Aminocarbonylation

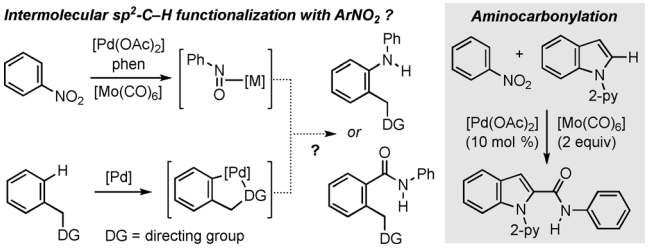
International Edition: DOI: 10.1002/anie.201612324
German Edition: DOI: 10.1002/ange.201612324

Nitroarenes as Nitrogen Source in Intermolecular Palladium-Catalyzed Aryl C–H Bond Aminocarbonylation Reactions

*Fei Zhou, Duo-Sheng Wang, Xinyu Guan, and Tom G. Driver**

Abstract: *A three-component palladium-catalyzed aminocarbonylation of aryl and heteroaryl sp^2 C–H bonds using nitroarenes as the nitrogen source was achieved using $Mo(CO)_6$ as the reductant and origin of the CO. This intermolecular C–H bond functionalization does not requires any exogenous ligand to be added, and our mechanism experiments indicate that the palladacycle catalyst serves two roles in the aminocarbonylation reaction: reduce the nitroarene to a nitrosoarene and activate the sp^2 C–H bond.*

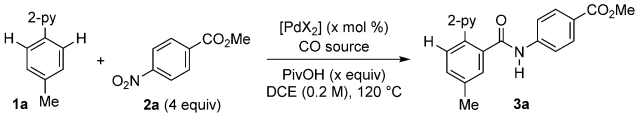
Intermolecular C–H bond functionalization of arenes and heteroarenes continues to be pursued because of its potential to selectively and efficiently increase the complexity of the substrate.[1] Although significant progress has been achieved,[2] the development of transition metal-catalyzed processes that transform C–H bonds into amides has lagged and often requires the use of isocyanates or other reactive reagents to effect bond construction.[3–5] Because of their ready availability, the use of nitroarenes in these C–H bond aminocarbonylation reactions would be enabling. During the course of our investigations into the reactivity of nitroarenes towards $[Mo(CO)_6]$ and palladium,[6] we were curious if we could achieve intermolecular C–H bond functionalization reactions, a reactivity pattern of electrophilic metal *N*-aryl catalytic intermediates, which had to date eluded our studies into aryl azides (Scheme 1).[7] Such a reaction, however, would require the unlocking the reactivity in both the nitroarene and the C–H bond to generate two reactive species that could potentially participate in undesired side reactions instead of reacting to produce the C–H bond functionalization product. Using $[Mo(CO)_6]$ also introduces a potential complication: its presence in the reaction mixture could enable insertion of a carbonyl fragment to achieve the formation of three new bonds from a single C–H bond (aminocarbonylation) in addition to C–H bond amination. While carbonylation reactions have a rich history in organic synthesis,[8] adding an additional C1 unit using CO in C–H bond functionalization processes remains rare.[9,10] Despite these challenges and potential pit falls, we report herein that the reactivity embedded in nitroarenes can be unlocked and controlled using $[Mo(CO)_6]$ and a palladium catalyst to achieve intermolecular C–H bond aminocarbonylation.



Scheme 1. Intermolecular C–H bond functionalization using nitroarenes.

To determine if a nitroarene could be used as the nitrogen source in intermolecular C–H bond functionalizations, 2-*para*-tolylpyridine **1a** was chosen because of its ubiquity in these types of reactions (Table 1).[11] While only trace C–H bond functionalization was observed in the absence of catalyst using $[Mo(CO)_6]$ as the reductant (entry 1), 20 mol% of palladium acetate produced amide **3a** in 76%

Table 1: Optimization of the C–H bond aminocarbonylation reaction.



