Cq each, C6″ and C7″), 117.5 and 117.5 (C5″ and C8″), 128.0 and 113.2 (C3 and C5), 109.8 (C4′), 15.8 (C3′-$CH_3$), 15.2 (C5′-$CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 162 MHz): $\delta$ 19.0 ($PPh_3$). IR (KBr pellets, cm$^{-1}$): $\nu$ 3442, 3051, 2706, 1604, 1478, 1435, 1406, 1358, 1186, 1089, 1030, 982, 910, 838, 828, 793, 746, 530, 515, 430. Anal. Calcd for $C_{53}H_{43}Cl_2N_7O_4P_2Ru{\cdot}2/3C_6H_{14}$: C, 60.41; H, 4.65; N, 8.65. Found: C, 60.12; H, 4.52; N, 8.78.

*Synthesis of **5a***. Under a nitrogen atmosphere, a mixture of complex **4a** (51.0 mg, 0.05 mmol) and $K_2CO_3$ (67.4 mg, 0.50 mmol) in 10 mL of dichloromethane was refluxed for 5 h. After cooling to ambient temperature the reaction mixture was passed through a short pad of Celite, which was then rinsed with 5 mL of dichloromethane. All the volatiles of the combined filtrate were evaporated under reduced pressure to give **5a** as a red solid (42.5 mg, 90% yield). Mp: >300 °C dec. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.89 (s, 1 H, 3-H), 7.38 (d, $J$ = 7.8 Hz, 1 H, 4-H), 6.33 (d, $J$ = 8.2 Hz, 1 H, 5-H), 7.32 and 6.96 (m each, 1:1 H, 8″-H and 5″-H), 7.20, 7.05, and 6.89 (m each, 12:6:12 H, 2 × $PPh_3$), 5.91(s, 1 H, 4′-H), 2.48 and 2.39 (s each, 3:3 H, C3″-$CH_3$ and C5″-$CH_3$), 2.31 and 2.31 (s each, 3:3 H, C7″-$CH_3$ and C6″-


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$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 156.7 and 155.9 (Cq each, C2 and C6), 155.3 and 144.4 (Cq each, C3′ and C5′), 150.5 (C2″), 145.5 and 130.5 (Cq each, C4″ and C9″), 141.0 (C4), 131.8 (Cq, 2 × $PPh_3$), 132.7, 127.5, and 126.2 (CH of 2 × $PPh_3$), 128.4 and 128.0 (Cq each, C7″ and C6″), 118.2 and 111.3 (C8″ and C5″), 117.0 and 114.6 (C3 and C5), 103.8 (C4′), 19.8 (C7″-$CH_3$), 19.5 (C6″-$CH_3$) 14.1 (C3′-$CH_3$), 14.1 (C5′-$CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.4 ($PPh_3$). IR (KBr pellets, $cm^{-1}$): $\nu$ 3057, 2917, 1960, 1607, 1574, 1554, 1503, 1435, 1349, 1323, 1285, 1188, 1158, 1093, 1029, 996, 926, 879, 859, 819, 786, 743, 698, 660, 459, 442. Anal. Calcd for $C_{55}H_{48}ClN_5P_2Ru$: C, 67.58; H, 4.95; N, 7.16. Found: C, 67.62; H, 4.99; N, 7.10.

*Synthesis of* ***6a***. Under a nitrogen atmosphere, a mixture of complex **4a** (470 mg, 0.45 mmol) and $K_2CO_3$ (621 mg, 4.5 mmol) in 20 mL of 2-propanol was refluxed for 3 h. After cooling to ambient temperature all the volatiles were removed under reduced pressure. A 8 mL amount of dichloromethane was then added to dissolve the crude product, and the solution filtered to remove the inorganic salts. The filtrate was concentrated under reduced pressure and then layered by *n*-hexane (1:3, v/v) for recrystallization at 25 °C to give **6a** as red-brown crystals (328 mg, 75% yield). Mp: >300 °C dec. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.85 (d, $J$ = 8.0 Hz, 1 H, 3-H), 7.41 (t, $J$ = 8.0 Hz, 1 H, 4-H), 7.24 and 6.33 (s each, 1:1 H, 5-H and 5″-H), 7.07 and 6.96 (m each, 6:1:24 H, 8″-H and 2 × $PPh_3$), 5.71(s, 1 H, 4′-H), 2.64 and 1.03 (s each, 3:3 H, C3″-$CH_3$ and C5″-$CH_3$), 2.21 and 2.04 (s each, 3:3 H, C7″-$CH_3$ and C6″-$CH_3$), −6.84 (t, $J$ = 26.4 Hz, Ru−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 159.2 and 153.1 (Cq each, C2 and C6), 152.9 and 144.4 (Cq each, C3′ and C5′), 148.7 (C2″), 145.8 and 132.0 (Cq each, C4″ and C9″), 140.7 (C4), 135.7 (Cq, 2 × $PPh_3$), 133.2, 128.1, and 127.3 (CH of 2 × $PPh_3$), 128.3 and 127.9 (Cq each, C7″ and C6″), 117.8 and 110.8 (C8″ and C5″), 117.6 and 115.8 (C3 and C5), 104.6 (C4′), 20.6 (C7″-$CH_3$), 20.2 (C6″-$CH_3$) 15.7 (C3′-$CH_3$), 15.3 (C5′-$CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): $\delta$ 43.3 (d, $J$(P, H) = 25.1 Hz, $PPh_3$). IR (KBr pellets, $cm^{-1}$): $\nu$ 3646, 3049, 2916, 1895, 1600, 1552, 1497, 1477, 1433, 1347, 1324, 1293, 1184, 1155, 1089, 1025, 999, 980, 857, 745, 619, 562, 443, 413. Anal. Calcd for $C_{55}H_{49}N_5P_2Ru\cdot 2/3C_6H_{14}$: C, 70.83; H, 5.87; N, 7.00. Found: C, 70.39; H, 5.76; N, 7.15.

**Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones.** The catalyst solution was prepared by dissolving complex **4b** (13.2 mg, 0.01 mmol) in 2-propanol (50.0 mL). Under a nitrogen atmosphere, a mixture of a ketone (2.0 mmol), 10.0 mL of the catalyst solution (0.002 mmol), and 2-propanol (9.6 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 by a syringe 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 subject to purification by silica gel column chromatography to afford the alcohol product, which was identified by comparison with the authentic sample through NMR and GC analyses.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00727.

NMR spectra of the new compounds (PDF)
X-ray crystallographic data for **4b** (CIF)
X-ray crystallographic data for **6a** (CIF)
All computed molecule Cartesian coordinates in a format for convenient visualization (XYZ)

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### Notes

The authors declare no competing financial interest.

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