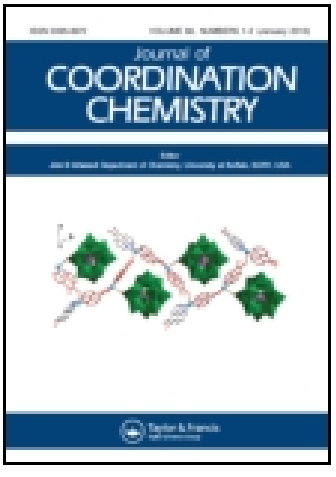


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, characterization, and transfer hydrogenation of Ru(II)-N-heterocyclic carbene complexes

S. Yaşar[a], S. Çekirdek[a] & İ. Özdemir[b]

[a] Department of Chemistry, Gaziosmanpaşa University, Tokat, Turkey

[b] Department of Chemistry, İnönü University, Malatya, Turkey

Accepted author version posted online: 04 Apr 2014.Published online: 29 Apr 2014.

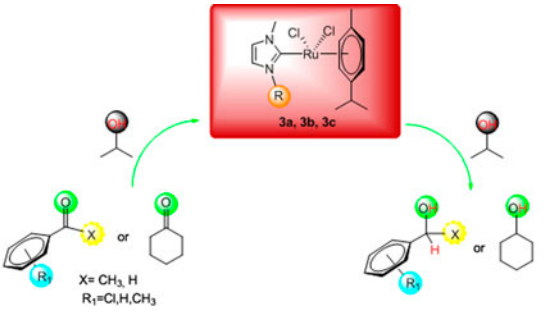
Journal of Coordination Chemistry, 2014
Vol. 67, No. 7, 1236–1248, http://dx.doi.org/10.1080/00958972.2014.911291

Synthesis, characterization, and transfer hydrogenation of Ru(II)-*N*-heterocyclic carbene complexes

S. YAŞAR*†, S. ÇEKIRDEK† and İ. ÖZDEMIR‡

†Department of Chemistry, Gaziosmanpaşa University, Tokat, Turkey
‡Department of Chemistry, İnönü University, Malatya, Turkey

(*Received 3 July 2013; accepted 26 February 2014*)



A new series of ruthenium(II) *N*-heterocyclic carbene complexes [RuL^{1,2,3}(*p*-cymene)Cl$_2$] (**3a–c**) (where L is a *N*-heterocyclic carbene), have been synthesized via transmetalation. The new ruthenium(II)-NHC complexes were applied to transfer hydrogenation of acetophenone derivatives and aldehydes using 2-propanol as a hydrogen source and KOH as a co-catalyst. The results show that the corresponding alcohols could be obtained in good yield with high catalyst activity (up to 100%) under mild conditions. [RuL^1(*p*-cymene)Cl$_2$] (**3a**) is much more active than the other complexes in transfer hydrogenation. Reactions, catalyzed by **3a–c**, showed the highest reaction rates and yields of alcohol when the substrates bear more electron-withdrawing substituents. All new compounds were characterized by IR, elemental analysis, LC–MS (ESI), and NMR spectroscopy.

Keywords: Ruthenium; Silver; *N*-Heterocyclic carbine; Transfer hydrogenation; Transmetalation

1. Introduction

Ligand effects are extremely important in homogeneous catalysis by metal complexes. Carbenes are both reactive intermediates and ligands in catalysis. After the first stable *N*-heterocyclic carbene ligands were reported by Arduengo *et al.*, *N*-heterocyclic carbenes

*Corresponding author. Email: sedat.yasar@gop.edu.tr

(NHCs) have been indispensable ligands for transition metals and homogeneous catalysis [1–3]. Due to their topological and electronic versatility, *N*-heterocyclic carbene-based ligands have widespread applications not only in organometallic chemistry but also in industrial applications of homogeneous catalysis. Strong σ-donation from NHCs increases the stability of the complexes and gives complexes with advantageous properties in catalytic reactions [1–15]. The first catalytic applications of NHC complexes were reported by Herrmann in 1995, together with the recognition that NHCs are excellent ligands for many homogeneous catalysts [2]. Different NHC complexes and their catalytic applications have been reported by many research groups [4–15]. Continued research has focused on synthesis of new functional NHC complexes. Functionality of the complexes depends on the steric and electronic effect of the ligands on the metal center. Ru–NHC complexes can be functionalized by N-substituted NHC ligands. In this context, our research group has focused on synthesis, characterization, and catalytic activity of functional *N*-heterocyclic carbene ligands and their metal complexes [16–19].

Synthesis of different alcohols is an important application for transition metal-catalyzed reactions for economical and environmental reasons [20]. Various Ir, Rh, and Ru complexes have catalyzed different types of ketone to alcohol conversions under mild reaction conditions [21, 22]. Ligand choice has a large effect on metal center selectivity and activity. So far, phosphine, *N*-heterocyclic carbene, and amine-based metal complexes have been catalysts for transfer hydrogenation reactions.

Based on our experience in the synthesis of *N*-heterocyclic carbene ligands and their applications in homogeneous catalysis, we explore the activity of new Ru–NHC (**3a–c**) complexes in transfer hydrogenation of ketones and aldehydes. All proposed structures are supported by NMR and IR spectra.

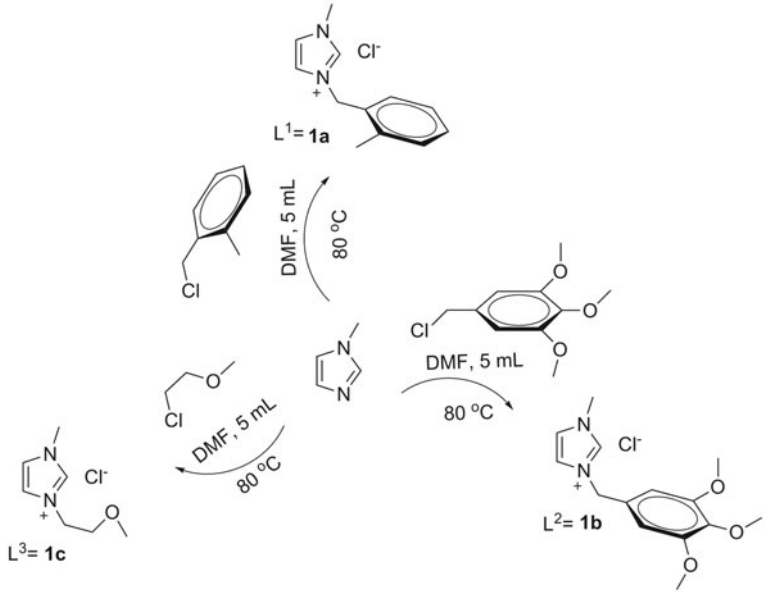


Figure 1. Synthesis of imidazolium salts (**1a–c**).