Entry	Catalyst	*x* [mol%]	CO source	*x* equiv	PivOH[a]	**3a** yield [%][b]
1	...	...	$[Mo(CO)_6]$	2	1.5	trace
2	$[Pd(OAc)_2]$	20	$[Mo(CO)_6]$	2	1.5	76
3	$[Pd(TFA)_2]$	20	$[Mo(CO)_6]$	2	1.5	52
4	$[Pd(dba)_2]$	20	$[Mo(CO)_6]$	2	1.5	42
5	$[Pd(OAc)_2]$	20	CO	1.5 atm	1.5	n.r.
6[c]	$[Pd(OAc)_2]$	20	CO	1.5 atm	1.5	n.r.
7[d]	$[Pd(OAc)_2]$	20	DMF	excess	1.5	dec.[f]
8[e]	$[Pd(OAc)_2]$	20	$CHCl_3$	6	1.5	dec.[f]
9	$[Pd(OAc)_2]$	20	$[Mo(CO)_6]$	2	0.5	82
10	$[Pd(OAc)_2]$	10	$[Mo(CO)_6]$	2	0.5	78
11	$[Pd(OAc)_2]$	5	$[Mo(CO)_6]$	2	0.5	74
12[f]	$[Pd(OAc)_2]$	10	$[Mo(CO)_6]$	2	0.5	80

[a] equiv. [b] As determined using ^1H NMR spectroscopy using CH_2Br_2 as the internal standard. [c] 20 mol% $[Mo(CO)_6]$ added. [d] DMF, imidazole, KO*t*-Bu, 180–190°C; ref. [12b]. [d] $CHCl_3$, $CsOH{\cdot}OH_2$; ref. [12c]; [e] Only urea observed. [f] Reaction performed under an air atmosphere. py = pyridine; PivOH = pivalic acid; DCE = 1,2-dichloroethane; Ac = acetyl; TFA = trifluoroacetate; dba = dibenylideneacetone; DMF = dimethylformamide.

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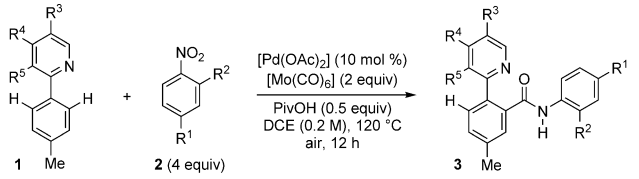
yield (entry 2). Changing the identity of the palladium counterion had a deleterious effect on the success of the reaction (entries 3–4). The identity of the reductant was also critical to the success of this reaction: no reaction was observed using 20 mol% of $[Mo(CO)_6]$ and CO, or if alternative sources of CO were used in place of $[Mo(CO)_6]$ (entries 5–8).[12] The yield of the aminocarbonylation could be improved if the amount of pivalic acid (PivOH) was reduced to 0.5 equivalents (entry 9). While PivOH appears necessary to promote a concerted metalation–deprotonation of the aryl C–H bond,[13] at too high of a concentration it has a negative effect on our transformation by favoring protonation of the pyridine to inhibit the desired C–H bond activation. To our delight, the transformation could be triggered successfully using lower loadings of $[Pd(OAc)_2]$ (entries 10 and 11). Finally, we were pleased to see that the reaction could be performed in air without reducing the yield of amide **3a** (entry 12).

Using these optimal conditions, the effect of changing the nitroarene and pyridine on the [Pd]-catalyzed amino-carbonylation reaction was examined (Table 2). The electronic

Table 2: Investigation of the effect of changing the nitroarene and pyridine directing group on the reaction outcome.



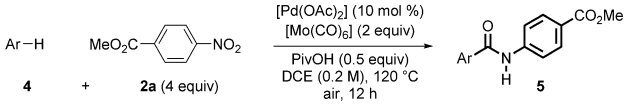
Entry	R^1	R^2	R^3	R^4	R^5	Compound	Yield [%][a]
1	CO_2Me	H	H	H	H	**3a**	80
2	CF_3	H	H	H	H	**3b**	70
3	Br	H	H	H	H	**3c**	68
4	Cl	H	H	H	H	**3d**	81
5	F	H	H	H	H	**3e**	72
6[b]	H	H	H	H	H	**3f**	63
7	Me	H	H	H	H	**3g**	66
8[b]	OMe	H	H	H	H	**3h**	30
9	H	Me	H	H	H	**3i**	n.r.
10	CO_2Me	H	Me	H	H	**3j**	89
11	CO_2Me	H	H	Me	H	**3k**	89
12	CO_2Me	H	H	H	Me	**3l**	90

