Syntheses, Structures, and Catalytic Properties of Ruthenium(II) Nitrosyl Complexes with Pyridine-Functionalized N-Heterocyclic Carbenes

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Ruthenium(II) nitrosyl complexes with pyridine-functionalized N-heterocyclic carbenes [(**L**)Ru(NO)Cl_3] [L = 3-*tert*-butyl-1-(2-pyridyl)imidazol-2-ylidene, **2a**; 3-*n*-butyl-1-(2-pyridyl)imidazol-2-ylidene, **2b**; 3-*tert*-butyl-1-picolylimidazol-2-ylidene, **2c**; 3-*n*-butyl-1-picolylimidazol-2-ylidene, **2d**; and 3-benzyl-1-picolylimidazol-2-ylidene, **2e**] have been prepared by transmetalation from the corresponding silver carbene complexes. Compounds **2a**−**c** have been characterized by single-crystal X-ray crystallography. Compounds **2a**−**e** show catalytic activities in transfer hydrogenation of ketones.

N-Heterocyclic carbenes (NHCs) have been receiving much attention for their wide applications in coordination chemistry and homogeneous catalysis.[1] Many types of interesting NHC-containing ligands have been designed to search for new efficient catalysts. In particular, functionalized NHC ligands and catalytic activities of their metal complexes have been the subject of intensive studies.[2] Incorporation of a classical donor into NHC compounds offers vast opportunities in the design of the functionalized NHC ligands. The noncarbon donor atom would act as a hemilabile arm, capable of reversible dissociation from the metal center. The hybrid NHC ligands containing nitrogen donors have attracted considerable interest, among which the bidentate pyridine-functionalized NHC ligands, **L**, have been most extensively studied. So far, many metal complexes including groups 9 (Rh,[3] Ir[3b−d,4]), 10 (Ni,[5] Pd[6]), and 11 (Cu,[7] Ag[3a,5a,8]) complexes of **L** have been prepared, some of which showed catalytic activities in hydrosilation of acetylenes,[4b] cyclizatioin of acetylenic carboxylic acids,[4b] transfer hydrogenation of ketones,[4b] reduction of nitrarenes,[4c] C−C coupling reactions,[6b,c] and olefin polymerization.[5a,6h] However, group 8 metal complexes with **L** have been rarely studied. Sun and coworkers have prepared dinuclear iron−carbonyl complexes with **L** as the 2Fe2S hydrogenase model.[9] The only known ruthenium complex with **L** is the half-sandwich ruthenium containing 1,2-dichalcogenolato-1,2-dicarba-closo-dococaborane, in which ligand **L** (n = 1, R = Me) is coordinated with carbene carbon and leaves the pyridyl nitrogen appeneded.[3d] Ruthenium nitrosyl complexes have been extensively studied due to their interesting

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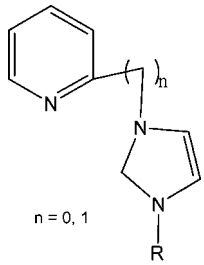
structures,[10] catalytic properties,[11] and biological significance.[12] However, ruthenium nitrosyl complexes with NHCs have only been scarcely reported. Lappert and co-workers prepared a series of ruthenium(osmium) nitrosyl complexes with the saturated NHCs via the reactions of electron-rich olefin and the metal precursors.[13] Recently, Lopes et al. reported the synthesis and the release of NO upon reduction of *trans*-$[Ru(NH_3)_4L(NO)]^{3+}$ (L = C-bound imidazole or its derivatives), where L is coordinated to ruthenium(II) through carbene C2.[14] It is of great interest to prepare and characterize new ruthenium nitrosyl complexes with pyridine-functionalized NHCs and to study their applications in catalysis. Herein, we report the synthesis of the ruthenium nitrosyl complexs with the pyridine-functionalized NHC, L, and their use in catalytic transfer hydrogenation of ketones.

