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Synthesis, Characterization and Catalytic Activity of New N-Heterocyclic Bis(carbene)ruthenium Complexes

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The reaction of $RuCl_2(PPh_3)_3$ with *t*BuOK-deprotonated *ortho*-xylyl-bis(*N*-imidazolinium) salts **1a–d** yields $RuCl_2(PPh_3)$[bis(imidazolidin-2-ylidene)] complexes (**2a–d**). Under similar conditions, $[RuCl_2(p\text{-cymene})]_2$ leads to the ruthenium complex **3** containing a tridentate η^6-arene-dicarbene ligand. All synthesized compounds were characterized by elemental analysis and NMR spectroscopy, and the molecular structures of **2a**, **2b** and **3** were determined by X-ray crystallography. The catalytic activity of $RuCl_2(PPh_3)$[bis(imidazolidin-2-ylidene)] complexes **2a–b** was evaluated in the direct arylation of 2-phenylpyridine with chlorobenzene derivatives.

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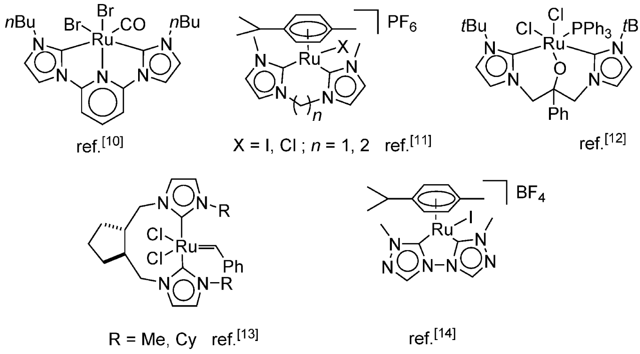
Introduction

Since the first characterization of metal complexes containing N-heterocyclic carbene (NHC) ligands by Öfele[1] and Wanzlick[2] in 1968, the development of metal-NHC complexes by Lappert in the early 1970s[3] and the seminal contribution of the group of Arduengo, who isolated the first stable free carbene in 1991,[4] NHCs have become the focus of intense study in the past decade through their application as ancillary ligands for catalytically active transition-metal complexes.[5]

NHCs show many interesting properties that make them valuable as ligands in catalysis. A combination of their powerful σ-donating and weak π-accepting character allows for the generation of a stronger bond to the metal than their phosphane homologues and leads to the formation of interestingly robust electron-rich metal complexes. Consequently, metal-NHC complexes tend to be air-stable, easy to handle and highly active in several catalytic transformations where harsh conditions are often required.[6] In recent years, an exceptionally large number of NHC complexes have emerged and have been used successfully in many catalytic transformations, notably the C–C and C–N cross-coupling reactions,[5,7] as well as the extremely useful metathesis reaction.[8]

The use of NHC ligands in catalysis continues to develop through the introduction of new NHC ligand architectures and the involvement of additional donor groups on NHC ligands to generate chelating ligands.[5b–5d,9] Among these, chelating bis-N-heterocyclic carbenes have been introduced as promising ligands.

Few examples of such ruthenium complexes and their applications in catalysis have been reported[10–14] (Scheme 1).



Scheme 1. Chelating bis(N-heterocyclic carbene)s in ruthenium complexes.

We report the synthesis of new ruthenium(II) complexes with bidentate electron-rich bis(carbene) ligands, arising from deprotonated *ortho*-xylyl-bis(*N*-imidazolinium) salts, upon reaction with $RuCl_2(PPh_3)_3$ and $[RuCl_2(p\text{-cymene})]_2$ precursors, and their application in catalytic C–H bond functionalization.

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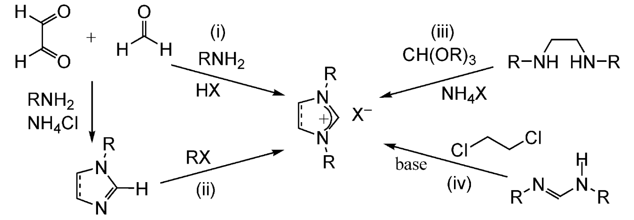
Results and Discussion

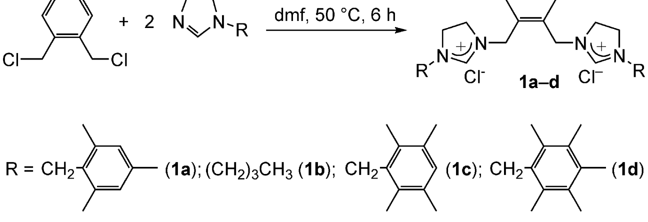
Preparation of Bis(imidazolinium) Salts

The increasing interest in transition-metal NHC complex precatalysts has contributed to the development of NHC ligand precursors, the azolium salts. Most often based on imidazole and imidazoline structures, these salts can be synthesized by various complementary synthetic routes: (i) the one-pot condensation of glyoxal, paraformaldehyde and primary amines to form imidazolium salts, (ii) alkylation of substituted imidazoles or imidazolines with an appropriate alkyl or aryl halide, (iii) the *ortho*-formate route to convert vicinal *N*,*N*-disubstituted-1,2-diamines into the corresponding imidazolinium salts under acidic conditions and (iv) reaction of a formamidine with dichloroethane and base under solvent-free reaction conditions (Scheme 2).[15]



Scheme 2. Synthetic methods leading to azolium salts.

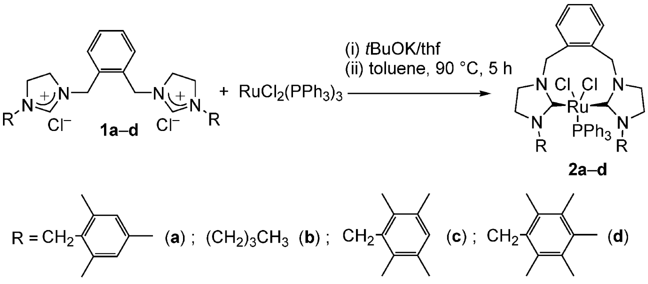
Whereas the first reported chelate bis(NHC)ruthenium complexes involve the imidazolylidene-type carbenes[10–14] (Scheme 1), we have focused our interest on the more electron-donating imidazolinylidene type with flexible *ortho*-xylyl N–CH_2–C_6H_4–CH_2–N bridges, in order to bring the two NHC groups closer together, with which the first dinuclear $(NHC\text{-}Rh)_2$ complexes have just been made.[16] However, the coordination of the two NHC units to the same rhodium site could not be achieved. We have prepared the bis(imidazolinium) salts **1a**–**d** according to route (ii) in Scheme 2. Thus, the new salts **1c**–**1d** were quantitatively prepared as **1a**–**1b**, the precursors of (NHC)-Rh complexes,[16] on reaction of 1,2-dichloromethylbenzene (5 mmol) with 1-alkylimidazoline in dmf at 50 °C, and isolated in 86–94% yields (Scheme 3).



