# **ORGANOMETALLICS**

# Activation of C–H Activation: The Beneficial Effect of Catalytic Amount of Triaryl Boranes on Palladium-Catalyzed C–H Activation

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**S** Supporting Information

**ABSTRACT:** Herein we report a novel approach to the acceleration of palladium-catalyzed C–H activation reactions. We demonstrated that the utilization of electron-deficient triaryl boranes as Lewis acidic cocatalysts of palladium enables the directed cross dehydrogenative coupling of aldehydes and anilides under mild reaction conditions. Study of the kinetic profile of the transformation reveals a unique, unexpectedly long induction period of the transformation.



# INTRODUCTION

Transition-metal-catalyzed C-H activation reactions are widely used, efficient synthetic tools for the direct functionalization of C-H bonds, even in complex molecules.<sup>1</sup> These C-H bond functionalization reactions typically require relatively high temperature. For the sake of wider applicability, activation of the catalytic system is desirable, which is in principle possible either by enhancing the catalytic activity of the transition metal or activation of the substrate itself. Based on the current mechanistic understanding of the reaction, the barriers of the elementary steps can be reduced through the development of new catalysts, better reaction conditions, and beneficial additives. Considering that the opening step of the C-H activation process may occur via concerted metalation deprotonation (CMD a.k.a. IES/AMLA) or electrophilic metalation pathways, the utilization of transition-metal catalysts with noncoordinating anions<sup>2</sup> such as  $BF_4^-$  or  $SbF_6^-$ , could facilitate the directed ortho-metalation by the participation of more electrophilic "naked" metal ion.

In the past few years, Pd-catalyzed  $C(sp^2)$ -H activation reactions on arenes bearing diverse ortho-directing groups have been widely studied, including ortho acylations<sup>1n,3</sup> using different acyl equivalents. In continuation of our recent studies on C-H activation,<sup>3j,k</sup> we aimed to examine the effect of Lewis acids on the palladium-catalyzed cross-dehydrogenative coupling of anilides and aldehydes, as a conceptually new approach for the activation of the catalytic system. For our studies of palladium-catalyzed oxidative coupling of anilides and aldehydes, we selected electron-deficient triarylboranes as welldefined organic Lewis acids rather than inorganic compounds, due to the simplification of the system and to avoid any redox interaction of different metals. We hypothesize that the presence of organic borane-based Lewis acidic additives in the reaction may also accelerate the C-H activation reaction via their interaction with the palladium catalyst.

Electron-deficient boron compounds represent a powerful and well-studied<sup>4</sup> group of Lewis acids in synthesis (Scheme 1). They are widely used in polymer chemistry<sup>5</sup> and aldol and Michael reactions.<sup>6</sup> Most recently, they serve as excellent Lewis acid partners for Frustrated Lewis Pair (FLP) systems.<sup>7</sup>





We aimed to study the effect of various borane derivatives with different electronic properties on the target palladiumcatalyzed transformation.

# RESULTS AND DISCUSSION

The Lewis acid-free model reaction was performed as a reference with the attempted coupling of acetanilide and 4-fluorobenzaldehyde in the presence of  $Pd(OAc)_2$  catalyst in dichloromethane (DCM) at 30 °C using <sup>t</sup>BuOOH (5.5 M solution in decane) as the oxidant. In the absence of Lewis acid, the reaction is sluggish, and the desired acetamidobenzophenone was formed only in 8% conversion even after 24 h. We tested four triarylborane derivatives with different properties as

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Received: December 18, 2015
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Lewis acid additives (Scheme 2). Among the mesityl substituted borane-based Lewis acids, trimesityl or the bis-

# Scheme 2. Conversions of the Same Reaction after 24 h with the Triaryl Boranes as Additives<sup>a</sup>



<sup>a</sup>Conversions were determined with GC.

tetrafluorophenyl derivative provide 5–7% conversion, whereas the more-electron-deficient bis-perfluorophenyl-mesitylborane provides coupled product in 94% conversion. Utilization of trispentafluorophenyl borane as the most Lewis acidic BR<sub>3</sub> additive ensured the full conversion of the reaction in 24 h at 30 °C.

In comparison to organic boranes, we tested simple inorganic boranes as hard Lewis acids. The reactions performed in the presence of hard Lewis acidic boron trihalides such as  $BCl_3$  and  $BBr_3$  did not provide the expected product. It is well-known that halide anions have a significant deleterious effect on the C–H activation step as these inorganic hard Lewis acids can serve as halide sources in the reaction and block the catalytic cycle. This comparative study revealed the special role and strong influence of electron deficient triaryl boranes on the palladium-catalyzed C–H activation.

