# Palladium-Catalyzed Carbonylative Coupling of Aryl lodides with **Alkenylaluminum Reagents**

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#### Supporting Information

ABSTRACT: A highly reactive catalytic system for the carbonylative coupling of aryl iodides with alkenylaluminum reagents has been developed. Various  $\beta$ -substituted  $\gamma$ , $\delta$ -unsaturated ketones were produced under mild conditions in good to excellent yields even under ppm level of palladium catalyst. Notably, this also represents the first example on carbonylative transformation of alkenylaluminum compounds. Additionally, by the addition of zinc salt, the selectivity of the product can be modified.

rganoaluminum reagents are a class of organometallic compounds with several attractive advantages, including low cost, low toxicity, ready availability, and broad tolerance of various important functional groups which benefit from the low ionic character of the carbon-aluminum bond.<sup>1</sup> As expected, these features have been recognized by various research groups. In 1976, Negishi's group reported the first example on using organoaluminum compounds in transitionmetal-catalyzed cross-coupling reactions.<sup>2</sup> In the subsequent decades, many cross-coupling reactions with organoaluminum compounds have been reported.<sup>3</sup> Notably, in 2010, Knochel's group reported a novel procedure for the preparation of organoaluminum reagents by directly inserting aluminum powder into Ar-X (X = I, Br) bonds in the presence of a catalytic amount of selected metallic chlorides (TiCl<sub>4</sub>, BiCl<sub>3</sub>,  $InCl_{3}$ , or PbCl<sub>2</sub>) together with LiCl as the promotor. The formed organoaluminum reagents were applied in palladiumcatalyzed cross-coupling and acylation reactions.<sup>3i</sup> More recently, Uchiyama's group performed a systematic study on nickel-catalyzed cross-coupling reactions of organoaluminum reagents with various electrophiles for new C-C bond formation.<sup>4</sup> Among the various organoaluminum compounds, alkenylaluminum compounds are attractive as they can be easily prepared from the corresponding alkynes by hydroalumination with aluminum hydrides such as DIBAL-H.<sup>5</sup> They are attractive reagents for new C-C bond formation and meanwhile introduce a new alkenyl group into the products.

Furthermore, since its discovery by Heck and co-workers in 1970s, palladium-catalyzed coupling reaction of aryl halides with CO and various nucleophiles has been widely used both in academia and industry for the production of carbonylcontaining compounds.<sup>6</sup> Even though many novel palladiumcatalyzed carbonylation reactions have been developed and applied, to our surprise, no example on using alkenylaluminum as the nucleophiles in carbonylation has been realized to date.



As attracted by the advantages of organoaluminum compounds and also in order to fill the mentioned gap, we become interested to develop a new carbonylative coupling procedure with alkenylaluminums. Initial investigations were carried out with iodobenzene and (E)-diisobutyl(oct-1-en-1yl)aluminum which was prepared by oct-1-yne with diisobutylaluminum hydride (DIBAL-H) as the model substrates. To our delight, the target (E)-3-hexyl-1-phenylundec-4-en-1-one can be successfully obtained with  $Pd(PPh_3)_4$ as the catalyst in THF at 60 °C for 16 h under 10 bar CO with 50% yield (Table 1, entry 1). Next, a set of solvents were tested, and decreased yields of 3aa were achieved (Table 1, entries 2-5). Notably, 45% yield of the desired product can still be obtained by using  $Pd(OAc)_2$  and  $PPh_3$  as the catalyst system (Table 1, entry 6). The combination of Pd/C and  $PPh_3$ can further increase the reaction outcome to 53% yield (Table 1, entry 7). The yield was able to be further improved to 60% when DPEphos was used as the ligand among all the tested systems (Table 1, entries 8-12). The model system was tested at 80 and 100 °C as well. The best results can be obtained by performing the reaction at 80 °C (Table 1, entry 13), whereas a slightly reduced yield of the target product was produced by performing the reaction at 100 °C (Table 1, entry 14). Interestingly, we found that decreasing the pressure of CO to 2 bar can further increase the yield (Table 1, entry 15). The reaction can be performed under 1 bar of carbon monoxide as well; however, considering the boiling point of solvent is lower than the reaction temperature, we decided to continue with 2 bar of CO for following studies. It is important to mention that the yield of the final product is maintained with prolonged reaction time, and decreased yield was obtained with short reaction time (10 h) because of the low conversion of iodobenzene.

