Catalysis in Water

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C–H Bond Functionalization in Water Catalyzed by Carboxylato Ruthenium(II) Systems**

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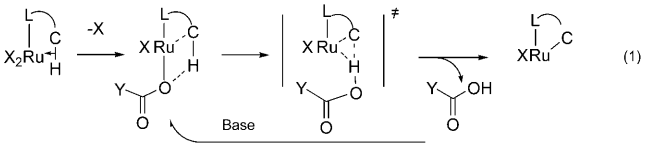
Direct metal-catalyzed C–H bond activation/functionalization reactions have become a topic of tremendous interest[1] owing to their potential to replace the classical catalytic cross-coupling reactions, without the intermediate formation of organometallic C–M species (M = metal center). Significant achievements in this field have already been reached using palladium[2,3] and rhodium[4] catalysts. Ruthenium(0)[5,6] and recently ruthenium(II)[7–11] systems have contributed to the functionalization of C–H bonds through two different processes. In parallel, the contribution of various metal catalysts for the functionalization of C–H bonds has also been reported.[12]

For the formation of C–C bonds directly from aromatic sp^2C–H bonds, initial studies suggested an electrophilic substitution reaction of the arene by Pd^{II} or Ru^{IV} species that are generated in situ from aryl bromide or aryl iodide oxidative addition to the Pd^0 and Ru^{II} catalysts. Significant recent contributions by Fagnou and co-workers[3a–d] and Echavarren, Maseras, and co-workers[13] based on both experimental studies with Pd^0 catalysts and density functional theory (DFT) calculations, support a concerted metalation–deprotonation mechanism. With ruthenium(II) catalysts, the influence of coordinated carbonate, as supported by DFT calculations, indicates a mechanism based on the cooperative actions of both the Ru^{II} site and the carbonate ligand for C–H bond deprotonation. This step generates a cyclometalated species before the oxidative addition of arylhalides.[9] [Eq. (1); X = halide, carboxylate; Y = OH, Me]. This result revealed the tremendous positive influence of coordinated carboxylate ligands, assisted by ruthenium(II), for C–H bond functionalization.[10] The beneficial influence of a carboxylate ligand coordinated to Pd^{II}[3] and Ru^{II} centers[8d] has also been demonstrated.

The concerted intramolecular deprotonation of inert C–H bonds with the assistance of a coordinated ligand appears to be a general phenomenon.[14,15]

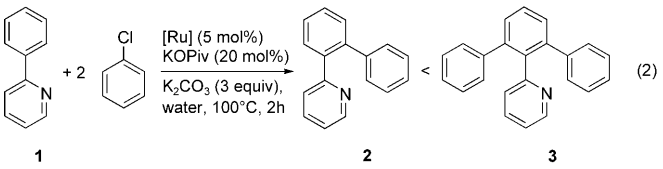


(1)

This intramolecular C–H bond deprotonation mechanism, rather than an electrophilic substitution, suggests that such a process could take place in water with ruthenium(II) catalytic systems, as some ruthenium(II) catalysts have already been shown to be stable for several catalytic transformations in water.[16] Catalysis in water is developing not only to avoid the use of organic solvents as reaction medium but also to reach better catalytic activity and regioselectivity.[17,18]

A few examples of palladium-catalyzed C–H bond functionalization in water have just been shown,[18,19] including the *ortho* C–H bond functionalization by Lipshutz and co-workers for the coupling of arylureas with aryl iodide and for the alkenylation of phenylamides in the presence of a surfactant.[19]

We now report that [$Ru(O_2CR)_2$(arene)] catalysts 1) can efficiently perform the direct *ortho* arylation of functional arenes with aryl chlorides in water, without the need for surfactant, 2) when they operate in water these catalysts can lead to a better catalyst activity than in an organic solvent (N-methylpyrrolidone (NMP)), and 3) they allow selective C–C bond formation leading to a variety of functional arenes and polyheterocycles including potential polydentate ligands [Eq. (2); KOPiv = potassium pivalate].



