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Transfer Hydrogenation of Ketones Catalyzed by 1-Alkylbenzimidazole Ruthenium(II) Complexes

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Summary. Six [$RuCl_2$(1-alkylbenzimidazole)(*p*-cymene)] complexes have been prepared and the new compounds characterized by C, H, N analyses, ^{1}H NMR, and ^{13}C NMR. The reduction of ketones to alcohols *via* transfer hydrogenation was achieved with catalytic amounts of the complexes in the presence of *t-Bu*OK.

Keywords. Ruthenium; Benzimidazole ligands; Transfer hydrogenation; Homogeneous catalysis.

Introduction

The design of new ligands for promoting high reactivity and selectivity in metal-catalyzed synthesis is a field of constant ongoing research. Nitrogen-containing heterocyclic ligands are receiving more and more attention in the fields of coordination chemistry, homogeneous catalysis, and organic synthesis because organometallic complexes containing nitrogen donor ligands usually exhibit high reactivities [1]. The coordination chemistry of imidazole and related compounds, including benzimidazoles, benzoxazoles, and benzothiazoles, has been extensively studied in part because of their role in aspects of catalysis and biomimetics. Also transition metal complexes with nitrogen-containing ligands have recently shown their potential to perform selective catalytic transformations of molecules with atom economy [2]. Especially, a variety of [RuX_2(arene)-(*L*)] complexes are promoting catalytic reactions such as nucleophilic addition to triple bonds to form furans (*L* = imidazoline, tetrahydropyrimidine [3], benzimidazole [4]), hydrogen transfer (*L* = amino acid [5], amino alcohol [6]), cyclopropanation (*L* = diamine [7]), or *Diels-Alder* cycloaddition and *Claisen* rearrangement (*L* = bisoxazoline [8, 9]). It is also well established that [$RuCl_2$(arene)(*L*)] complexes can easily be transformed *via* activation of propargylic alcohols into cationic ruthenium allenylidene complexes, which have shown catalytic properties in olefin metathesis [10]. These discoveries motivate the search for the new metal complexes with N-coordinated ligands and the evaluation of their catalytic properties.

Our contribution to this field has started with syntheses of 2-imidazoline and benzimidazole complexes of Pt(II), Rh(I), Ru(II), and Pd(II) which are capable of catalyzing the cyclopropanation of styrene with ethyl diazoacetate and intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran in good yields [11–14]. Recently, we have developed improved procedures for *Suzuki* reactions of aryl chlorides making use of novel ligands 1-alkylimidazoline and 1-alkylbenzimidazole [15, 16]. The 1-alkybenzimidazole complexes are insensitive to air and moisture and are thermally stable in both the solid state and in solution.

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The reduction of organic compounds is a subject of remarkable interest from both academic and industrial perspectives. Several viable methodologies have been established for this purpose, and most of them make use of a metal, in either stoichiometric or catalytic amounts, to promote the reaction between the reducing agent and the substrate. Transfer hydrogenation is a further one of these methodologies, and transition-metal catalyzed transfer hydrogenation of ketones is currently considered as a promising alternative to the widely used catalytic hydrogenation [17]. The reaction conditions for this important process are economic, relatively mild and environmentally friendly. The most commonly used catalysts for this reaction are ruthenium(II) complexes, but some rhodium and iridium derivatives have also been used [18]. Exploration of new ligands for construction of ruthenium(II) catalysts has been one of the greatest motivations for work in this area.

Based on these findings and our, continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of ruthenium-benzimidazole complexes for the transfer hydrogenation of ketones.

