Diethyl carbonate as a solvent for ruthenium catalysed C–H bond functionalisation†

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The ruthenium catalysed direct functionalisation of arene C–H bonds by aryl halides is reported. Reactions were performed in diethyl carbonate (DEC) instead of *N*-methylpyrrolidone (NMP), the solvent of choice used in most ruthenium catalysed C–H bond transformations. The use of diethyl carbonate facilitates the workup procedure thus reducing the amount of waste water. The slight loss of activity due to the use of diethyl carbonate is counterbalanced by the improvement of the catalyst efficiency achieved by a judicious choice of additives. Several arenes containing an *N*-heterocycle as a directing group have been diarylated.

Introduction

Transition metal catalysed functionalisation of C–H bonds[1] has received much attention over the last few years as a greener alternative to conventional cross-coupling reactions.[2] As compared to cross-coupling reactions, direct arene C–H bond arylation with aryl halides does not require the synthesis of metal containing substrates (Li, B, Sn, Zn, Mg, *etc.*) and does not produce by-products besides acid formation. Functionalisation of (hetero)arene C–H bonds is now possible under various catalytic conditions requiring in some cases a directing group. Palladium[3] and rhodium[4] have been extensively used for the functionalisation of sp^2 C–H bonds, however recent examples have emerged using ruthenium,[5] nickel,[6] rhenium,[7] copper,[8] iron,[9] iridium[10] and manganese catalysts.[11] A very efficient *in situ* generated ruthenium catalyst based on ruthenium(II)-acetate operating in *N*-methylpyrrolidinone (NMP) as solvent and allowing the direct arylation with inexpensive aryl chloride partners under very short reaction times has just been reported,[12] but as in most metal catalysed C–H bond functionalisation a reaction temperature as high as 120 °C was required to ensure high catalytic efficiency. Thus, in order to enable the transformation of usually reluctant substrates and to comply with the requirement of sustainable chemistry, catalysts with enhanced activity operating under milder conditions in non-toxic solvents are strongly desired. In addition, as is the case in most of the ruthenium catalysed directed arylations, the polar and high boiling point NMP is the solvent of choice, although catalytic C–H bond transformations were recently performed in toluene.[5b] So far, the use of more eco-friendly carbonate solvents has not been reported for such transformations. Consequently, we focused our efforts to perform C–H bond functionalisations in carbonate solvents which are known to be non-toxic and more environmentally acceptable.[13] Some examples of their use in homogeneous catalysis were recently reported by Börner *et al.* for asymmetric hydrogenation and allylic substitution reactions.[14] Several other catalytic transformations[15] including olefin metathesis[16] have also been reported in carbonate solvents. Here, the net benefit is not only the replacement of a solvent by a less toxic one, but the use of diethyl carbonate also reduces waste products by strongly facilitating the workup procedure. Herein we show for the first time that metal catalysed C–H bond functionalisation can be performed in diethyl carbonate and new ruthenium(II) based catalytic systems with improved efficiencies can allow these reactions to be performed at temperatures as low as 80 °C.

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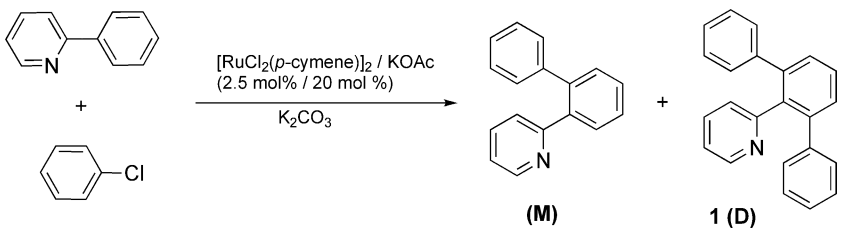
Results and discussion

The directed C–H bond functionalisation of phenylpyridine was selected as our model reaction as it is one of the benchmark substrates used to evaluate the efficiency of new catalysts (Scheme 1). In a typical experiment, phenylpyridine was reacted



Scheme 1 Ruthenium catalysed arylation of phenylpyridine.

