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The role of N-heterocyclic carbene substituents on ruthenium(II) complexes in the catalytic transfer hydrogenation of acetophenone

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Abstract: The novel ruthenium(II) complexes [$RuCl_2$(NHC)(p-cymene)], **3a**–**e**, containing 1-alkyl-3-benzylimidazol-2-ylidene ligands were prepared. All synthesized compounds were characterized by NMR spectroscopy and elemental analyses. Ru(II)-NHC complexes were tested as catalysts for the transfer hydrogenation of acetophenone, showing modest to high activity in this reaction. The results revealed that efficiencies depend on the substituents of the benzene ring of the benzyl on the N atom of the NHC ring.

Key words: N-heterocyclic carbene ligands, substituent effect, transfer hydrogenation, ruthenium complexes, silver-N-heterocyclic carbene complexes

1. Introduction

N-heterocyclic carbenes (NHCs), which have already been employed as supporting ligands for various metal-catalyzed reactions, are viewed as promising alternatives to phosphines[1,2] due to their strong σ-donating ability, and thermal and oxidative stability as well as electronic and steric tenability.[3–5] Recently, NHC ligands have been used in metal complex catalysts for both direct and transfer hydrogenation.[6] Transfer hydrogenation of unsaturated compounds is an important catalytic reduction for preparing the corresponding saturated products. This method is often more convenient and frequently less hazardous than direct hydrogenation with H_2 gas.[7,8] The first application on NHC complexes for the transfer hydrogenation reaction was reported by Nolan in 2001.[9] Moreover, transfer hydrogenation and different carbene or carbene-phosphine systems containing Rh,[10] Ir,[8] Ru,[11,12] and Ni[13] have been reported.

The transition metal complexes of NHC ligands bearing alkylated benzyl substituents on the N atom(s) of hetero rings are found to be more efficient catalysts than the simple benzyl substituted ones in C–C bond formation reactions.[14–16] Therefore, the main objective of this study was to investigate the influence of alkylated benzyl substituent while keeping the other N-substituent constant.

While we were doing this study, Yaşar and co-workers reported unsaturated Ru-NHC complexes containing alkylated benzyl substituent.[17] They focused on the synthesis, characterization, and catalytic application of these complexes.

In the present paper, a series of easily prepared new imidazol-2-ylidene ruthenium(II) complexes and their catalytic application in transfer hydrogenation reaction of acetophenone are reported. The characterization of the complexes was accomplished by analytical and spectral methods.

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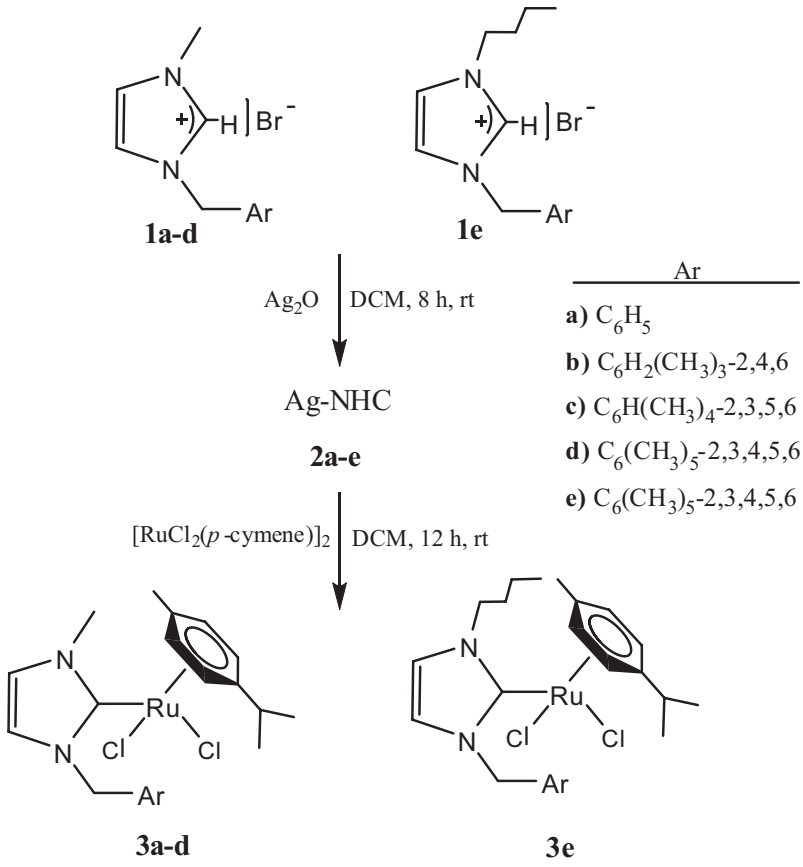
2. Results and discussion

2.1. Preparation of imidazolium salts (1a–e)

Unsymmetric dialkylimidazolium salts **1a**–**e** were prepared according to known methods[18,19] as conventional NHC precursors, starting from commercially available N-methylimidazole or N-buthylimidazole.

