Construction of Highly Active Ruthenium(II) NNN Complex Catalysts Bearing a Pyridyl-Supported Pyrazolyl-Imidazolyl Ligand for Transfer Hydrogenation of Ketones

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A family of hemilabile ruthenium(II) NNN complexes bearing a unsymmetrical 2-(benzoimidazol-2-yl)-6-(pyrazol-1-yl)pyridine ligand has been synthesized and exhibited good to excellent catalytic activity in transfer hydrogenation of ketones in refluxing 2-propanol, reaching final TOFs up to 7.2×10^5 h^{-1} with 0.05 mol % loading. The γ-NH effect of the benzoimidazol-2-yl moiety in the ligand and coordination modes of the metal center in a Ru(II) NNN complex has great influence on the catalytic activity of the complex catalyst in transfer hydrogenation of ketones. It has been demonstrated that one of the structural prerequisites for an active Ru(II) complex catalyst is the coordinatively unsaturated environment around the metal center in the complex or the precatalyst, and the catalytic activity of a complex catalyst can be enhanced by making its metal center cationic. This paper presents a methodology to construct new types of efficient Ru(II) complex catalysts for transfer hydrogenation of ketones.

Introduction

Hydrogen transfer (HT) catalysis is an attractive protocol for reduction of ketones to alcohols and has been extensively studied.[1] Ruthenium(II) complexes are usually applied as the most useful catalysts for transfer hydrogenation (TH) of ketones. The most important and significant catalysts are ruthenium(II) complexes containing monotosylated 1,2-diamines or aminoalcohols, discovered by Noyori and co-workers, which offer high catalytic activity and selectivity due to the presence of a N−H functionality (bifunctional catalysis).[2] A great number of related ligands and transition metal complex catalysts have been developed.[3] Recently, Baratta et al. reported a series of ruthenium(II) 2-(aminomethyl)pyridine (ampy) phosphane complex catalysts for TH of ketones which have demonstrated a remarkable acceleration effect by the ampy ligand.[4] In all the systems containing amine ligands, the presence of such a N−H functionality in the complex catalysts has been proven to be crucial for achieving highly efficient TH of ketones. Although a few active Ru(II) catalysts which do not feature an ancillary N−H functionality have also been documented for TH of ketones,[5] the need to develop new efficient catalysts is still strongly desired in this area. Planar tridentate N_3 ligands have recently been successfully developed,[6] but little attention has been paid to unsymmetrical planar tridentate ligands due to their complicated synthetic schemes. We have been interested in construction of new types of phosphine-free pyridyl-based 2,6-

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(1) For selected recent reviews, see: (a) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300. (b) Wu, X.; Xiao, J. L. *Chem. Commun.* **2007**, 2449. (c) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226. (d) Samec, J. S. M.; Bāckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237. (e) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201. (f) Everaere, K.; Mortreux, A.; Carpentier, J.-F. *Adv. Synth. Catal.* **2003**, *345*, 67. (g) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045. (h) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

(2) (a) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724. (b) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (c) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1997**, *36*, 285. (d) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916. (e) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 2521. (f) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562.

(3) (a) Schlattera, A.; Woggon, W.-D. *Adv. Synth. Catal.* **2008**, *350*, 995. (b) Huang, X. H.; Ying, J. Y. *Chem. Commun.* **2007**, 1825. (c) Canivet, J.; Süss-Fink, G. *Green Chem.* **2007**, *9*, 391. (d) Ma, G. B.; McDonald, R.; Ferguson, M.; Cavell, R. G.; Patrick, B. O.; James, B. R.; Hu, T. Q. *Organometallics* **2007**, *26*, 846. (e) Cheung, F. K.; Lin, C. X.; Minissi, F.; Criville, A. L.; Graham, M. A.; Fox, D. J.; Wills, M. *Org. Lett.* **2007**, *9*, 4659. (f) Cheung, F. K.; Graham, M. A.; Minissi, F.; Wills, M. *Organometallics* **2007**, *26*, 5346. (g) Morris, D. J.; Hayes, A. M.; Wills, M. *J. Org. Chem.* **2006**, *71*, 7035. (h) Zaitsev, A. B.; Adolfsson, H. *Org. Lett.* **2006**, *8*, 5129. (i) Vastila, P.; Zaitsev, A. B.; Wettergren, J.; Privalov, T.; Adolsson, H. *Chem.−Eur. J.* **2006**, *12*, 3218. (j) Schiffers, I.; Rantanen, T.; Schmidt, F.; Bergmans, W.; Zani, L.; Bolm, C. *J. Org. Chem.* **2006**, *71*, 2320.

(4) (a) Baratta, W.; Ballico, M.; Esposito, G.; Rigo, P. *Chem.−Eur. J.* **2008**, *14*, 5588. (b) Baratta, W.; Chelucci, G.; Herdtweck, E.; Magnolia, S.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7651. (c) Del Zotto, A.; Baratta, W.; Ballico, M.; Herdtweck, E.; Rigo, P. *Organometallics* **2007**, *26*, 5636. (d) Baratta, W.; Siega, K.; Rigo, P. *Chem.−Eur. J.* **2007**, *13*, 7479. (e) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214. (f) Baratta, W.; Da Ros, P.; Del Zotto, A.; Sechi, A.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3584.

(5) (a) Liu, D. L.; Xie, F.; Zhao, X. H.; Zhang, W. B. *Tetrahedron* **2008**, *64*, 3561. (b) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4732. (c) Reetz, M. T.; Li, X. G. *J. Am. Chem. Soc.* **2006**, *128*, 1044. (d) Leijondahl, K.; Fransson, A.-B. L.; Bāckvall, J.-E. *J. Org. Chem.* **2006**, *71*, 8622.

(6) (a) Lu, G.; Morimoto, H.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6847. (b) Milczek, E.; Boudet, N.; Blakey, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6825. (c) Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; Maarseveen, J. H. V. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777. (d) Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 2756. (e) Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 12645. (f) Gong, H.; Gagnè, M. R. *J. Am. Chem. Soc.* **2008**, *130*, 12177. (g) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745.

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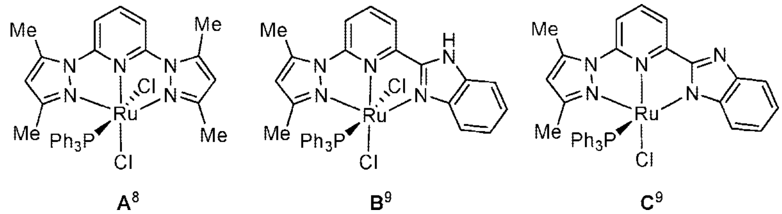
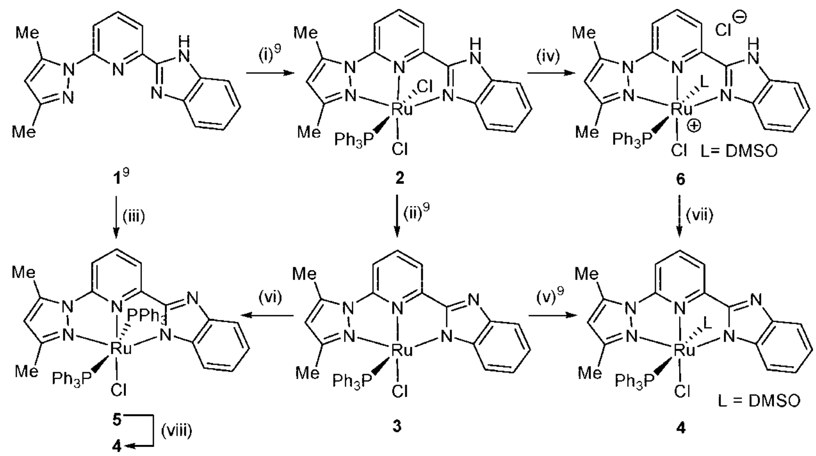
Scheme 1. Highly Active Ru(II) NNN Complex Catalysts for Transfer Hydrogenation of Ketones