2. Results and discussion

The hygroscopic imidazolium salts (**1a–c**) (figure 1) were characterized by ^{1}H and ^{13}C NMR mass, IR spectroscopy, and elemental analyses. The ^{1}H NMR spectra of the imidazolium salts supported the assigned structures; the resonances for acidic C(2)–H were observed as sharp singlets at 10.59, 10.48, and 10.28 ppm for **1a–c**, respectively. There was no direct effect of the R groups on the chemical shifts of the protons of **1a–c**. ^{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 137.2, 137.9, and 137.7 ppm for imidazolium salts (**1a–c**), respectively. The NMR values are similar to those found for other imidazolium salts [22].

Silver complexes of *N*-heterocyclic carbenes were prepared by the addition of Ag_2O to imidazolium salts solutions (**1a–c**) in CH_2Cl_2 (figure 2). The resulting suspension was stirred at room temperature overnight, filtered through Celite, and crystallized with CH_2Cl_2. White crystals (in 70–80% yield) were washed and dried in vacuum. When the white crystals were left in air, they began to slowly turn black. Low field signals attributed to acidic NC*H*N protons were not observed in the ^{1}H NMR spectra of the new Ag–NHC complexes (**2a–c**). This observation confirmed that the imidazolium salts were deprotonated. However, coordination of *N*-heterocyclic carbene ligands to the metal center resulted in low field resonances for carbene carbon at δ 180–181.2 ppm.

Ag–NHC complexes are widely used as transfer compounds. To show the feasibility of this approach for **2a–c**, a series of Ru(II)-NHC complexes were synthesized in good yield as stable dark red solids. **3a–c** were obtained by reaction of $[RuCl_2(p\text{-cymene})]_2$ with a solution of **2a–c** in the dark (figure 2). The low field resonance signals of Ag–C_{carb} shifted to higher field when NHC bonded to ruthenium. This observation confirms that Ru–NHC complexes were formed by transmetalation. The air and moisture-stable ruthenium *N*-heterocyclic carbene complexes (**3a–c**) were soluble in polar and halogenated solvents.

Transition metal-catalyzed transfer hydrogenation of ketones in 2-propanol has become an efficient method for synthesis of alcohols [22–29].

In order to show the usefulness of the catalysts in a more general manner, we employed **3a–c** in the transfer hydrogenation of acetophenone derivatives and aldehydes (figure 3). 2-Propanol and KOH were used as a hydrogen donor and promoter, respectively.

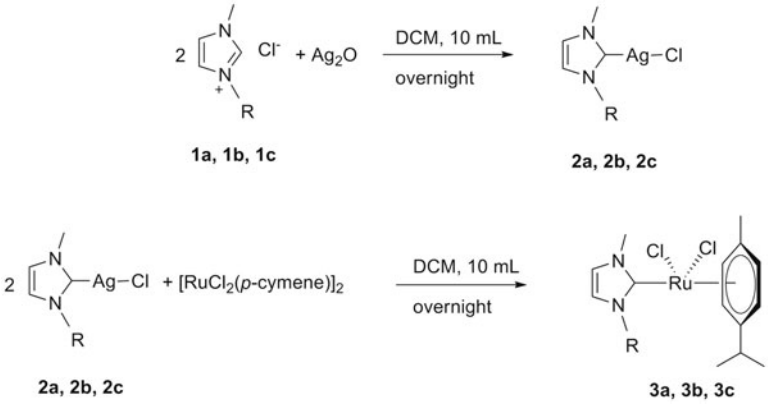


Figure 2. Synthesis of **2a–c** and **3a–c** NHC complexes.

The transfer hydrogenation reactions are very susceptible to the type of the base and its concentration. In order to confirm this, a blank reaction was carried out. As expected, no product was observed in the absence of base (table 1, entry 7). We screened the effect of base type and base ratio in the catalytic transfer hydrogenation. Different inorganic bases such as NaOH, Cs_2CO_3, *t*-BuOK, KOH, and K_2CO_3 were tested on this catalytic system; we obtained the best conversion rates with KOH. High concentrations of KOH promoted conversions but there was no conversion difference between 4 and 2 mM% of KOH (Conversion means conversion to the desired product; see table 1 footnote.). However, the lower base ratio (2 mM% KOH) was preferred for atom economy (table 1).

Electronically different acetophenone and aldehyde derivatives were selected as substrates for hydrogen transfer reactions. According to the literature, no decomposition or side reactions of these substrates have been detected in transfer hydrogenation [19].

As shown in table 2, these ketones and aldehydes were reduced to the corresponding secondary alcohols under mild conditions. Reaction time was determined as the time required for 90% conversion (determined by GC). Several factors play important roles in catalyst activity. Catalyst performance depends on the nature of substrates, the behavior of the ligands in the complexes, and concentration of the catalyst. Electrophilic effect of the substrate, nature of the catalysts, donor function, and flexibility of the backbone in the NHC ligands can be responsible for activity of the complexes. Steric and electronic properties of the substrates also affect conversions. Substrates bearing electron-withdrawing groups were reduced to secondary alcohols in better yield than substrates bearing electron-donating