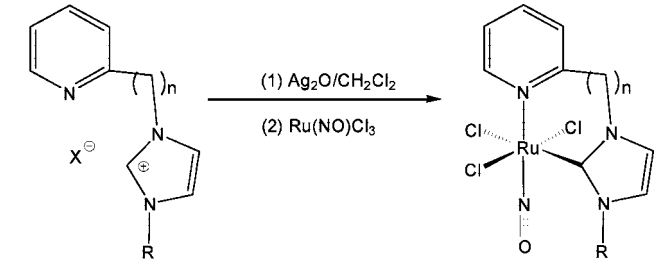


L

Results and Discussion

The transmetalation route using a silver NHC complex has proved to be useful in the preparation of a variety of NHC complexes.[15] In this study, we employed this route to prepare ruthenium nitrosyl complexes **2a**−**e** (Scheme 1). Reacting the imidazolium salts **1a**−**e** with an excess of Ag_2O in dichloromethane afforded the corresponding silver NHC complexes in situ, which were then treated with anhydrous $Ru(NO)Cl_3$ to yield the desired complexes **2a**−**e** with moderately low yields of 30−38%. The first step gave the intermediate silver NHC complex along with the formation of the byproduct water. Activated 4 Å molecular sieves were thus added to the reaction medium to remove the formed water, which was found to improve the yield and the purity of the product. In comparison, the desired products with only lower yields (10−20%) or impure products were obtained in the absence of molecular sieves. Complexes **2a**−**e** are very soluble in CH_3OH and CH_2Cl_2 but insoluble in diethyl ether and hydrocarbon solvents. The ^1H NMR spectra of **2a**−**e** do not exhibit the 2H-imidazolium proton

Scheme 1. Synthesis of Ruthenium(II) Nitrosyl Complexes 2a−e



n = 0, R = ^{t}Bu, X = Br, **1a**
n = 0, R = ^{n}Bu, X = Br, **1b**
n = 1, R = ^{t}Bu, X = Br, **1c**
n = 1, R = ^{n}Bu, X = Br, **1d**
n = 1, R = Bn, X = I, **1e**

n = 0, R = ^{t}Bu, **2a**
n = 0, R = ^{n}Bu, **2b**
n = 1, R = ^{t}Bu, **2c**
n = 1, R = ^{n}Bu, **2d**
n = 1, R = Bn, **2e**

signal at 10−12 ppm, indicating the coordination of the carbene carbon in **L** to ruthenium atom. The ^{13}C NMR signals for the carbene carbon atoms of **2a**−**e** (156.3−173.7 ppm) are located in the characteristic range reported for the carbene carbon signal of metal-NHC complexes.[3−8] It is well-known that ligands trans to the nitrosyl group influence the behavior of the nitrosyl group by interaction with the π^* orbitals of the nitrosyl group through the metal center.[10a,b] The nitrosyl group is located trans to the N atom of pyridine in **2a**−**e**. The nitrosyl stretching frequency in the IR spectra of **2a**−**e** (1865, 1872, 1875, 1872, and 1880 cm^{-1}, respectively) is shifted about 25−40 cm^{-1} to a lower frequency relative to the starting material anhydrous $RuNOCl_3$ (1905 cm^{-1}), an effect that illustrates the significant shift of electron density to NO by the pyridine groups in the functionalized NHCs. These nitrosyl stretching frequencies are within the characteristic range of the ruthenium nitrosyl complexes, indicating a linear coordination configuration of the nitrosyl group to d^6 Ru^{II} metal center.[10,12−12c]

The molecular structures of complexes **2a**−**c** have been established by single-crystal X-ray diffraction studies. For complex **2a**, the asymmetric unit contains four crystallographically nonequivalent molecules of **2a** and two cocrystallized methanol molecules. The structural parameters of these four molecules are almost the same, with only small differences in bond distances and bond angles. Therefore, only the structure of one molecule of **2a** is discussed below. The structures of **2a**−**c** are shown in Figures 1−3 with the selected bond lengths and angles given in the captions. The ORTEP drawings of **2a**−**c** show that the coordination geometry around the ruthenium atom can be rationalized as a slightly distorted octahedron with three chloride atom occupying mutually mer configuration. It is interesting to note that the NO group is located trans to the pyridine nitrogen. The Ru−NO bond lengths in **2a**−**c** are in the range of 1.708(3)−1.720(6) Å and are shorter than those in the reported ruthenium nitrosyl complexes with two nitrogen or phosphorus donor ligands *mer*-$[Ru(NO)Cl_3(L\text{-}L)]$ [L-L = bipyridine or diphosphine] (1.748−1.880 Å)[10c−f] but can be comparable to the Ru−NO bond length reported in *mer*-$[Ru(NO)Cl_3(DMSO)_2]$ (1.704 Å).[10g] The short Ru−NO bond lengths indicate stronger back bonding from Ru(II) to the NO ligands in **2a**−**c**. The $Ru-C_{carbene}$ distances Ru(1)−C(8) of 2.049(5) (**2a**), 2.015(3) (**2b**), and 2.098(3) Å (**2c**) are

