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Transfer Hydrogenation of Ketones by Ruthenium Complexes Bearing Benzimidazol-2-ylidene Ligands

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A series of benzimidazolium ligand precursors were metalated with $[RuCl_2(p\text{-cymene})]_2$ to give ruthenium(II) *N*-heterocyclic carbene complexes. All compounds were fully characterized by elemental analyses, ^1H NMR, ^{13}C NMR, and IR spectroscopy. The new benzimidazol-2-ylidene complexes have been found to be effective catalysis for the transfer hydrogenation of ketones by using 2-propanol as the hydrogen source in the presence of KOH.

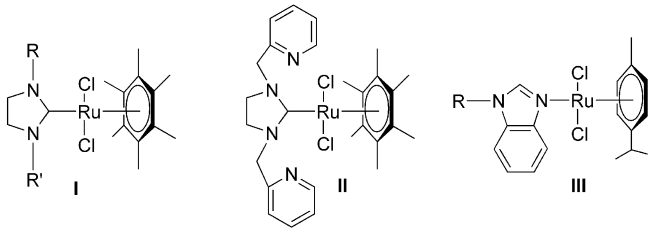
Introduction

Hydrogenation and transfer hydrogenation of unsaturated compounds are among the most important synthetic reactions not only from an academic standpoint but from an industrial standpoint as well, because these processes are operationally simple, environmentally friendly, and economic.[1] When compared to hydride reagents and hydrogen, these methods offer simple and safe operation and low costs, which are important, particularly on large-scale preparations. The processes involve hydrogen transfer from a donor to an unsaturated compound.[2]

Transfer hydrogenation of ketones catalyzed by metal complexes is one of the most important route to reduce ketones to alcohols, and it has been extensively investigated.[3] A broad range of alcohols are accessible by transfer hydrogenation under mild reaction conditions in the presence of various metal catalysts.[4] A large number of ruthenium complexes have been reported as catalyst precursors for the transfer hydrogenation of ketones and have shown high activity.[5] Several recent examples of ruthenium complexes bearing phosphanes,[6] *N*-heterocyclic carbenes (NHCs),[7] diamines,[8] diaminodiphosphanes or aminodiphosphanes,[9] amine–bis(phenolate)s,[10] chiral phosphanes,[11] nitrogen-containing chiral ligands,[12] and nitrogen-containing heterocyclic ligands[13] have become the most prominent members for the reduction of ketones in high yields.

Recently, research has also been devoted to the synthesis of functionalized ligands containing NHC moieties to modify ligand properties and catalytic activities.[14] The first application of NHC complexes for the transfer hydrogenation reaction was reported by Nolan in 2001.[15] With regard to transfer hydrogenations, different carbene or carbene–phosphane systems containing Rh,[16] Ir,[16,17] Ru,[18] and Ni[19] have been reported.

Previously, our laboratory reported the application of imidazolidin-2-ylidene ruthenium complexes **I**–**II** and benzimidazole ruthenium complexes **III** in the transfer hydrogenation of aromatic ketones.[20]



In view of the growing interest in the catalytic activities of ruthenium complexes to act as efficient catalysts in the transfer hydrogenation of ketones, we herein report the synthesis of new benzimidazol-2-ylidene ruthenium(II) complexes. The characterization of the complexes was accomplished by analytical and spectral methods. Further, the synthesized complexes were effectively used as catalysts in the transfer hydrogenation of ketones in the presence of 2-propanol and KOH as base.

Results and Discussion

Preparation of Benzimidazolium Salts

Dialkylbenzimidazolium salts **1a**–**e** were prepared according to known methods[21] as conventional NHC precur-