Scheme 2. Synthesis of Complexes 2−6[a]



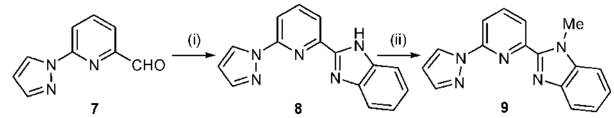
[a] Legend: (i) $RuCl_2(PPh_3)_3$, PhMe, 110 °C, 2 h, 91%. (ii) $NaHCO_3$, CH_2Cl_2/MeOH (v/v = 5:1), r.t., 5 h, 96%. (iii) $RuCl_2(PPh_3)_3$, Et_3N, PhMe, 110 °C, 2 h, 65%. (iv) DMSO/DMF (v/v = 5:1), 100 °C, 15 min, 77%. (v) DMSO/DMF (v/v = 5:1), 100 °C, 15 min, 60%. (vi) PPh_3, $CDCl_3$, r.t. (vii) $NaHCO_3$, CH_2Cl_2/MeOH (v/v = 5:1), r.t., 15 h, 96%. (viii) DMSO-d_6 or DMSO in $CDCl_3$, r.t.

(mixed *N*-heterocycles) ligands that can potentially provide a dynamic "on and off" chelating effect for the metal center during catalysis.[7,8] In a recent preliminary comunication, we reported a new class of highly active robust ruthenium(II) NNN complexes bearing a hemilabile unsymmetrical pyridyl-based pyrazolyl−imidazolyl ligand featuring no N−H functionality.[9] These Ru(II) complex catalysts showed exceptionally high catalytic activity in TH of ketones in 2-propanol, reaching 100% conversion for the ketone substrates and final TOFs up to 7.2 $\times$ 10^5 h^{-1} with 0.05 mol % catalyst at 82 °C and 55 800 h^{-1} with 0.1 mol % catalyst at room temperature. In our case,[9] formation of a coordinatively unsaturated ruthenium(II) center in the complex catalyst is the key factor in constructing a highly active Ru(II) NNN complex catalyst (Scheme 1). Herein, we report the detailed methodology for synthesis of these unsymmetrical and the related Ru(II) NNN complexes and exploration of their catalytic activity in transfer hydrogenation of ketones.

Results and Discussion

Synthesis of Complexes 2−6. Pyrazolyl-imidazolyl pyridine **1** was synthesized from the oxidative condensation of 1,2-phenylenediamine with 6-(3,5-dimethylpyrazol-1-yl)pyridine-2-carbaldehyde, which was prepared from the reaction of 2-bromo-6-(3,5-dimethylpyrazol-1-yl)pyridine and DMF in the presence of *n*-BuLi.[9] Reaction of **1** with 1.0 equiv of $RuCl_2(PPh_3)_3$ in refluxing toluene produced Ru(II) complex **2** in 91% yield; **2** was further transformed to 16-electron complex **3** in 96% yield by extrusion of 1 equiv of hydrogen chloride with base $NaHCO_3$. Complex **3** was easily converted to **4** by reacting with DMSO.[9] In the presence of triethylamine, treatment of **1** with $RuCl_2(PPh_3)_3$ in refluxing toluene formed complex **5**, whose structure was confirmed by X-ray crystallographic determinations. In polar solvent DMSO, **2** was transformed to cationic Ru(II) complex **6**, which could also be converted to the neutral complex **4** by using $NaHCO_3$ as the base. Dissolution of **5** in DMSO-d_6 or treatment of **5** with DMSO in $CDCl_3$ formed complex **4** (L = DMSO-d_6 or DMSO, Scheme 2), which was monitored and confirmed by $^{31}P\{^1H\}$ NMR determinations.

Scheme 3. Synthesis of Ligand 9[a]



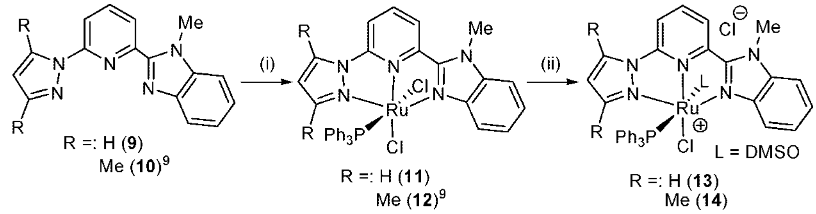
[a] Legend: (i) 1,2-phenylenediamine, nitrobenzene, 150 °C, 12 h, 53%. (ii) MeI, Cs_2CO_3, DMSO, rt, 3.0 h, 98%.

Synthesis of Ligand 9 and Complexes 11−14. In a fashion similar to the synthesis of **1**,[9] pyrazolyl−imidazolyl pyridine **8** and its N-methyl form **9** were prepared (Scheme 3). Treatment of ligands **9** and **10**[9] with 1.0 equiv of $RuCl_2(PPh_3)_3$ in refluxing toluene afforded the neutral 18-electron Ru(II) complexes **11** and **12**,[9] and heating of **11** and **12** in their DMSO/DMF solutions produced cationic Ru(II) complexes **13** and **14**, respectively (Scheme 4). It should be noted that complex **14** is hygroscopic in air.

NMR Characterization of the Complexes. The broadened proton resonance signals of the N−H moiety in **2** and **6** are shifted downfield by about 3 ppm as compared to that of the free ligand **1** (δ_{N-H}, 12.58 ppm), suggesting that the non-NH

(7) Zeng, F. L.; Yu, Z. K. *J. Org. Chem.* **2006**, *71*, 5274.
(8) (a) Sun, X. J.; Yu, Z. K.; Wu, S. Z.; Xiao, W.-J. *Organometallics* **2005**, *24*, 2959. (b) Deng, H. X.; Yu, Z. K.; Dong, J. H.; Wu, S. Z. *Organometallics* **2005**, *24*, 4110.
(9) Zeng, F. L.; Yu, Z. K. *Organometallics* **2008**, *27*, 2898.

Scheme 4. Synthesis of Complexes 11−14[a]



[a] Legend: (i) $RuCl_2(PPh_3)_3$, PhMe, 110 °C, 2 h, 85% (**11**), 92% (**12**). (ii) DMSO/DMF (v/v = 5:1), 100 °C, 15 min, 60% (**13**), 86% (**14**).

