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# Towards Iron-Catalysed Suzuki Biaryl Cross-Coupling: Unusual Reactivity of 2-Halobenzyl Halides

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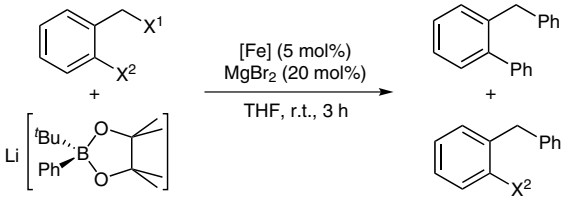


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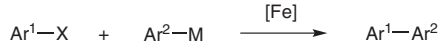
**Abstract** The reaction of 2-halobenzyl halides with the borate anion Li[(Ph)(*t*-Bu)Bpin] leads not only to the expected arylation at the benzyl position, but also to some Suzuki biaryl cross-coupling. Preliminary mechanistic investigations hint towards the intermediacy of benzyl iron intermediates that can either: (a) directly cross-couple with the aryl boron reagent to give observed monoarylated species, or (b) undergo oxidative addition of the aryl halide to generate the diarylated species on reaction with the boron-based nucleophile.

**Key words** iron, cross-coupling, aryl, Suzuki reaction, organoborate

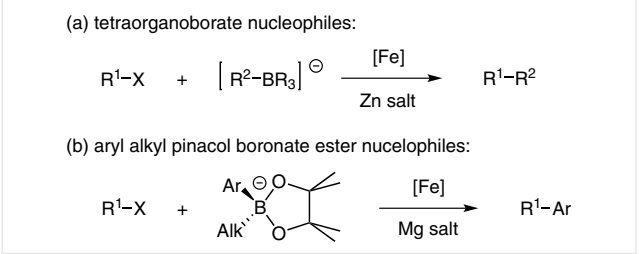
While the earliest reported iron-catalysed cross-coupling reaction dates back 70 years,[1] for much of the intervening period there was a lull in activity in the field, with only sporadic reports appearing before the early 2000s, notably from the groups of Kochi,[2] Molander[3] and Cahiez.[4] Since then there has been a renaissance in the field, with many excellent reports appearing over the last decade or so.[5] In many cases the activity, selectivity and coupling-partner tolerance obtained in iron-catalysed cross-couplings make such processes comparable to or better than palladium-catalysed counterparts. However, one area where this is not the case is biaryl bond formation (Scheme 1) where iron lags behind palladium in terms of both applicability and generality.




**Scheme 1** Iron-catalysed biaryl cross-coupling

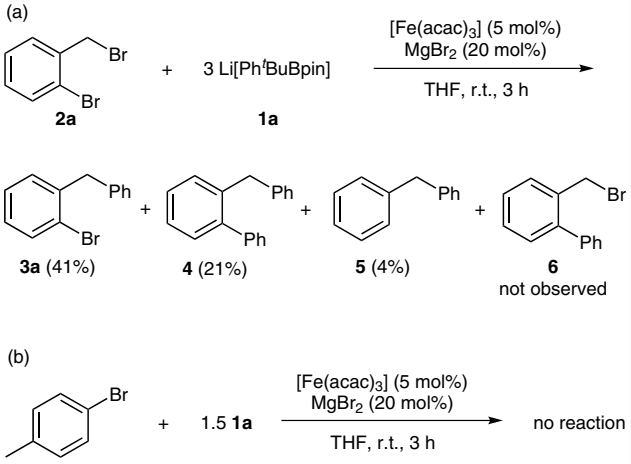
Fürstner found that while 2-halo-N-heterocyclic substrates couple with aryl Grignard reagents, the equivalent reaction between an activated aryl chloride and phenyl Grignard gives only a low yield of the cross-coupled product when [Fe(acac)$_3$] is used as the catalyst.[6] Subsequently, Nakamura showed that high yields could be obtained in the coupling of aryl chlorides with aryl Grignard reagents if an N-heterocyclic carbene/iron fluoride catalyst mixture is employed.[7] Recently, Chua and Duong showed that the dimeric alkoxide [Fe$_2$(O*t*-Bu)$_6$] can be used in place of iron fluorides.[8] Meanwhile Knochel and co-workers established that arylcuprates can be used as nucleophiles in iron-catalysed biaryl bond formation.[9]

