Carbonylation Hot Paper

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Selective Palladium-Catalyzed Aminocarbonylation of Olefins with Aromatic Amines and Nitroarenes**

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Molecular-defined catalysts allow for the refinement of readily available feedstocks to more complex functionalized products. Prime examples for such transformations are carbonylation processes, which make use of carbon monoxide—currently the most important C1 building block.[1] In fact, carbonylations represent industrial core reactions for converting various bulk chemicals into a diverse set of useful products for our daily life. More specifically, the transition-metal-catalyzed addition of carbon monoxide to olefins or alkynes in the presence of a suitable nucleophile, such as water, alcohols, and amines, leads to the formation of saturated or unsaturated carboxylic acid derivatives.[2] Nowadays, palladium is one of the most commonly employed metals in these transformations. Compared with the reaction of olefins, carbon monoxide, and alcohols (hydroesterification) or water (hydrocarboxylation),[3] related aminocarbonylations leading to amides have received much less attention. The same is also true compared to the well-studied aminocarbonylation of alkynes,[4] intramolecular aminocarbonylation of alkenes,[5] and aminocarbonylation of aryl and vinyl halides.[6] This is somewhat surprising as the aminocarbonylation of olefins provides a 100% atom-efficient route for producing carboxamides, which represent versatile building blocks and intermediates for the chemical, pharmaceutical, and agrochemical industries.[7]

In early studies of aminocarbonylations, cobalt-carbonyl complexes[8] or nickel cyanide[9] were used as catalysts. Iron-carbonyl complexes[10] and ruthenium chloride[11] also showed some catalytic activity. However, all these reactions were carried out under very severe conditions (>200 °C; >150 atm). Since the 1980s, more effective catalysts, such as ruthenium-carbonyl complexes[12] and cobalt on charcoal,[13] have been developed. Nevertheless, the substrate scope was limited and the reaction conditions were still harsh (150 °C; 70 atm). Notably, the formation of the corresponding formamide by-products was hardly suppressed. Hence, so far there exists no general and selective intermolecular aminocarbonylation of different olefins under mild conditions.

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Herein, we present an efficient homogeneous palladium-based catalyst system for the aminocarbonylation of olefins with a variety of (hetero)aromatic amines or nitro compounds under relatively mild conditions. Notably, the corresponding products were obtained in high yield with good regioselectivity, and unwanted formamides were not observed.

In our initial investigations we examined the effect of a series of phosphine ligands on the model reaction of 1-octene (**1a**) with aniline (**2a**) and carbon monoxide. When monodentate ligands were used, no conversion or just trace amounts of the desired products were observed (Table 1, entries 1–4). Commercially available bidentate ligands (e.g. BINAP, Dppp, **L2**, and **L4**) showed low activity in the formation of the desired product (Table 1, entries 5–14). Hence, some of our own developed *N*-phenylpyrrole-based bisphosphine ligands[14] with different steric properties were tested (Table 1, entries 15–17). To our delight, **L10** was identified as the most promising ligand and the reaction afforded the desired product **3aa** with moderate conversion, albeit with good selectivity. To improve the reaction further, we evaluated the influence of reaction parameters such as the molar ratio of **1a** to **2a**, acid co-catalyst, and solvent in the presence of **L10** as the ligand. As shown in Table 1, the yield of **3aa** was strongly affected by the molar ratio of **1a** to **2a** as a consequence of some isomerization of the olefin. Consequently, as the molar ratio of **1a** to **2a** increased to 2:1, the yield of **3aa** increased to 86% (Table 1, entry 18). Moreover, no reaction occurred in the absence of *para*-toluenesulfonic acid monohydrate (*p*-TsOH), thus indicating the importance of the acid for the generation of the catalytically active palladium hydride species (Table 1, entry 19).[15] Interestingly, changing the THF solvent to toluene resulted in full conversion of **2a** and gave nearly quantitative yields of the corresponding amides, as determined by GC (Table 1, entry 20). No conversion was observed and the starting materials were recovered in the absence of $[Pd(acac)_2]$ (acac = acetylacetonate) or when using other catalysts such as $[Rh(CO)_2(acac)]$, $[Co_2(CO)_8]$, [Ir(cod)(acac)] (cod = 1,5-cyclooctadiene), $[Ru_3(CO)_{12}]$, $[Fe_3(CO)_{12}]$, and $[Ni(acac)_2]$ (Table 1, entry 21).

