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Aryl-palladium-NHC complex: efficient phosphine-free catalyst precursors for the carbonylation of aryl iodides with amines or alkynes†

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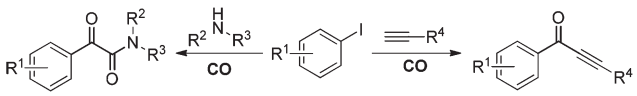
A series of aryl-palladium-NHC compounds was prepared according to the reported methods and their catalytic activity in the carbonylation of aryl iodides to synthesize α-keto amides and alkynones was examined. These practical aryl-palladium-NHC complexes have shown highly efficient catalyzed carbonylation and Sonogashira carbonylation reactions, with high turnover number in synthesis of α-keto amides (TON = 4300) and in synthesis of alkynones (TON = 980).

The carbonylation reaction represents an organic synthesis core technology for transforming raw materials and fine chemicals into a diverse set of useful compounds,[1] such as pharmaceuticals, agrochemicals, cosmetics and materials, in which CO acts as a most essential C1 building block for the preparation of carbonyl containing derivatives.[2] Among the carbonylation reactions, the transition metal-catalyzed carbonylation reaction is a widely used transformation that has been applied to the synthesis of acids, amides, alkynones, heterocycles and their derivatives.[3]

Over the past decades, effort has focused on the development of new efficient synthetic methods for the carbonylation reaction.[4] Phosphine ligands are usually required to promote the selectivity of the carbonylation reaction.[5] However, the air-sensitive phosphine ligands greatly limit the utility of the aforementioned transformations, especially on a large scale. To circumvent this drawback, much attention has been paid to stable N-heterocyclic carbenes (NHC) as ligands,[6] which have emerged as a class of ligands in transition-metal-catalyzed reactions due to their strong σ-donor properties compared with the phosphine ligand. Indeed, Pd- or Rh-NHC complexes have been successfully used as catalysts for some carbonylation reactions (Scheme 1).[7]

Recently, we disclosed a series of Pd-NHC complexes according to reported methods[8] as efficient catalysts for carbonylation reactions. Although a few examples have been reported for aryl-Pd-NHC catalyzed coupling reactions,[9] reports on the carbonylation reaction catalyzed by aryl-palladium-NHC complexes are rare. Inspired by these results[10] and in connection with our interests in developing carbonylation,[11] herein we disclose an efficient protocol for the aryl-Pd-NHC complex catalyzed carbonylation of aryl iodides with amines or alkynes converting to α-keto amides or alkynones.



Scheme 1 Palladium-catalyzed carbonylation reaction.

Towards this goal, the potential for a palladium-catalyzed iodobenzene carbonylation reaction was investigated (Table 1). This palladium-catalyzed carbonylation reaction depends greatly on the palladium species. To understand the nature of this reaction and to find the optimal reaction conditions, the effect of palladium complexes on the yield of **3aa** was examined. Fortunately, initial treatment of iodobenzene **1a** with diethylamine in the presence of $PdCl_2$, and K_2CO_3 in 1,4-dioxane at 80 °C for 12 hours to give α-keto amide **3aa** in 25% yield (Table 1, entry 1). It is noteworthy that when the palladium species was replaced by $PdCl_2(CH_3CN)_2$, the reaction proceeded with a much higher yield (47%) (Table 1, entry 2). To our delight, the use of the palladium complex containing Bmim and PPh_3 ligands as a catalyst efficiently improved the yield of **3aa** from 47% to 81% (Table 1, entry 3). Other palladium complexes containing NHC and N-ligand, such as **B** and **C** were also active, giving **3aa** in 90% and 74% yields, respectively (Table 1, entries 4 and 5). Further study revealed that palladium complex **D** containing IMes and aryl ligand, was also

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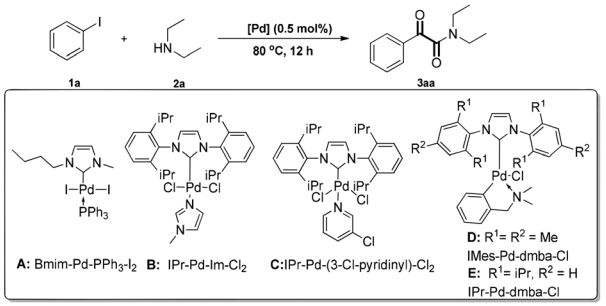
Table 1 Screening [Pd] catalysts of double carbonylation