Scheme 3. Synthesis of *ortho*-xylyl-bridged imidazolinium salts.

Preparation of (Dicarbene)ruthenium Complexes 2–3

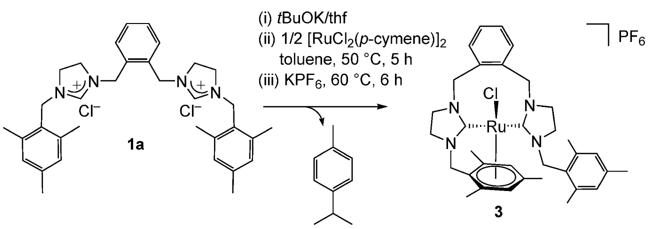
Several methods have been used for the formation of NHC-metal complexes. They are based on (i) in situ deprotonation of the azolium salts, (ii) complexation of the free NHC carbene or its protected form, (iii) thermal cleavage of electron-rich alkenes $(NHC)_2$ resulting from the dimerization of nonsterically hindered NHC, and formal insertion of the metal in a C=C bond, (iv) transmetallation from a silver-NHC complex or (v) direct oxidative addition to the metal centre.[17] Potentially chelating di- or triphosphane ligands almost always chelate if suitable labile sites are present at the metal centre. The lability of the M–P bond presumably allows the system to reach the thermodynamically preferred chelate product. A common problem in chelate and pincer NHC chemistry is that the NHC precursor often gives a kinetic product, in which each NHC azole ring binds to a different metal centre as in [M-NHC-linker-NHC-M].[10,16,18] Our failure to make [bridged-$(NHC)_2$]-rhodium complexes[16] led us to find ways to coordinate two NHC units to a single ruthenium site. The bis(carbene) ligand, arising from the deprotonation by *t*BuOK of the bis(imidazolinium) chlorides **1a**–**d** according to Lappert's procedure,[19] was treated with $RuCl_2(PPh_3)_3$ in toluene at 90 °C. After 5 h, the reaction was completed and mononuclear neutral ruthenium(II) complexes **2a**–**d** featuring a bidentate dicarbene ligand were obtained as red-brown crystalline solids in 79–89% yields (Scheme 4).



Scheme 4. Synthesis of bis(carbene)-ruthenium complexes **2a**–**d**.

The ruthenium complexes **2a**–**d** have been characterized by analytical and spectroscopic techniques. These new complexes show typical spectroscopic signatures, which are in line with those recently reported for other [$RuCl_2$(mono-NHC)(arene)] complexes.[20] They exhibit a characteristic $\nu_{(NCN)}$ infrared absorption typically at 1481–1497 cm^{-1}.[21] ^{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 207–217 ppm range and are similar to those found for other monocarbene-ruthenium complexes.[20] These values are much higher than those observed for the ruthenium complexes featuring bis(imidazolylidene) ligands (Scheme 1), which are located in the 170–200 ppm range.[10,11,13,14] However, whereas the structure is expected to be symmetrical, each of them shows two carbene carbon nuclei as doublets. For example, **2a** displays these doublets at δ = 217.2 (d, J = 9.0 Hz) and 210.5 (d, J = 16.0 Hz) ppm. Thus, we can expect in the structure a dissymmetry with different P–Ru–C(carbene) angles to explain the observed different [^{31}P–^{13}C] J values.

The reaction of $[RuCl_2(p\text{-cymene})]_2$ with the bis(carbene) arising from deprotonation of salt **1a** led to a very different complex type. After heating in toluene for 5 h, KPF_6 was added to favour chloride dissociation, and after further heating the ionic ruthenium(II) complex **3** was obtained in 75% yield (Scheme 5).



Scheme 5. Synthesis of bis(carbene)-arene-ruthenium complex **3**.

This complex also contains the chelating dicarbene ligand, but with additional η^6-coordination of one mesityl ring from the bis(carbene), arising from the displacement of the initial η^6-*p*-cymene ligand to benefit the intramolecular mesityl group coordination. A similar type of reaction had already been observed starting from $[RuCl_2(p\text{-cymene})]_2$ and monocarbene ligands leading to a bidentate 8-electron (η^6-arene–η^1-carbene) ligand.[21] The formation of complex **3** shows a unique example of a tridentate 10-electron (η^1-carbene-η^1-carbene-η^6-arene) donor ligand based on 2 NHCs and one arene moiety. The ruthenium complex **3** shows deshielded ^{13}C chemical shifts for the two carbene carbon nuclei as singlets at δ = 205.7 and 201.7 ppm in the 207–217 ppm range observed for mono-NHC-ruthenium complexes.[20]

X-ray Diffraction Study of Complexes 2a, 2b and 3

The molecular structures of complexes **2a**, **2b** and **3** have been confirmed by single-crystal X-ray diffraction analyses. Molecular structures of **2a**, **2b** and **3** with selected data are presented in Figures 1, 2 and 3, respectively, and Table 1 shows data for **2a**, **2b**.

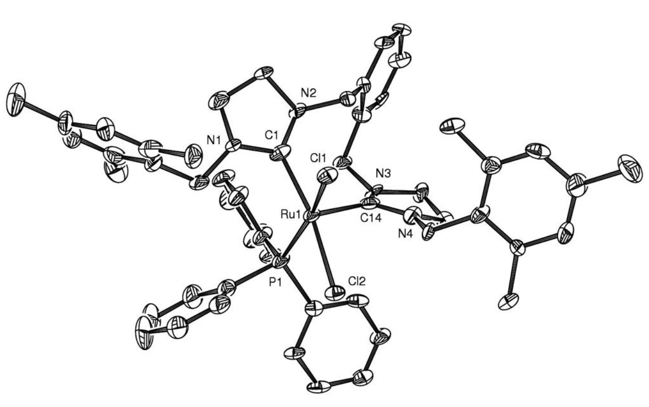


Figure 1. ORTEP drawing of complex **2a** showing 50% probability thermal ellipsoids. Selected bond lengths [Å]: Ru1–C1 2.024(10), Ru1–C14 2.000(12), Ru1–P 2.317(3), Ru1–Cl1 2.439(2), Ru1–Cl2 2.463(3); angles [°]: C14–Ru1–C1 97.7(4).

