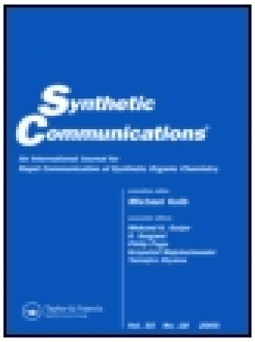

Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

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To cite this article: Ryo Akiyama, Mariko Sugaya, Hiraku Shinozaki & Tetsuya Yamamoto (2019): NHC-coordinated palladacycle catalyzed 1,2-addition of arylboronates to unactivated ketones, Synthetic Communications, DOI: 10.1080/00397911.2019.1594307

To link to this article: https://doi.org/10.1080/00397911.2019.1594307

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NHC-coordinated palladacycle catalyzed 1,2-addition of arylboronates to unactivated ketones

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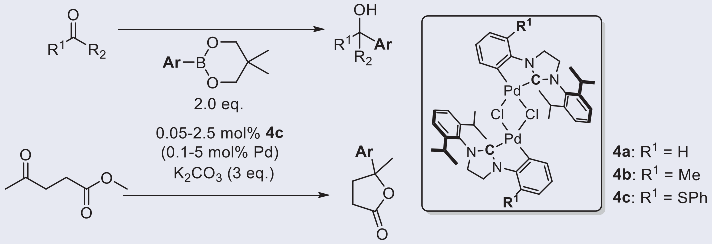
ABSTRACT

Palladium catalyzed intermolecular 1,2-addition of arylboronate to unactivated ketone was investigated. NHC-coordinated palladacycle **4c** exhibited catalytic activity for the reactions and provided the corresponding tertiary alcohols and γ,γ-disubstituted γ-lactones in good to excellent yields.

ARTICLE HISTORY
Received 5 February 2019

KEYWORDS
1,2-Addition; arylboronate; palladacycle; palladium catalysis; unactivated ketone

GRAPHICAL ABSTRACT



Introduction

In the past two decades, the transition metal such as Rh,[1] Pd,[2–4] Ni,[5] Ru,[6] Pt,[7] Co,[8] Cu,[9] Fe[10] or Ir[11] catalyzed 1,2-addition of organoboron compounds to carbonyl compounds such as aldehydes or ketones have been developed and is the attractive synthetic methods as an alternative to the Grignard reaction.[12] Because their catalytic 1,2-addition using organoboron compounds as nucleophilic reagents is tolerant to a more wide range of functional groups than using organomagnesium reagents. So but the reaction with unactivated ketones is limited to Rh or Ni catalysts. Previously, we and Hu independently reported phosphine coordinated organopalladium complexes such as phosphapalladacycles are suitable catalysts for the 1,2-addition of arylboronic acids to aldehydes and activated ketones.[3i] Although *N*-heterocyclic carbene (NHC) ligands show the electron-donation equal to or more effective than phosphine ligands for transition metal catalyst,[13] NHC coordinated palladacycles are rare and their catalysis have not been almost examined.[4,14] Thus, we demonstrated the facile synthesis of imidazoline-type NHC coordinated palladacycles and clarified their catalysis for

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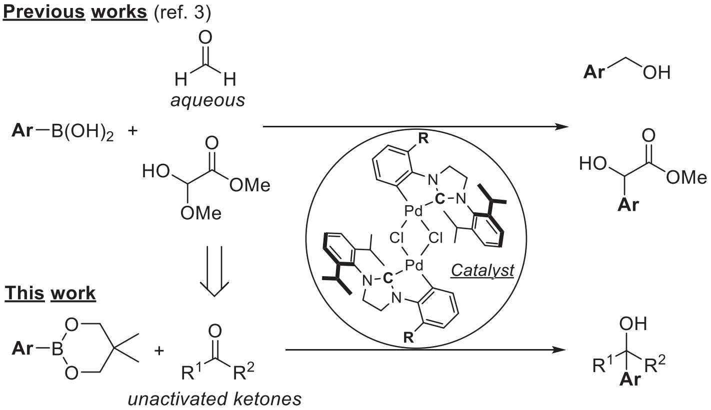


Scheme 1. Expansion of the substrate scope on the NHC-coordinated palladacycle catalyzed 1,2-addition.