To simplify the mechanistic studies, we first used <sup>19</sup>F NMR to examine the interaction of  $Pd(OAc)_2$  and  $B(C_6F_5)_3$  to find evidence for the supposed catalyst activation via acetate abstraction. Upon the addition of the palladium catalyst to the dichloromethane solution of the borane, new sets of two multiplets appeared immediately next to the parent borane ortho, meta, and para fluorine signals [133 ppm (ortho), 163 ppm (meta), 153 ppm (para).]. This appearance of new signals in the NMR spectra refers to the formation of new borane complex(es) in the solution (Figure 1. middle spectrum). To confirm the existence of borane-acetate Lewis acid-base interaction in the case of  $Pd(OAc)_2$ -B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, we also treated the tris-pentafluorophenyl borane with NH4OAc, under the same reaction conditions. The obtained <sup>19</sup>F-NMR spectra of this mixture provided the same pattern of the <sup>19</sup>F shifts such as the palladium-borane mixture (Figure 1, top spectrum). The pattern of the spectra obtained in these <sup>19</sup>F NMR experiments supports the hypothesis that the addition of Lewis acidic borane facilitates the formation of a more electrophilic palladium species via acetate abstraction and the formation of acetateborane Lewis acid-base adduct.

On the basis of the previous experiments, we suppose that acetate could interact with the borane, but we should also consider that there are several potential Lewis basic partners present in the reaction mixture to which the borane species can coordinate. It is known that the tris-pentafluorophenyl borane forms Lewis acid—base adducts with both aldehydes and



Figure 1.  $^{19}F$  NMR shifts of  $B(C_6F_5)_3$  (bottom) and effect of additional  $Pd(OAc)_2$  (middle) or  $NH_4OAc$  (top) in  $CD_2Cl_2$  under  $N_2$  atmosphere.

amides.<sup>8</sup> <sup>19</sup>F NMR studies were run to investigate the affinity of the borane toward each reagent. When the borane was mixed with one of the reagents, the formation of new borane species was observed in solution by <sup>19</sup>F NMR measurements (see SI, Chapter 4).

Next, we prepared the borane–benzaldehyde complex and measured the IR spectra of the compound in the solid form. The characteristic peak of carbonyl group in the complex was found at 1620 cm<sup>-1</sup>, which is in good agreement with the literature data.<sup>8</sup> However, when the IR spectra of the prepared complex was taken in DCM or toluene solution, the characteristic peak of carbonyl–borane interaction disappeared. This comparative study revealed that the interaction between the borane and the Lewis base is weaker in solution.

Nevertheless, we can still expect several possible interactions of the borane species with the LB partners present. It was demonstrated by Piers that the least basic component had the lowest tendency to interact with the LA to form Lewis acid–base adduct in the reaction mixture and the more Lewis basic components straightforwardly displaces the weaker one from their borane Lewis acid–base adduct.<sup>8</sup> This well-documented phenomenon, supports the preferred interaction of the more Lewis basic carbonyl compounds. However, interactions of other Lewis basic components with the free borane in equilibrium cannot be ruled out completely. Unfortunately, the monitoring of the full reaction mixture to determine any intermediates by <sup>19</sup>F NMR was not feasible due to the complexity of the NMR spectra.

To overcome the difficulties in finding and identifying interactions of the borane with any reactants and possible intermediates of the catalytic cycle, we aimed to examine the role of the borane in the catalytic transformation (Scheme 3).

To achieve this, we prepared the stable bimetallic palladium complex 4 and examined its reactivity toward aldehyde in the presence and absence of borane under the standard reaction conditions. The acetate-bridged palladacycle could not be isolated, and therefore, we used the more stable complex 4 for this study.<sup>9</sup> We observed similar conversions of complex 4 with the coupling of aldehyde (Scheme 3) either in the presence or the absence of borane (50% and 49% conversions; 39% and

Scheme 3. Reaction of Dimeric Palladium Complex 4 with 4-Fluorobenzaldehyde in the Absence and Presence of Triarylborane



42% isolated yield of **3a** after 20 h reaction time). The result of this comparative study supports our suggestion that the borane has influence only in the carbopalladation step.

After demonstrating the importance of triarylborane in the C–H activation, we aimed to determine the optimal palladium/ borane ratio for the reaction of 1a and 2a. When 2.5 mol % palladium was used, we observed low conversions independent from the borane loading (0–30 mol % range). An insignificant maximum was observed in the conversions when 7 mol %  $B(C_6F_5)_3$  was applied. However, in this case the conversion was only 23% (Figure 2, top).