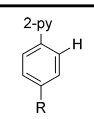
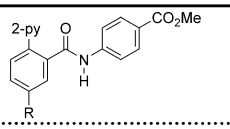
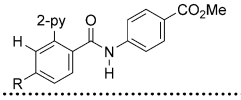
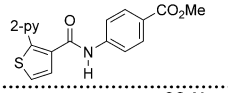
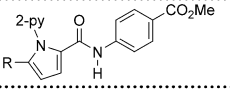
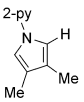
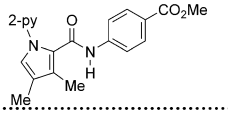
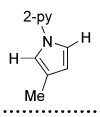
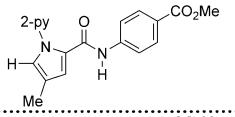
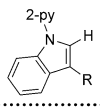
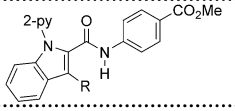
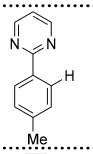
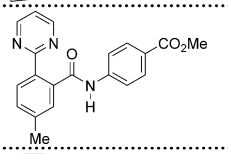
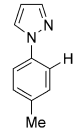
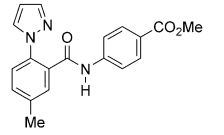
[a] Isolated after silica gel chromatography. [b] 1.0 equiv of PivOH added.

nature of the nitroarene impacted the success of the reaction (entries 1–8) with the highest yields observed when electron-deficient R^1-substituents were present on the nitroarene. Increasing the steric environment around the nitro group, however, had a detrimental effect on the reaction (entry 9). The pyridine-directing group could also be modified without adversely affecting the reaction: aminocarbonylation smoothly occurred when substituents were added to the 3-, 4- or 5-positions on the pyridine (entries 10–12).[14]

Next, the scope of the reaction was surveyed by varying the identity of the arene reaction site (Table 3). First, variation of the *para*-substituent of the 2-aryl group on **4** revealed that the aminocarbonylation reaction tolerated

Table 3: Examination of *N*-heteroarenes to determine scope and site selectivity.



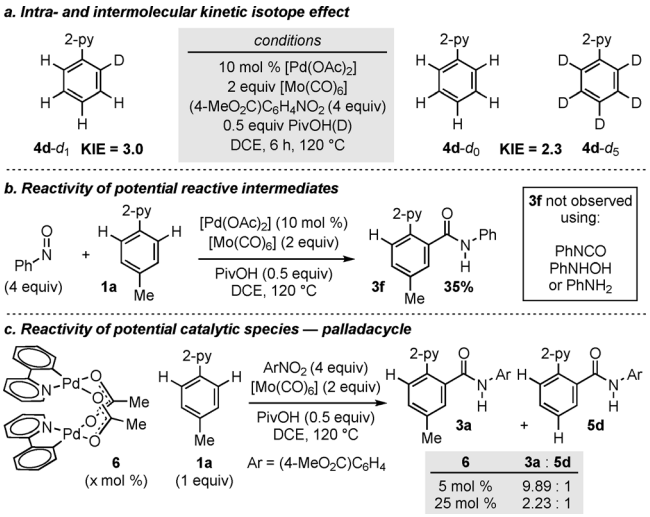
entry	*N*-heteroarene **4**	benzamide **5**	R	#	%, yield[a]
1[b]			OMe	**5a**	62
2[b]			OH	**5b**	55
3			SMe	**5c**	69
4			H	**5d**	66
5			Me	**5e**	79[c]
6			Cl	**5f**	50[c]
7			Br	**5g**	51[c]
8			...	**5h**	83
9			H	**5i**	58
10			Me	**5j**	70
11			...	**5k**	60
12[b]			...	**5l**	61[c]
13			H	**5m**	62
14			Me	**5n**	91
15			...	**5o**	58
16			...	**5p**	45

[a] Isolated after silica gel chromatography. [b] 1.0 equiv of PivOH added. [c] Regioselectivity determined using ^1H NMR spectroscopy; only product obtained.

