

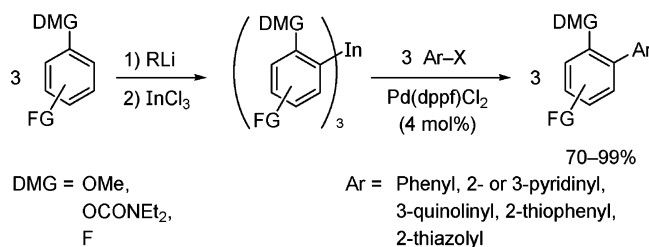
Palladium-Catalyzed Aryl–Aryl Cross-Coupling Reaction Using *ortho*-Substituted Arylium Reagents[†]

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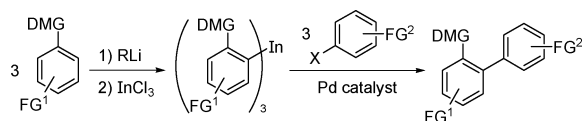


A range of biaryl compounds (aryl–aryl, aryl–heteroaryl, and heteroaryl–heteroaryl) can be efficiently prepared by a palladium-catalyzed cross-coupling reaction between *ortho*-substituted triarylium reagents and aryl halides. The triarylium reagents are prepared by directed *ortho*-lithiation and transmetalation to indium from the corresponding benzene derivatives using various directed metallation groups (DMGs). The reaction proceeds smoothly in high yields and short reaction times with high atom economy (the three aryl groups attached to indium are efficiently transferred).

Introduction

Transition metal-catalyzed cross-coupling reactions provide a unique methodology for carbon–carbon bond formation between unsaturated carbon bonds.¹ A representative example of the power of this methodology is the synthesis of biaryls by the reaction of aryl organometallics with aryl or heteroaryl halides.² Generally, these cross-coupling reactions are performed using organoboron³ or organozinc reagents,⁴ although other

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organometallics have also found some important applications.⁵ The resulting biaryl products are often essential building blocks in the synthesis of pharmaceuticals, agrochemicals, and new organic materials.⁶

Over the last few years, our group has been interested in the development of new applications of indium organometallics in organic synthesis.⁷ As part of this research program, we discovered the palladium-catalyzed cross-coupling reaction of triorganoindium compounds (R₃In) with organic halides.^{7b–h} In this reaction, R₃In showed interesting features such as high

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[†] This paper is dedicated to the memory of Prof. Marcial Moreno Mañas.

(1) (a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004. (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New York, 2002. (c) *Cross-Coupling Reactions. A Practical Guide*; Miyaura, N., Ed. *Top. Curr. Chem.* **2002**, *219*.

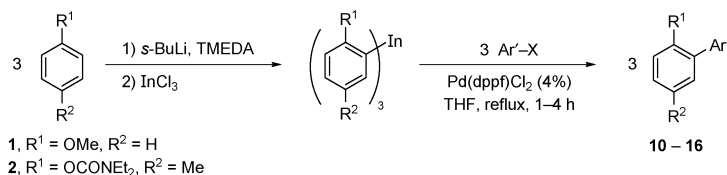
(2) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, C.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1469.

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TABLE 1. Palladium-Catalyzed Cross-Coupling Reaction of *ortho*-Oxygenated Triaryliindium Organometallics with Aryl and Heteroaryl Electrophiles^a

entry	Ar-H	Ar'-X	product	R ¹	R ²	yield (%) ^b	
1	1			10a	OMe	H	96
2	2			10b	OCONEt ₂	Me	99
3	1			11a	OMe	H	88 (85) ^c
4	2			11b	OCONEt ₂	Me	97 (94) ^c
5	1			12a	OMe	H	78
6	2			12b	OCONEt ₂	Me	70
7	1			13a	OMe	H	81
8	2			13b	OCONEt ₂	Me	85
9	1			14a	OMe	H	91
10	2			14b	OCONEt ₂	Me	85
11	1			15a	OMe	H	74
12	2			15b	OCONEt ₂	Me	88
13	1			16a	OMe	H	86
14	2			16b	OCONEt ₂	Me	70

^a Reactions were performed using 0.4 equiv of R₃In and 1 equiv of Ar'-X. ^b Isolated yield. ^c In parentheses, yields with **4b** (X = OTf) as electrophile.

reactivity, efficiency, versatility, and chemoselectivity, where all three organic groups attached to the metal were efficiently transferred to the electrophile. In addition, a wide variety of carbon groups (sp³, sp², and sp) can be transferred from the metal. The required organoindium reagents are usually prepared by transmetalation from the corresponding magnesium or lithium organometallics obtained from organic halides. In this article, we wish to report the palladium-catalyzed aryl-aryl cross-coupling reaction of *ortho*-substituted arylindium reagents,

which are prepared by directed *ortho*-metallation (DoM) of aryl and heteroaryl derivatives, with aryl and heteroaryl halides (Scheme 1).