With the optimized reaction conditions established (Table 1, entry 20), we examined the scope and limitations of this aminocarbonylation process with respect to various olefins (Table 2). Both short- and long-chain terminal olefins **1a**–**1e** provided the corresponding amides in good to excellent yields and with good regioselectivities (Table 2, entries 1–4). The more challenging internal olefin **1e** was transformed to C_9-amides in 53% yield. The linear amide is still formed preferentially because of isomerization of the olefin (66:34 *n*/*i* selectivity; Table 2, entry 5). Lower linear

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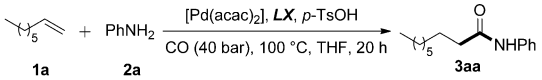
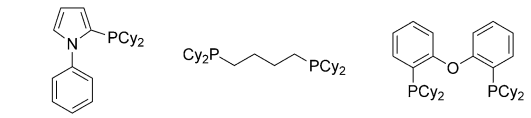
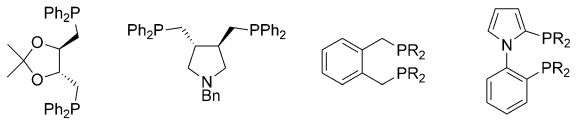
Table 1: Palladium-catalyzed aminocarbonylation of 1-octene (**1a**) with aniline (**2a**): Variation of reaction conditions.[a]





L1 L2 L3



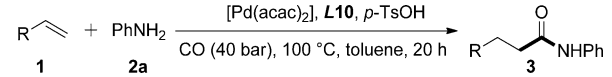
L4 **L5** **L6**: R=Ph; **L7**: R=*t*Bu; **L8**: R=Ph; **L9**: R=*t*Bu; **L10**: R=Cy

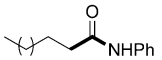
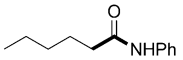
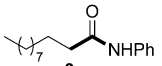
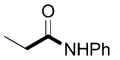
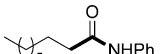
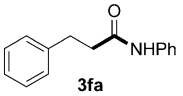
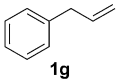
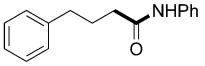
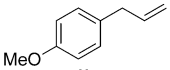
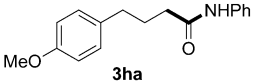
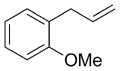
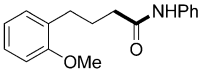
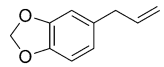
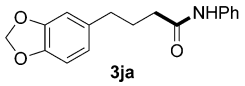
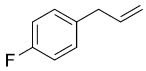
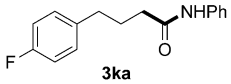
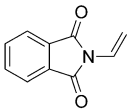
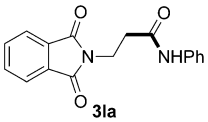
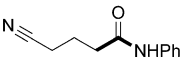
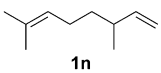
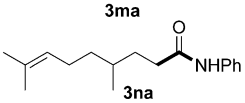
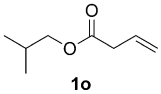
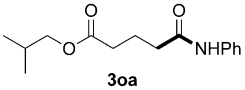
Entry	Ligand	Conversion [%][b]	Yield [%][c]	*n*/*iso*[d]
1	PPh_3		NR	
2	PCy_3		trace	
3	$BuPAd_2$		trace	
4	**L1**		trace	
5	Xantphos		trace	
6	Naphos		trace	
7	BINAP	8	3	77:23
8	Dppp	38	34	81:19
9	**L2**	32	28	87:13
10	**L3**		trace	
11	**L4**	22	18	82:18
12	**L5**		trace	
13	**L6**	5	1	–
14	**L7**		trace	
15	**L8**	7	3	86:14
16	**L9**		NR	
17	**L10**	50	46	88:12
18[e]	**L10**	89	86	88:12
19[f]	**L10**		NR	
20[g]	***L10***	***100***	***97***	***88:12***
21	**L10**		NR	

