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Selective Palladium-Catalyzed Aminocarbonylation of Aryl Halides with CO and Ammonia

Xiao-Feng Wu, Helfried Neumann, and Matthias Beller*[a]

Dedicated to Professor José Barluenga on the occasion of his 70th birthday

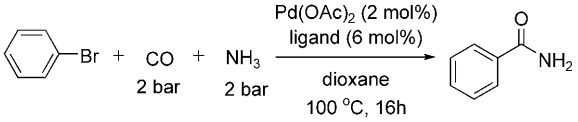
Primary aromatic amides are important intermediates in organic synthesis that are used as starting materials for engineering plastics, detergents, and lubricants.[1] Despite well-established methods of synthesis, there is continuing interest in the development of new, improved methodologies for their synthesis. In general, primary benzamides are synthesized either by hydration of the corresponding aromatic nitrile,[2] or by conversion of benzoic acids or acid chlorides with ammonia.[3] Less common synthetic strategies involve the transformation of benzaldehydes or benzaldoximes,[4] or the oxidation of primary benzyl amines or alcohols.[5]

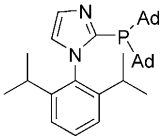
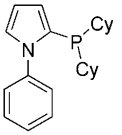
In recent years, the palladium-catalyzed carbonylation of aryl halides (Heck carbonylation) has become a powerful tool for the synthesis of substituted, aromatic, carboxylic acid derivatives.[6,7] However, there are few methods known that allow the synthesis of synthetically more useful primary amides. In general, these methods employ ammonia synthons as the nucleophilic partner in the carbonylation protocol. For example, the relatively expensive hexamethyldisilazane (HMDS) has been used for the aminocarbonylation of acyl chlorides, leading to primary amides in 52–92% yields.[8a] It has been shown that aryl iodides and triflates can also be converted into primary amides.[8b] Indolese and some of us,[9a] and later on Alterman and co-workers,[9b] succeeded in using formamide to give primary amides in moderate to good yields by the palladium-catalyzed aminocarbonylation of aryl bromides. Other ammonia sources that have been applied more recently to convert aryl iodides and bromides into primary amides are *N-tert*-butylamides[10] and hydroxylamine.[11] Interestingly, Mori and co-workers[12] utilized a titanium–nitrogen complex as a source of ammonia, which delivered primary amides in modest yields.

Clearly, the use of ammonia[13] in catalytic carbonylations would constitute the most straightforward method to synthesize primary amides from aryl halides. However, to date, there are no general methodologies available for this, apparently simple, transformation, because the lower basicity of ammonia renders it less reactive than primary and secondary amines. Ammonia, however, is inexpensive and has the advantage of being more atom economical than all previously employed ammonia equivalents. Based on our previous work on palladium-catalyzed carbonylations,[14] here we describe, for the first time, the use of ammonia for the aminocarbonylation of aryl halides under mild conditions.

Initially, the aminocarbonylation of bromobenzene was examined as a model system. Under low pressures of CO (2 bar) and NH_3 (2 bar) at 100 °C, the efficiency of different ligands was tested in the presence of $Pd(OAc)_2$ (2 mol%;

Table 1. Synthesis of benzamides: variation of ligands.[a]



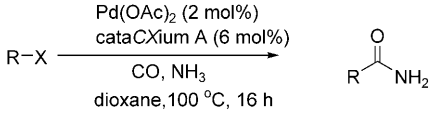
Entry	Ligands	Conversion [%][b]	Yield [%][b]
1	PPh_3	65	47
2	PCy_3	8	5
3	P(*o*-tolyl)$_3$	1	1
4		17	12
5		72	56
6	*n*-ButylP(Ad)$_2$[c]	100	86
7	HP(Ad)$_2$	22	10