ethers, thioethers, and even hydroxy groups (entries 1–4). Next, the selectivity of the C–H bond functionalization reaction was probed (entries 5–7). Our reaction proved to be site selective in that aminocarbonylation occurred only at the sterically more accessible C–H bond to produce amides **5e**–**5g** as single isomers. Changing the identity of the reaction site to a heteroarene did not diminish the efficiency of the Pd-catalyzed aminocarbonylation reaction: amides could be formed from thiophene-, pyrrole- or indole substrates (entries 8–14). In the latter two scaffolds, the *N*-pyridyl substituent can be removed by treating the amide product with MeOTf and PhSNa following the protocol reported by Ackermann and co-workers.[4c,15] A series of methyl-substituted pyrroles were investigated to provide insight into the

effect of increasing the steric environment around the reaction center. A C2-methyl group was tolerated in **4j**, and pyrrole **4k** demonstrated that aminocarbonylation could be achieved at a sterically congested site without loss of efficiency (entries 10 and 11). Despite the ability of the reaction to occur at this position, our C–H bond functionalization remained site selective: submission of C3-methyl-substituted pyrrole **4l** to reaction conditions produced amide **5l** as a single isomer (entry 12). Indoles **4m** and **4n** also proved to be competent substrates to produce C2-substituted **5m** and **5n** (entries 13 and 14). While the identity of the directing-group could be altered to either a pyrimidine or an indazole (entries 15 and 16), the yield of **5** was attenuated.

Several experiments were performed to provide more insight into the mechanism of the transformation (Scheme 2).

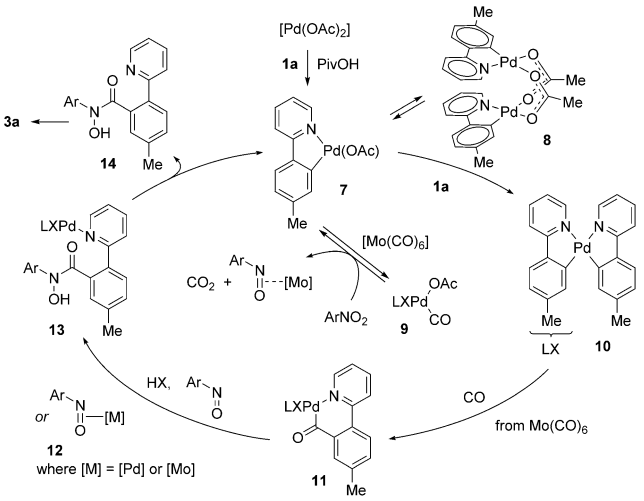


Scheme 2. Mechanistic experiments.

First, a control experiment established that no H/D exchange in substrate **4d** occurred if PivOD was used in place of PivOH.[16] Next, the reactivity of isotopologs [D_1]**4d** and [D_5]**4d** were examined. A primary kinetic isotope effect (KIE) of 3 was measured when 2-phenyl[D_1]pyridine was submitted to the reaction, and an intermolecular competition experiment between 2-phenylpyridine and 2-phenyl-[D_5]pyridine exhibited a KIE of 2.3. Together, these experiments suggest that the C–H bond activation step is both the product-determining and the turnover-limiting step.

Next, the reactivity of potential nitrogen and palladium catalytic intermediates were tested. To gain insight into the identity of the nitrogen reactive intermediate, several suspects were investigated (Scheme 2b). Aminocarbonylation was not observed using aniline, isocyanate, or *N*-hydroxyaniline as the nitrogen-source. The lack of amide formation from isocyanate was particularly surprising because it has been used as a reagent in metal-catalyzed amidation reactions;[4] isocyanate is well-established as the product of Pd-catalyzed reduction of nitroarenes with carbon monoxide;[17] and we observed the formation of *N*,*N*′-diarylurea as a by-product of our aminocarbonylation reaction. Instead, using stoichiometric- or substoichiometric amounts of isocyanate as the potential nitrogen source resulted in formation of only *N*,*N*′-diphenylurea.[11] In contrast, nitrosobenzene afforded the C–H bond functionalization product in 35% to suggest that it is being formed and consumed in the catalytic cycle. In the absence of [$Pd(OAc)_2$], however, no aminocarbonylation was observed using nitrosobenzene. Several experiments were performed to ascertain the identity of the active palladium species in the reaction (Scheme 2c). Towards this end, dinuclear palladium(II) complex **6** was prepared from the cyclopalladation of 2-phenylpyridine with [$Pd(OAc)_2$],[18] and was found to be a potent catalyst: exposure of 2-*para*-tolylpyridine to 5 mol% of **6** produced amide **3a** in 80% yield and amide **5d** in 88%. Increasing the stoichiometry of the palladacycle to 1 equiv, however, did not produce any amide product in the absence of the 2-arylpyridine.[19] The pyridylaryl ligand on **6** became labile once substrate was added: exposure of 0.25 equiv of palladacycle **6** to 1 equiv of 2-tolylpyridine and nitroarene produced a 2.23:1 mixture of amides **3a** and **5d**.