For iron to be seen to be truly competitive with palladium requires the development of an iron-catalysed variant of the Suzuki biaryl bond-forming reaction. There is one report in the literature that describes examples of such a process, conducted at very high pressure (15 kbar),[10] however, the extreme conditions employed render this interesting, but ultimately impractical. To date, the majority of more practical iron-catalysed Suzuki reactions occur between alkyl, benzyl and allyl halides and arylboron nucleophiles derived from either tetraorganoborates (Scheme 2, a)[11] or the alkyl aryl pinacol boronate esters **1** (Scheme 2, b)[12] formed by reaction of aryl pinacol boronate esters with *tert*-butyllithium or ethyl Grignard.




**Scheme 2** Iron-catalysed Suzuki cross-coupling reactions with organoborate reagents

While the former procedure can be used to couple 2-halo-N-heterocycles,[11a] to the best of our knowledge there are no reports that describe the Suzuki cross-coupling of aryl halides with arylboron-based nucleophiles under mild conditions. Indeed, when 2-halobenzyl halides are used as substrates in the reactions outlined in Scheme 2 (a), coupling occurs exclusively at the benzylic position.[11a] Therefore, we were surprised to find that the coupling of 2-bromobenzyl bromide (**2a**) with the pinacol borate anion **1a** led not only to coupling of the benzyl group to give the anticipated product **3a**, but also the aryl bromide function, furnishing the diarylated product **4**, albeit in low yield (Scheme 3, a). By contrast, no coupling was observed when 4-tolyl bromide was subjected to the same reaction conditions.[13]




**Scheme 3** (a) Iron-catalysed Suzuki arylation of **2a** with **1a**. Conversions into **3a**, **4**, **5** and **6** determined by GC (dodecane internal standard). *t*-BuBpin produced as co-product. (b) Attempted coupling of 4-bromotoluene.

Our first thought to try and explain the unusual reaction was that if **3a** forms first, the newly introduced arene substituent may then coordinate to the iron centre by an $\eta^n$-arene interaction, which may in turn direct C–Br bond activation. This suggestion is reminiscent of the one provided by Jacobi von Wangelin for the iron-catalysed coupling of aryl[14] or alkyl[15] Grignard reagents with chlorostyrenes (Figure 1, a), where initial coordination of the iron to an alkene is proposed to be followed by a haptotrophic shift and attack at the C–X bond. Figure 1 (b) shows the equivalent process that may occur here.

If this were the case then it would be anticipated that the concentration of **3a** would build up early in the reaction and there would be a lag in the production of **4**. However, the profile of product distribution against time (Figure 2) does not seem to support this hypothesis. Instead, it appears that the rates of production of the two species are independent of one another. This was further reflected in the fairly consistent ratio of mono- versus diarylated product obtained on changing the ratio of **2a**:**1a** in the reaction (Scheme 4).

