Heck Reaction

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General Olefin Synthesis by the Palladium-Catalyzed Heck Reaction of Amides: Sterically Controlled Chemoselective N–C Activation

*Guangrong Meng and Michal Szostak**

Abstract: *Metal-catalyzed reactions of amides proceeding via metal insertion into the N–CO bond are severely underdeveloped due to resonance stabilization of the amide bond. Herein we report the first Heck reaction of amides proceeding via highly chemoselective N–CO cleavage catalyzed by Pd^0 utilizing amide bond ground-state destabilization. Conceptually, this transformation provides access to a myriad of metal-catalyzed transformations of amides via metal insertion/decarbonylation.*

The Heck reaction is one of the most powerful methods for the catalytic construction of C–C bonds under mild conditions,[1,2] and has been widely utilized for the synthesis of small molecules, natural products, polymers and pharmaceuticals on both the laboratory and industrial scale.[3,4] Over the last four decades, a variety of aryl halides,[5a–d] aryl triflates,[5e] aryl phosphates,[5f] aryl diazonium salts,[5g,h] arylsulfonyl halides,[5i] aroyl halides,[5j,k] anhydrides[5l] and esters[5m] have been shown to participate as aryl electrophiles in this reaction.[6] Significant advances in the development of new catalytic systems[7] and mechanistic studies have been reported.[8] However, despite the reported advances, the use of amides as electrophilic coupling partners in the Heck reaction remains unknown.[1–8] There is little doubt that the successful application of bench-stable amide building blocks as olefination precursors would significantly broaden the scope of electrophilic partners for the Heck reaction and represent an attractive opportunity for the development of new activation modes of inert N–C bonds.[9]

Metal-catalyzed reactions of amides proceeding via metal insertion into the N–CO bond are severely underdeveloped due to $n_N \rightarrow \pi^*_{C=O}$ stabilization.[10] We recently questioned whether the use of amide ground-state distortion,[11] a well-recognized property of non-planar amides,[12] can be exploited to promote metal insertion into the amide N–CO bond under chemoselective conditions to deliver the acyl-metal intermediate capable of participating in a myriad of catalytic cross-coupling manifolds.[13] Recently, new methods for activation of amides by electronic means have been reported.[14] Steric activation of amides results in a general reactivity platform of amide bonds.[9–14] Furthermore, we have recently demonstrated that the N-/O-coordination aptitude in amides can be directly correlated with additive distortion parameters ($\Sigma\tau + \chi_N$),[15] which allows to rationally design arrays of amides for N–C scission via catalytic cross-coupling manifolds.[16] Expanding upon the N–C amide bond activation concept, we hypothesized that the acyl-Pd^{II} intermediate[17] formed after Pd^0 insertion into the inert amide N–CO bond might undergo selective decarbonylation[18] to give the aryl-Pd^{II} electrophile, thereby providing access a wide variety of valuable end-products by functionalization and/or elementary reactions (Figure 1).[19]