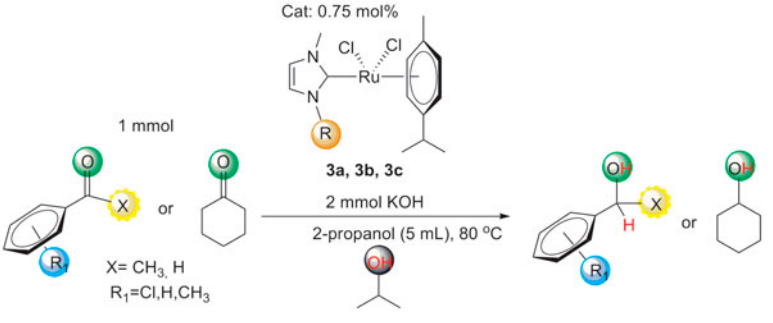


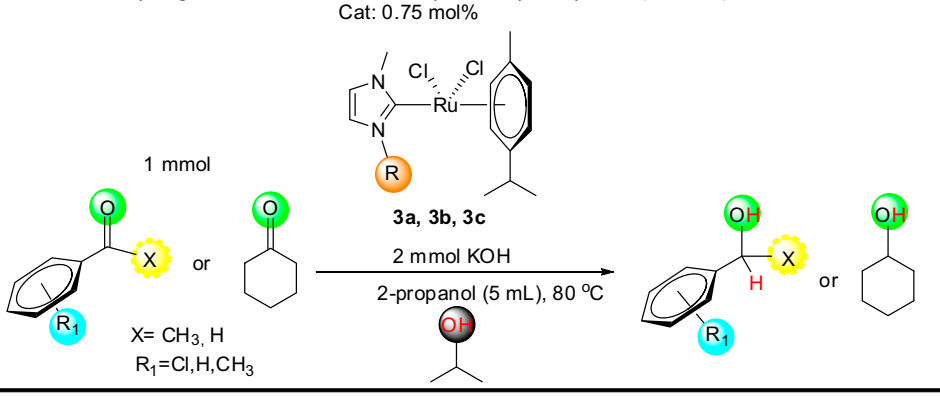
Figure 3. Transfer hydrogenation of ketones and aldehydes catalyzed by **3a–c**.

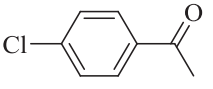
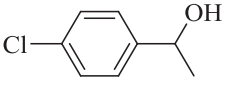
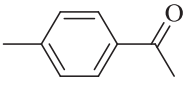
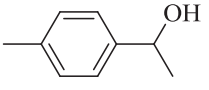
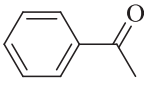
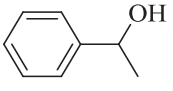
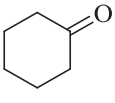
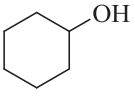
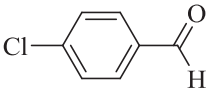
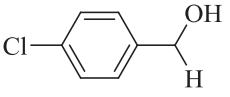
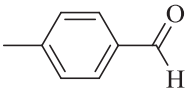
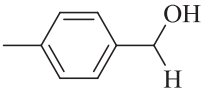
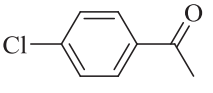
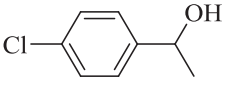
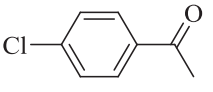
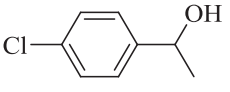
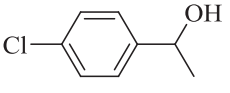
Table 1. Influence of the nature of the base co-catalyst with **3a** on the reduction of p-chloroacetophenone by transfer hydrogenation.[a]

Entry	Base	Base (mM)	Conversion (%)[b]
1	Cs_2CO_3	4	83
2	*t*BuOK	4	100
3	K_2CO_3	4	23
5	NaOH	4	90
4	KOH	4	100
5	KOH	2	100
6	KOH	1	85
7	–	–	0

[a]Reaction conditions: p-chloroacetophenone (1 mM), **3a** (0.75 M%), 80 °C, 30 min.
[b]Determined by GC.

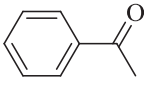
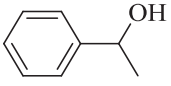
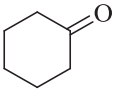
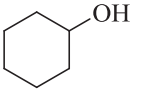
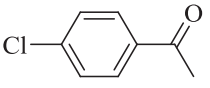
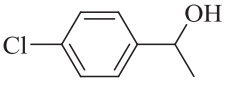
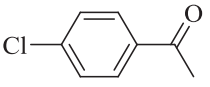
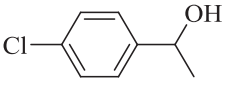
Table 2. Transfer hydrogenation of ketones and aldehydes catalyzed by **3a–c** (0.75 M%).



Entry	Catalyst	Substrate	Conversion[a]	Product
1	**3a**		100	
2	**3b**		97	
3	**3c**		92	
4	**3a**		91	
5	**3b**		88	
6	**3c**		87	
7	**3a**		93	
8	**3b**		96	
9	**3c**		85	
10	**3a**		100	
11	**3b**		100	
12	**3c**		100	
13	**3a**		100	
14	**3b**		100	
15	**3c**		100	
16	**3a**		100	
17	**3b**		100	
18	**3c**		100	
19	**3a**		93[c]	
20	**3b**		97[c]	
21	**3c**		90[c]	
22	**3c**		14[d]	
23	**3b**		19[d]	
24	**3a**		1[e]	
25	**3b**		3[e]	
26	**3c**		1[e]	
27	**3c**		65[b]	
28	–		20[f]	

(*Continued*)

Table 2. (*Continued*).

Entry	Catalyst	Substrate	Conversion[a]	Product
29	–		15[f]	
30	–		30[f]	
31	**3a**		0[g]	
32	**3a**		95[h]	
33	**3b**		94[h]	
34	**3c**		89[h]	
35	**3a**		65[h]	
36	**3b**		56[i]	
37	**3c**		51[i]	

[a]Reaction conditions: The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 1 : 0.0075 : 2, i-PrOH (5 mL), KOH (4 mM), **3a–c** (0.75 M%), 80 °C, 30 min. Purity of compounds is checked by GC and GC–MS (three independent catalytic experiments) and conversions are based on ketones. Conversions were determined by GC (three independent catalytic experiments).
[b]At normal atmospheric condition with undried 2-propanol.
[c]0.375 M% catalyst concentration.
[d]At 50 °C.
[e]At room temperature.
[f]No **3a–c** catalyst.
[g]No base.
[h]Catalyst concentration 0.1 M%.
[i]Catalyst concentration 0.025 M%.

groups (table 2, entry 1–3, 4–6, and 13–15). Considering yield and reaction time, **3a** and **3b** showed better performance than **3c** with acetophenone derivatives, presumably due to increased steric bulk around the metal or lower electron donation provided by the carbene ligands. When the bulkiness of R increased, catalyst activity did not change much (table 2, entry 1, 2, 4, 7, 8).

2-Propanol is used as hydrogen donor in transfer hydrogenation reactions due to its stability, low toxicity, and moderate boiling point. With 2-propanol, our results were promising when compared with literature as well as with our previous work [16–19, 30–36].