[a] Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), $[Pd(acac)_2]$ (0.5 mol%), monodentate ligand (2 mol%) or bidentate ligand (1 mol%), *p*-TsOH (2.5 mol%), THF (2 mL); NR = no reaction. [b, c] Conversion and yield (based on **2a**) determined by GC analysis using isooctane as the internal standard. [d] The ratios of linear to branched isomers were determined by GC-MS analysis. [e] **1a** (2 mmol). [f] **1a** (2 mmol) and without *p*-TsOH. [g] **1a** (2 mmol) and toluene as solvent. $BuPAd_2$ = *n*-butyldiadamantylphosphine; Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; Naphos = 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthalene; BINAP = *rac*-(±)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; Dppp = 1,3-bis(diphenylphosphino)propane; Ts = toluene-4-sulfanyl.

regioselectivity was observed when styrene **1f** was employed as a substrate because of stabilization of the benzylic palladium complex generated in situ (Table 2, entry 6). Interestingly, allylbenzene and different substituted allylbenzene derivatives were converted into the corresponding desired products in excellent yields and high regioselectivities (Table 2, entries 7–11). Selective aminocarbonylation reactions of functionalized olefins are known to be difficult. Gratifyingly, substrates having different functional groups such as phthalimide, nitrile, tri-substituted olefin, and ester

Table 2: Palladium-catalyzed aminocarbonylation of olefins (**1**) with aniline (**2a**).[a]



Entry	1	3	Yield [%] (*n*/*iso*)[b]
1	 **1a**	 **3aa**	85 (88:12)
2[c]	 **1b**	 **3ba**	84 (87:13)
3	 **1c**	 **3ca**	84 (88:12)
4[c]	**1d**	 **3da**	98
5[d]	 **1e**	 **3ea**	53 (66:34)
6	 **1f**	 **3fa**	75 (76:24)
7	 **1g**	 **3ga**	91 (92:8)
8	 **1h**	 **3ha**	87 (91:9)
9	 **1i**	 **3ia**	90 (92:8)
10	 **1j**	 **3ja**	91 (93:7)
11	 **1k**	 **3ka**	90 (92:8)
12	 **1l**	 **3la**	98 (99:1)
13	 **1m**	 **3ma**	92 (94:6)
14[e]	 **1n**	 **3na**	82 (99:1)
15[e]	 **1o**	 **3oa**	95 (95:5)

[a] Reaction conditions: **1** (2 mmol), **2a** (1 mmol), $[Pd(acac)_2]$ (0.5 mol%), **L10** (1 mol%), *p*-TsOH (2.5 mol%), toluene (2 mL). [b] Yield of isolated linear product based on **2a**; the regioselectivity was determined by GC-MS analysis. [c] **1** (20 mmol). [d] $[Pd(acac)_2]$ (1 mol%), [Pd]/**L10**/*p*-TsOH = 1:2:5; yield determined by GC analysis using isooctane as the internal standard. [e] $[Pd(acac)_2]$ (1 mol%), [Pd]/**L10**/*p*-TsOH = 1:2:5.

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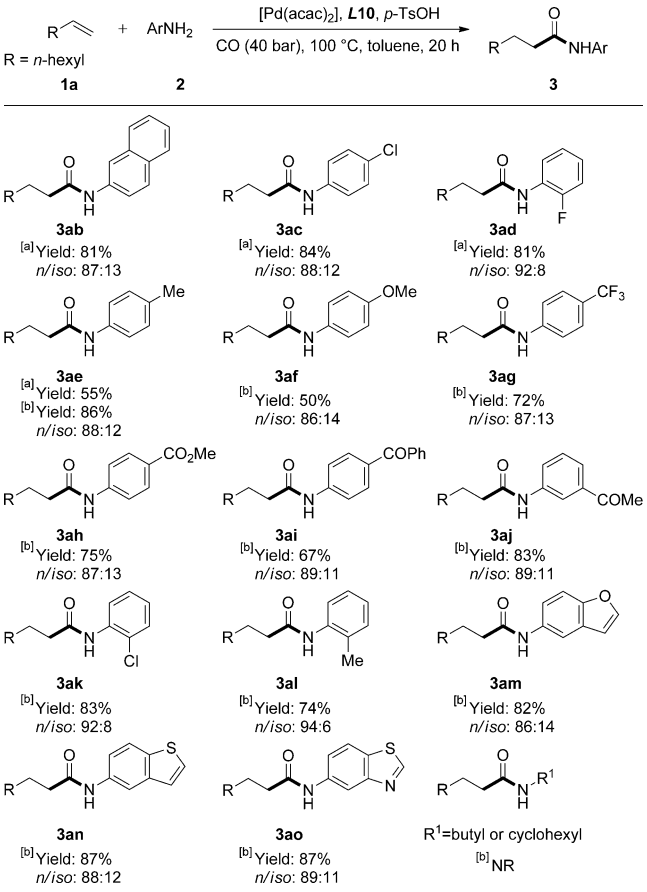
were well-tolerated, and smoothly transformed to the corresponding functionalized amides in good yields and high selectivities for the linear product (Table 2, entries 12–15). It is noteworthy that the corresponding formamides were not observed in any of these cases.

