Chemical Science

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Cross coupling of thioethers with aryl boroxines to construct biaryls *via* Rh catalyzed C–S activation†

Cite this: *Chem. Sci.*, 2013, **4**, 1573

Received 15th December 2012
Accepted 8th February 2013

DOI: 10.1039/c3sc22242j

www.rsc.org/chemicalscience

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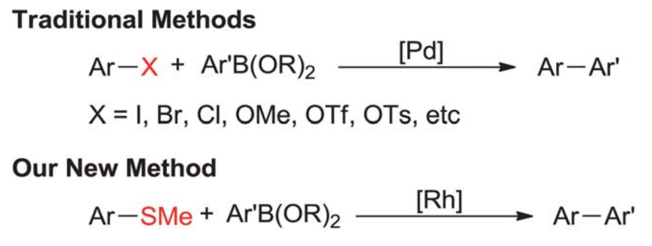
A novel rhodium-catalyzed C–C bond formation was developed to construct biaryls through unreactive aryl C–S bond cleavage of thioethers with aryl boroxines. This protocol provided a supplemental method of traditional Suzuki–Miyaura coupling.

Introduction

Biaryl structural units exist in a wide range of natural products, synthetic materials, pharmaceuticals and agrochemicals.[1] The Suzuki–Miyaura coupling has become one of the most useful tools to construct such units with the use of organohalides/pseudohalides and arylboronic acid derivatives (Scheme 1).[2] In the past several decades, *O*-based electrophiles have also been frequently applied in the Suzuki–Miyaura coupling.[3] Recently, arenes have been further explored with respect to direct coupling with arylboronic acid derivatives through oxidative coupling strategies.[4] Compared with other electrophiles, methyl aryl sulfides are also attractive due to their robustness and widespread existence in nature.[5] However, in general, the sulfur atom can be tightly bound to transition metals, which makes it poisonous towards transition metal catalysts. Although the cleavage of C–S bonds has been well studied with a vast range of transition metals as catalysts,[6] the construction of biaryl compounds through "inert" C–S bonds cleavage has been rarely reported. Herein, we present the first report of a successful example of the construction of carbon–carbon bonds through the cleavage of unreactive aryl C–S bond with aryl boroxines *via* Rh catalysis (Scheme 1).



Scheme 1 New strategy to construct biaryl compounds *via* aryl C–S activation.

As pioneers in the field of C–S activation, Liebeskind and co-workers have reported their successes in palladium or copper catalyzed cross-coupling reactions, starting from thioethers and thioesters.[7] Very recently, the cleavage of "inert" aryl C–SMe to deliver the carbothiolation of terminal alkynes was reported by Willis *et al.*[8] In our continued efforts towards the activation of C–H and C–C bonds, we found that rhodium catalysts showed advantages in cleaving "inert" bonds. Furthermore, the use of directing groups is a successful strategy to enable bond cleavage and further transformations.[9] Based on our experience and previous reports,[10] we envisioned that the cross-coupling could take place to construct C–C bonds through the cleavage of unreactive C–S bonds with the directing strategy in the presence of suitable Rh catalysts.

With the idea in mind, we first carried out the reaction with 1-(2-(methylthio)phenyl)ethanone (**1a**) as a model substrate under various conditions (Table 1). We found that, the desired product **3aa** was observed in 38% NMR yield with $[Rh(CO)_2Cl]_2$ as catalyst in the presence of Ag_2CO_3 and K_3PO_4 in toluene (entry 1). Moreover, the different solvents were tested (entries 1–4), and THF and DCE showed similar results. Further studies indicated that a mixed solvent (DCM–THF = 2 : 1) gave a better yield (entry 6). Among Rh catalysts, $[Rh(CO)_2Cl]_2$ presented the best yield (entry 6). To our delight, the homo-coupling of phenylboroxine was sufficiently suppressed under the optimized reaction conditions. Interestingly, Ni, Cu and Ru complexes also gave the desired product albeit in lower yields (entries 9–11). Different additives were examined, and Ag_2CO_3 gave the best results (entries 13 and 14). It is noteworthy that K_3PO_4 was the best base (entries 15–17). In the absence of either base or additive, the yields were sharply reduced (entries 18 and 19). Finally, complete conversion and a high yield were obtained by simply prolonging reaction time (entry 21).

