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Ruthenium(II) Acetate Catalyst for Direct Functionalisation of sp^2-C–H Bonds with Aryl Chlorides and Access to Tris-Heterocyclic Molecules

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Abstract: The *in situ* generated (*p*-cymene)ruthenium diacetate [$Ru(OAc)_2$(*p*-cymene)] catalyst **2**, prepared from the (*p*-cymene)ruthenium dichloride dimer {[$RuCl_2$(*p*-cymene)]$_2$, **1**} and potassium acetate (KOAc), acts as an excellent catalyst for *ortho* C–H bond functionalisation of 2-pyridylbenzene with unactivated aryl chlorides in the presence of potassium carbonate (K_2CO_3). Quantitative diarylation can be reached in 1 h at 120 °C. The diarylation of 2-pyridylbenzene with 2-halopyridines and 2- and 3-halothiophenes was performed with **1** in the presence of KOAc or K_2CO_3 under more drastic conditions to generate the potential tridentate ligands, tris[1,2,3-(2-pyridyl)]benzenes and bis(2,6-thiophenyl)2-pyridylbenzenes.

Keywords: arylation; C–H bond functionalization; pyridine derivatives; ruthenium acetate; ruthenium catalysts

The catalytic functionalisation of sp^2-C–H bonds is an emerging field[1] with the potential to replace one of the most useful catalytic reactions in synthetic methodology: the cross-coupling reaction.[2] Although the formation of C–C bonds directly from arenes, heterocycles or alkenes on reaction with an sp^2-carbon halide bond-containing substrates requires a base, it does not need the previous and costly regioselective formation of an organometallic compound as is the case for cross-coupling reactions.[2]

Direct arylations of functional arenes or alkenes have recently been performed using palladium(0) catalyst precursors.[3–5] Direct arylations of phenols[6] or heterocycles[7] can also be performed with rhodium[7] and iridium catalysts.[8] Recently, ruthenium(II) catalysts based on a $RuCl_2$(hydrocarbon) source associated with various ligands have emerged as possible catalysts for C–H bond arylation and allylation.[9–11] Efforts are currently being made to generate efficient ruthenium(II) catalysts for the functionalisation of arenes, heterocycles and alkenes.[12]

It was first believed that direct arylation with ArX proceeded by electrophilic substitution with palladium(II) or ruthenium(IV) species arising from oxidative addition of ArX to palladium(0) or ruthenium(II), respectively. However, recent studies supported a proton abstraction mechanism by a carbonate with palladium(II) species,[13] a process that is supported by several experimental observations.[5] DFT calculations also favour a proton abstraction mechanism from the substrate agostic C–H bond directly within the $RuCl_2$(L)(substrate) species, by cooperative actions of the ruthenium(II) centre and the coordinated carbonate[11] leading to the crucial *ortho*-metallated intermediate (Figure 1, Y = OH). In that latter case, the previous oxidative addition of the ArBr to ruthenium(II) is not required as for palladium(0) catalysts.[13] Other processes involving *proton abstraction* from a C–H bond *assisted* by coordinated ligand have also been reported.[14]

The proton abstraction mechanism with the Ru(II) centre[11] and the evidence for the carbonate coordina-

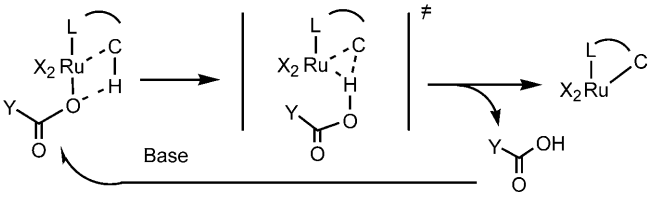


Figure 1. (Ligand)O-Ru(II)-assisted C–H bond cleavage mechanism for C–C bond formation.

tion,[15] led us to investigate the influence of an oxygen-containing ligand linked to the ruthenium(II) centre on proton abstraction of functional arenes and further arylation. The positive role of a carboxylic acid as additive has just been shown with palladium[5] and ruthenium[12g] catalysts.