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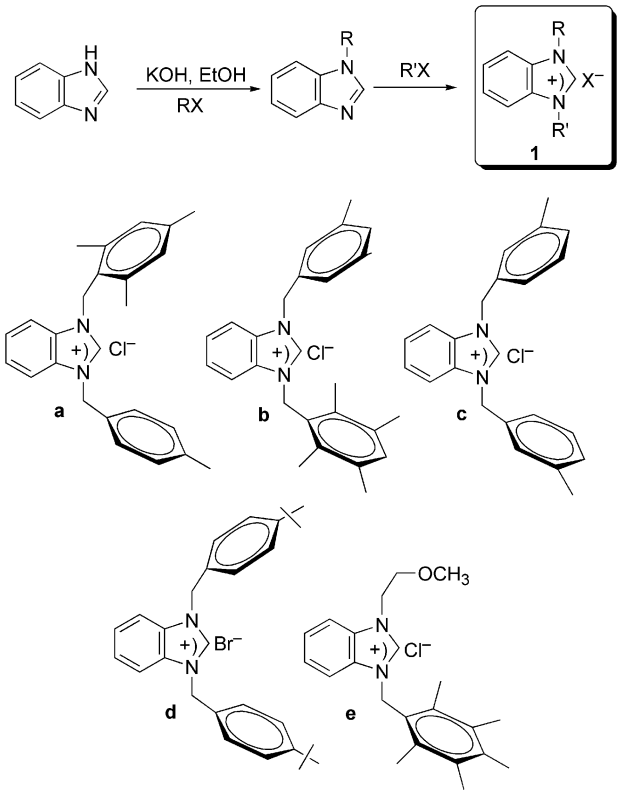
sors. Functionalized or bulky benzimidazolium salts **1a**–**e** were obtained upon reaction of a benzyl halides with 1-aklylbenzimidazole in dimethylformamide and isolated in 78–91% yield (Scheme 1).



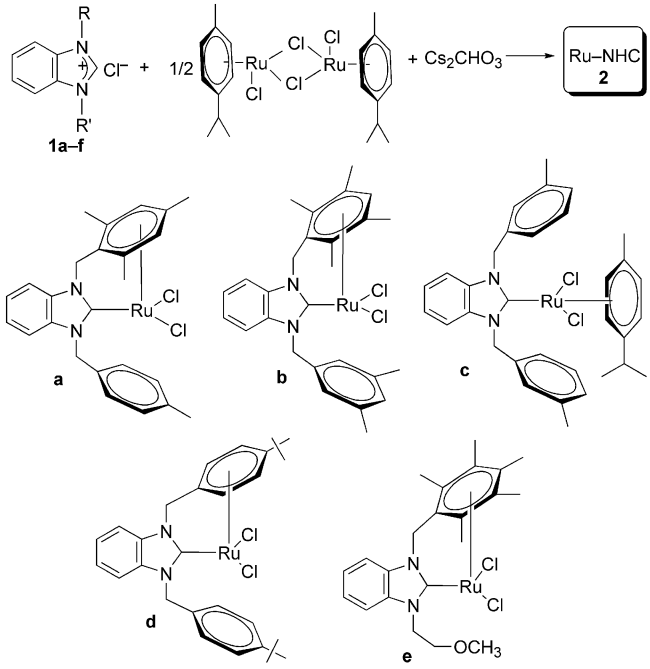
Scheme 1. Synthesis of 1,3-dialkylbenzimidazolium salts.

The salts are air and moisture stable both in the solid state and in solution and soluble in chlorinated solvents, alcohols, and water. Benzimidazolium salts **1a**–**e** were isolated as solids in very good yields and fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and elemental analyses, and their melting points were determined. ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon atom appeared as a typical singlet in the ^{1}H-decoupled mode at 143.7, 143.8, 144.8, 152.7, and 142.8 ppm, respectively, for benzimidazolium salts **1a**–**e**.

The ^{1}H NMR spectra of the benzimidazolium salts further supported the assigned structures; the resonances for C(2)-H were observed as sharp singlets at 11.63, 11.48, 11.83, 11.85, and 11.76 ppm, respectively, for **1a**–**e**. The IR data for benzimidazolium salts **1a**–**e** clearly indicate the presence of the –C=N– group with a ν(C=N) vibration at 1557, 1576, 1590, 1571, and 1580 cm^{-1}, respectively, for **1a**–**e**. The NMR values are similar to those found for other 1,3-dialkylbenzimidazolium salts.[22]

Preparation of Ruthenium–Carbene Complexes 2a–e

The in situ deprotonation of an azolium salt to produce the desired NHC has the advantage that the carbene does not have to be isolated, thus simplifying the reaction workup when the aim is to prepare the metal complex.[23] This method was used for the preparation of complexes **2a**–**e**. The carbene ligand, arising from deprotonation of benzimidazolium salts **1a**–**e** with the use of Cs_2CO_3 according to the literature,[24] was treated with $[RuCl_2(p\text{-cymene})]_2$ in toluene at 110 °C. After 5 h, the reaction was complete and mononuclear neutral ruthenium(II) complexes **2a**–**e** were obtained as red-brown crystalline solids in 72–87% yield (Scheme 2). Air- and moisture-stable ruthenium carbene complexes **2a**–**e** were soluble in halogenated solvents and insoluble in nonpolar solvents.



