Journal of Organometallic Chemistry 694 (2009) 4025–4031

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and catalytic properties of novel ruthenium *N*-heterocyclic-carbene complexes

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ARTICLE INFO

Article history:
Received 6 May 2009
Received in revised form 19 August 2009
Accepted 22 August 2009
Available online 27 August 2009

Keywords:
Ruthenium
Imidazolinium salts
N-heterocyclic carbene
C–H bond activation
Arylation

ABSTRACT

The reaction of $[RuCl_2(p\text{-cymene})]_2$ with 1,3-dialkylimidazolinium salts **1a–f** in the presence of a small excess of cesium carbonate yields chelated η^6-arene, η^1-carbene ruthenium complexes **2a–f**. All synthesised compounds were characterized by elemental analysis, NMR spectroscopy. The catalytic activity of $RuCl_2(\eta^6\text{-arene}, \eta^1\text{-imidazolinylidene})$ complexes **2a–f** was evaluated in the direct arylation of 2-phenylpyridine with chlorobenzene derivatives.

1. Introduction

The development of *N*-heterocyclic carbene (NHC) complexes in the 1960s [1] was followed by Lappert in the early 1970s [2], then eventual isolation and crystallographic characterization of a stable metal-free NHC by Arduengo group in 1991 [3]. *N*-heterocyclic carbenes have proven an alternative to tertiary phosphines in homogeneous catalysis, because of the strong σ-donating and negligible π-accepting character, NHCs can form stable bonds with various metals from main group to transition metals in different oxidation states and stabilize catalytically active intermediates [4]. Today, *N*-heterocyclic carbenes play a major role as ligands in organometallic chemistry. They make metal complexes suitable for a broad spectrum of catalytic applications [5]. For example, ruthenium complexes catalyze olefin metathesis [6] transfer hydrogenation [7], furan synthesis [8], palladium catalyzed cross-coupling reaction and related transformation [9,10] and rhodium catalyzed hydrosilylation [11] and hydroformylation [12]. It is expected that when the NHC orientation is perturbed in space, the catalytic activity of the linked metal site should be largely modified. This influence is leading to the design of new chelating NHC complexes. Examples of bis-NHC carbenes [13], mixed pyridine–carbene [14] and oxazoline–carbene [15] complexes have already been reported. The hemilable arm in such ligands is capable of reversible dissociation from the metal center. Such dynamic behaviour will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle, at the same time the strong donor moiety remains connected to the metal center. We have shown the route to metal complexes containing mixed arene and carbene ligands providing 8 electrons to the metal, and that the natural orientation of the carbene in the complex is significantly modified [16].

In recent years, transition metal-catalyzed C–H activation has emerged as a powerful tool to transform otherwise unreactive C–H bonds into carbon–carbon or carbon–heteroatom bonds [17]. Metal catalyzed direct arylation, through C–H bond activation has consequently received considerable attention as an efficient method of biaryl synthesis [18]. In recent years, significant progress has been made in direct arylation using complexes palladium [19], rhodium [20], ruthenium [21] and other metals [22].

We now report new 8 electron bridged η^6-arene, η^1-carbene ruthenium complexes from related electron-rich olefins bis-[1,3-imidazolin-2-ylidene] containing at least one arylmethylene group linked to a nitrogen atom. We also show that the resulting $(\eta^6\text{-arene}, \eta^1\text{-carbene})RuCl_2$ complexes can be used to for direct arylation of 2-phenylpyridine with chlorobenzene derivatives.

2. Results and discussion

1,3-Dialkylimidazolinium chlorides, (**1a–f**) are conventional NHC precursors. The preparation of 1,3-dialkylimidazolinium chloride was carried out according to the reported procedures (Scheme 1) [23]. The salts are air- and moisture-stable both in the solid state and in solution.