We now report that *in situ* generated ruthenium(II) acetate or Ru(II) carbonate catalysts dramatically promote the direct arylation of functional arenes, even with aryl chlorides, and that the reaction can be applied to the synthesis of tridentate ligands.[16]

We have first modified the $RuX_2(L)(arene)$ pre-catalysts by exchanging the halide (X = Cl) by oxygenated ligand such as carboxylate (X = OAc) in order to favour O···H intramolecular interaction between $MeCO_2$ ligand and the substrate *ortho* C–H bond, and to use the carboxylate ligand as a shuttle trapping the proton from the C–H bond (Figure 1, Y = Me) and releasing it to the external base as was observed for a palladium catalyst and pivalic acid.[5]

As the exchange of chloride with acetate easily takes place in $[RuCl_2(p\text{-cymene})]_2$ **1**, precatalyst **2**[17] was *in situ* prepared by stirring the binuclear complex **1** with 4 equivalents of KOAc in NMP, for 1 h at room temperature.[18] Then the base (K_2CO_3 or KOAc), 2-pyridylbenzene and aryl bromide or chloride were added and the mixture heated at 120 °C for various periods of time (Eq. 1). The results are compared in Table 1.

The catalytic reaction performed with catalyst **1** and only K_2CO_3 shows that complete diarylation with PhBr can be achieved at 120 °C in 20 h as a reference reaction (entries 1 and 2) but more importantly that K_2CO_3 also easily allows the diarylation with PhCl in only 3 h (entries 1, 3 and 2, 4).

The use of *in situ* prepared catalyst **2**, on reaction of **1** and KOAc,[18] using K_2CO_3 as an additional base leads to complete diarylation with ArCl of 2-pyridylbenzene after only 1 h heating at 120 °C (entries 6, 8, 10). It is noteworthy that the use of KOAc as additional base with **2** is not as efficient as K_2CO_3 (entries 5 and 6) and this shows that both the coordinated oxygenated ligand OAc and the strength of the additional base are cooperating, thus suggesting the shuttle role of the OAc ligand even when present in a catalytic amount.

These experiments allowed the isolation of diarylated products, from the less reactive but more easily available aryl chlorides, **5a** (81%), **5b** (88%) and **5c** (86%), under the conditions of entries 6, 8 and 10.

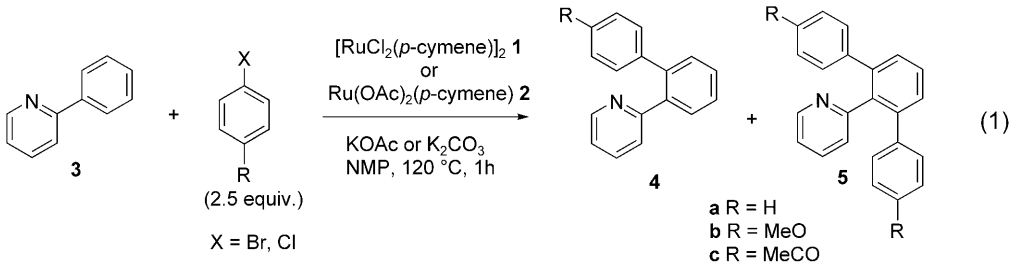


Table 1. Directed diarylation with ArBr and ArCl of 2-phenylpyridine with $[RuCl_2(p\text{-cymene})]_2$ **1** and *in situ* generated $Ru(OAc)_2(p\text{-cymene})$ **2**.