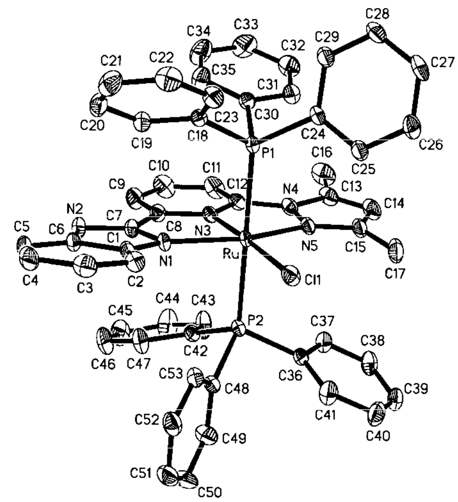


Figure 1. Perspective view of complex **5**.

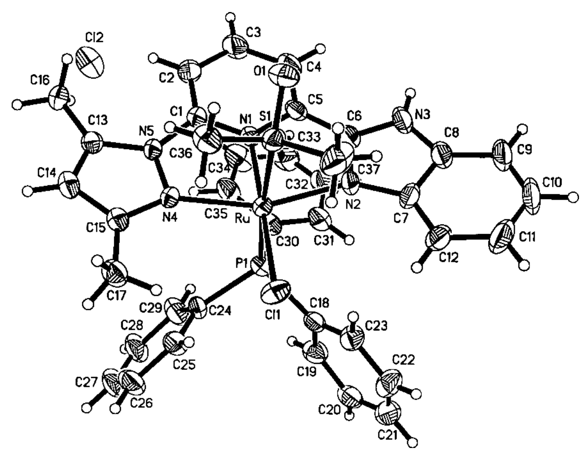


Figure 2. Perspective view of complex **6**.

nitrogen atom in the imidazolyl group is coordinated to the metal center. The ^{1}H NMR signals of the pyrazolyl-CH in the ligands appear at 6.15−6.18 ppm, and those of the Ru(II) complexes are shifted downfield to the region of 6.38−6.46 ppm, revealing that the pyrazolyl is also coordinated to the metal center. The ^{31}P NMR signals of complexes **2** and **6** appear at 31.5−31.9 ppm as singlets in DMSO-d_6, whereas those of **3** and **4** are shown at ca. 33.8 ppm. At ambient temperature, complex **5** exhibits one ^{31}P NMR signal at 22.0 ppm in $CDCl_3$, but in DMSO-d_6, it demonstrated one singlet at 33.7 ppm corresponding to that of **4** and the other signal at −6.5 ppm for free PPh_3, revealing that one coordinated PPh_3 ligand in **5** was dissociated from the complex in the DMSO-d_6 solution to form **4** (L = DMSO-d_6) (Figure 1). Coordination of a DMSO (or DMSO-d_6) molecule to the Ru(II) center in complexes **4** and **6** is concluded by the presence of a ^{13}C resonance signal at ca. 40.4

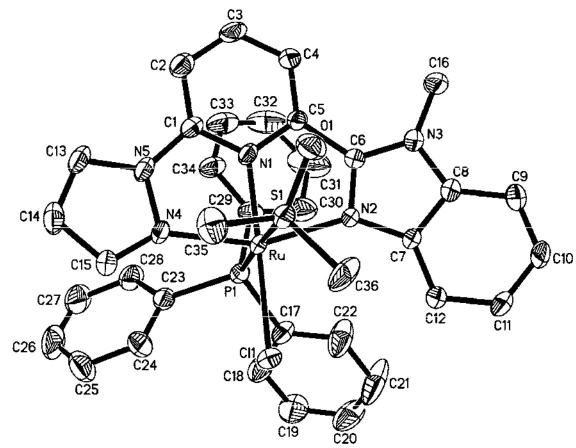


Figure 3. Perspective view of complex **13** with the dichloromethane molecule and chloride anion omitted for clarity.

ppm in their ^{13}C NMR spectra, and further confirmed by their X-ray single crystal structural analysis (Figure 2 and ref. 9). That dissolution of **5** in DMSO-d_6 or treatment of **5** with DMSO in $CDCl_3$ at ambient temperature afforded complex **4** further confirmed that DMSO or DMSO-d_6 can be easily coordinated to the metal center of **3** in solution. Reaction of **3** with PPh_3 also produced **5** at ambient temperature by ^{31}P NMR analysis. The proton and ^{13}C NMR features of complex **5** are similar to those of **3** and **4**.[9] The ^{31}P NMR signals of complexes **3** and **4** appear at 59.3 and 32.7 ppm in $CDCl_3$, respectively, suggesting different coordination environments around the metal center in these two complexes. Complex **3** is 16-electron with a five-coordinate metal center, whereas other complexes are 18-electron with a six-coordinate metal core.

The solid-state molecular structures of complexes **4**,[9] **12**,[9] **5**, **6**, and **13** were confirmed by X-ray crystallographic studies (Tables 1 and 2, Figures 1−3). The single crystal structure of **5** features a neutral ruthenium(II) center, and those of **6** and **13** reveal a cationic ruthenium(II) center in which the metal center is coordinated by the imidazolyl, pyridyl, and pyrazolyl nitrogen atoms. The ruthenium atom is in a distorted octahedral environment with one PPh_3 ligand and one DMSO (or PPh_3) trans to each other on the two sides of the NNN ligand plane. The unsymmetrical "pincer"-type NNN ligand occupies the three meridional sites with the three *N*-heterocyclic rings in a quasi-planar disposition, and the chloride ligand is positioned trans to the pyridyl nitrogen atom. A DMSO molecule is coordinated to the Ru(II) center through its sulfur atom in **6** or **13** and the Ru−S bond distances are 2.320(12) Å in **6** and 2.347(18) Å in **13**. The length difference between the $Ru-N_{imidazolyl}$ bond (2.111(4) Å) in **6** and those (2.088(17) and 2.084(5) Å) in **5** and **13** is attributed to the presence of a N−H functionality in **6**. The average Ru−P bond lengths in **5**, **6**, and **13** are almost the same (2.367(6), 2.369(13), and 2.361(19) Å), while the other Ru−P bond (2.415(6) Å) in **5** is longer than those in other

Table 1. Crystallographic Data and Refinement Details for 5, 6, and 13

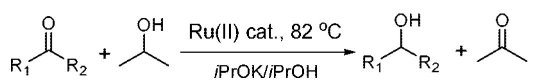
	5	**6**	**13**·CH_2Cl_2
Empirical formula	$C_{53}H_{44}ClN_5P_2Ru$	$C_{37}H_{36}Cl_2N_5OPRuS$	$C_{37}H_{36}Cl_4N_5OPRuS$
Formula weight	949.39	801.71	872.61
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	*P*2(1)/*n*	*P*2(1)2(1)2(1)	$P\bar{1}$
a (Å)	12.1008(7)	11.1431(6)	10.3359(10)
b (Å)	20.7883(11)	14.5034(8)	10.9327(11)
c (Å)	17.5491(10)	22.8917(13)	18.5189(19)
α (deg)	90	90	74.200(2)
β (deg)	96.5180(10)	90	74.175(2)
γ (deg)	90	90	85.627(2)
V (Å^3)	4386.0(4)	3699.6(4)	1937.2(3)
Z	4	4	2
Dc (gcm^{-3})	1.438	1.439	1.496
μ (mm^{-1})	0.536	0.705	0.813
F(000)	1952	1640	888
Crystal size (mm^3)	0.42 × 0.34 × 0.23	0.35 × 0.27 × 0.19	0.40 × 0.18 × 0.08
θ limits (deg)	1.95−27.00	1.66−27.00	1.18−26.50
No. of data collected	25557	22017	11170
No. of unique data	9509	8022	7867
R(int)	0.0665	0.0592	0.0676
No. of data observed with $I > 2\sigma(I)$	7795	6111	4179
No. of refined parameters	561	437	454
Goodness-of-fit on F^2	0.991	0.950	0.858
R (all data/obsd. data)	0.0483/0.0382	0.0582/0.0440	0.1004/0.0564
wR^2(all data/obsd. data)	0.0929/0.0890	0.1030/0.0984	0.1639/0.1331
Residual ρ_{max} (e Å^{-3})	0.829 (−0.509)	0.926 (−0.314)	1.819 (−0.834)

