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Aminocarbonylation of (Hetero)aryl Bromides with Ammonia and Amines using a Palladium/DalPhos Catalyst System

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Abstract: Variants of the DalPhos [2-aminophenylbisadamantyl)phosphine] ligand family were examined in a palladium-catalyzed carbonylative amination reaction using inexpensive carbon monoxide and ammonia as reagents. As a result of this survey, the Pyr-DalPhos ligand was identified as being effective for the selective aminocarbonylation of aryl bromides with ammonia, as well as primary and secondary alkylamines. A variety of primary aromatic, heteroaromatic and *N*-substituted benzamides were formed in moderate to good yields. As part of this study, a (Mor-DalPhos)Pd-benzoyl complex was prepared and crystallographically characterized, thereby showing the viability of the carbonyl insertion step.

Keywords: amides; ammonia; carbonylation; N,P ligands; palladium

Introduction

Palladium-catalyzed cross-coupling reactions have become an indispensable tool for the synthesis of natural products, pharmaceuticals and conjugated materials.[1] Among the most common and efficient of these reactions is Buchwald–Hartwig amination, a powerful method for the formation of C–N linkages from amines and aryl halides.[1c,g,2] However, only recently have these couplings and other transition metal-catalyzed processes been extended to the use of ammonia, an inexpensive and readily available starting material that is ideal for the synthesis of nitrogen-containing molecules.[3] Although palladium-catalyzed ammonia monoarylation has proven challenging for the vast majority of established catalyst systems used for Buchwald–Hartwig amination, due to the propensity for catalyst deactivation and/or uncontrolled polyarylation, new DalPhos ligands developed by the Stradiotto group have been found to circumvent these and similar issues pertaining to the functionalization of small molecules.[4]

Successful lead variants of this new ligand family include Me-DalPhos, for the cross-coupling of primary and secondary amines as well as ammonia,[5] and Mor-DalPhos, for the selective monoarylation of ammonia at mild temperatures,[6] the cross-coupling of hydrazine[7] and the α-arylation of acetone (Figure 1).[8]

Palladium-catalyzed carbonylative couplings of aryl and vinyl halides are gaining increasing interest among synthetic chemists as an important pathway for the construction of carboxylic acid derivatives.[9] Recent contributions from Beller and co-workers in this area include carbonylative Heck,[9a,10] Sonogashira[9a,11] and Suzuki[9a,12] couplings as well as aminocarbonylations.[9a,13] Carbonylative amination reactions had been restricted to primary and secondary amines until some of us reported for the first time the use of ammonia gas, giving direct access to synthetically useful primary aromatic and heteroaromatic amides.[14] The straightforward synthesis of primary

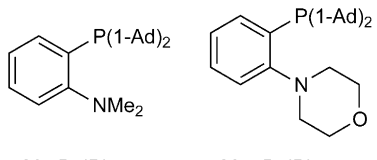


Figure 1. Structures of Me-DalPhos (*left*) and Mor-DalPhos (*right*) ligands used in Pd-catalyzed cross-coupling reactions.

aromatic amides *via* amincarbonylation of (hetero)aryl bromides and chlorides using palladium catalyst systems was developed based on either cata*CX*iumA (22 examples, GC yields 30–98%, 3 isolated yields 80–91%) or DPPF (22 examples, GC yields 30–98%, 3 isolated yields 85–90%).[14] An important feature of this reaction is the dual role of ammonia as both nucleophile and base. This protocol was later extended to phenols through the *in situ* generation of aryl nonaflates.[15] While effective approaches using benzoic acids or acid chlorides,[16] as well as ammonia surrogates [$NH(TMS)_2$, *t*-$BuNH_2$] have been reported,[17] these latter approaches lack the atom economy associated with using ammonia and carbon monoxide directly.[18]

Considering the utility of DalPhos ligands in challenging ammonia arylations,[5,6] and the recent establishment of aminocarbonylation protocols employing gaseous ammonia and carbon monoxide,[14] we became interested in evaluating the capabilities of DalPhos ligands in palladium-catalyzed aminocarbonylation. Herein, we describe our results on carbonylative amination reactions of (hetero)aryl bromides featuring ammonia and other amine coupling partners, utilizing a Pd/DalPhos catalyst system.

Results and Discussion

Our interest in palladium-catalyzed carbonylative amination reactions was initiated upon observation that [(κ^2-Mor-DalPhos)Pd(Ph)Cl] (**1**) was cleanly transformed into {(κ^2-Mor-DalPhos)Pd[C(O)Ph]Cl} (**2**) upon exposure to an atmosphere of CO [Eq. (1)]. This transformation establishes the validity of carbonyl insertion involving the putative oxidative addition catalytic intermediate **1**, and related DalPhos derivatives.

