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Hydride Transfer Enables the Nickel-catalyzed ipso-Borylation and Silylation of Aldehydes

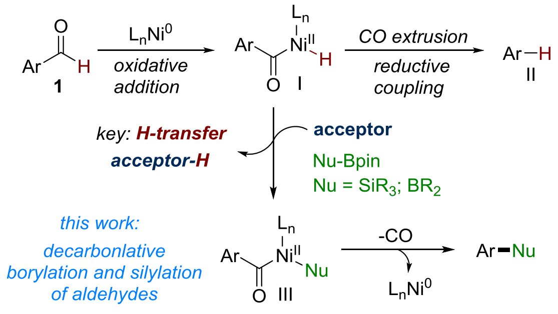
Watchara Srimontree, Lin Guo and Magnus Rueping*

Abstract: Nickel-catalyzed ipso-borylations and silylations of aldehydes are described for the first time. The new functional group interconversion protocol is characterized by its scalability, functional group tolerance and wide substrate scope, including examples of late-stage functionalization of complex molecules. The key for the successful reaction outcome is the use of a ketone as hydride acceptor which intercepts the nickel hydride to undergo a reductive pathway, thus allowing formation of the desired C-B and C-Si bonds.

Organoboron compounds play a crucial role as versatile key intermediates in organic synthesis for the elaboration of complex structures. Due to their stability, low toxicity, and ease of handling, boron containing-molecules are widely exploited in materials science and medicinal chemistry.[1] These compounds are classically prepared by the reaction of organolithium or Grignard reagents with boron electrophiles.[2] However, limitations regarding the functional group tolerance exist in the above-mentioned synthetic protocols. Yet, it is generally known that transition-metal-catalyzed cross-coupling reactions constitute a reliable and straightforward approach to construct C-C and C-heteroatom bonds,[3] including the carbon-boron bond formation.[4] To explore environmental friendly methods in this area, electrophiles bearing less reactive chemical bonds were recently evaluated instead of commonly used organohalides. Although arenes and heteroarenes are widely used as electrophiles in C-H borylation reactions for the synthesis of arylboronate esters,[4a-d] some protocols are not able to provide good regioselectivity and hence effective directing groups are necessary. Regarding these drawbacks, researchers focused on designing viable substrates which can be converted into boronate esters.[5-9] Recently, innovative strategies using carboxylic acid derivatives have been developed and the transition-metal-catalyzed decarbonylative borylation of carboxylic acid derivatives has been accomplished.[10] However, additional steps such as esterification, thioesterification and amidation are required for their synthesis from carboxylic acids. In addition stoichiometric amounts of by-products (phenols, thiols, amides) have to be removed. To overcome these disadvantages, a novel synthetic strategy is now considered.

Due to its stability, easy availability and low toxicity, aldehydes are regarded as one of the simplest functional groups which can be widely manipulated in organic synthesis. Surprisingly, the use of aldehydes in transition-metal-catalyzed cross-coupling reactions via a decarbonylative pathway has rarely been described. The existing precedents are currently restricted to reactions with alkenes or alkynes and make use of noble metal catalysts, such as rhodium and ruthenium.[11] Prompted by the recent prosperity of nickel catalyzed transformations and our recent work in the area,[12] we began to question whether a decarbonylative cross-coupling reaction of aldehydes, in particular a decarbonylative borylation and silylation, could be achieved via nickel catalysis. We anticipated that the successful validation of this strategy would make aldehydes an ideal synthetic building block which potentially could even be employed in late-stage modifications.