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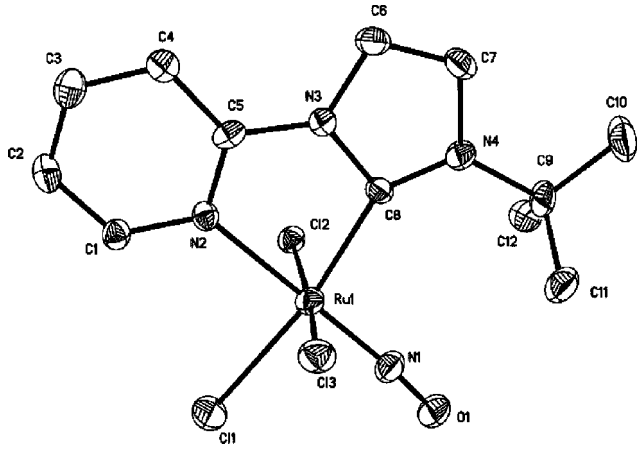


Figure 1. Structure of complex **2a** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−C8 = 2.049(5), Ru1−N1 = 1.720(6), Ru1−N2 = 2.104(5), Ru1−Cl1 = 2.4108(18), Ru1−Cl2 = 2.3702(17), and Ru1−Cl3 = 2.3796(17); N1−O1 = 1.155(7); and Ru1−N1−O1 = 171.8(6), N2−Ru1−C8 = 78.37(16).

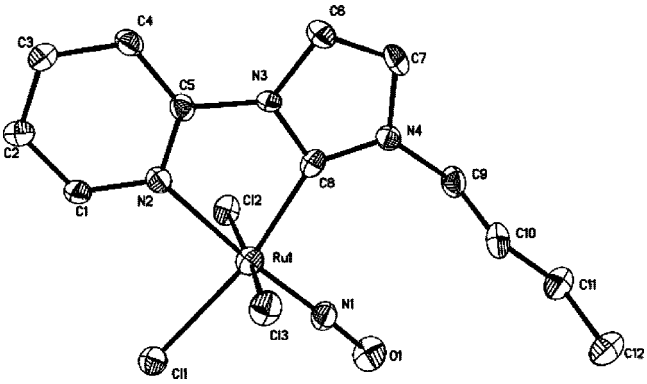


Figure 2. Structure of complex **2b** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−C8 = 2.015(3), Ru1−N1 = 1.708(3), and Ru1−N2 = 2.124(2); Ru1−Cl1 = 2.4128(8), Ru1−Cl2 = 2.3629(8), and Ru1−Cl3 = 2.3639(8); N1−O1 = 1.153(3); and Ru1−N1−O1 = 177.0(3), N2−Ru1−C8 = 76.64(10).

typical for Ru−NHC complexes.[3d,16] The Ru(1)−Cl(1) bond is longer than Ru(1)−Cl(2) and Ru(1)−Cl(3), indicating that the NHC carbons exert a strong trans influence, weakening the Ru−Cl bonds trans to carbene carbon due to their strong σ-donation.[6] The N(1)−O(1) distance [1.155(7) (**2a**), 1.153(3) (**2b**), and 1.145(4) Å (**2c**)] also lie in the range of other Ru−NO complexes.[10] Complexes **2a**−**c** have a linear Ru−N−O moiety with the respective angles Ru(1)−N(1)−O(1) 171.8(6)°, 177.0(3)°, and 172.8(3)°. These data confirmed the presence of the Ru^{II}−NO^{+} moiety in these ruthenium nitrosyl complexes,[10h−k] in which a high degree of positive charge resides on the coordinated nitrosyl; therefore, the