Scheme 2. Synthesis of ruthenium–carbene complexes.

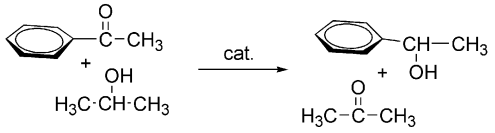
Complexes **2a**–**e** (except for **2c**) with the aryl group η^6-coordinated to the ruthenium atom was obtained in good yields (Scheme 2). These results show that Cs_2CO_3 is able to generate a ruthenium-coordinated benzimidazolinylidene group in refluxing toluene and that the *p*-cymene ligand can be displaced by an intramolecular aryl group. Complexes **2a**–**e**, which are very stable in the solid state, were characterized by analytical and spectroscopic techniques. Ruthenium complexes exhibit a characteristic ν_{NCN} band typically at 1404, 1418, 1409, 1410, and 1404 cm^{-1}, respectively, for **2a**–**e**.[24–26] The ^{13}C NMR chemical shifts provide a useful diagnostic tool for this type of metal carbene complex. The chemical shifts for the carbon atom fall in the 182–186 ppm region and are similar to those found in other ruthenium–carbene complexes.[24–26]

Catalytic Transfer Hydrogenation of Ketones

Catalytic reduction is preferred to stoichiometric reduction for large-scale industrial uses, and the catalytic hydrogenation of ketones is well known.[27] Hydrogen gas

presents considerable safety hazards, especially for large-scale reactions;[28] the use of a solvent that can donate hydrogen atoms overcomes this difficulty. 2-Propanol is a popular reactive solvent for transfer hydrogenation, as it is easy to handle (b.p. 82 °C) and is relatively nontoxic, environmentally benign, and inexpensive. The volatile acetone product can also be easily removed to shift an unfavorable equilibrium.[5b] Owing to their efficiency in the transfer hydrogenation of acetophenone derivatives, ruthenium(II) complexes **2a**–**e** were further investigated in the transfer hydrogenation of various methyl aryl ketones.

Ruthenium(II) complexes **2a**–**e** catalyze the reduction of ketones to the corresponding alcohols through hydrogen transfer from 2-propanol with KOH as the promoter. As the starting point, the performance of the catalysts in the transfer hydrogenation was screened by using acetophenone as a model substrate [Equation (1)].



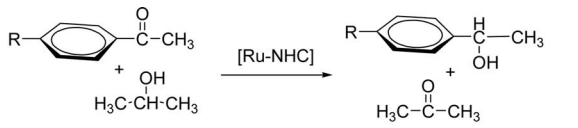
(1)

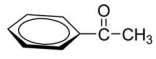
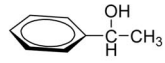
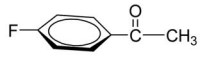
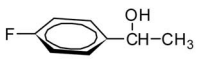
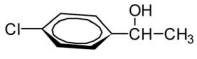
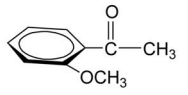
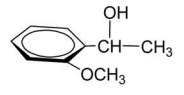
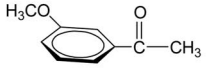
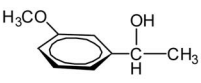
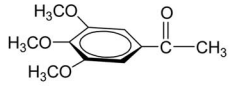
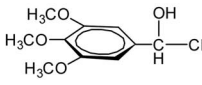
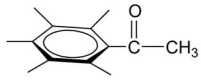
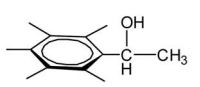
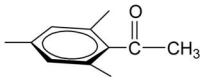
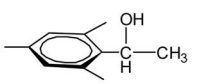
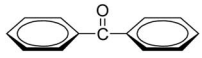
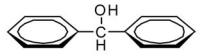
In a typical experiment, the preformed, isolated crystalline catalyst (0.01 mmol) was dissolved in 2-propanol. After the catalyst had completely dissolved, acetophenone (1.00 mmol) and a base (4 mmol) were added, and the reaction was heated at 80 °C. The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 1:0.01:4. For the choice of base, we surveyed Cs_2CO_3, K_2CO_3, KOH, NaOH, and *t*BuOK. Addition of bases like KOH or NaOH led to similar final conversions, but the highest rate was observed when KOH was employed. In the absence of a base, transfer hydrogenation of the ketones was not observed. Under the reaction conditions, complex **2d** proved to be more effective than **2a**, **2b**, **2c**, and **2e**. The reduction of acetophenone with **2d** was complete within 1 h in 97% conversion. In contrast, acetophenone was reduced within 1 h with the use of **2a**, **2b**, **2c**, and **2e** in 90, 90, 85, and 91% conversion, respectively (Table 1, Entries 1–5).