Complex **2**·0.5(CH_2Cl_2) was successfully isolated as an analytically pure solid in quantitative yield. Solution NMR characterization data agree with the proposed structure of **2** as being a square planar complex containing a benzoyl group.

Notably, the ^{13}C NMR resonance of the carbonyl group appears significantly more downfield (220.8 ppm) of the aromatic region in agreement with a Pd–C(O)Ph interaction and in direct contrast with typical benzoyl groups found in organic frameworks (i.e., benzamide 170 ppm, benzaldehyde 192 ppm, benzoic acid 172 ppm). Single crystal X-ray diffraction data obtained for crystals of **2**·CH_2Cl_2 support the solution NMR analyses; an ORTEP diagram of **2**·CH_2Cl_2 is shown in Figure 2.

Encouraged by the facile formation of **2**, we set out to screen a range of DalPhos ligands in the benchmark aminocarbonylation of bromobenzene forming benzamide (Scheme 1). The choice of conditions was based on those that had previously proven effective for such transformations [i.e., $Pd(OAc)_2$, ligand, 1,4-dioxane, 100 °C, 16 h].[14] Under the test conditions (2 mol% Pd, 6 mol% ligand, 2 bar CO, 2 bar NH_3), we were surprised to see that most catalysts featuring

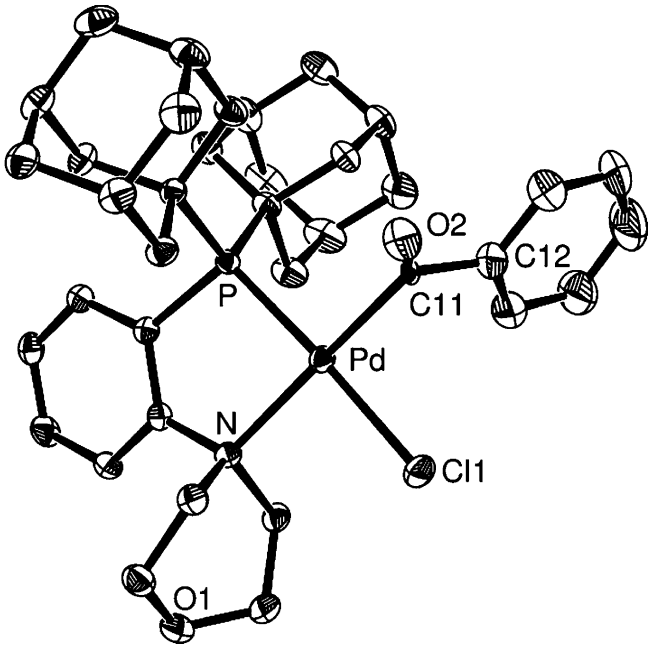
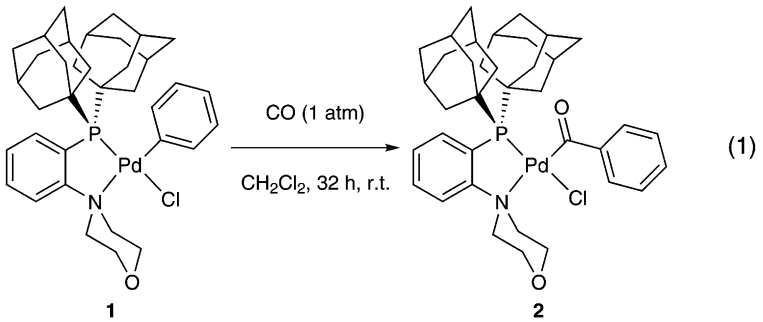
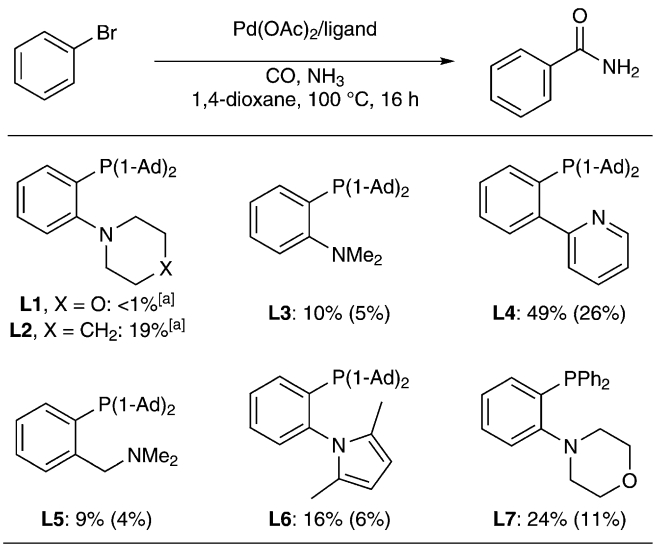