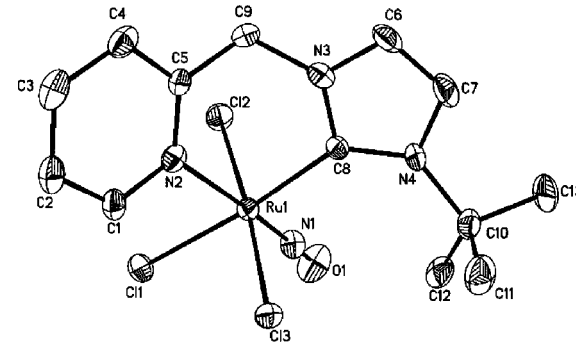
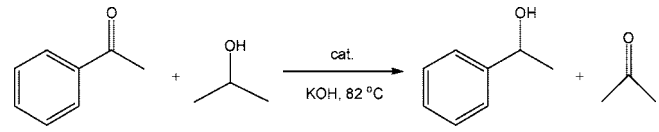


Figure 3. Structure of complex **2c** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1−C8 = 2.098(3), Ru1−N1 = 1.715(3), and Ru1−N2 = 2.152(3); Ru1−Cl1 = 2.4246(10), Ru1−Cl2 = 2.3912(10), and Ru1−Cl3 = 2.3746(9); N1−O1 = 1.145(4); and Ru1−N1−O1 = 172.8(3), N2−Ru1−C8 = 85.24(11).

complexes contain essentially ruthenium(II). Despite the fact that three structures are very similar, **2c** has a six-membered chelate ring with a relatively larger bite angle N2−Ru1−C8 of 85.24°, while only five-membered rings in **2a**,**b** with bite angles N2−Ru1−C8 of 78.37° and 76.64°.

Rutherium complexes have been used as active catalysts for transfer hydrogenation reactions;[17] however, only a very limited number of ruthenium−NHC complexes have been reported to be the catalysts for this transformation.[16e,f] Thus, complexes **2a**−**e** were studied as the catalysts for transfer hydrogenation of ketone. In the meantime, the ruthenium precursor $Ru(NO)Cl_3$ was examined under the same reaction conditions as to investigate the role of the pyridine-functionalized NHCs. The reduction of acetophenone to 1-phenylethanol by 2-propanol has been chosen as a model reaction in transfer hydrogenation, using 2-propanol as a hydrogen donor in the presence of base. To evaluate the difference between the various carbene complexes, the time-dependent conversions were followed (Figure 4).



It was found that complexes **2a**−**e** are much more active than anhydrous $Ru(NO)Cl_3$, suggesting that the presence of the pyridine-functionlaized carbene ligand is beneficial for the transfer hydrogenation of ketone. Compounds **2a**−**e** are active and reasonably efficient transfer hydrogenation catalysts, giving rise to nearly quantitative conversions (yield >96%) of acetophenone into 1-phenylethanol within 2−4 h. The complexes give >75% conversion after 1.0 h, and the relative activity sequence up to ~1.0 h is **2c** > **2a** > **2b** > **2d** > **2e**. It appeared that **2a**−**c** are more active than the other two complexes. It should be mentioned that the most active species **2a** and **2c** are bearing *t*-butyl group at the N atom of the imidazole moiety. Noyori and co-workers have shown that the true catalyst in transfer hydrogenation reaction is formally a 16-electron

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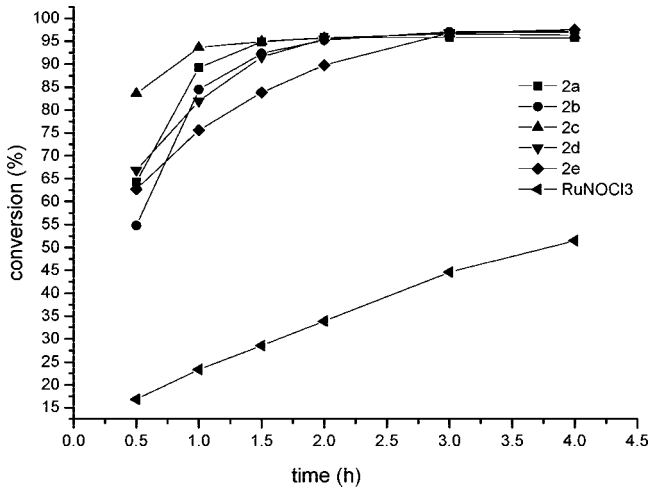
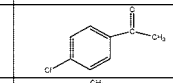
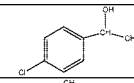
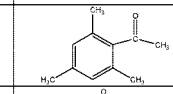
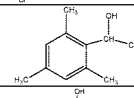
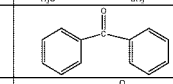
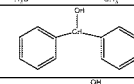
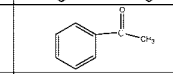
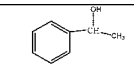
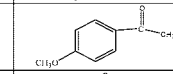
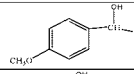
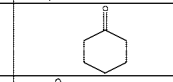
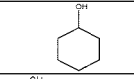
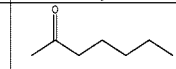
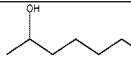


