DOI: 10.1002/adsc.200800414

Rhodium/N-Heterocyclic Carbene-Catalyzed Cross-Couplings of Aryl Arenesulfonates with Arylboronic Acids

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Received: July 4, 2008; Published online: September 26, 2008

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200800414.

Abstract: The combination of rhodium(I) and N-heterocyclic carbenes (NHC) was found to be effective as a catalyst for cross-coupling reactions of aryl arenesulfonates with arylboronic acids, which gave rise to the desired biaryl compounds in good yields.

Keywords: aryl arenesufonates; arylboronic acids; cross-couplings; N-heterocyclic carbenes; rhodium

Introduction

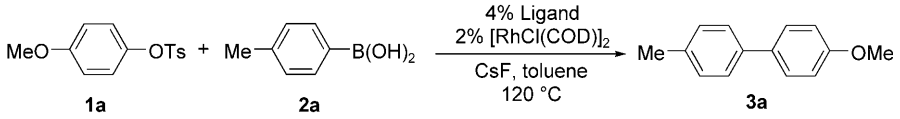
The transition metal-catalyzed cross-coupling reaction is known to be a powerful tool for C–C bond formation,[1] and this field is largely dominated by the use of palladium or nickel complexes as catalysts. An *electron-deficient* aryl-Pd(II) or aryl-Ni(II) intermediate is believed to be involved in the reaction process. However, a rhodium catalyst might also undergo oxidative addition of electrophilic aromatic substrates *via* an *electron-rich* arylrhodium intermediate, as demonstrated by the fact that the stoichiometric activation of aryl chlorides on a phenylrhodium complex could be realized.[2] The following report showed that arylboron compounds could be coupled efficiently with various aryl bromides and electron-deficient aryl chlorides in the presence of an appropriate rhodium-based catalyst system.[3] Moreover, a rhodium catalyst has been employed in the cross-coupling of arylboron reagents with acid anhydrides,[4] as well as in the coupling of arylzinc reagents with aryl iodides.[5]

Among the electrophiles employed in transition metal-catalyzed cross-coupling reactions, aryl arenesulfonates, which could be easily accessible from cheap, readily available phenols and arenesulfonyl chloride, are emerging as important alternatives to aryl halides and triflates.[6] Moreover, they are less expensive, more stable and easier to handle than the corresponding triflates. In recent years, cross-coupling reactions employing aryl arenesulfonates as electrophiles have been realized although they are relatively unreactive compared with the corresponding aryl halide and triflate counterparts.[6] For instance, several examples have been reported of Suzuki–Miyaura[7] reactions by using palladium[6b] or nickel[6a] catalysts. Prompted by the development of Rh-catalyzed cross-coupling reactions, we envisioned that an electron-rich arylrhodium intermediate might be employed in cross-coupling reactions of aryl arenesulfonates. Herein, we report the first example utilizing rhodium as the catalyst in the cross-coupling reactions of aryl arenesulfonates with boronic acids.

Results and Discussion

To verify the practicability of this projected route, a set of experiments was carried out using 4-methoxyphenyl tosylate **1a** and 4-tolylboronic acid **2a** as model substrates. This preliminary survey, carried out in the presence of $[RhCl(COD)]_2$ as the catalyst at 120 °C, allowed us to evaluate and optimize the most efficient catalytic system (Table 1). In an initial experiment, only a trace amount of product was detected when the reaction was performed in the presence of $[RhCl(COD)]_2$ (2 mol%) and CsF in toluene (Table 1, entry 1). All the phosphine ligands investigated gave the desired product in markedly poor yields (Table 1, entries 2–11). In view of the inferior oxidative addition capability of aryl arenesulfonates to a rhodium(I) intermediate, we conceived that a strong σ-donation from the supporting ligand might

Table 1. Screening of ligands for rhodium-catalyzed coupling reaction of aryl tosylates **1a** with arylboronic acid **2a**.[a]