Results and Discussion

During the past decade, the directed *ortho*-metallation cross-coupling nexus has been shown as an efficient protocol for the synthesis of biaryl compounds.⁸ This methodology has been exploited with the main organometals used in cross-coupling reactions, but the utility of organoindium remains unexplored. For the application of this methodology to indium organometallics, we started from benzene derivatives furnished with various directed metallation groups (DMGs). As electrophiles, we chose common aryl and heteroaryl halides.

The first candidate for the *ortho*-metallation-transmetalation sequence was anisole (methoxybenzene, **1**, Table 1). The *ortho*-metallation of anisole (1.2 equiv) with *s*-BuLi (1.2 equiv) and

(7) Conjugate addition reactions: (a) Pérez, I.; Pérez Sestelo, J.; Maestro, M. A.; Mouriño, A.; Sarandeses, L. A. *J. Org. Chem.* **1998**, *63*, 10074–10076. Cross-coupling reactions: (b) Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. *Org. Lett.* **1999**, *1*, 1267–1269. (c) Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 4155–4160. (d) Pena, M. A.; Pérez, I.; Pérez Sestelo, J.; Sarandeses, L. A. *Chem. Commun.* **2002**, 2246–2247. (e) Pena, M. A.; Pérez Sestelo, J.; Sarandeses, L. A. *Synthesis* **2003**, 780–784. (f) Pena, M. A.; Pérez Sestelo, J.; Sarandeses, L. A. *Synthesis* **2005**, 485–492. Allylic substitution reactions: (g) Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *J. Org. Chem.* **2003**, *68*, 2518–2520. (h) Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *J. Org. Chem.* **2004**, *69*, 8136–8139. Propargylic substitution reactions: (i) Riveiros, R.; Rodríguez, D.; Pérez Sestelo, J.; Sarandeses, L. A. *Org. Lett.* **2006**, *8*, 1403–1406.

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TABLE 2. Palladium-Catalyzed Cross-Coupling Reaction of *ortho*-Fluorinated Triarylindium Organometallics with Aryl Electrophiles^a

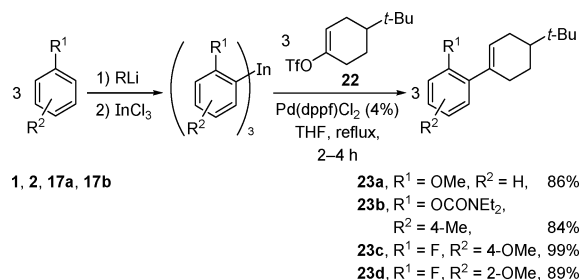
entry	Ar–H	Ar'–X	product	yield (%) ^b
1	17a	3	18	94
2		4a	19	90
3		4b	20	87
4	17b	3	21	96
5		4a	21	96
6		4b	21	88

^a Reactions were performed using 0.4 equiv of R₃In and 1 equiv of Ar'–X. PMDTA: *N,N,N',N',N'*-pentamethyldiethylenetriamine. ^b Isolated yield.

TMEDA (1.2 equiv), followed by transmetalation to indium by the addition of InCl₃ (0.4 equiv), and reaction with 4-iodotoluene (**3**, 1 equiv), in the presence of Pd(PPh₃)₂Cl₂ (4%) as catalyst, afforded the *ortho*-substituted biaryl product **10a** in 58% yield after 4 h. Optimizing the reaction conditions, we observed that the use of other palladium catalysts such as Pd(PPh₃)₄ gave similar yields, but interestingly, the reaction in the presence of Pd(dppf)Cl₂ (4%) improved the yield up to 96% in just 1 h (Table 1, entry 1). In this process, the high efficiency of the transmetalation step together with the relatively mild reaction conditions (THF, reflux), short reaction times, and high atom economy are noteworthy since the three methoxyphenyl groups attached to the indium were transferred.

After this encouraging result, the previous optimized reaction conditions were applied to other organic electrophiles. To our delight, we observed that tri-(2-methoxyphenyl)indium reacted chemoselectively with 4-bromoacetophenone (**4a**), providing the *ortho*-substituted biphenyl **11a** in 88% yield within 1 h (Table 1, entry 3). A similar yield was obtained using aryl triflate **4b** as electrophile (85%).