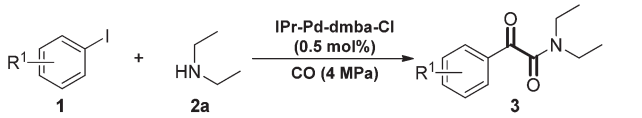
Entry	[Pd]	Yield[a] (%)
1	$PdCl_2$	25
2	$PdCl_2(CH_3CN)_2$	47
3	Bmim-Pd-PPh_3-I_2	81
4	IPr-Pd-Im-Cl_2	74
5	IPr-Pd-(3-Cl-pyridinyl)-Cl_2	90
6	IMes-Pd-dmba-Cl	86
7	IPr-Pd-dmba-Cl	91

[a] General conditions: **1a** (1.0 mmol), **2a** (5.0 mmol), [Pd] (0.5 mol%), K_2CO_3 (2.0 mmol), 1,4-dioxane (5.0 mL), CO (4.0 MPa), 80 °C, 12 h. Isolated yield.

effective giving **3aa** in 86% yield (Table 1, entry 6).[12] Meanwhile, the hindrance on the phenyl ring of NHC had a slight effect on the efficiency. Gratifyingly, the aryl palladium complex **E** containing the sterically demanding IPr-ligand is the most effective in forming **3aa** with 91% isolated yield (Table 1, entry 7).

With the optimized reaction conditions in hand, we next investigated the substrate scope of this carbonylation.[10] As shown in Table 2, electron-donating and electron-withdrawing groups contained in the phenyl ring were tolerated well. A series of functional groups, such as methyl, methoxy, halide, methoxycarbonyl, acetamide and nitro were compatible with the optimized aryl-Pd-NHC catalytic system, and the desired products were isolated in good to excellent yields (**3aa–3qa**), which indicated that the present reaction had a good functional group tolerance. Among these functional groups, the surviving halide groups could be valuable for further manipulation (**3ia–3ka**). An obvious steric hindrance effect on the reactivity was observed, which was demonstrated by the reactivity of **1b–d** *vs.* **1e**. Using very highly sterically hindered **1e** as the substrate, the single carbonylation product and deiodination product of *m*-xylene were also detected by GC-MS under standard conditions. Notably, 1-bromo-4-iodobenzene containing dihalide groups survived well in the standard procedure, leading to **3ka** in excellent 87% yield and the symmetrical product, 2,2′-(1,4-phenylene)bis(*N*,*N*-diethyl-2-oxoacetamide), **3ka′** in 11% yield. Although free phenolic hydroxyl and amino groups, such as 4-iodophenol and 2-iodoaniline, did not react with amines under these conditions and single carbonylation products and 4-amino-*N*-(4-iodophenyl)benzamide, 4-iodophenyl 4-hydroxybenzoate could detected by GC-MS as by-products, 4-iodoaniline and *N*-(4-iodophenyl)acetamide are

Table 2 Substrate scope of palladium-catalyzed double carbonylation of aryl iodides[a]



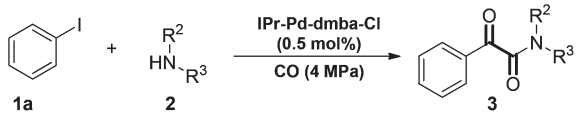
Entry	R^1	Yield (%)
1	H	**3aa**, 92
2	4-CH_3	**3ba**, 79
3	3-CH_3	**3ca**, 73
4	2-CH_3	**3da**, 95
5	2,6-$(CH_3)_2$	**3ea**, 12
6	4-CH_3O	**3fa**, 78
7	3-CH_3O	**3ga**, 70
8	2-CH_3O	**3ha**, 98 (10 : 1)[b]
9	4-F	**3ia**, 95
10	4-Cl	**3ja**, 97
11	4-Br	**3ka**, 87 (**3ka′**, 11)[c]
12	4-OH	**3la**, <5
13	4-NH_2	**3ma**, 16
14	2-NH_2	**3na**, <5
15	4-NHAc	**3oa**, 47
16	4-$COOCH_3$	**3pa**, 98
17	4-NO_2	**3qa**, 58
18	1-Naphthyl	**3ra**, 92
19	3-Pyridinyl	**3sa**, 92
20	4-Pyridinyl	**3ta**, <5
21	2-Thiophenyl	**3ua**, 99 (9 : 1)[b]