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5, 6 and 13

		complex **5**			
Ru−N(1)	2.088(17)	Ru−N(3)	1.981(19)	Ru−N(5)	2.094(18)
Ru−P(1)	2.415(6)	Ru−P(2)	2.367(6)	Ru−Cl(1)	2.470(6)
N(1)−Ru−N(5)	156.88(8)	P(1)−Ru−P(2)	178.76(2)		
N(3)−Ru−Cl(1)	177.40(6)	P(1)−Ru−Cl(1)	92.00(2)		
		complex **6**			
Ru−N(1)	1.999(3)	Ru−N(2)	2.111(4)	Ru−N(4)	2.077(3)
Ru−S(1)	2.320(12)	Ru−P(1)	2.369(13)	N(2)−Ru−N(4)	156.55(15)
N(1)−Ru−S(1)	87.42(11)	N(1)−Ru−P(1)	91.34(11)	S(1)−Ru−P(1)	174.84(5)
N(1)−Ru−Cl(1)	173.97(11)				
		complex **13**			
Ru−N(1)	1.975(5)	Ru−N(2)	2.084(5)	Ru−N(4)	2.092(5)
Ru−S(1)	2.347(18)	Ru−P(1)	2.361(19)	N(4)−Ru−N(2)	156.84(19)
N(1)−Ru−S(1)	89.09(14)	N(1)−Ru−P(1)	93.26(14)	S(1)−Ru−P(1)	177.14(6)
N(1)−Ru−Cl(1)	177.49(16)				

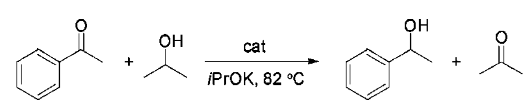
complexes, suggesting that the two PPh_3 ligands in **5** have great *trans* influences to each other. The Ru−N$_{imidazolyl}$, Ru−N$_{pyridyl}$, and Ru−P bonds in **13** are shorter than those in other complexes, implying that complex **13** is structurally more stable.

Catalytic Transfer Hydrogenation of Ketones (eq 1).



(1)

Reduction of acetophenone to 1-phenylethanol by 2-propanol was chosen as the model reaction to test the catalytic activity of the Ru(II) NNN complexes (eq 2, Table 3). The catalytic reactions were carried out using a 0.1 M solution of acetophenone in refluxing 2-propanol with 0.05−0.3 mol % of the complex as catalyst, and freshly prepared *i*PrOK as the base under nitrogen atmosphere. Complexes **2** and **3** exhibited the same exceptionally high catalytic activity, achieving 98% conversion for acetophenone and a final TOF of 705 600 h^{-1} within 10 s (Table 3, entries 1 and 2). Complex **6** can be considered as a precursor to complex **4** that they demonstrated the same high catalytic activity, reaching 98% conversion for the ketone and a final TOF of 117 600 h^{-1} within one minute (Table 3, entries 3 and 5), presumably due to the instant transformation of **6** to **4** under the basic conditions. However, complex **5** only showed a moderate catalytic activity even with a higher loading, e.g., 0.1 mol %, yielding the reduction product in 97% yield with a final TOF of 3880 h^{-1} over a period of 15 min (Table 3, entry 4). With 0.3 mol % loading, complexes **11**−**13** exhibited much lower catalytic activity than complexes **2**−**6** (Table 3, entries 6−8), and acetophenone was reduced to



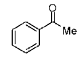
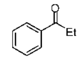
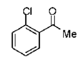
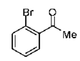
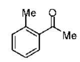
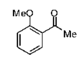
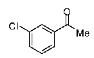
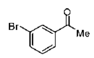
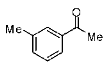
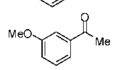
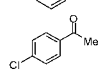
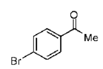
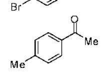
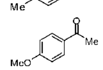
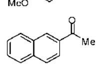
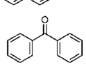
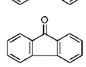
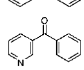
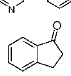
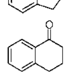
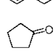
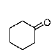
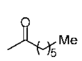
(2)

Table 3. Transfer Hydrogenation of Acetophenone Catalyzed by Complexes 2−6 and 11−14[a]

entry	complex (mol %)	time (min)	conversion (%)[b]	final TOF (h^{-1})
1[9]	**2** (0.05)	1/6	98	705 600
2	**3** (0.05)	1/6	98	705 600
3[9]	**4** (0.05)	1	98	117 600
4	**5** (0.1)	15	97	3880
5	**6** (0.05)	1	98	117 600
6	**11** (0.3)	10	98	1960
7	**12** (0.3)	10	98	1960
8	**13** (0.3)	10	96	1920
9	**14** (0.1)	5	98	11 760

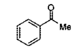
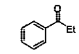
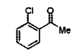
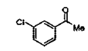
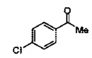
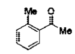
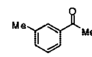
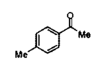
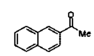
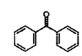
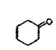
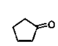
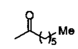
[a] Conditions: acetophenone, 2.0 mmol (0.1 M in 20 mL i PrOH); *i*PrOK/cat = 20/1; 0.1 MPa, 82 °C. [b] GC yield of the corresponding alcohol.

Table 4. Transfer Hydrogenation of Ketones Catalyzed by 3[a]

entry	ketone	time (min)	conversion (%)[b]	final TOF (h^{-1})
1		1/6	98	705600
2		1/6	99	712800
3		1/6	100	720000
4		1/6	100	720000
5		1/6	99	712800
6		1/6	99	712800
7		1/6	99	712800
8		1/6	99	712800
9		1/6	97	698400
10		1/6	99[c]	712800
11		1/6	98	705600
12		1/6	98	705600
13		1/6	96	691200
14		1/6	89	640800
15		1/6	93	669600
16		1/6	97[c]	698400
17		1/6	93[c]	669600
18		15	98	7840
19		30	78	3120
20		30	20	800
21		1/6	100	720000
22		1/6	100	720000
23		1/6	98	705600

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); complex **3**, 0.05 mol%; ketone/*i*PrOK/cat.= 2000:20:1; 0.1 MPa, 82 °C. [b] By GC analysis. [c] By ^{1}H NMR.

