TÜBİTAK

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2017) 41: 29 – 39

doi:10.3906/kim-1604-62

N-heterocyclic carbenes bearing a naphthyl substituent and their metal complexes: synthesis, structure, and application in catalytic transfer hydrogenation

Aylin ATİK, Lütfiye GÖK PEZÜK, Hayati TÜRKMEN*
Department of Chemistry, Faculty of Science, Ege University, İzmir, Turkey

Received: 21.04.2016 • **Accepted/Published Online:** 21.07.2016 • **Final Version:** 22.02.2017

Abstract: A series of unsymmetrical imidazolinium bromides (**3a**–**d**) bearing naphthyl and benzyl groups (R' = $CH_2C_6H_2(CH_3)_3$-2,4,6 (**a**); $CH_2C_6H(CH_3)_4$-2,3,5,6 (**b**); $CH_2C_6(CH_3)_5$ (**c**); $CH_2C_6F_5$ (**d**)) at the N^1 and N^3 positions were successfully synthesized. $[RuCl_2(NHC)(p\text{-cymene})]$ (NHC= N-heterocyclic carbene) complexes (**4a**–**d**) were prepared by the reaction of $[RuCl_2(p\text{-cymene})]_2$ with imidazolinium salts (**3a**–**d**). The new salts (**3a**–**d**) and their ruthenium(II) complexes (**4a**–**d**) were characterized by ^1H, ^{13}C, ^{19}F NMR, and elemental analysis. The ruthenium(II) complexes (**4a**–**d**) were employed as catalysts for the transfer hydrogenation (TH) of ketones in the presence of KOH using 2-propanol as a hydrogen source and the results were compared. The best results in the transfer hydrogenation of ketones were obtained with **4b**. [MCl(NHC)L] (M = Ir, L = Cp^*) (**5b**), cod (**6b**); M = Rh, L= Cp^* (**5b'**), and cod (**6b'**) complexes were prepared and investigated in the TH of ketones. The reactivity of Rh complexes in comparison to those of Ir also appears to be somewhat better. The catalysis appears to be homogeneous.

Key words: Arene ruthenium(II) complexes, N-heterocyclic carbene, transfer hydrogenation, naphthyl substituent

1. Introduction

The chemistry of N-heterocyclic carbenes (NHCs) has a long tradition based on preliminary work by Wanzlick,[1] Öfele,[2] and Lappert[3] and the isolation and identification of a stable NHC by Arduengo et al. in 1991.[4] Since then, a tremendous number of different NHCs have been prepared and characterized.[5–10] They are strong σ-donors and significant π-acceptor ligands.[10] The electronic properties can be modified by varying the number, nature, and position of the substituents on both the nitrogen atoms and the backbone of NHCs. Variations in substituents bound to the nitrogen atoms or to the backbone give unsymmetrical NHCs (uNHCs). The properties of ligands directly influence the catalyst's performance. They have become highly popular in catalysis owing to their ability to stabilize transition metals and their use in homogeneous catalysis, such as C–C coupling,[11,12] olefin metathesis,[13] and hydrogenation.[14–16] Transfer hydrogenation is also a potentially useful protocol for the reduction of ketones and aldehydes to their corresponding alcohols and transfer hydrogenation of ketones has been extensively studied.[17–21] The method is attractive as an alternative to hydrogenation because it requires neither the hazardous hydrogen gas nor pressure vessels, and it is easy to execute. Transition metal complex-catalyzed transfer hydrogenation of ketones is usually carried out in refluxing 2-propanol (IPA) under an inert

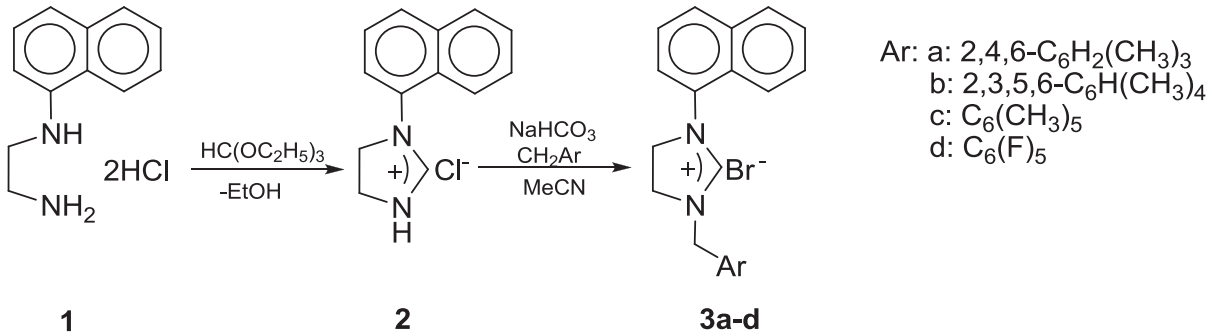
*Correspondence: hayatiturkmen@hotmail.com

atmosphere in order to keep the catalysts active during the reaction. IPA, HCOOH/NEt_3, or HCOONa are the most frequently used hydrogen donors. In fact, both acetone and IPA are environmentally friendly and therefore make somewhat green chemistry.[22] The TH of C=O groups catalyzed by the complexes of Ru, Ir, and Rh with diamine, phosphine, and NHCs has been investigated.[23–35] These intense research efforts have resulted in advances in the development of new catalysts of higher activity and selectivity. In previous works, we introduced ruthenium(II) complexes with pyrazole,[36] diamine,[37,38] 1-R-imidazo[4,5-*f*][1,10]-phenanthroline(R= alkyl),[39] and iridium(I) and rhodium(I) complexes with benzimidazol-2-ylidene[21] and annulated saturated NHC[28] ligands. Their catalytic properties were studied in TH reactions. We now report the preparation of Ru(II), Rh(I), and Ir(I) complexes with naphthyl substituted imidazolin-2-ylidene ligand. They are catalytically active catalysts for the reduction of ketones.

2. Results and discussion

2.1. Synthesis and characterization of naphthyl-substituted imidazolinium ligands

Naphthyl-substituted imidazolinium salts were synthesized according to the steps illustrated in Scheme 1. N-(naphthyl)-ethylenediamine dihydrochloric acid (**1**) was purchased. The second step involved naphthyl-substituted imidazolinium chloride (**2**) synthesis upon ring closing of **1**. Unsymmetrical imidazolinium derivatives (**3a**–**d**) were prepared by deprotonation of **2** in the presence of $NaHCO_3$ followed by treatment with alkyl bromides. The synthesized imidazolium salts were characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of these salts were consistent with the proposed structures: C_2–H resonance at δ = 8.25–9.63 ppm as sharp singlets. The formation of the salts was also supported by resonance at δ = 156.9–159.4 ppm in the ^{13}C NMR spectrum for the C_2–H carbon atom.

