



Borylation using group IV metallocene under mild conditions

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ABSTRACT

A borylation reaction of aromatic diazonium salts has been optimized using titanocene and zirconocene derivatives as catalysts. The reaction employs diisopropylaminoborane as a borylating agent and proceeds smoothly at room temperature to provide arylboronates after methanolysis and transesterification with pinacol. The reaction mechanism has been found to proceed via a radical pathway.

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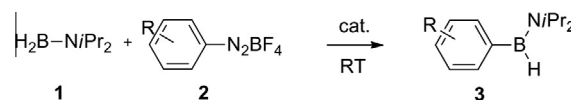
Boron derivatives are used in a plethora of domain and serve as efficient building block in synthesis.¹ Traditional organometallic addition to trialkylborate aside, carbon–boron bond formation is mostly achieved through two main reactions: hydroboration and catalyzed borylation.² Both have witnessed tremendous improvements over the last two decades with the introduction of transition metal catalysts, leading to better selectivities and easier product access. The main borylation methods have been developed using palladium activation of carbon–halide bond (Miyaura borylation)^{3–6} or Ar–H activation using iridium catalysts (Hartwig borylation).^{7–14} Both are very efficient and use traditional pinacolborane or pinacolatodiboron as boron source. Recently, we reported that the aminoboranes used in the same type of palladium catalyzed borylation^{15–20} could be used in combination with iron catalysis.^{21–23} Here, we would like to present the extension of our research related to the use of other metallocene to perform the same reactions.

We started to investigate group IV derived metallocene as they have been shown by Manners to activate dehydrogenation of the monoalkylamine borane complex into B–N oligomers.^{24,25} Hence, we envisioned that the activation of the B–H bond by those complex could advantageously be used to create a carbon boron bond. We chose aryldiazonium salts (Scheme 1) as they often appear to be the most reactive partners in coupling reaction owing to the irreversible generation of nitrogen during oxidative addition. They have additionally successfully been used for borylation reaction using pinacolatodiboron as coupling agent.^{26–29} More recently, they have been shown to add to bis(pinacolato)diboron

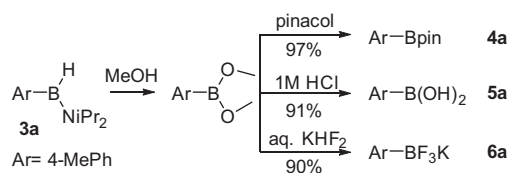
upon activation with peroxide when generated in situ from anilines.³⁰ Fundamentally, the presence of a B–H bond in the borylation reagent is likely to induce more competitive reduction of the substrate into the corresponding arene or the aniline.

Starting with the system described by Manners,²⁴ we evaluated the reaction of $i\text{Pr}_2\text{N}=\text{BH}_2$ **1** in the presence of 1% of $[\text{Cp}_2\text{Ti}]$ generated *in situ* by the addition of 2 equiv of $n\text{-BuLi}$ on Cp_2TiCl_2 .²⁴ By reaction with 4-MeC₆H₄N₂BF₄ **2a**, it led to the formation of the arylaminoborane 4-MeC₆H₄BHNiPr₂ **3a** in 30% yield. This compound, stable enough to be fully characterized by NMR, can advantageously be transformed into other boron derivatives using previously reported methods (Scheme 2).

This first catalytic system led to 15% of toluene as a reduction by-product, probably originating from the competitive hydride



Scheme 1. Borylation of arenediazonium salts with diisopropyl amino borane.

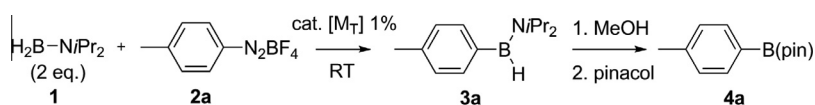


Scheme 2. Transformation of arylaminoboranes.

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Table 1
Catalytic system optimization



Entry	Catalyst	Solvent	Yield ^a (%)
1	—	THF	0
2	[TiCp ₂]	THF	30
3	[TiCp ₂]	CH ₃ CN	56
4	TiCp ₂ (CO) ₂	CH ₃ CN	60
5	(Cp ⁺ tBu) ₂ TiCl ₂	CH ₃ CN	61
6	Cp ⁺ TiCl ₃	CH ₃ CN	62
7	TiCp ₂ Cl ₂	CH ₃ CN	72
8	Cp ⁺ TiCl ₃	CH ₃ CN	67
9	TiCp ⁺ * ₂ Cl ₂	CH ₃ CN	61
10	(Indenyl) ₂ ZrCl ₂	CH ₃ CN	75
11	(tBuCp) ₂ ZrCl ₂	CH ₃ CN	68
12	Cp ₂ ZrCl ₂	CH ₃ CN	68
13	Cp ₂ ZrHCl	CH ₃ CN	74
14	[Cp ₂ Co]PF ₆	CH ₃ CN	61
15	Cp ₂ Co	CH ₃ CN	69
16	Cp ₂ Ni	CH ₃ CN	76
17	Cp ₂ Ru	CH ₃ CN	74

^a Isolated yield after pinacol treatment and purification.

transfer. A quick solvent screening showed that polar solvent favored greatly the reaction, most likely because of the poor diazonium solubility in apolar media. Most titanocene derivatives were found to efficiently catalyze the coupling reaction (Table 1, entries 3–9). Addition of alkyl lithium species to TiCp₂Cl₂ in various quantities led to minor differences in catalytic activities. Effect of cyclopentadienyl (Cp) ring replacement by the permethyl analog (Cp⁺) was unclear (Table 1, entries 8 and 9). Overall the titanocene dichloride was found to be the most active and practical complex to use.