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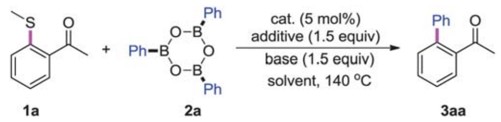
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3sc22242j

Table 1 Cross-coupling of 1-(2-(methylthio)phenyl)ethanone (**1a**) with phenylboroxine (**2a**) under various conditions[a]

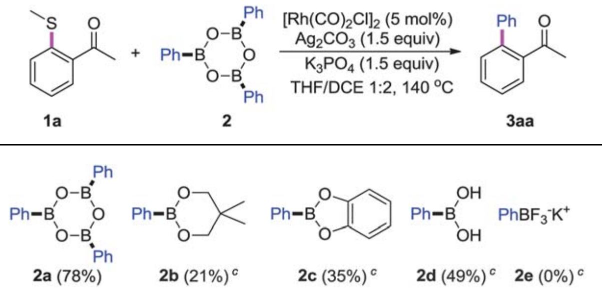


Entry	Catalyst	Additive	Base	Solvent	**3aa**[b] (%)
1	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	Toluene	38%
2	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	Dioxane	48%
3	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF	53%
4	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	DCE	56%
5	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 1	59%
6	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	83%
7	$Rh(COD)Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	42%
8	$Rh(acac)_3$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	0
9	$Pd(OAc)_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	62%
10	$Ni(PCy_3)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	5%
11	$Ru(COD)Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	47%
12	CuI	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	0
13	$Rh(CO)_2Cl_2$	Ag_2O	K_3PO_4	THF–DCE 1 : 2	17%
14	$Rh(CO)_2Cl_2$	$Cu(OAc)_2$	K_3PO_4	THF–DCE 1 : 2	26%
15	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_2CO_3	THF–DCE 1 : 2	46%
16	$Rh(CO)_2Cl_2$	Ag_2CO_3	Na_3PO_4	THF–DCE 1 : 2	18%
17	$Rh(CO)_2Cl_2$	Ag_2CO_3	CsOAc	THF–DCE 1 : 2	29%
18	$Rh(CO)_2Cl_2$	Ag_2CO_3	—	THF–DCE 1 : 2	19%
19	$Rh(CO)_2Cl_2$	—	K_3PO_4	THF–DCE 1 : 2	16%
20	—	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	0
21[c]	$Rh(CO)_2Cl_2$	Ag_2CO_3	K_3PO_4	THF–DCE 1 : 2	88% (78%)

[a] The reactions were conducted with 0.20 mmol of **1a** and 0.30 mmol of **2a** for 24 h unless otherwise noted. [b] GC yields are given using dodecane as the internal standard, and the isolated yield is shown in parentheses. [c] 48 h.

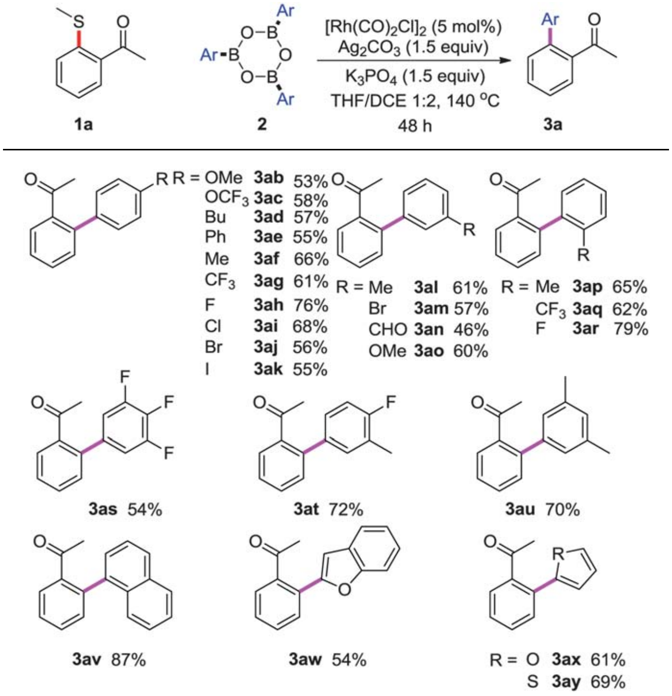
Compared with phenylboroxine **2a**, other phenylboronic acid derivatives showed much lower efficiency (Table 2). Phenylboronic esters **2b** and **2c** also reacted with **1a** albeit in lower yields. Phenylboronic acid **2d** also underwent this transformation in a moderate yield. However, potassium phenyltrifluoroborate **2e** completely failed to produce the desired product under the same conditions.