2.2. Preparation of silver-carbene complexes (2a–e)

All silver complexes were prepared by deprotonation of imidazolium salts (**1a**–**e**) with the mild base Ag_2O in dichloromethane at room temperature.[19] For complexes **2a**–**e**, a stoichiometry of one half equivalent of Ag_2O for one equivalent of ligand precursor was used (Scheme 1). The formation of the silver(I) complexes (**2a**–**e**) was confirmed by the absence of the ^{1}H NMR resonance of the acidic imidazolium C2 proton. The silver(I) bound carbene carbon is identified in the ^{13}C NMR spectra of the complexes at the typically high-frequency shift at around 180 ppm, indicating the successful formation of the desired complexes.[20] However, resonances for benzylic protons were observed at around 5.22–5.36 ppm in all spectra.



Scheme 1. Synthesis of $[RuCl_2(NHC)(p\text{-cymene})]$ complexes, **3**.

2.3. Preparation of ruthenium carbene complexes (3a–e)

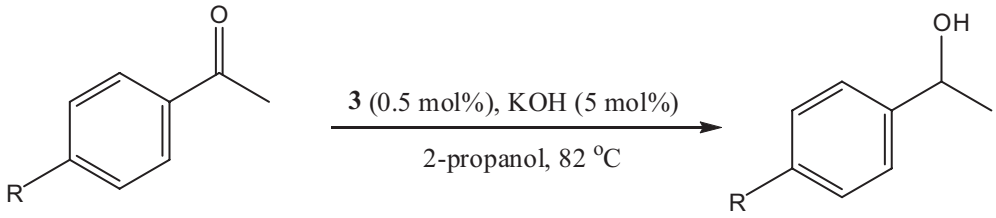
The ruthenium(II)-carbene complexes (**3a**–**e**) were synthesized in quantitative yields at a milder condition by transmetallation using Ag(I) complexes (**2a**–**e**) as a carbene transfer reagent (Scheme 1). Compounds

1a–**e** were first reacted with silver(I) oxide to form silver carbene complexes **2a**–**e** and then treatment of **2a**–**e** with $[RuCl_2(p\text{-cymene})]_2$ in CH_2Cl_2 led to formation of a precipitate (AgBr), affording the Ru(II)-NHC complexes. After 24 h stirring, the mixtures were filtered through Celite and the crude products were purified by flash column chromatography and recrystallized from CH_2Cl_2/Et_2O as orange solids. It is also possible to synthesize these ruthenium(II) complexes via in situ transmetallation with Ag(I)-NHCs. The successful carbene transfer is confirmed by analytical methods. The most indicative result is shown by a typical carbene carbon signal at around 171.9–174.4 ppm in ^{13}C NMR spectroscopy.

There is a possibility that the *p*-cymene ligand can be displaced by an aryl group of the benzyl to generate a bidentate ligand.[21,22] In order to eliminate the existence of such species in catalytic media, we have the complex **3d** under catalytic conditions. The control experiment (heating a solution of **3d** in $^{i}PrOH$ for 2 h at 82 °C) indicated essentially no change in ^{1}H NMR. This shows that the imidazole moiety is more resistant than the saturated analogue (imidazolidin moiety).

2.4. Catalytic studies

Complexes **3a**–**e** were tested as catalysts for transfer hydrogenation of acetophenone to 1-phenylethanol using 2-propanol in the presence of KOH (Scheme 2). The catalytic experiments were carried out using 4 mmol of acetophenone, 0.02 mmol (0.5 mol%) of NHC-ruthenium complexes (**3a**–**e**), 0.2 mmol of KOH, and 5 mL of 2-propanol. The catalyst was added to a solution of 2-propanol containing KOH, which was kept at 82 °C for 30 min and acetophenone was added to this solution.



Scheme 2. Transfer hydrogenation of acetophenone.

The results in Table 1 (entries 1–6) show that the role of base affects the transfer hydrogenation reaction. In contrast to KOH, other bases such as Na_2CO_3, NaOAc, triethylamine, pyridine, and K_2CO_3 showed less conversion and the completion of the reaction was much longer than that achieved with KOH. This revealed that, among the bases, KOH is the most suitable for the transfer hydrogenation reaction. The role of Ru-NHC complex was screened and a control experiment (Table 2) produced only a trace amount of alcohol in the absence of Ru-NHC complex.