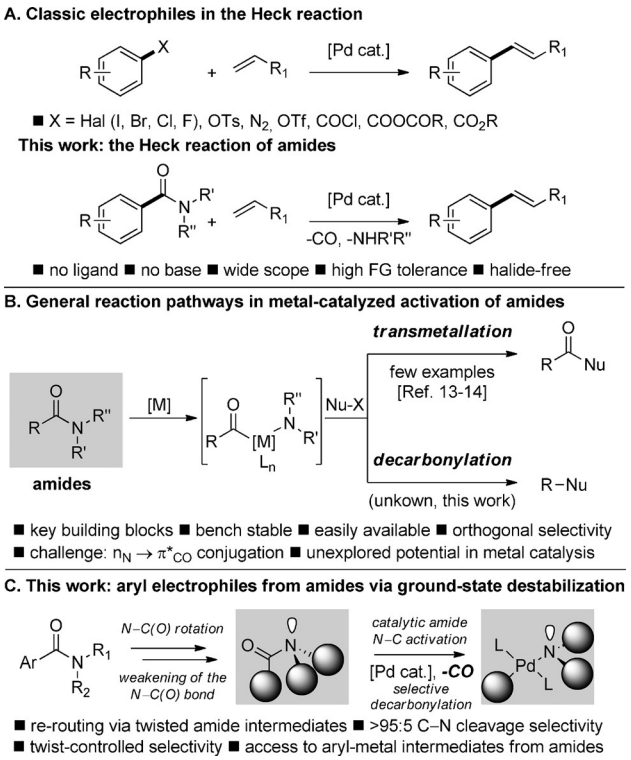

Figure 1. A) Electrophiles in the Heck reaction. B) Transition-metal catalyzed activation of amides. C) This work: the first Heck reaction of amides via ground-state distortion.

Herein, we document the first Heck reaction of amides proceeding via highly chemoselective N–CO cleavage catalyzed by Pd^0, utilizing amide bond ground-state destabilization as a new strategy for organic synthesis. The following features are noteworthy: 1) The reaction proceeds with an excellent N–CO bond cleavage selectivity (> 95:5 in all cases examined).[11c] 2) The protocol is characterized by a broad substrate scope with respect to amide and alkene coupling partners.[5j–m] 3) High yields and coupling selectivity are

[*] G. Meng, Prof. Dr. M. Szostak
Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102 (USA)
E-mail: michal.szostak@rutgers.edu

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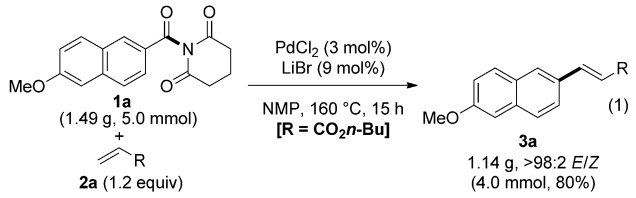
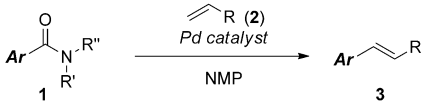
achieved under base-free and ligand-free conditions, leading to an operationally simple protocol, reduction of waste and cost of the process.[5l] 4) Stoichiometric corrosive halide waste is not formed in the reaction.[4a] 5) This reaction constitutes the first general method for the synthesis of aryl electrophiles from amides under catalytic conditions.[9–14] Notably, this transformation represents a significant advance in the construction of C–C bonds directly from amides via N–C activation[20] with potential applications ranging from functionalization of biomolecules (amino acids, peptides, proteins)[21] to large scale industrial olefinations for the production of specialty and bulk chemicals.[4b]

The following gram scale procedure is representative: a mixture of **1a** (1.49 g, 5 mmol), olefin (0.77 g, 6 mmol), and $PdCl_2$ (26.6 mg, 0.15 mmol) was stirred in the presence of LiBr (39.1 mg, 0.45 mmol) in NMP at 160 °C to afford 1.14 g of **3a** (80 % yield) [Eq. (1)].

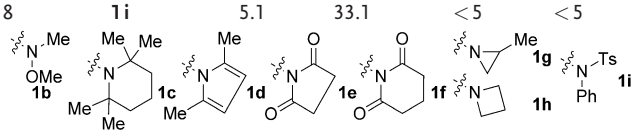


Our initial efforts focused on screening a range of electronically and sterically distorted amides in the reactions with *n*-butyl acrylate as a coupling partner in the presence of palladium catalytic systems under various conditions (Table 1). We hypothesized that 1) metal insertion into the N–C bond in amides in which the sum of distortion parameters ($\Sigma\tau + \chi_N$) is close to 50° should be thermodynamically favorable;[15] 2) less coordinating ligands and high temperatures should favor decarbonylation of the acyl-metal intermediate;[18c] 3) the leaving group should regenerate Pd^0,[1,2] thus obviating the need for a stoichiometric amount of external base.[9]