One of the most important challenges in the aryl–aryl cross-coupling reaction is the use of heteroaryls either as nucleophiles or as electrophiles. For this reason, we studied the reactivity of tri-(2-methoxyphenyl)indium with electron-deficient aromatic heterocycles such as halopyridines or haloquinolines. Thus, the cross-coupling reaction of tri-(2-methoxyphenyl)indium with 2-bromo-5-nitropyridine (**5**), 3-bromopyridine (**6**), and 3-bromoquinoline (**7**) gave the corresponding cross-coupling products **12a** (78%), **13a** (81%), and **14a** (91%), respectively, in good yields (Table 1, entries 5, 7, and 9). In addition, the cross-coupling reaction of the same triorganoinidium reagent with electron-rich heterocyclic halides, such as 2-bromothiophene (**8**) or 2-bromothiazole (**9**), also provided the aryl–heteroaryl

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coupling compounds **15a** and **16a** in good yields, 74 and 86%, respectively (Table 1, entries 11 and 13). Remarkably, the results obtained in the synthesis of heterobiaryls improved the previously reported synthesis using other organometallics.⁹ This set of results demonstrates the important synthetic utility of indium reagents and their high efficiency in the directed *ortho*-metallation–transmetalation–cross-coupling nexus.

In a new step forward, taking advantage of the different groups that can be used in the directed *ortho*-metallation, we extended our methodology to other substituted arenes. For this purpose, we tried the *O*-aryl carbamate functionality, which can act not only as DMG but also as a leaving group in nickel-catalyzed cross-coupling reactions with Grignard reagents.¹⁰ Under the previous experimental conditions, the *ortho*-metallation and transmetalation sequence with the *O*-aryl carbamate **2** also proceeded cleanly, and the palladium-catalyzed cross-coupling reactions with all the electrophiles tested before gave the corresponding aryl–aryl and aryl–heteroaryl coupling products in good to excellent yields (70–99%, Table 1, entries 2, 4, 6, 8, 10, 12, and 14).

As a directing metallation group, we also employed the fluoro group in benzene derivatives. The regioselective metallation of 1-fluoro-4-methoxybenzene (**17a**) under Schlosser's conditions,¹¹ in the *ortho*-position to the fluorine atom,¹² followed by transmetalation to indium, and palladium-catalyzed cross-coupling with the aryl halides **3** and **4a** and triflate **4b**, afforded the corresponding fluorobiaryls **18** and **19** in excellent yields (87–94%, Table 2, entries 1–3). In addition, the regioselective metallation of 1-fluoro-2-methoxybenzene (**17b**), in the *ortho*-position to the fluorine atom,¹² under the same conditions as before, followed by transmetalation to indium and palladium-catalyzed cross-coupling with aryl iodide **3**, aryl bromide **4a**, or aryl triflate **4b**, afforded the corresponding fluorobiaryls **20** and **21** in high yields (88–96%, Table 2, entries 4–6).

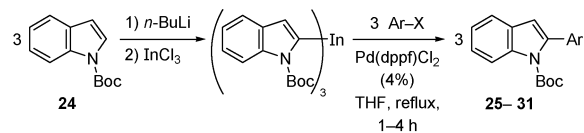
The excellent results obtained in the cross-coupling reactions of *ortho*-substituted arylindium organometallics with aryl and heteroaryl electrophiles led us to extend the scope of these reactions by studying their reactivity with nonaromatic electrophiles such as vinyl triflates, which are useful electrophiles

(9) (a) Sonesson, C.; Lindborg, J. *Tetrahedron Lett.* **1994**, *35*, 9063–9066. (b) Mongin, F.; Mojovic, L.; Guillaumet, B.; Trécourt, F.; Quéguiner, G. *J. Org. Chem.* **2002**, *67*, 8991–8994. (c) Ishikura, M.; Oda, I.; Terashima, M. *Heterocycles* **1985**, *23*, 2375–2386. (d) Xia, M.; Chen, Z.-C. *Synth. Commun.* **1999**, *29*, 2457–2465. (e) Jensen, J.; Skjaerbaek, N.; Vedso, P. *Synthesis* **2001**, 128–134.

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(12) The regioselectivity in the metallation of **17a** and **17b** was confirmed by reaction of the metallated species with CO₂. For further details, see the Supporting Information.