Table 1 Arylation of phenylpyridine with $[RuCl_2(p\text{-cymene})]_2$/KOAc and various additives[a]

Entry	Solvent	Additive[b]	*t*/h	Conv. (%)[c]	M : D[d]	**1** (%)[e]
1	NMP	—	1	100	0 : 100	95
2	DEC	—	5	83	40 : 60	—
3	DEC	—	9	100	0 : 100	96
4	DEC	NMP (10 mol%)	4	87	30 : 70	—
5	DEC	NMP (20 mol%)	4	94	29 : 71	65
6	DEC	**A**	4	100	0 : 100	95
7	DEC	**B**	4	100	0 : 100	—
8	DEC	**C**	2	100	0 : 100	96
9	DEC	**D**	2	100	0 : 100	94
10	DEC	**E**	2	93	30 : 70	68
11	DEC	**F**	4	62	46 : 54	—
12	DEC	**G**	4	63	55 : 45	—
13	DEC	**H**	4	60	60 : 40	—

[a] Phenylpyridine (0.5 mmol), PhCl (1.25 mmol, 2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), KOAc (10 mol%), 2 mL of solvent, K_2CO_3 (3 equiv.), 120 °C. [b] 20 mol%. [c] Conversion determined by gas chromatography using tetradecane as internal standard. [d] Ratio monoarylated : diarylated (**1**) products determined by gas chromatography. [e] Isolated yields.

with an excess of phenyl chloride in the presence of ruthenium acetate catalyst prepared *in situ* from $[RuCl_2(p\text{-cymene})]_2$ and KOAc.[17] The efficiency of the reaction was reflected by the phenylpyridine conversion and the ratio of mono (M) and disubstituted (D) products (Scheme 1).

The catalytic system based on $[RuCl_2(p\text{-cymene})]_2$/KOAc was first tested in diethyl carbonate at 120 °C. We were pleased to observe that the reaction proceeded to completion in 9 h affording the diarylated product **1** in 96% yield (Table 1, entry 3). Since the same reaction required only 1 h in NMP as solvent (Table 1, entry 1), we evaluated the influence of NMP as an additive in diethyl carbonate. Thus, the reactions were performed with 10 and 20 mol% of NMP in diethyl carbonate resulting in improved conversions (Table 1, entries 2, 4 and 5). Encouraged by these results, several other amide and carbamate additives were tested (Fig. 1).

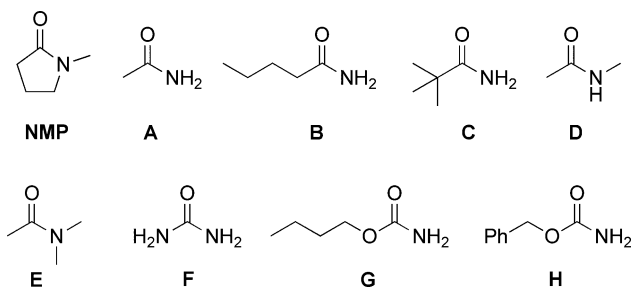


Fig. 1 Additives tested in the $[RuCl_2(p\text{-cymene})]_2$/KOAc catalysed arylation of phenylpyridine.

This screening unambiguously showed the superiority of amides as additives. In particular acetamide **A** and pivalamide **C** allowed complete diarylation in 4 h and 2 h leading to 95 and 96% isolated yield of **1**, respectively, *i.e.* in a short reaction time considering the use of phenyl chloride (Table 1, entries 6 and 8). *N*-Methyl acetamide **D** also increased the catalyst performances but not to a sufficient extent with regard to its toxicity and was therefore discarded (Table 1, entry 9). These results show that amides act as catalyst partners in diethyl carbonate.

With this efficient system in hand we then focused on the nature of the carboxylate salt as it was demonstrated that carboxylates play a crucial role in the C–H bond activation *via* a ligand or base assisted proton abstraction.[18] This type of mechanism was recently invoked for palladium by Lafrance and Fagnou[3f] and ruthenium[5b] C–H bond functionalisation. In both cases a carboxylic acid was initially used and supposed to *in situ* generate a metal–carboxylate complex. Having obtained very good results using potassium acetate with amide additives, we evaluated a similar procedure using potassium pivalate and acetamide **A** or pivalamide **C** as additives. The results depicted in Table 2 show that at 120 °C the catalytic system generated *in situ* from $[RuCl_2(p\text{-cymene})]_2$ and KOPiv is as efficient as the three-components system based on $[RuCl_2(p\text{-cymene})]_2$, KOAc and amide additives. However in that case amide additives did not improve the efficiency of the KOPiv system (Table 2 and Table 1, entries 3, 6 and 8).

The efficiency of the new ruthenium carboxylate catalysts has been evaluated at lower temperatures using acetamide and pivalamide as additives in 20 mol% amounts (Table 3). At

Table 2 Arylation of phenylpyridine at 120 °C in DEC with $[RuCl_2(p\text{-cymene})]_2$/KOPiv catalyst[a]

Entry	Additive[b]	*t*/h	Conv. (%)[c]	M : D[d]	**1** (%)[f]
1	—	2	100	0 : 100	96
		1	100	6 : 94	
		4	100	7 : 93[e]	
2	**A**	2	100	0 : 100	94
		1	100	10 : 90	
3	**C**	1	100	10 : 90	—