Table 5. Transfer Hydrogenation of Ketones Catalyzed by Complexes 4−6 and 14[a]

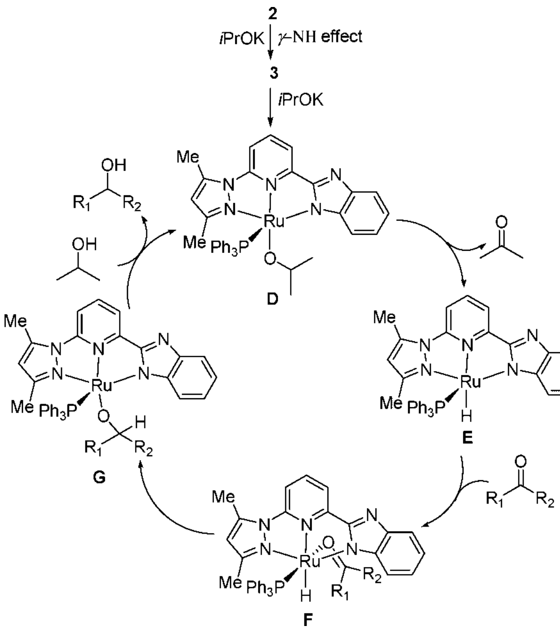
entry	ketone	cat.	time (min)	conversion (%)[b]	final TOF (h^{-1})
		4	1	98	117600
1		5	15	97	3880
		6	1	98	117600
		14	5	98	11760
		4	2	98	58800
2		5	60	98	980
		6	2	98	58800
		14	5	97	11640
		5	120	98	490
3		6	2	99	59400
		14	15	98	3920
		5	5	98	11760
4		6	1	99	118800
		14	15	98	3920
		5	10	98	5880
5		6	0.5	98	235200
		14	15	98	3920
		5	60	95	950
6		6	1	99	118800
		14	5	99	11880
		5	180	95	317
7		6	1	97	116400
		14	30	94	1880
		4	2	95	57000
8		5	15	95	3800
		6	2	96	57600
		14	30	94	1880
		4	2	93	55800
9		5	10	96	5760
		6	2	96	57600
		14	5	95	11400
		5	15	99[b]	3960
10		6	1	99[b]	118800
		14	5	99[b]	11880
		4	0.5	97	232800
11		5	5	98	11760
		6	0.5	100	240000
		14	2	97	29100
		5	10	98	5880
12		6	1	98	117600
		14	15	96	3840
		5	240	94	118
13[c]		6	5	98	5880
		14	60	97	485

[a] Conditions: ketone, 2.0 mmol (0.1 M in 20 mL *i*PrOH); catalyst: **4** and **6**, 0.05 mol%; **5** and **14**, 0.1 mol%; *i*PrOK:cat. = 20:1; 0.1 MPa, 82 °C. [b] GC yield of the corresponding alcohol. [c] By ^{1}H NMR. [d] Catalyst (0.2 mol %).

the corresponding alcohol in 96−98% yields over a period of 10 min. Unexpectedly, the cationic form of the neutral complex **12**, that is, **14**, exhibited much higher catalytic activity than its parent complex **12**, achieving 97% conversion for the ketone with a final TOF of 11 760 h^{-1} within 5 min using 0.1 mol % of the complex as catalyst (Table 3, entry 9).

Under the typical conditions for TH of ketones (82 °C, 0.1 M ketone in 2-propanol), transfer hydrogenation of various ketones was explored by means of complexes **3**−**6** and **14** as the catalysts (Tables 4 and 5). As reported in the preliminary communication,[9] complex **3** nearly exhibited the same catalytic activity as complex **2** did in the TH of ketones, reaching >98% conversion for most of the ketone substrates with final TOFs up to 720 000 h^{-1} within 10 s (Table 4, entries 3, 4, 21, and 22). Complexes **4**−**6** and **14** demonstrated good to excellent catalytic activities in TH of ketones (Table 5). **4** and **6** almost exhibited the same high catalytic activity and reached 95−100% conversion for the ketones and final TOFs up to 240 000 h^{-1} within 0.5−5 min, presumably due to the instant conversion of **6** to **4** under the reaction conditions (Table 5, entries 1, 2, 8, 9, and 11). Complex **5** only exhibited good catalytic activity as compared with those of complexes **2**−**4** and **6** but showed better catalytic activity than Ru(II) complex **A** bearing a symmetrical NNN ligand[8] (Scheme 1). Although the neutral Ru(II) complex **12** only showed fairly good catalytic activity in TH of acetophenone (entry 7, Table 3), its cationic form, that is, complex **14**, exhibited good to excellent catalytic activity in the TH of various ketone substrates (Table 5) and achieved final TOFs up to 29 400 h^{-1}. To date, the highest TOF value in TH

Scheme 5. Proposed Mechanism



of ketones, that is, 2.5 × 10^6 h^{-1} (at 50% conversion of the ketone, 82 °C), has been reported in TH of 3-chloroacetophenone by using 0.005 mol% Baratta's Ru(II) CNN catalyst featuring a N−H functionality.[4e] Stradiotto's cationic Ru(II) catalyst featuring no N−H functionality has also shown very high catalytic activity in TH of ketones with 0.05 mol % loading (TOFs up to 2.2 × 10^5 h^{-1}).[5b] In our cases, both the neutral complexes **2** and **3** exhibited exceptionally high catalytic activity, complex **4** and its cationic form **6**, and the cationic complex **14** also demonstrated excellent catalytic activity in TH of ketones. Complexes **2** and **3** are among the three most efficient complex catalysts for transfer hydrogenation of ketones to date.[4e,5b]

On the basis of the behaviors of complexes **2-6** and **11-14** in solution and the transformations as shown in Scheme 2, an inner-sphere mechanism[10] is proposed for TH of ketones catalyzed by **2** or **3** (Scheme 5). Thus, TH of a ketone can be initiated directly from **3** or *in situ* generated **3** by extrusion of one equivalent of hydrogen chloride from **2** with the base, that is, *i*PrOK. Complex **3** interacts with the base to form Ru(II)-alkoxide **D** which undergoes *β*-H elimination to result in a Ru−H intermediate **E** and releases of acetone. Coordination of a ketone substrate to **E** produces species **F** and is followed by insertion of the coordinated ketone carbonyl into the Ru−H bond to form Ru(II)-alkoxide **G** which is then reacted with 2-propanol to afford the alcohol product and regenerate species **D**. Ru(II) hydride **E** is presumably considered as the catalytically active species although it was not successfully isolated by reacting **3** with EtONa or *i*PrOK in refluxing ethanol (or 2-propanol). Formation of Ru−H complexes from Ru−Cl precursors has been well-documented,[11] and such *in situ* formed Ru−H species can act as the active catalysts for TH of ketones.[1,5c,11,12] In the present case, the presence of a $Ru-N_{imidazolyl}$ bond and the coordinatively unsaturated 16-electron environment around the ruthenium center in **3** are crucial to the exceptionally high catalytic activity of complex **3**.

(10) Comas-Vives, A.; Ujaque, G.; Lledós, A. *Organometallics* **2007**, *26*, 4135.