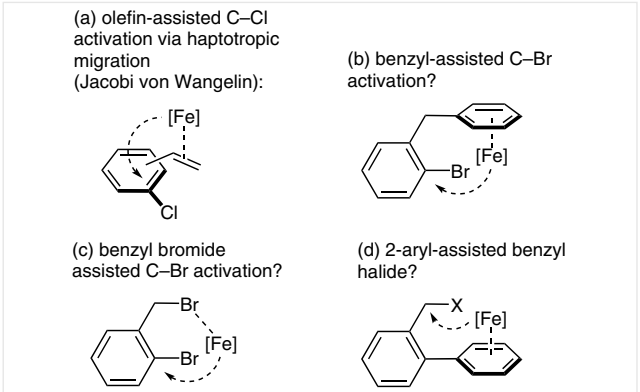



**Figure 1** Possible modes of coordination-directed C–X functionalisation

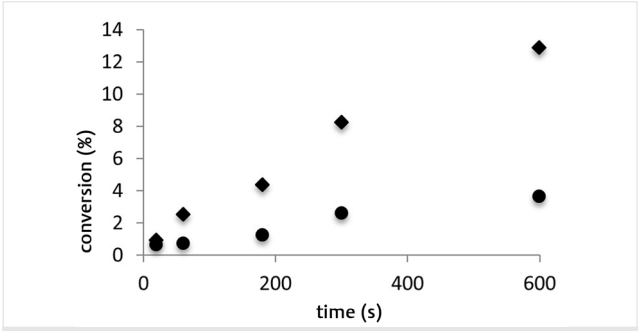
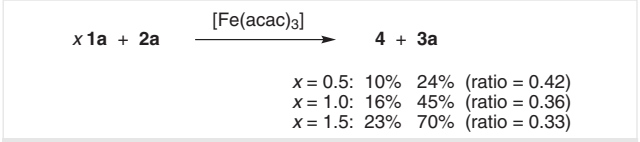



**Figure 2** Conversion into **3a** (◆) and **4** (●) during first ten minutes of the reaction of **1a** with **2a**




**Scheme 4** Effect of varying **1a**:**2a** on the ratio of mono- **3a** and diarylated **4** products. Conditions as per Scheme 3, conversions based on amount of benzyl halide converted into products, determined by GC analysis (dodecane standard).

Furthermore, subjecting isolated **3a** and its aryl chloride counterpart, **3b**, to the same reaction conditions in the presence of four different iron catalysts (Table 1) gave little or none of the diarylated product **4**. In some cases, using **3a** as substrate, modest amounts the hydrodehalogenated species **5** were obtained. Taken together, the data strongly suggests that **3a** is not an intermediate in the formation of **4**.

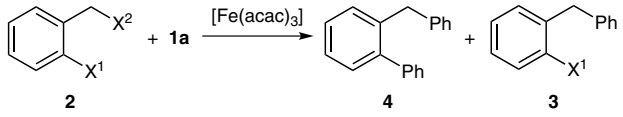
**Table 1** Reaction of **1a** with 2-$XC_6H_4CH_2Ph$ [X = Br (**3a**) or Cl (**3b**)] with Various Iron Catalysts[a]

| Entry | Substrate | [Fe] | Yield (%) of **4** | Yield (%) of **5** |
|---|---|---|---|---|
| 1 | **3a** | $[Fe(acac)_3]$ | 1 | 16 |
| 2 | **3a** | $[FeCl_2(dppe)]$ | 1 | 8 |
| 3 | **3a** | $[FeCl_2(dpbz)_2]$ | 0 | 1 |
| 4 | **3a** | $[FeCl_2(dppp)]$ | 3 | 44 |
| 5 | **3b** | $[Fe(acac)_3]$ | 0 | 2 |
| 6 | **3b** | $[FeCl_2(dppe)]$ | 0 | 0 |
| 7 | **3b** | $[FeCl_2(dpbz)_2]$ | 0 | 1 |
| 8 | **3b** | $[FeCl_2(dppp)]$ | 1 | 6 |

[a] Conditions as per Scheme 3; dppe: 1,2-bis(diphenylphosphino)ethane; dpbz: 1,2-bis(diphenylphosphino)benzene; dppp: 1,3-bis(diphenylphosphino)propane.

If the arene introduced into the benzylic position is not responsible for directing the aromatic C–Br bond activation, then could coordination of the benzyl bromide perform a similar role (Figure 1, c)? If this were the case, then replacing the benzyl bromide with other benzyl halides may also facilitate biaryl bond formation. It is clear from the results in Table 2 that replacing the benzyl bromide (entries 1 and 3) with a benzyl chloride function (entries 2 and 4) leads to greater conversion to the diarylated product **4a**, however, no activity is seen with a benzyl fluoride based substrate (entry 6). With regards coupling of the aryl halide, it appears the order is Br > Cl > I.