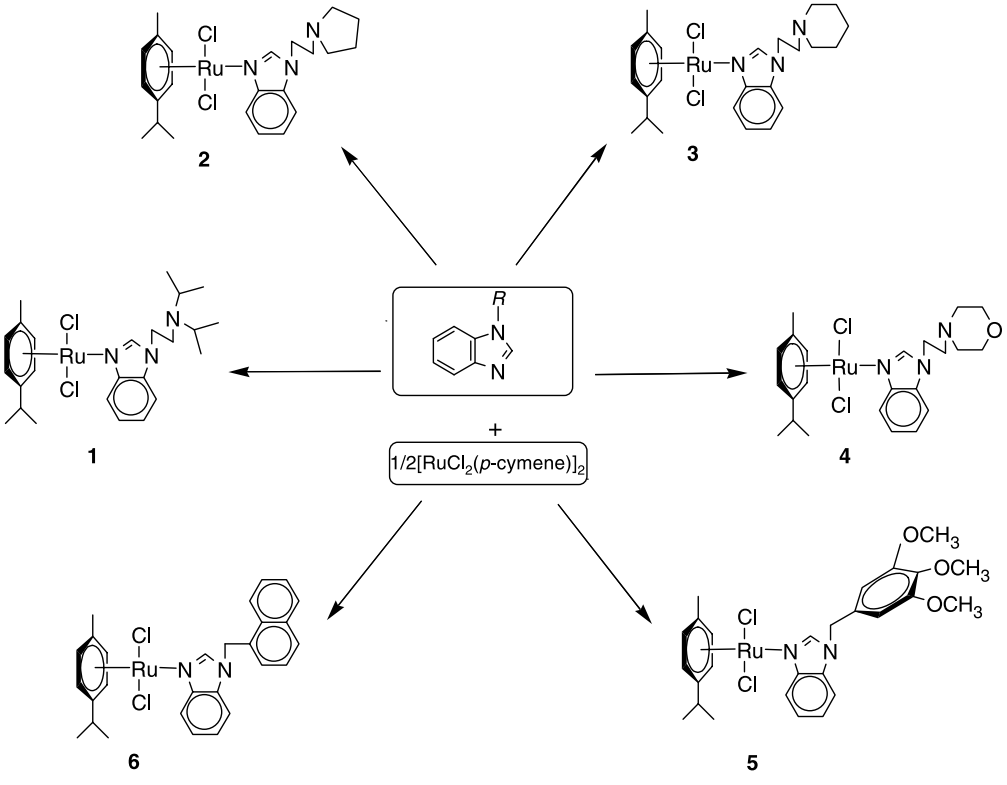
Results and Discussion

The reaction of 1-alkylbenzimidazole with the binuclear $[RuCl_2(p\text{-cymene})]_2$ complex proceeded smoothly in refluxing toluene to give the $[RuCl_2$(1-alkylbenzimidazole)$(p$-cymene)] complexes **1–6** as crystalline solids in 78–92% yields (Scheme 1).

The complexes **1–6** which are very stable in the solid state, were characterized by analytical and spectroscopic data. The spectroscopic properties indicate that they all are N(3)-bonded.

The nature of the bonding in the benzimidazole complexes **1–6** was readily shown by NMR spectroscopy. ^{13}C NMR spectroscopy was the most useful tool for structure elucidation.

Thus, from our previous experience [19–21] we expected that C-coordination would result in a shift of the carbene carbon nucleus signal toward low field *i.e.*, 190–212 ppm, while N-coordination would result in a high field shift towards 155 ppm. ^{13}C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode at 145.7, 145.8, 145.8, 145.7, 145.7, and 145.2 ppm for **1–6**. The ^{1}H NMR spectra of the complexes further



Scheme 1. Synthesis of 1-alkylbenzimidazoleruthenium(II) complexes

supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets at 8.43, 8.43, 8.50, 8.47, 8.45, and 8.30 ppm for **1**–**6**. The IR data for **1**–**6** clearly indicate the presence of the –C=N– group with a $\bar{\nu}$(C=N) vibration at 1510, 1509, 1515, 1516, 1514, and 1511 cm^{-1} for **1**–**6**. The NMR and IR values are similar to those found for N-coordinated metal complexes [3, 4, 11–14].

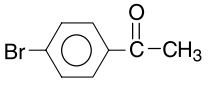
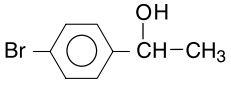
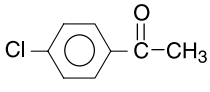
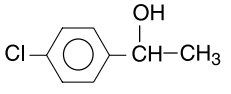
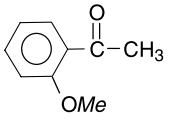
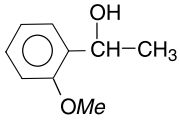
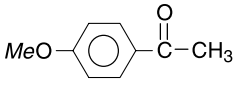
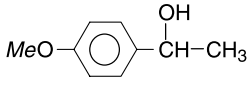
Catalytic reduction is preferred to stochiometric reduction for large scale industrial processes of ketones hydrogenation and they are well known [22]. Hydrogen gas presents considerable safety hazards especially for large scale reactions [23]. The use of a solvent that can donate hydrogen overcomes these difficulties. 2-Propanol is a popular reactive solvent for transfer hydrogenation reactions since it is easy to handle (bp 82°C) and is relatively non-toxic, environmentally benign, and inexpensive. The volatile acetone by-product can also be easily removed to shift unfavourable equilibria.

