### C–N Cross-coupling Reactions of Amines with Aryl Halides Using Amide-Based Pincer Nickel(II) Catalyst

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#### Abstract

An approach to C–N cross-coupling reactions of aryl halides with amines in the presence of an amide-based pincer nickel(II) catalyst (**2**) is described. For 3 h reactions at 110 °C with 0.2 mol% catalyst, aryl bromides gave higher turnover numbers (TON) than the corresponding chlorides or iodides. Both primary and secondary amines could be used with the former giving higher TON. However, sterically hindered amines showed lower TON. In elucidating the mechanism of this nickel complex-catalyzed C–N cross coupling reaction it was found that the rate of reaction was unchanged in the presence of radical quenchers and a plausible Ni(I)–Ni(III) pathway is proposed.

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**Graphic Abstract** 



Nickel pincer catalyst proved to be excellent catalyst for the C-N cross-coupling reaction with the high turnover number (TON) for  $1^{\circ}$  and  $2^{\circ}$  amines and different nonactivated aryl halides under optimum conditions.

Keywords Nickel catalyst · Pincer catalyst · Cross-coupling · Aryl halides · Amination

#### 1 Introduction

Using transition metal complexes for amination of aryl halides to form arylamines has become a prevailing methodology [1]. In this context, heterocyclic compounds containing nitrogen atoms are of significant importance due to their abundance in natural products and their roles in biological and bio-inspired reactions [2]. Carbon–nitrogen (C–N) bond-containing aromatic and aliphatic compounds have also found multiple applications as polymers, dyes, and agrochemicals [3, 4]. However, one of the primary avenues for exploration of C–N bond-containing molecules is their value in medicinal chemistry [5]. Some prevalent pharmaceutical compounds containing C–N bonds are shown in Fig. 1. Due to these and many more potential applications, it is highly desirable to develop improved methodologies for facile and economical generation of C–N bonds.

Development of versatile catalyzed processes for arylamine synthesis took chemists over a century to achieve

success. In 1903, Ullmann and Goldberg showed that copper salts enabled reactions of activated aryl halides with anime nucleophiles [6, 7]. However, these reactions used stoichiometric copper and typically harsh reaction conditions. In the 1990s, Buchwald [8, 9] and Hartwig [10, 11] worked independently to successfully develop palladium catalyzed *N*-arylation using phosphine ligands. Since that time the Buchwald–Hartwig amination has brought great advances in C–N cross-coupling reactions [12, 13]. In attempts to reduce catalyst loading and reaction times, design of new catalysts for efficient C–N coupling reactions continues as a vigorous research area [14]. In a recent example, aryl chlorides, bromides and iodides could be efficiently coupled using 1 mol% CuBr with a simple 8-oxyquinoline N-oxide ligand [15].

With a view to performing C–N coupling catalysis on larger scales, recent interest has focused on advancing nickel catalysis [16–18] beyond the original reports [19–21]. In contrast to Pd and Cu catalysts, nickel catalyzed C–N bond-forming reactions often proceed through paramagnetic Ni(I)/





(III) intermediates via redox processes [22–24] although systems have been developed recently to favor Ni(0)/(II) [17, 25]. Therefore, developing new nickel-based catalysts with geometrical constraints enforced by pincer ligands may allow for improved catalysts. We have previously used a diamidopyridine-ligated nickel complex for cross-coupling reactions of multiple C–Cl bonds [26] and activation of  $sp^3$ and  $sp^2$  C–H bonds in alkylation and arylation [27]. In this study, we show that the nickel complex affects the selective cross-coupling amination of unactivated aryl halides with various aliphatic and aromatic amines with low catalyst loading and short reaction times.

#### 2 Experimental Section

#### 2.1 Materials and Instrumentation

All reactions were carried out under an inert (Ar) atmosphere using oven-dried glassware. All solvents and chemicals such as anhydrous dimethylsulfoxide (DMSO), amines, anhydrous aryl halides, KO<sup>t</sup>Bu, and all chemicals for ligand synthesis were obtained from Sigma-Aldrich, USA, Acros Organics, USA, and Alfa Aesar, USA and were used as

received without any further purification unless otherwise stated. All amines were purified by passing through activated alumina prior to use. Gas chromatography-mass spectrometry (GC–MS) spectra were collected using a Shimadzu QP2010 GC–MS, where parameters were maintained at 275 °C interface, 3 injections at 24 and 50 min. Characterization of the ligand and metal catalyst were performed by electrospray ionization mass spectrometry (ESI–MS), Fourier transform infrared spectrometer (FT/IR), and nuclear magnetic resonance (NMR) as reported previously [26, 27].