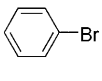
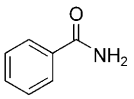
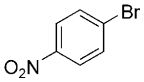
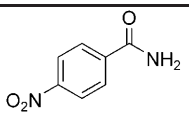
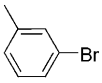
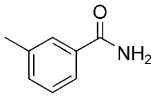
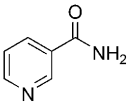
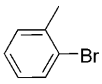
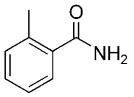
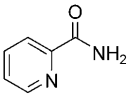
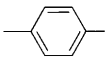
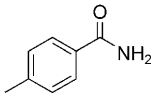
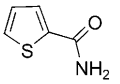
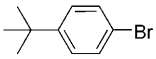
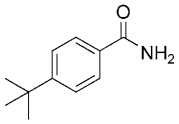
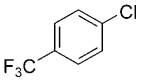
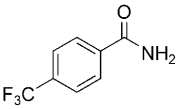
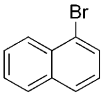
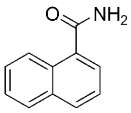
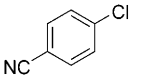
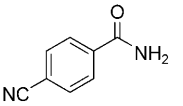
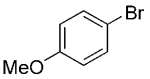
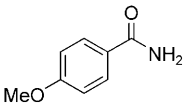
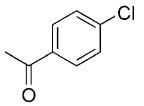
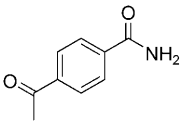
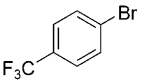
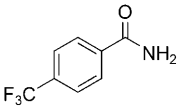
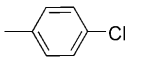
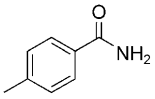
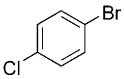
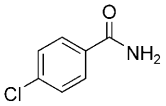
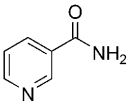
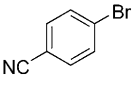
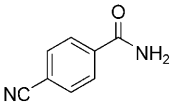
[a] General conditions: bromobenzene (1 mmol), CO (2 bar), NH_3 (2 bar), $Pd(OAc)_2$ (0.02 mmol), ligand (0.06 mmol), dioxane (2 mL), 100 °C, 16 h; Ad = Adamantyl; Cy = cyclohexyl. [b] Conversion and yield were determined by GC by using hexadecane as an internal standard and based on bromobenzene. [c] Cata*CX*ium A.

[a] X.-F. Wu, Dr. H. Neumann, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de

Table 1). While PPh_3 yielded benzamide in 47% yield (Table 1, entry 1), other standard ligands, such as PCy_3 and tri(*o*-tolyl)phosphine, gave only 5 and 1% yields, respectively, of the product (Table 1, entries 2 and 3). The application of our recently developed ligands *N*-(2,6-diisopropylphenyl)-2-[di-(1-adamantyl)phosphino]imidazole and 2-(dicyclohexylphosphino)-1-phenyl-*1H*-pyrrole, which show excellent reactivity in C–O coupling reactions[15] and direct aminations with ammonia,[16] gave only 12 and 56% yields of benzamide in this model aminocarbonylation (Table 1, entries 4 and 5). To our delight, we observed full conversion and an 86% yield of benzamide in the presence of *n*BuP(1-Ad)$_2$ (cata*CX*ium A) as the ligand (Table 1, entry 6). It is interesting to note that cata*CX*ium A is also an efficient ligand for pal-

Table 2. Aminocarbonylation of various aryl and heteroaryl halides.[a]



Entry	Aryl halides	Primary amides	Yield [%] (selec.[%])[b]	Entry	Aryl halides	Primary amides	Yield [%] (selec.[%])[b]
1			80 (80)[c]	12			52 (52)[e,f]
2			98 (98)	13			90 (90)
3			90 (90)	14			75 (75)[d]
4			88 (88)[c]	15			30 (59)
5			91 (91)[c]	16			48 (65)[e]
6			98 (98)	17			32 (33)[e]
7			93 (93)	18			34 (40)[e]
8			86 (86)	19			38 (72)[g]
9			83 (83)	20			40 (95)[e]
10			53 (53)[d]	21			60 (95)[e]
11			57 (57)[d]	22			40 (>99)[g]

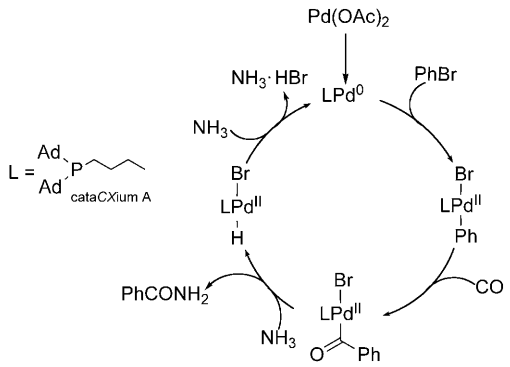
[a] General conditions: Aryl or heteroaryl halide (1 mmol), CO (2 bar), NH_3 (2 bar), $Pd(OAc)_2$ (0.02 mmol), cata*CX*ium A (0.06 mmol), dioxane (2 mL), 100 °C, 16 h. [b] Selectivity and yield were determined by GC by using hexadecane as the internal standard. [c] Isolated yield. [d] 80 °C, 30 h. [e] 130 °C, 20 h. [f] 40% Yield of 4-aminobenzamide. [g] $Pd(OAc)_2$ (0.05 mmol), cata*CX*ium A (0.15 mmol), 150 °C, 40 h, 20 bar N_2.

ladium-catalyzed alkoxycarbonylations,[17] reductive carbonylations,[18] and Suzuki carbonylations,[19] as well as in non-carbonylative coupling reactions.[20] However, if the secondary di-(1-adamantyl)phosphine ($HPAd_2$), which forms the corresponding phenyldi-(1-adamantyl)phosphine in situ, was used as the ligand, benzamide was obtained in only a 10% yield (Table 1, entry 7).