To achieve this goal several challenges need to be addressed. Nickel catalysts readily undergo oxidative addition to aldehydes **1** to provide acylnickel hydride species (**I**)[13] that can easily undergo CO migration and reductive elimination to provide the corresponding arenes (**II**). However, the decarbonylative/reductive process may be intercepted by a suitable hydride acceptor which would prevent the formation of the arene. Hence, upon hydride transfer and transmetallation the nicke(II)-complex (**III**) would be formed and subsequent CO extrusion and reductive elimination would result in the formation of the desired silylated or borylated products. Thus, key for the overall nickel catalyzed *ipso*-borylation/silylation of aldehydes is the hydride acceptor that needs to be readily available and compatible with the overall reaction sequence. Furthermore, the reaction conditions need to be mild in order to prevent further reaction. In addition, the use of strong base needs to be avoided, guaranteeing a good functional group tolerance.



Scheme 1. Concept of the Ni-catalyzed *ipso*-borylation and silylation of aldehydes using a hydride transfer as key step.

Based on the above, ketones were considered as possible H-acceptors as they would suit all of these requirements (they are readily available, stable, compatible, and good H-acceptors for the hydride-transfer step, and the formed alcoholate is a also good activator for the transmetalation.

Therefore, our initial efforts in this study focused on evaluating the reaction of 2-naphthaldehyde (**1a**) and bis(pinacolato)diboron (**2**) in the presence of $Ni(cod)_2$ and different ketones as H-acceptors. From the different ketones tested, 2,2,2-trifluoro-1-(4-fluorophenyl)-

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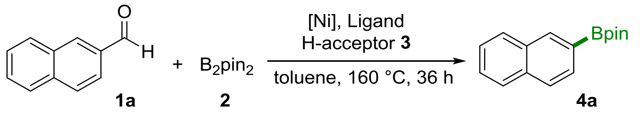
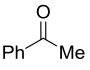
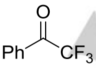
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) ethanone (**3c**) provided the best results (Table 1). Ligands play an important role in cross-coupling reactions. Use of bidentate phosphine and *N*-heterocyclic carbene ligands did not provide the desired product **4a** (entries 1-4), whereas the utilization of a trialkylphosphine ligand PCy_3 provided **4a** (entry 5). The yield increased significantly when PCy_3 was substituted by other tri(*n*-alkyl)phosphines (P*n*-Bu_3 and P*n*-Oct_3), affording **4a** in 69% and 71% yield, respectively (entries 6 and 7). Attempts to use other nickel catalysts, did not result in any improvement (entries 8 and 9).

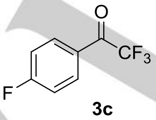
Table 1. Optimization of the reaction conditions.[a]

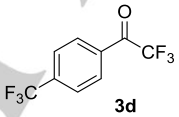


Entry	[Ni] Cat. (10 mol%)	Ligand (x mol%)	Hydride Acceptor	Yield (%)[b]
1	Ni(cod)$_2$	dcype (10)	**3c**	0
2[c]	Ni(cod)$_2$	SIPr·HCl (20)	**3c**	trace
3[c]	Ni(cod)$_2$	IPr·HCl (20)	**3c**	12
4[c]	Ni(cod)$_2$	IMes·HCl (20)	**3c**	trace
5	Ni(cod)$_2$	PCy_3 (20)	**3c**	32
6	Ni(cod)$_2$	P^nBu_3 (20)	**3c**	69
7	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3c**	71
8	Ni(cod)$_2$	-	**3c**	0
9	Ni(acac)$_2$	P(Oct)$_3$ (20)	**3c**	trace
10	Ni(OAc)$_2$·4H$_2$O	P(Oct)$_3$ (20)	**3c**	34
11	-	P(Oct)$_3$ (20)	**3c**	0
12	Ni(cod)$_2$	P(Oct)$_3$ (20)	-	0
13	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3a**	0
14	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3b**	64
15	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3d**	34
16[d]	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3c**	64
17[e]	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3c**	62
18[f]	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3c**	63
19[g]	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3c**	53
20[h]	Ni(cod)$_2$	P(Oct)$_3$ (20)	**3c**	82(79)[i]
21[h,j]	**Ni(cod)$_2$**	**P(Oct)$_3$ (10)**	**3c**	**81(77)[i]**


