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## Letter

# Palladium-Catalyzed Cross-Coupling of Arenediazonium Salts with Organoindium or Organobismuth Reagents

Α

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• R<sup>1</sup> = Ac, NO<sub>2</sub>, NHAc, F, OH, OCH<sub>3</sub>, Br, CN, CO<sub>2</sub>CH<sub>3</sub>

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**Abstract** Arylindium and isolated triarylbismuth compounds generated in situ react as nucleophiles with arenediazonium salts in palladium-catalyzed cross-coupling reactions to give substituted biphenyls.

Key words palladium catalysis, cross-coupling, arenediazonium salts, organobismuth compounds, organoindium compounds

In spite of recent interesting developments in the synthesis of biaryl compounds, such as C-H activation,<sup>1</sup> hydroarylations of arynes generated in situ,<sup>2</sup> and dehydro-Diels-Alder reactions,<sup>3</sup> transition-metal-catalyzed crosscoupling reactions remain the most general and reliable methods.4-6 The most commonly used cross-coupling reaction for this synthetic application is the Suzuki-Miyaura reaction,<sup>7</sup> which uses arylboronic acids<sup>8</sup> or their derivatives<sup>9</sup> as nucleophilic partners. Less common, but still intensively investigated, are arylsilicon,<sup>10</sup> arylzinc,<sup>11</sup> aryltin,<sup>12</sup> and arylmagnesium<sup>13</sup> compounds. In most cross-coupling reactions, aryl halides have been used as the electrophilic coupling partners, with triflates or nonaflates providing alternatives.<sup>14</sup> A recent addition to the group of fluorinated sulfate leaving groups is the fluorosulfate group, which has also found application in cross-coupling reactions.<sup>15</sup> Arenediazonium salts are useful but underinvestigated alternatives to aryl halides or triflates in Pd-catalyzed coupling and cross-coupling reactions.<sup>16-19</sup> Although the majority of Pdcatalyzed coupling reactions investigated for these reagents are Heck-type reactions,<sup>20–25</sup> there have also been reports on their use in cross-coupling reactions, in particular Suzuki-Miyaura couplings.<sup>19,26-30</sup> Apart from organoboron compounds, surprisingly few other organometallic reagents have been tested in cross-coupling reactions with arenediazonium salts.<sup>31-34</sup> Kikukawa et al. reported that the Stille coupling of *p*-toluenediazonium tetrafluoroborate with phenyl(tributyl)tin resulted in the formation of the desired cross-coupling product in fair yields, but these products were accompanied by large amounts of homocoupling products.<sup>35</sup> Dughera investigated the same reaction, but with the less common o-benzenedisulfonimide counterion instead of tetrafluoroborate; he reported significantly higher yields of biaryls and only minor amounts of homocoupling products for this and several other examples.<sup>36</sup> We are aware of only one report that describes a Pd-catalyzed cross-coupling of arenediazonium salts with organometallic reagents other than organoboron or organotin compounds. Dughera and co-workers found that the abovementioned arenediazonium benzenedisulfonimides can be coupled with triarylindium reagents generated in situ to give diazenes or biaryls in the absence or presence of a Pd catalyst, respectively.<sup>37</sup> Our interest in the synthesis of biaryls with at least one phenol or methoxybenzene ring<sup>38,39</sup> as potential phytoalexins<sup>40</sup> prompted us to explore arylindium<sup>41</sup> and arylbismuth<sup>42-44</sup> reagents as alternatives to organoboron compounds in cross-coupling reactions with arenediazonium salts. Both classes of organometallic reagents have previously found applications in Pd-catalyzed cross-coupling reactions, but mostly with aryl, vinyl, or benzyl halides.<sup>45</sup> We are not aware of any reports describing cross-coupling reactions of arenediazonium salts with organobismuth reagents.

We started this investigation with 4-hydroxybenzenediazonium tetrafluoroborate (**3a**) and 4-methoxybenzenediazonium tetrafluoroborate (**3b**) as test substrates. As the nucleophilic cross-coupling partner, the phenylindium reagent **2a**, synthesized in situ from phenylmagnesium bromide (equimolar amount to the diazonium salt) and  $InCl_3$  (0.5 equiv), was employed.<sup>37</sup> In previous investigations on Suzuki–Miyaura-type<sup>29</sup> and Heck-type couplings<sup>46</sup> with arenediazonium salts, we found that the solvent and the

<sup>•</sup>  $R^2 = OCH_3$ , F

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Table 1 Optimization of the Cross-Coupling Reaction of Diazonium Salts and Arylindium Reagents



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<sup>a</sup> GC/MS yield; determined by using 1,2-dimethoxybenzene as a standard for calibration.