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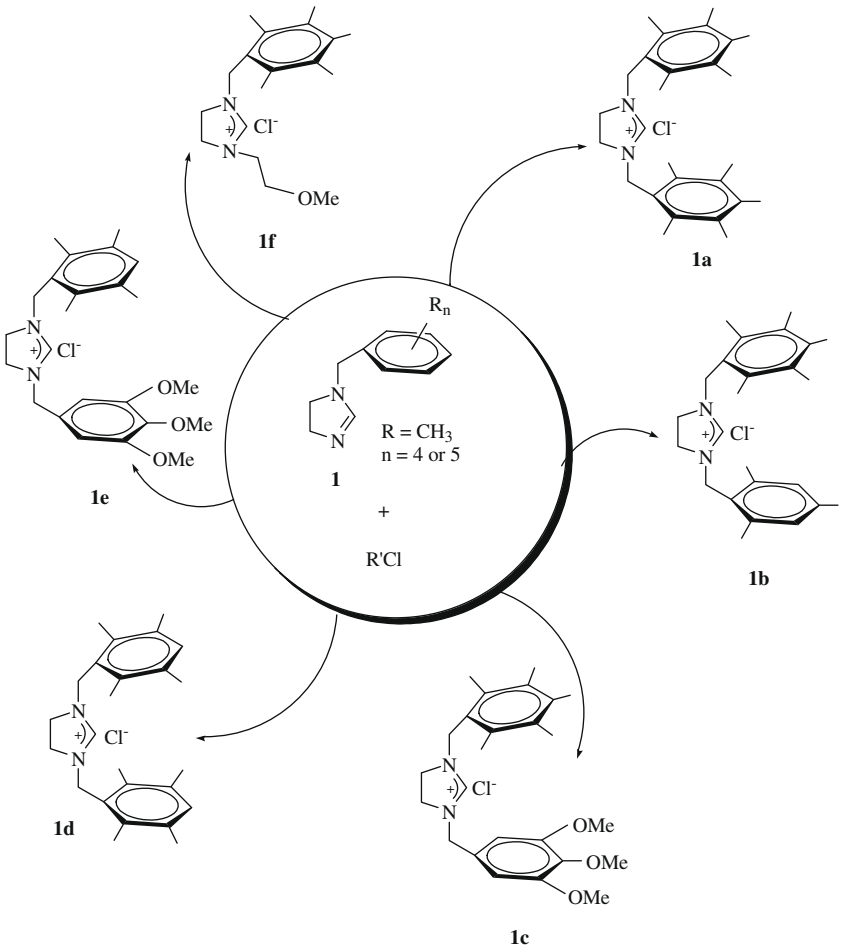
doi:10.1016/j.jorganchem.2009.08.030



Scheme 1. Synthesis of substituted imidazolinium salts.

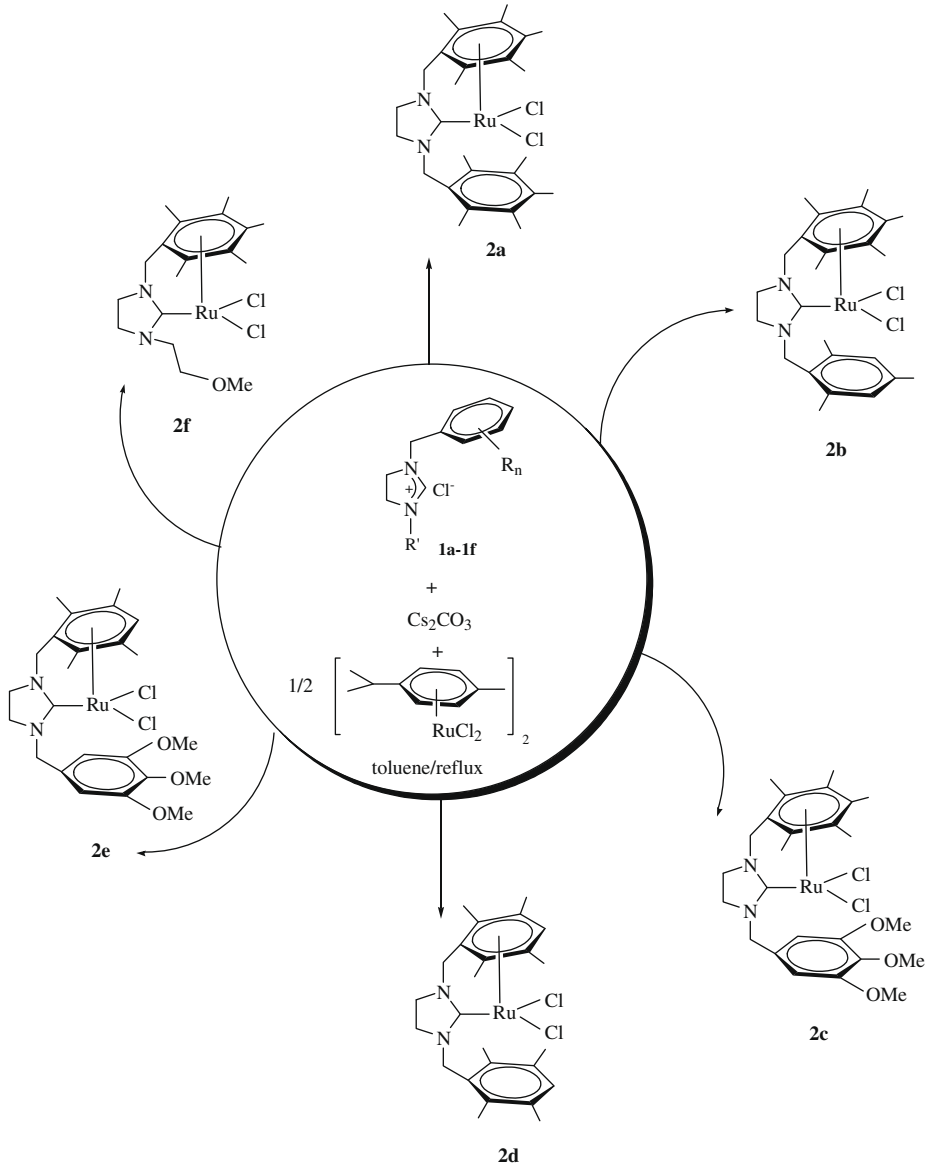
The structures of **1a–f** were determined by their characteristic spectroscopic data and elemental analyses. ^{13}C NMR chemical shifts were consistent with the proposed structure, the imino carbon appeared as a typical singlet in the ^{1}H-decoupled mode in the 157.3, 157.9, 158.4, 157.9 158.7 and 158.2 ppm, respectively for imidazolinium chlorides **1a–f**. The ^{1}H NMR spectra of the imidazolinium salts further supported the assigned structures; the resonances for C(2)–H were observed as sharp singlets in the 9.39, 9.85, 10.38, 9.67, 10.49 and 9.32 ppm, respectively for **1a–f**. The IR data for imidazolinium salts **1a–f** clearly indicate the presence of the –C=N– group with a ν(C=N) vibration at 1630, 1629, 1661, 1630, 1653 and 1653 cm^{-1}, respectively for **1a–f**. The NMR values are similar to those found for other 1,3-dialkylimidazolinium salts [24].