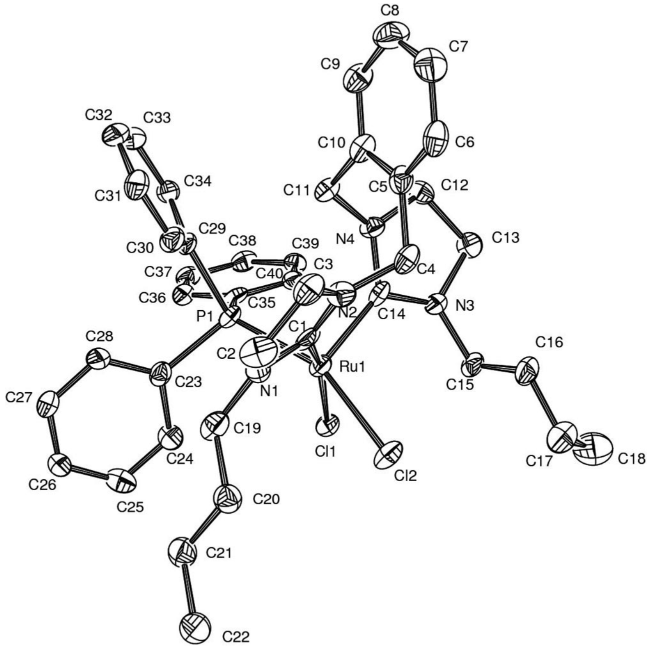


Figure 2. ORTEP drawing of complex **2b** showing 50% probability thermal ellipsoids. Selected bond lengths [Å]: Ru1–C1 2.001(5), Ru1–C14 1.954(5), Ru1–P 2.308 (12), Ru1–Cl1 2.448(13), Ru1–Cl2 2.418(12); angles [°]: C14–Ru1–C1 96.9(2).

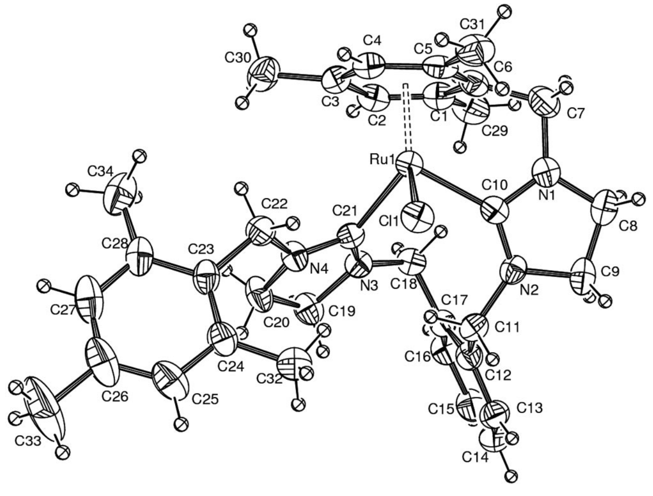


Figure 3. ORTEP drawing of complex **3** showing 50% probability thermal ellipsoids. Selected bond lengths [Å]: Ru1–C10 2.028(4), Ru1–C21 2.066(4), Ru1–Cl1 2.4112(10), Ru1–C1 2.201(4), Ru1–C2 2.195(4), Ru1–C3 2.340(4), Ru1–C4 2.297(4), Ru1–C5 2.234(4), Ru1–C6 2.154(4); angles [°]: C10–Ru1–C21 97.21(15), C21–Ru–Cl1 92.10(10), C10–Ru–Cl1 82.89(11), C10–N1–C7 123.1(4), C21–N4–C22 125.7(3), C10–N2–C11 127.7(3), C21–N3–C18 127.8(3), N1–C7–C6 106.5(4), N4–C22–C23 112.8(3), N2–C11–C12 112.1(3), N3–C18–C17 111.8(3).

From data comparison in Table 1 for **2a** and **2b** it appears that the chloride ligands are in *cis* position with a Cl–Ru–Cl angle around 90°, and that the Ru–C distances in **2a** are slightly longer than in **2b**. This shows that the nature of the NHC (only a benzyl group changed by a *N*-butyl group) has an influence on the Ru–C(carbene) bond length.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2a** and **2b**.

	2a	**2b**
Ru1–C14	2.000(12)	1.954(5)
Ru1–C1	2.024(10)	2.001(5)
Ru1–P1	2.317(3)	2.308(12)
Ru1–Cl1	2.439(2)	2.448(13)
Ru1–Cl2	2.463(3)	2.418(12)
N1–C1	1.372(14)	1.341(6)
N2–C1	1.352(14)	1.356(6)
N3–C14	1.365(15)	1.374(5)
N4–C14	1.355(13)	1.362(5)
C14–Ru1–C1	97.7(4)	96.9(2)
C14–Ru1–P1	92.7(3)	93.8(12)
C1–Ru1–P1	101.7(3)	99.7(12)
C14–Ru1–Cl1	103.5(3)	97.3(14)
C1–Ru1–Cl1	80.9(3)	164.3(15)
P1–Ru1–Cl1	163.12(11)	85.84(4)
C14–Ru1–Cl2	97.5(3)	107.71(12)
C1–Ru1–Cl2	163.8(3)	82.81(11)
P1–Ru1–Cl2	83.20(9)	157.86(5)
Cl1–Ru1–Cl2	90.05(9)	86.60(4)

Each complex has two different carbenes: one carbene is almost orthogonal to the Ru–P bond and the other one gives a larger P–Ru–C angle. For **2a**, the angle C14–Ru1–P1 is 92.7(3)° and the angle C1–Ru1–P1 is 101.7(3)°. This angle difference is likely reflected in the ^{13}C NMR spectra, which show different [^{13}C–^{31}P] J values, the larger being attributed to the larger angle.

The structure of complex **3** shows very different data with a small C–Ru–C angle (97.21°) that forces the flexible xylyl bridge to adopt a twisted position. Thus, NHC coordinating sites force the bridge to adopt its conformation, not the ligand to impose a larger C14–Ru–C1 bite angle.