There are some applications for hydrogen transfer reactions with metal-free catalytic systems. However, metal-free catalytic systems cannot compete in terms of efficiency and time with metal-based systems [37–40]. Therefore, a blank reaction was tested in the absence of the **3a–c** complexes and results agreed with the literature (table 2, entry 28–30).

The stability of metal carbene complexes against moisture and oxygen were reported previously by Schultz *et al.* [14]. Addition of water to the catalyst system (10 M%) decreased conversions and yields [14]. Observations made on the basis of our experiments are in agreement (table 2, entry 27). The performance of **3a–c** was negatively affected by moisture in 2-propanol with lower yields observed when 2-propanol was not stirred over CaH_2 overnight before distillation. However, **3c** gave 65% conversion (table 2, entry 27). Temperature has a potent effect on the catalyst performance for transfer hydrogenation [41]; catalyst performance of **3a–c** was very low at low temperatures (table 2, entry 22–26).

To compare catalyst performance, **3a–c** were tested under the same conditions. 4-Chloroacetophenone was reduced to almost 100% of the corresponding alcohol in 30 min by 0.75 M% **3a–c**. At lower **3a–c** concentration (0.375, 0.1, and 0.025 M%) with 4-chloroacetophenone, very high conversions were obtained (table 2, entry 19–21, 32–37). Although **3a–c** gave excellent performance with all substrates, there were slight differences in performance due to the *N*-heterocyclic carbene ligands at the metal center.

A plot of conversion *versus* time for **3a–c** with 4-chloroacetophenone is shown in figure 4. The reaction was monitored by taking small portions from the reaction mixture under a nitrogen atmosphere at set intervals and the percentage conversion was determined. It is clear that this sampling of the reaction medium and reduction in the concentration of catalyst negatively affected the catalyst performance (figure 4).

When the catalytic reactions were performed without interruption (table 2, entry 1–3), the results were clearly better than the interrupted reactions.

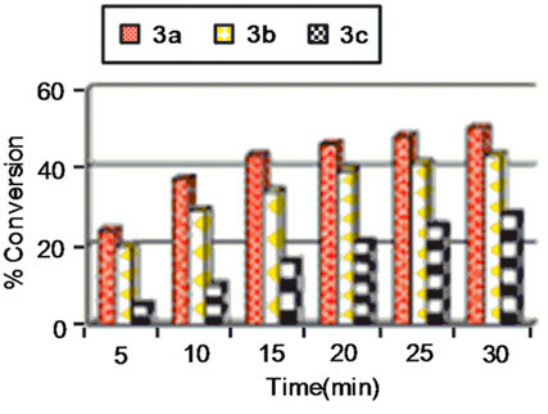


Figure 4. Time dependence of the catalytic transfer hydrogenation of 4-chloroacetophenone catalyzed by **3a–c** (0.75 M%) in 2-propanol at 80 °C with KOH as base. Every 5 min reactions were stopped and small portions taken for analyses.

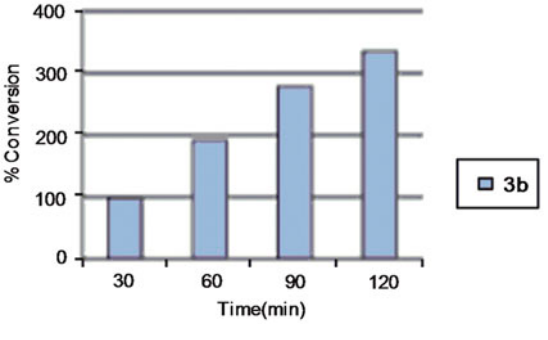


Figure 5. Lifetime study for **3b** (0.75 M%) with 4-chloroacetophenone. Catalytic run was initiated using standard conditions but after 30 min operating time, when >90% conversion had been obtained, an additional 1 mM of substrate was added to the solution and the reaction monitored for a further 30 min (total conversion (99 + 93%)), after which time a third aliquot of substrate was added and the reaction monitored for further 30 min (total conversion (99 + 93 + 87%)), after which time a fourth aliquot of substrate was added and the reaction again monitored (total conversion (99 + 93 + 87 + 56%)).

Stability, activity, and continuity of **3b** for hydrogen transfer were tested with 4-chloroacetophenone under normal operating conditions. After 30 min, an additional 1 mM of 4-chloroacetophenone was added to the reaction mixture and reaction monitored, and after 90 min, a third aliquot of substrate was loaded. Although catalyst concentration was reduced, catalyst performance of **3b** hardly decreased with time (figure 5).

The catalytic activities of **3a–c** are comparable with previously reported catalyst systems and our previous results [20, 30–36]. In our previous studies [17], concentrations of catalysts and KOH were higher and reaction times were longer than in our current study. With this catalysis system, we developed reaction parameters such as reaction time, conversion, and catalyst quantity. Catalyst systems **3a–c** showed excellent activity with different substrates and **3b** performed with very high catalyst stability.

In summary, a new series of *N*-heterocyclic carbene ligands (**1a–c**), silver-NHC complexes (**2a–c**), and ruthenium-NHC complexes (**3a–c**) have been synthesized. To demonstrate the efficiency of **3a–c** as catalyst precursors, transfer hydrogenations of ketones and aldehydes were performed. Excellent activity and good catalyst stability were observed under mild reaction conditions. Structural differences in **3a–c** did not affect yields significantly. The Ru–NHC catalysts described here gave one of the highest conversion rates to date for transfer hydrogenation reaction catalyzed by Ru–NHC complexes with low base loading.

3. Experimental setup

3.1. *Materials and methods*

All procedures were carried out under an inert atmosphere using standard Schlenk line techniques. Chemicals and solvents were purchased from Sigma Aldrich Co. (Dorset, UK). The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: Et_2O (Na/K alloy), CH_2Cl_2 (CaH_2), hexane, and toluene (Na). Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab. NMR spectra and mass spectrometry (ESI) were recorded at Gaziosmanpasa University. IR spectra were recorded at Gaziosmanpasa University on a Perkin Elmer Paragon 1000 FT-IR Spectrometer employing a KBr disk. All reactions involving silver compounds were performed with the exclusion of light.

3.2. *Melting point determination*

Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected.

3.3. *NMR spectroscopy*

^{1}H NMR and ^{13}C NMR spectra were recorded using a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00). Coupling constants (J values) are given in Hz.

3.4. *Gas chromatography*

GC analyses of reactions mixtures have been done using a Shimadzu GC 2010-Plus GC-FID system. Column: TeknokromaTRB-5 capillary column, 30 m × 0.32 mm × 0.25 µm. Initial temperature at 50 °C, held for 1 min, ramp 2 °C/min next 90 °C, held for 3 min, ramp 40 °C/min next 240 °C held for 10 min. The temperature of the injector and detector were held at 240 °C.