Entry	ArX	Catalyst	Base, time [h]	Conversion [%][c] (isolated%)[d]	Product ratio[c]
1[a]	C_6H_5Br	**1**	K_2CO_3 (3 h)	82	**4a/5a:** 23/77
2[a]	C_6H_5Br	**1**	K_2CO_3 (20 h)	100 (94%)[d]	**4a/5a:** 0/100
3[a]	C_6H_5Cl	**1**	K_2CO_3 (1 h)	73	**4a/5a:** 50/50
4[a]	C_6H_5Cl	**1**	K_2CO_3 (3 h)	100 (81)[d]	**4a/5a:** 0/100
5[a]	C_6H_5Cl	**1**	KOAc (1 h)	100	**4a/5a:** 48/52
6[b]	C_6H_5Cl	**2**[b]	K_2CO_3 (1 h)	100 (81)[d]	**4a/5a:** 0/100
7[a]	*p*-$MeOC_6H_4Cl$	**1**	K_2CO_3 (1 h)	62	**4b/5b:** 58/42
8[b]	*p*-$MeOC_6H_4Cl$	**2**[b]	K_2CO_3 (1 h)	100 (88)[d]	**4b/5b:** 0/100
9[a]	*p*-$MeCOC_6H_4Cl$	**1**	K_2CO_3 (1 h)	77	**4c/5c:** 25/75
10[b]	*p*-$MeCOC_6H_4Cl$	**2**[b]	K_2CO_3 (1 h)	100 (86)[d]	**4c/5c:** 0/100

[a] *Reaction conditions:* $[RuCl_2(p\text{-cymene})]_2$ **1** (0.0125 mmol), 2-phenylpyridine (0.5 mmol), ArX (1.25 mmol), base (1.5 mmol), NMP (1.5 mL), 120 °C.

[b] **2** is *in situ* prepared from KOAc (0.05 mmol) and precatalyst **1** (0.0125 mmol), stirred in NMP (1.5 mL) at room temperature for 1 h,[18] then base (1.5 mmol), 2-phenylpyridine (0.5 mmol) and ArX (1.25 mmol) were added.

[c] Determined by GC-analysis.

[d] Isolated yields after column chromatography.

Comparison of experiments with K_2CO_3 only (entries 3, 7, 9) shows that the diarylation with aryl chlorides is only slightly favoured by a *para* electron-withdrawing group R (R = MeCO > H > MeO).

The above results show that the *in situ* prepared $Ru(OAc)_2$(*p*-cymene) catalyst **2** with the base K_2CO_3 allows the most efficient diarylation of 2-pyridylbenzene with aryl chlorides.

It is noteworthy that precatalyst **1** with $MesCO_2H$ as additive has been successfully used for the direct arylation of arenes containing a heterocyclic functional group, in non-polar toluene at 100–120 °C for 16–20 h, under conditions also allowing the use of aryl chlorides.[12g]

The Ru acetate- and Ru carbonate-based[15] catalysts were then evaluated for the preparation of tridentate molecules containing three heterocyclic groups with tripodal ligand potential, the bis-(2,6-heteroaryl)(2-pyridyl)benzenes.

The reaction of 2-halopyridine **10a** with phenylpyridine was first attempted to prepare the tripodal tris-1,2,3-(2-pyridyl)benzene [Eq. (2)], and the results are displayed in Table 2. As expected from the use of 2-halopyridine in cross-coupling reactions,[19] the 2-halo-

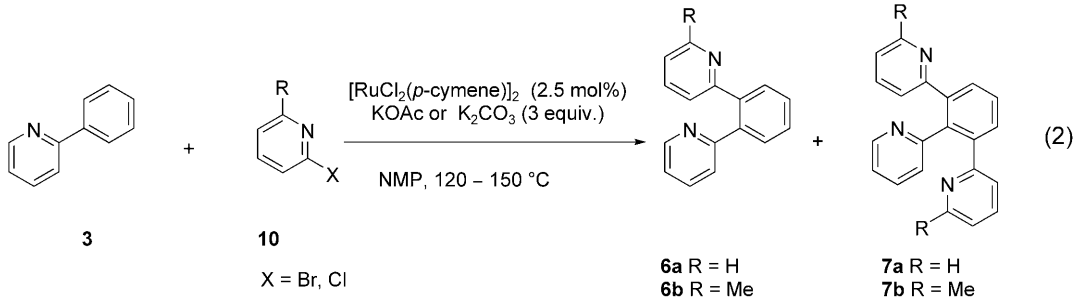
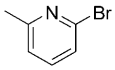
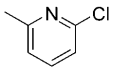
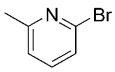
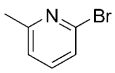
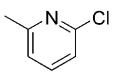
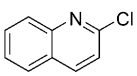


Table 2. Catalytic coupling of 2-phenylpyridine with 2-haloazaheterocycles.