The activity of complexes **3a**–**e** largely depends on the nature of *N*-substituents and decreases in the order **3d** > **3c** ∼ **3e** > **3b** > **3a**, indicating that **3d** shows the most noticeable activity and a maximum yield of 93% was achieved after 4 h (Table 2; Figure). The essential features for efficient transfer hydrogenation with Ru-NHC catalysts appear to include a flexible and sterically demanding benzyl substituent on the N atom of NHC. The successful introduction of alkylated benzyl substituent to the nitrogen of imidazole ligand offers additional options for fine-tuning $[RuCl_2(NHC)(p\text{-cymene})]$ catalyst precursors. Comparing the values observed here with literature values,[23] it is shown that the turnover-frequency (TOF) values were low due to the reduction of the activity of these catalysts. With the same catalytic conditions, acetophenone substrate was

catalyzed by $[RuCl_2(p\text{-cymene})]_2$ metal complex (Table 2, entry 6). However, the $[RuCl_2(p\text{-cymene})]_2$ gave very low conversion in 240 min. On the other hand, electronic properties of the substituents on the phenyl ring of the ketone caused the changes in the reduction rate. A *para*-substituted acetophenone with an electron-donor substituent, i.e. 4-methyl, is reduced more slowly than acetophenone (Table 2, entry 7).[24] In addition, the introduction of electron-withdrawing substituents, such as Cl, to the *para*-position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved, giving rise to easier hydrogenation (Table 2, entry 8).[25,26]

Table 1. Performance of the **3d** catalyst in the transfer hydrogenation of acetophenone in the presence of different bases (temperature = 80 °C).

Entry	Base used	Solvent	Reaction time	Product yield (%)
1	KOH	IPA	4	93
2	Na_2CO_3	IPA	15	45
3	NaOAc	IPA	15	40
4	Triethlyamine	IPA	15	20
5	Pyridine	IPA	15	30
6	K_2CO_3	IPA	15	40

Table 2. Catalytic activity of Ru(II)-NHC complexes for transfer hydrogenation[a] of acetophenone.

Entry	Catalyst	R	cat. (%)	t (min)	Conv. (%)[b,c]	TOF (h^{-1})[d]
1	**3a**	H	0.5	240	34	17.0
2	**3b**	H	0.5	240	45	22.5
3	**3c**	H	0.5	240	85	42.5
4	**3d**	H	0.5	240	**93**	**46.5**
5	**3e**	H	0.5	240	81	40.5
6	$\mathbf{[RuCl_2(p\text{-cymene})]_2}$	H	0.5	240	14	7.0
7	**3d**	CH_3	0.5	240	27	13.5
8	**3d**	Cl	0.5	240	56	28.0
9	–	H	–	240	5[e]	–

[a]Reactions were carried out at 82 °C using a 0.1 M acetophenone solution in 2-propanol and KOH.
[b]Determined by GC analysis with an HP-5 capillary column. Yields are based on aryl ketone.
[c]Internal standard was not used.
[d]Referred to the reaction time indicated in column; TOF = (mol product/mol Ru(II) cat.) × h^{-1}.
[e]No catalyst.

Herein, we report the synthesis and catalytic application of Ru-NHC complexes, which have different steric and electronic properties. Although catalytic activities of complexes bearing similar groups were quite close to each other, **3d** containing a NHC with a small methyl group exhibited better catalytic performance than the others.

3. Conclusions

From readily available N-methylimidazole or N-butylimidazole, $[RuCl_2(NHC)(p\text{-cymene})]$ complexes (**3a**–**e**) were readily prepared by transmetallation from Ag-NHC complexes and their catalytic activity was investigated in the transfer hydrogenation reaction of acetophenone. The best catalyst among the examined compounds was $[RuCl_2(NHC)(p\text{-cymene})]$ (**3d**) for transfer hydrogenation reactions. It is clear that the introduction of the

alkylated benzyl group to the nitrogen atom increased transfer hydrogenation performance. Presumably, the flexible character of N-benzyl systems might be electronically more sensitive and tunable to the need of the substrates to enhance the transfer hydrogenation performance,[27] and the Ar group of the alkylated benzyl substituent may protect the active center via π-interactions.[28]