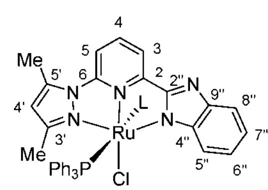
Conclusions

In summary, hemilabile ruthenium(II) NNN complexes bearing a unsymmetrical pyridyl-supported pyrazolyl-imidazolyl ligand have been synthesized and exhibited exceptionally high catalytic activity in transfer hydrogenation of ketones at 82 °C, demonstrating rare examples of highly active Ru(II) NNN complex catalysts that do not feature a N−H functionality.[13] The hemilability feature of the unsymmetrical NNN ligand and the coordinatively unsaturated environment around the Ru(II) center in the complex or precatalyst provide the complex catalyst with a remarkable acceleration effect during the TH reactions of ketones.

Experimental Section

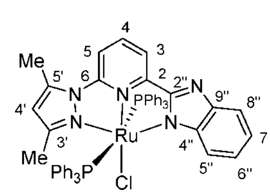
General Considerations. Unless otherwise noted, all the starting materials were commercially available and used without further purification. The catalytic reactions were carried out under a nitrogen atmosphere. All the solvents were dried prior to use according to the standard procedures. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$NMR spectra were obtained with a 400 MHz NMR spectrometer.

X-Ray Crystallographic Studies. Single crystal X-ray diffraction studies for compounds **5**, **6**, and **13** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic data and refinement details for **5**, **6**, and **13** are listed in Table 1, and the selected bond lengths and angles are given in Table 2.

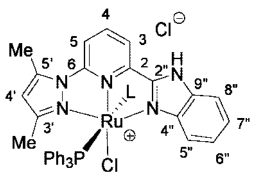


L = DMSO

Synthesis of Complex 4[9] from its Cationic Form 6. A mixture of complex **6** (0.26 g, 0.32 mmol) and $NaHCO_3$ (0.27 g 3.20 mmol) in dichloromethane/methanol (20 mL, v/v = 5:1) was stirred at ambient temperature for 15 h. The resultant mixture was filtered through a short pad of celite and the filtrate was collected. All the volatiles were removed under reduced pressure to afford complex **4** (0.24 g, 96%).

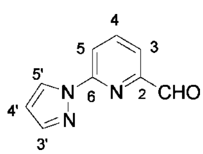


Synthesis of Complex 5. 2.1 mL of triethylamine (1.52 g, 15.0 mmol) was added to a slurry of $RuCl_2(PPh_3)_3$ (1.44 g, 1.5 mmol) and benzoimidazole **1**[9] (0.43 g, 1.5 mmol) in toluene (50 mL) with stirring and the mixture was refluxed for 2 h. The mixture was cooled to ambient temperature and the resultant solid was filtered off, washed with *i*PrOH (2 × 50 mL) and diethyl ether (50 mL), and dried in vacuum to afford compound **5** as an orange microcrystalline solid (0.93 g, 65%). Red single crystals suitable for X-ray crystallographic study were grown by diffusion of diethyl ether vapor into a saturated solution of the complex in CH_2Cl_2/MeOH (v/v = 4:1) at ambient temperature. mp: dec > 240 °C. ^{1}H NMR (CD_2Cl_2, 23 °C): δ 8.29 and 7.39 (d each, J = 7.1 and 7.1 Hz, 1:1 H, 3-H and 5-H), 8.08 (s, 1 H, 4-H), 7.11 and 6.88 (m each, 33 H, Ph in PPh_3, 6″-H, 7″-H, and 8″-H), 6.48 (d, J = 8.3 Hz, 1 H, 5″-H), 5.90 (s, 1 H, 4′-H), 2.36 (s, 3 H, C3′-CH_3), 2.30 (s, 3 H, C5′-CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 23 °C): δ 157.2 and 151.2 (s and Cq each, C2 and C6), 151.9 and 143.4 (s and Cq each, C3′ and C5′), 143.1, 131.8 and 131.5 (s and Cq each, C2″, C4″, and C9″), 132.8, 132.8, 128.7 and 127.2 (s each, Phenyl CH in PPh_3), 131.7 (s, C4), 122.9, 121.6, 114.4 and 112.4 (s each, Phenyl CH), 120.4 and 118.7 (s each, 1:1 CH, C3 and C5), 107.6 (s, C4′), 14.6 (s, C3′-CH_3), 14.4 (s, C5′-CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 23 °C): δ 21.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C): δ 22.0. Anal. calcd for $C_{53}H_{44}ClN_5P_2Ru$: C, 67.05; H, 4.67; N, 7.38. Found: C, 66.73; H, 4.71; N, 7.42.

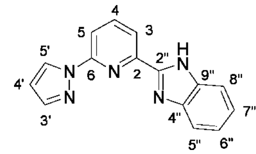


L = DMSO

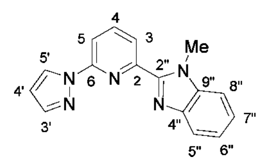
Synthesis of Complex 6. A mixture of complex **2**[9] (0.35 g, 0.47 mmol) and DMF/DMSO (20 mL, v/v = 5:1) was stirred at 100 °C for 15 min. After cooling to ambient temperature, the resultant solution was layered with diethyl ether and recrystallized at −20 °C to afford complex **6** as red crystals (0.30 g, 77%). mp: dec > 210 °C. ^{1}H NMR (DMSO-d_6, 23 °C) δ 15.49 (s, 1 H, NH), 8.40 and 8.23 (d each, J = 8.0 and 8.0 Hz, 1:1 H, 3-H and 5-H), 7.93 (t, J = 16.4 Hz, 1 H, 4-H), 7.64 (m, 2 H, 5″-H and 8″-H), 7.48 (m, 2 H, 6″-H and 7″-H), 7.25 and 7.11 (m each, 9:6 H, Ph in PPh_3), 6.45 (s, 1 H, 4′-H), 2.72 (s, 3 H, C3′-CH_3), 2.58 (s, 3 H, C5′-CH_3), 2.54 (s, 6 H, DMSO). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C) δ 158.0 and 151.9 (s and Cq each, C2 and C6), 151.8 and 142.1 (s and Cq each, C3′ and C5′), 149.5, 146.0 and 134.1 (s and Cq each, C2″, C4″, and C9″), 137.0 (s, C4), 132.7 (d, *o*-C of PPh_3), 130.8 (d, *i*-C of PPh_3), 129.8 (s, *p*-C of PPh_3), 128.1 (d, *m*-C of PPh_3), 125.5, 124.3, 113.5 and 113.2 (s each, C5", C6″, C7″, and C8″), 119.3 and 119.1 (s each, C3 and C5), 111.2 (s, C4′), 40.4 (s, CH_3 of DMSO), 14.4 (s, C3′-CH_3), 14.2 (s, C5′-CH_3). ^{31}P{^{1}H} NMR (DMSO-d_6, 23 °C) δ 31.9. Anal. calcd for $C_{37}H_{36}Cl_2N_5OPRuS$: C, 55.43; H, 4.53; N, 8.74. Found: C, 55.40; H, 4.50; N, 8.77.