Table 2 Cross-coupling of **1a** with various organoboron reagents (**2**)[a,b]



[a] The reactions were conducted with 0.20 mmol of **1a** for 48 h. [b] GC yields were given using dodecane as an internal standard. [c] 4.5 equiv. of the organoboron reagent was added.

Table 3 Cross-coupling of **1a** with aryl boroxines **2**[a]

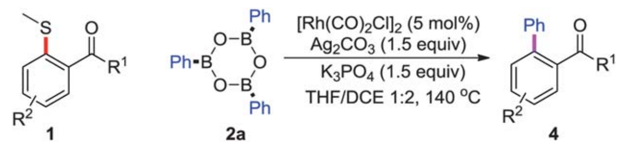


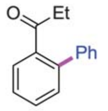
[a] The reactions were conducted with 0.20 mmol of **1a** and 0.30 mmol of **2** for 48 h. Isolated yields are given unless otherwise noted.

With the optimized conditions, we set out to explore different aryl boroxines substrates **2** (Table 3). The results showed that the cross coupling was not sensitive to the electronic effects of the aryl boroxines. Boroxines bearing both electron donating and withdrawing groups, provided good results (**3ab** to **3ag**). Notably, sterically hindered aryl boroxines did not reduce the efficacy of the reaction and the desired products were obtained in excellent yields (**3ap**, **3aq**, and **3ar**). Halide substituents were well tolerated, which provides the potential for further orthogonal functionalization (**3ah**, **3ai**, **3aj**, and **3ak**).[11] Moreover, heteroaryl boroxines could also be applied, affording the products in moderate yields (**3aw**, **3ax**, **3ay**).

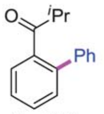
A variety of thioethers were further investigated (Table 4). The reaction proved to have a broad substrate scope, tolerating a variety of functional groups with different electronic and steric properties. We first changed the directing group and found that other directing groups, such as propionyl (**4a**), isobutyryl (**4b**), heptanoyl (**4c**), cyclohexanecarbonyl (**4d**), and benzoyl (**4e**) can be applied as directing groups to facilitate this transformation. It is important to note that methyl ester (**4f**) also acted as a directing group, which greatly expands the potential application of this method. Different substituents on the phenyl ring were examined, showing that both electron rich and electron deficient groups were compatible. Other functional groups, such as fluoro (**4g**) and trifluoromethyl (**4h**), also survived well. Notably, the methylthio group at the *para*-position also survived under these conditions, allowing discrimination of different thioether groups in the same molecule. This result also demonstrated the key role of the directing group.