Figure 2. ORTEP diagram of **2**·CH_2Cl_2 shown with 50% displacement ellipsoids. All hydrogen atoms and the dichloromethane solvate have been omitted for clarity. Selected interatomic distances (Å): Pd–P, 2.2630(7); Pd–N, 2.233(2); Pd–Cl, 2.3796(7); P–C_{aryl}, 1.846(3); N–C_{aryl}, 1.464(3); Pd–C(O)C_{Ph}, 2.055(3); PdC(O)–C_{Ph}, 1.553(4).



(1)



[a] No product observed.

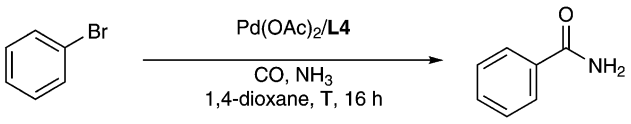
Scheme 1. Ligand screening for the palladium-catalyzed aminocarbonylation of bromobenzene. *General conditions:* bromobenzene (1 mmol), $Pd(OAc)_2$ (0.02 mmol), ligand (0.06 mmol), CO (2 bar), NH_3 (2 bar), 1,4-dioxane (2 mL), 100 °C, 16 h; Ad = adamantyl. Conversion and yield (indicated in parentheses) determined by GC based on bromobenzene using hexadecane as an internal standard.

phenylene P,N ligands achieved little to no conversion of the starting material and/or poor yield of benzamide. Among the ligands surveyed, the pyridine-derived ligand **L4** (Pyr-DalPhos) proved most effective, affording nearly 50% conversion and a promising yield. Although they both perform well in ammonia arylation,[6] Mor-DalPhos (**L1**) and the related derivative **L2** afforded only poor conversions with no product, while Me-DalPhos (**L3**), benzyl (**L5**) and pyrrole (**L6**) variants gave both little conversion and product. Interestingly, the diphenylphosphino-substituted ligand **L7** was more effective than Mor-DalPhos under these test conditions, affording modest conversion and yield. On the basis of the results obtained with **L4**, optimization was continued with this ligand in an effort to achieve full conversion (Table 1).

The use of increased pressures of CO and NH_3 was first examined in an attempt to push the reaction towards full consumption of bromobenzene. However, this change in pressure was not beneficial for the **L4** catalyst system (Table 1, entry 1). At a higher temperature (120 °C), conversion was greatly improved, affording a significant increase in yield (Table 1, entry 2). A modest decrease in the conversion was observed when less ligand was used (Table 1, entry 3), although the yield did not suffer (68 *vs.* 62%). When the Pd loading was doubled (4 mol%), near complete conversion was obtained; however, similar results were obtained when using standard loading (2 mol%) and 1 M concentration of bromobenzene in 1,4-dioxane (Table 1, entries 4 and 5). Continuing at the higher concentration, good conversion but only moderate yield resulted when using a decreased Pd:L ratio (Table 1, entry 6), while an increase to 3 mol% Pd gave access to the best yields (Table 1, entries 7 and 8). Thus, isolated yields (72 *vs.* 79%) determined the optimal Pd:L ratio (1:3).

Once Pd/**L4** catalyst mixtures had been identified as being effective for the standard aminocarbonylation of bromobenzene, we then proceeded to survey the scope of reactivity with CO and NH_3 (Table 2). It is worth mentioning that in order to fully establish

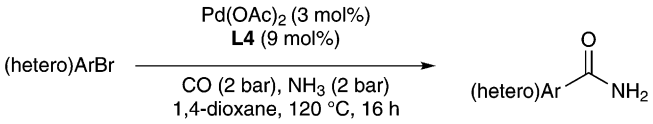
Table 1. Optimization of reaction conditions: variation of pressure, temperature, palladium loading and concentration.[a]

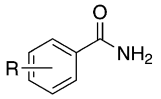
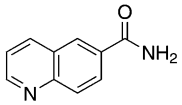
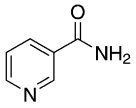
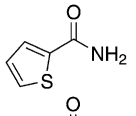
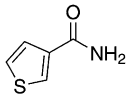