(2)

Our preliminary study showed that the direct arylation of 2-phenylpyridine **1** in water preferentially takes place according to the sequence of arylhalides PhCl > PhBr > PhI, a result of decreasing arylhalide solubility, and bases K_2CO_3 > $KHCO_3$ > Me_4NOH (see Tables S1 and S2 in the Supporting Information). 2-Phenylpyridine **1** (0.5 mmol) was treated with phenylchloride (1.25 mmol) in the presence of 5 mol% of various ruthenium(II) catalysts in the presence of 2 equivalents of KO_2CR ligand precursor in distilled water (2 mL), with 3 equivalents of K_2CO_3 as a base at 100 °C for 2 h. The results displayed in Table 1 show that ruthenium(II) catalysts

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Table 1: Direct arylation of 2-phenylpyridine with PhCl in water.[a]

Entry	Catalyst	Conv. [%]/*t* [h]	**2/3**
1	$RuCl_3 \cdot 3H_2O$	–	–
2	[RuCl(dppb)(*p*-cymene)]Cl	68/2	75/25
3	$RuCl_2\{P(OMe)_3\}$(*p*-cymene)]	100/2	58/42
4	$[RuCl_2(PPh_3)$(*p*-cymene)]	100/2	74/26
5	$[RuCl_2(PPh_3)_3]$	–	–
6	$[\{RuCl_2$(*p*-cymene)$\}_2]$ (**A**)[b]	100/2	9/91
7	$[\{RuCl_2$(*p*-cymene)$\}_2]$ (**A**)[b]	100/4	0/100
8	$[\{RuCl_2$(*p*-cymene)$\}_2]$ (**A**)[c]	100/6	9/91
9	$[Ru(O_2CtBu)_2$(*p*-cymene)] (**B**)[d]	99/1	6/96
10	$[Ru(O_2CtBu)_2$(*p*-cymene)] (**B**)[d]	100/2	0/100

[a] 2-phenylpyridine (0.5 mmol), ruthenium catalyst (5 mol%), K_2CO_3 (3 equiv), tetradecane (10 μL as GC internal standard), potassium pivalate (20 mol%), chlorobenzenze (1.25 mmol), and distilled water (2 mL). [b] 2.5 mol% of **A**. [c] 1 mol% of **A**. [d] 10 mol% of isolated **B**.[20]

Table 2: Ligand influence on reaction of 2-phenylpyridine (**1**) with phenyl chloride in water with ruthenium catalyst **A**.[a]

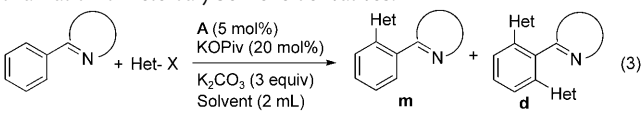
Entry	Solvent	KO_2CR	*T* [°C]	*T* [h]	Conv [%]	**2/3**
1	water	KOAc	100	2	100	26/74
2	water	KOPiv	100	2	100	0/100
3	water	–	100	2	97	21/79
4	water	KOAc[b]	100	2	92	77/23
5	water	KOPiv[c]	100	2	62	93/7
6	NMP	KOPiv	100	2	100	25/75
7	DEC	KOPiv	100	2	100	45/55
8	water	KOPiv	80	4	100	0/100
9	water	KOPiv	60	24	100	9/91
10	water	KOPiv	25	62	100	17/83

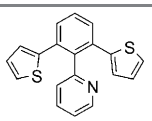
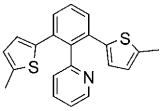
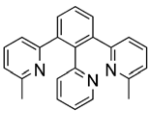
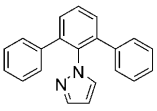
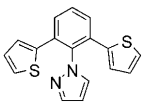
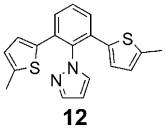
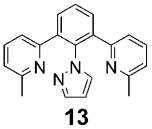
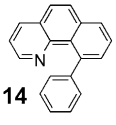
[a] **1** (0.5 mmol), **A** (5 mol%), KO_2CR (20 mol%), K_2CO_3 (3 equiv), PhCl (1.25 mmol), 2 mL of water or other solvent. [b] No K_2CO_3 but 3 equivalents of KOAc. [c] No K_2CO_3 but 3 equivalents of KOPiv.