TABLE 3. Palladium-Catalyzed Cross-Coupling Reaction of Tri-(*N*-Boc-2-indolyl)indium with Aryl and Heteroaryl Electrophiles^a

entry	Ar-X	product	yield (%) ^b
1	3		80
2	4a		76
3	4b		76
4	5		74
5	6		74
6	7		93
7	8		70
8	9		75

^a Reactions were performed using 0.4 equiv of R₃In and 1 equiv of Ar-X. ^b Isolated yield.

in cross-coupling reactions.¹³ As a representative example of this type of compound, we chose vinyl triflate **22**. As shown in Scheme 2, the palladium-catalyzed cross-coupling reaction of the *ortho*-substituted organoindium reagents derived from anisole (**1**), carbamate **2**, and fluorides **17a** and **17b**, with vinyl triflate **22** (0.4 equiv), afforded the corresponding coupling products in high yields (86–99%) and short reaction times (2–4 h). These results show the ability of arylindium reagents to couple with alkenyl triflates, providing new attractive compounds for organic synthesis.

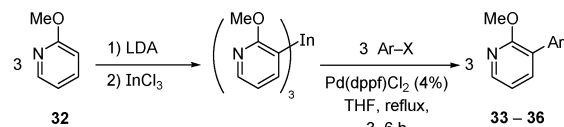
Although the use of heteroaryl compounds as electrophiles in cross-coupling reactions is quite common, the examples using heteroaryls as nucleophiles is more limited. To fill this gap, we investigated the reactivity of heteroarylindium reagents generated by DoM in cross-coupling reactions. For this purpose, we chose the indole and pyridinyl rings, important motifs in medicinal chemistry.¹⁴

The synthesis of 2-arylandoles had been traditionally performed by de novo construction of the indole nucleus,¹⁵ despite

(13) (a) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *2*, 47–54. (b) Ritter, K. *Synthesis* **1993**, 735–762.

(14) Toyota, M.; Ihara, N. *Nat. Prod. Rep.* **1998**, *15*, 327–340.

(15) See, as an example: Thummel, R. P.; Hegde, V. *J. Org. Chem.* **1989**, *54*, 1720–1725.

TABLE 4. Palladium-Catalyzed Cross-Coupling Reaction of Tri-(2-Methoxy-3-pyridinyl)indium with Aryl and Heteroaryl Electrophiles^a

entry	Ar-X	product	yield (%) ^b
1	3		67
2	4a		65
3	6		65
4	7		73

^a Reactions were performed using 0.4 equiv of R₃In and 1 equiv of Ar-X. ^b Isolated yield.

that the cross-coupling reaction may constitute an efficient way to prepare such compounds.^{16,17} Unfortunately, the Stille coupling using 2-indolylstannanes proceeds with moderate yields,¹⁶ and the Suzuki coupling with 2-indolylboronic acids takes place with some *N*-deprotection.¹⁷ In our case, the *N*-Boc-protected indole **24** was efficiently and regioselectively metalated at the C-2 position with *n*-BuLi and transmetalated with InCl₃ (0.4 equiv), and the palladium-catalyzed cross-coupling reaction with 4-iodotoluene (**3**) afforded the 2-arylandole **25** in 80% yield (Table 3, entry 1). This methodology was successfully extended to other aryl and heteroaryl halides. Thus, the reaction with acetophenones **4a** or **4b** afforded the cross-coupling product **26** in 76% yield (Table 3, entries 2 and 3). Additionally, the cross-coupling reaction using heteroaromatic electrophiles (pyridines **5** and **6**, quinoline **7**, thiophene **8**, and thiazole **9**) provided an interesting set of 2-heteroarylindoles (**27–31**) in good yield (70–93%, Table 3, entries 4–8).

Finally, we also studied the preparation of pyridinylindium reagents, by *o*-lithiation and transmetalation to indium, and their utility as nucleophiles in cross-coupling reactions. The examples using the pyridinyl nucleus as substrate for DoM are rare¹⁸ since the method of choice for the metallation is the halogen–metal exchange reactions.¹⁹ In our case, the treatment of 2-methoxy-pyridine (**32**, Table 4) with LDA at 0 °C,¹⁸ followed by

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(17) (a) Johnson, C. N.; Stemp, G.; Anand, N.; Stephen, S. C.; Gallagher, T. *Synlett* **1998**, 1025–1027. (b) Kudo, N.; Perseghini, M.; Fu, G. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1282–1284.

(18) (a) Parry, P. R.; Bryce, M. R.; Tarbit, B. *Synthesis* **2003**, 1035–1038. (b) Thompson, A. E.; Hughes, G.; Batsanov, A. S.; Bryce, M. R.; Parry, P. R.; Tarbit, B. *J. Org. Chem.* **2005**, *70*, 388–390.