Entry	Variations from the initial conditions	Conv. [%][b]	Yield [%][c]
1	Increase pressure to 10 bar CO, 4 bar NH_3	7	5
2	120 °C instead of 100 °C	85	62
3[c]	Pd:L = 1:2	78	68
4[c]	4 mol% Pd, 12 mol% L	98	87
5[c]	[PhBr] = 1 M	99	83
6[c]	Pd:L = 1:2, 1 M	93	61
7[c,d]	3 mol% Pd, 6 mol% L	97	>99 (72)
8[c,d]	3 mol% Pd, 9 mol% L	97	>99 (79)

[a] *Initial reaction conditions:* bromobenzene (1 mmol), $Pd(OAc)_2$ (0.02 mmol), **L4** (0.06 mmol), CO (2 bar), NH_3 (2 bar), 1,4-dioxane (2 mL), 100 °C, 16 h.
[b] Conversion and yield were determined by GC based on bromobenzene using hexadecane as an internal standard.
[c] 120 °C.
[d] [PhBr] = 1 M (isolated yield in parentheses).

Table 2. Palladium-catalyzed aminocarbonylation of aryl bromides.[a]



Entry	Product	Yield [%][b]
		
1	R = H	79
2	R = 4-Me	89
3	R = 2-Me	70
4	R = 4-OMe	96
5	R = 4-CF_3	76
6	R = 4-CN	40
7[c]	R = 4-NHMe	56
8		84
9		76
10		59
11		76

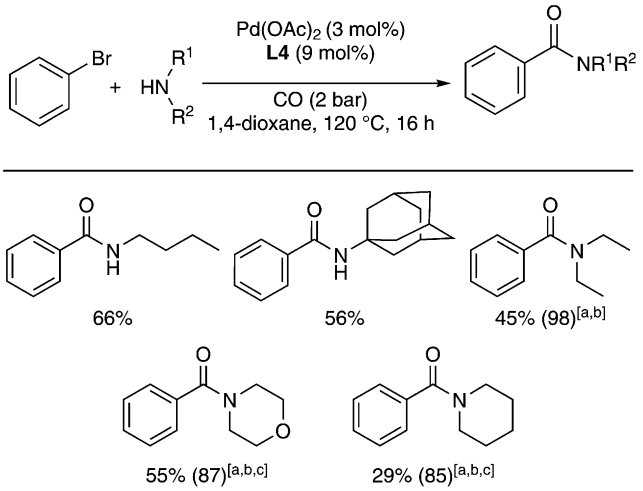
[a] *General reaction conditions:* aryl bromide (1 mmol), $Pd(OAc)_2$ (0.03 mmol), **L4** (0.09 mmol), CO (2 bar), NH_3 (2 bar), 1,4-dioxane (1 mL), 120 °C, 16 h.
[b] Isolated yield.
[c] Heated at 140 °C.

the practical synthetic utility of this process, isolated yields were obtained for all examples. We were pleased to find that the reaction was tolerant of activated and deactivated bromoarenes, *ortho*-substitution as well as some heterocycles. Electron-donating substituents such as Me and OMe (Table 2, entries 2 and 4) gave the best yields (89 and 96%, respectively), while electron-deficient ring systems were also coupled successfully (Table 2, entries 5 and 6). Nitrogen-containing heterocycles 6-quinoline (Table 2, entry 8) and 3-pyridine (Table 2, entry 9) worked well in the reaction, as did 2- and 3-substituted thiophene derivatives (Table 2, entries 10 and 11). Notably, an NH-containing substrate (Table 2, entry 7) was accommodated under the reaction conditions, displaying the chemoselective capabilities of the reaction.

Other sterically congested bromide substrates were not as well-tolerated in aminocarbonylation as was 2-bromotoluene (Table 2, entry 3; 70% yield). 1-Bromonaphthalene resulted in poor yield, 2-bromo-*N*-methylaniline afforded only low conversion and 2-bromomesitylene did not form any desired product under these reaction conditions. Furthermore, aryl chlorides proved to be unreactive substrates using either the optimized conditions or with increased temperature and time (i.e., 140 °C/20 h). When compared to the previously published reports of such aminocarbonylations using either Pd/cata*CX*iumA or Pd/DPPF catalysts,[14] this current system provides similar efficiency for those substrates previously reported (Table 2, entries 1–6, 9 and 10). New examples applied herein to this aminocarbonylation method include heterocyclic aryl amides obtained in high isolated yields (Table 2, entries 8 and 11), a potentially competitive aniline derivative (Table 2, entry 7) and also *N*-alkyl (di)substituted amides (Scheme 2).