A variety of ketones were transformed into the corresponding secondary alcohols. Typical results are shown in Table 1. Under those conditions, *p*-methoxyacetophenone, *o*-methoxyacetophenone, *m*-methoxyacetophenone, *p*-fluoroacetophenone, and 3,4,5-trimethoxyacetophenone reacted very cleanly and in goods yields with 2-propanol (Table 1, Entries 10, 22, 25, and 15). Enhancement in activity, although less significant, was further observed by employing *o*-methoxyacetophenone instead of *p*-methoxyacetophenone (Table 1 Entries 6–10, 20–22).

As shown in Table 1, the reduction is more efficient for 4-fluoroacetophenone than for 2-chloroacetophenone, and among the complexes, **2e** was the most active, giving 96% conversion after 1 h (Table 1, Entries 15 and 19). The ruthenium complexes also catalyzed the transfer hydrogenation of benzophenone very effectively (Table 1 Entries 34–36).

Table 1. Transfer hydrogenation of ketones catalyzed by **2a**–**e**.[a]



Entry	Cat.	Substrate	Product	Yield [%]
1	**2a**			90
2	**2b**			90
3	**2c**			85
4	**2d**			97
5	**2e**			91
6	**2a**			87
7	**2b**			97
8	**2c**			93
9	**2d**			91
10	**2e**			98
11	**2a**			93
12	**2b**			94
13	**2c**			94
14	**2d**			92
15	**2e**			96
16	**2b**			68
17	**2c**			58
18	**2d**			30
19	**2e**			78
20	**2c**			97
21	**2d**			80
22	**2e**			99
23	**2c**			77
24	**2d**			97
25	**2e**			98
26	**2a**			90
27	**2b**			89
28	**2e**			91
29	**2a**			–
30	**2b**			–
31	**2a**			43
32	**2b**			65
33	**2c**			76
34	**2a**			86
35	**2b**			84
36	**2e**			93

[a] Reaction conditions: substrate (1.0 mmol), *i*PrOH (10 mL), KOH (4 mmol), Ru–NHC (0.01 mmol), 80 °C, 1 h. Purity of compounds was checked by GC and GC–MS and yields are based on ketones.

The conversions of ketones with bulky substituents on the aromatic ring were not observed or were slightly lower. For example, when a ketone with a pentamethyl group on the aromatic ring was used in the transfer hydrogenation, con-

version was not observed (Table 1, Entries 29 and 30), and when 2,4,6-trimethylphenyl methyl ketone was used, the conversion was lower (Table 1, Entries 31–33).

Among the tested complexes, complex **2e** is highly efficient in the transfer hydrogenation of ketones to secondary alcohols. The data indicate clearly the superiority of the complexes with pentamethyl benzyl substituents at the ring nitrogen atom.

Conclusions

The above results show that benzimidazolinylidene ligands containing an arylmethyl-*N* group (except for **1c**) on reaction with $[RuCl_2(p\text{-cymene})]_2$ displace the *p*-cymene ligand to give chelate ruthenium complexes. The complexes show high activity in the catalytic transfer hydrogenation of ketones with the use of 2-propanol in the presence of KOH. Complex **2e** is the most active complex. The procedure is simple and efficient towards various aryl ketones. Although all of the complexes are active catalysts for the transfer hydrogenation of ketones, conversion was not observed with very substituted ketones such as 2′,3′,4′,5′,6′-pentamethylacetophenone. Also, we obtained moderate yields with 2′,4′,6′-trimethylacetophenone. We are currently investigating the scope and application of these complexes as catalysts for various organic reactions.

Experimental Section

General Methods: All reactions for the preparation benzimidazolium salts **1** and ruthenium–NHC complexes **2** were carried out under an atmosphere of argon in flame-dried glassware by using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under an atmosphere of argon: Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FTIR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} with an ATI UNICAM 1000 spectrometer. ^1H and ^{13}C NMR spectra were recorded by using a Varian AS 400 Merkur spectrometer operating at 400 (^1H) and 100 MHz (^{13}C) in $CDCl_3$ and [D$_6$]DMSO with tetramethylsilane as an internal reference. Column chromatography was performed by using silica gel 60 (70–230 mesh). Elemental analyses were performed by Turkish Research Council (Ankara, Turkey) Microlab.