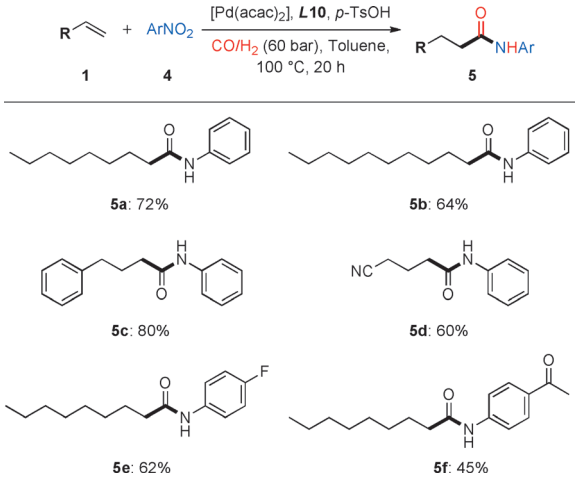
Next, we varied the amine substrate and using 1-octene (**1a**) as a standard coupling partner (Scheme 1). In general, the aminocarbonylation reaction was sensitive to steric and electronic effects of the substituent(s) on the aniline. Aniline



Scheme 1. Palladium-catalyzed aminocarbonylation of 1-octene (**1a**) with aniline derivatives **2**. [a] Reaction conditions: **1a** (2 mmol), **2** (1 mmol), $[Pd(acac)_2]$ (0.5 mol%), **L10** (1 mol%), *p*-TsOH (2.5 mol%), toluene (2 mL); yield of isolated linear product based on **2**; the regioselectivity was determined by GC-MS analysis. [b] $[Pd(acac)_2]$ (1 mol%), **L10** (2 mol%), *p*-TsOH (5 mol%).

derivatives such as 2-naphthylamine, 4-chloroaniline, and 2-fluoroaniline gave full conversion and around 80% yield of the expected linear product in the presence of only 0.5 mol% catalyst (Scheme 1, **3ab**–**3ad**). Electron-rich substituted anilines such as *p*-toluidine and *p*-anisidine are more sensitive and led to lower conversion and yields of the corresponding *N*-aryl C_9-amides (Scheme 1, **3ae**). However, when the catalyst loading was increased to 1.0 mol%, all the reactions of the anilines substituted with electron-rich or electron-deficient groups proceeded smoothly and afforded the desired products in moderate to good yields and high regioselectivities (Scheme 1, **3ae**–**3aj**). Higher linear regioselectivity is observed when *ortho*-substituted anilines were employed as substrates, probably because of steric effects (Scheme 1, **3ad**, **3ak**, and **3al**). Moreover, heteroaromatic amines proved to be efficient coupling partners and gave the corresponding products in good yields with high regioselectivities (Scheme 1, **3am**–**3ao**). No conversion was observed when aliphatic amines such as butyl- or cyclohexylamine were used. Apparently, the active Pd-H species is not formed in the presence of the more basic aliphatic amines, as indicated by the absence of any isomerization side reaction.

Subsequently, we became interested in the aminocarbonylation of olefins by utilizing inexpensive nitroarenes. Of course, most of the anilines are prepared from the corresponding nitroarenes. Hence, this transformation would allow the elimination of at least one process step and makes use of less-expensive starting materials. Gratifyingly, all the individual reaction steps proceeded smoothly when molecular hydrogen was used as the reducing agent and afforded the desired product in acceptable to good yields (Scheme 2). Substrates having functional groups such as nitrile and even



Scheme 2. Palladium-catalyzed aminocarbonylation of olefins (**1**) with nitroarenes (**4**). [a] Reaction conditions: **1** (2 mmol), **4** (1 mmol), $[Pd(acac)_2]$ (1 mol%), **L10** (2 mol%), *p*-TsOH (5 mol%), toluene (2 mL); yield of isolated linear product based on **4**.

ketone (Scheme 2, **5d** and **5f**) were well-tolerated under these reducing conditions. In general, this latter protocol provides a useful and benign alternative for the synthesis of *N*-aryl carboxamides. To the best of our knowledge such aminocarbonylations of olefin with nitroarenes has not been explored before.