Next, we studied the coupling of acetanilide 1a and 4fluorobenzaldehyde (2a) in the presence of 5 mol % Pd(OAc)<sub>2</sub> in dichloromethane (DCM) at 30 °C. The borane loading effect was examined in the range of 0-100 mol % (Figure 2. middle). Interestingly, we found an optimum for the borane loading. The transformation reached the highest conversion after 24 h reaction time, when the reaction was carried out in the presence of 7 mol %  $B(C_6F_5)_3$ . The borane amountconversion curves show either the lower or the higher amount of borane has a deleterious effect on the transformation. We suppose that the Lewis acidic species may facilitate the formation of the more electrophilic palladium species by its interaction of the acetate ion brought by the metal, whereas overloading is undesirable as it gives way to coordination of the Lewis acid to several reactants blocking the optimal reaction pathway.

Interestingly, when 10 mol % palladium acetate was used as catalyst, the optimal borane loading was 30 mol % to reach almost full conversion in 24 h. In this case, we also observed the same phenomenon regarding the influence of different Lewis acid/palladium catalyst ratios on the reaction. Low borane loading does not facilitate the reaction, but overloading of the borane leads again to inhibition of the reaction (Figure 2, bottom).

The effect of the palladium/borane ratio on the conversion measured after 24 h, initiated us to gain deeper insight into the transformation. First, we monitored the coupling of the anilide and the aldehyde in the presence of 5 mol %  $Pd(OAc)_2$  and 7 mol % borane by sampling and GC analysis. To our surprise, the time–conversion curve gave an unusual profile (Figure 3).

We observed that the homogeneous catalytic reaction has an unexpectedly long induction period. We found no transformation in the first 6 h of the reaction, but after this period, the coupling reaction started and completed in 24 h overall reaction time.

In order to exclude the accidental effect of sampling on the transformation, we followed the coupling reaction of acetanilide and 4-fluorobenzaldehyde at 30  $^{\circ}$ C with the aid of real time IR spectroscopic analysis. Fortunately, two IR bands of the



Figure 2. Effect of  $B(C_6F_5)_3$  loading on the palladium-catalyzed coupling: 2.5 mol %  $Pd(OAc)_2$  (top), 5 mol %  $Pd(OAc)_2$  (middle), 10 mol %  $Pd(OAc)_2$  (bottom). Conversions were measured after 24 h and determined with GC.

product (1637 and 925  $\text{cm}^{-1}$ ) enabled the monitoring of its formation (Figure 4).

In situ IR spectroscopy studies supported the previous results obtained by GC analysis. The unexpected progress of the product formation including unusually long induction period was also confirmed with this study. Our study showed that in reaction with 5%  $Pd(OAc)_2$  and 7.2%  $B(C_6F_5)_3$  the initiation



Figure 3. Progress of the formation of product 3a monitored by gas chromatography.



Figure 4. Appearance and evolution of characteristic IR bands of product 3a: (top) 1637, (bottom) 925 cm<sup>-1</sup> during the first 16 h of the coupling reaction.

period takes about 5.5 h. After this period of time, the catalytic process starts and the formation of the coupling product was observed. Although , at this point, we are not able to explain the occurrence of the unprecedentedly long induction period, with the aid of IR data analysis, the formation and decomposition of a transient species was suspected during the initial period of the catalytic transformation. While we did not detect any other species in the reaction mixture during this initial period, we suppose that the formation and decomposition of this transient species prior to the formation of the product is important for the transformation.

Reaction conditions: acetanilide (0.5 mmol), 4-fluorobenzaldehyde (1 mmol, 105  $\mu$ L), Pd(OAc)<sub>2</sub> (0.025 mmol, 5.6 mg), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.036 mmol, 18 mg), TBHP (5.5 M in decane, 4 Å M.S.) (1 mmol, 200  $\mu$ L), anh. DCM (1 mL), nitrogen atmosphere, 30 °C, 24 h. Yields of isolated materials are indicated.

After the demonstration of the significant effect of borane type Lewis acids on the coupling, we aimed to explore the generality of the phenomenon in this palladium-catalyzed C–H activation reaction. We performed several coupling reactions of diverse anilides and aldehydes using tris-perfluorophenylborane as the borane-based Lewis acid under mild reaction conditions (DCM, 30 °C). Acylation of the electron-rich acetanilide derivatives with 4-fluorobenzaldehyde in the presence of borane provided the appropriate benzophenone derivatives (**3a**, **3c**, **3d**, and **3f**) in 40–99% yield (Scheme 4). Ortho-substituted and





electron-deficient anilides are more challenging substrates for this palladium-catalyzed reaction. *Ortho*-subtituted substrates afforded *ortho*-acylated products **3b** and **3e** in 21 and 32% yield, respectively, in the Lewis acid-accelerated coupling. Anilides bearing chloro and fluoro function, as well as the naphthyl derivative **3g**-**j** were also coupled with 4-fluorobenzaldehyde, and the desired products were obtained in 31–65% yield.