are operative in water, even with the least-reactive arylchloride. As an attempt to reach diarylation, the best system appears to be the in-situ-generated catalyst from $[\{RuCl_2(p\text{-cymene})\}_2]$ (**A**) with 2 equivalents of potassium pivalate (KO_2CtBu) per ruthenium atom, which was shown to give the complex $[Ru(O_2CtBu)_2(p\text{-cymene})]$ (**B**).[20] Complete diarylation can be reached with this catalyst at 100 °C for 4 h with only 2.5 mol% of **A** and without surfactant (Table 1; entry 7). The use of well-defined (that is, isolated) **B** led to only slightly better results than the in-situ-prepared catalyst **B** from **A**[20] (Table 1; entries 7 vs. 10) and thus justifies the use of the more convenient in situ preparation of catalysts from ruthenium precursor and potassium carboxylates.

It is noteworthy that phosphine complexes (Table 1; entry 4), while promoting good conversion, favor monoarylation over diarylation. Based on the highest efficiency of the catalyst precursor **A**, the influence of carboxylate ligands in water on arylation of **1** with phenylchloride [Eq. (2)] has been investigated (Table 2). In water with **A**, the pivalate ligand is more efficient that the acetate one (Table 2; entries 1 and 2). Without K_2CO_3, 3 equivalents of KOAc per Ru atom, as the only base *and* ligand precursor, is not as efficient as the combination of 20 mol% KOAc (2 equivalents per ruthenium atom) and 3 equivalents of K_2CO_3 (Table 2; entries 1 and 4). Similar

Table 3: Functionalization of heteroarylbenzene derivatives.[a]



Entry	*T* [°C]	Solvent	*T* [°C]	Conv [%]	Product	**m**/**d**(yield)[b]
1	100	H_2O	10	100		1/99 (89)
		NMP	10	99	**7**	2/98
2	100	H_2O	10	100		1/99 (92)
		NMP	10	99	**8**	3/97
3	100	H_2O	20	100		0/100 (41)
		NMP	20	70	**9**	38/62
4	100	H_2O	2	100		0/100 (94)
	40	H_2O	62	100	**10**	3/97 (90)
5	100	H_2O	10	100		4/96 (90)
					11	
6	100	H_2O	100	100		3/97 (95)
		NMP	95	95	**12**	64/36
7	100	H_2O	100	100		3/97 (48)
		NMP	95	95	**13**	17/83
8	100	H_2O	100	100		– (83)
					14	

[a] Heteroarylbenzene (0.5 mmol), **A** (5 mol%) KOPiv (20 mol%), K_2CO_3 (3 equiv). Het-X (1.25 mmol; see text for the identity of Het-X in each entry), 2 mL of water. [b] Yield of isolated product in parenthesis.

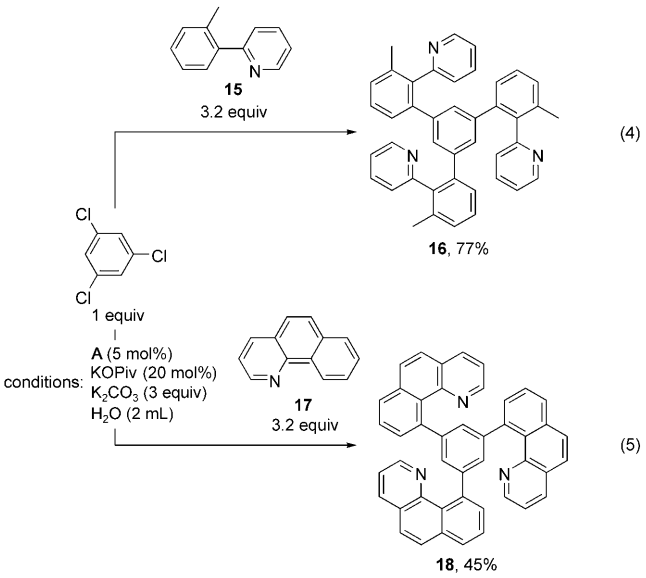
behavior is observed for pivalate with and without K_2CO_3 (Table 2; entries 2 and 5). K_2CO_3 alone without KO_2CR ligand is efficient at promoting the ruthenium(II) catalyst activity in water, but not as much as with the pivalate ligand (Table 2; entries 2 and 3). However, this result is an indication of the coordination of carbonate, as it also took place in other solvents.[9,21]