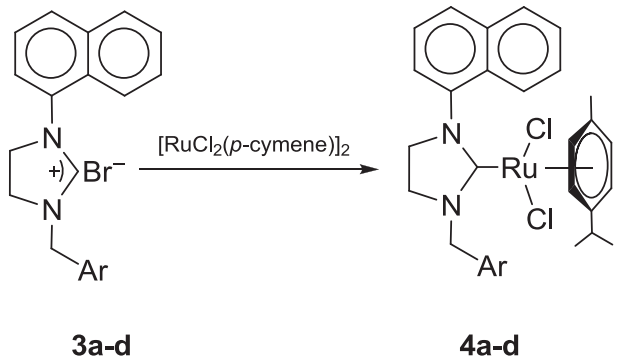


Scheme 1. Synthesis of imidazolinium salts.

2.2. Synthesis and characterization of Ru(II) complexes

Metal complexes with NHC ligand can be prepared by three major methods: (i) the free carbene ligands, (ii) the carbene transfer reactions from silver carbene complexes to other transition metals, (iii) in situ deprotonation of azolium salts by complexes with basic ligands or counterions like OAc^- and OR^-. The first method was used for preparation of [$RuCl_2$(NHC)(*p*-cymene)] complexes (**4a**–**d**). The complexes **4a**–**d** were synthesized by reaction of [Ru(*p*-cymene)Cl_2]$_2$ with naphthyl-substituted imidazolinium salts (**3a**–**d**) in the presence of NaH/KO^{t}Bu in THF (Scheme 2). All new complexes were isolated as orange and air-stable solids and all complexes were soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. The complexes **4a**–**d** were fully identified by spectroscopic techniques. The characteristic signals for the C_2–H proton of the imidazolinium

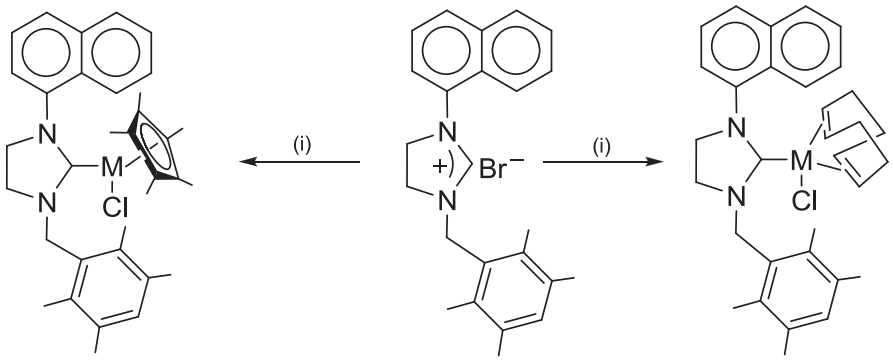
salts (**3a**–**d**) disappeared in the ^{1}H NMR spectra of Ru(II) complexes. The benzylic-CH_2 protons of ruthenium complexes (**4a**–**d**) were observed to shift towards lower fields as compared to respective ligands (**3a**–**d**). Values of δ ($^{13}C_{carbene}$) were in the 221.7–224.8 ppm range.



3a-d **4a-d**

Scheme 2. Synthesis of ruthenium(II) complexes (**4a**–**d**).

The Rh(I) and Ir(I) complexes (**5**, **6**) were made in an analogous manner to the synthesis described above (Scheme 3). As expected, the complexes lacked the NCHN proton resonance of the precursor imidazolinium salt. The ^{13}C NMR spectra showed the characteristic resonances for the imidazolin-2-ylidene carbene carbon atom in the range δ = 195.5, 195.9 ppm (for iridium complexes **5b**, **6b**) and δ = 204.3, 215.2 ppm (for rhodium complexes **5b′**, **6b′**). Coupling constants $J(^{103}$Rh-^{13}C) for the new rhodium complexes **5b′** and **6b′** are comparable to those found for rhodium-NHC complexes described previously.[27,28]



5b M: Ir
5b' M: Rh

3b

6b M: Ir
6b' M: Rh

Scheme 3. Synthesis of rhodium(I) and iridium(I) complexes (**5** and **6**), (i) KOH, KO^tBu, $[MCl_2(L)]_2$, THF, R.T.

2.3. Catalytic studies

Recently, the transfer hydrogenation of ketones to alcohols has been extensively investigated. At the same time, studies are continuously aiming to obtaining better catalysts. Herein, we prepared a series of novel ruthenium (**4a**–**d**), iridium (**5b**, **6b**), and rhodium (**5b′**, **6b′**) complexes and employed them as catalysts for the transfer hydrogenation of ketones (Table 1). The Ru(II)-NHC complexes (**4a**–**d**) were screened as catalyst for transfer hydrogenation of different aryl-ketones to aryl-ethanols using 2-propanol as hydrogen donor in the presence of KOH. The catalytic experiments were carried out using 1 mmol of ketone, 0.01 mmol of ruthenium complexes

4a–**d** as a catalyst, and 2 mmol of KOH in 5 mL of 2-propanol. The transfer hydrogenation reactions were carried out in the presence of KOH, which was reported earlier to be the best inorganic base for such reactions.[28,29] The complex **4b** was found to be the most active catalyst among all of these complexes tested. Better behavior of the tetramethylbenzyl derivatives was observed against other complexes. Presumably, the presence of a hydrogen atom at the *p*-position of the arene ring plays an important role in the TH. The sequence of activity is **4b** > **4d** > **4c** > **4a**.

Table 1. Transfer hydrogenation of ketones using complexes.

		Yield, %							
Entry	Substrate	**4a**	**4b**	**4c**	**4d**	**5b**	**5b′**	**6b**	**6b′**
1	acetophenone	61	91	69	72	37	57	69	88
2	4-methoxyacetophenone	54	88	70	73	40	59	70	83
3	4-chloroacetophenone	65	93	77	76	52	66	69	87
4	4-bromoacetophenone	66	94	86	80	55	64	71	84
5	3,4-dimethylacetophenone	54	87	76	73	33	56	59	78
Reaction conditions: Substrate (1 mmol), ^{i}PrOH (5 mL), KOH (2.0 mmol), catalyst (0.01 mmol), 82 $^{\circ}$C, 2 h.									