(19) See, as an example: (a) Schubert, U. S.; Eschbaumer, C.; Heller, M. *Org. Lett.* **2000**, *2*, 3373–3376. (b) Lützen, A.; Hapke, M. *Eur. J. Org. Chem.* **2002**, 2292–2297.

transmetalation to indium and a palladium-catalyzed cross-coupling reaction with 4-iodotoluene (**3**), afforded 2-methoxy-3-tolylpyridine (**33**, Table 4, entry 1) in 67% yield. In addition, the reactions using 4-bromoacetophenone (**4a**), 3-bromopyridine (**6**), and 3-bromoquinoline (**7**) as electrophiles afforded the corresponding heterobiaryls **34–36** in good yield (65–73%, Table 4, entries 2–4). Remarkably, these results improve the metallation–transmetalation–cross-coupling sequence previously reported in the preparation of the analogous boronic esters from 2-methoxypyridine.¹⁸ In conclusion, the examples shown with the pyridinylindium and indoylindium reagents demonstrate the ability of indium organometallics to transfer heterocyclic aromatic groups in palladium-catalyzed cross-coupling reactions.

Conclusion

In summary, this work establishes that arylindium reagents can be efficiently prepared from substituted arenes and heteroarenes by *ortho*-metallation and transmetalation to indium. The palladium-catalyzed aryl–aryl cross-coupling reaction of the preformed arylindium reagents with aryl and heteroaryl halides provides an interesting body of *ortho*-substituted biaryl compounds (aryl–aryl, aryl–heteroaryl, and heteroaryl–heteroaryl) in good yields. The reaction proceeded under relatively mild conditions, with short reaction times and high atom efficiency since the three organic groups attached to the metal were transferred to the electrophile. Therefore, the results obtained can be successfully compared with those obtained using the most usual organometallics in cross-coupling reactions and confirm indium organometallics as an important tool for the synthesis of biaryl and heterobiaryl compounds.

Experimental Section²⁰

Triorganoindium Reagents. The triarylindium compounds were prepared, by treatment of the corresponding aryllithium species (3 equiv, ~0.5 M in dry THF) with a solution of InCl₃ (1.1 equiv, ~0.05 M in dry THF) at –78 °C and warming to room temperature.

(20) For general experimental methods, see reference 7g.

(21) Rennels, R. A.; Maliakal, A. J.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 421–422.

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The aryllithium reagents were prepared, according literature procedures, as follows: organolithium reagents derived from anisole (**1**)²¹ and *p*-tolyl diethylcarbamate (**2**)²² were prepared by dropwise addition of *s*-butyllithium (1.0 equiv, 1.4 M in cyclohexane) to a solution of **1** or **2** (1.0 equiv, ~0.5 M in dry THF) and *N,N,N',N'*-tetramethylethylenediamine (1.0 equiv) at –78 °C and stirring for 2 h. The *o*-lithiation of 4- and 2-fluoroanisole (**17a** and **17b**)¹¹ was performed by treatment of a solution of **17a** or **17b** (1.0 equiv, ~0.5 M in dry THF) with *n*-butyllithium (1.0 equiv, 2.5 M in hexanes) at –78 °C, followed by the addition of *N,N,N',N',N''*-pentamethyldiethylenetriamine (1.0 equiv) and stirring for 2 h. The *N*-(*t*-butoxycarbonyl)indole (**24**) was lithiated^{16a} by the dropwise addition of a solution of *n*-butyllithium (1.0 equiv, 2.5 M in hexanes) to a solution of **24** (1.0 equiv, ~0.5 M in dry THF) at –78 °C and stirring for 2 h at the same temperature. Lithiation of 2-methoxypyridine (**32**)^{18b} was performed by slow addition of a solution of **32** (1.0 equiv, 1.7 M in dry THF) to a solution of LDA (1 equiv, 1.3 M in dry THF) at 0 °C and stirring for 1 h at the same temperature.

General Procedure for the Palladium-Catalyzed Cross-Coupling Reaction of *ortho*-Substituted Tri(hetero)arylindium Organometallics with Aryl and Heteroaryl Electrophiles. To a solution of Pd(dppf)Cl₂ (33 mg, 0.04 mmol) and the electrophile (1 mmol) in dry THF (4 mL), a solution of R₃In (0.4 mmol, ~0.04 M in dry THF) was slowly added. The resulting mixture was refluxed until the starting material was consumed (1–4 h, TLC monitoring). The reaction was quenched by the addition of a few drops of MeOH, the mixture was concentrated in vacuo, and Et₂O (25 mL) was added. The organic phase was washed with saturated aq NH₄Cl (15 mL), dried, filtered, and concentrated in vacuo. The residue was purified by flash chromatography to afford, after concentration and high vacuum-drying, the corresponding biaryl products.

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Supporting Information Available: Relevant spectral data and copies of NMR spectra for compounds prepared. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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