3.5. *General preparation of 1,3-dialkylimidazolium salts*

New unsymmetrical 1,3-dialkylimidazolium salts (**1a–c**) were prepared according to known methods [23]. The unsymmetrical NHC precursors were prepared according to the general reaction pathway shown in figure 1. To a solution of 1-methyl imidazole (0.78 g, 10.0 mM) in DMF (5 mL) was added slowly the corresponding alkyl or aryl halogen (12.0 mM) compounds, and the resulting mixture was stirred at 80 °C for 24 h. Diethyl ether (10 mL) was added to obtain a creamy hydroscopic solid. The creamy solids were washed with diethyl ether (3 × 10 mL) and the corresponding imidazolium chlorides obtained in (80–85%) yields after drying under vacuum.

3.5.1. 1-Methyl-3-(2-methylbenzyl)imidazolium chloride, 1a. Yield: 1.77 g (80%). $\nu_{(CN)}$ = 1475 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 2.26 [s, 3H, $CH_2C_6H_4(CH_3)$-2]; 4.04 [s, 3H, NCH_3]; 5.51 [s, 2H, $CH_2C_6H_4(CH_3)$-2]; 7.11–7.23 [m, 5H, NC*H*CHN and $CH_2C_6H_4(CH_3)$-2]; 7.69 [s, 1H, NCHC*H*N]; 10.59 [s, 1H, NC*H*N]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.5 [$CH_2C_6H_4(CH_3)$-2]; 35.9 [NCH_3]; 50.8 [$CH_2C_6H_4(CH_3)$-2]; 120.8, 123.2; 126.2, 129.0, 129.1 and 130.1 [$CH_2C_6(CH_3)$-2]; 130.5 and 136.2 [NCHCHN]; 137.2 [NCHN]. LC–MS (ESI): *m/z* (%) 187.2 (100) $[M–Cl]^+$. Anal. Calcd for $C_{12}H_{15}N_2Cl$ (%): C, 64.71; H, 6.79; N, 12.58. Found: C, 64.78; H, 6.85; N, 12.68.

3.5.2. 1-Methyl-3-(3,4,5-trimethoxybenzyl)imidazolium chloride, 1b. Yield: 2.5 g (85%). $\nu_{(CN)}$ = 1432 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 3.79 [s, 3H, $CH_2C_6H_2(OCH_3)$-4]; 3.86 [s, 6H, $CH_2C_6H_2(OCH_3)$-3,5]; 4.02 [s, 3H, NCH_3]; 5.45 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.83 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 7.39 and 7.46 [s, 2H, NCHCHN]; 10.48 [s, 1H, NCHN]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 35.9 [NCH_3]; 52.8 [$CH_2C_6H_2(OCH_3)$-4]; 55.8 [$CH_2C_6H_2(OCH_3)$-3,5]; 60.1 $CH_2C_6H_2(OCH_3)_3$-3,4,5]; [105.8, 121.2, 122.5; 153.1, [$CH_2C_6(OCH_3)_3$-3,4,5]; 128.1 and 138.0 [NCHCHN]; 137.1 [NCHN]. Anal. Calcd for $C_{14}H_{19}N_2ClO_3$ (%): C, 56.28; H, 6.41; N, 9.38. Found: C, 56.36; H, 6.45; N, 9.38.

3.5.3. 1-Methyl-3-(2-metoxhyethyl)imidazolium chloride, 1c [23]**.** Yield: 1.4 g (82%). $\nu_{(CN)}$ = 1432 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 3.25 [s, 3H, $CH_2CH_2OCH_3$]; 3.36 [t, J = 4 Hz, 2H, $CH_2CH_2OCH_3$]; 4.00 [s, 3H, NCH_3]; 4.49 [t, J = 4 Hz, 2H, $CH_2CH_2OCH_3$]; 7.54 [s, 1H, NCHCHN]; 7.58 [s, 1H, NCHCHN]; 10.28 [s, 1H, NCHN]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 36.4 [$CH_2CH_2OCH_3$]; 49.6 [$CH_2CH_2OCH_3$]; 59.0 [NCH_3]; 70.1 [$CH_2CH_2OCH_3$]; 123.2 [NCHCHN]; 137.7 [NCHN]. LC–MS (ESI): *m/z* (%) 141.22 (100) $[M–Cl]^+$. Anal. Calcd for $C_7H_{13}N_2OCl$ (%): C, 47.60; H, 7.42; N, 15.86. Found: C, 47.54; H, 7.35; N, 15.80.

3.6. *General procedure for the preparation of the silver-NHC complexes (2a–c)*

The silver-NHC complexes were prepared via reaction of Ag_2O (5 mM) with dialkyl imidazolium salts (10 mM) (**1a–c**) in CH_2Cl_2 (20 mL) and stirred overnight at room temperature (figure 2). Overnight stirred Ag–NHC solutions were filtered through Celite and diethyl ether added to get white crystals. The white crystals slowly turn black in 3–4 days when standing in light. The molecular structure of Ag–NHC complexes was determined by spectroscopic techniques.

3.6.1. Chloro-[1-methyl-3-(2-methylbenzyl)imidazole-2-ylidene]silver(I), 2a. Yield: 2.5 g (76%), m.p.: 146–147 °C. $\nu_{(CN)}$ = 1604 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 2.28 [s, 3H, $CH_2C_6H_4(CH_3)$-2]; 3.86 [s, 3H, NCH_3]; 5.27 [s, 2H, $CH_2C_6H_4(CH_3)$-2]; 7.11–7.23 [m, 6H, NCHCHN and $CH_2C_6H_4(CH_3)$-2]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 19.6 [$CH_2C_6H_4(CH_3)$-2]; 39.0 [NCH_3]; 54.0 [$CH_2C_6H_4(CH_3)$-2]; 121.0, 122.1; 126.9, 128.6, 129.1 and 131.3 [$CH_2C_6H_4(CH_3)$-2];133.1 and 136.6 [NCHCHN]; 180.7 [Ag–C_{carb}]. LC–MS(ESI): m/z = 480.2 [$(L_2Ag)AgCl_2$-$AgCl_2$]. Anal. Calcd for $AgC_{12}H_{14}N_2Cl$ (%): C, 43.73; H, 4.28; N, 8.50. Found: C, 43.70; H, 4.23; N, 8.45%.