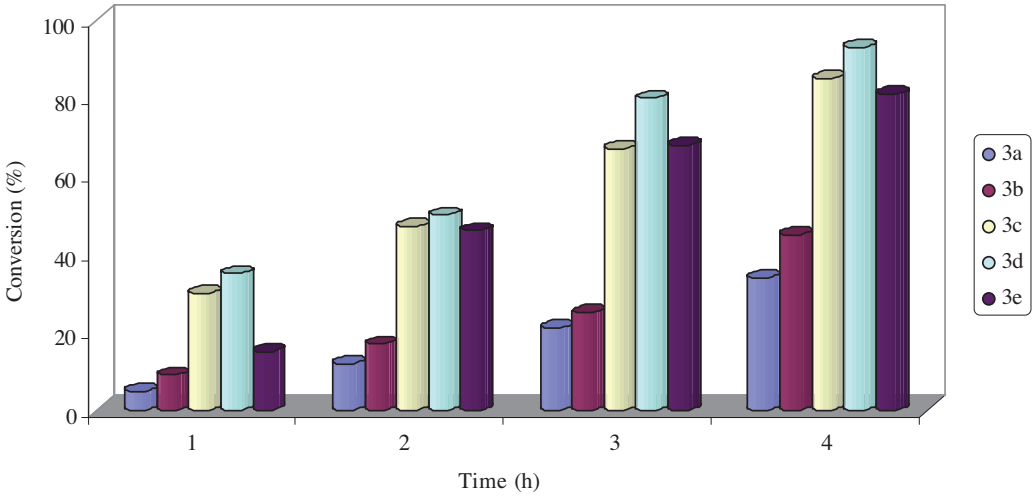


Figure. Time dependence of the catalytic transfer hydrogenation of acetophenone.

4. Experimental

4.1. General methods and materials

All reactions were performed under Ar using standard Schlenk techniques. Solvents were dried prior to use. All chemicals were obtained from commercial sources and were used as received. Benzyl bromides[29] and **1a**[30] (**1b**–**d**)[31] were synthesized according to the literature. ^{1}H and ^{13}C NMR measurements were performed using a Varian AS 400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^{1}H and ^{13}C NMR spectra. All catalytic reactions were monitored on an Agilent 6890N GC system by GC-flame ionization detection with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness. The GC parameters for transfer hydrogenation of ketone were as follows: initial temperature, 60 °C; temperature ramp, 10 °C/min; final temperature, 280 °C; final time 15.00 min; injector port temperature, 110 °C; detector temperature, 300 °C; injection volume, 1.0 μL. Melting points were measured in open capillary tubes with a Stuart SMP 30 melting point apparatus. Elemental analyses were performed by ODTÜ Microlab (Ankara, Turkey).

4.2. Synthesis of imidazolium salt, 1e

To a solution of N-butylimidazole (10 mmol) in toluene (10 mL) was added slowly 2,3,4,5,6-pentamethylbenzyl bromide (10 mmol) at 25 °C over 24 h. Diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 15 mL) and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O.

1e: Yield: 3.25 g (89%), mp 117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, 3H, J = 7.4 Hz, $CH_3CH_2CH_2CH_2N$); 1.29 (m, 2H, $CH_3CH_2CH_2CH_2N$); 1.83 (m, 2H, $CH_3CH_2CH_2CH_2N$); 2.13 (s, 6H, $C_6(CH_3)_5$-o-CH_3); 2.14 (s, 6H, $C_6(CH_3)_5$-m-CH_3); 2.17 (s, 3H, $C_6(CH_3)_5$-p-CH_3); 4.29 (t, 2H, J = 7.2

Hz, $CH_3CH_2CH_2CH_2N$); 5.57 (s, 2H, $NCH_2C_6(CH_3)_5$); 6.83 (t, 1H, J = 1.7 Hz, $NCHCHN$); 7.54 (t, 1H, J = 1.7 Hz, $NCHCHN$); 10.14 (s, 1H, $NCHN$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 ($CH_3CH_2CH_2CH_2N$); 16.8 ($CH_3CH_2CH_2CH_2N$); 16.9 ($C_6(CH_3)_5$-o-CH_3); 17.2 ($C_6(CH_3)_5$-m-CH_3); 19.4 ($C_6(CH_3)_5$-p-CH_3); 32.1 ($CH_3CH_2CH_2CH_2N$); 49.0 ($CH_3CH_2CH_2CH_2N$); 50.0 ($NCH_2C_6(CH_3)_5$); 120.8 ($NCHCHN$); 122.2 ($NCHCHN$); 125.3 ($C_6(CH_3)_5$); 133.5 ($C_6(CH_3)_5$); 133.7 ($C_6(CH_3)_5$); 136.4 ($C_6(CH_3)_5$); 137.2 ($NCHN$).