Entry	Ligand	Yield [%][b]	Entry	Ligand	Yield [%][b]
1	none	trace	13	IMes·HCl	42
2	Ph_3P	trace	14	IMes·HBF_4	49[d]
3	Cy_3P	7	15	SIMes·HCl	14[d]
4	CyJohnPhos	2	16	IPr·HCl	trace[d]
5	JohnPhos	7	17	SIPr·HCl	11[d]
6	S-Phos	12	18	IXy·HCl	56[d]
7	dppf	9	19	SIXy·HCl	27[d]
8	dppp	trace	20	IEt·HCl	trace[d]
9	Xantphos	trace	21	ITol·HCl	trace[d]
10	S-Phos	7[c]	22	I-2-Tol·HCl	trace[d]
11	S-Phos	14[d]	23	I*t*Bu·HCl	31[d]
12	IMes·HCl	81[d]	24	ICy·HCl	trace[d]

[a] *Reaction conditions:* $MeOC_6H_4OTs$ **1a** (0.25 mmol), $MeC_6H_4B(OH)_2$ **2a** (1.1 equiv.), CsF (4.0 equiv.), toluene (1 mL).
[b] Isolated yield based on **1a**.
[c] 8 mol% ligand.
[d] $[RhCl(COD)]_2$, ligand, CsF and toluene were stirred at room temperature for 30 min before the reactants were added.

enhance the electron density of the metal center. It seemed that N-heterocyclic carbenes (NHC) should be a good choice. Since their first introduction as ligands for catalysis by Herrmann in 1995, NHCs are attracting increasing interest in transition metal-catalyzed reactions,[8] due to their variable steric bulk and ease of synthesis, as well as their excellent σ-donor power. Interestingly, although no reaction occurred in the presence of a palladium catalyst and an NHC as reported by Buchwald,[6b] the combination of Rh(I) and NHC, in contrast to that with phosphines, was proven to be the catalyst of choice in our investigation of the Suzuki–Miyaura coupling of aryl tosylates. As shown in Table 1, in an effort to access a phosphine-free catalyst system, the air-stable, easily available imidazolium salts and imidazolinium salts were examined as precursors of N-heterocyclic carbene ligands (Figure 1). To our delight, use of the catalyst system arising from IMes·HCl resulted in a satisfactory isolated yield (81% yield, Table 1, entry 12). Deprotonation of the imidazolium salt at room temperature with CsF as a mild base was crucial for such an efficiency (entry 13). Further screening of solvents and bases revealed that CsF and toluene were the best choices (data not shown in Table 1). Decreasing the temperature retarded the reaction.

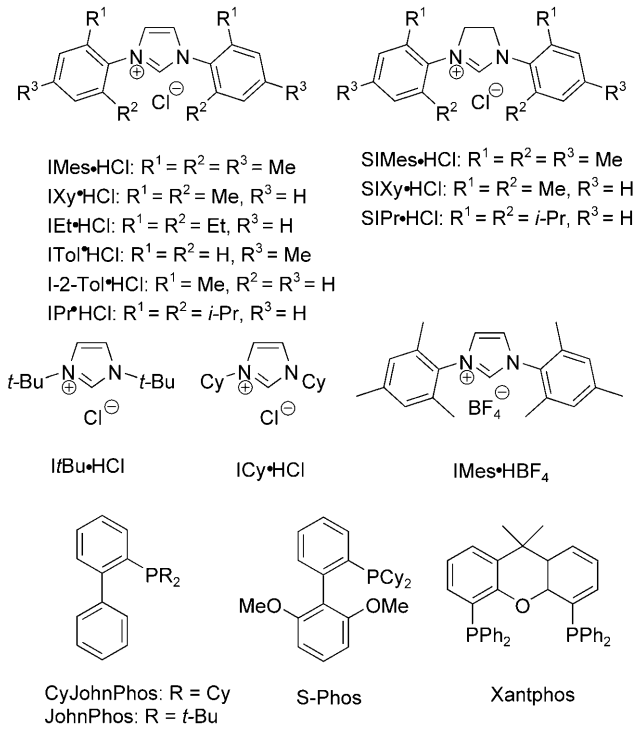
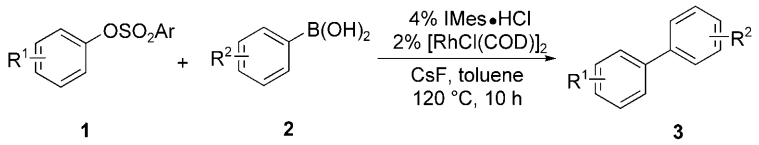


Figure 1. Ligands for screening.