General Method for the Preparation of Benzimidazolium Salts: To a solution of *N*-alkylbenzimidazole (10.0 mmol) in DMF (5 mL) was added slowly the alkyl or aryl halide (10.0 mmol), and the resulting mixture was stirred at room temperature for 5 h. Ethyl ether (10 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 10 mL) and dried under vacuum, and the crude product was recrystallized from ethanol/diethyl ether.

1-(2,4,6-Trimethylbenzyl)-3-(4-methylbenzyl)benzimidazolium Chloride (1a): Yield: 3.21 g (82%); m.p. 216–217 °C. IR: $\tilde{\nu}$ = 1557 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.19 [s, 6 H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.26 [s, 6 H, $CH_2C_6H_2(CH_3)_3$-4, $CH_2C_6H_4(CH_3)$-4], 5.84 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.85 [s, 2 H, $CH_2C_6H_4(CH_3)$-4], 6.89 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.09–7.55 [m, 8 H, $CH_2C_6H_4(CH_3)$-4 and C_6H_4], 11.63 (s, 1 H, NC*H*N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 20.3 [$CH_2C_6H_2(CH_3)_3$-2,6], 21.1 [$CH_2C_6H_2(CH_3)_3$-4], 21.2 [$CH_2C_6H_4(CH_3)$-4], 51.3 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.4 [$CH_2C_6H_4(CH_3)$-4], 113.8, 125.1, 126.9, 127.1, 128.1, 128.3, 129.9, 130.0, 130.2, 131.4, 131.5, 137.9, 139.3, 139.7 [$CH_2C_6H_2(CH_3)_3$-2,4,6, $CH_2C_6H_4(CH_3)$-4, C_6H_4], 143.7 (NCHN) ppm. $C_{25}H_{27}ClN_2$ (390.95): calcd. C 76.80, H 6.96, N 7.17; found C 76.80, H 7.01, N 7.19.

1-(3,5-Dimethylbenzyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium Chloride (1b): Yield: 3.36 g (80%); m.p. 214–215 °C. IR: $\tilde{\nu}$ = 1576 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.20 [s, 12 H, $CH_2C_6H_4(CH_3)_2$-3,5; $CH_2C_6H(CH_3)_4$-3,5], 2.24 [s, 6 H, $CH_2C_6H(CH_3)_4$-2,6], 5.82 [s, 2 H, $CH_2C_6H_3(CH_3)_2$-3,5], 5.93 [s, 2 H, $CH_2C_6H(CH_3)_4$-2,3,5,6], 6.92–7.56 [m, 8 H, $CH_2C_6H(CH_3)_3$-2,3,5,6; $CH_2C_6H_3(CH_3)_2$-3,5 and C_6H_4], 11.48 (s, 1 H, NC*H*N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 16.1 [$CH_2C_6H(CH_3)_4$-2,6], 21.2 [$CH_2C_6H_3(CH_3)_2$-3,5 and $CH_2C_6H(CH_3)_4$-3,5], 48.0 [$CH_2C_6H_4(CH_3)_2$-3,5], 51.5 [$CH_2C_6H_4(CH_3)_2$-2,3,5,6], 113.8, 125.7, 126.9, 127.1, 127.8, 130.7, 131.5, 131.6, 132.8, 133.6, 134.0, 135.1, 138.9 [$CH_2C_6H_4(CH_3)_2$-3,5; $CH_2C_6H(CH_3)_4$-2,3,5,6 and C_6H_4], 143.8 (NCHN) ppm. $C_{27}H_{31}ClN_2$ (419.00): calcd. C 77.40, H 7.46, N 6.69; found C 77.45, H 7.42, N 6.72.

1,3-Bis(3-methylbenzyl)benzimidazolium Chloride (1c): Yield: 2.83 g (78%); m.p. 135–136 °C. IR: $\tilde{\nu}$ = 1590 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.28 [s, 6 H, $CH_2C_6H_4(CH_3)$-3], 5.82 [s, 2 H, $CH_2C_6H_4(CH_3)$-3], 7.09–7.98 [m, 12 H, $CH_2C_6H_4(CH_3)$-3 and C_6H_4], 11.83 (s, 1 H, NC*H*N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 21.5 [$CH_2C_6H_2(CH_3)_3$-3], 51.8 [$CH_2C_6H_4(CH_3)$-3], 125.5, 129.0, 129.4, 130.2, 131.6, 132.8, 139.5 [$CH_2C_6H_4(CH_3)$-3 and C_6H_4], 144.8 (NCHN) ppm. $C_{23}H_{23}ClN_2$ (362.90): calcd. C 76.12, H 6.39, N 7.72; found C 76.10, H 6.36, N 7.75.