**Table 2** Coupling of **2** with **1a** Catalysed by $[Fe(acac)_3]$[a]




2 4 3

| Entry | $X^1$ | $X^2$ | Yield (%) of **4** | Yield (%) of **3** |
|---|---|---|---|---|
| 1 | Br | Br (**2a**) | 21 | (**3a**, $X^1$ = Br) 41 |
| 2 | Br | Cl (**2b**) | 41 | (**3a**) 12 |
| 3 | Cl | Br (**2c**) | 17 | (**3b**, $X^1$ = Cl) 36 |
| 4 | Cl | Cl (**2d**) | 27 | (**3b**) 34 |
| 5 | I | Cl (**2e**) | 9 | (**3c**, $X^1$ = I) 0 |
| 6 | Br | F (**2f**) | 0 | (**3a**) 0 |

[a] Conditions as per Scheme 3.

While these data are consistent with coordination of the benzyl halide directing the oxidative addition of the aryl halide, there are a couple of inconsistencies that suggest such a pathway may not be operative.

Firstly, it might be imagined that substituting the benzyl bromide for other potentially coordination-directing groups would facilitate biaryl coupling. However, this appears not to be the case: none of the substrates shown in Figure 3, which contain a range of potentially directing donor groups, are arylated by **1a** under the standard reaction conditions.

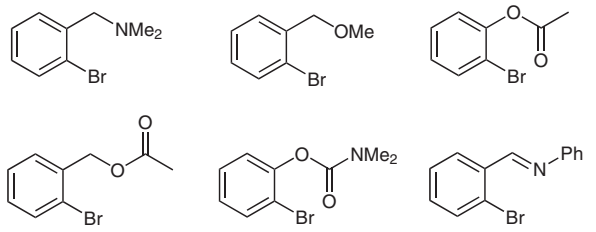
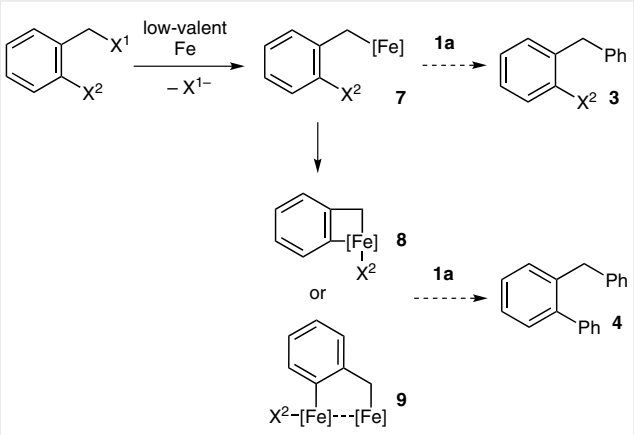



**Figure 3** Substrates that show no biaryl bond formation with **1a** (conditions as per Scheme 3, analysed by GC-MS)

Secondly, if aryl coupling does indeed precede benzylic coupling, one might expect to observe the formation of 2-phenylbenzyl halides, such as **6**. These, however, were never seen, even when the amount of borate used in the reaction was restricted to sub-stoichiometric amounts (0.5 equivalent with respect to **2a**, Scheme 4). It is possible that the rate of coupling at the benzylic position is accelerated by the introduction of the 2-aryl function, perhaps by $\eta^n$-coordination of the iron to the 2-aryl group (Figure 1, d).