Transfer hydrogenations of ketones were carried out in 2-propanol at 80°C with *in situ* prepared complexes **1′**–**6′**, which were obtained from **1**–**6** by exchanging a chloro ligand to a triflate group, as the catalysts and *tBu*OK as the base. The results were summarized in Table 1.

Complexes **3**–**6** showed high activity for most of the ketones listed in Table 1 (entries: 3, 4, 8, 9, 11, 13, 15, and 21). The introduction of electron-withdrawing substituents, such as Cl and Br to the *para* position of the aryl ring of the ketone decreased the electron density on the C=O bond so that the activity (entries 3, 15) was improved giving rise to easier hydrogenation.

In conclusion, from readily available starting materials, such as 1-alkylbenzimidazole, six ruthenium-benzimidazole complexes **1**–**6** were prepared and characterized. *In situ* prepared [RuCl(1-alkylbenzimidazole)(*p*-cymene)]O*Tf* (**1′**–**6′**) complexes exhibited very high catalytic efficiency in the transfer hydrogenation of ketones. The procedure is simple and efficient towards various aryl ketones. Studies on the reactivity of the new complexes, extension of the methodology

Table 1. Catalytic transfer hydrogenation of acetophenones with 1-benzimidazole ruthenium(II) complexes

Entry	Catalyst	Substrate	Product	Yield/%[a,b]
1	**1**			91
2	**2**			90
3	**3**			95
4	**4**			88
5	**5**			95
6	**6**			96
7	**1**			97
8	**2**			98
9	**3**			100
10	**4**			98
11	**5**			98
12	**6**			96
13	**1**			95
14	**2**			96
15	**3**			98
16	**4**			91
17	**5**			86
18	**6**			88
19	**1**			82
20	**2**			88
21	**3**			90
22	**4**			86
23	**5**			87
24	**6**			84

[a] Catalyst (0.01 mmol), AgO*Tf* (0.01 mmol in 2 cm^3 CH_2Cl_2), substrate (1 mmol), ^iPrOH (10 cm^3), KOBu^t (5 mmol%), 80°C, 12 h
[b] Purity of compounds is checked by NMR and GC, and yields are based on methyl aryl ketone

to other transition metals and the synthesis of other functionalised 1-alkylbenzimidazole and imidazoline ligands with a variety of other donor functionalities is under way. Future investigations are aiming at the development of an asymmetric version of this process.

Experimental

Methylene chloride was purchased from Merck and distilled from P_2O_5 prior to use. Toluene and *n*-hexane were purchased from Aldrich or Merck and distilled from Na/benzophenone. 2-Propanol was purchased from Aldrich or Acros Chemicals. AgO*Tf* was purchased from Aldrich. All manipulations were carried out using standard *Schlenk* techniques under an inert atmosphere of N_2 or Ar. The complex $[RuCl_2(p\text{-cymene})]_2$ [24] and 1-alkylbenzimidazoles were prepared according to known methods [16]. FT-IR spectra were recorded as KBr pellets in which 10 mg samples were mixed with KBr and pelleted under 5 ton cm^{-2} pressure in the range of 400–4000 cm^{-1} on a ATI UNICAM 2000 model spectrometer. All ^1H and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker AM 400 WB FT spectrometer. ^1H NMR spectra were collected at 400.0 MHz using a 6000 Hz spectral width, a relaxation delay of 3s, 30k data points, a pulse width of 35°, and ^{13}C NMR spectra were collected at 100.0 MHz and chemical shifts were referenced to residual solvent $CDCl_3$. All NMR samples were prepared under an Ar atmosphere prior to the analyses. Microanalyses were performed by the TÜBITAK Analyses Center; results agreed with calculated values. Gas chromatographic analyses were performed on an Agilent 6890N instrument equipped with a 30 m capillary column of 5% phenylmethylsilicone.