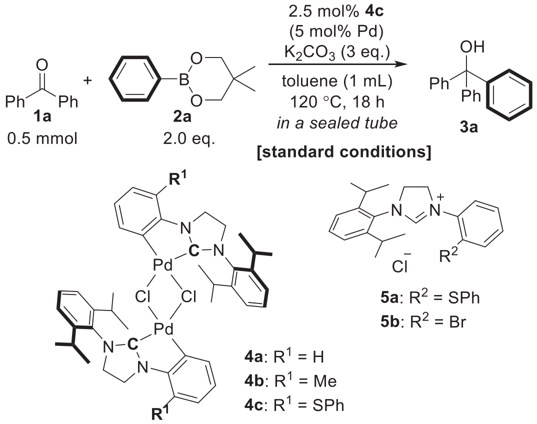
1,2-addition of arylboronic acids with aldehyde and activated hemiacetals.[4] Herein, we report the first examples of the Pd-catalyzed intermolecular 1,2-addition of arylboronates to unactivated ketones using NHC coordinated palladacycles as catalyst (Scheme 1). Additionally, we applied the catalytic system to the γ,γ-disubstituted γ-lactones synthesis.

Results and discussion

The optimization of reaction conditions of Pd-catalyzed 1,2-addition of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane **2a** to benzophenone **1a** is summarized in Table 1. Phenylthio-substituted NHC coordinated complex **4c** provided the corresponding alcohol in excellent yields (entry 1). The use of **4a** and **4b** instead of **4c** resulted in lower yields even 10 mol% catalyst loading (entries 2 and 3). Previously, we and Kuriyama and coworkers independently reported the combination of imidazolinium salts **5** and $[PdCl(\eta^3\text{-allyl})]_2$ exhibited high activity for the addition of arylboronic acid to aldehydes.[2] However, these catalyst systems are not effective in this reaction (entries 4 and 5). By the use of Cs_2CO_3, Na_2CO_3 and K_3PO_4 the corresponding product **3a** was obtained in less yields (entries 6–8). Phenylboronic acid afforded no product in this addition (entry 9). The yield was declined in ether solvents such as 1,4-dioxane and 1,2-dimethoxyethylene (entries 10 and 11).

The scope and limitation of the **4c**-catalyzed 1,2-addition of phenylboronate **2a** to unactivated ketones are listed in Table 2. Acyclic type alkylarylketones such as 2-acetylnaphthalene **1b** provided the corresponding alcohols in excellent yields under less than 1 mol% Pd catalyst loadings and reacted more easily than diarylketone **1a** (entry 1). Although acyclic type dialkylketones such as 4-phenyl-2-butanone **1c** needed 3 mol% catalyst loading in this phenylation, the reaction of cyclic type dialkylketones such as cycloheptanone **1d**, 1,4-dioxaspiro[4.5]decan-8-one **1e** and *tert*-butyl 4-oxopiperidine-1-carboxylate **1f** proceeded smoothly in excellent yields (entries 3–6). Methyl 4-oxo-pentanoate **1g** as one of acyclic type dialkylketones needed 5 mol% catalyst loading in this addition and was transformed to the corresponding γ,γ-disubstituted γ-lactone **3g** in

Table 1. Optimization of Pd-catalyzed 1,2-addition of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane **1a** to benzophenone **2a**.