Synthesis of 6-(Pyrazol-1-yl)pyridine-2-carbaldehyde (7). Compound **7** was prepared using a procedure different from the reported method.[14] A mixture of 6-bromopyridine-2-carbaldedyhyde (3.72 g, 20.00 mmol), pyrazole (1.77 g, 26.00 mmol), 1,10-phenanthroline monohydrate (0.79 g, 4.00 mmol), CuI (0.38 g, 2.00 mmol, 10 mol %), and K_2CO_3 (3.04 g, 20.00 mmol) in toluene (80 mL) was stirred at 120 °C for 24 h. After cooling to ambient temperature, the mixture was filtered through celite, and all the volatiles were removed under reduced pressure. Isolation by silica gel column chromatography (petroleum ether (60−90 °C)/ethyl acetate, v/v = 40:1) afforded **7** as white solid (2.50 g, 72%). ^{1}H NMR ($CDCl_3$, 23 °C) δ 10.05 (s, 1 H, CHO), 8.68 (d, J = 2.4 Hz, 1 H, 3′-H), 8.23 and 7.84 (d each, J = 8.0 and 7.6 Hz, 2 H, 3-H and 5-H), 7.99 (t, J = 15.6 Hz, 1 H, 4-H), 7.78 (s, 1 H, 5′-H), 6.52 (s, 1 H, 4′-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C) δ 192.7 (s, CHO), 151.9 and 151.2 (s and Cq each, C2 and C6), 142.8, 139.9 and 108.5 (s each, 3 × CH, C3′, C4′, and C5′), 127.4 (s, C4), 119.2 and 117.0 (s each, 2 × CH, C3 and C5).



Synthesis of 2-(Benzoimidazol-2-yl)-6-(pyrazol-1-yl)pyridine (8). A mixture of aldehyde **7** (0.50 g, 2.89 mmol) and 1,2-phenylenediamine (0.31 g, 2.89 mmol) in nitrobenzene (50 mL) was stirred at 150 °C for 12 h. All the volatiles were removed under reduced pressure and the resultant residue was subject to purification by flash silica gel column chromatography (CH_2Cl_2/ethyl acetate, v/v = 3:1), affording compound **8** as a pale yellow solid (0.40 g, 53%). mp: 208−209 °C. ^{1}H NMR (DMSO-d_6, 23 °C) δ 13.10 (s, 1 H, NH), 9.26 (s, 1 H, 3′-H), 8.22 (d, J = 7.6 Hz, 1 H, 3-H), 8.15 (t, J = 16.0 Hz, 1 H, 4-H), 7.99 (d, J = 8.4 Hz, 1 H, 5-H), 7.88 (s, 1 H, 5′-H), 7.75 and 7.64 (d each, J = 8.0 and 9.2 Hz, 1:1 H, 5″-H and 8″-H), 7.31 and 7.25 (m each, 2 H, 6″-H and 7″-H), 6.70 (d, J = 1.2 Hz, 1 H, 4′-H). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C) δ 150.5 and 149.9 (s and Cq each, C2 and C6), 147.0, 144.0 and 134.7 (s and Cq each, C2″, C4″, and C9″), 142.6 and 140.9 (s each, C3′ and C5′), 128.2 (s, C4), 123.6, 122.1, 112.2 and 111.9 (s each, phenyl CH), 119.6 and 118.7 (s each, C3 and C5), 108.2 (s, C4′). HRMS calcd for C15H11N5: 261.1014. Found: 261.1019.



Synthesis of 2-(*N*-Methyl-benzoimidazol-2-yl)-6-(pyrazol-1-yl)pyridine (9). A mixture of benzoimidazole **8** (0.68 g, 2.60 mmol) and Cs_2CO_3 (1.69 g, 5.20 mmol) in 50 mL DMSO was stirred at 80 °C for 30 min and cooled to ambient temperature. Iodomethane (0.55 g, 3.90 mmol) was then added, and the reaction was continued at ambient temperature for 3 h. Dichloromethane (100 mL) was added, and the resultant mixture was washed with water (3 × 100 mL). The organic phase was separated, dried over anhydrous $MgSO_4$, and filtered. All the volatiles were evaporated from the filtrate under reduced pressure, and the resultant residue was subject to purification by flash silica gel column chromatography (CH_2Cl_2/ethyl acetate, v/v = 3:1), affording **9** as a white solid (0.70 g, 98%). M.p.: 134−135 °C. ^{1}H NMR (DMSO-d_6, 23 °C) δ 8.73 (d, J = 2.1 Hz, 1 H, 3′-H), 8.25 (d, J = 7.7 Hz, 1 H, 3-H), 8.16 (t, J = 15.8 Hz, 1 H, 4-H), 8.02 (d, J = 8.1 Hz, 1 H, 5-H), 7.89 (s, 1 H, 5′-H), 7.75 and 7.69 (d each, J = 8.0 and 8.0 Hz, 1:1 H, 5″-H and 8″-H), 7.35 and 7.29 (m each, 2 H, 6″-H and 7″-H), 6.65 (d, J = 1.6 Hz, 1 H, 4′-H), 4.29 (s, 3 H, N-CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C) δ 150.0 and 148.5 (s and Cq each, C2 and C6), 148.8, 142.0 and 137.1 (s and Cq each, C2″, C4″, and C9″), 142.6 and

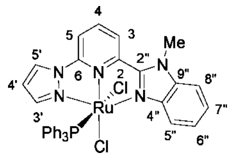
(11) Li, T.; Churlaud, R.; Lough, A. J.; Abdur-Rashid, K.; Morris, R. H. *Organometallics* **2004**, *23*, 6239.

(12) (a) Casey, C. P.; Clark, T. B.; Guzei, I. A. *J. Am. Chem. Soc.* **2007**, *129*, 11821. (b) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805. (c) Chowdhury, R. L.; Bāckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063. (d) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bāckvall, J.-E. *Chem. Commun.* **1999**, 351.

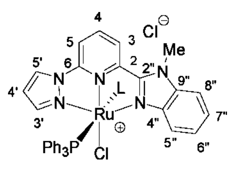
(13) Enthaler, S.; Hagemann, B.; Bhor, S.; Anilkumar, G.; Tse, M. K.; Bitterlich, B.; Junge, K.; Erre, G.; Beller, M. *Adv. Synth. Catal.* **2007**, *349*, 853.

(14) Vacher, B.; Bonnaud, B.; Funes, P.; Jubault, N.; Koek, W.; Assie, M.-B.; Cosi, C. *J. Med. Chem.* **1998**, *41*, 5070.

140.6 (s each, C3′ and C5′), 127.5 (s, C4), 123.4, 122.5, 112.2 and 110.9 (s each, phenyl CH), 120.0 and 119.6 (s each, C3 and C5), 108.7 (s, C4′), 33.0 (s, N-CH_3). HRMS calcd for C16H13N5: 275.1171. Found: 275.1171.