Figure 4. Conversion vs reaction time of the catalytic transfer hydrogenation of acetophenone. Experimental conditions: 8 μmol of catalyst (**2a**−**e**,**s**), 0.2 mmol of KOH, 2 mmol of acetophenone, solvent ^{i}PrOH (10 mL), and T = 355 K.

intermediate species.[19] It is possible that the bulky ligand helps the formation of a stable of 16-electronic intermediates, which shows high activity in transfer hydrogenation process. To determine the fate of nitrosyl ligand in the catalytic reaction, we have attempted to probe if the nitrosyl ligand still existed in the coordination sphere of ruthenium for the catalytic reduction of acetophenone with **2a** and **2c**. After the catalytic reaction, the reaction mixture was evaporated to give a solid. The IR spectra of the isolated solids showed the absence of nitrosyl ligand around the ruthenium atom, indicating that the nitrosyl group did not survive in the reaction conditions. The active catalytic species apparently do not contain the nitrosyl group. It is thus reasonable to assume that complexes **2a**−**e** just acted as precursors to the active catalyts and that the nitrosyl ligands probably play no role in transfer hydrogenation reactions.

Because complex **2c** was found to be the most efficient catalyst in transfer hydrogenation of acetophenone, we decided to further explore its catalytic potential in the reduction of other aryl and alkyl ketones with the reaction condition similar to those used in the transfer hydrogenation of acetophenone (Table 1). It was found that **2c** is efficient in transfer hydrogenation of cyclohexanone to cyclohexanol (93.99% conversion after 2 h, entry 6) and 4-chloroacetophenone to 4-chlorophenylethanol (97.9% conversion after 6 h, entry 1), reasonably active in the case of diphenylketone (63.67% after 6 h, entry 3) and 2-heptanone (66.84% after 6 h, entry 7), but shows a poor activity to transfer hydrogenation of 4-methoxyacetophenone to 4-methoxyphenylethanol (21.00% after 6 h, entry 5) and the reduction of 2,4,6-trimethylacetophenone (35.35% after 6 h, entry 2). These different activities in these substrates may be attributed to the electron and steric effects of the substituents on the ketones.

Table 1. Catalytic Transfer Hydrogenation of Ketones with Complex 2c[a]

entry	Ketone	Alcohol	Conversion% (h)[b]
1			97.90(6)
2			35.35(6)
3			63.67(6)
4			96.34(4)
5			21.00(6)
6			93.99(2)
7			66.84(6)

[a] Experimental conditions: Reactions were carried out at 82 °C; acetophenoe (2 mmol), complex **2c** (8 μmol), and KOH (0.2 mmol) in 2-propanol (10 mL); ketone/Ru/KOH = 1000/4/100. [b] The conversion was determined by GC analysis.

Experimental Section

General Procedures. Unless otherwise noted, all reactions and manipulations were performed under a dry nitrogen atmosphere using a standard Schlenk technique. The solvents were purified using standard methods and degassed before use. Methanol was dried over Mg, and dichloromethane was dried over P_2O_5 and then distilled under nitrogen. Other chemicals were purchased from commercial sources and used without further purification. The starting materials $[Ru(NO)Cl_3(H_2O)_2]$,[10k] 1-*t*-butyl imidazole,[18] 3-*t*-butyl-1-(2-pyridyl)imidazolium bromide (**1a**),[8] 3-*n*-butyl-1-(2-pyridyl)imidazolium bromide (**1b**),[6c] 3-*t*-butyl-1-(2-picoly)imidazolium bromide (**1c**),[8] 3-*n*-butyl-1-(2-picoly)-imidazolium bromide (**1d**),[8] and 3-benzyl-1-(2-picoly)imidazolium iodide (**1e**)[5a] were prepared according to the literature methods. Elemental analysis was performed in an Elementar Vario ELIII elemental analyzer. NMR measurements were obtained in $CDCl_3$ and DMSO-d_6 on a Bruker AM-500 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^{1}H and ^{13}C NMR. The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000−400 cm^{-1} region. The GC analyses of the catalytic mixture were performed on a Shimadzu GC-2010.