[a] General conditions: **1** (1.0 mmol), **2a** (2.0 mmol), [Pd] (0.5 mol%), K_2CO_3 (2.0 mmol), 1,4-dioxane (5.0 mL), CO (4.0 MPa), 80 °C, 12 h. Isolated yield. [b] Ratios of regioisomers was determined by ^{1}H NMR analysis. Major isomers are shown. [c] **3ka′**: 2,2′-(1,4-phenylene)bis(*N*,*N*-diethyl-2-oxoacetamide).

suitable for this reaction, affording the corresponding products **3ma** and **3oa**, respectively, in decent yields. These results indicated that anilines and phenols could act as stronger nucleophilic reagents for this the double carbonylation reaction. It is worth noting that heterocyclic derivatives are usable for the present reaction, affording the corresponding products **3sa** and **3ua** in excellent yields as well. The reaction of 1-iodo-2-methoxybenzene **1h** and 2-iodothiophene **1u** afforded **3ha** and **3ua** as a mixture of regioisomers (double carbonylation : single carbonylation) in a ratio of 10 : 1 and 9 : 1.

Furthermore, the scope of the amines was also explored and the results are shown in Table 3. Symmetrical secondary amines containing alkyl, allyl and benzyl groups reacted smoothly to give the corresponding products in high yields (**3aa–3ae**). Notably, the surviving allyl group could be valuable for further manipulation. Furthermore, the challenging cyclic secondary amines successfully underwent this carbonylation reaction to provide the desired products **3af–3ai** in 48–92% yields. Among these secondary amines, morpholine showed the highest reactivity with an almost quantitative conversion of iodobenzene in 92% yield for the desired α-keto amide. The unsymmetrical secondary amines, such as **2i** and **2j** were also successfully transformed into the corresponding products in good yields. In addition to secondary amines, primary

Table 3 Substrate scope of palladium-catalyzed double carbonylation of amines[a]



1a 2 3

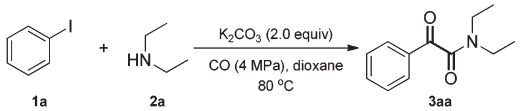
Entry	R^3	R^2	Yield (%)
1	Et	Et	**3aa**, 92
2	*n*-Pr	*n*-Pr	**3ab**, 85
3	*n*-Bu	*n*-Bu	**3ac**, 84
4	Allyl	Allyl	**3ad**, 82
5	Bn	Bn	**3ae**, 63
6	Pyrrolidinyl		**3af**, 69
7	Piperidinyl		**3ag**, 48
8	Morpholino		**3ah**, 92
9	3,4-Dihydroisoquinolin-2(1*H*)-yl		**3ai**, 66
10	*n*-Pr	Bn	**3aj**, 53
11	H	*n*-Bu	**3ak**, 83
12	H	Ph	**3al**, 31[b]

[a] General conditions: **1** (1.0 mmol), **2a** (2.0 mmol), [Pd] (0.5 mol%), K_2CO_3 (2.0 mmol), dioxane (5.0 mL), CO (4.0 MPa), 80 °C, 12 h. Isolated yield. [b] **3al**: *N*-phenylbenzamide.

alkyamine was also compatible with this process, furnishing the desired product **3ak** in good yield. However, when aniline **2l** was employed as the carbonylation partner, only the single carbonylation product *N*-phenylbenzamide **3al** was obtained in 31% yield.

We next turned our efforts toward investigation of the practicality of this aryl-Pd-NHC-catalyzed double carbonylation reaction (Scheme 2). This transformation provides many opportunities for applications in organic synthesis. Notably, we conducted the reaction of iodobenzene **1a** and diethylamine **2a** on a 10 mmol scale with a catalyst loading of 0.05 mol% and elongated time, and α-keto amide **3aa** was isolated in a very good 90% yield (1.8 g), which greatly increased the practicality of this palladium catalyzed carbonylation reaction. And importantly, when we further decreased the catalyst loading to 0.01 mol%, α-keto amide **3aa** was obtained in a very good (43%) yield (2.2 g). Notably, this result represents a TON of 4300, which is the highest among those reported for the aryl Pd-NHC catalyzed carbonylation reaction.