Entry	Heterocycle-X	Conditions[a,b]	Conversion of **3** [%][c]	Products[d]
1	**10a** 	[a] KOAc, 120 °C, 24 h	67	60/40 (**6a**/**7a**)
2	**10a** 	[a] K_2CO_3, 150 °C, 48 h	55	76/24 (**6a**/**7a**) (30)/(10) (**6a**/**7a**)[e]
3	**10b** 	[a] KOAc, 120 °C, 24 h	47	100/0 (**6a**/**7a**)
4	**10c** 	[b] KOAc (10 mol%), K_2CO_3, 120 °C, 21 h	90	20/80 (**6b**/**7b**)
5	**10d** 	[b] KOAc (10 mol%), K_2CO_3, 120 °C, 24 h	55	42/58 (**6b**/**7b**)
6	**10c** 	KOAc, 120 °C, 24 h	77	55/45 (**6b**/**7b**) (29)/(21) (**6b**/**7b**)[e]
7	**10c** 	[a] K_2CO_3, 150 °C, 48 h	100	10/90 (**6b**/**7b**)
8	**10d** 	[a] K_2CO_3, 150 °C, 24 h	99	10/90 (**6b**/**7b**)
9	**10e** 	[a] K_2CO_3, 150 °C, 48 h	100	35/65 (**8**/**9**)[d] (17)/(36) (**8**/**9**)[e]

[a] *Reaction conditions:* $[RuCl_2(p\text{-cymene})]_2$ **1** (0.0125 mmol), 2-phenylpyridine (0.5 mmol), Het-X (1.25 mmol), KOAc or K_2CO_3 (1.5 mmol), NMP (1.5 mL), 120 °C.

[b] KOAc (10 mol%) and $[RuCl_2(p\text{-cymene})]_2$ **1** were stirred in NMP at room temperature for 1 h, then the base, 2-phenylpyridine (0.5 mmol), and 2-halopyridine **10** (1.25 mmol), were added.

[c] Determined on the basis of GC analysis.

[d] Determined on the basis of ^{1}H NMR analysis of the mixture.

[e] Yield of product isolated by column chromatography.

pyridines **10a–e** are not as reactive as aryl halides as the disubstitution is not completed after 24 h at 120 °C (entries 1 and 3).

The *in situ* prepared catalyst **2**, from **1** and KOAc,[18] is more active than **1** with only K_2CO_3 (entries 1 and 2). In this case the 2-chloropyridine appears much less reactive than the 2-bromopyridine (entries 1 and 3).

The 2-halo-6-methylpyridines **10c** and **d** are slightly more active than **10a** and **b** (entries 1, 6 and 2, 7). In the case of bromopyridine, the *in situ* prepared catalyst **2** in the presence of K_2CO_3 only slightly favours the direct functionalisation (entries 4 and 6). Thus an increase of the temperature to 150 °C is required to reach complete conversion of **3**, with **1**/K_2CO_3 after 48 h (entries 7 and 8), with high yield of diarylation product formation **7b** (90%). Quinolines **8** and **9** can also be obtained from 2-chloroquinoline but in lower yields (entry 9).

These results are consistent with a determining step which is now the oxidative addition, difficult to be performed with 2-halopyridines, rather than the easier formation of the *ortho*-metallated intermediate as with aryl halides (Table 1, Figure 1).

The ruthenium acetate-based catalyst **2** was evaluated with respect to the catalyst precursor **1** with K_2CO_3 for the preparation of tridentate ligands bis(2,6-thiophenyl)(2-pyridyl)benzenes [Eqs. (3) and (4)]. 2-Chloro- and 2-bromothiophenes react with 2-pyridylbenzene **3** in the presence of [$RuCl_2$(*p*-cymene)]$_2$ **1** and *in situ* made Ru(OAc)$_2$(*p*-cymene) **2** to afford tripodal molecules containing two thiophenyl groups separated by a 2-pyridyl group linked to a benzene ring: **13a, 13d** and **13c** [Eqs. (3) and (4), Table 3). The reaction conditions are much milder than those required for the reactions with halopyridynes (Table 2) as the dithiophenylated products **13a** and **13b** can be quantitatively obtained after 12 h at 120 °C.(Table 3, entries 5, 8, 9).