The [(NHC)M] (M= Rh, Ir) complexes bearing 1,5-cyclooctadiene (cod) or pentamethylcyclopentadienyl (Cp*) have been successfully applied in TH in recent years.[40−45] Rhodium and iridium complexes, particularly half-sandwich types, have been less explored for transfer hydrogenation than ruthenium species. In most cases, the catalytic reactions in 2-propanol necessitate high temperature and an inert atmosphere.[46−48] We explored the effectiveness of catalysts (**5b**, **5b′**, **6b**, **6b′**) on aryl ketones reduction under hydrogen transfer conditions. Complexes (**6b**, **6b′**) having cod in coordination with Rh/Ir were slightly more efficient catalysts as corresponding compounds (**5b**, **5b′**) involving Cp* in coordination, as conversions are somewhat higher with the former. Moreover, the Rh(I) species (**5b′**, **6b′**) appear to more efficient than their Ir(I) analogues (**5b**, **6b**).

We also performed an additional experiment to assess whether the reaction system is homogeneous or heterogeneous; mercury and PPh_3 poisoning tests[49−52] were carried out. The suppression of catalysis by Hg(0) is evidence for a heterogeneous catalyst; if Hg(0) does not suppress catalysis, that is evidence for a homogeneous catalyst. The Hg(0) test with catalyst **4b** and acetophenone in basic IPA showed no significant inhibition of conversion to products. Thus, the present catalysis appears to be homogeneous in nature (Table 2).

Table 2. The Hg(0) and PPh_3 poisoning tests for ATH of acetophenone to 1-phenylethanol.

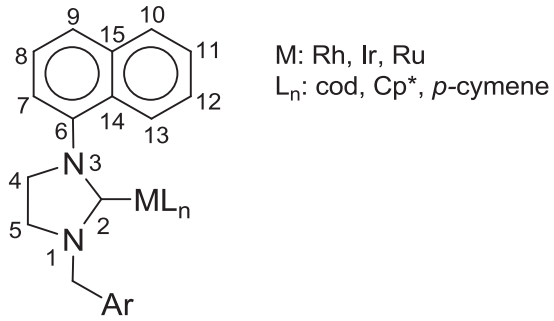
Entry	**4b**/Hg$^{\circ}$	Conversion, %
1	1/0	91
2	1/1	90
3	1/300	89
	4b/PPh_3	
4	1/1	90
5	1/5	86

The PPh_3 poisoning test was also used. In the presence of 5 equiv of PPh_3, the reaction occurred with only a 5% decrease in percent conversion (entry 5). The homogeneous nature of catalysis is supported as inferred on the basis of the Hg test.

In summary, we have disclosed the synthesis and full characterization of new ruthenium, rhodium, and iridium complexes bearing unsymmetrically NHCs, in which a substituted benzyl arm was present on one nitrogen. The Ru(II) complexes revealed differences in their behavior as precatalysts for transfer hydrogenation of different ketones. The best result in the transfer hydrogenation of ketones was obtained with **4b**. Presumably, the presence of a H atom at the *p*-position of the arene ring or benzylic protons played an important role in the transfer hydrogenation reaction. The catalytic processes of Rh complexes were more efficient than those of the corresponding Ir complexes. The homogeneous nature of transfer hydrogen was supported by poisoning tests. Further investigation into the different catalytic reactions of each complex is currently ongoing.

3. Experimental

Reactions involving air-sensitive components were performed using a Schlenk-type flask under argon atmosphere and high vacuum-line techniques. The glass equipment was heated under vacuum in order to remove oxygen and moisture and then it was filled with argon. The solvents were analytical grade and distilled under argon atmosphere from sodium (ethanol, methanol, toluene, tetrahydrofuran, diethylether, pentane) and P_2O_5 (dichloromethane). THF (Sigma, Aldrich), dichloromethane (Merck), N-(1-naphthyl)ethylenediamine dihydrochloric acid (Merck), pentane, diethylether, 2-propanol, methanol (J. T. Baker), $RuCl_3.3H_2O$ (Johnson Matthey), and α-phellandrene (Alfa Aesar) were used as received. $[RuCl_2(p\text{-cymene})]_2$[53], $[M(cod)Cl_2)]_2$, and $[Cp^*MCl_2)]_2$ (M = Rh, Ir)[54–56] were synthesized according to the published procedures. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer (Scheme 4). *J* values were given in Hz. Elemental analysis data were recorded with CHNS elemental analysis.



Scheme 4. The numbering of M(NHC) complexes.

Compound 2: N-(1-naphthyl)-ethylenediamine dihydrochloric acid (1.5 g, 5.78 mmol) and triethyl orthoformate (10.0 mL) were heated in a distillation apparatus until the ethanol distillation ceased. The temperature of reaction mixture reached 120 °C. After cooling to RT, 30.0 mL of ether was added to the reaction mixture. A precipitated white solid was collected by filtration. Purification was achieved by repeated recrystallizations from ethanol/ether. Yield: 0.89 g, 66%. ^1H NMR (400 MHz, DMSO): δ 9.51 (s, 1H, NC*H*N), 8.40 (d, 1 H, J = 7.4 Hz, naph.- H^{13}), 8.15 (t, 1 H, J = 7.4 Hz, naph.- H^{10}), 7.95 (d, 1 H, J = 7.4 Hz, naph.- H^{11}), 7.79 (m, 1 H, naph.- H^{12}), 7.72 (t, 1 H, J = 7.4 Hz, naph.- H^{8}), 7.69 (d, 1 H, J = 7.4 Hz, naph.- H^{9}), 7.54 (t, 1 H, J = 7.4 Hz, naph.- H^{7}), 4.77 (m, 2 H, N(H_2C)$_2$N), 4.17 (m, 2 H, N(H_2C)$_2$N). ^{13}C

NMR (100 MHz, DMSO): δ 164.2 (NCHN), 144.5 (naph.-C^{6}), 129.4 (naph.-C^{8}), 129.2 (naph.-C^{15}), 128.1 (naph.-C^{13}), 127.3 (naph.-C^{14}), 127.1 (naph.-C^{10}), 126.4 (naph.-C^{6}), 122.8 (naph.-C^{12}), 107.9 (naph.-C^{9}), 104.0 (naph.-C^{7}), 45.6, 42.5 (N(H$_2C$)$_2$N). Anal. Calc. for $C_{13}H_{13}ClN_2$ (M = 232.71): C, 67.10; H, 5.63; N, 12.04; Found C, 67.14; H, 5.72; N, 12.31%.

3.1. General procedure for the preparation of 3a–3d

2 (1.0 g, 4.31 mmol) and $NaHCO_3$ (0.36 g, 4.31 mmol) were dissolved in acetonitrile (10.0 mL). The mixture was stirred 1 h at 25 °C and benzyl bromide derivative (4.31 mmol) was added and refluxed for 24 h at 80 °C. The solvent was removed under vacuum and then the residue was dissolved with DCM (5.0 mL) and filtered by cannula. Diethyl ether was added to the solution. The obtained cream precipitate was filtered and dried under vacuum.

