

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

Orsolya Tischler, Zsófia Bokányi, Zoltán Novák*

MTA-ELTE "Lendület" Catalysis and Organic Synthesis Research Group, Institute of Chemistry.
Eötvös Loránd University, Pázmány Péter stny. 1/a, Budapest, 1117, Hungary

Supporting Information Placeholder

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 co-catalyst 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 molecules¹. These C-H bond functionalization reactions typically require relatively high temperature. For the sake of wider applicability the activation of the catalytic system is needed which is in principle possible either by enhancing 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 anions² such as BF_4^- or SbF_6^- , facilitates the directed *ortho*-metallation by the participation of more electrophilic "naked" metal ion.

In the past few years, Pd-catalyzed $\text{C}(\text{sp}^2)\text{-H}$ activation reactions on arenes bearing diverse *ortho*-directing groups have been widely studied, including *ortho* acylations^{1n, 3} using different acyl equivalents. In continuation of our recent studies on C-H activation,^{3i, 3k} 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 well-defined 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-studied⁴ group of Lewis acids in synthesis (Scheme 1). They are widely used in polymer chemistry,⁵ aldol and Michael reactions⁶. Most recently, they serve as excellent Lewis acid partners for Frustrated Lewis Pair (FLP)⁷ systems.

Scheme 1. Synthetic applications of $\text{B}(\text{C}_6\text{F}_5)_3$

We aimed to study the effect of various borane derivatives on the target palladium catalyzed transformation, considering the electronic effects of the borane center

RESULTS AND DISCUSSION

The Lewis acid free model reaction as a reference was performed with the attempted coupling of acetanilide and 4-fluorobenzaldehyde in the presence of $\text{Pd}(\text{OAc})_2$ catalyst in dichloromethane (DCM) at 30 °C using $t\text{BuOOH}$ (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 hours. As Lewis acid additive we tested four triarylborane derivatives with different properties (Scheme 2). Amongst the mesityl substituted borane-based Lewis acids trimesityl or the bis-tetrafluorophenyl derivative provide 5-7% conversion, while the more electron deficient bis-perfluorophenyl-mesitylborane provides coupled product in 94% conversion.

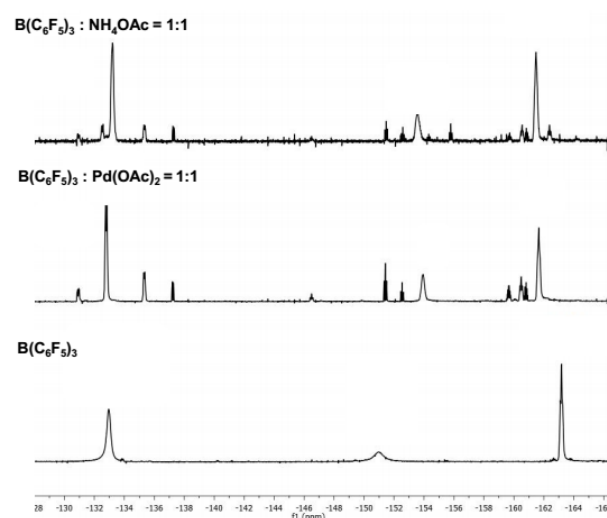
Scheme 2. Conversions of the same reaction after 24 hours with the triaryl boranes as additives. Conversion were determined with GC.

Utilization of tris-pentafluorophenyl borane as the most Lewis acidic BR_3 additive ensured the full conversion of the reaction in 24 hours 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 at all. It is well known that halide anions have significant deleterious effect on the C-H activation step, and 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, first we examined the interaction of $\text{Pd}(\text{OAc})_2$ and the $\text{B}(\text{C}_6\text{F}_5)_3$ to find evidence of the supposed catalyst activation via acetate abstraction. To achieve this we performed ^{19}F NMR measurements and examined the interactions between $\text{Pd}(\text{OAc})_2$ and tris-pentafluorophenyl borane. Upon the addition of the palladium catalyst to the dichloromethane solution of the borane three 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 (Scheme 3. middle spectrum). To confirm the existence of borane-acetate Lewis acid base interaction in case of $\text{Pd}(\text{OAc})_2\text{-B}(\text{PhF}_5)_3$ we treated the tris-pentafluorophenyl borane also with NH_4OAc , under the same reaction conditions. The