1,3-Bis(4-*tert*-butylbenzyl)benzimidazolium Bromide (1d): Yield: 4.23 g (89%); m.p. 236–237 °C. IR: $\tilde{\nu}$ = 1571 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 1.25 {s, 18 H, $CH_2C_6H_4[C(CH_3)_3$-4],} 5.82 {s, 2 H, $CH_2C_6H_4[C(CH_3)_3$-4]}, 7.35–7.46 {m, 12 H, $CH_2C_6H_4[C(CH_3)_3$-4] and C_6H_4}, 11.85 (s, 1 H, NC*H*N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 31.4 {$CH_2C_6H_4[C(CH_3)_3$-4]}, 34.9 {$CH_2C_6H_4[C(CH_3)_3$-4]}, 51.5 [$CH_2C_6H_4(CH_3)_2$-3,5], 114.0, 126.5, 127.3, 128.4, 129.8 and 131.6 {$CH_2C_6H_4[C(CH_3)_3$-4] and C_6H_4}, 152.7 (NCHN) ppm. $C_{29}H_{35}BrN_2$ (491.51): calcd. C 70.87, H 7.18, N 5.70; found C 70.85, H 7.20, N 5.77.

1-(Methoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium Bromide (1e): Yield: 3.14 g (84%); m.p. 186–187 °C. IR: $\tilde{\nu}$ = 1580 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.18 [s, 6 H, $CH_2C_6(CH_3)_5$-2,6], 2.25 [s, 3 H, $CH_2C_6(CH_3)_5$-4], 2.23 [s, 6 H, $CH_2C_6(CH_3)_5$-3,5], 3.30 (s, 3 H, OCH_3), 3.89 (t, J = 4.5 Hz, 2 H, NCH_2CH_2O), 4.96 (t, J = 4.5 Hz, 2 H, NCH_2CH_2O), 5.79 [s, 2 H, $CH_2C_6(CH_3)_5$-2,3,4,5,6], 7.29–7.93 (m, 4 H, C_6H_4), 11.76 (s, 1 H, NC*H*N) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 17.0, 17.1 [$CH_2C_6(CH_3)_5$-2,3,5,6], 17.3 [$CH_2C_6(CH_3)_5$-4], 47.9 [$CH_2C_6(CH_3)_5$-2,3,4,5,6], 70.5 (OCH_3), 59.0 (NCH_2CH_2O), 47.9 (NCH_2CH_2O), 113.11, 114.3, 124.8, 127.0, 131.2, 132.5, 133.6, 134.0, 137.4 [$CH_2C_6(CH_3)_5$-2,3,4,5,6 and C_6H_4], 142.8 (NCHN) ppm. $C_{22}H_{29}BrN_2O$ (417.38): calcd. C 63.31, H 7.00, N 6.71; found C 63.35, H 7.05, N 6.76.

General Method for the Preparation of Ruthenium Complexes 2a–e: A suspension of benzimidazolium salt (2.10 mmol), Cs_2CO_3 (2.14 mmol), and $[RuCl_2(p\text{-cymene})]_2$ (0.82 mmol) was heated under reflux in degassed toluene (20 mL) for 5 h. The reaction mixture was then filtered while hot, and the volume was reduced to about 10 mL before addition of *n*-hexane (15 mL). The precipitate

formed was crystallized from CH_2Cl_2/hexane (5:15 mL) to give red-brown crystals.