The results in Table 3 show that the *in situ* generated RuOAc catalyst again strongly favours the direct arene substitution with halothiophene with respect to the use of catalyst precursor **1** with K_2CO_3 (entries 1, 3 and 4, 5).

The actions of **1** with KOAc or **2** with K_2CO_3 are similar (entries 5 and 6), but surprisingly the chloro derivative seems to be more active than the bromo derivative (entries 2, 4 and 3, 5) and than the 2-iodothiophene (entry 7).

Thus, the reaction starting with chlorothiophene under entry 5 conditions allows the isolation of **13a** in 86% yield. The reaction can be applied to 3-chlorothiophene [Eq. (4), Table 3, entries 8 and 9) and derivative **13b** was isolated in 86% yield.

On reaction of **3** with the bromothiophenyl ketone **11e** and KOAc in the presence of **1**, the dithiophenylated product **13c** can be isolated in 89% yields (entry 10).

In conclusion, the above results show that the *in situ* generated catalyst Ru(OAc)$_2$(*p*-cymene) is very active for the *ortho* C–H bond diarylation of 2-pyridylbenzene with unactivated aryl chlorides with 1.5 equivalents of K_2CO_3 at 120 °C for 1 h. This catalytic system strongly favours the *ortho* C–H bond cleavage by cooperative assistance of the coordinated (OAc) oxygen atom and the ruthenium(II) centre to generate the *ortho*-metallated intermediate[11] that further allows oxidative addition of even aryl chlorides and reductive elimination with C–C bond formation.

The *ortho* difunctionalisation of 2-pyridylbenzene with 2-halopyridines and with 2- or 3-halothiophenes can be achieved to generate tris(2-pyridyl) ligands and a mixed tridentate 2-pyridylbis(thiophenyl) ligand. However, the conditions are more drastic with 2-halopyridines than for halothiophenes. The results with unreactive 2-halopyridines suggest that the determining step of the reaction is no longer the formation of the *ortho*-metallated intermediate but the more difficult to perform oxidative addition of the 2-haloheterocycles.

Ruthenium(II) carboxylate catalysts with functional arenes appear to favour the *ortho*-metallation inter-

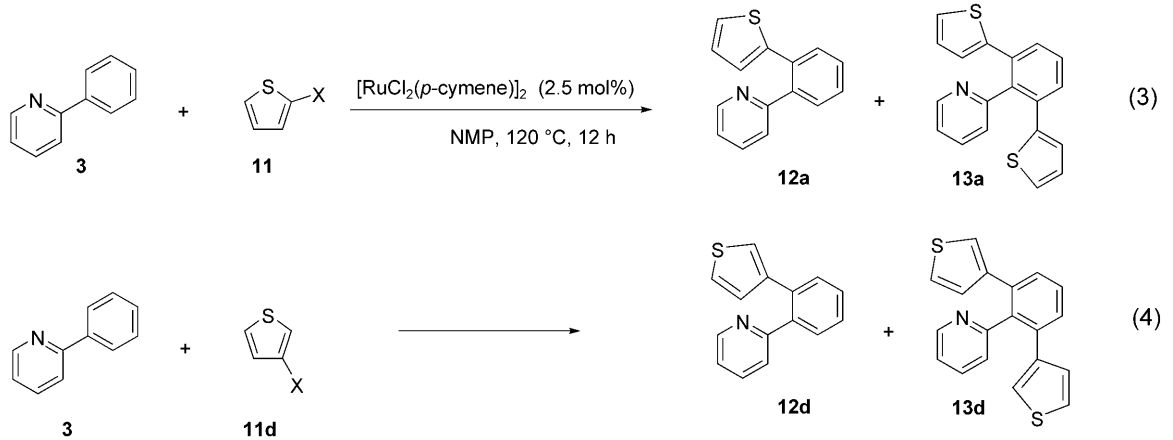
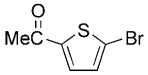


Table 3. Catalytic coupling of 2-phenylpyridine with 2- or 3-halothiophenes.