obtained ^{19}F -NMR spectra of this mixture provided the same pattern of the ^{19}F shifts such as the palladium-borane mixture (Figure 1. top spectrum). However, we were not able to identify any other species in solution the pattern of the spectra obtained in these ^{19}F NMR experiments supports the hypothesis that the addition of Lewis acidic borane may facilitate the formation of more electrophilic palladium species via acetate abstraction and the formation of acetate-borane Lewis acid-base adduct.

Figure 1. ^{19}F NMR shifts of $\text{B}(\text{C}_6\text{F}_5)_3$ (bottom) and effect of additional $\text{Pd}(\text{OAc})_2$ (middle) or NH_4OAc (top) in CD_2Cl_2 under N_2 atmosphere



Beyond the existence of the key interaction for accelerated C-H activation we should consider that there are several potential Lewis basic partners present in the reaction mixture for the borane species to coordinate to. It is known that the tris-pentafluorophenyl borane forms Lewis acid-base adducts both with aldehydes and amides.⁸ ^{19}F NMR studies were run to investigate the affinity of the borane towards each reagent. When coordination to a Lewis basic partner takes place native symmetry of the three perfluoroaryl rings is distorted resulting in split and additional signs (see SI). In contrast, we were not able to identify any interaction between the borane and the carbonyl substrates with in situ IR studies. Although, the observed NMR shifts were identical with the finding of Piers⁸ the expected IR band shift from 1703cm^{-1} to 1620cm^{-1} of aldehyde carbonyl was not observed in solution. Next, we prepared the borane-benzaldehyde complex and measured the IR spectra of the compound in solid form. The characteristic peak of carbonyl function in the complex was found at 1620cm^{-1} , which is in good agreement with the literature data. 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 borane has no significant and characteristic interaction with the aldehyde carbonyl function in solution. However, we can expect several possible interactions of the borane species with the LB partners present. It was demonstrated by Piers⁸ 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 elaborates the weaker one from their borane Lewis acid-base adduct. This well documented phenomenon, supports the preferred interaction of more Lewis basic acetate ion with the borane even in the presence of less 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 ¹⁹F 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 towards aldehyde in the presence and absence of borane under the standard reaction conditions. Acetate bridged palladacycle could not be isolated, therefore we used the more stable complex **4** for this study⁹. As the result, 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%). The result of this comparative study supports our suggestion that the borane has influence only in the carbopalladation step.

Scheme 3. Reaction of dimeric palladium complex **4 with 4-fluorobenzaldehyde in the absence and presence of triarylborane**

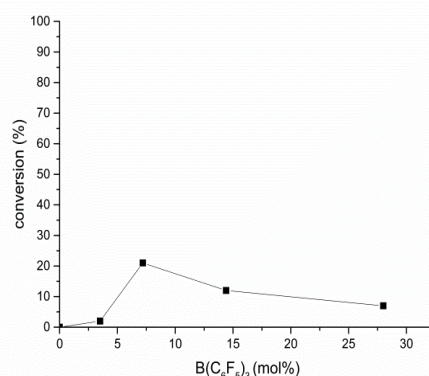
After demonstrating the importance of triarylborane in the C-H activation we aimed to determine the optimal palladium:borane ratio for the reaction of **1a** and **2a**. When 2.5 mol% palladium was used we observed low conversions independently from the borane loading (0-30 mol% range). An insignificant maximum was observed in the conversions when 7 mol % B(C₆F₅)₃ was applied. However, in this case the conversion was only 23% (Figure 2. top).