Several general methods have been utilized for the preparation of transition metal–NHC complexes. They are based on (i) *in situ* deprotonation of the azolium salts, (ii) complexation of the free, or protected form of the NHC carbene, (iii) thermal cleavage of electron-rich olefin $(NHC)_2$ resulting from the dimerization of non-sterically hindered NHC, and formal insertion of the metal in a C=C bond, (iv) transmetallation from a silver–NHC complex, (v) direct oxidative addition to the metal center or (vi) the nucleophilic attack at the carbon atom of a coordinated isocyanide [25].

It has recently been shown that the heating in toluene of $[RuCl_2(p\text{-cymene})]_2$, imidazolinium salt, and Cs_2CO_3 afforded an *in situ* prepared catalyst for enyne or alkene metathesis more active that the isolated complex $RuCl_2$(imidazolinylidene)(*p*-cymene) complex [26]. It was suggested that the catalyst resulted from the coordination of the *in situ* formed carbene, on imidazolium salt deprotonation with Cs_2CO_3, with concommittant displacement of the (*p*-cymene) ligand. Thus the imidazolinium salts **1a–f** in the presence of a small excess of cesium carbonate was heated with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ in toluene at 110 °C for 6 h. The complexes 2a–**f** with the aryl group η^6-coordinated to the ruthenium atom was obtained in good yields (Scheme 2). This result shows that Cs_2CO_3 is able to generate a ruthenium coordinated imidazolinylidene group in refluxing toluene and that the *p*-cymene ligand can be intramolecularly displaced by an aryl group to generate a bidentate ligand.

All products **2a–f** were obtained as orange-brown crystalline complexes in 65–88% yields. The air and moisture-stable ruthenium carbene complexes (**2a–f**) were soluble in halogenated solvents and insoluble in non-polar solvents. The ruthenium complexes **2a–f** have been characterized by analytical and spectroscopic techniques. Ruthenium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1500–1669 cm^{-1} [8,27]. ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of $\delta(^{13}C_{carb})$ are in the 198.5–201.5 ppm range and are similar to those found for other carbene complexes. These complexes show typical spectroscopic signatures, which are in line with those recently reported for other $[RuCl_2$(mono-NHC)(arene)] complexes [28].

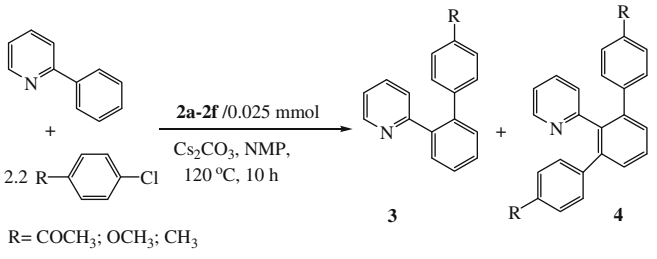
We have recently shown that NHC–ruthenium(II) species *in situ* generated from of $[RuCl_2(p\text{-cymene})]_2$ and monoazolium salts under basic conditions were able to catalyze the direct arylation of



Scheme 2. Synthesis of chelated η^6-arene, η^1-carbene ruthenium(II) complexes.

2-phenylpyridine by aryl bromides [29]. The mechanism study showed that the first step of the reaction deals with the *ortho*metallation of the 2-phenylpyridine-ruthenium(II) adduct *via* a cooperative action of both the ruthenium(II) site and the coordinated carbonate. We have found that the (dicarbene)ruthenium complexes **2a–f** can also act as catalyst precursors for the direct diarylation of 2-phenylpyridine, used as model substrate, directed in *ortho*-position by the *N*-atom of the pyridine group according to Scheme 3.