Compound 3a: Yield: 1.62 g, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1 H, NCHN), 7.99 (d, 1 H, J = 6.8 Hz, H^{13}), 7.94 (d, 1 H, J = 6.8 Hz, H^{10}), 7.90 (d, 1 H, J = 6.8 Hz, H^{12}), 7.88 (d, 1 H, J = 6.8 Hz, H^{11}), 7.64 (t, 1 H, J = 6.8 Hz, H^{8}), 7.57 (t, 1 H, J = 6.8 Hz, H^{9}), 7.48 (t, 1 H, J = 6.8 Hz, H^{14}), 6.90 (s, 2 H, Ar-CH), 5.12 (s, 2 H, NCH_2Ar), 4.58 (m, 2 H, N(H_2C)$_2$N), 4.39 (m, 2 H, N(H_2C)$_2$N), 2.45 (s, 6 H, Ar-CH_3), 2.44 (s, 3 H, Ar-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4 (NCHN), 139.3 (naph.-C^{6}), 138.3 (Ar-C), 134.4 (naph.-C^{15}), 132.2 (Ar-C), 130.4 (Ar-CH), 129.9 (naph.-C^{8}), 128.9 (naph.-C^{14}), 128.7 (naph.-C^{13}), 128.3 (naph.-C^{10}), 127.3 (Ar-C), 125.7 (naph.-C^{12}), 125.5 (naph.-C^{11}), 125.1 (naph.-C^{9}), 121.6 (naph.-C^{7}), 55.6, (NCH$_2$Ar), 49.6, 47.2 (N(H$_2C$)$_2$N), 21.1, 20.5 (Ar-CH$_3$). Anal. Calc. for $C_{23}H_{25}BrN_2$ (M = 409.36): C, 67.48; H, 6.16; N, 6.84; Found C, 68.92; H, 6.86; N, 7.01%.

Compound 3b: Yield: 1.53 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1 H, NCHN), 8.03 (d, 1 H, J = 8.0 Hz, H^{13}), 7.97 (d, 1 H, J = 8.0 Hz, H^{10}), 7.91 (d, 1 H, J = 8.0 Hz, H^{12}), 7.89 (d, 1 H, J = 8.0 Hz, H^{11}), 7.63 (t, 1 H, J = 8.0 Hz, H^{8}), 7.57 (t, 1 H, J = 8.0 Hz, H^{9}), 7.50 (t, 1 H, J = 8.0 Hz, H^{14}), 7.01 (s, 1 H, Ar-CH), 5.14 (s, 2 H, NCH_2Ar), 4.61 (m, 2 H, N(H_2C)$_2$N), 4.46 (m, 2 H, N(H_2C)$_2$N), 2.38 (s, 12 H, Ar-CH_3).^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1 (NCHN), 134.9 (naph.-C^{6}), 134.4 (naph.-C^{15}), 134.2 (Ar-C), 133.1 (Ar-CH), 132.2 (Ar-C), 130.5 (Ar-C), 129.0 (naph.-C^{8}), 128.6 (naph.-C^{14}), 128.3 (naph.-C^{13}), 128.2 (naph.-C^{10}), 127.3 (naph.-C^{12}), 125.8 (naph.-C^{11}), 125.0 (naph.-C^{9}), 121.5 (naph.-C^{7}), 53.6 (NCH$_2$Ar), 50.1, 49.7 (N(H$_2C$)$_2$N), 20.6, 16.4 (Ar-CH$_3$). Anal. Calc. for $C_{24}H_{27}BrN_2$ (M = 423.39): C, 68.08; H, 6.43; N, 6.62; Found C, 68.14; H, 6.38; N, 6.60%.

Compound 3c: Yield: 1.80 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1 H, NCHN), 8.03 (d, 1 H, J = 8.0 Hz, H^{1}), 7.97 (d, 1 H, J = 8.0 Hz, H^{4}), 7.91 (d, 1 H, J = 8.0 Hz, H^{2}), 7.89 (d, 1 H, J = 4.0 Hz, H^{3}), 7.63 (t, 1 H, J = 8.0 Hz, H^{8}), 7.57 (t, 1 H, J = 8.0 Hz, H^{7}), 7.50 (t, 1 H, J = 8.0 Hz, H^{6}), 5.12 (s, 2 H, NCH_2Ar), 4.65 (m, 2 H, N(H_2C)$_2$N), 4.53 (m, 2 H, N(H_2C)$_2$N), 2.42 (s, 15 H, Ar -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9 (NCHN), 136.8 (naph.-C^{10}), 134.4 (naph.-C^{5}), 133.8, 133.7, 132.3, 130.4 (Ar-C), 128.9 (naph.-C^{8}), 128.7 (naph.-C^{6}), 128.3 (naph.-C^{1}), 127.3 (naph.-C^{4}), 125.8 (naph.-C^{2}), 125.7 (naph.-C^{3}), 125.2 (naph.-C^{7}), 121.6 (naph.-C^{9}), 53.8 (NCH$_2$Ar), 50.1, 48.9 (N(H$_2C$)$_2$N), 20.6, 17.3, 17.0 (Ar-CH$_3$). Anal. Calc. for $C_{25}H_{29}BrN_2$ (M = 437.42): C, 68.65; H, 6.68; N, 6.40; Found C, 68.69; H, 6.72; N, 6.43%.

Compound 3d: Yield: 1.75 g, 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1 H, NCHN), 8.05 (d, 1 H, J = 7.6 Hz, H^{13}), 8.00 (d, 1 H, J = 7.6 Hz, H^{10}), 7.96 (d, 1 H, J = 7.6 Hz, H^{12}), 7.88 (d, 1 H, J = 7.6 Hz,

H^{11}), 7.62 (t, 1 H, J = 7.6 Hz, H^{8}), 7.55 (t, 1 H, J = 7.6 Hz, H^{9}), 7.46 (t, 1 H, J = 7.6 Hz, H^{14}), 5.42 (s, 2 H, NCH_2Ar), 4.61 (m, 2 H, N(H_2C)$_2$N), 4.46 (m, 2 H, N(H_2C)$_2$N). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (NCHN), 134.2 (naph.-C^{6}), 131.8 (naph.-C^{15}), 130.7, 129.1, 128.8, 128.5 (Ar-CF), 128.4 (naph.-C^{8}), 128.3 (naph.-C^{14}), 127.5 (naph.-C^{13}), 127.3 (naph.-C^{10}), 125.7 (naph.-C^{12}), 125.2 (naph.-C^{11}), 124.5 (naph.-C^{9}), 121.8 (naph.-C^{7}), 53.8 (NCH$_2$Ar), 50.4, 48.6 (N(H$_2C$)$_2$N). ^{19}F NMR (376 MHz, $CDCl_3$) δ 123.7–123.5 (m, 2 F, Ar-CF), 112.8–112.6 (m, 1 F, Ar-CF), 104.9–104.8 (m, 2 F, Ar-CF). Anal. Calc. for $C_{20}H_{14}BrF_5N_2$ (M = 457.24): C, 52.54; H, 3.09; N, 6.13; Found C, 52.63; H, 3.11; N, 6.19%.