<sup>b</sup> No GC/MS yields determined because TLC indicated formation of a complex mixture of products.

<sup>c</sup> Isolated yield of pure product.

<sup>d</sup> n.d.: not determined.

presence (or absence) of a base are critical parameters. In addition, reaction conditions for hydroxybenzenediazonium salts are often complementary to those required for diazonium salts lacking a phenolic hydroxy group. For these reasons, we tested the cross-coupling-reactions in methanol or acetonitrile under basic or base-free conditions. A well-tried base for Pd-catalyzed couplings of arenediazonium salts is NaOAc, which was also used in this study (Table 1).

All reactions were monitored by GC/MS and, unless otherwise stated, the yields reported in Table 1 are GC yields calculated by using 1,2-dimethoxybenzene as a standard for calibration. In methanol as a solvent (entries 1, 2, 5, and 6), conversion to the desired cross-coupling products 4 was very low, both the presence or absence of NaOAc. Addition of NaOAc led to increased formation of the homocoupling products, biphenyl (5) and the biaryl 6a (entry 1) or 6b (entry 5). As mentioned in the introduction, homocoupling products were also detected by Kikukawa et al.<sup>35</sup> and by Dughera<sup>36</sup> in their studies on the Stille cross-couplings of arenediazonium salts. A plausible explanation for the formation of homocoupling products is a rapid exchange of aryl groups between various Pd-aryl σ-complexes in combination with a comparatively slow reductive elimination step.<sup>35</sup> Changing the solvent to acetonitrile did not improve the selectivity of the cross-coupling reaction under basefree conditions (entries 4 and 8). However, if NaOAc was added to the reaction mixture, the selectivity toward the formation of cross-coupling products was sufficiently high to allow isolation of the biaryls 4aa and 4ab in synthetically useful yields (entries 3 and 7). Correia and co-workers proved that acetonitrile is a coordinating ligand in Pd-catalyzed Heck-type reactions of arenediazonium salts by monitoring these reactions with ESI-MS.<sup>47</sup> In our case, coordination of acetonitrile to the intermediate σ-complex Ar-Pd-Ar' should accelerate the reductive elimination step in the catalytic cycle over aryl ligand exchange. NaOAc, which promotes the regeneration of the Pd(0)-complex in Heck-type reactions by deprotonation of the Pd hydride resulting from the  $\beta$ -hydride elimination step, probably plays a different role in our reaction. Acetate can serve as a stabilizing ligand for cationic Pd intermediates, but it might also promote transfer of the phenyl substituent from the organoindium reagent to the Pd by coordination of the Pd-bound acetate to the Lewis acidic indium. A precedent for this oxo-type mechanism exists in Suzuki-Miyaura coupling reactions.<sup>48</sup>

The successful conditions for the cross-coupling of diazonium salts **3a** and **3b** with the phenylindium reagent **2a** were applied to four other arenediazonium tetrafluoroborates **3c-f** (Scheme 1). Ketone (**4ac**), ester (**4af**), and amide groups (**4ae**) were well tolerated as functional groups in the arenediazonium coupling partner, but the reaction failed completely with a carboxylic acid-substituted diazonium salt (not shown). Moderate yields were obtained for **4ad** and **4ba**.

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**Scheme 1** Examples of cross-coupling reactions of arylindium reagents with arenediazonium tetrafluoroborates

A disadvantage of arylindium reagents is that they are not isolable and, consequently, their structures and compositions are rather ill defined. For this reason, we investigated triarylbismuth compounds as alternative cross-coupling partners. These are isolable and can be conveniently synthesized, purified and characterized; moreover, some are even commercially available. In addition, they are less toxic than most other heavy-metal compounds.<sup>49</sup> We investigated the cross-coupling of **3b** and  $BiPh_3$  (**7a**) as a test reaction (Table 2). The reactions were monitored by HPLC. Unfortunately, the amount of the homocoupling product biphenyl (**5**) could not be quantified because its retention time was identical with that of triphenylbismuth under the optimized HPLC conditions. However, an analysis of the reaction mixtures by NMR spectroscopy revealed that biphenyl (**5**) is indeed a byproduct of these cross-coupling reactions.