Table 4 Cross-coupling of different methyl(phenyl)sulfanes **1** with phenylboroxine **2a**[a]

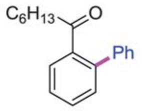




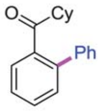
4a 60%



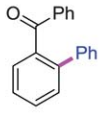
4b 58%



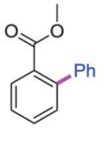
4c 64%



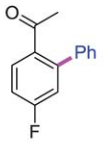
4d 58%



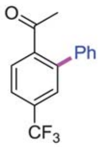
4e 44%



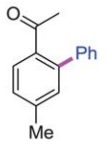
4f 70%



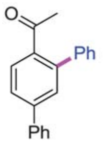
4g 59%



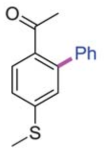
4h 81%



4i 64%



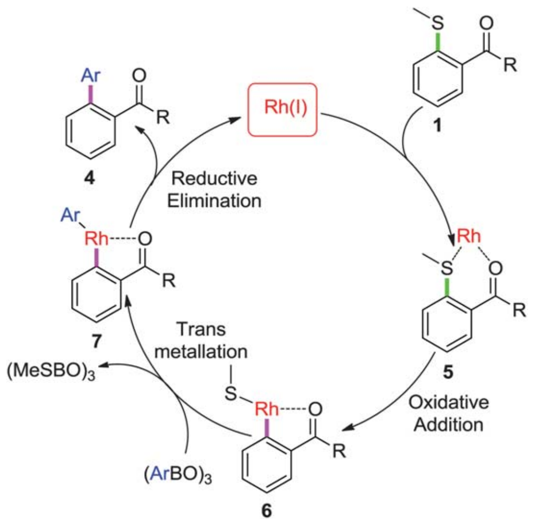
4j 72%



4k 71%

[a] The reactions were conducted with 0.20 mmol of **1** and 0.30 mmol of **2a** for 48 h. Isolated yields are given unless otherwise noted.

Based on these studies, a reaction mechanism was proposed (Scheme 2). Rhodium complex **2** first coordinates with the sulfur atom and the carbonyl group to form complex **5**. Like the traditional Suzuki–Miyaura cross coupling, the subsequent oxidative addition of C–S to Rh(I) takes place and key intermediate **6** is formed. With the assistance of a suitable base, the phenyl group is transferred from the aryl boroxine to the Rh(III) center to form biaryl Rh(III) intermediate **7**. Finally, the reductive elimination occurs to construct the C–C bond and produce the desired product **4**, accompanied by regeneration of the Rh(I) catalyst to complete the catalytic cycle.



Scheme 2 A plausible mechanism for Rh-catalyzed C–C bond formation *via* cleavage of the unreactive aryl C–S bond of thioanisole derivatives with aryl boroxines.

Experimental procedure for the cross-coupling reactions

The reactions were carried out in Schlenk tubes, which were dried by heating under vacuum. Under an air atmosphere, $[Rh(CO)_2Cl]_2$ (0.005 mmol, 1.9 mg), Ag_2CO_3 (0.30 mmol, 82.6 mg), and **1a** (0.2 mmol) were added to a Schlenk tube. K_3PO_4 (0.3 mmol, 63.7 mg) and **2a** (0.3 mmol) were transferred into the Schlenk tube in a glove box under a dry N_2 atmosphere. THF (1 mL) and DCE (0.5 mL) were added by syringe. The mixture was stirred under an air atmosphere at 140 °C for 48 h (unless otherwise specified), and then cooled to room temperature. The resultant mixture was filtered through a short plug of silica gel and further concentrated *in vacuo*. The crude product **3aa** was purified using flash chromatography on silica gel eluting with petroleum ether–ethyl acetate (v/v = 50/1) to afford the desired product **3aa** in 78% yield.

Conclusions

In conclusion, we have reported the first construction of biaryls *via* rhodium-catalyzed C–C bond formation through unreactive aryl C–S bond cleavage by coupling with aryl boroxines. This protocol exhibits broad substrate scope with respect to both aryl boroxines and thioether derivatives, affording products in good to excellent yields. As a supplement to the traditional Suzuki–Miyaura coupling, this method for the first time provides an alternative route based on the activation of C–S bonds with the methylthioethers as electrophiles. Further studies to address the detailed reaction mechanism and its applications are currently ongoing.

Acknowledgements

We acknowledge financial support from the National Basic Research Program of China (973 Program, 2009CB825300) and the NSF of China (no. 20925207 and 21002001).

Notes and references

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