The results from these experiments were used to construct a potential catalytic cycle centered on the hypothesis that palladium is required to reduce the nitroarene as well as activate the *ortho*-C–H bond (Scheme 3). Our mechanistic



Scheme 3. Possible catalytic cycle for Pd-catalyzed aminocarbonylation.

experiments suggest that the active catalyst is palladacycle **7**.[18] This species is formed from the directed C–H bond activation of 2-*para*-tolylpyridine, which is in equilibrium with the dimer **8**.[20] Palladacycle **7** first reacts with CO liberated from [$Mo(CO)_6$] to produce palladium carbonyl complex **9**,[21] which reduces the nitroarene to produce nitrosoarene and reform **7**.[22] The second role of palladacycle **7** is to trigger the C–H bond activation of the substrate (**1a**) to produce biscyclometallated **10**.[23] The lack of H/D scrambling in the recovered 2-arylpyridine substrate when PivOD is used indicates that this step is irreversible. Insertion of CO into the Pd–aryl bond forms **11**, which reacts with nitrosoarene to form **13**.[24] Reduction of the N–O bond in **14** by molybdenum or palladium then produces the product amide. This reduction could occur before or after dissociation of the palladacycle

catalyst. Alternatively, the amide could be formed from the reaction of palladacycle **10** with arylisocyanate,[4,5] which could be formed from the $[Mo(CO)_6]$-mediated reduction of the nitroarene,[17] or from the reaction of aniline or *N*-hydroxy-aniline with acyl-Pd species **11**. The lack of amide formation when isocyanate, aniline, or *N*-hydroxyaniline are used as the nitrogen source, however, strongly suggests that bond formation does not occur through these two potential pathways.

We have shown that Pd-catalyzed intermolecular C–H bond aminocarbonylation of 2-aryl- or 2-heteroarylpyridines can be achieved using nitroarenes as the nitrogen source and $[Mo(CO)_6]$ as the carbonyl source. Our mechanistic studies revealed that the active catalyst is a palladacycle, which serves to both reduce the nitroarene to a nitrosoarene as well as activate the aryl C–H bond. Our future studies will build on these results by exploring the reactivity of palladacycles towards nitroarenes to trigger intermolecular C–N bond-forming reactions to rapidly and efficiently build complexity of simple heteroarenes.

Acknowledgements

We are grateful to the National Science Foundation CHE-1564959, University of Illinois at Chicago, Office of the Vice-Chancellor for Research, Huaqiao University Xiamen, and the Fujian Hundred Talents Plan for their generous financial support. We thank Mr. Furong Sun (UIUC) for HRMS data.

Conflict of interest

The authors declare no conflict of interest.

Keywords: aminocarbonylation · C–H functionalization · homogeneous catalysis · nitroarenes · palladium

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[14] No aminocarbonylation was observed when a 6-methyl substituent was present on the 2-arylpyridine substrate.

[15] Using this sequence the pyridine on benzamide **5j** was removed to produce the product pyrrole in 75%.

[16] No deuterium was exchanged into 2-phenylpyridine when it was submitted to $[D_1]$pivalic acid, $[Mo(CO)_6]$ and $[Pd(OAc)_2]$.

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Manuscript received: December 20, 2016
Revised: February 16, 2017
Final Article published: ■■ ■■, ■■■■

Communications

Aminocarbonylation

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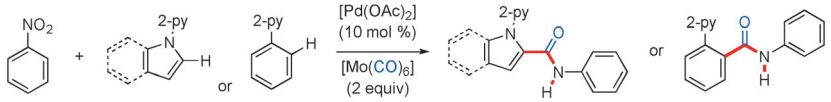
Nitroarenes as Nitrogen Source in Intermolecular Palladium-Catalyzed Aryl C–H Bond Aminocarbonylation Reactions



C–H functionalization: A three-component palladium-catalyzed aminocarbonylation of sp^2 C–H bonds using nitroarenes as the nitrogen source was achieved using $Mo(CO)_6$ as the reductant and origin of the CO. This intermolecular C–H bond functionalization does not require any exogenous ligand to be added.