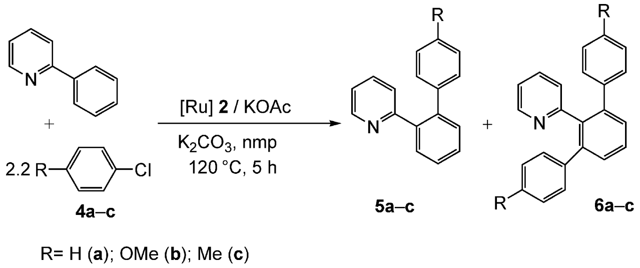
Some data show striking differences with the chelating diimidazolylideneruthenium complexes.[10–14] The comparison of structure data of complexes **2a**, **2b** and **3** containing a diimidazolinylidene chelating ligand with the reported ruthenium complexes containing a diimidazolylidene chelating group (Scheme 1)[10–14] shows that:

(i) in the former complexes **2**–**3** the Ru–C(carbene) bonds are slightly shorter than in those shown in Scheme 1. This may reflect the electron-donating capability of the NHC groups. As examples, in Scheme 1, Ru–C(carbene) bond lengths are 2.062(5) and 2.056(5) Å for the complex in ref.[10], and 2.083(15) and 2.049(15) Å for the complex described in ref.[11] (n = 2).

(ii) The C–Ru–C angles of complexes represented in Scheme 1 are much smaller than in **2**–**3** (see Scheme 1): C–Ru–C [°]: 83.6(3) (n = 1) and 87.2(6) (n = 2)[11] and 76.8(3),[14] whereas in **2**–**3** the larger angles are C–Ru–C: 97.7(4) (**2a**); 96.9(2) (**2b**); 97.4(15) (**3**) [°].

Application in Catalysis. Direct Arylation of 2-Phenylpyridine through C–H Bond Activation

We have recently shown that NHC-ruthenium(II) species in situ generated from [RuCl$_2$(p-cymene)]$_2$ and monoazolium salts under basic conditions were able to catalyze the direct arylation of 2-phenylpyridine by aryl bromides.[22] The mechanism study showed that the first step of the reaction deals with the *ortho*-metallation of the 2-phenylpyridine-ruthenium(II) adduct through a cooperative action of both the ruthenium(II) site and the coordinated carbonate.[23] The direct functionalization of sp^2 C–H bonds for C–C bond formation is an emerging field.[24] The potential of ruthenium catalyst precursors to promote this useful reaction has already been seen[25] and we have initiated mechanism studies with this metal.[22] Thus, we have explored the new (dicarbene)ruthenium complexes **2a**–**d** as catalyst precursors in the presence of coordinating bases (KOAc, K$_2$CO$_3$) for the direct diarylation of 2-phenylpyridine, used as a model substrate directed to the *ortho*-position by the N atom of the pyridine group according to Scheme 6.



Scheme 6. Direct arylation of 2-phenylpyridine with aryl chlorides.

The importance of the coordination of the required base in the catalyst intermediate[22,23] led us to first explore the influence of Cs$_2$CO$_3$, K$_2$CO$_3$ and tBuOK in the presence of a precatalyst **2**. We found that K$_2$CO$_3$ in nmp (N-methyl-2-pyrrolidinone) at 120 °C provided the best conditions and that initial treatment of the ruthenium precatalyst **2** with KOAc was beneficial.[26] We first investigated the arylation of 2-pyridylbenzene with chlorobenzene (**4a**) in the presence of [RuCl$_2$(PPh$_3$)(dicarbene)] (**2a**–**d**) as catalyst precursor and extended the scope of the reaction to the *para*-substituted methoxy- (**4b**), and methyl- (**4c**) chlorobenzenes. The results are reported in Table 2 (entries 1–6).

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. The alkyl-N-substituted bis(carbene) ligand in **2b** led to a less efficient catalyst to perform the second arylation as the **5**/**6** ratio was around 30:70. The most selective catalytic system towards the formation of bis-*ortho*-arylated 2-phenylpyridine was obtained when the bis(carbene) ligand contained the bulky benzyl substituent in **2d** (Table 2, entries 6, 10 and 14). It is worth noting that these new catalytic systems based on (dicarbene)ruthenium precursors in the presence of both potassium acetate and carbonate make possible arylation with chloroarene derivatives, which are more easily available than bromoarenes, but

Table 2. Direct arylation of 2-phenylpyridine with ArCl.[a]

Entry	Catalyst	ArCl	Conversion [%][b]	**5a–c**/**6a–c** (%:%)[b]
1	**2a**	**4a**	66[c]	**5a**/**6a** (18:82)
2	**2a**	**4a**	77[d]	**5a**/**6a** (14:86)
3	**2a**	**4a**	100	**5a**/**6a** (12:88)
4	**2b**	**4a**	100	**5a**/**6a** (27:73)
5	**2c**	**4a**	100	**5a**/**6a** (9:91)
6	**2d**	**4a**	100	**5a**/**6a** (5:95)
7	**2a**	**4b**	100	**5b**/**6b** (10:90)
8	**2b**	**4b**	100	**5b**/**6b** (31:69)
9	**2c**	**4b**	100	**5b**/**6b** (11:89)
10	**2d**	**4b**	100	**5b**/**6b** (8:92)
11	**2a**	**4c**	100	**5c**/**6c** (9:91)
12	**2b**	**4c**	100	**5c**/**6c** (29:71)
13	**2c**	**4c**	100	**5c**/**6c** (10:90)
14	**2d**	**4c**	100	**5c**/**6c** (3:97)

[a] Reaction conditions: KOAc (0.05 mmol), ruthenium complex **2** (0.025 mmol), nmp as solvent, room temp. for 1 h, then 2-phenylpyridine (0.5 mmol), ArCl (1.1 mmol), $\mathrm{K_2CO_3}$ (1.5 mmol), 120 °C, 5 h. [b] Conversion of 2-phenylpyridine and **5a–c**/**6a–c** ratio determined by ^{1}H NMR and by GC. [c] After 1 h of reaction. [d] After 3 h of reaction.

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.[22]

Conclusions

From readily available starting materials, such as *ortho*-xylyl-bis(*N*-alkylimidazolinium) salts, four novel $\mathrm{RuCl_2}$(d-icarbene)($\mathrm{PPh_3}$) complexes (**2a–d**) and the unprecedented [RuCl(η^1-carbene-η^1-carbene-η^6-arene)]$\mathrm{PF_6}$ complex **3** have been prepared and characterized. Complexes **2a**, **2b** and **3** have been characterized by single-crystal X-ray diffraction studies. The efficiency of complexes **2a–d** as catalyst precursors for the bis-*ortho*-arylation of 2-phenylpyridine with aryl chlorides has been established.