3.6.2. Chloro-[1-methyl-3-(3,4,5-trimethoxybenzyl)imidazole-2-ylidene]silver(I), 2b. Yield: 3 g (75%), m.p.: 158–159 °C. $\nu_{(CN)}$ = 1602 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 3.84 [m, 12H, NCH_3 and $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 3.86 [s, 6H, $CH_2C_6H_2(OCH_3)$-3,5]; 5.17 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.52 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 7.01 [s, 2H, NCHCHN]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 38.9 [NCH_3]; 56.1 [$CH_2C_6H_2(OCH_3)$-4]; 56.4 [$CH_2C_6H_2(OCH_3)$-3,5]; 60.8 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; [105.3, 121.1, 122.6; 153.6, [$CH_2C_6(OCH_3)_3$-3,4,5]; 131.1 [NCHCHN]; 180.2 [Ag–C_{carb}]. LC–MS (ESI): m/z = 631.2 [$(L_2Ag)AgCl_2$-$AgCl_2$]. Anal. Calcd for $AgC_{14}H_{18}N_2ClO_3$ (%): C, 41.45; H, 4.47; N, 6.91. Found: C, 41.39; H, 4.43; N, 6.88.

3.6.3. Chloro-[1-methyl-3-(2-metoxhyethyl)imidazole-2-ylidene]silver(I), 2c. Yield: 2 g (76%), m.p.: 74 °C. $\nu_{(CN)}$ = 1608 cm^{-1}. ^1H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 3.22 [s, 3H, $CH_2CH_2OCH_3$]; 3.38 [t, J = 4 Hz, 2H, $CH_2CH_2OCH_3$]; 4.08 [s, 3H, NCH_3]; 4.55 [t, J = 4 Hz, 2H, $CH_2CH_2OCH_3$]; 7.54–7.58 [m, 2H, NCHCHN]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 36.9 [$CH_2CH_2OCH_3$]; 50.0 [$CH_2CH_2OCH_3$]; 59.6 [NCH_3]; 72.1 [$CH_2CH_2OCH_3$]; 123.6 [NCHCHN]; 181.2 [Ag–C_{carb}]. LC–MS (ESI): m/z = 388.2 [$(L_2Ag)AgCl_2$-$AgCl_2$]. Anal. Calcd for $AgC_7H_{12}N_2OCl$ (%): C, 29.66; H, 4.27; N, 9.88. Found: C, 29.62; H, 4.22; N, 9.81.

3.7. *General method for the preparation of the ruthenium-NHC complexes (3a–c)*

The ruthenium-NHC complexes (**3a–c**) were synthesized through transmetalation via silver NHC complexes (**2a–c**) with the method reported by Wang and Lin [36]. We reacted Ag–NHC complexes (5 mM) with $[RuCl_2(p\text{-cymene})]_2$ (10 mM) in the dark and the mixture was stirred for 24 h at room temperature. The solution was filtered through Celite and crystallized from dichloromethane:diethyl ether (1 : 2) at room temperature (figure 2).

3.7.1. Dichloro-[1-methyl-3-(2-methylbenzyl)imidazole-2-ylidene](p-cymene)ruthenium (II), 3a. Yield: 0.3 g (60%), m.p.: 207–208 °C. $\nu_{(CN)}$ = 1612 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 1.25 [d, J = 6.9 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$]; 2.03 [s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$]; 2.40 [s, 3H, $CH_2C_6H_4(CH_3)$-2]; 2.88 [h, J = 6.9 Hz, 1H, p-$CH_3C_6H_4CH(CH_3)_2$]; 4.07 [s, 3H, NCH_3]; 4.92 [s, 2H, $CH_2C_6H_4(CH_3)$-2]; 5.30 and 6.12 [s, 4H, p-$CH_3C_6H_4CH(CH_3)_2$]; 6.91 and 7.06 [d, J = 2 Hz, 2H, NCHCHN]; 7.14–7.25 [m, 4H, $CH_2C_6H_4(CH_3)$-2]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.6 [p-$CH_3C_6H_4CH(CH_3)_2$]; 19.4 [p-$CH_3C_6H_4CH(CH_3)_2$]; 30.7 [p-$CH_3C_6H_4CH(CH_3)_2$]; 39.8 [$CH_2C_6H_4(CH_3)$-2], 52.7 [NCH_3]; 76.6 [$CH_2C_6H_4(CH_3)$-2]; 98.6, 107.8, 123.5, 123.9 [NCHCHN and p-$CH_3C_6H_4CH(CH_3)_2$]; 125.9, 126.3, 127.7, 130.6, 135.7 and 136.6 [$CH_2C_6H_4(CH_3)$-2]; 174.6 (Ru–Ccarb). LC–MS (ESI): m/z (%) 457.1 (100) $[M–Cl]^+$. Anal. Calcd for $RuC_{22}H_{28}N_2Cl_2$ (%): C, 53.66; H, 5.73; N, 5.65. Found: C, 53.70; H, 5.78; N, 5.85.

3.7.2. Dichloro-[1-methyl-3-(3,4,5-trimethoxybenzyl)imidazole-2-ylidene](p-cymene)-ruthenium(II), 3b. Yield: 0.4 g (71%), m.p.: 196–197 °C. $\nu_{(CN)}$ = 1614 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 1.25 [d, J = 6.9 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$]; 2.09 [s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$]; 2.97 [h, J = 6.9 Hz, 1H, p-$CH_3C_6H_4CH(CH_3)_2$]; 3.84 [s, 6H, $CH_2C_6H_2(OCH_3)_3$-3,5]; 3.85 [s, 3H, $CH_2C_6H_2(OCH_3)_3$-4]; 4.05 [s, 3H, NCH_3]; 5.10 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 5.40 and 5.98 [s, 4H, p-$CH_3C_6H_4CH(CH_3)_2$]; 6.65 [s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5]; 6.89 and 6.99 [s, 2H, NCHCHN]; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.8 [p $CH_3C_6H_4CH(CH_3)_2$]; 30.9 [p-$CH_3C_6H_4CH(CH_3)_2$]; 39.8 [p-$CH_3C_6H_4CH(CH_3)_2$]; 55.0 [$CH_2C_6H_2(OCH_3)_3$-4]; 56.4 [$CH_2C_6H_2(OCH_3)_3$-3,5]; 60.9 [NCH_3]; 76.6 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 99.2103.2, 105.6, 108.9 [p-$CH_3C_6H_4CH(CH_3)_2$]; 122.5 123.8 [NCHCHN]; 132.5, 137.7, 153.5 [$CH_2C_6H_2(OCH_3)_3$-3,4,5]; 174.4 (Ru–Ccarb). LC–MS (ESI): m/z (%) 533.2 (100) $[M–Cl]^+$. Anal. Calcd for $RuC_{24}H_{32}N_2Cl_2O_3$ (%): C, 50.70; H, 5.67; N, 4.93. Found: C, 50.68; H, 5.60; N, 4.89.