Entry	Catalyst	Base	Solvent	Yield (%)[a]
1	2.5 mol% **4c** (5 mol% Pd)	K_2CO_3	Toluene	90
2	5 mol% **4a** (10 mol% Pd)	K_2CO_3	Toluene	55
3	5 mol% **4b** (10 mol% Pd)	K_2CO_3	Toluene	78
4	5 mol% $[PdCl(\eta^3\text{-allyl})]_2$ and 10 mol% **5a**	K_2CO_3	Toluene	2
5	5 mol% $[PdCl(\eta^3\text{-allyl})]_2$ and 10 mol% **5b**	K_2CO_3	Toluene	4
6	2.5 mol% **4c** (5 mol% Pd)	Cs_2CO_3	Toluene	4
7	2.5 mol% **4c** (5 mol% Pd)	Na_2CO_3	Toluene	3
8	2.5 mol% **4c** (5 mol% Pd)	K_3PO_4	Toluene	32
9[b]	2.5 mol% **4c** (5 mol% Pd)	K_2CO_3	Toluene	NO[c]
10	2.5 mol% **4c** (5 mol% Pd)	K_2CO_3	1,4-dioxane	60
11	2.5 mol% **4c** (5 mol% Pd)	K_2CO_3	1,2-dimethoxyethylene	70

[a] Isolated yields.
[b] Phenylboronic acid was used instead of **2a**.
[c] Not obtained.

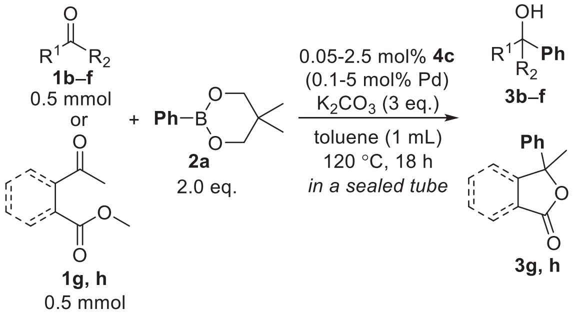
moderate yield. In contrast, methyl 2-acetylbenzoate **1h** was not reacted in this condition (entries 7 and 8).

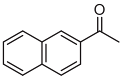
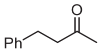
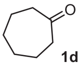
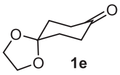
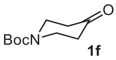
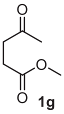
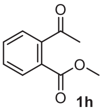
The scope and limitation of the **4c**-catalyzed arylation of *tert*-butyl 4-oxopiperidine-1-carboxylate **1f** and methyl 4-oxo-pentanoate **1g** are summarized in Table 3. Electron-rich arylboronic acid such as methoxyphenyl boronates were converted to the corresponding products in excellent yields (entries 1 and 7). The reaction of 2-methylphenylboronate **2c** was a little difficult due to more sterically bulky and less electron-rich than 2-methoxyphenylboronate **2b** (entries 2 *vs.* 3). Weakly electron withdrawing groups such as fluoro atom substituted arylboronate reacted smoothly to give the desired alcohols in excellent yields under 1 mol% Pd catalyst loadings, while strongly electron withdrawing group such as trifluoromethyl group substituted arylboronate **3n** required 6 mol% of catalyst (entries 4 and 5). Failed substrate was 4-bromophenylboronate **2g** afforded a complex mixture of products (entry 6).

Conclusion

In conclusion, we found the imidazoline-type NHC coordinated palladacycle **4c** has remarkable catalytic activity for the addition of arylboronates to unactivated ketones.

Table 2. The scope and limitations of the **4c**-catalyzed 1,2-addition of **2a** to unactivated ketones.



Entry	**4c** (mol%)	Ketone **1**	Product **3**	Yield (%)[a]
1	0.5	 **1b**	**3b**	93
2	1.5	 **1c**	**3c**	93
3	0.5	 **1d**	**3d**	70
4	0.05	 **1e**	**3e**	97
5	0.05	 **1f**	**3f**	95
6[b]	2.5	 **1g**	**3g**	66
7[b]	2.5	 **1h**	**3h**	N.R.[c]

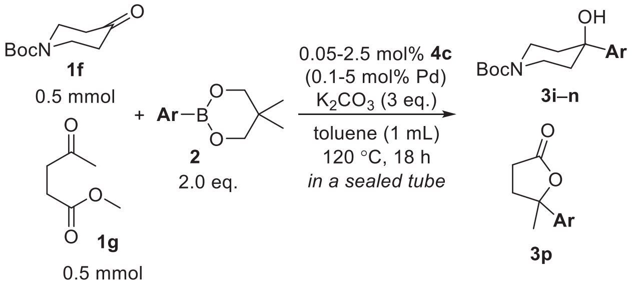
[a] Isolated yields.
[b] The reactions were stirred for 24 h.
[c] No reaction.