Experimental Section

All reactions for the preparation of bis(imidazolinium) salts (**1**) and *o*-xylyl-linked ruthenium(NHC) complexes **2a–d** were carried out under argon in flame-dried glassware using standard Schlenk techniques. Melting points were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus. FTIR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} with a ATI UNICAM 1000 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian AS 400 Merkur spectrometer operating at 400 MHz (^{1}H), 100 MHz (^{13}C) in $\mathrm{CDCl_3}$ with tetramethylsilane as an internal reference. Column chromatography was performed using silica gel 60 (70–230 mesh). Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey) Microlab and Centre Régional de Mesures Physiques de l′Ouest, Université de Rennes. X-ray diffraction analyses were carried out with a X8-APEX II Bruker AXS instrument for complex **2a**, and a CCD Saphire 3 Xcalibur diffractometer for complexes **2b** and **3**.

General Procedure for the Preparation of the Bis(imidazolinium) Salts (1c–d): Salts **1a** and **1b** were prepared according to our previous report.[16] 1,2-Dichloromethylbenzene (5 mmol) was slowly added to a solution of 1-alkylimidazoline (10 mmol) in dmf (10 mL) at 25 °C, and the resulting mixture was stirred at 50 °C for 6 h. Diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 15 mL) and dried under vacuum. The crude product was recrystallized from EtOH/$\mathrm{Et_2O}$.

***o*-Xylyl-bis(*N*-2,3,5,6-tetramethylbenzylimidazolinium) Dichloride (1c):** Yield: 2.58 g (85%); m.p. 288–289 °C. IR: $\tilde{\nu}_{\mathrm{(CN)}}$ = 1657 cm^{-1}. $\mathrm{C_{36}H_{48}Cl_2N_4}$ (607.70): calcd. C 71.15, H 7.96, N 9.22; found C 71.19, H 7.91, N 9.17. ^{1}H NMR (399.9 MHz, $\mathrm{CDCl_3}$): δ = 10.28 (s, 2 H, NC*H*N), 7.36–7.26 (m, 4 H, o-$\mathrm{CH_2C_6}H_4\mathrm{CH_2}$), 7.24 [s, 2 H, $\mathrm{CH_2C_6}H\mathrm{(CH_3)_4}$-2,3,5,6], 5.51 (s, 4 H, o-$\mathrm{C}H_2\mathrm{C_6H_4C}H_2$), 4.98 [s, 4 H, $\mathrm{C}H_2\mathrm{C_6H(CH_3)_4}$-2,3,5,6], 3.77–3.91 (m, 8 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 2.32 and 2.26 [s, 24 H, $\mathrm{CH_2C_6H\ (C}H_3)_4$-2,3,5,6] ppm. ^{13}C NMR (100.5 MHz, $\mathrm{CDCl_3}$): δ = 158.7 (N*C*HN), 132.9, 129.6 and 129.3 (o-$\mathrm{CH_2}C_6\mathrm{H_4CH_2}$), 134.8, 133.9, 132.5 and 128.1 [$\mathrm{CH_2}C_6\mathrm{H(CH_3)_4}$-2,3,5,6], 50.1 ($o$-$\mathrm{CH_2C_6H_4}C\mathrm{H_2}$), 47.2 [$C\mathrm{H_2C_6H\ (CH_3)_4}$-2,3,5,6], 47.8 and 47.7 ($\mathrm{N}C\mathrm{H_2}C\mathrm{H_2N}$), 20.6 and 16.1 [$\mathrm{CH_2C_6H(C}H_3)_4$-2,3,5,6] ppm.

***o*-Xylyl-bis(*N*-2,3,4,5,6-pentamethylbenzylimidazolinium) Dichloride (1d):** Yield: 2.87 g (94%); m.p. 282–283 °C. IR: $\tilde{\nu}_{\mathrm{(CN)}}$ = 1655 cm^{-1}. $\mathrm{C_{38}H_{52}Cl_2N_4}$ (635.75): calcd. C 71.79, H 8.24, N 8.81; found C 70.65, H 8.62, N 9.14. ^{1}H NMR (399.9 MHz, $\mathrm{CDCl_3}$): δ = 10.19 (s, 2 H, NC*H*N), 7.34–7.24 (m, 4 H, o-$\mathrm{CH_2C_6}H_4\mathrm{CH_2}$), 5.51 (s, 4 H, o-$\mathrm{C}H_2\mathrm{C_6H_4C}H_2$), 4.99 [s, 4 H, $\mathrm{C}H_2\mathrm{C_6\ (CH_3)_5}$-2,3,4,5,6], 3.75–3.92 (m, 8 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 2.36, 2.26 and 2.24 [s, 30 H, $\mathrm{CH_2C_6(C}H_3)_5$-2,3,4,5,6] ppm. ^{13}C NMR (100.5 MHz, $\mathrm{CDCl_3}$): δ = 158.5 (N*C*HN), 132.5, 129.6 and 129.3 (o-$\mathrm{CH_2}C_6\mathrm{H_4CH_2}$), 136.5, 133.6, 133.5 and 125.5 [$\mathrm{CH_2}C_6\ \mathrm{(CH_3)_5}$-2,3,4,5,6], 50.1 ($o$-$\mathrm{CH_2C_6H_4}C\mathrm{H_2}$), 47.6 [$C\mathrm{H_2C_6\ (CH_3)_5}$-2,3,4,5,6], 47.8 and 47.7 ($\mathrm{N}C\mathrm{H_2}C\mathrm{H_2N}$), 17.2, 17.1 and 16.9 [$\mathrm{CH_2C_6(C}H_3)_5$-2,3,4,5,6] ppm.