Next, we examined the reactivity of different aldehydes toward acetanilide in Lewis acid-accelerated C–H activation reactions (Scheme 5). We found that benzaldehyde derivatives bearing electron-donating or electron-withdrawing substituents on the phenyl ring provide the appropriate products (3k-v) in 44–91% yield. 2-Naphtaldehyde, phenylacetaldehyde, and aliphatic aldehydes also were compatible with the reaction conditions and the benzophenone derivatives (3w-z) were isolated in 17–63% yield.

We envisioned the following putative catalytic cycle for the transformation (Scheme 6). The highly electrophilic palladium monoacetate cation forms from  $Pd(OAc)_2$  via acetate abstraction by the assistance of the Lewis acidic triarylborane. In the following step, the amide-directed *ortho* C–H activation takes place resulting the carbopalladated species. Next, we propose that the monomeric palladium complex dimerizes and a bimetallic palladium intermediate forms. In our earlier work, we demonstrated by quantum chemical calculations that the

Scheme 5. Reactions of Different Aldehydes with Acetanilide



Scheme 6. Proposed Mechanistic Picture



formation of dimeric palladium complex provides an energetically more favorable pathway compared with the cycle based upon a monomeric species.

Reaction conditions: acetanilide (0.5 mmol, 67.5 mg), aldehyde (1 mmol),  $Pd(OAc)_2$  (0.025 mmol, 5.6 mg),  $B(C_6F_5)_3$  (0.036 mmol, 18 mg), TBHP (5.5 M in decane, 4 Å M.S.) (1 mmol, 200  $\mu$ L), anh. DCM (1 mL), nitrogen atmosphere, 30 °C, 24 h. Yields of isolated materials are indicated.

Benzoyl radical generated from the aldehyde with TBHP reacts with the dimer palladium complex, and the formed benzoyl palladium species provides the acetamido benzophenone derivative in a reductive elimination step.

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Summarizing our results, we have demonstrated for the first time that addition of electron-deficient tris-perfluorophenylborane as a Lewis acid additive has a significant influence on a palladium-catalyzed C-H activation reaction. We have found that the Lewis acid acceleration facilitates palladium-catalyzed cross dehydrogenative couplings of aromatic and aliphatic aldehydes with N-arylacetamide derivatives to access aminobenzophenones. On the basis of NMR, IR spectroscopic and experimental results, we hypothesize that a specific affinity of the borane toward the transition metal catalyst giving way to the evolution of a more electrophilic palladium species as active catalyst. This should be adjusted by fine-tuning of the electrophilicity of the Lewis acid. We have revealed the importance of the optimal borane/palladium catalyst ratio for the coupling, and we identified a catalytic transformation with unique and unusual induction period. The mechanistic studies of the transformation and the extension of this Lewis acid effect in the field of C-H activation reactions are in progress in our laboratory.

### EXPERIMENTAL SECTION

General Method. Under nitrogen atmosphere (in glovebox), a flame-dried screw cap 4 mL vial with a stirring bar was charged with amide (0.5 mmol, 1 equiv) and  $Pd(OAc)_2$  (0.025 mmol, 5.6 mg, 5 mol %) and the mixture was dissolved in anhydrous dichloromethane (1 mL). Tris(pentafluoro)phenyl borane (0.036 mmol, 18 mg, 7.2 mol %), 4-fluorobenzaldehyde (1 mmol, 105  $\mu$ L, 2 equiv), and TBHP solution (5.5 M in decane, 4 Å M.S.) (1 mmol, 200  $\mu$ L, 2 equiv) were added, and the vial was closed with a septum screw cap. The reaction mixture was removed from the glovebox and stirred at 30 °C for 18 h under inert atmosphere. The mixture was diluted with DCM, washed with 1 N HCl solution and water. The collected organic phases were dried with anhydrous sodium sulfate, and the solvent was removed in vacuum. The product was purified by column chromatography and dried in vacuum.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.Sb01017.

Experimental procedures, optimization studies, characterization data, and NMR spectra for all compounds (PDF)

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# Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This project was supported by the "Lendület" Research Scholarship of the Hungarian Academy of Sciences (LP2012-48/2012) and research grant by National Research, Development and Innovation Office TÉT-10-1-2011-0245. The generous donation of mesytilboranes, help, and technical support of Dr. Tibor Soós and co-workers at the Hungarian Academy of Sciences is gratefully acknowledged. The authors also thank Prof. Tim Peelen (Lebanon Valley College) for the proofreading of this manuscript.

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