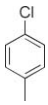
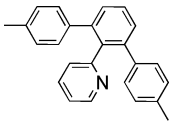
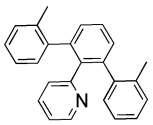
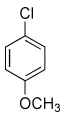
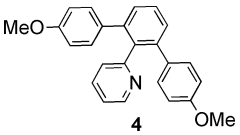
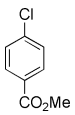
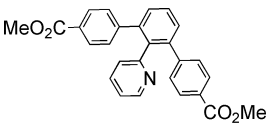
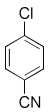
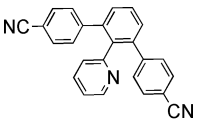
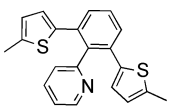
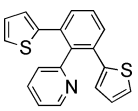
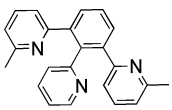
[a] Phenylpyridine (0.5 mmol), PhCl (1.25 mmol, 2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), KOPiv (10 mol%), K_2CO_3 (3 equiv.), DEC (2 mL), 120 °C. [b] 20 mol%. [c] Conversion determined by gas chromatography using tetradecane as internal standard. [d] Ratio monoarylated : diarylated (**1**) products determined by gas chromatography. [e] $[RuCl_2(p\text{-cymene})]_2$ (1 mol%), DEC (2 mL), K_2CO_3 (3 equiv.), additive (4 mol%), 120 °C. [f] Isolated yields.

Table 3 Arylation of phenylpyridine in DEC at 100 °C and 80 °C with $[RuCl_2(p\text{-cymene})]_2/KO_2CR$[a]

Entry	*T*/°C	KO_2CR[b]	Additive	*t*/h	Conv. (%)[c]	M : D[d]
1	100	KOAc	—	4	53	55 : 45
			A	10	98	15 : 85
				16	100	0 : 100
			C	4	91	29 : 71
				6	100	0 : 100
2	100	KOPiv	—	4	100	7 : 93
			A	4	100	1 : 99
			C	4	100	1 : 99
3	80	KOAc	—	16	24	59 : 41
			A	16	64	46 : 54
			C	10	70	47 : 53
				20	100	0 : 100
4	80	KOPiv	—	14	98	30 : 70
				18	100	0 : 100
			A	14	100	34 : 66
			C	14	100	20 : 80

[a] Phenylpyridine (0.5 mmol), PhCl (1.25 mmol, 2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), KOAc or KOPiv (10 mol%), K_2CO_3 (3 equiv.), DEC (2 mL). [b] 20 mol%. [c] Conversion determined by gas chromatography using tetradecane as internal standard. [d] Ratio monoarylated : diarylated (**1**) products determined by gas chromatography.

Table 4 $[RuCl_2(p\text{-cymene})]_2$/KOPiv catalysed arylation of phenylpyridine in DEC[a]

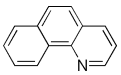
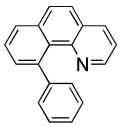
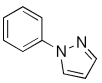
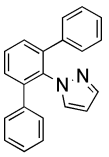
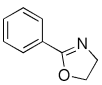
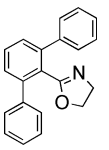
Entry	Ar–X	T/°C	t/h	C (%)[b]	Product	M : D[c]	Y (%)[d]
1		100 80	16 61	100 100	 **2**	1 : 99 1 : 99	97
2		120	24	100	 **3**	8 : 92	90
3		100 80	24 61	100 100	 **4**	1 : 99 1 : 99	92 —
4		100	16	100	 **5**	0 : 100	82
5		120 100	24 16	100	 **6**	4 : 96 20 : 80	80
6		120	16	100	 **7**	1 : 99	96
7		100	10	100	 **8**	3 : /97	94
8		120 80	16 61	100 100	 **9**	8 : 92 7 : 93	38[e]

[a] Phenylpyridine (0.5 mmol), ArCl (1.25 mmol, 2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), KOPiv (10 mol%), K_2CO_3 (3 equiv.), DEC (2 mL). [b] Conversion determined gy gas chromatography using tetradecane as internal standard. [c] Ratio monoarylated : diarylated (**1**) products determined by gas chromatography. [d] Diarylated product isolated yield. [e] Product partially decomposed during purification on SiO_2 or Al_2O_3.

100 °C, **1** was obtained quantitatively in 6 h using the catalytic system based on KOAc/pivalamide (Table 3, entry 1) and in only 4 h with KOPiv (Table 3, entry 2). Lowering further the reaction temperature to 80 °C resulted in a loss of activity but it is noteworthy that **1** could still be obtained in a reasonable time of 20 h with the KOAc/pivalamide system (Table 3, entry 3) and in 18 h with KOPiv only (Table 3, entry 4). In both cases, the benefit of using amide additives was only observed with the system based on acetate. Further studies are ongoing to understand the origin of this amide effect. It can be postulated that the steric hindrance of the pivalate ligands may prevent the coordination of amides to the ruthenium site whereas this coordination is not prevented by acetate ligands.