An alternative tentative mechanism that accounts for many of the experimental observations is summarised in Scheme 5. In this scenario, a low-valent iron centre[16] reacts with the benzyl halide residue to yield the iron benzyl intermediate **7**.[17] This intermediate could then undergo reaction with **1a** to generate the simple cross-coupled product **3**. Alternatively the intermediate **7** could undergo either mono- or binuclear oxidative addition of the 2–X′-aryl function to generate the metallacyclobutene intermediate **8** or a dinuclear intermediate **9**. Subsequent reactions with **1a** would liberate the diarylated product **4**.




**Scheme 5** Tentative mechanism for the iron-catalysed mono- and diarylation of 2-halobenzyl halides

In summary, we have shown that the reaction of 2-halobenzyl halides with the boronate anion **1a** leads not only to the anticipated arylation of the benzyl position, but also to a unique iron-catalysed Suzuki biaryl bond formation under mild conditions. This does not seem to occur by the benzylic aryl group directing the second C–X bond cleavage. Instead our current hypothesis is that either the benzyl halide acts as a directing group or, perhaps more likely, a benzyl ligand is formed on iron, then the aryl C–X bond undergoes oxidative addition in either a mono- or dimetallic process. Probing this mechanism more deeply should allow us to understand the reaction and thus maximise its scope, and these studies are ongoing.

All reactions involving air- or moisture-sensitive reagents or products were carried out under an atmosphere of $N_2$ using standard Schlenk line techniques. Solvents were dried and purified using Anhydrous Engineering double alumina columns and alumina-copper catalyst drying columns. GC analysis was conducted using an Agilent Technologies 7820A, using calibration curves obtained from a minimum of five different concentrations of genuine samples of the products, with dodecane as an internal standard. GC-MS analysis was performed on a Varian Saturn 2100T. Substrates **2a**, **c** and **d** were purchased and used as received, as was intermediate **3b**.

## Preparation of Substrates

### THF Solution of Li[(Ph)(*t*-Bu)Bpin] (1a)

Anhydrous THF (6 mL) was added to 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.408 g, 2.0 mmol) and the solution stirred and cooled to –40 °C. *t*-BuLi (1.10 mL, 1.7 M in pentane, 1.87 mmol) was added dropwise at –40 °C and then the mixture stirred at this temperature for 30 min, then at 0 °C for a further 30 min before allowing to warm to r.t. The solution of **1a** was used without purification in the catalytic reactions.

### 2-Bromobenzyl Chloride (2b)

A solution of 2-bromobenzyl alcohol (0.94 g, 5 mmol) in THF (3 mL) was cooled to 0 °C. $SOCl_2$ (1.81 mL, 25 mmol) was added dropwise with vigorous stirring. The mixture was stirred for a further 3 h, then warmed to r.t. and concentrated in vacuo affording **2b**; yield: 0.97 g (95%); white solid.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 4.70 (s, 2 H, ArC$H_2$), 7.18 (t, *J* = 7.6 Hz, 1 H, ArH), 7.32 (t, *J* = 7.6 Hz, 1 H, ArH), 7.47 (d, *J* = 7.6 Hz, 1 H, ArH), 7.58 (d, *J* = 7.6 Hz, 1 H, ArH).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 46.3, 124.3, 128.0, 130.2, 131.0, 133.3, 136.8.

NMR data consistent with previously reported data.[18]

### 2-Iodobenzyl Chloride (2e)

Prepared in the same manner as described for **2b**, using 2-iodobenzyl alcohol (1.17 g, 5 mmol), which afforded **2e**; yield: 1.12 g (89%); white solid.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.9 Hz, 1 H), 7.46 (d, *J* = 7.7 Hz, 1 H), 7.34 (t, *J* = 7.6 Hz, 1 H), 6.99 (t, *J* = 7.7 Hz, 1 H), 4.66 (s, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 51.2, 99.7, 129.0, 130.2, 130.3, 139.9, 140.0.