3a


3b

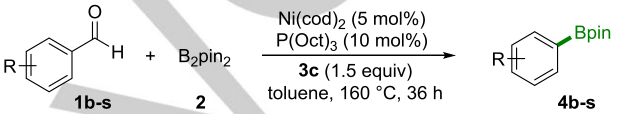

3c

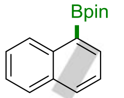
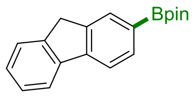
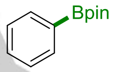
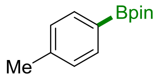
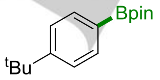
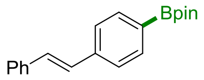
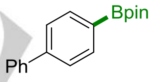
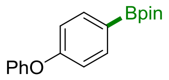
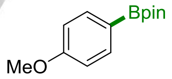
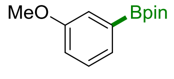
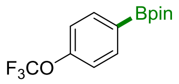
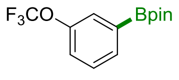
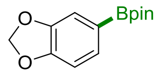
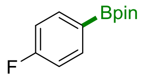
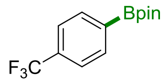
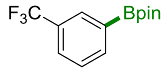
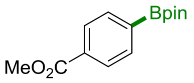
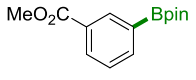

3d

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Ni(cod)$_2$ (10 mol%, 0.02 mmol), ligand (10~20 mol%, 0.02-0.04 mmol), **3** (0.3 mmol), toluene (1 mL), 160 °C, 36 h. [b] Determined by ^1H NMR spectroscopy using 1,3,5-$(OMe)_3C_6H_3$ as an internal standard. [c] NaO^{t}Bu (40 mol%) as base. [d] Using 1,4-dioxane. [e] At 150 °C. [f] At 140 °C. [g] Running for 16 h. [h] Using 1.2 equiv of **2**. [i] Yield after isolation. [j] Using Ni(cod)$_2$ (5 mol%, 0.01 mmol), P(Oct)$_3$ (10 mol%, 0.02 mmol). P(Oct)$_3$ = trioctylphosphine, dcype = 1,2-bis(dicyclohexylphosphino)-ethane, SIPr·HCl = 1,3-bis(2,6-diisopropylphenyl) imidazolinium chloride, IPr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride. IMes·HCl = 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride.

Although different oxidants or hydrogen acceptors were investigated, they were not able to furnish a better yield (entries 13-15). Performing the reaction in 1,4-dioxane, afforded the expected product **4a** in 64% yield (entry 16). Neither lower temperatures nor shorter reaction time could provide better yields (entries 17-19). Surprisingly, when the amount of bis(pinacolato)diboron (**2**) was decreased to 1.2 equiv, the expected product was obtained in 79% yield (entry 20). Similarly, product **4a** was detected in 77% after isolation when 5 mol% Ni(cod)$_2$ was used (entry 21). As anticipated, control experiments revealed that the transformation does not proceed in the absence of catalyst, ligand or hydride acceptor (entries 8, 11, and 12).

Table 2. Substrate scope for nickel-catalyzed decarbonylative borylation of aldehydes.[a]