Having screened a variety of aryl bromides, we then turned our attention to the use of different amines, in place of ammonia, to form *N*-substituted amides using the Pd/**L4** catalyst system. Electron-rich amines were successfully coupled to afford both secondary and tertiary amides. The secondary amines required *N,N,N,N*-tetramethylethylenediamine (TMEDA) as the base in order to achieve good conversions for these reactions.

For the primary amines, *n*-butyl and 1-adamantyl groups gave moderate yields of the corresponding amides, where the amines acted as both nucleophile



[a] Conversion (in parentheses) determined by GC based on bromobenzene using hexadecane as an internal standard.
[b] TMEDA (0.75 equiv.) was used as base.
[c] Heated at 140 °C, 20 h.

Scheme 2. Palladium-catalyzed aminocarbonylation of bromobenzene with alkylamines. *Reaction conditions:* bromobenzene (1 mmol), amine (2 mmol if solid or 0.4–0.9 mL if liquid), $Pd(OAc)_2$ (0.03 mmol), **L4** (0.09 mmol), CO (2 bar), 1,4-dioxane (0.6–1 mL), 120 °C, 16 h; isolated yields provided.

and base. It should be noted that this lower reactivity of the primary and secondary amines compared to ammonia provides the basis to perform selective monoarylation reactions.

Conclusions

In summary, a palladium catalyst system featuring the ligand **L4** (Pyr-DalPhos) was successfully employed for the aminocarbonylation of (hetero)aryl bromides with ammonia, as well as primary and secondary alkyl amines as reactive partners. It is important to note the dual role of ammonia in these reactions as both a nucleophile and base. In view of the successful results shown here and the promising conversions obtained with other ligands in the initial ligand screen, we will continue to investigate related catalyst systems for this and other carbonylative cross-coupling processes.

Experimental Section

General Information

Unless otherwise stated, all reactions were set up using standard Schlenk techniques under argon. Chemicals were purchased from Fluka, Aldrich, Alfa Aesar and Strem and used as received. 1,4-Dioxane was distilled over CaH_2 and stored under argon, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was distilled/stored under air, and *n*-butylamine and morpholine were distilled/stored under argon. Gas chromatography was performed on a Hewlett Packard HP 6890N chromatograph with an HP5 column. ^1H and ^{13}C NMR characterization data were collected at 300 K on Bruker AV-300 and AV-400 spectrometers operating at 300.1 and 75.5 MHz or 400.1 and 100.6 MHz (respectively) and with chemical shifts reported in parts per million downfield relative to the internal standard solvent peak. Mass spectra were in general recorded on an AMD 402/3 or an HP 5989A mass selective detector. CCDC 877542 contains the supplementary crystallographic data for this paper (for **2**·CH_2Cl_2). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

General Procedure

To six 4-mL glass vials were added $Pd(OAc)_2$ (3 mol%, 6.7 mg), Pyr-DalPhos (**L4**; 9 mol%, 41.0 mg), aryl bromide (1.00 mmol, if solid) and a magnetic stir bar. All vials were placed in a metal alloy plate, sealed with a cap containing a Teflon-rubber faced septum and an inlet needle, and then the vials were evacuated/backfilled with argon three times. 1,4-Dioxane (1.00 mL) and aryl bromide (1.00 mmol, if liquid) were injected into each vial, stirred briefly and the alloy plate with vials was transferred into a 300-mL autoclave (Parr Instruments 4560 series) under an atmosphere of argon. The autoclave was then flushed with NH_3 three times, followed by addition of NH_3 (2 bar) and CO (2 bar) at room temperature. The autoclave was heated at 120 °C for 16 h, at which point the autoclave was cooled and the pressure slowly released at room temperature. All reaction vials were removed from the autoclave, the contents of each were filtered over Celite, the filter was washed with a sufficient amount of EtOAc and CH_2Cl_2 (10–20 mL of each) and the resulting filtrate concentrated to dryness on silica powder. The crude material was then purified by column chromatography (heptane/ethyl acetate) to afford the desired aryl amide as a solid.

Preparation of Benzamide

Bromobenzene was used as the aryl bromide and the crude material was purified with 0–50% ethyl acetate/heptane to afford the desired product as an off-white solid; yield: 95.5 mg (0.788 mmol, 79%). ^1H NMR (DMSO-d_6): $\delta = 7.98$ (br s, 1H), 7.89–7.85 (m, 2H), 7.55–7.41 (m, 3H), 7.37 (br s, 1H); $^{13}C\{^1H\}$ NMR (DMSO-d_6): $\delta = 168.0$ (C=O), 134.3 (C_{quat}), 131.3, 128.3, 127.5, in agreement with that previously reported in the literature.[14a]

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