Dichloro-[1-(2,4,6-trimethylbenzyl)-3-(4-methylbenzyl)benzimidazol-2-ylidene]ruthenium(II) (2a): Yield: 0.56 g (84%); m.p. 283–284 °C. IR: $\tilde{\nu}$ = 1404 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.19 [s, 6 H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.15 [s, 3 H, $CH_2C_6H_2(CH_3)_3$-4] 2.19 [s, 3 H, $CH_2C_6H_4(CH_3)$-4], 5.50 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 5.11 [s, 2 H, $CH_2C_6H_4(CH_3)$-4], 5.55 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 6.94–7.87 [m, 8 H, $CH_2C_6H_4(CH_3)$-4 and C_6H_4] ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 16.9 [$CH_2C_6H_2(CH_3)_3$-2,6], 17.5 [$CH_2C_6H_2(CH_3)_3$-4], 21.2 [$CH_2C_6H_4(CH_3)$-4], 45.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 51.4 [$CH_2C_6H_4(CH_3)$-4], 90.1, 93.3, 98.3, 101.1 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 110.9, 112.4, 123.3, 123.8, 127.9, 129.0, 133.5, 134.0,134.5, 136.8 [$CH_2C_6H_4(CH_3)$-4, C_6H_4], 185.3 (C_{carb}) ppm. $C_{25}H_{26}Cl_2N_2Ru$ (526.46): calcd. C 57.03, H 4.98, N 5.32; found C 57.05, H 5.00, N 5.36.

Dichloro-[1-(2,3,5,6-tetramethylbenzyl)-3-(3,5-dimethylbenzyl)benzimidazol-2-ylidene]ruthenium(II) (2b): Yield: 0.58 g (88%); m.p. 384–385 °C. IR: $\tilde{\nu}$ = 1418 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.14 [s, 12 H, $CH_2C_6H_4(CH_3)_2$-3,5; $CH_2C_6H(CH_3)_4$-3,5], 2.0 [s, 6 H, $CH_2C_6H(CH_3)_4$-2,6], 5.34 [s, 2 H, $CH_2C_6H_3(CH_3)_2$-3,5], 5.51 [s, 2 H, $CH_2C_6H(CH_3)_4$-2,3,5,6], 6.54–7.68 [m, 8 H, $CH_2C_6H(CH_3)_3$-2,3,5,6; $CH_2C_6H_3(CH_3)_2$-3,5 and C_6H_4] ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 13.8 [$CH_2C_6H(CH_3)_4$-2,6], 18.2 and 21.4 [$CH_2C_6H_3(CH_3)_2$-3,5 and $CH_2C_6H(CH_3)_4$-3,5], 46.3 [$CH_2C_6H_4(CH_3)_2$-3,5], 51.5 [$CH_2C_6H_4(CH_3)_2$-2,3,5,6], 85.0, 98.9, 109.6, 112.4, 122.0, 124.5, 126.0, 128.4, 129.0, 133.4, 134.4, 135.5, 137.9 [$CH_2C_6H_4(CH_3)_2$-3,5; $CH_2C_6H(CH_3)_4$-2,3,5,6 and C_6H_4], 185.4 (C_{carb}) ppm. $C_{27}H_{30}Cl_2N_2Ru$ (554.52): calcd. C 58.48, H 5.45, N 5.05; found C 58.44, H 5.41, N 5.01.

Dichloro-[1,3-bis(3-methylbenzyl)benzimidazol-2-ylidene](*p*-cymene)-ruthenium(II) (2c): Yield: 0.72 g (72%); m.p. 294–295 °C. IR: $\tilde{\nu}$ = 1609 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 1.30 [d, J = 13.8 Hz, 6 H, *p*-$CH_3C_6H_4CH(CH_3)_2$], 1.26 [s, 6 H, $CH_2C_6H_4(CH_3)$-3], 1.27 [s, 3 H, *p*-$CH_3C_6H_4CH(CH_3)_2$], 1.63 [p, J = 6.6 Hz, 1 H, *p*-$CH_3C_6H_4CH(CH_3)_2$], 5.13 [s, 4 H, $CH_2C_6H_4(CH_3)$-3], 4.81–7.31 [m, 16 H, $CH_2C_6H_4(CH_3)$-3, *p*-$CH_3C_6H_4CH(CH_3)_2$ and C_6H_4] ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 19.1 [*p*-$CH_3C_6H_4CH(CH_3)_2$], 21.5 [$CH_2C_6H_2(CH_3)_3$-3 and $CH_3C_6H_4CH(CH_3)_2$], 29.7 [*p*-$CH_3C_6H_4CH(CH_3)_2$], 53.0 [$CH_2C_6H_4(CH_3)$-3], 75.4, 87.4, 99.8, 109.6, 113.3, 114.6, 123.4, 124.0, 125.0, 128.6, 133.0, 134.8, 136.4, 137.8 5 [$CH_2C_6H_4(CH_3)$-3, *p*-$CH_3C_6H_4CH(CH_3)_2$ and C_6H_4], 182.1 (C_{carb}) ppm. $C_{32}H_{35}Cl_2N_2Ru$ (619.61): calcd. C 62.03, H 5.69, N 4.52; found C 62.06, H 5.73, N 4.56.