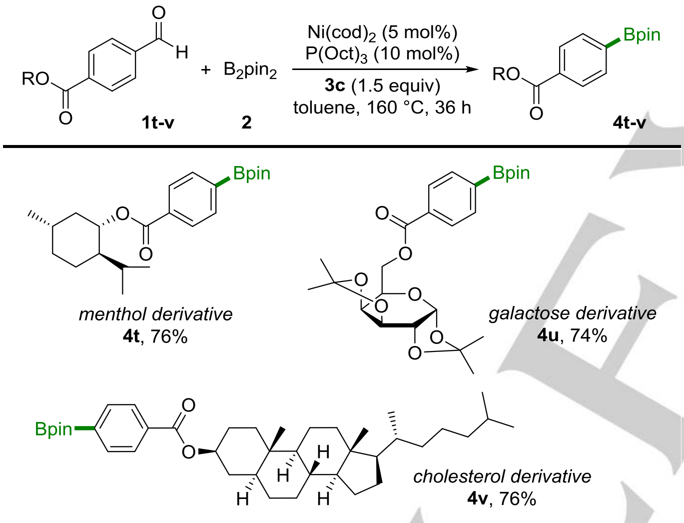


	**4b**, 64%		**4c**, 55%
	**4d**, 75%		**4e**, 77%
	**4f**, 74%		**4g**, 63%
	**4h**, 80%		**4i**, 75%
	**4j**, 60%		**4k**, 87%
	**4l**, 51%		**4m**, 58%
	**4n**, 54%		**4o**, 62%
	**4p**, 48%		**4q**, 52%
	**4r**, 61%[b]		**4s**, 59%

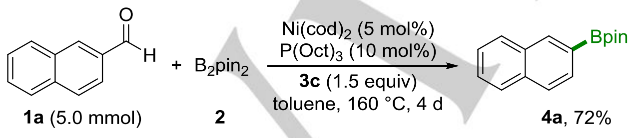
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), Ni(cod)$_2$ (0.01 mmol), P(Oct)$_3$ (0.02 mmol), **3c** (0.3 mmol), toluene (1 mL), 160 °C, 36 h, yield after isolation. [b] At 170 °C.

With the optimized conditions in hand, the substrate scope of the nickel-catalyzed decarbonylative borylation of aromatic aldehydes was evaluated and the results are summarized in Table 2. For aromatic aldehydes **1b**-**d**, the transformations gave the corresponding aryl boronate esters **4b**-**d** in 64-77% yield. Further electron-donating and -withdrawing groups on the phenyl ring were considered and use of aldehydes containing alkyl, alkenyl, and phenyl substituents provided **4e**-**h** in good to high yields. In addition, the reaction tolerates substrates bearing phenoxy, alkoxy, and trifluoromethoxy and fluorinated groups, leading to the borylated products **4i**-**q**. Interestingly, a selective bond cleavage occurs if ester groups are present, leaving the ester groups untouched (**4r**-**s**). Regarding the mentioned chemoselectivity, bifunctional natural product derivatives such as menthol, galactose, and cholesterol derivatives **1t**-**v** were also applied in the new ipso-borylation (Table 3). Selective borylation afforded the corresponding products **4t**-**v** in good yields. To demonstrate that the standard reaction conditions can be scaled up, compound **4a** was prepared on a large scale (5.0 mmol) in good yield in the presence of low catalyst loading (Scheme 2).

Table 3. Decarbonylative borylation of complex molecules.[a]



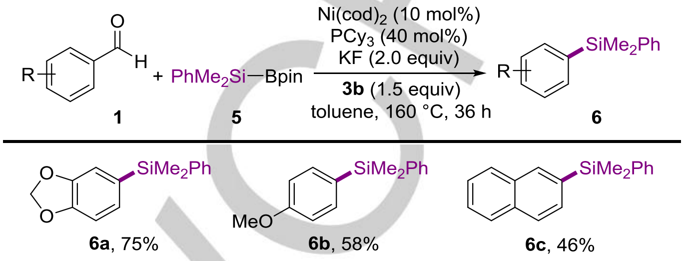
[a] Reaction conditions: **1** (0.2 mmol), **2** (0.24 mmol), $Ni(cod)_2$ (0.01 mmol), $P(Oct)_3$ (0.02 mmol), **3c** (0.3 mmol), toluene (1 mL), 160 °C, 36 h, yield after isolation.



Scheme 2. Scalability of nickel-catalyzed decarbonylative borylation.