Subsequently, twenty two different aryl and heteroaryl halides were aminocarbonylated in the presence of cata*CX*ium A to demonstrate the general applicability of this novel carbonylation. As shown in Table 2 the corresponding primary amides are obtained in moderate to excellent yield. The *ortho*-, *meta*- and *para*-alkyl-substituted benzenes and 1-bromonaphthalene were successfully transformed into the corresponding primary amides in high yields (90–98%; Table 2, entries 2–6). Both electron-rich and electron-deficient aryl bromides gave good yields (83–93%) of the primary amide products (Table 2, entries 7–9). More difficult substrates, such as cyano-, acetyl-, and nitro-functionalized aryl bromides furnished the desired amides in full conversion and 52–57% yields (Table 2, entries 10–12). In the case of 1-bromo-4-nitrobenzene, 4-aminobenzamide was obtained as a by-product in 40% yield if we increased the temperature to 130°C.

Among the carbonylation reactions of aryl halides, those of heteroaryl halides are of special interest to industrial research groups because the attachment of carbonyl functionalities to heterocyclic frameworks by replacing bromide or chloride substituents provides easy access to valuable intermediates for the manufacture of herbicides and pharmaceuticals.[22] Hence, we were pleased to see that heteroaryl substrates were also efficiently transformed. For example, nicotinamide can be smoothly prepared from 3-bromopyridine in 90% yield (Table 2, entry 13). Similarly, 2-bromopyridine gave picolinamide in 75% yield. However, in the latter reaction 2,2′-bipyridine is observed in 10% yield as a homocoupling by-product. Finally, the catalyst system was successfully applied in the aminocarbonylation of both activated and nonactivated aryl chlorides (Table 2, entries 16–22). In general, yields of 30–60% and selectivities of 33–99% were achieved.

The proposed mechanism of our aminocarbonylation is shown in Scheme 1. In agreement with previous studies on the catalytic carbonylation of aryl halides,[21] we suppose that the oxidative addition is the rate determining step at high CO pressure. Hence, aryl chlorides react more slowly than aryl bromides (see Table 2). It is important to note that ammonia is both a reagent and a base in this transformation.



Scheme 1. Proposed mechanism of the palladium-catalyzed carbonylation.

In summary, a general palladium-catalyzed aminocarbonylation of aryl and heteroaryl halides with CO and ammonia has been established. Primary amides are accessible, under comparably mild conditions, in good yields. The general applicability and functional group tolerance of the presented system is shown by the aminocarbonylation of 22 different aryl and heteroaryl halides.

Experimental Section

General information: All reactions were performed by using standard Schlenk techniques (argon). Gas chromatography was performed on a Hewlett Packard HP 6890N chromatograph with an HP5 column. Chemicals were purchased from Fluka, Aldrich, and Strem and used as received. The cataCXium A ligand is available from Strem or directly from Solvias. Dioxane was distilled over CaH_2.

General Procedure: A Schlenk flask (25 mL) was charged with $Pd(OAc)_2$ (31.4 mg, 2 mol%), $P(1\text{-}Ad)_2nBu$ (150.6 mg, 6 mol%), and dioxane (14 mL) to form a clear yellow stock solution. Subsequently, hexadecane (1.17 mL, internal GC standard) and the stock solution (2.2 mL) were transferred into 6 vials (4 mL reaction volume) equipped with a septum, small cannula, stirring bar and the aryl bromide (1 mmol). The vials were placed in an alloy plate, which was transferred to an autoclave (300 mL) of the 4560 series from Parr Instruments, under an argon atmosphere. After flushing the autoclave three times with NH_3, NH_3 (2 bar) and CO (2 bar) were added at ambient temperature and the reaction was performed for 16 h at 100°C. After the reaction an aliquot of the mixture was subjected to GC and GC-MS analysis for determination of the yield and conversion. All products are known compounds.

Representative purification procedure for the model reaction: After the sample had been collected and washed with water, the mixture was extracted with ethyl acetate (3×3 mL), dried with $MgSO_4$, and purified by flash column chromatography (*n*-heptane/ethyl acetate, 1:1–1:2). A white solid (97 mg; 80% yield) was obtained. Spectroscopic data: ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 7.97$ (s, 1H), 7.88 (d, $J = 7.2$ Hz, 2H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.45 (m, 2H), 7.35 ppm (s, 1H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 167.9$, 134.3, 131.2, 128.2, 127.4 ppm.

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