The two component system $[RuCl_2(p\text{-cymene})]_2$ and KOPiv in diethyl carbonate was selected to further extend the scope of the reaction to various aryl halide substrates. As depicted in Table 4,

Table 5 Arylation of *N*-containing heteroaromatics[a]

Entry	Substrate	PhX	*T*/°C	*t*/h	Conv. (%)[b]	Product	M : D[c]	Y (%)[d]
1		X = Cl X = Br X = Br	120 120 120	24 24 68	52 78 94	 **10**	— —	— 70
2		X = Cl X = Cl	120 80	10 24	100 100	 **11**	4 : 96 7 : 93	91 89
3		X = Cl X = Cl	120 100	16 61	100 43	 **12**	0 : 100 1 : 99	96

[a] Heteroaromatic derivative (0.5 mmol), PhCl (1.25 mmol, 2.5 equiv.), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), KOPiv (10 mol%), DEC (2 mL), K_2CO_3 (3 equiv.). [b] Conversion determined gy gas chromatography using tetradecane as internal standard. [c] Ratio Monoarylated/diarylated (**1**) products determined by gas chromatography, (diarylated product isolated yield). [d] Diarylated product isolated yield except for entry 1.

the reaction proceeded with high efficacy with electron-donating or electron-withdrawing substituted aryl chlorides. With electron-donating *p*-substituted aryl derivatives the reaction proceeded in 16 h or 24 h at 100 °C (Table 4, entries 1 and 3) and could even be performed at 80 °C (Table 4, entries 1 and 3). The sterically hindered *o*-chlorobenzene required higher reaction temperature to reach full conversion in 24 h with high selectivity for the bis-arylated product **3** (Table 4, entry 2). The transformation of aryl halides bearing electron-withdrawing groups was also found to proceed with high efficacy. For instance, the ester substituted derivative reacted under mild conditions in 16 h to provide **5** in high yield (Table 4, entry 4). The more electron-withdrawing cyano substituted derivative could also be transformed efficiently, however this reaction required 24 h heating at 120 °C (Table 4, entry 5).

The ruthenium carboxylate catalysed C–H bond functionalisation in diethyl carbonate was also applicable to heteroaromatic halides leading to an efficient transformation of 2-chlorothiophenes and a bromo pyridine derivative. In particular the mixed thiophene–pyridine compound **8** and the tris-pyridine derivative **9** were obtained with high conversions at 100 °C, 120 °C and 80 °C (Table 4, entries 7 and 8).

The $[RuCl_2(p\text{-cymene})]_2$/KOPiv catalyst was then considered for the arylation of other *N*-heterocyclic substrates of interest as pharmaceutical building blocks or dyes (Table 5). α-Benzoquinoline was found difficult to arylate and the use of the bromide derivative was in this particular case necessary to obtain high conversion and yield at 120 °C in 24 h (Table 5, entry 1). On the other hand, phenyl pyrazole and phenyloxazoline were more efficiently arylated at lower temperatures. Arylation of phenyl pyrazole could be achieved at 80 °C in 24 h providing **11** in 89% yield (Table 5, entry 2). Phenyloxazoline could also be arylated at low temperature using phenyl chloride but higher temperature was necessary to ensure high conversion in 16 h providing **12** in high yield (Table 5, entry 3).

As mentioned earlier, in all the experiments presented herein, the use of diethyl carbonate strongly facilitated the workup procedure and also contributed to the reduction of wastes. Indeed, diethyl carbonate can easily be removed by distillation and recycled whereas efficient removal of *N*-methylpyrrolidinone, the solvent of choice for ruthenium catalysed C–H bond functionalisations, requires numerous water washings.

Conclusion

In summary, we have presented two new catalytic systems for sp^2 C–H bond functionalisation with enhanced performances operating in diethyl carbonate, an eco-friendly solvent. These catalysts based on the easily available $[RuCl_2(p\text{-cymene})]_2$ and potassium carboxylates allow the efficient transformation of inexpensive aryl halides at temperatures as low as 80 °C. Depending on the nature of the carboxylate used, amide additives were shown to boost the catalyst activity to a large extent. The activity of the $[RuCl_2(p\text{-cymene})]_2$/KOAc system was strongly increased by the addition of amides whereas the $[RuCl_2(p\text{-cymene})]_2$/KOPiv system was not influenced by the addition of the same amides. The use of diethyl carbonate instead of NMP also contributed to the reduction of wastes by avoiding fastidious water extractions source of large amounts of waste.

Experimental

Typical experimental procedures, spectroscopic and analytical data are provided as supplementary data.†

Acknowledgements

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