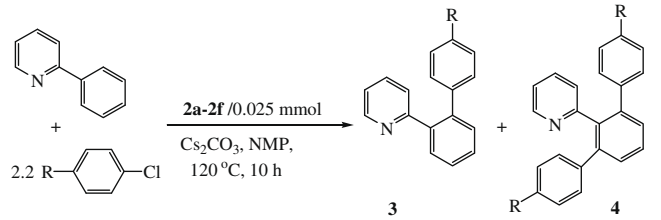
The importance of the coordination of the required base in the catalyst intermediate [29,30] led us to explore first the influence of Cs_2CO_3, K_2CO_3, and $KOBu^t$ in the presence of a precatalyst **2**. We found that Cs_2CO_3 in NMP at 120 °C provided the best conditions, and that initial treatment of the chelated η^6-arene, η^1-carbene ruthenium(II) complexes. We first investigated the arylation of 2-phenylpyridine with 4-chloroacetophenone in the presence of [(η^6-arene, η^1-carbene)$RuCl_2$] (**2a–f**) as catalyst precursor, and extended the scope of the reaction to the *para*-substituted methoxy-, and methylchorobenzenes. The results are reported in Table 1.



Scheme 3. Direct arylation of 2-phenylpyridine with aryl chlorides.

Control experiments indicated that the arylation of 2-phenylpyridine with chlorobenzene reaction did not occur in the absence of **2a**. Under the optimum reaction conditions, the chlorobenzene substrates reacted with 2-phenylpyridine to selectively afford the major di-*ortho*-arylated products in excellent yields (Table 1 entries 5, 10 and 16). It is worth noting that these new catalytic systems based on (carbene)ruthenium precursors in the presence of cesium carbonate make possible the arylation with chloroarene

Table 1
Direct arylation of chloro benzene derivatives with 2-phenylpyridine.[a]



Entry	[Ru–NHC]	Ar	Yield 3/4 (%)[b]
1	**2a**	4-MeCOC$_6$H$_4$	25/75
2	**2b**	4-MeCOC$_6$H$_4$	30/70
3	**2c**	4-MeCOC$_6$H$_4$	17/83
4	**2d**	4-MeCOC$_6$H$_4$	12/88
5	**2e**	4-MeCOC$_6$H$_4$	10/90
6	**2f**	4-MeCOC$_6$H$_4$	28/72
7	**2a**	4-MeOC$_6$H$_4$	37/63
8	**2b**	4-MeOC$_6$H$_4$	31/69
9	**2c**	4-MeOC$_6$H$_4$	19/81
10	**2d**	4-MeOC$_6$H$_4$	13/87
11	**2e**	4-MeOC$_6$H$_4$	24/76
12	**2f**	4-MeOC$_6$H$_4$	35/65
13	**2a**	4-MeC$_6$H$_4$	20/80
14	**2b**	4-MeC$_6$H$_4$	15/85
15	**2c**	4-MeC$_6$H$_4$	13/87
16	**2d**	4-MeC$_6$H$_4$	7/93
17	**2e**	4-MeC$_6$H$_4$	25/75
18	**2f**	4-MeC$_6$H$_4$	28/72

[a] Reaction conditions: ruthenium complex **2** (0.025 mmol), 2-phenylpyridine (0.5 mmol), ArCl (1.25 mmol), Cs_2CO_3 (1.5 mmol), NMP as solvent, 120 °C, 10 h.
[b] Conversion of 2-phenylpyridine and **3**/**4** ratio determined by ^{1}H NMR and by GC.

derivatives that are more easily available than bromoarenes, but much less reactive than the corresponding bromides, as the second step of the catalytic reaction involves an oxidative addition to the *ortho*metallated ruthenium(II) intermediate [29].

3. Conclusion

The above results show that imidazolinylidene ligands containing an arylmethyl-*N* group on reaction with $[RuCl_2(p\text{-cymene})]_2$ always displace the *p*-cymene to give (η^1-carbene, η^6-arene)$RuCl_2$ complexes. We have investigated the arylation of 2-phenylpyridine with aryl chlorides in the presence of the Ru–NHC complexes resulting in the formation of the corresponding arylated pyridine derivatives and further applications of the present catalytic system are ongoing and will be reported in due course.

4. Experimental

4.1. General procedures

All reactions for the preparation imidazolinium salts (**1**) and ruthenium(NHC) complexes (**2**) were carried out under argon in flame-dried glassware using standard Schlenk techniques. Complex **1f** was synthesized according to known procedure [31]. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar:Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na). Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI UNICAM 1000 spectrometer. ^{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. Column chromatography was performed using silica gel 60 (70-230 mesh). Elemental analyses were carried out by analytical service of TÜBİTAK with a Carlo Erba Strumentaziona Model 1106 apparatus.