3.2. General procedure for the preparation of metal complexes

A mixture of imidazolium salt **3** (1.0 mmol), NaH (1.5 mmol), and a catalytic amount of KO^{t}Bu was added to dry THF (50.0 mL) under inert conditions. The reaction mixture was stirred at room temperature for 1 h. When the color of the mixture turned from yellow to orange, [$RuCl_2$(p-cymene)]$_2$ or [MCl_2(L)]$_2$ (M = Rh, Ir; L = Cp*, cod) (0.5 mmol) was added and the mixture was stirred at room temperature for 2 h. The mixture was filtered by cannula and the solvent was removed in vacuo. The residue was purified by column chromatography (silica, eluted with dichloromethane) to give an orange solid.

Compound 4a: Yield: 0.30 g, 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, 1 H, J = 8.0 Hz, H^{13}), 7.92 (d, 1 H, J = 8.0 Hz, H^{10}), 7.75 (d, 1 H, J = 8.0 Hz, H^{7}), 7.31 (d, 1 H, J = 8.0 Hz, H^{11}),7.23 (t, 1 H, J = 8.0 Hz, ^{H12}), 7.16, (t, 1 H, J = 8.0 Hz, H^{8}), 7.04 (t, 1 H, J = 8.0 Hz, H^{9}), 6.94 (s, 2 H, Ar-CH), 5.68 (d, 1 H, J = 7.2 Hz, p-cym$-$CH), 5.65 (d, 1 H, J = 7.2 Hz, p-cym$-$CH), 5.50 (d, 1 H, J = 7.2 Hz, p-cym-CH), 5.48 (s, 2 H, NCH_2Ar), 5.36 (d, 1 H, J = 7.2 Hz, p-cym$-$CH), 4.62 (m, 2 H, N(H_2C)$_2$N), 4.34 (m, 2 H, N(H_2C)$_2$N), 3.55 (m, 1 H,p-cym-^{iPr}CH), 2.47 (s, 12 H, p-cym-CH_3, Ar-CH_3), 0.95 (d, 3 H, J = 8.0 Hz,$p-$cym-^{iPr}CH_3), 0.85 (d, 3 H, J = 8.0 Hz,$p-$cym-^{iPr}CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 222.1 (C$_{carbene}$), 160.6 (naph.-C^{6}), 142.6 (naph.-C^{15}), 140.2 (Ar-C), 138.2 (Ar-CH), 134.8 (Ar-C), 132.4 (Ar-C), 129.5 (naph.-C^{8}), 129.2 (naph.-C^{14}), 129.0 (naph.-C^{13}), 123.9 (naph.-C^{10}), 122.6 (naph.-C^{12}), 119.8 (naph.-C^{11}), 105.6 (naph.-C^{9}), 100.4 (naph.-C^{7}), 95.3, 92.4, 88.3, 84.2 (p-cym$-C$H), 50.3 (NCH$_2$Ar), 49.3, 49.0 (N(H$_2C$)$_2$N), 31.4 (p-cym$-^{iPr}C$H), 23.4 (p-cym-CH$_3$), 21.9, 21.2 (p-cym-^{iPr}CH$_3$), 20.9, 19.8 (Ar-CH$_3$). Anal. Calc. for $C_{33}H_{38}Cl_2N_2Ru$ (M = 634.64): C, 62.45; H, 6.04; N, 4.41; Found C, 62.32; H, 6.18; N, 4.56%.

Compound 4b: Yield: 0.33 g, 51%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, 1 H, J = 8.4 Hz, H^{13}), 7.92 (d, 1 H, J = 8.4 Hz, H^{10}), 7.75 (d, 1 H, J = 8.4 Hz, H^{7}), 7.31 (d, 1 H, J = 8.0 Hz, H^{11}), 7.23 (t, 1 H, J = 8.4 Hz, H^{12}), 7.16 (t, 1 H, J = 8.4 Hz, H^{8}), 7.04 (t, 1 H, J = 8.4 Hz, H^{9}), 7.03 (s, 1 H, Ar-CH), 5.70 (d, 1 H, J = 3.6 Hz, p-cym$-$CH), 5.67 (s, 2 H, NCH_2Ar), 5.65 (d, 1 H, J = 3.6 Hz, p-cym$-$CH), 5.51 (d, 1 H, J = 3.6 Hz, p-cym$-$CH), 5.41 (d, 1 H, J = 3.6 Hz, p-cym$-$CH), 4.62 (m, 2 H, N(H_2C)$_2$N), 4.34 (m, 2 H, N(H_2C)$_2$N), 3.59 (m, 1 H, p-cym-^{iPr}CH), 2.40 (s, 15 H, Ar-CH_3, p-cym-CH_3), 0.96 (d, 3 H, J = 8.0 Hz, $p-$cym$-^{iPr}$CH_3), 0.85 (d, 3 H, J = 8.0 Hz, $p-$cym$-^{iPr}$CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.9 (C$_{carbene}$), 160.6 (naph.-C^{6}), 142.6 (naph.-C^{15}), 140.3 (Ar-C), 132.4 (Ar-CH), 132.1 (Ar-C), 131.9 (Ar-C), 130.4 (naph.-C^{8}), 129.2 (naph.-C^{14}), 123.9 (naph.-C^{13}), 122.0 (naph.-C^{10}), 120.6 (naph.-C^{12}), 119.8 (naph.-C^{11}), 105.5 (naph.-C^{9}), 100.5 (naph.-C^{7}), 95.2, 92.5, 88.2, 84.3 (p-cym$-C$H), 50.4 (NCH$_2$Ar), 49.9, 49.0 (N(H$_2C$)$_2$N), 31.5 ($p-$cym$-^{iPr}C$H), 23.2 (p-cym-CH$_3$), 21.9, 21.0 ($p-$cym$-^{iPr}C$H$_3$), 20.7, 19.9 (Ar-CH$_3$). Anal. Calc. for $C_{34}H_{40}Cl_2N_2Ru$ (M = 648.67): C, 62.95; H, 6.22; N, 4.32; Found C, 62.85; H, 6.19; N, 4.11%.