The scope of this reaction was then investigated under optimized conditions, and the results are summarized in Table 2. For all cases, aryl arenesulfonates **1** reacted with arylboronic acids **2** leading to the corresponding products **3** in moderate to good yields. For instance, reaction of 4-benzylphenyl tosylate **1b** with 4-methylphenylboronic acid **2a** gave rise to the desired product **3b** in 75% yield (Table 2, entry 2). α- or β-naphthyl tosylate was also a suitable partner for this Rh-catalyzed reaction of 4-methylphenylboronic acid **2a** (Table 2, entries 7 and 8). Reaction of 4-trifluoromethylphenyl tosylate proceeded well under the conditions to generate the coupling product **3m** in 80%

Table 2. Rhodium/NHC-catalyzed coupling reactions of aryl tosylates **1** with arylboronic acids **2**.[a]



1 **2** **3**

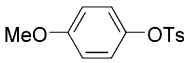
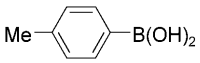
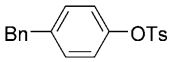
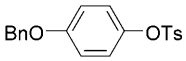
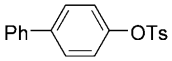
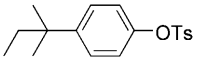
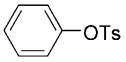
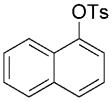
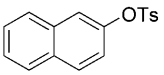
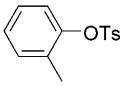
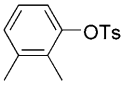
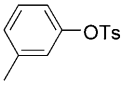
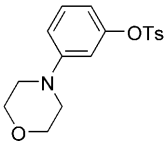
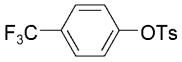
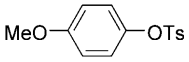
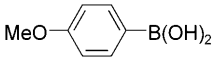
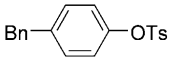
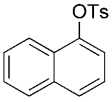
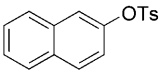
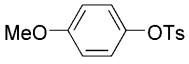
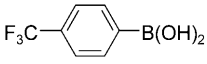
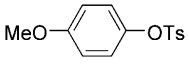
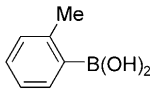
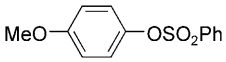
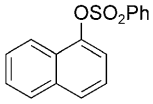
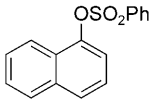
Entry	Arenesulfonate		Arylboronic acid		Product	Yield [%][b]
1	**1a**		**2a**		**3a**	81
2	**1b**		**2a**		**3b**	75
3	**1c**		**2a**		**3c**	55
4	**1d**		**2a**		**3d**	60
5	**1e**		**2a**		**3e**	43
6	**1f**		**2a**		**3f**	80
7	**1g**		**2a**		**3g**	86
8	**1h**		**2a**		**3h**	81
9	**1i**		**2a**		**3i**	61
10	**1j**		**2a**		**3j**	63
11	**1k**		**2a**		**3k**	70
12	**1l**		**2a**		**3l**	70
13	**1m**		**2a**		**3m**	80[c]
14	**1a**		**2b**		**3n**	46
15	**1b**		**2b**		**3o**	65
16	**1g**		**2b**		**3p**	61
17	**1h**		**2b**		**3q**	71
18	**1a**		**2c**		**3r**	32
19	**1a**		**2d**		**3s**	52

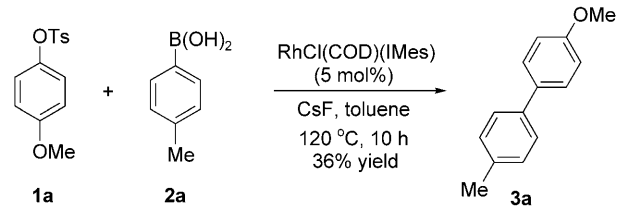
Table 2. (Continued)