4.2. General synthesis of imidazolinium salts

To a solution of *N*-substituted imidazoline (**1**) (5.0 mmol) in DMF (10 mL) was added slowly alkyl or aryl halide (5.0 mmol) and the resulting mixture was stirred at 70 °C for 10 h. Diethylether (10 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethylether (3×10 mL) dried under vacuum and the crude product was recrystallized from ethanole/diethylether.

4.2.1. 1,3-Bis(2,3,4,5,6-pentamethylbenzyl)imidazolinium chloride, **1a**

Yield: 3.93 g (92%), m.p.: 332–333 °C, $\upsilon_{(CN)}$: 1630 cm^{-1}. Anal. Calc. for $C_{27}H_{39}N_2Cl$: C, 75.93; H, 9.20; N, 6.56. Found: C, 75.98; H, 9.15; N, 6.62%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 9.39 (s, 1H, NC*H*N), 4.93 (s, 4H, CH_2C$_6$(CH$_3$)$_5$-2,3,4,5,6), 3.78 (s, 4H, NCH_2CH_2N), 2.26, 2.22 and 2.19 (s, 30H, CH$_2$C$_6$(CH_3)$_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 157.3 (N*C*HN), 136.4, 133.5, 133.2 and 125.6 (CH$_2$C$_6$(CH$_3$)$_5$-2,3,4,5,6), 47.8 (N*C*H$_2$*C*H$_2$N), 47.4 (*C*H$_2$-C$_6$(CH$_3$)$_5$-2,3,4,5,6), 17.2, 16.9 and 16.8 (CH$_2$C$_6$(*C*H$_3$)$_5$-2,3,4,5,6).

4.2.2. 1-(2,3,4,5,6-Pentamethylbenzyl)-3-(2,4,6-trimethylbenzyl) imidazolinium chloride, **1b**

Yield: 3.71 g (93%), m.p.: 298–299 °C, $\upsilon_{(CN)}$: 1629 cm^{-1}. Anal. Calc. for $C_{25}H_{35}N_2Cl$: C, 75.25; H, 8.84; N, 7.02. Found: C, 75.19; H, 8.86; N, 7.06%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 9.85 (s, 1H, NC*H*N), 6.87 (s, 2H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 4.97 (s, 2H, CH_2C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 4.90 (s, 2H, CH_2C$_6$(CH$_3$)$_5$-2,3,4,5,6), 3.79–3.64 (m, 4H, NCH_2CH_2N), 2.33, 2.29, 2.25, 2.23 and 2.21 (s, 24H, CH$_2$C$_6$(CH_3)$_5$-2,3,4,5,6 and CH$_2$C$_6$H$_2$(CH_3)$_3$-2,4,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 157.9 (N*C*HN), 136.5, 133.6, 133.3 and 125.5 (CH$_2$C$_6$(CH$_3$)$_5$-2,3,4,5,6), 139.0, 137.8, 129.8 and 125.4 (CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 47.5 (*C*H$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6), 47.4 (N*C*H$_2$*C*H$_2$N), 46.3 (*C*H$_2$C$_6$(CH$_3$)$_5$-2,3,4,5,6), 20.9 (CH$_2$C$_6$H$_2$(*C*H$_3$)$_3$-2,*4*,6), 20.1 (CH$_2$C$_6$H$_2$(*C*H$_3$)$_3$-*2*,4,6), 17.2, 16.9 and 16.8 (CH$_2$C$_6$(CH$_3$)$_5$-2,3,4,5,6).

4.2.3. 1-(2,3,4,5,6-Pentamethylbenzyl)-3-(3,4,5-trimethoxybenzyl) imidazolinium chloride, **1c**

Yield: 4.02 g (90%), m.p.: 256–257 °C, $\upsilon_{(CN)}$: 1661 cm^{-1}. Anal. Calc. for $C_{25}H_{35}N_2O_3Cl$: C, 67.17; H, 7.89; N, 6.27. Found: C, 67.21; H, 7.93; N, 6.25%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 10.38 (s, 1H, NC*H*N), 6.74 (s, 2H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,5), 4.97 (s, 2H, CH_2C$_6$H$_2$(OCH$_3$)$_3$-3,4,5), 4.80 (s, 2H, CH_2C$_6$(CH$_3$)$_5$-2,3,4,5,6), 3.89 (s, 6H, CH$_2$C$_6$H$_2$(OCH_3)$_3$-3,4,5), 3.82 (s, 3H, CH$_2$C$_6$H$_2$(OCH_3)$_3$-3,*4*,5), 3.79-3.62 (m, 4H, NCH_2CH_2N), 2.29, 2.23 and 2.20 (s, 15H, CH$_2$C$_6$(CH_3)$_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 158.4 (N*C*HN), 153.8, 138.4, 128.4 and 106.2 (CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,5), 136.6, 133.6, 133.3 and 125.5 (CH$_2$C$_6$(CH$_3$)$_5$-2,3,4,5,6), 60.8 (CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,*4*,5), 56.6 (CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,*5*), 52.5 (*C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-3,4,5), 47.5 and 47.4 (NCH$_2$CH$_2$N), 47.3 (*C*H$_2$C$_6$(CH$_3$)$_5$-2,3,4,5,6), 17.2, 16.9 and 16.8 (CH$_2$C$_6$(*C*H$_3$)$_5$-2,3,4,5,6).