4.3. General procedure for the synthesis of silver-NHC complexes (2a–e)

A solution of imidazolium salt (**1a**–**e**, 1 mmol) and Ag_2O (0.5 mmol) in dichloromethane was stirred at room temperature for 8 h in the dark. The color of the suspension gradually changed from black to colorless. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure to give a white solid. The crude product was recrystallized from CH_2Cl_2/Et_2O at room temperature.

2a: Yield: 0.282 g (70%), mp 165–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 6H, NCH_3); 5.28 (s, 4H, $NCH_2C_6H_5$); 6.93 (d, J = 2.0 Hz, 2H, $NCHCHN$); 6.98 (d, J = 2.0 Hz, 2H, $NCHCHN$); 7.22–7.24 (dd, J = 7.0 Hz, J = 2.0 Hz, 4H, C_6H_5); 7.30–7.33 (m, 6H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9 (NCH_3); 55.6 ($NCH_2C_6H_5$); 121.2 ($NCHCHN$); 122.6 ($NCHCHN$); 127.8 (C_6H_5); 128.6 (C_6H_5); 129.1 (C_6H_5); 135.6 (C_6H_5); 181.9 (Ag-$C_{carbene}$).

2b: Yield: 0.282 g (70%), mp 168–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 12H, $C_6H_2(CH_3)_3$-o-CH_3); 2.22 (s, 6H, $C_6H_2(CH_3)_3$-p-CH_3); 3.79 (s, 6H, NCH_3); 5.22 (s, 4H, $NCH_2C_6H_2(CH_3)_3$); 6.47 (d, 2H, J = 4.0 Hz, $NCHCHN$); 6.84 (d, 2H, J = 4.0 Hz, $NCHCHN$); 6.85 (s, 4H, $C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 ($C_6H_2(CH_3)_3$-o-CH_3); 21.2 ($C_6H_2(CH_3)_3$-p-CH_3); 39.2 (NCH_3); 49.7 ($NCH_2C_6H_2(CH_3)_3$); 120.1 ($NCHCHN$); 122.0 ($NCHCHN$); 127.8 ($C_6H_2(CH_3)_3$); 129.9 ($C_6H_2(CH_3)_3$); 138.0 ($C_6H_2(CH_3)_3$); 139.2 ($C_6H_2(CH_3)_3$); 181.8 (Ag-$C_{carbene}$). Elemental analyses (%) calc. for $C_{28}H_{36}Ag_2Br_2N_4$: C, 41.82; H, 4.51; N, 6.97; found: C, 42.27; H, 5.02; N, 6.81.

2c: Yield: 0.271 g (65%), mp 185–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (s, 12H, $C_6H(CH_3)_4$-o-CH_3); 2.25 (s, 12H, $C_6H(CH_3)_4$-m-CH_3); 3.86 (s, 6H, NCH_3); 5.36 (s, 4H, $NCH_2C_6H(CH_3)_4$); 6.57 (d, 2H, J = 4.0 Hz, $NCHCHN$); 6.90 (d, 2H, J = 4.0 Hz, $NCHCHN$); 7.04 (s, 2H, $C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.1 ($C_6H(CH_3)_4$-o-CH_3); 20.7 ($C_6H(CH_3)_4$-m-CH_3); 39.3 (NCH_3); 50.4 ($NCH_2C_6H(CH_3)_4$); 120.4 ($NCHCHN$); 121.8 ($NCHCHN$); 130.6 ($C_6H(CH_3)_4$); 132.9 ($C_6H(CH_3)_4$); 134.0 ($C_6H(CH_3)_4$); 134.9 ($C_6H(CH_3)_4$); 182.2 (Ag-$C_{carbene}$). Elemental analyses (%) calc. for $C_{30}H_{40}Ag_2Br_2N_4$: C, 43.30; H, 4.84; N, 6.73; found: C, 42.71; H, 5.00; N, 6.87.

2d: Yield: 0.323 g (75%), mp 215–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 12H, $C_6(CH_3)_5$-o-CH_3); 2.16 (s, 12H, $C_6(CH_3)_5$-m-CH_3); 2.20 (s, 6H, $C_6(CH_3)_5$-p-CH_3); 3.78 (s, 6H, NCH_3); 5.28 (s, 4H, $NCH_2C_6(CH_3)_5$); 6.52 (d, 2H, J = 4.0 Hz, $NCHCHN$); 6.83 (d, 2H, J = 4.0 Hz, $NCHCHN$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.0 ($C_6(CH_3)_5$-o-CH_3); 17.1 ($C_6(CH_3)_5$-m-CH_3); 17.4 ($C_6(CH_3)_5$-p-CH_3); 39.3 (NCH_3); 50.8 ($NCH_2C_6(CH_3)_5$); 120.5 ($NCHCHN$); 121.8 ($NCHCHN$); 127.8 ($C_6(CH_3)_5$); 133.6 ($C_6(CH_3)_5$); 133.7 ($C_6(CH_3)_5$); 136.7 ($C_6(CH_3)_5$); 181.4 (Ag-$C_{carbene}$). Elemental analyses (%) calc. for $C_{32}H_{44}Ag_2Br_2N_4$: C, 44.68; H, 5.16; N, 6.51; found: C, 43.95; H, 5.27; N, 6.48.