Table 1: Optimization of the amide bond geometry.[a]



Entry	NR′R″	τ [deg]	χ_N [deg]	Conv. [%]	Yield [%]
1	**1b**	1.2	16.3	< 5	< 5
2	**1c**	34.1	17.0	< 5	< 5
3	**1d**	39.7	8.4	< 5	< 5
4	**1e**	45.9	10.7	< 5	< 5
5	**1f**	87.8	6.8	> 98	95
6	**1g**	14.3	69.6	< 5	< 5
7	**1h**	5.1	33.1	< 5	< 5
8	**1i**	5.1	33.1	< 5	< 5



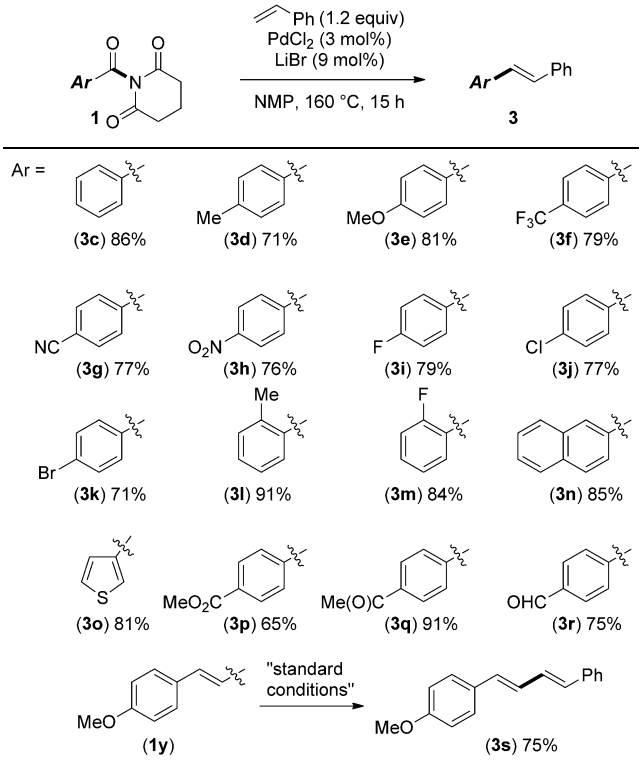
[a] Conditions: R = CO_2nBu (1.2 equiv), $PdCl_2$ (3 mol%), LiBr (9 mol%), NMP (0.25 M), 160 °C. See Supporting Information for full details.

The optimization results in Table 1 revealed that no reaction or low yields were observed with Weinreb amides (entry 1),[22a] tmp amides (entry 2),[22b] acylpyrroles (entry 3),[22c] and five-membered imide derivatives (entry 4).[22d] However, we were delighted to find that by using the six-membered imide derivative **1f** (entry 5),[22d] the proposed Heck reaction was indeed feasible delivering the desired olefin in excellent 95 % yield (2,1/1,2 > 98:2; E/Z > 98:2). Pyramidalized aziridinyl (entry 6) and azetidinyl (entry 7) amides[22e] resulted in no product formation. Furthermore, it is worth noting that N–C bond activation was not observed using electronically-activated amide substrates (entry 8),[14] which presents an attractive opportunity for chemoselective transformations using complementary amide bond activation modes. Overall, the results in Table 1 validate the feasibility of the N–C activation/decarbonylation platform of sterically-activated amides. The results show a unique behavior of twisted imide **1f**, and suggest that the ground-state destabilization may not be the only factor contributing to the observed reactivity.[13] Importantly, under these conditions reductive elimination from the acyl-Pd intermediate was not observed, suggesting that decarbonylation is facile.