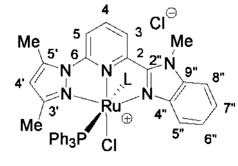


Synthesis of Complex 11. A mixture of $RuCl_2(PPh_3)_3$ (0.34 g, 0.36 mmol) and *N*-methyl-benzoimidazole **9** (0.10 g, 0.36 mmol) in toluene (8 mL) was refluxed for 2 h, forming a red-brown microcrystalline solid. The mixture was cooled to ambient temperature and the solid was filtered off, washed with diethyl ether (3 × 30 mL), and dried in vacuum to afford complex **11** (0.22 g, 85%) as a red-brown crystalline solid. mp>280 °C. ^{1}H NMR (DMSO-d_6, 23 °C) δ 9.19 and 8.32 (d each, J = 3.2 and 1.8 Hz, 1:1 H, 3′-H and 5′-H), 8.39 (d, J = 9.0 Hz,1 H 5-H), 8.03 (m, 3 H, 3-H, 4-H and 5″-H), 7.88 (d, J = 9.0 Hz,1 H, 8″-H), 7.55 (m, 2 H, 6″-H and 8″-H), 7.26 and 7.12 (m each, 9:6 H, Ph in PPh_3), 6.88 (t, J = 5.0 Hz,1 H, 4′-H), 4.26 (s, 3 H, N-CH_3). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C) δ 151.3 and 150.9 (s and Cq each, C2 and C6), 148.5, 141.0 and 136.0 (s and Cq each, C2″, C4″, and C9″), 147.1 and 136.8 (s each, C3′ and C5′), 133.2 (s, C4), 132.7 (d, *o*-C of PPh_3), 130.2 (s, *p*-C of PPh_3), 129.8 (d, *i*-C of PPh_3), 128.2 (d, *m*-C of PPh_3), 125.6, 124.5, 112.3 and 111.2 (s each, phenyl CH), 121.0 and 119.6 (s each, C3 and C5), 110.9 (s, C4′), 32.8 (s, N-CH_3). ^{31}P{^{1}H} NMR (DMSO-d_6, 23 °C) δ 32.8. Anal. calcd for $C_{34}H_{28}Cl_2N_5PRu$: C, 57.55; H, 3.98; N, 9.87. Found: C, 57.30; H, 4.06; N, 10.00.



L = DMSO

Synthesis of Complex 13. A mixture of complex **11** (0.30 g, 0.42 mmol) and DMF/DMSO (15 mL, v/v = 5:1) was stirred at 100 °C for 15 min. After cooling to ambient temperature, all the volatiles were removed under reduced pressure and the resultant residue was dissolved in 20 mL CH_2Cl_2. The resultant solution was layered with diethyl ether and recrystallized at −20 °C to afford complex **11** as red crystals (0.20 g, 60%). M.p.: dec > 210 °C °C.^{1}H NMR (DMSO-d_6, 23 °C) δ 9.21 and 8.32 (d each, J = 3.0 and 1.8 Hz, 1:1 H, 3′-H and 5′-H), 8.39 (d, J = 9.2 Hz, 1 H, 5-H), 8.07 (m, 2 H, 3-H, and 5″-H), 8.00 (t, J = 16.0 Hz, 1 H, 4-H), 7.88 (d, J = 6.0 Hz, 1 H, 8″-H), 7.54 (m, 2 H, 6″-H and 8″-H), 7.26 and 7.12 (m each, 9:6 H, PPh_3), 6.88 (t, J = 5.1 Hz, 1 H, 4′-H), 4.26 (s, 3 H, N-CH_3), 2.53 (s, 6 H, DMSO). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C) δ 151.3 and 150.9 (s and Cq each, C2 and C6), 148.5, 141.0 and 136.0 (s and Cq each, C2″, C4″, and C9″), 147.1 and 136.8 (s each, C3′ and C5′), 133.3 (s, C4), 132.7 (d, *o*-C of PPh_3), 130.2 (s, *p*-C of PPh_3), 129.8 (d, *i*-C of PPh_3), 128.2 (d, *m*-C of PPh_3), 125.6, 124.5, 112.4 and 111.2 (s each, phenyl CH), 121.1 and 119.6 (s each, C3 and C5), 111.0 (s, C4′), 40.4 (s, CH_3 of DMSO), 32.8 (s, N-CH_3). ^{31}P{^{1}H} NMR (DMSO-d_6, 23 °C) δ 32.8. $C_{36}H_{34}Cl_2N_5OSPRu \cdot 0.5CH_2Cl_2$: C, 52.81; H, 4.25; N, 8.44. Found: C, 52.53; H, 4.30; N, 8.55.



L = DMSO

Synthesis of Complex 14. A mixture of complex **12**[9] (0.74 g, 1.00 mmol) and 20 mL DMSO was stirred at 100 °C for 15 min. After cooling to ambient temperature, diethyl ether (300 mL) was added to precipitate the crude product. The resultant brown solid was dried in vacuum to afford compound **14** (0.70 g, 86%). Compound **14** is hydroscopic in air. mp: dec > 210 °C. ^{1}H NMR (DMSO-d_6, 23 °C) δ 8.54 and 8.08 (d each, J = 7.0 and 8.1 Hz, 1:1 H, 3-H and 5-H), 7.88 (m, 2 H, 4-H and 5″-H), 7.75 (d, J = 8.6 Hz, 1 H, 8″-H), 7.53 (m, 2 H, 6″-H and 7″-H), 7.24 and 7.12 (m each, 9:6 H, Ph in PPh_3), 6.45 (s, 1 H, 4′-H), 4.25 (s, 3 H, N-CH_3), 2.76 (s, 3 H, C3′-CH_3), 2.57 (s, 3 H, C5′-CH_3), 2.54 (s, 6 H, CH_3 of DMSO). ^{13}C{^{1}H} NMR (DMSO-d_6, 23 °C) δ 157.9 and 152.3 (s and Cq each, C2 and C6), 150.9 and 141.2 (s and Cq each, C3′ and C5′), 149.1, 146.1 and 136.1 (s and Cq each, C2″, C4″, and C9″), 136.7 (s, C4), 132.7 (d, *o*-C of PPh_3), 130.8 (d, *i*-C of PPh_3), 129.8 (s, *p*-C of PPh_3), 128.0 (d, *m*-C of PPh_3), 125.5, 124.5, 113.4, and 112.3 (s each, phenyl CH), 120.6 and 119.7 (s each, C3 and C5), 111.6 (s, C4′), 40.4 (s, CH_3 of DMSO), 32.9 (N-CH_3), 14.6 (s, C3′-CH_3), 14.0 (s, C5′-CH_3). ^{31}P{^{1}H} NMR (DMSO-d_6, 23 °C): δ 31.5 (s, PPh_3). $C_{38}H_{38}Cl_2N_5OSPRu \cdot H_2O$: C, 54.74; H, 4.84; N, 8.40. Found: C, 54.48; H, 4.91; N, 8.58.

General Procedure for Catalytic Transfer Hydrogenation of Ketones. The catalyst solution was prepared by dissolving complex **14** (16.3 mg, 20.0 μmol) in 2-propanol (40.0 mL). Under nitrogen atmosphere, the mixture of a ketone substrate (2.0 mmol), 4.0 mL of the catalyst solution (0.1 mol % catalyst **14**), and 2-propanol (15.6 mL) was stirred at 82 °C for 5 min. Then, 0.4 mL of 0.1 M *i*PrOK (0.04 mmol) solution in 2-propanol was introduced to initiate the transfer hydrogenation of the ketone. At the stated time, 0.1 mL of the reaction mixture was sampled and diluted with 0.5 mL of 2-propanol precooled at 0 °C for immediate GC analysis. After the reaction was complete, the reaction mixture was condensed under reduced pressure and subject to purification by flash silica gel column chromatography to afford the alcohol product. The alcohol products were identified by comparison of their GC traces with the authentic samples and/or by proton NMR measurements.

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Supporting Information Available: X-ray crystallographic data of **5**, **6**, and **13**, also in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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