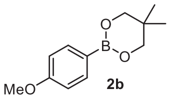
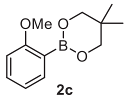
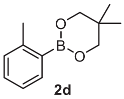
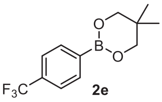
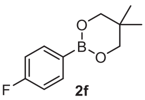
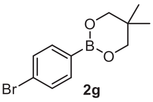
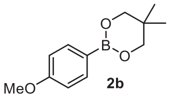
Further examinations of asymmetric catalytic reaction using chiral NHC palladium complexes are underway in our laboratory.

Experimental

All reactions were carried out under an argon atmosphere. TLC was performed on aluminum silica gel 60 F254 (Merck) sheets, which were visualized by the quenching of

Table 3. The scope and limitation of the **4c**-catalyzed 1,2-addition of arylboronates to **1f** or **1g**.



Entry	4c (mol%)	Ketone 1	Arylboronate 2	Product 3	Yield (%)[a]
1	0.05	**1e**	 **2b**	**3j**	96
2	0.05	**1e**	 **2c**	**3k**	96
3	0.1	**1e**	 **2d**	**3l**	76
4	3	**1e**	 **2e**	**3m**	62
5	0.5	**1e**	 **2f**	**3n**	91
6	1.0	**1e**	 **2g**	**3o**	C.M.[b]
7	2.5	**1j**	 **2b**	**3p**	96

[a] Isolated yields.
[b] Complex mixture.

UV fluorescence (254 nm). Column chromatography was conducted on silica gel (Cica, 60–210 mesh, spherical, neutral). ^{1}H, ^{13}C and ^{19}F spectra were recorded on a Brucker DPX-300 (300.13 MHz) or AVANCE III 400 spectrometer (400.13 MHz) at ambient temperature. The chemical shifts of ^{1}H were reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane (0.0 ppm). Chemical shifts of ^{13}C were reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$. Commercially available organic and inorganic compounds were used without purification. Palladacycles (**4a–c**),[4b] imidazolinium chloride **5a**[15] and **5b**[2a] were prepared according to the literature procedures.

General procedure for palladium catalyzed 1,2-addition of arylboronate 2 to ketone 1

Ketone **1** (0.5 mmol), arylboronate **2** (1.0 mmol), **4c** (0.00025–0.0125 mmol/Pd 0.0005–0.025 mmol) and K_2CO_3 (207 mg, 1.5 mmol) were charged in a 10 mL screw-top test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon. This sequence was repeated five times. Then toluene (1.0 mL) was added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The sealed test tube was placed into an oil bath preheated at 120 °C. After the reaction mixture was stirred for 18 h, the reaction mixture was cooled to room temperature. The obtained crude was purified by passing it through a silica gel column with a hexane/ethyl acetate.

Triphenylmethanol (3a)

Benzophenone **1a** (91.1 mg, 0.5 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane **2a** (190 mg, 1.0 mmol), **4c** (13.9 mg, 0.0125 mmol [0.025 mmol Pd]) and K_2CO_3 (207 mg, 1.5 mmol) were used. The crude product was purified by column chromatography (silica gel, hexane/EtOAc 4:1) to afford **3a** (117 mg, 90%) as a white solid. mp 161–163 °C [lit. 161–165 °C]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.33–7.24 (m, 15H), 2.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 146.9, 127.9, 127.9, 127.3, 82.0.

Funding

This work was supported in part by the Research Institute for Science and Technology, Tokyo Denki University Grant Number Q16E-02.

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