Entry	Arenesulfonate	Arylboronic acid	Product	Yield [%][b]
20	**1n** 	**2a**	**3a**	60
21	**1o** 	**2a**	**3g**	75
22	**1o** 	**2b**	**3p**	50

[a] *Reaction conditions:* 2 mol% $[RhCl(COD)]_2$, 4 mol% IMes·HCl, CsF (4.0 equiv.), toluene (1 mL), room temperature, 30 min; then aryl arenesulfonate **1** (0.25 mmol) and arylboronic acid **2** (1.1 equiv.) were added, 120 °C, 10 h.
[b] Isolated yield based on aryl arenesulfonate **1**.
[c] KOH used as base.

yield (Table 2, enrty 13). Other arylboronic acids were employed in the reactions of aryl tosylates and similar results were observed (Table 2, entries 14–18). Meanwhile, aryl benzenesulfonates were examined for the Rh/NHC-catalyzed coupling reactions. 4-Methoxyphenyl benzenesulfonate **1n** reacted with 4-methylphenylboronic acid **2a** leading to the desired product **3a** in 60% yield (Table 2, entry 19). When α-naphthyl benzenesulfonate **1o** was employed in the reaction with 4-methylphenylboronic acid **2a** or 4-methoxyphenylboronic acid **2b**, a 75% or 50% yield of the corresponding product was obtained, respectively (Table 2, entries 20 and 21). We also tested other boronic acids, such as 4-chlorophenylboronic acid or 4-nitrophenylboronic acid in the reaction with 4-methoxyphenyl tosylate **1a** under the standard conditions. However, the results were inferior and the yields ranged form 20–30%.

In the reaction process, an RhCl(COD)(IMes) complex generated *in situ* might be the active species. The RhCl(COD)(IMes) complex has been reported in the literature and the structure was identified.[9] We also synthesized this complex according to the reported method and applied it in the reaction of tosylate **1a** with 4-methylphenylboronic acid **2a**. The desired product **3a** was generated as expected although the yield was lower (Scheme 1).



Scheme 1.

Conclusions

In conclusion, the combination of Rh(I) and NHC was found to be effective for cross-coupling reactions of aryl arenesulfonates with arylboronic acids. The results not only demonstrate the efficiency of the rhodium catalyst in cross-coupling reactions of aryl arenesulfonates, but also provide an interesting complement to the phosphine-based palladium or nickel catalyst systems.

Experimental Section

General Procedure for the Suzuki–Miyaura Couplings of Aryl Arenesulfonates

A mixture of $[RhCl(COD)]_2$ (2.5 mg), IMes·HCl (3.4 mg) and CsF (152 mg) in 1 mL toluene was stirred for 30 min at room temperature. Under a nitrogen flow, aryl arenesulfonate **1** (0.25 mmol) and arylboronic acid **2** (1.1 equiv.) were added. The Schlenk tube was put into a 120 °C oil bath and the mixture stirred for 10 h. After quenching with brine, the reaction mixture was extracted with ethyl acetate. The organic layer was directly subjected to flash chromatography on silica gel to yield the desired products **3**.

Data of a selected example 4-(4-methylphenyl)anisole (**3a**):[6a] ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 2.39$ (s, 3H), 3.85 (s, 3H), 6.97 (d, $J = 8.7$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.52 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (100 MHz): $\delta = 159.0$, 138.1, 136.5, 133.8, 129.5, 128.1, 126.7, 114.2, 55.4, 21.2; for further details, please see Supporting Information.

Supporting Information

Experimental procedure, characterization data, as well as copies of the ^1H and ^{13}C NMR spectra of compound **3** are available as Supporting Information.

Acknowledgements

Financial support from National Natural Science Foundation of China (20772018), Shanghai Pujiang Program, and Program for New Century Excellent Talents in University (NCET-07–0208) is gratefully acknowledged.

References

[1] a) J. Tsuji, *Palladium Reagents and Catalysts*, 2nd edn., John Wiley & Sons, Chichester, **2004**; b) A. de Meijere, F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, 2nd edn., John Wiley & Sons, Weinheim, **2004**.