Preparation of Anhydrous Trichloronitrosylruthenium. Anhydrous $Ru(NO)Cl_3$ was prepared by the dehydration of the complex $[RuNOCl_3(H_2O)_2]$ in $SOCl_2$. Newly distilled $SOCl_2$ (30 mL) was added to the $[RuNOCl_3(H_2O)_2]$ (7.75 g, 28.3 mmol), and gases HCl and SO_2 were immediately released. The solution was refluxed at 80 °C for 2 days under N_2. Filtration gave the brick-red solid powder of anhydrous $Ru(NO)Cl_3$. The product was dried in vacuo and stored in a glovebox. Yield, 5.65 g (84%). IR: ν (NO) 1905 cm^{-1}.

Preparation of Ruthenium Complexes 2a−e. A suspension of the ligand precursor **1a**−**e** (1.0 mmol), silver oxide (0.24 g, 1.0 mmol), and some activated 4 Å molecular sieves was stirred in dichloromethane (30 mL) at 40 °C for 24 h. The product mixture was then filtered to remove the unreacted silver oxide. Anhydrous $Ru(NO)Cl_3$ (0.24 g, 1.0 mmol) was added to the solution and stirred at 40 °C for another 24 h. The formed silver halide was removed by filtration. The filtrate was subsequently concentrated and purified by column chromatography. Elution with dichloromethane/methanol (40: 1) afforded the separation of a purple band that contained the desired product. Recrystallization from a saturated solution of methanol gave pure products suitable for elemental analysis and crystal for X-ray diffraction (for **2a**−**c**).

Compound 2a. Yield, 0.12 g, 30%. Anal. calcd for $C_{12}H_{15}Cl_3N_4ORu$: C, 32.85; H, 3.45; N, 12.77. Found: C, 33.04; H, 3.66; N, 12.76. IR: ν (NO) 1865 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.43 (d,

(18) Liu, J. P.; Ren, Z. Y.; Zhao, Y. H.; Zhang, H. B. *Chin. J. Org. Chem.* **2004**, *24*, 1091–1094.

(19) Haack, K. J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285–288.

1H, 6-*H* of py), 8.75 and 8.02 (d, 2 × 1H, 4,5-imidazol-2-ylidene *H*), 8.52 and 8.42 (dt, 2 × 1H, 3,5-*H* of py), 7.77 (dt, 1H, 4-*H* of py), 1.76 (9H, s, [C(CH_3)$_3$]). ^{13}C NMR (DMSO-d_6): δ 171.7 (2-imidazol-2-ylidene *C*), 150.1, 148.6, 145.2 (py *C*), 124.8, 124.2, 117.7, 113.7 (py and 4,5-imidazol-2-ylidene *C*), 60.2[*C*(CH$_3$)$_3$], 30.7 [C(*C*H$_3$)$_3$].

Compound 2b. Yield, 0.13 g, 30%. Anal. calcd for $C_{12}H_{15}Cl_3N_4ORu$: C, 32.85; H, 3.45; N, 12.77. Found: C, 32.67; H, 3.30; N, 12.82. IR: ν (NO) 1872 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.33 (d, 1H, 6-*H* of py), 8.71 and 7.97 (d, 2 × 1H, 4,5-imidazol-2-ylidene *H*), 8.51 and 8.38 (dt, 2 × 1H, 3,5-H of py), 7.75 (dt, 1H, 4-*H* of py), 4.25 (t, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.88 (quintet, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.40 (sextet, 2H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.95 (t, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (DMSO-d_6): δ 173.7 (2-imidazol-2-ylidene *C*), 150.3, 148.9, 144.9 (py *C*), 127.3, 123.9, 118.9, 113.5 (py and 4,5-imidazol-2-ylidene *C*), 50.5, 32.7, 19.4, 13.8 (N*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$).