Compound 4c: Yield: 0.35 g, 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, 1 H, J = 8.0 Hz, H^{13}), 7.93 (d, 1 H, J = 8.0 Hz, H^{10}), 7.76 (d, 1 H, J = 8.0 Hz, H^{7}), 7.32 (d, 1 H, J = 8.0 Hz, H^{11}), 7.23 (t, 1 H, J = 8.0 Hz, H^{12}), 7.16 (t, 1 H, J = 8.0 Hz, H^{8}), 7.05 (t, 1 H, J = 8.0 Hz, H^{9}), 5.51 (s, 2 H, NCH_2Ar), 5.68 (d, 1 H, J = 6.0 Hz, p-cym$-$CH), 5.64 (d, 1 H, J = 6.0 Hz, $p-$cym$-$CH), 5.51 (d, 1 H, J = 6.0 Hz, p-cym$-$CH), 5.41 (d, 1 H, J = 6.0 Hz, p-cym$-$CH), 4.62 (m, 2 H, N(H_2C)$_2$N), 4.34 (m, 2 H, N(H_2C)$_2$N), 3.61 (m, 1 H, p-cym-CH), 2.42 (s, 18 H, Ar-CH_3, p-cym-CH_3), 0.97 (d, 3 H, J = 8.0 Hz, $p-$cym$-^{iPr}$CH_3), 0.88 (d, 3 H, J = 8.0 Hz, p-cym-^{iPr}CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.7 ($C_{carbene}$), 160.6 (naph.-C^{6}), 142.7 (naph.-C^{15}), 140.6, 135.6, 133.5, 132.3 (Ar-C), 129.1 (naph.-C^{8}), 123.9 (naph.-C^{14}), 122.0 (naph.-C^{13}), 120.5 (naph.-C^{10}), 119.7 (naph.-C^{12}), 105.0 (naph.-C^{11}), 102.4 (naph.-C^{9}), 100.6 (naph.-C^{7}), 94.9, 92.6, 88.1, 83.9 (p-cym$-$$C$H), 50.2 (NC$H_2$Ar), 48.9, 46.6 (N($H_2C$)$_2$N), 31.4 ($p$-cym$-^{iPr}$$C$H), 23.4 ($p$-cym-C$H_3$), 22.0, 19.8 ($p$-cym-^{iPr}C$H_3$), 17.6, 17.2, 17.0 (Ar-CH_3). Anal. Calc. for $C_{35}H_{42}Cl_2N_2Ru$ (M = 662.70): C, 63.43; H, 6.39; N, 4.23; Found C, 63.34; H, 6.42; N, 4.49%.

Compound 4d: Yield: 0.33 g, 49%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, 1 H, J = 8.0 Hz, H^{13}), 7.90 (d, 1 H, J = 8.0 Hz, H^{10}), 7.78 (d, 1 H, J = 8.0 Hz, H^{7}), 7.34 (d, 1 H, J = 8.0 Hz, H^{11}), 7.23 (t, 1 H, J = 8.0 Hz, H^{12}), 7.19 (t, 1 H, J = 7.4 Hz, H^{8}), 6.18 (d, 1 H, J = 8.0 Hz, H^{9}), 5.72 (s, 2 H, NCH_2Ar), 5.69 (d, 1 H, J = 5.6 Hz, p-cym$-$CH), 5.63 (d, 1 H, J = 5.6 Hz, p-cym$-$CH), 5.55 (d, 1 H, J = 5.6 Hz, p-cym$-$CH), 5.50 (d, 1 H, J = 6.0 Hz, p-cym$-$CH), 4.70 (m, 2 H, N(H_2C)$_2$N), 4.52 (m, 2 H, N(H_2C)$_2$N), 3.80 (m, 1 H, p-cym-CH), 2.14 (s, 3 H, p-cym-CH_3), 0.89 (d, 3 H, J = 6.4 Hz,$p-$cym$-^{iPr}$CH_3), 0.80 (d, 3 H, J = 6.4 Hz, $p-$cym$-^{iPr}$CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.8 ($C_{carbene}$), 161.7 (naph.-C^{6}), 147.0, 142.4, 140.0 (Ar-CF), 132.3 (naph.-C^{15}), 129.2 (naph.-C^{8}), 124.2 (naph.-C^{14}), 122.4 (naph.-C^{13}), 122.3 (naph.-C^{10}), 121.0 (naph.-C^{12}), 119.6 (naph.-C^{11}), 110.2 (naph.-C^{9}), 106.1 (naph.-C^{7}), 100.5 (Ar-C), 95.9, 92.4, 88.4, 84.0 (p-cym$-$$C$H), 51.4 (NC$H_2C_6(F)_5$), 49.6, 48.1 (N($H_2C$)$_2$N), 31.3 ($p$-cym$-^{iPr}$$C$H), 23.3 ($p$-cym-C$H_3$), 21.8, 19.8 ($p$-cym-^{iPr}C$H_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ 123.7–123.6 (m, 2 F, Ar-CF), 112.8–112.6 (m, 1 F, Ar-CF), 104.9–104.8 (m, 2 F, Ar-CF). Anal. Calc. for $C_{30}H_{27}Cl_2F_5N_2Ru$ (M = 682.52): C, 52.79; H, 3.99; N, 4.10; Found C, 52.44; H, 3.91; N, 4.23%.

Compound 5b: Yield: 0.43 g, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 1 H, J = 8.2 Hz, H^{13}), 7.83 (d, 1 H, J = 8.2 Hz, H^{10}), 7.78 (d, 1 H, J = 8.2 Hz, H^{7}), 7.35 (d, 1 H, J = 8.2 Hz, H^{11}), 7.25 (t, 2 H, J = 8.2 Hz, $H^{12,8}$), 7.17 (t, 1 H, J = 8.2 Hz, H^{9}), 7.02 (s, 1 H, Ar-CH), 5.53 (d, 1 H, J = 13.6 Hz, NCH_2Ar), 5.06 (d, 1 H, J = 13.6 Hz, NCH_2Ar), 4.66 (m, 1 H, N(H_2C)$_2$N), 4.16 (m, 1 H, N(H_2C)$_2$N), 3.73 (m, 1 H, N(H_2C)$_2$N), 3.53 (m, 1 H, N(H_2C)$_2$N), 1.87 (s, 12 H, Ar-CH_3), 1.53 (s, 15 H, Cp*-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5 ($C_{carbene}$), 143.1 (naph.-C^{6}), 140.0 (naph.-C^{15}), 138.3 (Ar-C), 135.4 (Ar-CH), 132.1 (Ar-C), 131.9 (Ar-C), 131.6 (naph.-C^{8}), 128.8 (naph.-C^{14}), 123.6 (naph.-C^{13}), 122.0 (naph.-C^{10}), 121.6 (naph.-C^{12}), 121.2 (naph.-C^{11}), 119.8 (naph.-C^{9}), 92.8 (naph.-C^{7}), 92.3 (Cp*-C_5), 50.4 (NCH_2Ar), 49.4, 48.6 (N(H_2C)$_2$N), 20.4, 18.7 (Ar-CH_3), 10.3, 9.0 (Cp*-CH_3). Anal. Calc. for $C_{34}H_{41}ClN_2Ir$ (M = 705.37): C, 57.89; H, 5.86; N, 3.97; Found C, 57.76; H, 5.64; N, 3.82%.