Table 1-SI (SI = Supporting Information) presents selected results obtained during optimization of the reaction using **1f** and styrene. Palladium chloride was identified as the most active precatalyst. NMP was found to be the optimum solvent. Phosphane ligands and base were not required for the efficient coupling. Catalytic halide salts[7a] exerted small but beneficial effect on the reaction selectivity, consistent with the ligand effect on the olefin insertion step during the catalytic cycle (see below).[8a] Optimization of the temperature revealed that catalytic turnover of Pd ensues at lower temperatures, but the process is less efficient. Other products resulting from the acyl-Pd^{II} intermediate were not detected in the reaction. As for related cross-couplings,[5j–m] the addition to styrene is not completely regioselective; however, the observed selectivity compares very favorably with other reported olefinations.[1,2] Notably, olefin overaddition products were not detected in the reaction.

With the optimized conditions in hand, we explored the scope of the reaction using styrene as a standard olefin (Table 2). The reaction exhibits an excellent chemoselectivity profile, tolerating a wide range of functional groups. The observed coupling selectivity (2,1/1,2 see SI) is good to excellent in all cases examined. In all cases, single olefin isomers were obtained (E/Z > 98:2). Electron-donating (**3d**, **3e**) and electron-withdrawing (**3f**–**3h**) substituents are well-tolerated. Amides containing sensitive functional groups at the para position of the aromatic ring such as cyano (**3g**), nitro (**3h**), fluoro (**3i**), chloro (**3j**), and bromo (**3k**) were all successfully coupled in high yields, providing a synthetic handle for further functionalization. Steric hindrance in the *ortho*-position was well-tolerated (**3l**–**3m**). Naphthyl (**3n**) and heteroaromatic amides (**3o**) underwent olefination in high yields. Remarkably, the reaction was fully chemoselective for the C–N bond activation in the presence of other

Table 2: Amide scope in the Pd-catalyzed Heck reaction of amides.[a,b]

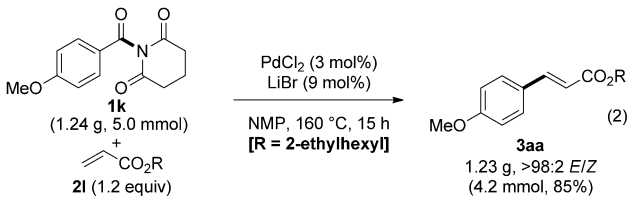


[a] See Table 1. [b] Yields of isolated products. See SI for full details.

Table 3: Olefin scope in the Pd-catalyzed Heck reaction of amides.[a,b]

Entry	1	2	Olefin	Yield [%]	Regio-selectivity
1	**1f**	**2b**	Ph	86	15:1
2	**1f**	**2c**	CO_2Me	84	>20:1
3	**1f**	**2a**	CO_2n-Bu	81	>20:1
4	**1f**	**2d**	CONH*t*-Bu	86	>20:1
5	**1f**	**2e**	CN	93	13:1
6	**1f**	**2f**	n-C_8H_{17}	85	–[c]
7	**1f**	**2g**		94	4:1
8	**1f**	**2h**		80	13:1
9	**1f**	**2i**		89	10:1
10	**1f**	**2j**	TMS	91	9:1

[a,b] See Table 2. [c] Olefin isomers (1:0.4:1:1). See SI for full details.



typically more reactive carboxylic acid derivatives such as esters (**3p**), ketones (**3q**) and aldehydes (**3r**); these moieties are poised for further functional group manipulation. The chemoselective coupling of amides nicely illustrates the synthetic potential of the amide bond activation platform via distortion.[12] Finally, the decarbonylative Heck reaction could be readily extended to the α,β-unsaturated amide substrate to yield the diene product with excellent selectivity ($E/Z > 98{:}2$) (**3s**).