Preparation of $RuCl_2$(p-cymene)(1-(2-diisopropylaminoethyl) benzimidazole) (**1**)

A solution of 0.276 g 1-(2-diisopropylaminoethyl)benzimidazole (1.0 mmol) and 0.31 g $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) in 10 cm^3 toluene was heated under reflux for 4 h. Upon cooling to room temperature, orange crystals of **1** were obtained. The crystals were filtered off, washed with diethyl ether (3 × 10 cm^3), and dried under vacuum. The yield was 0.51 g, 92%, mp 215.5–216°C. IR: $\bar{\nu}_{(CN)} = 1510\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 0.92$ (d, $J = 12.8$ Hz, 12H, $NCH_2CH_2N(CH(CH_3)_2)_2$), 1.31 (d, $J = 13.6$ Hz, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.16 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.98 (hept, $J = 12.7$ Hz, 2H, $NCH_2CH_2N(CH(CH_3)_2)_2$), 2.98 (hept, $J = 12.7$ Hz, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.81 and 4.04 (t, $J = 20.4$ Hz, 4H, $NCH_2CH_2N(CH(CH_3)_2)_2$), 5.38 and 5.54 (d, $J = 12$ Hz, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 7.36–8.20 (m, 4H, C_6H_4-*o*), 8.43 (s, 1H, 2-C*H*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 19.0$, 22.8, 31.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 21.3, 44.9, 47.3, 49 (NCH_2CH_2N-(CH$(CH_3)_2)_2$), 81.6, 83.2, 97.8, 103.2 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 111, 121.1, 123.7, 124.3, 142.8 (C_6H_4-*o*), 145.7 (2-*C*H) ppm.

Preparation of $RuCl_2$(p-cymene)1-(pyrrolidinoethyl) benzimidazole (**2**)

Compound **2** was prepared in the same way as **1** from 0.229 g 1-pyrrolidinoethylbenzimidazole (1.0 mmol) and 0.31 g $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) to give 0.41 g orange crystals of **2**, 78% yield, mp 204.5–205°C. IR: $\bar{\nu}_{(CN)} = 1509\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.84$ (d, $J = 7.0$ Hz, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.09 and 2.77 (m, 8H, pyrrolidin), 2.56 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.86 and 4.09 (t, $J = 6.0$ Hz, 2H, NCH_2CH_2N), 2.89 (hept, $J = 6.0$ Hz, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.37 and 5.53 (d, J = 6.0 Hz, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 7.31–8.04 (m, 4H, C_6H_4-*o*), 8.43 (s, 1H, 2-C*H*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.9$, 22.8, 31.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 15.5, 23.8 (pyrrolidin), 23.9, 54.3 (NCH_2CH_2N), 81.6, 83.3, 98.0, 103.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 111.4, 120.9, 123.8, 124.5, 132.7, 133.9 (C_6H_4-*o*), 145.8 (2-*C*H) ppm.

Preparation of $RuCl_2$(p-cymene)1-(piperidinoethyl) benzimidazole (**3**)

Compound **3** was prepared in the same way as **1** from 0.245 g 1-piperidinoethylbenzimidazole (1.0 mmol) and 0.31 g $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) to give 0.46 g orange crystals of **3**, 86% yield, mp 211–211.5°C. IR: $\bar{\nu}_{(CN)} = 1515\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.42$, 1.47 and 2.36 (m, 10H, piperidin), 1.46 (d, $J = 6.8$ Hz, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.11 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.52 and 4.19 (m, 4H, NCH_2CH_2N), 2.89 (hept, $J = 6.8$ Hz, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.41 and 5.56 (d, $J = 5.8$ Hz, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 7.01–8.03 (m, 4H, C_6H_4-*o*), 8.50 (s, 1H, 2-C*H*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.9$, 22.8, 31.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 18.8, 22.7, 35.1 (piperidin), 53.8, 57.4 (NCH_2CH_2N), 81.6, 83.4, 97.9, 103.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 110.9, 120.8, 120.9, 123.8, 124.3, 132.5 (C_6H_4-*o*), 145.8 (2-*C*H) ppm.

Preparation of $RuCl_2$(p-cymene)1-(morpholinoethyl) benzimidazole (**4**)

Compound **4** was prepared in the same way as **1** from 0.231 g 1-morpholinoethylbenzimidazole (1.0 mmol) and 0.31 g $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) to give 0.43 g orange crystals of **4**, 80% yield, mp 232–232.5°C. IR: $\bar{\nu}_{(CN)} = 1516\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.28$ (d, $J = 7.0$ Hz, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.11 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.44 and 3.66 (m, 8H, CH_2CH_2-morpholin), 2.63 and 3.99 (m, 4H, CH_2CH_2-morpholin), 2.89 (hept, $J = 7.0$ Hz, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.40 and 5.56 (d, $J = 5.6$ Hz, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 7.28–7.99 (m, 4H, C_6H_4-*o*), 8.47 (s, 1H, 2-C*H*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.9$, 22.7, 31.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 42.9, 53.9, 57.4, 67.1 ($CH_2CH_2N(CH_2CH_2)_2O$), 81.7, 83.3, 97.9, 103.1 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 111.3, 120.8, 123.5, 124.4, 132.6, 142.5 (C_6H_4-*o*), 145.7 (2-*C*H) ppm.