3.7.3. Dichloro-[1-methyl-3-(methoxyethyl)imidazole-2-ylidene](p-cymene)ruthenium(II), 3c. Yield: 0.33 g (75%), m.p.: 146–147 °C. $\nu_{(CN)}$ = 1621 cm^{-1}. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ (ppm) = 1.26 [d, J = 6.9 Hz, 6H, p-$CH_3C_6H_4CH(CH_3)_2$]; 2.10 [s, 3H, p-$CH_3C_6H_4CH(CH_3)_2$]; 2.93 [h, J = 6.9 Hz, 1H, p-$CH_3C_6H_4CH(CH_3)_2$]; 3.33 [s, 3H, $CH_2CH_2(OCH_3)$]; 3.71 [m, 2H, $CH_2CH_2(OCH_3)$]; 3.99 [s, 3H, NCH_3]; 4.26 and 4.76 [m, 2H, $CH_2CH_2(OCH_3)$]; 5.15 and 5.42 [s, 4H, p-$CH_3C_6H_4CH(CH_3)_2$]; 6.97 [d, J = 2 Hz, 1H, NCHCHN]; 7.32 [d, J = 2 Hz, 1H, NCHCHN]. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.5 [p-$CH_3C_6H_4CH(CH_3)_2$]; 30.7 [p-$CH_3C_6H_4CH(CH_3)_2$]; 39.5 [p-$CH_3C_6H_4CH(CH_3)_2$]; 51.5 [$CH_2CH_2(OCH_3)$]; 53.48 [$CH_2CH_2(OCH_3)$]; 58.8 [$CH_2CH_2(OCH_3)$]; 73.2 [NCH_3]; 82.6, 85.1, 99.5, 108.6 [p-$CH_3C_6H_4CH(CH_3)_2$]; 122.8 and 123.6 [NCHCHN]; 173.7 (Ru–Ccarb). LC–MS (ESI): m/z (%) 411.1 (100)$[M–Cl]^+$. Anal. Calcd for $RuC_{17}H_{26}N_2Cl_2O$ (%): C, 45.74; H, 5.87; N, 6.28. Found: C, 45.69; H, 5.78; N, 6.22.

3.8. *General method for transfer hydrogenation of ketones and aldehydes*

Ketones or aldehydes (1 mM) were added to a mixture of the ruthenium catalyst, **3a–c** (0.75 M%) and KOH (2 mM) in i-PrOH (3 mL), and the mixture was heated to 80 °C for 30 min (figure 3). Solution was cooled to room temperature and passed through silica gel. Then volatiles were removed under reduced pressure and conversion distribution was determined by ^{1}H NMR spectroscopy and GC.

Acknowledgement

This work was financially supported by Gaziosmanpasa University Research Fund (GOP. B.A.P: 2010/84, 2011/51 and 2011/105).