Entry	Het-X	Conditions[a,b]	Conversion [%][c] (isolated yield [%])[d]	**12/13**[c]
1	**11b** 	[a] K_2CO_3, 120 °C, 24 h	53	80/20 (**12a**/**13a**)
2	**11b** 	[a] K_2CO_3, 120 °C, 12 h	25	40/60 (**12a**/**13a**)
3	**11b** 	[a] KOAc, 120 °C, 24 h	100	2/98 (**12a**/**13a**)
4	**11a** 	[a] K_2CO_3, 120 °C, 12 h	73	23/77 (**12a**/**13a**)
5	**11a** 	[a] KOAc, 120 °C, 12 h	100 (86)[d]	2/98 (**12a**/**13a**)
6	**11a** 	[b] KOAc (10 mol%), K_2CO_3, 120 °C, 12 h	97	5/95 (**12a**/**13a**)
7	**11c** 	[a] K_2CO_3, 150 °C, 48 h	54	66/34 (**12a**/**13a**)
8	**11d** 	[b] KOAc (10 mol%), K_2CO_3, 120 °C, 24 h	100 (83)[d]	0/100 (**12b**/**13b**)
9	**11d** 	[a] KOAc, 120 °C, 12 h	100 (86)[d]	0/100 (**12b**/**13b**)
10	**11e** 	[a] KOAc, 120 °C, 12 h	100 (89)[d]	0/100 (**12c**/**13c**)

[a] *Reaction conditions:* $[RuCl_2(p\text{-cymene})]_2$ **1** (0.0125 mmol), 2-phenylpyridine (0.5 mmol), halothiophene (1.25 mmol), KOAc or K_2CO_3 (1.5 mmol), NMP (1.5 mL), 120 °C.
[b] KOAc (10 mol%) and $[RuCl_2(p\text{-cymene})]_2$ **1** were stirred in NMP at room temperature for 1 h, then the base, 2-phenylpyridine (0.5 mmol), and 2-halothiophene (1.25 mmol), were added.
[c] Determined on the basis of GC analysis.
[d] Yield of product isolated by column chromatography.

mediate formation and it can be proposed that they will be efficient for the catalytic functionalisation of the C–H bond when oxidative addition of an sp^2-C–X bond on the *ortho*-metallated intermediate will be easily feasible.

Experimental Section

General Procedure for the Catalytic Diarylation of 2-Pyridylbenzene with Aryl Chlorides

Catalytic system **2** was *in situ* prepared from KOAc (0.05 mmol) and $[RuCl_2(p\text{-cymene})]_2$ **1** (7.7 mg, 0.0125 mmol), on stirring in NMP (1.5 mL) at room temperature for 1 h, then the base KOAc or K_2CO_3 (1.5 mmol), 2-phenylpyridine (0.5 mmol) and aryl chloride (1.25 mmol) were added. The resulting mixture was stirred at 120 °C for 1 h. Water (35 mL) and ethyl acetate (25 mL) were added to the cold reaction mixture. The separated organic phase was washed with water (2×25 mL). The combined aqueous layers were extracted with ethyl acetate (3×25 mL). The remaining residue was purified by column chromatography on silica gel. Compounds **5a, 5b**, and **5c** were thus obtained in 81, 88 and 86% yields, respectively.

General Procedure for the Catalytic Disubstitution of 2-Pyridylbenzene with 2-Haloheterocycles

To the mixture of $[RuCl_2(p\text{-cymene})]_2$ **1** (7.7 mg, 0.0125 mmol), base KOAc or K_2CO_3 (1.5 mmol) and NMP (1.5 mL), 2-phenylpyridine (78 mg, 0.5 mmol) and 2-haloheterocycle (1.25–1.5 mmol) were added. The resulting mixture was stirred at the temperature and for the time indicated in the tables and the compounds were isolated as mentioned above. After 12 h of reaction at 120 °C of 2-phenylpyridine with chlorothiophenes, compounds **13a, 13b** and **13c** were thus isolated in 86, 86 and 89% yields, respectively.

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