4.2.4. 1,3-Bis(2,3,5,6-tetramethylbenzyl)imidazolinium chloride, **1d**

Yield: 3.39 g (85%), m.p.: 337–338 °C, $\upsilon_{(CN)}$: 1630 cm^{-1}. Anal. Calc. for $C_{25}H_{35}N_2Cl$: C, 75.25; H, 8.84; N, 7.02. Found: C, 75.29; H, 8.80; N, 7.09%. ^{1}H NMR (399.9 MHz, $CDCl_3$) δ = 9.67 (s, 1H, NC*H*N), 7.01 (s, 2H, CH$_2$C$_6$*H*(CH$_3$)$_4$-2,3,5,6), 4.97 (s, 4H, CH_2C$_6$H(CH$_3$)$_4$-2,3,5,6), 3.73 (s, 4H, NCH_2CH_2N), 2.25 and 2.24 (s, 24H, CH$_2$C$_6$H(CH_3)$_4$-2,3,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 157.9 (N*C*HN), 134.6, 133.8, 132.8 and 128.2 (CH$_2$C$_6$H(CH$_3$)$_4$-

2,3,5,6), 47.6 (NCH_2CH_2N), 46.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 20.5 and 15.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6).

4.2.5. 1-(2,3,5,6-Tetramethylbenzyl)-3-(3,4,5-trimethoxybenzyl) imidazolinium chloride, 1e

Yield: 3.85 g (89%), m.p.: 247–248 °C, $\upsilon_{(CN)}$: 1653 cm^{-1}. Anal. Calc. for $C_{24}H_{33}N_2O_3Cl$: C, 66.57; H, 7.68; N, 6.47. Found: C, 66.65; H, 7.72; N, 6.45%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 10.49 (s, 1H, NC*H*N), 6.99 (s, 1H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 6.75 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.98 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.80 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 3.90 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.83 (s, 3H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.79–3.62 (m, 4H, NCH_2CH_2N), 2.26 and 2.23 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 158.7 (NCHN), 153.8, 138.4, 128.4 and 106.2 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 134.8, 133.8, 132.8 and 128.1 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 60.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 56.6 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 52.5 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 47.5 ve 47.4 (NCH_2CH_2N), 46.8 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 20.5 and 16.0 ($CH_2C_6H(CH_3)_4$-2,3,5,6).

4.2.6. 1-(2,3,4,5,6-Pentamethylbenzyl)-3-(2-methoxyethyl) imidazolinium chloride, **1f**

Yield: 2.76 g (85%), m.p.: 149–150 °C, $\upsilon_{(CN)}$: 1653 cm^{-1}. Anal. Calc. for $C_{18}H_{29}N_2OCl$: C, 66.54; H, 9.00; N, 8.62. Found: C, 66.57; H, 9.05; N, 8.59%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 9.32 (s, 1H, NC*H*N), 4.89 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 4.06 (t, 2H, J = 8.0 Hz, $NCH_2CH_2OCH_3$), 3.86–3.78 (m, 4H, NCH_2CH_2N), 3.63 (t, 2H, J = 8.0 Hz, $NCH_2CH_2OCH_3$), 3.33 (s, 3H, $CH_2CH_2OCH_3$), 2.28, 2.23 and 2.20 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 158.2 (NCHN), 136.5, 133.6 133.4 and 125.5 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 69.2 ($NCH_2CH_2OCH_3$), 58.9 ($CH_2CH_2OCH_3$), 49.4 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 48.1 ($NCH_2CH_2OCH_3$), 48.0 and 47.3 (NCH_2CH_2N), 17.2 and 16.9 ($CH_2C_6(CH_3)_5$-2,3,4,5,6).

4.3. General synthesis of η^6-arene, η^1-carbene ruthenium(II) complexes

A suspension of imidazolinium salt (**1a–1f**) (2.10 mmol), Cs_2CO_3 (2.14 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.82 mmol) was heated under reflux in degassed toluene (20 mL) for 6 h. The reaction mixture was then filtered while hot, and the volume was reduced to about 10 mL before addition of n-hexane (15 mL). The precipitate formed was crystallized from CH_2Cl_2/hexane (5:15 mL) to give of orange-brown crystals.