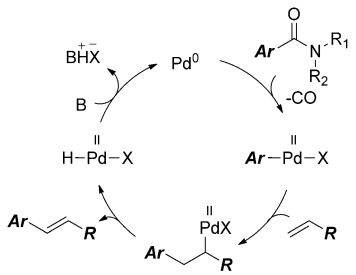
The scope of olefin coupling partners is also very broad (Table 3). Styrenes and electron deficient olefins provide the products in high yields and with excellent regioselectivity.[23] Acrylic esters (entries 2 and 3), amides (entry 4) and nitriles (entry 5) are well-tolerated.[23a] Terminal olefins can be used as substrates (entry 6);[23b] however, olefin isomerization results in a mixture of isomers, in agreement with previous studies.[5l] Cyclooctane, the only cyclic olefin examined, gave isomeric arylcyclooctenes (entry 7).[5l] Notably, sterically demanding *n*-butyl methacrylate and α-methylstyrene were arylated in high yields (entries 8 and 9);[23c] double bond isomerization constituted a minor reaction pathway. Finally, the synthetically valuable *E*-stilbenes are accessible in high yields by using trimethylvinylsilane as an ethylene equivalent (entry 10).[23d] Formation of styrenes was not observed under these conditions.

We demonstrated the synthetic utility of this new protocol in the gram scale synthesis of **3aa**, which is a common UV-B sunscreen produced on an industrial scale [Eq. (2)].[4a]

Extensive studies on the Heck reaction of aryl anhydrides demonstrated that the reaction involves a cationic palladium complex with decarbonylation as the rate limiting step.[24] The presence of halide accelerates the reaction and increases the selectivity by acid to halide exchange. We conducted several studies to gain preliminary insight into the mechanism of the Heck reaction of amides (see SI). 1) Intermolecular competition experiments with differently substituted amides revealed that electron-deficient arenes are more reactive substrates; however, the relative reactivity suggests that oxidative addition is not the rate-determining step in the reaction.[25] 2) Competition experiments with sterically-demanding ortho aryl substrates revealed that steric effects may play an important role in accelerating the reaction.[18c] 3) Intermolecular competition experiments with different olefins ($H_2C{=}CHR$) established the following order of reactivity: CO_2nBu > Ph > n-C_8H_{17}, which follows the reactivity in Heck reactions of aryl halides.[1,2] 4) Competition experiments established the following reactivity order: Ar-I > Ar-C(O)NR_2 ≫ Ar-Br. Moreover, we established the following reactivity order of carboxylic acid electrophiles: Ar-C(O)NR_2 ≈ (Ar-CO)$_2$O ≫ Ar-CO_2R. 5) Electrospray ionization mass spectrometry (ESI/MS) analysis using stoichiometric palladium was performed.[26] Intermediates corresponding to the aryl-Pd^{II} species containing halide and amine ligands were detected. 6) The role of halide was probed by preliminary kinetic studies using styrene and acrylate nucleophile.[5k] The effect of halide salt on the cross-coupling rate was found

to be negligible in both classes of olefins, consistent with amine coordination to the metal throughout the catalytic cycle.

Overall, the preliminary mechanistic studies are consistent with amide activation by ground-state distortion. It is particularly noteworthy that activation of the inert N–C bond takes place in the absence of electron-rich ligands on metal. Decarbonylation of the acyl-Pd intermediate is favored by the coordination of sterically-demanding anionic amine ligand. Reductive elimination appears to be a kinetically relevant step in the reaction (Scheme 1). The alternative catalytic cycle



Scheme 1. Proposed mechanism. B = base (glutarimide); X = halide, glutarimide (ESI-MS experiments).

$Pd^{II/IV}$ cannot be excluded at this point.[27] Further studies to elucidate the mechanism are ongoing.

In conclusion, we have documented the first Heck reaction of amides via chemoselective N–C bond activation using amide ground-state destabilization. The ability of amides to engage in catalytic manifolds as aryl electrophiles sets the stage for the design of new catalytic reactions via metal insertion/decarbonylation beyond the coupling described herein.

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Keywords: amide bonds · base-free Heck reaction · Heck reaction · N–C activation · twisted amides

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