Compound 2c. Yield, 0.17 g, 38%. Anal. calcd for $C_{13}H_{17}Cl_3N_4ORu$: C, 34.49; H, 3.78; N, 12.38. Found: C, 34.37; H, 3.86; N, 12.22. IR: ν (NO) 1875 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.56 (d, 1H, 6-*H* of py), 7.92 and 7.81 (d, 2 × 1H, 4,5-imidazol-2-ylidene *H*), 8.24 and 7.75 (dt, 2 × 1H, 3,5-*H* of py), 7.72 (dt, 1H, 4-*H* of py), 6.15 (s, 2H, pyC*H*$_2$im), 1.87 (9H, s, [C(C*H*$_3$)$_3$]). ^{13}C NMR (DMSO-d_6): δ 156.3 (2-imidazol-2-ylidene *C*), 155.9, 154.3, 142.9 (py *C*), 125.6, 124.9, 124.8, 124.6 (py and 4,5-imidazol-2-ylidene *C*), 62.8 [*C*(CH$_3$)$_3$], 55.2(py*C*H$_2$im), 32.3 [C(*C*H$_3$)$_3$].

Compound 2d. Yield, 0.15 g, 33%. Anal. calcd for $C_{13}H_{17}Cl_3N_4ORu$: 34.49; H, 3.78; N, 12.38. Found: C, 34.19; H, 3.90; N, 11.98. IR: ν (NO) 1872 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.50 (d, 1H, 6-*H* of py), 8.24 (t, 1H, 4-H of Py), 7.78−7.72 (2 × 1H, 4,5-imidazol-2-ylidene, 2 × 1H, 3,5-*H* of py; 1H, 4-*H* of py), 6.04 (s, 2H, pyC*H*$_2$im), 4.22 (t, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.85 (quintet, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.43 (sextet, 2H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.94 (t, 3H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (DMSO-d_6): δ 158.3 (2-imidazol-2-ylidene *C*), 155.5, 153.7, 142.5 (py *C*), 125.8, 124.8, 124.6, 123.7 (py and 4,5-imidazol-2-ylidene *C*), 53.6 (py*C*H$_2$im), 49.9, 33.2, 19.8, 14.0 (N*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$).

Compound 2e. Yield, 0.19 g, 36%. Anal. calcd for $C_{16}H_{15}Cl_3N_4ORu$: C, 39.48; H, 3.11; N, 11.51. Found: C, 39.94; H, 3.09; N, 11.21. IR: ν (NO) 1880 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.53 (d, 1H, 6-*H* of py), 8.25 and 7.75 (dt, 2 × 1H, 3,5-*H* of py), 7.81 (2 × 1H, 4,5-imidazol-2-ylidene *H*), 7.36 (dt, 1H, 4-*H* of py), 7.50, 7.42, 7.15 (1*H*, 2*H*, 2*H*, Ph), 6.12 (s, 2H, NC*H*$_2$), 5.61 (s, 2H, NC*H*$_2$). ^{13}C NMR (DMSO-d_6): δ 160.5 (2-imidazol-2-ylidene *C*), 155.9, 154.1, 142.9 (py *C*), 137.2, 124.9, 129.9, 128.9 (py and 4,5-imidazol-2-ylidene *C*), 127.3, 126.3, 125.4, 125.1 (Ph, *C*), 54.1 (NCH$_2$, *C*), 53.2 (NCH$_2$, *C*).

General Procedure for the Catalytic Transfer Hydrogenation Studies. The transfer hydrogenation experiments were carried out using standard Schlenk glassware. Organic substrate ketone (2.0 mmol) and ruthenium complex (8 μmol) were dissolved in ^{i}PrOH (8 mL) in a Schelenk tube. The solution was allowed to warm to 82 °C for 30 min under nitrogen. By addition of 2 mL of a 0.1 M KOH in ^{i}PrOH, the reaction started immediately. The reaction progress was monitored by GC analysis.

Acknowledgment. We are grateful for the financial support from the National Basic Research Program of China (Nos. 2006CB806104 and 2007CB925102), Natural Science Grant of China (Nos. 20721002 and 10676012), and the U.S. National Science Foundation.

Supporting Information Available: Detailed X-ray structure determination procedures, summary of crystallographic data (Table 1S), bond lengths and bond angles (Table 2S), and CIF files giving crystallographica data for **2a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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