NMR data consistent with previously reported data.[18]

### 2-Bromobenzyl Fluoride (2f)

Prepared according to a synthesis of benzyl fluoride.[19]

A solution of 2-bromobenzyl alcohol (1.87 g, 10 mmol) in anhydrous $CH_2Cl_2$ (10 ml) was added to a Deoxo-Fluor® solution (50% in THF, 4.73 mL, 11 mmol) in $CH_2Cl_2$ (10 mL) at –78 °C and the resultant mixture stirred for 3 h. The mixture was quenched by a slow addition of sat. aq $NaHCO_3$ (25 mL) over 10 min and extracted with $CH_2Cl_2$ (3 × 15 mL), dried ($Na_2SO_4$) and concentrated in vacuo to afford a yellow oil, which was purified by flash chromatography (hexane–EtOAc); yield: 1.06 g (56%).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 5.49 (d, *J* = 47.2 Hz, 2 H, ArC$H_2$), 7.23 (t, *J* = 7.9 Hz, 1 H, ArH), 7.37 (t, *J* = 7.6 Hz, 1 H, ArH), 7.49 (d, *J* = 7.6 Hz, 1 H, ArH), 7.58 (d, *J* = 7.9 Hz, 1 H, ArH).

## Preparation of Reference Samples of Products

### 2-Benzyl-1-bromobenzene (3a)[20]

Benzene (20 mL) was added slowly to 2-bromobenzyl alcohol (8.0 g, 42 mmol) and $FeCl_3$ (3.2 g, 20 mmol), then the mixture was heated at reflux for 12 h. Once cooled to r.t., the solvent was removed under reduced pressure and the residual solid purified by column chromatography (eluent: pentane) affording **3a** as a white solid; yield: 4.67 g (55%).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.0, 1.2 Hz, 2 H, ArH), 7.32 (t, *J* = 7.6 Hz, 2 H, ArH), 7.26–7.21 (m, 4 H, ArH), 7.16 (dd, *J* = 7.6, 1.7 Hz, 1 H, ArH), 7.10 (td, *J* = 8.0, 1.7 Hz, 1 H, ArH), 4.14 (s, 2 H, ArC$H_2$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 41.6, 124.9, 126.2, 127.4, 127.8, 128.5, 129.0, 131.0, 132.8, 139.9, 140.4.

### 2-Benzyl-1,1′-biphenyl (4)

$NiCl_2$ (13.1 mg, 0.101 mmol), $Cy_3P$ (57.7 mg, 0.202 mmol) and **3a** (0.5 g, 2.02 mmol) were stirred for 10 min in anhydrous THF (4 mL). A solution of phenylmagnesium chloride (1.52 mL, 3.04 mmol, 2.0 M) in THF was added dropwise at 0 °C with vigorous stirring and the resultant mixture stirred for a further 2 h. The reaction was quenched with sat. aq $NH_4Cl$ (20 mL) at 0 °C, extracted with $Et_2O$ (3 × 10 mL), dried ($MgSO_4$) and the solvent removed under reduced pressure to afford **4**; yield: 74.3 mg (15%); white solid.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.42 (m, 12 H, ArH), 7.00 (d, *J* = 7.4 Hz, 2 H, ArH), 3.98 (s, 2 H, ArC$H_2$).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 39.18, 125.91, 126.30, 127.61, 128.17, 128.37, 129.00, 129.44, 130.26, 130.44, 138.34, 141.59, 141.79, 142.40.

NMR data consistent with previously reported data.[21]

### Catalytic Reactions; General Procedure

A mixture of the appropriate iron catalyst (0.025 mmol), $Et_2O{\cdot}MgBr_2$ (1.0 mL, 0.1 M) in THF and the appropriate 2-halobenzyl halide (0.5 mmol) was stirred for 5 min. The borate anion solution **1a** in THF (5 mL, 1.5 mmol, 0.33 M) was added dropwise over 5 min with vigorous stirring. The reaction mixture was allowed to stir for 3 h before the addition of dodecane as an internal standard (110 µL, 0.50 mmol). An aliquot (~0.5 mL) was taken and passed through a plug of silica gel before being diluted with THF (0.5 mL) and analysed by GC.

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