4.3.1. $RuCl_2[\eta^1$-CN{$CH_2(\eta^6$-$C_6(CH_3)_5$-2,3,4,5,6)}CH_2CH_2N-$(CH_2C_6(CH_3)_5$-2,3,4,5,6)], **2a**

Yield: 478 mg (85%), m.p.: 337–338 °C, $\upsilon_{(CN)}$: 1507 cm^{-1}. Anal. Calc. for $C_{27}H_{38}N_2RuCl_2$: C, 57.67; H, 6.81; N, 4.98. Found: C, 57.69; H, 6.88; N, 4.93%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 5.19 (s, 2H, free $CH_2C_6(CH_3)_5$-2,3,4,5,6), 4.14 (s, 2H, coord. $CH_2C_6(CH_3)_5$-2,3,4,5,6), 3.59 and 3.27 (t, 4H, J = 9.6 Hz, NCH_2CH_2N), 2.22, 2.17, 2.12, 2.07 and 2.03 (s, 30H, $CH_2C_6(CH_3)_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 200.9 (Ru–$C_{carbene}$), 134.2, 134.1, 133.4 and 129.9 (free $CH_2C_6(CH_3)_5$-2,3,4,5,6), 105.9, 99.2, 94.2 and 88.2 (coord. $CH_2C_6(CH_3)_5$-2,3,4,5,6), 48.9 (serbest $CH_2C_6(CH_3)_5$-2,3,4,5,6), 48.5 and 48.1 (NCH_2CH_2N), 47.4 (coord. $CH_2C_6(CH_3)_5$-2,3,4,5,6), 17.0 and 16.8 (free $CH_2C_6(CH_3)_5$-2,3,4,5,6), 15.6, 14.9 and 14.8 (coord. $CH_2C_6(CH_3)_5$-2,3,4,5,6).

4.3.2. $RuCl_2[\eta^1$-CN{$CH_2(\eta^6$-$C_6(CH_3)_5$-2,3,4,5,6)}$CH_2CH_2N(CH_2C_6H_2$-$(CH_3)_3$-2,4,6)], **2b**

Yield: 465 mg (87%), m.p.: 313–314 °C, $\upsilon_{(CN)}$: 1506 cm^{-1}. Anal. Calc. for $C_{25}H_{34}N_2RuCl_2$: C, 56.17; H, 6.41; N, 5.24. Found: C, 56.21; H, 6.38; N, 5.23%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 6.71 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 5.04 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 4.11 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 3.57 and 3.23 (t, 4H, J = 9.3 Hz, NCH_2CH_2N), 2.21 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.17 (s, 3H, $CH_2C_6H_2(CH_3)_3$-2,4,6), 2.07, 2.01 and 1.97 ($CH_2C_6(CH_3)_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 201.2 (Ru–$C_{carbene}$), 138.3, 136.8, 129.6 and 129.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 106.0, 99.3, 94.3 and 86.2 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 48.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 48.8 and 47.5 (NCH_2CH_2N), 47.3 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 20.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 20.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6), 15.6, 14.9 and 14.8 ($CH_2C_6(CH_3)_5$-2,3,4,5,6).

4.3.3. $RuCl_2[\eta^1$-CN{$CH_2(\eta^6$-$C_6(CH_3)_5$-2,3,4,5,6)}$CH_2CH_2N(CH_2C_6H_2$-$(OCH_3)_3$-3,4,5)], 2c

Yield: 513 mg (88%), m.p.: 281–282 °C, $\upsilon_{(CN)}$: 1515 cm^{-1}. Anal. Calc. for $C_{25}H_{34}N_2O_3RuCl_2$: C, 51.55; H, 5.88; N, 4.81. Found: C, 51.62; H, 5.85; N, 4.84%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 6.76 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.74 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.15 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 3.82 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.80 (s, 3H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.74–3.67 and 3.55–3.48 (m, 4H, NCH_2CH_2N), 2.13, 2.05 and 2.02 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 200.7 (Ru–$C_{carbene}$), 152.9, 137.1, 132.2 and 106.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 107.2, 98.3, 94.7 and 85.7 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 60.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 56.3 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 53.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 49.2 and 48.5 (NCH_2CH_2N), 47.7 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 15.6, 14.9 and 14.8 ($CH_2C_6(CH_3)_5$-2,3,4,5,6).

4.3.4. $RuCl_2[\eta^1$-CN{$CH_2(\eta^6$-$C_6H(CH_3)_4$-2,3,5,6)}$CH_2CH_2N(CH_2C_6H$-$(CH_3)_4$-2,3,5,6)], **2d**