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Received: August 17, 2019
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Table 1. Selected Results of the Optimization of the Reaction Conditions $^{a}$ 

			n-Hex	
Ĺ	1a	Al( <i>i</i> -Bu) <sub>2</sub> (Pd) CO	Jaaa O T	n-Hex
entry	catalyst	ligand	solvent	yield % <sup>b</sup>
1	$Pd(PPh_3)_4$	-	THF	50
2	$Pd(PPh_3)_4$	-	dioxane	17
3	$Pd(PPh_3)_4$	-	PhCl	35
4	$Pd(PPh_3)_4$	-	DMF	22
5	$Pd(PPh_3)_4$	-	DCE	43
6	$Pd(OAc)_2$	PPh <sub>3</sub>	THF	45
7	Pd/C	PPh <sub>3</sub>	THF	53
8	Pd/C	-	THF	trace
9	Pd/C	Xantphos	THF	53
10	Pd/C	DPPE	THF	5
11	Pd/C	PCy <sub>3</sub>	THF	20
12	Pd/C	DPEphos	THF	60
13 <sup>d</sup>	Pd/C	DPEphos	THF	78
14 <sup>e</sup>	Pd/C	DPEphos	THF	69
15 <sup>d,f</sup>	Pd/C	DPEphos	THF	80 (76 <sup>°</sup> )

<sup>*a*</sup>Reaction conditions: **1a** (0.5 mmol), **2a** (1.25 mmol in hexane), catalyst (1 mol %), ligand (1 mol % for bidentate ligand, 2 mol % for monophosphine ligand), solvent (1.0 mL), 10 bar CO, 60 °C, 16 h. <sup>*b*</sup>NMR yield. <sup>*c*</sup>Isolated yield. <sup>*d*</sup>80 °C. <sup>*e*</sup>100 °C. <sup>*f*</sup>2 bar CO.

With the optimal reaction conditions in hand, we explored the scope of this carbonylative cascade reaction. First, we tested the generality of aryl iodides for this reaction. As shown in Scheme 1, iodobenzene with electron-donating or -withdrawing substituents can be well tolerated and delivers the desired products in good to excellent yields (3aa-3qa). Notably, monoketone and diketone product could be achieved, respectively, by controlling the equivalent of alkenylaluminum added (3la, 3ma). Additionally, carbonylative cascade reactions with heterocyclic and polycyclic iodides also proceed smoothly and gave the target products in moderate yields (3ra-3ta). Then we tested some functional group substituted iodobenzenes including ester, cyano, alkenyl, alkynyl, azido, indole, and sulfonyl groups which may be sensitive to alkenylaluminum. Gratifyingly, for these compounds, the reaction could also give the expected products in good to excellent yields (3ua-3aba).

Subsequently, we examined different types of alkenylaluminum reagents for this carbonylative cascade reaction (Scheme 2). Several aliphatic alkenylaluminum reagents which were prepared by reacting aliphatic alkynes with DIBAL-H proceeded well to afford the desired products in moderate to good yield (3ab-3ah). Aromatic alkenylaluminum compounds can be tolerated as well, and moderate yields of the corresponding products can be isolated (3ai-3ak). Interestingly, diene aluminum compounds can also work well in this reaction and gave the desired product in 72% yield (3al). When indole-substituted alkenylaluminum reagent was subjected to the reaction conditions, a 64% yield of the corresponding product was achieved (3am). It is also interesting to mention that attempting to produce a mixed 3-R-5-R'-type enone product from two different alkenyl reagents was unsuccessful. The reaction leads to no selectivity. Additionally, we tried to prepare *cis*-alkenylaluminum reagent,