Compound 5b': Yield: 0.36 g, 59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, 1 H, J = 8.4 Hz, H^{13}), 7.92 (d, 1 H, J = 8.6 Hz, H^{10}), 7.86 (d, 1 H, J = 8.1 Hz, H^{7}), 7.78 (d, 1 H, J = 8.4 Hz, H^{11}), 7.38 (t, 1 H, J = 8.4 Hz, H^{12}), 7.27 (t, 1 H, J = 8.4 Hz, H^{8}), 7.01 (s, 1 H, Ar-CH), 6.67 (d, 1 H, J = 8.4 Hz, H^{9}), 5.62 (d, 1 H, J = 13.6 Hz, NCH_2Ar), 5.05 (d, 1 H, J = 13.6 Hz, NCH_2Ar), 4.35 (m, 1 H, N(H_2C)$_2$N), 3.76

(m, 1 H, N(H_2C)$_2$N), 3.44 (m, 1 H, N(H_2C)$_2$N), 3.34 (m, 1 H, N(H_2C)$_2$N), 1.80 (s, 12 H, Ar-CH_3), 1.47 (s, 15 H, Cp*-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.3 (d, $J_{Rh-Carbene}$ = 52.8 Hz, C$_{carbene}$), 143.0 (naph.-C^6), 140.1 (naph.-C^{15}), 139.4 (Ar-C), 136.7 (Ar-CH), 135.8 (Ar-C), 134.5 (Ar-C), 133.5 (naph.-C^8), 132.0 (naph.-C^{14}), 131.7 (naph.-C^{13}), 128.9 (naph.-C^{10}), 127.2 (naph.-C^{12}), 124.6 (naph.-C^{11}), 123.7 (naph.-C^9), 122.1 (naph.-C^7), 99.2 (d, J_{Rh-C} = 4.5 Hz, Cp*-C_5), 50.4 (NCH$_2$Ar), 49.4, 48.6 (N(H$_2C$)$_2$N), 20.4, 20.0 (Ar-CH$_3$), 10.2 (Cp*-CH$_3$). Anal. Calc. for C$_{34}$H$_{41}$ClN$_2$Rh (M = 616.06): C, 66.29; H, 6.71; N, 4.55; Found C, 66.34; H, 6.63; N, 4.42%.

Compound 6b: Yield: 0.46 g, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 1 H, J = 8.4 Hz, H^{13}), 7.87 (d, 1 H, J = 8.4 Hz, H^{10}), 7.57 (t, 1 H, J = 8.4 Hz, H^7), 7.52 (m, 4 H, J = 8.4 Hz, H^{12,11,9,8}), 6.99 (s, 1 H, Ar-CH), 6.99 (s, 1 H, Ar-CH), 5.51 (d, 1 H, J = 14.4 Hz, NCH_2Ar), 5.33 (d, 1 H, J = 14.4 Hz, NCH_2Ar), 4.45 (br, 2 H, cod-CH), 4.19 (m, 1 H, N(H_2C)$_2$N), 3.65 (m, 1 H, N(H_2C)$_2$N), 3.36 (m, 2 H, N(H_2C)$_2$N), 3.21 (m, 1 H, cod-CH), 2.40 (s, 6 H, Ar-CH_3), 2.28 (s, 6 H, Ar-CH_3), 2.11 (m, 1 H, cod-CH) 1.44–1.35 (m, 4 H, cod$-$CH_2), 0.97–0.77 (m, 4 H, cod$-$CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.9 (C$_{carbene}$), 143.2 (naph.-C^6), 138.3 (naph.-C^{15}), 135.4 (Ar-C), 132.1 (Ar-CH), 131.9 (Ar-C), 131.6 (Ar-C), 128.8 (naph.-C^8), 123.6 (naph.-C^{14}), 122.0 (naph.-C^{13}), 121.6 (naph.-C^{10}), 121.2 (naph.-C^{12}), 119.8 (naph.-C^{11}), 92.8 (naph.-C^9), 92.3 (naph.-C^7), 53.0, 51.8 (cod-CH), 50.4 (NCH$_2$Ar), 49.4, 48.3 (N(H$_2C$)$_2$N), 33.2, 30.3, 29.7, 28.5 (cod-CH$_2$), 20.4, 20.1 (Ar-CH$_3$). Anal. Calc. for C$_{32}$H$_{38}$ClN$_2$Ir (M = 678.33): C, 56.66; H, 5.65; N, 4.13; Found C, 56.77; H, 5.49; N, 4.27%.

Compound 6b': Yield: 0.39 g, 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 1 H, J = 8.2 Hz, H^{13}), 7.93 (d, 1 H, J = 8.2 Hz, H^{10}), 7.90 (d, 1 H, J = 8.2 Hz, H^7), 7.65 (t, 1 H, J = 8.2 Hz, H^{11}), 7.52 (m, 3 H, H^{12,9,8}), 6.99 (s, 1 H, Ar-CH), 5.62 (d, 1 H, J = 14.2 Hz, NCH_2Ar), 5.60 (d, 1 H, J = 14.2 Hz, NCH_2Ar), 4.94 (br, 2 H, cod-CH), 4.14 (m, 1 H, N(H_2C)$_2$N), 3.62 (m, 2 H, cod-CH), 3.34 (m, 1 H, N(H_2C)$_2$N), 3.27 (m, 2 H, N(H_2C)$_2$N), 2.39 (s, 6 H, Ar-CH_3), 2.28 (s, 6 H, Ar-CH_3), 1.72 (m, 2 H, cod$-$CH_2), 1.57 (m, 2 H, cod$-$CH_2), 1.16 (m, 2 H, cod$-$CH_2), 0.84 (m, 2 H, cod$-$CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2 (d, $J_{Rh-Carbene}$ = 46.6 Hz, C$_{carbene}$), 138.6 (naph.-C^6), 134.5 (naph.-C^{15}), 134.3 (Ar-C), 134.2 (Ar-CH), 132.1 (Ar-C), 131.9 (naph.-C^8), 130.6 (Ar-C), 130.1 (naph.-C^{14}), 130.1 (naph.-C^{13}), 129.0 (naph.-C^{10}), 128.1 (naph.-C^{12}), 126.8 (naph.-C^{11}), 126.1 (naph.-C^9), 122.5 (naph.-C^7), 98.3 (d, J_{Rh-C} = 6.7 Hz, cod-CH), 97.9 (d, J_{Rh-C} = 6.7 Hz, cod-CH), 69.9 (d, J_{Rh-C} = 6.7 Hz, cod-CH), 67.8 (cod-CH), 52.9 (NCH$_2$Ar), 49.8, 48.7(N(H$_2C$)$_2$N), 33.5, 31.2, 28.9, 28.5 (cod-CH_2), 20.7, 16.6 (Ar-CH$_3$). Anal. Calc. for C$_{32}$H$_{38}$ClN$_2$Rh (M = 589.02): C, 65.25; H, 6.50; N, 4.76; Found C, 65.36; H, 6.61; N, 4.79%.