In our first experiments, a 3:1 ratio of diazonium salt 3b and BiPh<sub>3</sub> was used with 5 mol% of Pd(OAc)<sub>2</sub> as a precatalyst. As solvents methanol, acetonitrile, THF, 1,4-dioxane, and DMF were tested at an initial substrate concentration of 0.1 M. For each solvent, the HPLC yield was determined with and without added NaOAc. From this initial solvent screening, only the results for acetonitrile are shown in Table 2 (entries 1 and 2) because for all other solvents, the HPLC yields were lower than 30%. Addition of NaOAc is essential, as it increased the HPLC yield of **4ab** from 8% (entry 1) to 51% (entry 2). We also tested several other Pd precatalysts, such as  $Pd(PPh_3)_4$  (39%) or  $Pd_2(dba)_3$ ·CHCl<sub>3</sub> (28%), under these conditions (not shown), but we found that only Pd(acac)<sub>2</sub> gave the product in a comparable yield and selectivity (entry 3). A wide range of alternative bases known to be efficient promotors of Suzuki-Miyaura couplings (KOAc, CsOAc, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, KF, Bu<sub>4</sub>NF) were investigated, but none was as efficient as NaOAc. Reducing the initial substrate concentration to 0.01 M resulted in a notably lower yield of 4ab (35%) and 6b (11%), even after a reaction

| Table 2 Optimization | n of the Cross-Coupling React | tion of BiPh <sub>3</sub> ( <b>7a</b> ) and Ar | enediazonium salt <b>3b</b> . |
|----------------------|-------------------------------|--|-------------------------------|
|----------------------|-------------------------------|--|-------------------------------|

| $H_{3}CO + N_{2}^{\Theta} + H_{3}CO + H_$ |                           |                           |                                      |          |                  |                                      |                                     |  |  |
|---|---------------------------|---------------------------|--------------------------------------|----------|------------------|--------------------------------------|-------------------------------------|--|--|
|   | 30                        |                           |                                      | tab      | 5                | 00                                   |                                     |  |  |
| Entry   | BiPh <sub>3</sub> (equiv) | Catalyst (mol%)           | Concentration (mol·L <sup>-1</sup> ) | Time (h) | Additive (equiv) | Yield <sup>a</sup> (%) of <b>4ab</b> | Yield <sup>a</sup> (%) of <b>6b</b> |  |  |
| 1 <sup>b</sup>  | 0.33                      | $Pd(OAc)_2(5)$            | 0.10                                 | 16       | -                | 8                                    | 2                                   |  |  |
| 2   | 0.33                      | $Pd(OAc)_2(5)$            | 0.10                                 | 16       | -                | 51                                   | 20                                  |  |  |
| 3   | 0.33                      | Pd(acac) <sub>2</sub> (5) | 0.10                                 | 16       | -                | 49                                   | 19                                  |  |  |
| 4   | 0.33                      | $Pd(OAc)_2(5)$            | 0.01                                 | 48       | -                | 35                                   | 11                                  |  |  |
| 5   | 0.33                      | $Pd(OAc)_2(5)$            | 0.10                                 | 16       | TBAB (1.0)       | 26                                   | 24                                  |  |  |
| 6   | 0.33                      | $Pd(OAc)_2(5)$            | 0.10                                 | 16       | TBACI (1.0)      | 29                                   | 19                                  |  |  |
| 7   | 0.33                      | $Pd(OAc)_2(5)$            | 0.10                                 | 16       | TBAF (1.0)       | 3                                    | 1                                   |  |  |
| 8   | 0.50                      | $Pd(OAc)_2(5)$            | 0.10                                 | 2.5      | -                | 50                                   | 19                                  |  |  |
| 9   | 1.00                      | Pd(OAc) <sub>2</sub> (10) | 1.00                                 | 18       | -                | 55                                   | 9                                   |  |  |
| 10  | 1.00                      | $Pd(acac)_2$ (10)         | 1.00                                 | 18       | -                | 66 <sup>c</sup>                      | 11                                  |  |  |
| 11  | -                         | $Pd(OAc)_2$ (5)           | 0.10                                 | 16       | _                | -                                    | 1                                   |  |  |

<sup>a</sup> HPLC yield; determined by using 4,4'-di-tert-butylbiphenyl for calibration.

<sup>b</sup> Reaction without added NaOAc.