Although the detailed mechanism of the palladium-catalyzed aminocarbonylation of olefins is still under investigation, we suggest the following catalytic cycle based on our preliminary observations and the known work on carbonylations of olefins and alkynes (Scheme 3).[16] Initially, the active cationic palladium hydride species **A** should be formed in situ from the reaction of $[Pd(acac)_2]$, **L10**, and *p*-TsOH.[15] Next, π coordination of the olefin to the metal center, followed by insertion into the hydrogen–palladium bond,

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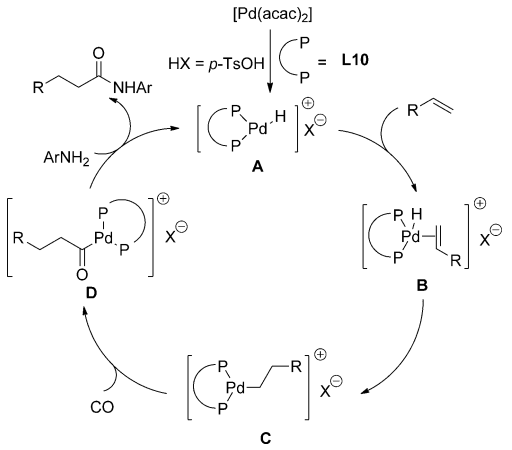
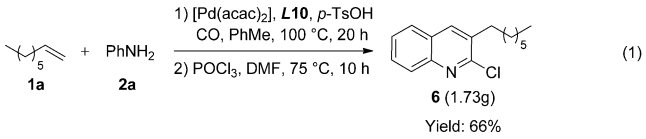


Scheme 3. Proposed catalytic cycle for this reaction.

should afford the alkyl-palladium intermediate **C**. Subsequent insertion of CO into the palladium–alkyl bond leads to the corresponding acyl palladium complex **D**. Finally, aminolysis leads to the desired product and regenerates the palladium hydride species **A**.

It should be noted that our new procedure for the preparation of all kinds of *N*-aryl carboxamides also allows for an efficient synthesis of important heterocycles. For example, the aminocarbonylation of olefins followed by the established Vilsmeier–Haack formylation should give rise to a variety of bioactive quinolines. Indeed, the one-pot synthesis of **6**, which has been used as an intermediate for 5-hydroxytryptamine antagonists, proceeded smoothly on a gram scale. Starting from inexpensive **1a** and aniline (**2a**), **6** was obtained in 66% yield after successive aminocarbonylation and cyclization with $POCl_3$ and DMF [Eq. (1)].[17]



(1)

In summary, we have developed a palladium-based catalyst system for a general and selective aminocarbonylation of olefins with (hetero)aromatic amines to alkanamides. Notably, a wide range of olefins are efficiently transformed to the corresponding *N*-(hetero)aryl amides in good yields and often with high regioselectivity. Combining this procedure with established functionalizations of the resulting products allows the efficient preparation of quinolines. Furthermore, we reported the first catalytic aminocarbonylations of olefins by utilizing easily accessible nitroarenes. We believe these procedures will inspire chemists to use carbonylation reactions more frequently in organic synthesis.

Experimental Section

Typical procedure for the preparation of **3**: A vial (4 mL) was charged with $[Pd(acac)_2]$ (1.5 mg, 0.5 mol%), **L10** (5.4 mg, 1 mol%), *p*-TsOH (4.75 mg, 2.5 mol%), and a stirring bar. Then, toluene (2 mL), olefin **1** (2 mmol), and aniline (**2a**, 1 mmol) were injected by syringe. The vial was placed in an alloy plate, which was transferred into an autoclave (300 mL) of the 4560 series from Parr Instruments under an argon atmosphere. After flushing the autoclave three times with nitrogen, the pressure of CO was increased to 40 bar CO at ambient temperature. The reaction was performed for 20 h at 100 °C. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released and isooctane (internal standard) was added to the solution. The yield and regioselectivity were measured by GC and GC-MS, respectively. After removing the solvent by vacuum, the residue was directly purified by flash chromatography on silica gel (eluent: *n*-heptane/ethyl acetate = 5:1) to give the desired product **3**.

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