2e: Yield: 0.364 g (77%), mp 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, 6H, J = 7.2 Hz, $CH_3CH_2CH_2CH_2N$); 1.31 (m, 4H, $CH_3CH_2CH_2CH_2N$); 1.77 (m, 4H, $CH_3CH_2CH_2CH_2N$); 2.18 (s, 12H, $C_6(CH_3)_5$-o-CH_3); 2.21 (s, 12H, $C_6(CH_3)_5$-m-CH_3); 2.24 (s, 6H, $C_6(CH_3)_5$-p-CH_3); 4.08 (t, 4H,

J = 7.2 Hz, $CH_3CH_2CH_2CH_2N$); 5.33 (s, 4H, $NCH_2C_6(CH_3)_5$); 6.56 (d, 2H, J = 2.0 Hz, $NCHCHN$); 6.88 (d, 2H, J = 2.0 Hz, $NCHCHN$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 ($CH_3CH_2CH_2CH_2N$); 16.7 ($CH_3CH_2CH_2CH_2N$); 16.8 ($C_6(CH_3)_5$-o-CH_3); 17.1 ($C_6(CH_3)_5$-m-CH_3); 20.0 ($C_6(CH_3)_5$-p-CH_3); 33.4 ($CH_3CH_2CH_2CH_2N$); 50.6 ($CH_3CH_2CH_2CH_2N$); 52.0 ($NCH_2C_6(CH_3)_5$); 120.0 ($NCHCHN$); 127.6 ($C_6(CH_3)_5$); 133.2 ($C_6(CH_3)_5$); 133.4 ($C_6(CH_3)_5$); 136.3 ($C_6(CH_3)_5$); 180.1 (Ag-$C_{carbene}$). Elemental analyses (%) calc. for $C_{38}H_{56}Ag_2Br_2N_4$: C, 48.33; H, 5.98; N, 5.93%. Found: C, 48.12; H, 5.94; N, 6.00%.

4.4. General procedure for the synthesis of ruthenium-NHC complexes (3a–e)

The ruthenium complexes were prepared by means of the Ag-carbene transfer method developed by Wang and Lin.[32,33] The silver carbene complexes, which should subsequently serve as a carbene-transfer agent, were synthesized by the reaction of Ag_2O with 2 equiv. of salts (**1a**–**e**) in CH_2Cl_2 at ambient temperature. We conveniently reacted Ag-NHC with $[RuCl_2(p\text{-cymene})]_2$ in the dark and the mixture was allowed to stir for 12 h at room temperature. The solution was filtered through Celite, and the solvent was removed under vacuum to afford the product as a red-brown powder. The crude product was recrystallized from CH_2Cl_2/Et_2O at room temperature.

3a: Yield: 0.276 g (90%), mp 165–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, J = 4.0 Hz, 6H, (p-cymene)-$CH(CH_3)_2$); 2.04 (s, 3H, (p-cymene)-CH_3); 2.16 (NCH_3); 2.90 (m, 1H, (p-cymene)-$CH(CH_3)_2$); 4.02 (s, 2H, $NCH_2C_6H_5$); 4.99 (m, 1H, (p-cymene-CH); 5.32 (m, 1H, (p-cymene-CH); 5.65 (s, 2H, (p-cymene-CH)); 6.84 (d, J = 4.0 Hz, 1H, $NCHCHN$), 6.98 (d, J = 4.0 Hz, 1H, $NCHCHN$); 7.24 (m, 1H, C_6H_5), 7.33 (m, 4H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.6 (p-cymene-$CH(CH_3)_2$); 30.7 (p-cymene-CH_3); 39.7 (p-cymene-$CH(CH_3)_2$); 39.7 (NCH_3); 54.8 ($CH_2C_6H_4$); 99.0 (p-cymene-C); 108.5 (p-cymene-CH), 123.0 ($NCHCHN$); 123.9 ($NCHCHN$); 127.6 (C_6H_5); 127.9 (C_6H_5); 128.8 (C_6H_5); 137.7 (C_6H_5); 174.4 (Ru-$C_{carbene}$). Elemental analyses (%) calc. for $C_{21}H_{26}Cl_2N_2Ru$: C, 52.72; H, 5.48; N, 5.86; found: C, 52.57; H, 5.53; N, 5.96.