<sup>c</sup> Isolated yield: 66%.

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time of 48 hours (entry 4). Further attempts to improve the yield were therefore made at the higher substrate concentration. First, we tested the addition of tetraalkylammonium halides (entries 5-7), because halides are known to stabilize catalytically active Pd species.<sup>50</sup> This approach turned out to be unsuccessful: addition of the bromide or chloride (entries 5 and 6) led to a lower yield of the cross-coupling product and an increased proportion of the homocoupling product 6b. Addition of fluoride led to near complete inhibition of the reaction (entry 7). Next, we tried using BiPh<sub>3</sub> in slight excess (entry 8), but we obtained virtually identical yields of **4ab** and **6b**. Increasing the amount of BiPh<sub>2</sub> to one equivalent and the amount of Pd(OAc)<sub>2</sub> to 10 mol% resulted in an improved yield of the cross-coupling product and, more importantly, a notable reduction in that of the homocoupling product (entry 9). Replacing Pd(OAc)<sub>2</sub> by Pd(acac)<sub>2</sub> led eventually to the best reaction conditions, which gave 4ab in 66% HPLC yield (isolated yield 61%), together with 11% (HPLC) of 6b (entry 10).



**Scheme 2** Examples of cross-coupling reactions of BiAr<sub>3</sub> reagents and arenediazonium tetrafluoroborates

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To gain some insight into the mechanism of the formation of homocoupling product **6b**, we undertook a control experiment. Diazonium salt **3b** was submitted to the reaction conditions listed in Table 2, entry 1, but in the absence of the cross-coupling partner BiPh<sub>3</sub> (entry 11). After 16 hours, the HPLC yield of **6b** was only 1%. From this observation, we conclude that the homocoupling product of the arenediazonium partner is not formed through a sequence of reduction and radical dimerization, but more likely through an exchange of aryl groups between Pd– $\sigma$ -aryl complexes and reductive elimination.

The optimized conditions were applied to eight other diazonium salts **3**, which were successfully coupled with BiPh<sub>3</sub> (**7a**) and three other triarylbismuth reagents **7b–d**. The lowest yields were obtained with the *ortho*-substituted arenediazonium salt **3g** (example **4ag**) and the electron-deficient *para*-nitro-substituted arenediazonium salt **3d** (examples **4ad** and **4cd**). Compound **4ah** was obtained reproducibly in yields of less than 10% and could not be purified. All other yields were better (40–62%, Scheme 2).<sup>51</sup>

In summary, we have identified conditions for the Pdcatalyzed cross-coupling of arylindium or triarylbismuth reagents with arenediazonium salts. The solvent, the base, and the initial substrate concentration have significant effects on the yield and selectivity of the reactions.

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## **Supporting Information**

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- (51) Methyl 4-Hydroxy-3'-methoxybiphenyl-3-carboxylate (4cf); Typical Example

The diazonium salt **3f** (134 mg, 0.50 mmol), triarylbismuthane **7c** (265 mg, 0.50 mmol, 1.0 equiv),  $Pd(acac)_2$  (15.2 mg, 0.05 mmol, 10 mol%), and NaOAc (123 mg, 1.50 mmol, 3.0 equiv) were suspended in MeCN (0.5 mL, 1.0 M), and the mixture was stirred for 16–18 h at r.t. The mixture was then diluted with EtOAc (30 mL), washed with H<sub>2</sub>O (30 mL), dried (MgSO<sub>4</sub>), and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, PE--EtOAc) to give a colorless oil; yield: 66 mg (51%, 0.26 mmol).

IR (ATR): 2999 (bw), 1738 (w), 1675 (m), 1204 (s), 1170 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 10.78 (s, 1 H), 8.07 (d, *J* = 2.2 Hz, 1 H), 7.70 (dd, *J* = 8.6, 2.2 Hz, 1 H), 7.35 (t, *J* = 7.9 Hz, 1 H), 7.13 (d, *J* = 7.7 Hz, 1 H), 7.09–7.03 (m, 2 H), 6.88 (dd, *J* = 8.2, 2.2 Hz, 1 H), 3.98 (s, 3 H), 3.87 (s, 3 H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 170.7, 161.2, 160.2, 141.6, 134.6, 132.4, 130.0, 128.4, 119.3, 118.2, 112.7, 112.6, 112.4, 55.5, 52.5. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>14</sub>NaO<sub>4</sub>: 281.0784; found: 281.0787.