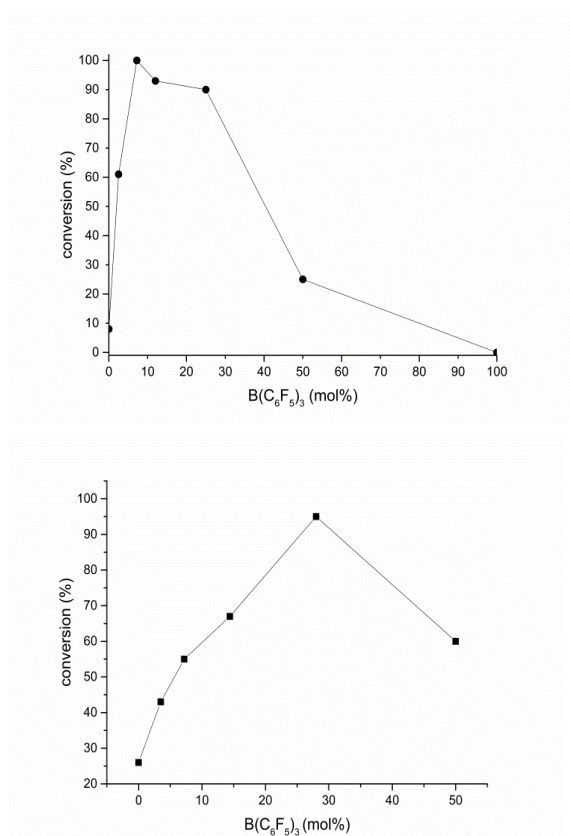
Next, we studied the coupling of acetanilide **1a** and 4-fluorobenzaldehyde (**2a**) in the

presence of 5 mol% Pd(OAc)₂ 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 hours reaction time, when the reaction was carried out in the presence of 7 mol% B(C₆F₅)₃. The borane amount-conversion curves show either the lower or the higher amount of borane has deleterious effect on the transformation. Regarding the explanation of the significant influence of the electron deficient triaryl borane on the reaction 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. On the other hand 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 hours. 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).

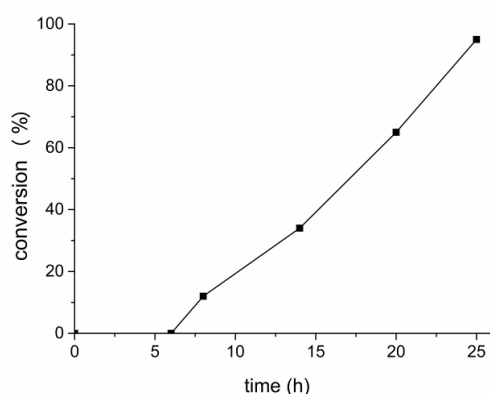
Figure 2. Effect of B(C₆F₅)₃ loading on the the palladium catalyzed coupling. 2.5 mol% Pd(OAc)₂ (top), 5mol% Pd(OAc)₂ (middle), 10mol% Pd(OAc)₂ (bottom) Conversions were measured after 24 hours, and determined with GC.





The revealed effect of the palladium:borane ratio on the conversion measured after 24 hours, initiated us to gain deeper insight to 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 special profile (Figure 3.).

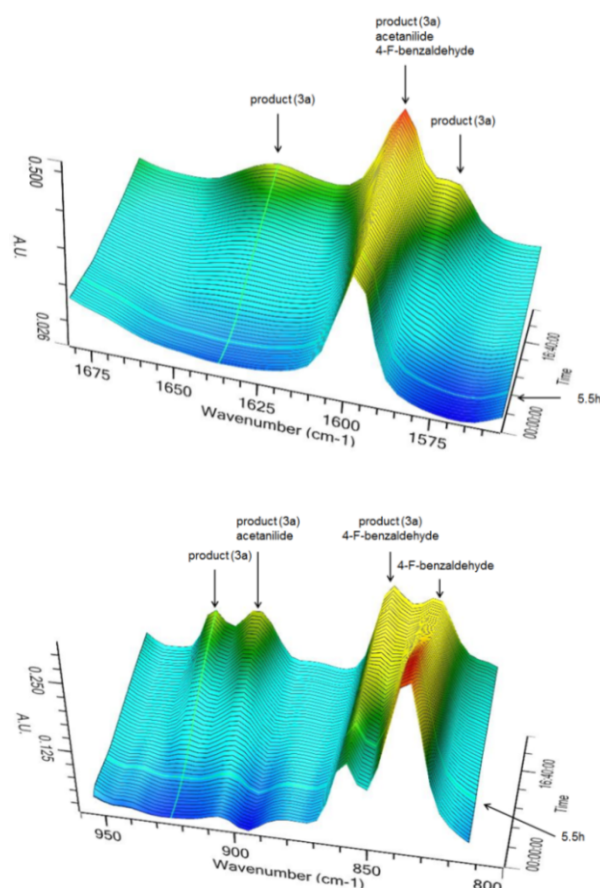
Figure 3. Progress of the formation of product 3a monitored by gas chromatography.