Dichloro-[1,3-bis(4-*tert*-butylbenzyl)benzimidazol-2-ylidene]ruthenium(II) (2d): Yield: 0.50 g (87%); m.p. 314–315 °C. IR: $\tilde{\nu}$ = 1609 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 1.26 {s, 9 H, $CH_2C_6H_4[C(CH_3)_3$-4]}, 1.54 {s, 9 H, $CH_2C_6H_4[C(CH_3)_3$-4]}, 4.99 {m, 2 H, coord. $CH_2C_6H_4[C(CH_3)_3$-4]}, 6.20 {m, 2 H, $CH_2C_6H_4[C(CH_3)_3$-4]}, 5.83–5.31{m, 4 H, coord. $CH_2C_6H_4[C(CH_3)_3$-4]} 7.35–7.46 {m, 8 H, $CH_2C_6H_4[C(CH_3)_3$-4 and C_6H_4] ppm}. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 31.0 {$CH_2C_6H_4[C(CH_3)_3$-4]}, 31.3 {coord. $CH_2C_6H_4[C(CH_3)_3$-4]}, 34.4 {$CH_2C_6H_4[C(CH_3)_3$-4]}, 35.0 {coord. $CH_2C_6H_4[C(CH_3)_3$-4]}, 50.6 [coord. $CH_2C_6H_4(CH_3)_2$-3,5], 53.5 [$CH_2C_6H_4(CH_3)_2$-3,5], 96.2, 96.6, 99.7, 100.0 {coord. $CH_2C_6H_4[C(CH_3)_3$-4]}, 109.6, 112.4, 113.2, 123.3, 124.0, 125.1, 127.2, 132.9, 133.5, 134.8, {$CH_2C_6H_4[C(CH_3)_3$-4 and C_6H_4]}, 185.3 (C_{carb}) ppm. $C_{29}H_{34}Cl_2N_2Ru$ (582.57): calcd. C 59.79, H 5.88, N 4.81; found C 59.76, H 5.92, N 4.82.

Dichloro-[1-(2,3,4,5,6-pentamethylbenzyl)-3-(2-methoxyethyl)benzimidazol-2-ylidene]ruthenium (II) (2e): Yield: 0.91 g (72%); m.p. 291–292 °C. IR: $\tilde{\nu}$ = 1404 (ν_{CN}) cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 2.08 [s, 6 H, $CH_2C_6(CH_3)_5$-2,6], 2.29 [s, 6 H, $CH_2C_6(CH_3)_5$-4], 2.02 [s, 3 H, $CH_2C_6(CH_3)_5$-3,5], 3.28 (s, 3 H, OCH_3), 3.76 (t, J = 4.8 Hz, 2 H, NCH_2CH_2O), 4.67 (t, J = 4.8 Hz, 2 H, NCH_2CH_2O), 5.06 [s, 2 H, $CH_2C_6(CH_3)_5$-2,3,4,5,6], 7.70–7.27 (m, 4 H, C_6H_4) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 15.0, 15.7 [$CH_2C_6(CH_3)_5$-2,3,5,6], 14.9 [$CH_2C_6(CH_3)_5$-4], 48.0 [$CH_2C_6(CH_3)_5$-2,3,4,5,6], 65.9 (OCH_3), 46.4 (NCH_2CH_2O), 58.8 (NCH_2CH_2O), 94.5, 98.1, 132.9, [$CH_2C_6(CH_3)_5$-2,3,4,5,6] 107.8, 109.1, 113.4, 123.1, 123.5, 136.0 (C_6H_4), 186.2 (C_{carb}) ppm. $C_{22}H_{28}Cl_2N_2ORu$ (508.45): calcd. C 51.97, H 5.55, N 5.51; found C 51.99, H 5.58, N 5.55.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones: Under an inert atmosphere, a mixture containing the ketone (1 mmol), ruthenium catalyst **2a**–**e** (0.01 mmol), and KOH (4 mmol) was heated at reflux in *i*PrOH (10 mL) for 1 h. The solvent was then removed under reduced pressure, and the product distribution was determined by ^1H NMR spectroscopy and GC and GC–MS.

Acknowledgments

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