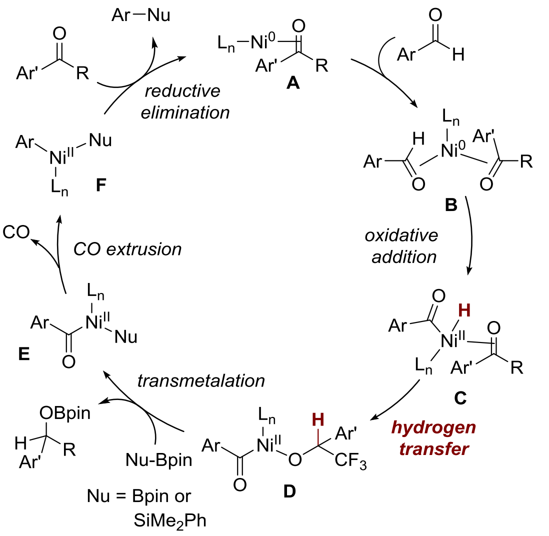
After having accomplished a decarbonylative ipso-borylation of aldehydes for the first time, we wondered whether this newly developed strategy could be applied to other useful C-heteroatom bond forming reactions such as the C-Si bond formation.[14] As shown in Table 4, this was indeed the case, and differently substituted aldehydes could be applied together with silylborane **5** under minor modification of the standard reaction conditions. Changing the ligand from $P(Oct)_3$ to PCy_3 and the acceptor from **3c** to **3b**, afforded arylsilanes **6a-c** in moderate to good yields. This transformation showed the great potential of our decarbonylative strategy for building various carbon-heteroatom bonds.

Table 4. Nickel-catalyzed decarbonylative silylation of aldehydes.[a]



[a] Reaction conditions: **1** (0.2 mmol), **5** (0.3 mmol), $Ni(cod)_2$ (0.02 mmol), PCy_3 (0.08 mmol), KF (0.4 mmol), **3b** (0.3 mmol), toluene (1 mL), 160 °C, 36 h, yield after isolation.

Based on our previous results[15] a proposed mechanism for the above transformations is depicted in Scheme 3. Complex **B** is generated by the coordination of nickel(0) with the carbonyl moieties of the aldehyde and ketone. Oxidative addition of Ni(0) species to the C(acyl)-H bond of aldehyde produces the acylnickel(II) hydride species **C** which subsequently undergoes the key hydrogen transfer process to form acylnickel(II) alkoxide **D**. The resulting complex **D** undergoes a transmetalation step with bis(pinacolato)diboron (**2**) or dimethyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (**5**), in the later case, the step being facilitated by the KF. The subsequent CO extrusion releases intermediate **F**. Finally, reductive elimination leads to the borylated or silylated products while regenerating the active Ni(0) species coordinating to ketone **3c** which then initiates a next catalytic cycle.



Scheme 3. Proposed mechanism for the nickel-catalyzed decarbonylative cross-coupling.

In summary, we have developed a new protocol for the nickel-catalyzed ipso-borylation and ipso-silylation of aldehydes. This new method relies on the use of readily available aldehydes in combination with low amounts of a nickel catalyst and provides the borylated and silylated products in one step under base-free conditions. Previously reported protocols for the synthesis of organoborons and organosilicons often use pre-formed or more sensitive organometallic reagents which may not always be compatible with functional groups. Thus, the reported base-free protocol constitutes a valuable complementary approach which can also be applied for the interconversion of more complex aldehydes in which the carbonyl group has been used as a directing group for C-H functionalizations[16] prior to the ipso-substitution. Importantly, this protocol shows good functional group tolerance and broad substrate scope including natural product derivatives, which unlocks the opportunity to be utilized in the late-stage modification of more sophisticated molecules. Regarding the mechanism of this so far unprecedented ipso-functionalization of aldehydes we postulate that the reaction proceeds through C(acyl)-H bond activation with subsequent hydride transfer as a key step. Given the simplicity and practicability of the strategy, it is anticipated that it should find further applications in synthesis, retrosynthesis, and late-stage functionalization.

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Keywords: Borylation • Silylation • Aldehyde • Decarbonylative cross-coupling • Nickel catalysis

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