$\mathrm{RuCl_2(PPh_3)}$[bis(imidazolidin-2-ylidene)] Complex 2a: The preparation was adapted from the Lappert procedure.[19] A solution of the bis(imidazolinium) salt (**1a**) (10 mmol) and *t*BuOK (22 mmol) in thf (20 mL) was stirred at room temperature for 12 h, and volatiles were removed under vacuum. Toluene (20 mL) was added and the suspension was filtered. After removal of toluene from the filtrate, a colourless oil corresponding to the carbene dimerization alkene was obtained in quantitative yield. This bis(carbene) (0.50 g, 1 mmol) and ruthenium complex $\mathrm{RuCl_2(PPh_3)_3}$ (0.95 g, 1 mmol) were heated in degassed toluene (15 mL) at 90 °C for 5 h. After the reaction mixture had been cooled to 25 °C and filtered, the filtrate was kept at –25 °C, and reddish brown crystals were obtained. Yield: 86% (0.81 g), m.p. 191–192 °C. IR: $\tilde{\nu}_{\mathrm{(CN)}}$ = 1481 cm^{-1}. $\mathrm{C_{52}H_{57}Cl_2N_4PRu}$ (940.99): calcd. C 66.37, H 6.11, N 5.95; found C 66.49, H 6.02, N 5.84. ^{1}H NMR (399.9 MHz, $\mathrm{CDCl_3}$): δ = 7.63 [t, J = 8.6 Hz, 6 H, $\mathrm{P(C_6}H_5)_3$], 7.26–7.36 [m, 9 H, $\mathrm{P(C_6}H_5)_3$], 7.10–7.21 (m, 4 H, o-$\mathrm{CH_2C_6}H_4\mathrm{CH_2}$), 6.69–6.75 [m, 4 H, $\mathrm{CH_2C_6}H_2\mathrm{(CH_3)_3}$-2,4,6], 6.55 and 5.13 [d, J = 15.2 Hz, 2 H, $\mathrm{C}H_2\mathrm{C_6H_2(CH_3)_3}$-2,4,6], 4.76 and 4.35 [d, J = 12.0 Hz, 2 H, $\mathrm{C}H_2\mathrm{C_6H_2(CH_3)_3}$-2,4,6], 5.30 (d, J = 14.4 Hz, 1 H, o-$\mathrm{C}H_2\mathrm{C_6H_4C}H_2$), 4.89 (d, J = 14.8 Hz, 1 H, o-$\mathrm{C}H_2\mathrm{C_6H_4C}H_2$), 3.78 (d, J = 15.6 Hz, 1 H, o-$\mathrm{C}H_2\mathrm{C_6H_4C}H_2$), 2.28 (d, J = 14.4 Hz, 1 H, o-$\mathrm{C}H_2\mathrm{C_6H_4C}H_2$), 2.57-2.74 (m, 2 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 2.95–3.07 (m, 2 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.09–3.15 (m, 2 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.27–3.38 (m, 2 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 2.43 [s, 6 H, $\mathrm{CH_2C_6H_2(C}H_3)_3$-2,*4*,6], 2.21 [s, 12 H, $\mathrm{CH_2C_6H_2(C}H_3)_3$-*2*,4,*6*] ppm. ^{13}C NMR (100.5 MHz, $\mathrm{CDCl_3}$): δ = 217.2 (d, J = 9.0 Hz) and 210.5 (d, J = 16.0 Hz, C_{carbene}), 128.1, 129.5, 129.6, 134.5 and 134.6 [$\mathrm{P(}C_6\mathrm{H_5)_3}$], 128.2, 130.3, 136.2 and 136.3 (*o*-

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$CH_2\mathit{C}_6H_4CH_2$), 128.8, 129.2, 131.0, 131.9, 136.6, 137.5, 137.9 and 139.7 [$CH_2\mathit{C}_6H_2(CH_3)_3$-2,4,6], 52.3 and 53.9 (*o*-$\mathit{C}H_2C_6H_4\mathit{C}H_2$), 48.2 and 52.0 [$\mathit{C}H_2C_6H_2(CH_3)_3$-2,4,6], 46.7, 47.4, 48.0 and 49.8 ($N\mathit{C}H_2\mathit{C}H_2N$), 21.29 [$CH_2C_6H_2(\mathit{C}H_3)_3$-2,*4*,6], 21.1 [$CH_2C_6H_2(\mathit{C}H_3)_3$-2,4,*6*] ppm.

$RuCl_2(PPh_3)$[bis(imidazolidin-2-ylidene)] Complex 2b: Compound **2b** was prepared in the same way as **2a**, from a solution of the electron-rich olefin (0.35 g, 1 mmol) in dry toluene (15 mL) and $RuCl_2(PPh_3)_3$ (0.95 g, 1 mmol). Red-brown crystals were obtained: 79% (0.62 g), m.p. 114–115 °C. IR: $\tilde{\nu}_{(CN)}$ = 1483 cm^{-1}. $C_{40}H_{49}Cl_2N_4PRu$ (788.79): calcd. C 60.91, H 6.26, N 7.10; found C 61.07, H 6.12, N 7.24. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 7.22–7.69 [m, 15 H, $P(C_6\mathit{H}_5)_3$], 7.10–7.19 (m, 4 H, *o*-$CH_2C_6\mathit{H}_4CH_2$), 5.13 (d, J = 15.6 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 4.80 (d, J = 14.4 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 3.72 (d, J = 16.0 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 2.58 (d, J = 14.4 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 3.33–3.70 (m, 6 H, $NC\mathit{H}_2C\mathit{H}_2N$), 3.90–3.94 (m, 1 H, $NC\mathit{H}_2C\mathit{H}_2N$), 4.99–5.07 (m, 1 H, $NC\mathit{H}_2C\mathit{H}_2N$), 3.24–3.32 (m, 2 H, $C\mathit{H}_2CH_2CH_2CH_3$), 0.90–1.51 (m, 8 H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.85 (t, J = 7.2 Hz, 3 H, $CH_2CH_2CH_2C\mathit{H}_3$), 0.71 (t, J = 7.2 Hz, 3 H, $CH_2CH_2CH_2C\mathit{H}_3$) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 216.8 (d, J = 9.0 Hz) and 207.0 (d, J = 15.8 Hz, $C_{carbene}$), 127.8, 129.2, 130.3, 134.3, 134.5 and 137.0 [$P(\mathit{C}_6H_5)_3$], 127.9, 130.5, 135.6 and 136.5 (*o*-$CH_2\mathit{C}_6H_4CH_2$), 52.7 and 53.5 (*o*-$\mathit{C}H_2C_6H_4\mathit{C}H_2$), 52.0 and 52.8 ($\mathit{C}H_2CH_2CH_2CH_3$), 46.3, 48.9, 49.9 and 50.6 ($N\mathit{C}H_2\mathit{C}H_2N$), 31.3, 31.1, 19.9 and 19.7 ($CH_2\mathit{C}H_2\mathit{C}H_2CH_3$), 14.3 and 13.8 ($CH_2CH_2CH_2\mathit{C}H_3$) ppm.