More importantly the C–H bond activation with ruthenium(II) catalysis performed in water appears to be more efficient than in organic solvents, such as *N*-methylpyrrolidone (NMP) or diethyl carbonate (DEC) (Table 2; compare entries 6, 7, and 2). It is noteworthy that in water, the temperature of the reaction can be decreased to 60 °C and even to room temperature but extended reaction times are necessary to reach complete conversion and high diarylation ratio (Table 2; entries 8–10). No efficient C–H bond functionalization could take place with Ru^{II} systems at these low temperatures in organic solvents.[8a,10b]

The best conditions (Table 2, entry 2) were used for the introduction of two heterocyclic groups in the *ortho* positions of heteroarylbenzene derivatives [Eq. (3) in Table 3). The formation of the disubstituted (**d**) product rather than the monosubstituted (**m**) one was attempted. Thus from 2-phenylpyridine **1** the C–C coupling of two thiophenyl groups and two 2-(6-methyl)(pyridyl) can be achieved in water with 2-chlorothiophene (**4**), 5-methyl-2-chlorothiophene (**5**; Table 3; entries 1, 2) and 6-bromo-2-picoline (**6**; Table 3; entry 3) leading, respectively, to the tridentate ligand 1,2,3-trisheteroaryl benzenes **7**, **8** and **9** which could be isolated in good yields. Note that the formation of these compounds in water was easier than in NMP (Table 3; entries 1–3).

N-phenyl pyrazole was employed and its *ortho*-diphenyl derivative **10** was isolated in 94 % yield (100 °C, 2 h) (Table 3; entry 4). The two bis-(*ortho*-2-thienyl) derivatives **11** and **12** were quantitatively formed and obtained in 90 % and 95 % yield upon reaction with 2-chlorothiophene (**4**), 5-methyl-2-chlorothiophene (**5**), respectively (Table 3; entries 5, 6). From *N*-phenyl pyrazole and 6-bromo-2-picoline (**6**) the bis 2-pyridyl derivative **13** was formed and identified by GC/MS but decomposed during separation on silica (Table 3; entry 7). The monoarylation of 7,8-benzoquinoline with phenylchloride performed in water produced the derivative **14** in 83 % yield (Table 3; entry 8). The same transformation in DEC led only to 53 % conversion after 24 h at 120 °C.

Polydentate ligands containing pyridyl coordinating groups are receiving interest for their use in catalysis,[22] but now more importantly for molecular material for optics.[23] Their importance thus requires that new methods of direct preparation are found. The easy direct arylation with arylchlorides in water led us to extend this reaction to the arylation of 2-(2-pyridyl)toluene (**15**) with 1,3,5-trichlorobenzene for the production of the tridentate ligand **16**. The reaction in water under reflux for 36 h led to the isolation of the 1,3,5-trispyridylbenzene (**16**) in 77 % yield, [Eq. (4)] whereas in NMP at 150 °C for 24 h only 45 % of **16** were formed. The reaction of benzoquinoline (**17**) with 1,3,5-trichlorobenzene in refluxing water for 36 h led to the isolation of trisbenzoquinoline (**18**) in 45 % yield [Eq. (5)] whereas 40 % were obtained in NMP after 24 h at 150 °C.



The above results show that it is now possible to perform ruthenium(II) catalyzed sp^2C–H bond functionalization of functional arenes in water without surfactant on reaction even with aryl and heteroaryl chlorides. The preferential influence of $[Ru(O_2CtBu)_2(p\text{-cymene})]$ (**B**) is shown in the presence of K_2CO_3. The activity of these catalyst systems in water is compatible with concerted C–H bond deprotonation process and appears to be higher than in organic solvent (NMP) allowing transformation at low temperature, including room temperature. Thus the reaction allows the grafting of two aryl or heteroaryl groups at the *ortho* positions of the arene functionality (pyridines, pyrazole) and trisheteroaryl benzene compounds can be directly produced from simple chloroheterocycles. The nature of the ruthenium catalyst operating in water from these precursors, with the non-innocent carbonate base, needs to be elucidated.

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