3b: Yield: 0.233 g (90%), mp 210–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, J = 4.0 Hz, 6H, (p-cymene)-$CH(CH_3)_2$); 2.14 (s, 6H, $C_6H_2(CH_3)_3$-p-CH_3, (p-cymene)-CH_3); 2.23 (s, 6H, $C_6H_2(CH_3)_3$-o-CH_3); 2.28 (NCH_3); 2.95 (m, 1H, (p-cymene)-$CH(CH_3)_2$); 4.01 (s, 2H, $NCH_2C_6H_2(CH_3)_3$); 5.23 (m, 2H, (p-cymene-CH)); 5.57 (d, J = 4.0 Hz, 2H, (p-cymene-CH)); 6.33 (s, 1H, $NCHCHN$); 6.81 (s, 1H, $NCHCHN$); 6.90 (s, 2H, $C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 (p-cymene-$CH(CH_3)_2$); 20.1 ($C_6H_2(CH_3)$-o-CH_3, $C_6H_2(CH_3)$-p-CH_3); 21.0 (p-cymene-CH_3); 30.9 (NCH_3); 39.8 ((p-cymene)-$CH(CH_3)_2$); 49.5 ($NCH_2C_6H_2(CH_3)_3$); 84.6 (p-cymene-C); 99.6 (p-cymene-CH); 107.9 (p-cymene-C); 120.5 ($NCHCHN$); 122.6 ($NCHCHN$); 128.5 ($C_6H_2(CH_3)_3$); 129.4 ($C_6H_2(CH_3)_3$); 138.5 ($C_6H_2(CH_3)_3$), 172.4 (Ru-$C_{carbene}$). Elemental analyses (%) calc. for $C_{24}H_{32}Cl_2N_2Ru$: C, 55.38; H, 6.20; N, 5.38; found: C, 55.70; H, 6.65; N, 5.65.

3c: Yield: 0.212 g (80%), mp 225–226 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (d, J = 4.0 Hz, 6H, (p-cymene)-$CH(CH_3)_2$); 2.15 (s, 6H, $C_6H(CH_3)_4$-o-CH_3); 2.17 ((p-cymene)-CH_3); 2.25 (s, 9H, $C_6H(CH_3)_4$-m-CH_3, NCH_3); 2.98 (m, 1H, (p-cymene)-$CH(CH_3)_2$); 4.04 (s, 2H, $NCH_2C_6H(CH_3)_4$); 5.25 (d, J = 4.0 Hz, 2H, (p-cymene-CH)); 5.50 (d, J = 4.0 Hz, 2H, (p-cymene-CH)); 6.35 (s, 1H, $NCHCHN$); 6.81 (s, 1H, $NCHCHN$); 7.01 (s, 2H, $C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9 ($C_6H(CH_3)_4$-o-CH_3); 18.8 (p-cymene-$CH(CH_3)_2$); 20.4 ($C_6H(CH_3)_4$-m-CH_3, p-cymene-CH_3); 30.9 (NCH_3); 39.8 ((p-cymene)-$CH(CH_3)_2$); 50.2 ($NCH_2C_6H(CH_3)_4$); 84.5 (p-cymene-C); 99.5 (p-cymene-C); 107.7 (p-cymene-CH); 120.9

(NCHCHN); 122.5 (NCHCHN); 131.3 (C_6H(CH_3)$_4$); 132.2 (C_6H(CH_3)$_4$); 134.3 (C_6H(CH_3)$_4$); 172.1 (Ru-$C_{carbene}$). Elemental analyses (%) calc. for $C_{25}H_{34}Cl_2N_2Ru$: C, 56.17; H, 6.41; N, 5.24; found: C, 56.49; H, 5.88; N, 5.27.