Letter



<sup>+</sup>Reaction conditions: **1** (0.5 mmol), **2a** (1.25 mmol in hexane which is prepared by oct-1-yne with DIBAL-H), Pd/C (1 mol %), DPEphos (1 mol %), THF (1.0 mL), 2 bar CO, 80 °C, 16 h, isolated yields. "1,4-Diiodobenzene (0.25 mmol).

but failed. However, according to previous works on alkenes,<sup>7</sup> cis or trans should have no effect on the outcome of this reaction.

To gain some insight into the reaction pathway, control experiments were performed (Scheme 3). Under identical conditions but using alternative metals such as Fe, Ni, Co, Cu, and others as catalysts, no desired product 3aa could been

# Scheme 2. Substrate Scope of Various Alkenylaluminum Compounds $^{\dagger}$



<sup>+</sup>Reaction conditions: **1a** (0.5 mmol), **2** (1.25 mmol in hexane which were prepared by corresponding alkynes with DIBAL-H), Pd/C (1 mol %), DPEphos (1 mol %), THF (1.0 mL), 2 bar CO, 80 °C, 16 h, isolated yields.

detected. This indicates the unique role of palladium catalyst in this reaction. Using (*E*)-styrylboronic acid which was a common alkenylation reagent instead of alkenylaluminum compound, no reaction occurred under our standard conditions. It implied alkenylaluminum possessed specific activity in this reaction. Finally, the cross-coupling compound 4a could be achieved almost quantitatively when combining (*E*)-chalcone with (*E*)-diisobutyl(oct-1-en-1-yl)aluminum in THF at room temperature for 0.5 h (Scheme 3, eq a). The reaction also proceeds when benzoyl chloride was applied in the presence of palladium catalyst (Scheme 3, eq b vs eq c).

Interestingly, when  $Zn(OAc)_2$  was added into our model system, the selectivity can be modified, and an 82% yield of 3methyl-1-phenylbutan-1-one was isolated under CO pressure (30 bar). In the variation of aryl iodide substrates, good yields and good functional groups tolerance can be obtained (Scheme 4). The substrates that failed with aluminum reagent can proceed well under these conditions. In our control experiments, we found that transmetalation occurred between zinc salt and aluminum reagent primarily and was then catalyzed by palladium to give the final product (Scheme 3, eq. d-f).

On the basis of our results and literature,<sup>8-10</sup> a plausible reaction pathway is proposed in Scheme 5. First the oxidative addition of aryl iodide to palladium provides the arylpalladium

#### Scheme 3. Control Experiments



Scheme 4. Carbonylative Synthesis of Ketones<sup>7</sup>



<sup>\*</sup>Reaction conditions: **1** (0.5 mmol), **2a** (0.6 mmol in hexane), Pd(PPh<sub>3</sub>)<sub>4</sub> (1 mol %), Zn(OAc)<sub>2</sub> (0.6 mmol), THF (1.0 mL), 30 bar CO, 80 °C, 16 h, isolated yields. <sup>*a*</sup>1,4-Diiodobenzene (0.5 mmol), **2a** (1.2 mmol), Zn(OAc)<sub>2</sub> (1.2 mmol).

complex **A**, which is followed by migratory insertion of carbon monoxide giving the acylpalladium complex **B**. This acylpalladium **B** will undergo transmetalation with the alkenylalumi-

# Scheme 5. Proposed Reaction Mechanism



num compound to form the complex **C**, which will undergo reductive elimination to form the key enone intermediate **D**. Meanwhile the active palladium species will be regenerated and ready for the next catalytic cycle. At the same time, the formed  $\alpha,\beta$ -unsaturated ketone **D** undergoes 1,4-Michael addition to give the final obtained product **E**. For the formation of product **5**, the in situ production of organozinc reagent occurred.