Preparation of $RuCl_2$(p-cymene)(1-(3,4,5-trimethoxybenzyl) benzimidazole) (**5**)

Compound **5** was prepared in the same way as **1** from 0.247 g 1-(3,4,5-trimethoxybenzyl)benzimidazole (1.0 mmol) and 0.31 g $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) to give 0.56 g orange crystals of **5**, 92% yield, mp 228.5–229°C. IR: $\bar{\nu}_{(CN)} = 1514\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.21$ (d, $J = 6.8$ Hz, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.07 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.52 and 4.19 (m, 4H, NCH_2CH_2N), 2.71 (hept, $J = 6.8$ Hz, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 3.77 and 3.79 (s, 9H, 3,4,5-

($H_3CO)_3$ $C_6H_2CH_2$), 4.99 (s, 2H, 3,4,5-$(H_3CO)_3C_6H_2CH_2$), 5.37 and 5.53 (d, $J = 5.8$ Hz, 4H, $(CH_3)_2$ $CHC_6H_4CH_3$-*p*), 6.42 (s, 2H, 3,4,5-$(H_3CO)_3C_6H_2CH_2$), 7.28–8.04 (m, 4H, C_6H_4-*o*), 8.45 (s, 1H, 2-C*H*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.9$, 22.7, 31.1 (($CH_3)_2CHC_6H_4CH_3$-*p*), 50.1, 56.8, 61.3 (3,4,5-$(H_3CO)_3$ $C_6H_2CH_2$), 81.4, 83.6, 98.2, 102.7 (($CH_3)_2CHC_6H_4CH_3$-*p*), 105.3, 130.7, 138.5, 145.3 (3,4,5-$(H_3CO)_3C_6H_2CH_2$), 111.9, 120.8, 123.9, 124.8, 134.1, 142.9 (C_6H_4-*o*), 154.1 (2-*C*H) ppm.

Preparation of $RuCl_2$(p-cymene) (1-naphthalenomethyl) benzimidazole (**6**)

Compound **6** was prepared in the same way as **1** from 0.298 g 1-naphthalenomethylbenzimidazole (1.0 mmol) and 0.31 g $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) to give 0.50 g orange crystals of **6**, 89% yield, mp 248.5–249°C. IR: $\bar{\nu}_{(CN)} = 1511$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 0.97$ (d, $J = 6.4$ Hz, 6H, $(CH_3)_2CH$ $C_6H_4CH_3$-*p*), 2.03 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.49 (hept, $J = 6.4$ Hz, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.28 and 5.37 (d, $J =$ 6.4 Hz, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.66 (s, 2H, $C_{10}H_7CH_2$), 7.31–8.10 (m, 11H, C_6H_4-*o* and $C_{10}H_7CH_2$), 8.30 (s, 1H, 2-C*H*) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.6$, 22.5, 30.7 (($CH_3)_2$ CHC_6 H_4CH_3-*p*), 47.8 ($C_{10}H_7CH_2$), 81.1, 83.2, 98.4, 102.2 (($CH_3)_2$ $CHC_6H_4CH_3$-*p*), 111.2, 121.1, 123.9, 124.6, 134.1, 142.8 (C_6H_4-*o*), 122.4, 125.8, 126.5, 127.3, 127.4, 129.5, 129.6, 130.0, 130.9, 134.2 ($C_{10}H_7CH_2$), 145.2 (2-*C*H) ppm.

Typical Procedure for the Transfer Hydrogenation of Ketones

The complexes [$RuCl_2$(1-alkylbenzimidazole)(*p*-cymene)] **1**–**6** (0.01 mmol) and AgO*Tf* (0.01 mmol, 2.57 mg) were introduced into a *Schlenk* tube under Ar. Dry and degassed CH_2Cl_2 (3 cm^3) was added, the suspension were stirred at room temperature for 30 min, and the solvent was removed by vacuum to give [RuCl(1-alkylbenzimidazole)(*p*-cymene)]O*Tf* (**1′**–**6′**). After that 10 cm^3 2-propanol, *t-Bu*OK (5 mmol%), and 1 mmol of the substrate were added to **1′**–**6′**. The resulting solution was heated at 80°C for 12 h. The solvent was then removed under reduced pressure and product distribution was determined by ^{1}H NMR spectroscopy and GC.

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