3d: Yield: 0.232 g (85%), mp 235–236 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (d, J = 4.0 Hz, 6H, (p-cymene)-CH(CH_3)$_2$); 2.17 (s, 3H, (p-cymene)-CH_3); 2.20 (s, 6H, C$_6$(CH_3)$_5$-o-CH_3); 2.23 (s, 6H, C$_6$(CH_3)$_5$-m-CH_3); 2.27 (s, 6H, C$_6$(CH_3)$_5$-p-CH_3, NCH_3); 2.97 (m, 1H, (p-cymene)-CH(CH$_3$)$_2$); 4.03 (s, 2H, NCH_2C$_6$(CH$_3$)$_5$); 5.26 (d, J = 4.0 Hz, 2H, (p-cymene-CH)); 5.48 (d, J = 4.0 Hz, 2H, (p-cymene-CH)); 6.40 (s, 1H, NCHCHN); 6.80 (s, 1H, NCHCHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8 (C$_6$(CH$_3$)$_5$-o-CH_3, p-cymene-CH_3); 17.0 (C$_6$(CH$_3$)$_5$-m-CH_3); 17.1 (C$_6$(CH$_3$)$_5$-p-CH_3); 18.8 (p-cymene-CH(CH_3)$_2$); 30.9 (NCH_3); 39.8 ((p-cymene)-CH(CH$_3$)$_2$); 50.7 (NCH_2C$_6$(CH$_3$)$_5$); 84.4 (p-cymene-CH); 99.3 (p-cymene-CH); 107.7 (p-cymene-C); 121.0 (NCHCHN); 122.4 (NCHCHN); 128.7 (C_6(CH$_3$)$_5$); 133.1 (C_6(CH$_3$)$_5$); 135.7 (C_6(CH$_3$)$_5$); 171.9 (Ru-$C_{carbene}$). Elemental analyses (%) calc. for $C_{26}H_{36}Cl_2N_2Ru$: C, 56.93; H, 6.61; N, 5.11; found: C, 57.24; H, 6.10; N, 5.14.

3e: Yield: 0.196 g (76%), mp 125–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.20 Hz, 3H, NCH$_2$CH$_2$CH$_2$CH_3); 1.28 (d, J = 6.65 Hz, 6H, (p-cymene)-CH(CH_3)$_2$); 1.42 (m, 2H, NCH$_2$CH$_2$CH_2CH_3); 1.72 (m, 2H, NCH$_2$CH_2CH$_2$CH_3); 2.15 (s, 3H, (p-cymene)-CH_3); 2.19 (s, 6H, C$_6$(CH$_3$)$_5$-o-CH_3); 2.23 (s, 6H, C$_6$(CH$_3$)$_5$-m-CH_3); 2.27 (s, 6H, C$_6$(CH$_3$)$_5$-p-CH_3); 2.35 (s, 2H, NCH_2CH$_2$CH$_2$CH_3); 2.94 (m, 1H, (p-cymene)-CH(CH$_3$)$_2$); 4.78 (m, 2H, NCH_2C$_6$(CH$_3$)$_5$); 5.24 (br, 2H, (p-cymene-CH)); 5.49 (br, 2H, (p-cymene-CH)); 6.41 (d, J = 1.96 Hz, 1H, NCHCHN); 6.87 (d, J = 1.96 Hz, 1H, NCHCHN). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (NCH$_2$CH$_2$CH$_2$CH_3); 16.8 (C$_6$(CH$_3$)$_5$-o-CH_3, p-cymene-CH_3); 17.0 (C$_6$(CH$_3$)$_5$-p-CH_3); 17.1 (C$_6$(CH$_3$)$_5$-m-CH_3); 18.7 (p-cymene-CH(CH_3)$_2$); 20.2 (NCH$_2$CH$_2$CH_2CH$_3$); 30.9 (NCH_3); 33.8 ((p-cymene)-CH(CH$_3$)$_2$); 50.7 (NCH_2C$_6$(CH$_3$)$_5$); 51.5 (NCH$_2$CH_2CH$_2$CH_3); 60.1 (NCH_2CH$_2$CH$_2$CH_3); 84.6 (p-cymene-CH); 99.2 (p-cymene-CH); 107.0 (p-cymene-C); 120.0 (NCHCHN); 121.2 (NCHCHN); 128.8 (C_6(CH$_3$)$_5$); 132.8 (C_6(CH$_3$)$_5$); 135.7 (C_6(CH$_3$)$_5$); 171.9 (Ru-$C_{carbene}$). Elemental analyses (%) calc. for $C_{29}H_{42}Cl_2N_2Ru$: C, 58.97; H, 7.17; N, 4.74; found: C, 58.74; H, 7.53; N, 4.96.

4.5. General procedure for transfer hydrogenation experiments

NHC-Ru(II) complex (0.02 mmol-0.5 mol%, **3a**–**e**) and KOH (0.2 mmol) were introduced into a Schlenk tube under argon. Then 2-propanol (5 mL) was added to the reaction vessel. After stirring at 82 °C for 30 min under argon, acetophenone (4 mmol) was added. After the desired reaction time the solution was allowed to cool and quenched with 1 M HCl, extracted with diethyl ether, and the organic phase separated. The resulting organic phase was filtered to remove insoluble inorganic material and the reaction progress was monitored by GC. The product yield was determined by GC. The results for each experiment are averages over two runs.

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