[2] V. V. Grushin, W. J. Marshall, *J. Am. Chem. Soc.* **2004**, *126*, 3068–3069.

[3] K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2005**, *7*, 2229–2231.

[4] a) K. Oguma, M. Miura, M. Nomura, *J. Organomet. Chem.* **2002**, *648*, 297–301; b) T. Sugihara, T. Satoh, M. Miura, M. Nomura, *Angew. Chem. Int. Ed.* **2003**, *42*, 4672–4674; c) T. Sugihara, T. Satoh, M. Miura, M. Nomura, *Adv. Synth. Catal.* **2004**, *346*, 1765–1772; d) C. G. Frost, K. J. Wadsworth, *Chem. Commun.* **2001**, 2316–2317; e) L. J. Goossen, J. Paetzold, *Adv. Synth. Catal.* **2004**, *346*, 1665–1668; f) M. Yamane, K. Uera, K. Narasaka, *Chem. Lett.* **2004**, 424–425.

[5] K. M. Hossain, K. Takagi, *Chem. Lett.* **1999**, 1241–1242.

[6] For selected examples, see: a) Z.-Y. Tang, Q.-S. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 3058–3059; b) H. N. Nguyen, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 11818–11819; c) V. Percec, J.-Y. Bae, D. H. Hill, *J. Org. Chem.* **1995**, *60*, 1060–1065; d) D. Zim, V. R. Lando, J. Dupont, A. L. Monteiro, *Org. Lett.* **2001**, *3*, 3049; e) M. K. Lakshman, P. F. Thomson, M. A. Nuqui, J. H. Hilmer, N. Sevova, B. Boggess, *Org. Lett.* **2002**, *4*, 1479–1482; f) V. Percec, G. M. Golding, J. Smidrkal, O. Weichold, *J. Org. Chem.* **2004**, *69*, 3447–3452; g) J. M. Baxter, D. Steinhuebel, M. Palucki, I. W. Davies, *Org. Lett.* **2005**, *7*, 215–218; h) D. Steinhuebel, J. M. Baxter, M. Palucki, I. W. Davies, *J. Org. Chem.* **2005**, *70*, 10124–10127; i) M. R. Netherton, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 3910–3912; j) L. Zhang, T. Meng, J. Wu, *J. Org. Chem.* **2007**, *72*, 9346–9349; k) A. H. Roy, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 8704–8705; l) A. Fürstner, A. Leitner, M. Mendez, H. Krause, *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863; m) J. Zhou, G. C. Fu, *J. Am. Chem. Soc.* **2003**, *125*, 12527–12530.

[7] For reviews, see: a) N. Miyaura, *Top. Curr. Chem.* **2002**, *219*, 11–59; b) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147; c) D. A. Culkin, J. F. Hartwig, *Acc. Chem. Res.* **2003**, *36*, 234–245; d) J. Hassan, M. Sevigon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1470; e) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, 9633–9695.

[8] For selected examples, see: a) F. Glorius, (Ed.), *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer, Berlin, **2007**; b) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; c) O. Navarro, R. A. , III Kelly, S. P. Nolan, *J. Am. Chem. Soc.* **2003**, *125*, 16194–16195; d) G. A. Grasa, S. P. Nolan, *Org. Lett.* **2001**, *3*, 119–122; e) M. R. Fructos, T. R. Belderrain, M. C. Nicasio, S. P. Nolan, H. Kaur, M. M. Diaz-Requejo, P. J. Perez, *J. Am. Chem. Soc.* **2004**, *126*, 10846–10847; f) C. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1511–1514; g) R. Singh, M. S. Viciu, N. Kramareva, O. Navarro, S. P. Nolan, *Org. Lett.* **2005**, *7*, 1829–1832; h) G. A. Grasa, A. C. Hillier, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1077–1080; i) M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens, S. P. Nolan, *Organometallics* **2002**, *21*, 5470–5472.

[9] X, Yu, B. O. Patrick, B. R. James, *Organometallics* **2006**, *25*, 2359–2363.