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

In order to exclude the accidental effect of sampling on the transformation we intended to follow the coupling reaction of acetanilide and 4-fluorobenzaldehyde at 30 °C with the aid of real time IR spectroscopic analysis. Fortunately, two IR bands of the product (1637 cm^{-1} and 925 cm^{-1}) enabled the monitoring of its formation (Figure 4.).

Figure 4. Appearance and evolution of characteristic IR bands of product 3a: (top) 1637 , (bottom) 925 cm^{-1} during the first 16 hours of the coupling reaction.



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. As we registered, in case of 5% $Pd(OAc)_2$ and 7.2% $B(C_6F_5)_3$ the initiation period takes about 5.5 hours. 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.

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.).

Scheme 4. Reactions of different N-aryl acetamides. Reaction conditions: acetanilide (0.5 mmol), 4-fluorobenzaldehyde (1 mmol, 105 μ L), Pd(OAc)₂ (0.05mmol, 5.6 mg), B(C₆F₅)₃ (0.036 mmol, 18 mg), TBHP (5.5 M in decane, 4 \AA M.S.) (1 mmol, 200 μ L), anh. DCM (1 mL), nitrogen atmosphere, 30°C, 24 h. Yields of isolated materials are indicated.

Ortho substituted and electron deficient anilides are more challenging substrates for this palladium-catalyzed reaction. Ortho-substituted 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, and 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.

Scheme 5. Reactions of different aldehydes with acetanilide. Reaction conditions: acetanilide (0.5 mmol, 67.5 mg), aldehyde (1 mmol), Pd(OAc)₂ (0.05mmol, 5.6 mg), B(C₆F₅)₃ (0.036 mmol, 18 mg), TBHP (5.5 M in decane, 4 \AA M.S.) (1 mmol, 200 μ L), anh. DCM (1 mL), nitrogen atmosphere, 30°C, 24 h. Yields of isolated materials are indicated.

We envisioned a 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 guided *ortho* C-H activation takes place resulting the carbopalladated species. Next, the monomeric palladium complex dimerizes and supposedly a bimetallic palladium intermediate forms. In our earlier work we demonstrated by quantumchemical calculations that the formation of dimeric palladium complex opens energetically more favourable path over the cycle which is based on monomeric species. 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.

Scheme 6. Supposed mechanistic steps of the catalytic process

CONCLUSION

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. Based on NMR, IR spectroscopic and experimental results we hypothesize that a specific affinity of the borane towards 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 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 glove-box) 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 anhyd. dichloromethane (1 mL). Tris(pentafluorophenyl) borane (0.036 mmol, 18 mg, 7.2 mol%), 4-fluorobenzaldehyde (1 mmol, 105 µL, 2 equiv.) and TBHP solution (5.5M in decane, 4 Å M.S.) (1 mmol, 200 µL, 2 equiv.) were added afterwards and the vial was capped with septum screw cap. Taken into fume hood from the glove-box the reaction mixture was magnetically stirred at 30°C for 18 hours under inert atmosphere. The mixture was diluted with DCM, washed with 1N HCl solution and water. The unified organic phases were dried with anhyd. sodium sulphate and solvent was removed in vacuum. The product was purified by column chromatography and dried in vacuum.

ASSOCIATED CONTENT

Supporting Information

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

The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* novakz@elte.hu

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