Yield: 363 mg (68%), m.p.: 381–382 °C, $\upsilon_{(CN)}$: 1500 cm^{-1}. Anal. Calc. for $C_{25}H_{34}N_2RuCl_2$: C, 56.17; H, 6.41; N, 5.24. Found: C, 56.15; H, 6.48; N, 5.19%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 8.33 (s, 1H, coord. $CH_2C_6H(CH_3)_4$-2,3,5,6), 7.04 (s, 1H, free $CH_2C_6H(CH_3)_4$-2,3,5,6), 4.68 (s, 2H, coord. $CH_2C_6H(CH_3)_4$-2,3,5,6), 3.71 (s, 2H, free $CH_2C_6H(CH_3)_4$-2,3,5,6), 3.61 and 3.08 (t, 4H, J = 10.5 Hz, NCH_2CH_2N), 2.21 and 2.15 (s, 24H, free and coord. $CH_2C_6H(CH_3)_4$-2,3,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 198.5 (Ru–$C_{carbene}$), 134.3, 133.6, 132.6 and 129.4 (free $CH_2C_6H(CH_3)_4$-2,3,5,6), 108.3, 99.0, 90.6 and 84.1 (coord. $CH_2C_6H(CH_3)_4$-2,3,5,6), 48.8 and 48.3 (NCH_2CH_2N), 47.7 (free $CH_2C_6H(CH_3)_4$-2,3,5,6), 47.2 (coord. $CH_2C_6H(CH_3)_4$-2,3,5,6), 20.6 and 16.1 (free $CH_2C_6H(CH_3)_4$-2,3,5,6), 18.0 and 13.7 (coord. $CH_2C_6H(CH_3)_4$-2,3,5,6).

4.3.5. $RuCl_2[\eta^1$-CN{$CH_2(\eta^6$-$C_6H(CH_3)_4$-2,3,5,6)}$CH_2CH_2N(CH_2C_6H_2$-$(OCH_3)_3$-,3,4,5)], **2e**

Yield: 426 mg (75%), m.p.: 335–336 °C, $\upsilon_{(CN)}$: 1507 cm^{-1}. Anal. Calc. for $C_{24}H_{32}N_2O_3RuCl_2$: C, 50.70; H, 5.67; N, 4.93. Found: C, 50.75; H, 6.63; N, 4.98%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 6.72 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 5.49 (s, 1H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 4.77 (s, 2H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 4.19 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6), 3.84 (s, 6H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.81 (s, 3H, $CH_2C_6H_2(OCH_3)_3$-3,4,5), 3.74–3.68 and 3.56–3.50 (m, 4H, NCH_2CH_2N), 2.08 and 2.03 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 199.7 (Ru–$C_{carbene}$), 152.9, 137.1, 132.4 and 106.7 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 109.9, 98.1, 90.7 and 83.8 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 60.8 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 56.3 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 53.9 ($CH_2C_6H_2(OCH_3)_3$-3,4,5), 49.2 and 47.9 (NCH_2CH_2N), 47.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6), 18.3 and 13.7 ($CH_2C_6H(CH_3)_4$-2,3,5,6).

4.3.6. $RuCl_2[\eta^1$-CN{$CH_2(\eta^6$-$C_6(CH_3)_5$-2,3,4,5,6)}CH_2CH_2N $(CH_2CH_2OCH_3)$], **2f**

Yield: 299 mg (65%), m.p.: 153–154 °C, $\upsilon_{(CN)}$: 1669 cm^{-1}. Anal. Calc. for $C_{18}H_{28}N_2ORuCl_2$: C, 46.96; H, 6.13; N, 6.08. Found: C, 47.01; H, 6.15; N, 6.04%. ^1H NMR (399.9 MHz, $CDCl_3$) δ = 4.15 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 3.84 (t, 2H, J = 4.2 Hz, $NCH_2CH_2OCH_3$),

3.98–3.91 and 3.75–3.69 (m, 4H, NCH_2CH_2N), 3.55 (t, 2H, J = 4.2 Hz, $NCH_2CH_2OCH_3$), 3.27 (s, 3H, $CH_2CH_2OCH_3$), 2.12, 2.03 and 1.99 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 201.5 (Ru–$C_{carbene}$), 107.6, 97.6, 95.3 and 85.0 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 74.7 ($NCH_2CH_2OCH_3$), 58.5 ($CH_2CH_2OCH_3$), 51.8 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 49.5 ($NCH_2CH_2OCH_3$), 48.5 and 48.1 (NCH_2CH_2N), 15.6, 14.9 and 14.8 ($CH_2C_6(CH_3)_5$-2,3,4,5,6).

4.4. General procedure for the arylation of 2-phenylpyridine

Ruthenium complex (**2a–f**) (0.025 mmol), 2-phenylpyridine (0.5 mmol), aryl chloride (1.25 mmol) and Cs_2CO_3 (1.50 mmol) were stirred in NMP (2 mL) at 120 °C for 10 h. H_2O and EtOAc were added to the cold reaction mixture. The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel (pentane/diethylether mixture) to yield the orthoarylated products. Conversion and ratio were determined by ^1H NMR and by GC analyses.

Acknowledgements

This work was financially supported by the Technological and Scientific Research Council of Turkey TUBİTAK-CNRS [TBAG-U/181 (106T716)], Inönü University Research Fund.

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