$RuCl_2(PPh_3)$[bis(imidazolidin-2-ylidene)] Complex 2c: Compound **2c** was prepared in the same way as **2a**, from a solution of the electron-rich olefin (0.53 g, 1 mmol) in dry toluene (15 mL) and $RuCl_2(PPh_3)_3$ (0.95 g, 1 mmol). Red-brown crystals were obtained. Yield: 82% (0.79 g), m.p. 225–226 °C. IR: $\tilde{\nu}_{(CN)}$ = 1493 cm^{-1}. $C_{54}H_{61}Cl_2N_4PRu$ (969.04): calcd. C 66.93, H 6.34, N 5.78; found C 66.89, H 6.30, N 5.82. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 7.55 [t, J = 1.5 Hz, 6 H, $P(C_6\mathit{H}_5)_3$], 7.25–7.52 [m, 9 H, $P(C_6\mathit{H}_5)_3$], 7.12–7.22 (m, 4 H, *o*-$CH_2C_6\mathit{H}_4CH_2$), 6.91 and 6.84 [s, 2 H, $CH_2C_6\mathit{H}(CH_3)_4$-2,3,5,6], 6.72 [d, J = 7.2 Hz, 1 H, $C\mathit{H}_2C_6H(CH_3)_4$-2,3,5,6], 5.37 [d, J = 15.0 Hz, 1 H, $C\mathit{H}_2C_6H(CH_3)_4$-2,3,5,6], 4.91 [d, J = 11.4 Hz, 1 H, $C\mathit{H}_2C_6H(CH_3)_4$-2,3,5,6], 4.95 [d, J = 13.5 Hz, 1 H, $C\mathit{H}_2C_6H(CH_3)_4$-2,3,5,6], 6.56 (d, J = 15.0 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 5.34 (d, J = 15.6 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 4.43 (d, J = 12.0 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 3.83 (d, J = 15.9 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 2.51–3.17 (m, 8 H, $NC\mathit{H}_2C\mathit{H}_2N$), 2.41, 2.37, 2.21, 2.15 and 2.12 [s, 24 H, $CH_2C_6H(C\mathit{H}_3)_4$-2,3,5,6] ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 216.9 (d, J = 9.0 Hz) and 209.8 (d, J = 15.8 Hz, $C_{carbene}$), 128.0, 129.4, 130.1, 134.3, 134.5 and 135.5 [$P(\mathit{C}_6H_5)_3$], 128.1, 130.7, 136.0 and 136.1 (*o*-$CH_2\mathit{C}_6H_4CH_2$), 128.3, 129.0, 131.5, 131.7, 133.1, 133.3, 136.7 and 137.3 [$CH_2\mathit{C}_6H(CH_3)_4$-2,3,5,6], 52.3 and 53.7 (*o*-$\mathit{C}H_2C_6H_4\mathit{C}H_2$), 46.3, 47.4, 47.9 and 49.6 ($N\mathit{C}H_2\mathit{C}H_2N$), 48.4 and 52.1 [$\mathit{C}H_2C_6H(CH_3)_4$-2,3,5,6], 20.8, 20.6, 20.4, 20.3, 17.1, 16.5, 15.5 and 15.3 [$CH_2C_6H(\mathit{C}H_3)_4$-2,3,5,6] ppm.

$RuCl_2(PPh_3)$[bis(imidazolidin-2-ylidene)] Complex 2d: Compound **2d** was prepared in the same way as **2a**, from a solution of the electron-rich olefin (0.56 g, 1 mmol) in dry toluene (15 mL) and $RuCl_2(PPh_3)_3$ (0.95 g, 1 mmol). Red-brown crystals were obtained. Yield: 89% (0.91 g), m.p. 243–244 °C. IR $\tilde{\nu}_{(CN)}$ = 1497 cm^{-1}. $C_{58}H_{65}Cl_2N_4PRu$ (1021.11): calcd. C 68.22, H 6.42, N 5.49; found C 68.26, H 6.45, N 5.55. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 7.67 [t, J = 8.4 Hz, 6 H, $P(C_6\mathit{H}_5)_3$], 7.25–7.39 [m, 9 H, $P(C_6\mathit{H}_5)_3$], 7.12–7.22 (m, 4 H, *o*-$CH_2C_6\mathit{H}_4CH_2$), 6.72 [d, J = 7.2 Hz, 1 H, $C\mathit{H}_2C_6(CH_3)_5$-2,3,4,5,6], 5.46 [d, J = 15.3 Hz, 1 H, $C\mathit{H}_2C_6(CH_3)_5$-2,3,4,5,6], 4.90–4.97 [m, 2 H, $C\mathit{H}_2C_6(CH_3)_5$-2,3,4,5,6], 6.54 (d, J = 15.3 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 5.354 (d, J = 15.6 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 4.43 (d, J = 12.0 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 3.84 (d, J = 15.6 Hz, 1 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 2.50–3.45 (m, 8 H, $NC\mathit{H}_2C\mathit{H}_2N$), 2.42, 2.38, 2.22, 2.21, 2.18, 2.15 and 2.13 [s, 30 H, $CH_2C_6(C\mathit{H}_3)_5$-2,3,4,5,6] ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 216.8 (d, J = 9.0 Hz) and 209.6 (d, J = 16.5 Hz, $C_{carbene}$), 127.9, 129.0, 129.3, 134.3, 134.4 and 135.5 [$P(\mathit{C}_6H_5)_3$], 128.0, 130.1, 136.0 and 136.8 (*o*-$CH_2\mathit{C}_6H_4CH_2$), 128.2, 128.9, 130.7, 131.9, 132.3, 136.2, 137.3 and 137.9 [$CH_2\mathit{C}_6(CH_3)_5$-2,3,4,5,6], 52.6 and 53.7 (*o*-$\mathit{C}H_2C_6H_4\mathit{C}H_2$), 46.3, 47.5, 48.7 and 49.6 ($N\mathit{C}H_2\mathit{C}H_2N$), 48.1 and 52.1 [$\mathit{C}H_2C_6(CH_3)_5$-2,3,4,5,6], 16.5, 16.6, 16.7, 16.8, 16.9, 17.0, 17.1, 17.4, 17.5 and 18.1 [$CH_2C_6(\mathit{C}H_3)_5$-2,3,4,5,6] ppm.