3.3. General method for transfer hydrogenation of acetophenone using Ru(II) complexes

A mixture of acetophenone (1 mmol), the catalyst (0.01 mmol), and KOH (2.0 mmol) was stirred in 2-propanol (5.0 mL) at 82 °C for 2 h. At the desired reaction times, aliquots were withdrawn from the reaction vessel to follow the reaction by ^{1}H NMR spectroscopy. The yields were obtained by integration areas of methyl peaks assigned to acetophenone and racemic 1-phenylethanol. The results for each experiment are averages over two runs.

Acknowledgments

Financial support was from Ege University (Project 2012-BİL-042; 2010-FEN-046). We thank Prof Dr S Astley at Ege University Chemistry Department for reading the manuscript and Mr Salih Günnaz for NMR analyses.

References

1. Wanzlick, H. W.; Kleiner, H. J. *Angew. Chem.* **1961**, *73*, 493-498.
2. Öfele, K. *J. Organomet. Chem.* **1968**, *12*, 42-43.
3. Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185-213.
4. Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
5. Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 3122-3172.
6. Glorius, F. *N-Heterocyclic Carbenes in Transition Metal Catalysis*. Springer Verlag: Berlin, Germany, 2007.
7. Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*. Wiley-VCH: Weinheim, Germany, 2006.
8. Diez-Gonzalez, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874-883.
9. Herrmann, W. A. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1290-1309.
10. Schuster, O.; Yang, L.; Raubenheimer, H. G.; Albrecht, M. *Chem. Rev.* **2009**, *109*, 3445- 3478.
11. Kantchev, E. A. B.; O'Brien, J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768-2813.
12. Gürbüz, N.; Karaca, E. Ö.; Özdemir, İ.; Çetinkaya, B. *Turk. J. Chem.* **2015**, *39*, 1115-1157.
13. Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18-29.
14. Lee, H. M.; Jiang, T.; Stevens, L. E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 1255- 1258.
15. Powell, M. T.; Hou, D.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878-8879.
16. Perry, M. C.; Cui, X.; Hou, D. R.; Reibenspies, H. J. *J. Am. Chem. Soc.* **2003**, *125*, 113- 123.
17. Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97-102.
18. Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226-236.
19. Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300-1308.
20. Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201-2237.
21. Samec, J. S. M.; Bäckvall, J. E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237-248.
22. Alfonsi, K.; Colberg, J.; Dunn, P. J.; Fevig, T.; Jennings, S.; Johnson, T. A.; Kleine, H. P.; Knight, C.; Nagy, M. A.; Perry, D. A.; et al. *Green Chem.* **2008**, *10*, 31-36.
23. Canivet, J.; Lapat, G.; Stoeckli- Evans, H.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2005**, 4493-4500.
24. Baratta, W.; Chelucci, G.; Gladiali, S., Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem. Int. Ed.* **2005**, *44*, 6214-6219.
25. Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P. *Organometallics* **2005**, *24*, 1660-1669.
26. Del Zotto, A.; Baratta, W.; Ballico, M.; Herdtweck, E.; Rigo, P. *Organometallics* **2007**, *26*, 5636-5642.
27. Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246-4252.
28. Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. *Organometallics* **2008**, *27*, 571-575.
29. Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2008**, *36*, 5418- 5423.
30. Gülcemal, S.; Daran, J. C.; Çetinkaya, B. *Inorg. Chim. Acta* **2011**, *365*, 264-268.
31. Wylie, W. N. O.; Lough, A. J.; Morris, R. H. *Organometallics* **2012**, *31*, 2137-2151.
32. Özdemir, İ.; Yaşar, S.; Çetinkaya, B. *Trans. Metal Chem.* **2005**, *30*, 831-835.

33. Yigit, M.; Yigit, B.; Özdemir, İ.; Çetinkaya, E.; Çetinkaya, B. *Appl. Organomet. Chem.* **2006**, *20*, 322-327.
34. Gürbüz, N.; Yaşar, S.; Özcan, E. Ö.; Özdemir, İ.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2010**, 3051-3056.
35. Oruç, Z. İ.; Gök, L.; Türkmen, H.; Şahin, O.; Büyükgüngör, O.; Cetinkaya, B. *J. Organomet. Chem.* **2016**, *807*, 36-44.
36. Kırkar, B. T.; Türkmen, H.; Kani, İ.; Çetinkaya, B. *Tetrahedron* **2012**, *68*, 8655-8662.
37. Türkmen, H.; Kani, İ.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2012**, 4494-4499.
38. Türkmen, H. *Appl. Organometal. Chem.* **2012**, *26*, 731-735.
39. Gök, L.; Türkmen, H. *Tetrahedron* **2013**, *69*, 10669-10674.
40. Marr, A. C.; Pollock, C. L.; Saunders, G. C. *Organometallics* **2007**, *26*, 3283-3285.
41. Gnanamgari, D.; Sauer, E. L. O.; Schley, N. D.; Butler, C.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2009**, *28*, 321-325.
42. Gong, X.; Zhang, H., Li, X. *Tetrahedron Lett.* **2011**, *52*, 5596-5600.
43. Gülcemal, S. *Appl. Organometal. Chem.* **2012**, *26*, 246-251.
44. Zinner, S. C.; Rentzsch, C. F., Herdtweck, E.; Herrmann, W. A.; Kühn, F. E. *Dalton Trans.* **2009**, 7055-7062.
45. Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246- 4252.
46. Cortez, N. A.; Aguirre, G.; Parra-Hake, M.; Somanathan, R. *Tetrahedron Lett.* **2009**, *50*, 2228-2231.
47. Wu, X.; Xiao, J. *Chem. Commun.* **2007**, *46*, 2449-2466.
48. Raja, M. U.; Ramesh, R.; Ahn, K. H. *Tetrahedron Lett.* **2009**, *50*, 7014-7017.
49. Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713-6725.
50. Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855-859.
51. Eberhard, M. R. *Org. Lett.* **2004**, *6*, 2125-2128.
52. Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317-341.
53. Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233-241.
54. Lin, Y.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1993**, *32*, 6040-6045.
55. Giordano, G.; Crabtree, R. H. *Inorganic Synthesis* **1990**, *28*, 90-92.
56. Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301-307.