As other metals were used for dehydrogenation of amine borane complexes, they were evaluated in the borylation process. Indeed zirconium based catalysts³¹ also efficiently promote the borylation reaction (Table 1 entries 10–13). Among all tested complexes the Schwartz's reagent turned out to be one of the most efficient (Table 1 entry 13) despite few differences within the results. Other metallocene derivatives were tried, including cobaltocene (Table 1 entry 15), cobaltocenium hexafluorophosphate (Table 1 entry 14), nickelocene (Table 1 entry 16), and ruthenocene (Table 1 entry 17) led to interesting results. As Schwartz's reagent is known to react with nitrile, we evaluated the imino zirconium complex formed by reaction between Cp₂ZrHCl and acetonitrile, it gave similar yields than without preformation.

This reaction was then extended to the use of other aryldiazonium salts. Overall the reaction proceeds smoothly with electron donating or withdrawing group. In most cases yields remain in the 60–80% range, which is quite decent considering they originate from a multistep sequence: aminoborylation, alcohol solvolysis, and transesterification by pinacol. In addition to methoxy groups (Table 2, entries 2–5), electron poor arylboronates, bearing nitro group (Table 2, entries 6 and 10), trifluoromethyl groups (Table 2, entries 7 and 9), cyano groups (Table 2, entry 8) can be obtained using this method. Not surprisingly, 4-benzoyl substituent led only to reduction product (benzophenone, Table 2, entry 25).

One advantage of this methodology is the complete compatibility with halide-substituted aryldiazonium salts. If fluorine arylboronates can be easily accessible using classical methods (Table 2, entries 12–14), the presence of chlorine, bromine and even more iodine, can lead to selectivity issues when performing borylation with classical reagents (organolithium or palladium/nickel catalysis). In our cases, chlorine (Table 2 entries 15–19) or bromine (Table 2 entries 20–22) substituted diazonium salts led to the corresponding boronates in similar yields to those obtained with

other substituents. Even iodobenzenboronates can be synthesized using our method (Table 2, entries 23 and 24).

Overall, apart from arylketo and carboxaldehyde substituted diazonium salts, this method was found to be quite general in terms of chemical substitution, likely owing to the mild conditions used during the process. Additionally, this method offers a preparation of boron derivatives which could appear more versatile than the previous methodologies using bis(pinacolato)diboron. Indeed, the resulting aryl amino borane can be transformed at will, depending on the work up of the borylation reaction, into the boronic acid, boronates, or trifluoroborate salts. As an example, diisopropylamino-(4-methyl)phenylborane **3a** is transformed by treatment with a MeOH/aq HCl mixture affording the corresponding boronic acid **5a** in 91% yield. Trifluoroborate salts are obtained from the same intermediate by treatment with a saturated aqueous solution of KHF₂ leading to the borate **6a** in 90% yield. Considering the safety issues associated with diazonium salts manipulation, we performed an experiment generating the salt in situ by reaction of the 4-methylaniline with isoamyl nitrite and BF₃·Et₂O. Yields were comparable (70%) but the reaction was slower than with the isolated diazonium salt (4 vs 2 h).

Even if our first rational for this reaction was based on the activation of the B–H bond by zirconocene and titanocene, we were deeply intrigued by the fact that any zirconocene and titanocene seem to promote this reaction. Moreover other metallocenes (Table 1 entries 14–17) led to the same conversion. We then performed a series of experiment to rule out the possibility of a classical ionic metal centered mechanism. In the case of a titanium centered mechanism the reaction is likely to start with the oxidative addition of the aryl diazonium salt to the metallocene (Scheme 3, A¹). The aryl transfer from the metal center onto the boron could proceed through an addition leading to an amidoborane (Scheme 3, A²)³² or via a metal assisted σ-bond metathesis (Scheme 3, A³).³³

However, despite our tries we never succeeded to obtain the cationic metallocenium by reacting titanocene (generated in situ from TiCp₂Cl₂) or zirconocene with a diazonium salt. In all cases, degradation occurred, mostly via arylation of the Cp ring. Moreover reaction of zirconocene dichloride **7** with one equivalent of phenyl lithium led to the phenylzirconocenium chloride **8**, which underwent an ion metathesis by the addition of silver tetrafluoroborate **9**. This sequence provided us a reference compound which was never observed during the standard reaction. Moreover, we never

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