Compound 3: A solution of bis(imidazolium) salt **1a** was deprotonated by *t*BuOK in thf according to Lappert's procedure[19] (see deprotonation of **1a** in the preparation of **2a**). The resulting carbene dimer (0.50 g, 1 mmol) and ruthenium complex [$RuCl_2$(*p*-cymene)]$_2$ (0.31 g, 0.5 mmol) were stirred in degassed toluene (15 mL) at room temperature for 1 h. Then the mixture was heated at 50 °C for 5 h and then cooled to room temperature. KPF_6 (0.37 g, 2.0 mmol) was added and the mixture was heated at 60 °C for 8 h. After cooling, toluene was removed under vacuum. The crude solid was crystallized from a dichloromethane/diethyl ether (1:2) mixture and yellow crystals were obtained. Yield: 75% (0.62 g), m.p. 321–322 °C. $C_{34}H_{42}ClF_6N_4PRu\cdot 0.5CH_2Cl_2$ (830.68): calcd. C 49.88, H 5.22, N 6.74; found C 49.92, H 5.25, N 6.70. ^1H NMR (399.9 MHz, $CDCl_3$): δ = 7.21–7.48 (m, 4 H, *o*-$CH_2C_6\mathit{H}_4CH_2$), 6.79 [s, 2 H, free $CH_2C_6\mathit{H}_2(CH_3)_3$-2,4,6], 5.20 and 5.95 [s, 2 H, coord. $CH_2C_6\mathit{H}_2(CH_3)_3$-2,4,6], 5.40 (crystallize $C\mathit{H}_2Cl_2$), 4.06 and 6.26 [d, J = 14.7 Hz, 2 H, coord. $C\mathit{H}_2C_6H_2(CH_3)_3$-2,4,6], 4.56–4.77 (m, 4 H, *o*-$C\mathit{H}_2C_6H_4C\mathit{H}_2$), 4.37 and 4.23 [d, J = 12.6 Hz, 2 H, free $C\mathit{H}_2C_6H_2(CH_3)_3$-2,4,6], 3.79–3.96 (m, 4 H, $NC\mathit{H}_2C\mathit{H}_2N$), 3.43–3.52 (m, 4 H, $NC\mathit{H}_2C\mathit{H}_2N$), 2.33 [s, 6 H, free $CH_2C_6H_2(C\mathit{H}_3)_3$-2,4,*6*], 2.30 [s, 3 H, free $CH_2C_6H_2(C\mathit{H}_3)_3$-2,*4*,6], 2.16, 2.20 and 2.42 [s, 9 H, coord. $CH_2C_6H_2(C\mathit{H}_3)_3$-2,4,6] ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 205.7 and 201.7 ($C_{carbene}$), 128.3, 128.8, 131.5, 133.5 and 136.6 (*o*-$CH_2\mathit{C}_6H_4CH_2$), 128.1, 131.1, 133.0 and 137.1 [free $CH_2\mathit{C}_6H_2(CH_3)_3$-2,4,6], 86.3, 92.9, 100.7, 102.6, 102.8 and 106.8 [coord. $CH_2\mathit{C}_6H_2(CH_3)_3$-2,4,6], 53.2 (crystallize $\mathit{C}H_2Cl_2$), 51.4 and 52.3 (*o*-$\mathit{C}H_2C_6H_4\mathit{C}H_2$), 45.2 and 48.1 [$\mathit{C}H_2C_6H_2(CH_3)_3$-2,4,6], 46.0, 46.4, 47.7 and 47.9 ($N\mathit{C}H_2\mathit{C}H_2N$), 19.6 [free $CH_2C_6H_2(\mathit{C}H_3)_3$-2,*4*,6], 20.1 [free $CH_2C_6H_2(\mathit{C}H_3)_3$-2,4,*6*], 15.5, 16.5 and 20.1 [coord. $CH_2C_6H_2(\mathit{C}H_3)_3$-2,*4*,*6*] ppm.

General Procedure for the Arylation of 2-Phenylpyridine: KOAc (0.05 mmol) and the ruthenium complex (**2a**–**d**) (0.025 mmol) were stirred in nmp (2 mL) at room temp. for 1 h. Then 2-phenylpyridine (0.5 mmol), aryl chloride (1.25 mmol) and K_2CO_3 (1.50 mmol) were added. The resulting mixture was stirred at 120 °C for 5 h. H_2O and EtOAc were added to the cold reaction mixture. The organic phase was dried with $MgSO_4$ and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel (pentane/diethyl ether mixture) to yield the *ortho*-arylated products. Conversion and ratio were determined by ^1H NMR spectroscopic and by GC analyses.

X-ray Crystallography: Crystallographic data are given in Table 3.

CCDC-284181 (for **2a**), -665238 (for **2b**) and -675471 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for complexes **2a**, **2b**, and **3**.

	2a	**2b**	**3**
Empirical formula	$C_{56}H_{67}Cl_2N_4OPRu$	$C_{40}H_{49}Cl_2N_4PRu$	$C_{34.50}H_{43}Cl_2F_6N_4$ PRu
Molecular mass [g mol^{-1}]	1015.08	788.77	830.67
Crystal size [mm]	0.28 × 0.28 × 0.08	0.22 × 0.12 × 0.12	0.20 × 0.08 × 0.08
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [Å]	20.0076(5)	13.6970(8)	12.8351(6)
b [Å]	11.2504(3)	11.8906(3)	11.6572(6)
c [Å]	22.6674(6)	22.5674(8)	24.5510(10)
β [°]	94.1450(10)	91.013(3)	95.123(3)
Volume [Å^3]	5088.9(2)	3674.9(3)	3658.7(3)
Z	4	4	4
Density [g cm^3]	1.325	1.426	1.508
Temperature [K]	100(1)	110(2)	220(2)
$F(000)$	2128	1640	1700
Wavelength [Å]	0.71069	0.71073	0.71069
Absorption coefficient [mm^{-1}]	0.488	0.650	0.680
θ range [°]	2.55–27.51	2.88–33.46	2.55–32.27
Index ranges	$-25 \le h \le 25$	$-20 \le h \le 20$	$-19 \le h \le 18$
	$-14 \le k \le 13$	$-17 \le k \le 18$	$-11 \le k \le 17$
	$-29 \le l \le 29$	$-33 \le l \le 33$	$-36 \le l \le 36$
Reflections collected	95514	36926	32084
Independent reflections	11490 [$R_{\text{int}} = 0.0819$]	10101 [$R_{\text{int}} = 0.1002$]	11417 [$R_{\text{int}} = 0.0537$]
Reflections [$I > 2\sigma(I)$]	7732	3945	4735
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	11490/0/586	10101/0/433	11417/0/451
Goodness-of- fit on F^2	1.026	0.830	0.807
Final R indices	$R_1 = 0.0468$	$R_1 = 0.0604$	$R_1 = 0.0511$
[$I > 2\sigma(I)$]	$wR_2 = 0.1021$	$wR_2 = 0.1056$	$wR_2 = 0.1346$
R indices (all data)	$R_1 = 0.0918$	$R_1 = 0.1851$	$R_1 = 0.1409$
	$wR_2 = 0.1253$	$wR_2 = 0.1267$	$wR_2 = 0.1488$
Largest diff. peak and hole [e Å^{-3}]	1.328 and –1.360	1.296 and –1.219	1.021 and –0.689

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