To extend the scope of the aryl-Pd-NHC catalytic system, we also tested carbonylation of aryl iodides with alkynes to synthesize alkynones catalyzed by the aryl-Pd-NHC. With previous experiences in mind, we initially conducted the reaction of iodobenzene **1a** and ethynylbenzene **3a**, with triethylamine (2 equiv.) as the base.



1a 2a 3aa

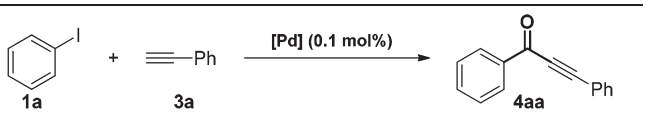
1a	[Pd]	t (hours)	Yield (%)	TON
10.0 mmol	(0.05 mol%)	48	90 (1.8 g)	1800
25.0 mmol	(0.01 mol%)	60	43 (2.2 g)	4300

Scheme 2 Determination in TON of palladium-catalyzed double carbonylation of amines.

Although the polymer form of palladium chloride did not react with ethynylbenzene, $PdCl_2(CH_3CN)_2$ is suitable for this reaction, affording the corresponding products **4aa** in 27% yield (Table 4, entries 1 and 2). Much to our delight, the reaction efficiency was improved to a good yield (81%) by using Bmim-Pd-PPh_3-I_2 (Table 4, entry 3). Other palladium species, such as IPr-Pd-Im-Cl_2 and IPr-Pd-(3-Cl-pyridinyl)-Cl_2 did not effectively improve the carbonylation reactivity (Table 4, entries 4 and 5). Further investigation of the palladium catalyst precursors revealed that the reactivity was affected by the nature of the NHC ligands, and the best result was achieved with IPr-Pd-dmba-Cl as the catalyst precursor (Table 4, entries 6 and 7). After screening reaction conditions, we can concluded that the reaction was carried out by stirring a toluene solution of iodobenzene, ethynylbenzene, 0.1 mol% of aryl-Pd-NHC, and two equivalents of Et_3N at 100 °C under 2 MPa of CO for 18 hours to give the product in the best yield.[12] Notably, this result represents a TON of 980, which is the highest among those reported for aryl Pd-NHC catalyzed Sonogashira carbonylation reaction.

As shown in Table 5, the reactions of aryl iodides **1** bearing an electron-donating or electron-withdrawing group at the *ortho*, *meta*, or *para* position of the phenyl ring proceeded smoothly to give the corresponding products **4aa**–**4la** in 39 to 98% yields. An obvious steric hindrance effect on the reactivity was observed, which was demonstrated by the reactivities of **1c** *vs.* **1d** and **1f** *vs.* **1g**. Fortunately, the free amino group survived well in the standard procedure, leading to carbonylation product **4ha** in excellent yield. This result revealed that aniline acted as a weak nucleophilic reagent for the Sonogashira carbonylation reaction. In addition to substituted aryl iodides, naphthyl-substituted iodide was also compatible with this process, furnishing the desired product **4oa** in good yield. It is worth noting that heterocyclic derivatives are suitable for the

Table 4 Screening [Pd] catalysts of single carbonylation

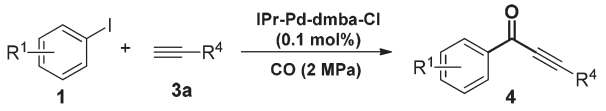


1a 3a 4aa

Entry	[Pd]	Yield **4aa**[a] (%)
1	$PdCl_2$	NR
2	$PdCl_2(CH_3CN)_2$	27
3	Bmim-Pd-PPh_3-I_2	81
4	IPr-Pd-Im-Cl_2	63
5	IPr-Pd-(3-Cl-pyridinyl)-Cl_2	79
6	IMes-Pd-dmba-Cl	87
7	IPr-Pd-dmba-Cl	98

[a] General conditions: **1a** (1.0 mmol), **3a** (1.2 mmol), [Pd] (0.1 mol%), triethylamine (2.0 mmol), toluene (5.0 mL), CO (2.0 MPa), 100 °C, 18 h. Isolated yield.