The developed procedures for the organometallic related carbonylative coupling reactions usually require loading 1-10 mol % of catalysts.<sup>6</sup> Therefore, the discovery of more effective conditions, for the organometallic carbonylation under low catalyst loading conditions (less than 0.1 mol %), would be a considerable advantage for industrial applications and also for sustainable development. Hence, we tested different catalyst loading conditions as shown in Table 2. Notably, we found even 0.01 mol % Pd(PPh<sub>3</sub>)<sub>4</sub> was enough to catalyze this reaction. Additionally, the practicability of the presented methodology was demonstrated with a 5 mmol scale reaction in the presence of 0.005 mol % palladium catalyst (1 ppm)

#### Table 2. Catalyst Loading Variation<sup>a</sup>

entry	catalyst loading	yield <sup>b</sup>
1	0.1 mol % Pd(PPh <sub>3</sub> ) <sub>4</sub>	81%
2	0.1 mol % $Pd(PPh_3)_4$ and 1 mol % $PPh_3$	88%
3	0.01 mol % Pd(PPh <sub>3</sub> ) <sub>4</sub>	22%
4	0.01 mol % $Pd(PPh_3)_4$ and 1 mol % $PPh_3$	86%
5	0.001 mol % $Pd(PPh_3)_4$ and 1 mol % $PPh_3$	10%
6	0.0001 mol % $Pd(PPh_3)_4$ and 1 mol % $PPh_3$	2%

<sup>*a*</sup>Reaction conditions: **1a** (0.5 mmol), **2a** (1.25 mmol in hexane which is prepared by oct-1-yne with DIBAL-H), THF (1.0 mL), 2 bar CO, 80 °C, 16 h. <sup>*b*</sup>NMR yields.

concentration), and good yield of the product **3aa** was obtained with very high TON up to 15600 (Scheme 6).

#### Scheme 6. Gram-Scale Synthesis



Interestingly, these two selectivities can be combined in one reaction as well (Scheme 7). By using 1,4-diiodobenzene as the





substrate, after the first step reaction,  $Zn(OAc)_2$  (1 mmol) was added to the reaction vial, and then the reaction was placed back under 30 bar of carbon monoxide at 80 °C for 16 h; subsequently, 43% of the designed product 6 can be isolated.

In conclusion, we have developed a general and convenient palladium-catalyzed cascade carbonylation procedure for the synthesis of  $\beta$ -substituted  $\gamma$ , $\delta$ -unsaturated ketones. Started from readily available aryl iodides and alkenylaluminum reagents, the desired products were obtained in good yields in general. Various iodides with different functional groups were transformed to the corresponding products under mild conditions. To the best of our knowledge, this is the first procedure for the carbonylation of alkenylaluminums, which can even be performed under ppm level of palladium catalyst. Additionally, by the addition of zinc salt, the selectivity of the product can modified.

### GENERAL PROCEDURE

Under an argon atmosphere, a 4 mL screwcap vial was charged with Pd/C (1 mol %), DPEphos (1 mol %), iodobenzene (0.5 mmol), toluene (1 mL), and an oven-dried stirring bar and then injected with alkenylaluminum solutions which were prepared by corresponding alkynes with DIBAL-H. The vial was closed by a Teflon septum and a phenolic cap and connected to the atmosphere through a needle. Then the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL). At room temperature, the autoclave is flushed with carbon monoxide for three times, and 2 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction was heated at 80 °C for 16 h. Afterward, the autoclave was cooled to room temperature, and the pressure was carefully released. After removal of the solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate 30:1).

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b02923.

General comments, analytic data, and NMR spectra for products (PDF)

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#### Funding

C.B. thanks the Chinese Scholarship Council (CSC) for financial support.

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

The analytical support of Dr. W. Baumann, Dr. C. Fisher, S. Buchholz, and S. Schareina (all in LIKAT) is gratefully acknowledged.

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