References

[1] (a) N. Marion, S. Diez-Gonzalez, S.P. Nolan. *Angew. Chem. Int. Ed.*, **46**, 2988 (2007); (b) D. Enders, O. Niemeier, A. Henseler. *Chem. Rev.*, **107**, 5606 (2007); (b) V. Nair, S. Bindu, V. Sreekumar. *Angew. Chem. Int. Ed.*, **43**, 5130 (2004).
[2] (a) S.P. Nolan. *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2006); (b) F. Glorius. *N-Heterocyclic Carbenes in Transition Metal Catalysis Topics in Organometallic Chemistry*, Springer-Verlag, Berlin (2007); (c) W.A. Herrmann, C. Kocher. *Angew. Chem. Int. Ed.*, **36**, 2162 (2007); (d) W.A. Herrmann, M. Elison, J. Fischer, C. Kocher, G.R.J. Artus. *Angew. Chem. Int. Ed. Engl.*, **34**, 2371 (1995).
[3] A.J. Arduengo, H.L. Harlow, M. Kline. *J. Am. Chem. Soc.*, **113**, 361 (1991).
[4] (a) E. Peris, R.H. Crabtree. *Coord. Chem. Rev.*, **248**, 2239 (2004); (b) M.C. Perry, K. Burgess. *Tetrahedron: Asymmetry*, **14**, 951 (2003).
[5] A.J. Arduengo, R.L. Harlow, M. Kline. *J. Am. Chem. Soc.*, **113**, 361 (1991).
[6] C.W.K. Gstottmayr, V.P.W. Bohm, E. Herdtweck, M. Grosche, W.A. Herrmann. *Angew. Chem. Int. Ed.*, **41**, 1363 (2002).
[7] V. Lavallo, Y. Canac, A. De Hope, B. Donnadieu, G. Bertrand. *Angew. Chem. Int. Ed.*, **44**, 7236 (2005).
[8] K. Vehlow, S. Maechling, S. Blechert. *Organometallics*, **25**, 25 (2006).
[9] (a) J.W. Sprengers, J. Wassenaar, N.D. Clement, K.J. Cavell. *Angew. Chem. Int. Ed.*, **44**, 2026 (2005); (b) N.D. Clement, K.J. Cavell. *Angew. Chem. Int. Ed.*, **43**, 3845 (2004).
[10] (a) A. Furstner, O.R. Thiel, C.W. Lehmann. *Organometallics*, **21**, 331 (2002); (b) A. Furstner, L. Ackermann, A. Beck, H. Hori, D. Koch, K. Langemann, M. Liebl, C. Six, W. Leitner. *J. Am. Chem. Soc.*, **123**, 9000 (2001).
[11] G. Altenhoff, R. Goddard, C.W. Lehmann, F. Glorius. *J. Am. Chem. Soc.*, **126**, 15195 (2001).
[12] (a) T.W. Funk, J.M. Berlin, R.H. Grubbs. *J. Am. Chem. Soc.*, **128**, 1840 (2006); (b) J.P. Morgan, R.H. Grubbs. *Org. Lett.*, **2**, 3153 (2000).
[13] N. Marion, O. Navarro, J. Mei, E.D. Stevens, N.M. Scott, S.P. Nolan. *J. Am. Chem. Soc.*, **128**, 4101 (2006).
[14] (a) M.J. Schultz, S.S. Hamilton, D.R. Jensen, M.S. Sigman. *J. Org. Chem.*, **70**, 3343 (2005); (b) C.M. Crudden, D.P. Allen. *Coord. Chem. Rev.*, **248**, 2247 (2004).
[15] (a) R.H. Grubbs. *Handbook of Olefin Metathesis*, VCH-Wiley, Weinheim (2003); (b) S. Beligny, S. Blechert. In *N-Heterocyclic Carbenes in Synthesis*, S.P. Nolan (Ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2004).
[16] (a) I. Ozdemir, B. Yigit, B. Cetinkaya, D. Ulku, M.N. Tahir, C. Arici. *J. Organomet. Chem.*, **633**, 27 (2001); (b) S. Yasar, I. Ozdemir, B. Cetinkaya, J.L. Renaud, C. Bruneau. *Eur. J. Org. Chem.*, **1**, 2142 (2008).
[17] (a) I. Ozdemir, S. Yasar, B. Cetinkaya. *Transition Met. Chem.*, **30**, 831 (2005); (b) M. Yigit, B. Yigit, I. Ozdemir, E. Cetinkaya, B. Cetinkaya. *Appl. Organomet. Chem.*, **20**, 322 (2006).
[18] (a) S. Yaşar, K.J. Cavell, B.D. Ward, B. Kariuki. *Appl. Organomet. Chem.*, **25**, 374 (2011); (b) N. Gurbuz, I. Ozdemir, S. Demir, B. Cetinkaya. *J. Mol. Catal. A: Chem.*, **209**, 23 (2004).
[19] I. Ozdemir, E.O. Ozcan, S. Gunal, N. Gurbuz. *Molecules*, **15**, 2499 (2010).
[20] M. Beller, C. Bolm. *Transition Metals for Organic Synthesis*, 2nd Edn, Wiley-VCH, Weinheim (2004); (b) B. Cornils, W.A. Herrmann. *Applied Homogeneous Catalysis with Organometallic Compounds*, Wiley-VCH, Weinheim (2007).
[21] S. Gladiali, E. Alberico. *Chem. Soc. Rev.*, **35**, 226 (2006).
[22] (a) N. Gürbüz, E.Ö. Özcan, I. Özdemir, B. Çetinkaya, O. Şahin, O. Büyükgüngör. *Dalton Trans.*, 2330 (2012); (b) E.Ö. Özcan, D. Mercan, N. Gürbüz, E. Çetinkaya, B. Çetinkaya, I. Özdemir. *Turk. J. Chem.*, **35**, 699 (2011); (c) N. Gürbüz, S. Yaşar, E.Ö. Özcan, I. Özdemir, B. Çetinkaya. *Eur. J. Inorg. Chem.*, 3051, (2010).
[23] L.C. Branco, J.N. Rosa, J.J.M. Ramos, C.A.M. Afonso. *Chem. Eur. J.*, **8**, 3671 (2002).
[24] (a) I. Ozdemir, S. Demir, S. Yasar, B. Cetinkaya. *Appl. Organomet. Chem.*, **19**, 55 (2005); (b) I. Ozdemir, S. Demir, B. Cetinkaya. *Synletters*, **6**, 889 (2007); (c) N. Gurbuz, I. Ozdemir, B. Cetinkaya. *Tetrahedron Lett.*, **46**, 2273 (2005).
[25] E. Peris. In *Topics in Organometallic Chemistry*, F. Glorius (Ed.), Vol. 21, Springer, Heidelberg (2007).
[26] M.R.L. Furst, C.S.J. Cazin. *Chem. Commun.*, **46**, 6924 (2010).
[27] (a) L. Delaude, X. Sauvage, A. Demonceau, J. Wouters. *Organometallics*, **28**, 4056 (2009); (b) A.M. Voutchkova, L.N. Appelhans, A.R. Chianese, R.H. Crabtree. *J. Am. Chem. Soc.*, **127**, 17624 (2005).
[28] D.S. McGuinness, K.J. Cavell. *Organometallics*, **19**, 741 (2000).

[29] (a) D. Semeril, C. Bruneau, P.H. Dixneuf. *Adv. Synth. Catal.*, **344**, 585 (2000); (b) B. Cetinkaya, S. Demir, I. Ozdemir, L. Toupet, D. Semeril, C. Bruneau, P.H. Dixneuf. *Chem. Eur. J.*, **9**, 2323 (2003).
[30] M. Albrecht, J.R. Miecznikowski, A. Samuel, J.W. Faller, R.H. Crabtree. *Organometallics*, **21**, 3596 (2002).
[31] S.C. Zinner, C.F. Rentzsch, E. Herdtweck, W.A. Herrmann, F.E. Kuhn. *Dalton Trans.*, 7055 (2009).
[32] (a) H. Turkmen, T. Pape, F.E. Hahn, B. Cetinkaya. *Organometallics*, **27**, 571 (2008); (b) H. Turkmen, T. Pape, F.E. Hahn, B. Cetinkaya. *Eur. J. Inorg. Chem.*, 5418 (2008).
[33] E. Mas-Marza, M. Sanau, E. Peris. *Inorg. Chem.*, **44**, 9961 (2005).
[34] J.F. Sun, F. Chen, B.A. Dougan, H.J. Xu, Y. Cheng, Y.Z. Li, X.T. Chen, Z.L. Xue. *J. Organomet. Chem.*, **694**, 2096 (2009).
[35] A. Binobaid, M. Iglesias, D. Beetstra, A. Dervisi, I. Fallis, K.J. Cavell. *Eur. J. Inorg. Chem.*, 5426 (2010).
[36] H.M.J. Wang, I.J.B. Lin. *Organometallics*, **17**, 972 (1998).
[37] V. Polshettiwar, R.S. Varma. *Green Chem.*, **11**, 1313 (2009).
[38] A. Ouali, J.P. Majoral, A.M. Caminade, M. Taillefer. *Chem. Cat. Chem.*, **1**, 504 (2009).
[39] J. Sedelmeier, S.V. Ley, I.R. Baxendale. *Green Chem.*, **11**, 683 (2009).
[40] M.I. Ikhile, V.O. Nyamori, M.D. Bala. *Tetrahedron Lett.*, **53**, 4925 (2012).
[41] E. Gross, J.H.C. Liu, F.D. Toste, G.A. Somorjai. *Nat. Chem.*, **4**, 947 (2012).