Table 5 Substrate scope of palladium-catalyzed carbonylation[a]



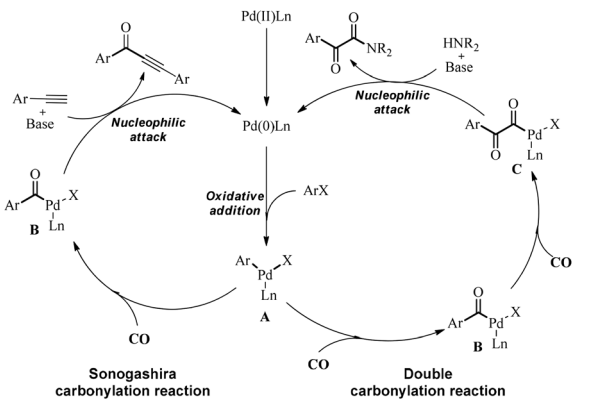
Entry	R^1	R^4	Yield (%)
1	H	Ph	**4aa**, 98
2	4-CH_3	Ph	**4ba**, 82
3	3-CH_3	Ph	**4ca**, 96
4	2-CH_3	Ph	**4da**, 63
5	4-OCH_3	Ph	**4ea**, 60
6	3-OCH_3	Ph	**4fa**, 83
7	2-OCH_3	Ph	**4ga**, 71
8	2-NH_2	Ph	**4ha**, 90
9	4-NHAc	Ph	**4ia**, 39
10	4-F	Ph	**4ja**, 78
11	4-Cl	Ph	**4ka**, 72
12	4-NO_2	Ph	**4la**, 92
13	4-C(O)CH_3	Ph	**4ma**, 40
14	4-C(O)OCH_3	Ph	**4na**, 49
15	1-Naphthyl	Ph	**4oa**, 82
16	3-Pyridine	Ph	**4pa**, 54
17	H	4-CH_3Ph	**4ab**, 97
18	H	4-CH_3OPh	**4ac**, 93
19	H	4-*n*-Bu-Ph	**4ad**, 65
20	H	3-F-Ph	**4ae**, 95
21	H	4-CN-Ph	**4af**, 96

[a] General conditions: **1** (1.0 mmol), **2a** (1.2 mmol), [Pd] (0.1 mol%), triethylamine (2.0 mmol), toluene (5.0 mL), CO (2.0 MPa), 100 °C, 18 h. Isolated yield.

present reaction, affording the corresponding product **4pa** in high yield as well.

To extend the scope of our catalytic system, we also tested carbonylation of **1a** with alkynes under the standard procedure. Alkynes containing electron-rich or -deficient functional groups reacted smoothly to give the corresponding products in excellent yields. Typical functional groups such as methyl, methoxy, halide and cyano groups were compatible with the reaction conditions.

On the basis of the results we obtained here and previous reports, a plausible mechanism for the present process can be proposed as shown in Scheme 3. Initial oxidative addition of aryl iodide to a Pd(0) species formed *in situ* from catalyst precursors of aryl-Pd-NHC reductively eliminates the dmba to give aryl palladium species **A**. Then CO insertion into the Pd–C bond of **A** gives aroyl palladium species **B**. In double carbonylation, CO insertion into **B** gives the intermediate **C**. Subsequently, the α-keto amide or alkynone is produced by nucleophilic attack in the palladium species **C** or **B** and regenerates the active Pd(0) species for the next catalytic cycle.



Scheme 3 Plausible mechanism.

In summary, we have developed an efficient and facile aryl Pd-NHC catalytic system that allows the direct formation of α-keto amide and alkynones from commercially available aryl iodide *via* carbonylation under mild conditions. A series of aryl palladium NHC compounds was prepared and their catalytic activity in the carbonylation of aryl iodides to synthesize α-keto amides and alkynones was examined. The method is compatible with a variety of functional groups and can be used to prepare a range of α-keto amide and alkynone derivatives. Notably, this aryl Pd-NHC-catalyzed carbonylation exhibits high reactivities, which afford TONs of 4300 and 980, respectively. The protocol would be practical for use as an economical synthetic method and offers an alternative synthetic strategy for the practical construction of α-keto amide and alkynone derivatives. Further investigations on application of the aryl Pd-NHC catalytic system in other carbonylation reactions are currently under way in our laboratory.

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12 See ESI for details on optimized reaction conditions.