#### 2.2 Synthesis of *N*,*N*'-bis(2,6-di-isopropylphenyl)-2, 6-pyridinedicarboxamide (1)

The ligand was synthesized according to a previous synthetic route with slight modifications [26, 27]. In a 100 mL round bottom flask with a stir bar, 2,6-pyridinedicarboxylic acid (5 g, 0.03 mol) and 15 mL 1,2-dimethoxyethane were added followed by addition of thionyl chloride (5 mL, 0.07 mol). The reaction mixture was refluxed for 3 h. After completion, the excess solvent and thionyl chloride were removed under reduced pressure to obtain a white product, followed by crystallization from concentrated hexane to obtain 2,6-pyridinedicarbonyl dichloride. The acid chloride was then treated with 2,6-diisopropylaniline and triethylamine of anhydrous





tetrahydrofuran (THF) cooled to 0 °C and stirred for 3 h. On warming the reaction was further stirred at room temperature for another 9 h. The reaction mixture was then filtered and THF was removed under reduced pressure to obtain the crude ligand (1) (Fig. 2).

#### 2.3 Synthesis of Pincer Nickel(II) Complex (2)

Our previous work has described the synthesis of pincer nickel(II) complex (**2**) (Fig. 2) [26, 27]. In short, a 100 mL Schlenk flask fitted with a magnetic stir bar was charged with **1**. The flask was sealed with a septum and stirred for 5 min while purging with N<sub>2</sub>. Dry THF was added using a gas tight syringe, and *n*-butyllithium was added to the ice bath-cooled (0 °C) reaction mixture to deprotonate the ligand, followed by addition of anhydrous nickel(II) chloride to yield the deep red nickel(II) complex **2**. The catalyst was characterized using <sup>1</sup>H-NMR, ESI–MS, FT/IR, and ultraviolet–visible (UV–Vis) spectroscopy as described in the previous reports [26, 27].

#### 2.4 General Amination Procedure of Aryl Halides Using Different Amines

A representative amination method using chlorobenzene, pentylamine, and KO<sup>t</sup>Bu in DMSO is described here. All other amination reactions including different aryl halides, primary  $(1^{\circ})$  and secondary  $(2^{\circ})$  amines, solvents and bases were performed using a similar method. A 4 mL reaction vial containing a magnetic stir bar was charged with 1.4 mL of anhydrous DMSO. The reaction vial, after being sealed with a septum and parafilm, was purged with Ar for 10 min. Chlorobenzene [0.4 mL, 3.9 mmol, 2.25 equivalent (eq.)], pentylamine (0.21 mL, 1.8 mmol, 1.0 eq.), anhydrous powdered KO<sup>t</sup>Bu (70 mg, 0.63 mmol, 0.3 eq.), and 2 (2 mg, 0.2 mol%) were added sequentially. The reaction mixture was stirred for 5 min while continually purging with Ar. The vial was then sealed with a Teflon screw cap. The reaction mixture was stirred for 3 h at 110 °C in a preheated oil bath, then allowed to cool to room temperature and filtered by passing through Celite to remove the base and the catalyst. 30 µL of the solution was then dissolved in 1 mL absolute

ethanol, and 10  $\mu$ L of decane was added as an internal standard. Turn over number (TON) was determined using GC–MS.

#### **3** Results and Discussion

#### 3.1 Optimization of Reaction Solvent and Base

To best facilitate the amination, reactions conditions were optimized by changing solvents and bases (Table 1). Many solvents gave low TON (Entries 1–3) most likely due to the low solubility of the catalyst and/or base. The low boiling point of the solvents may also have played a role in the product conversion. Solvents with high polarity and boiling point, such as dimethylacetamide (DMA), produced moderate results (TON 69) (Entry 6). whereas none of the desired product was obtained using dimethylformamide (DMF) (Entry 1), presumably due to thermal decomposition. DMSO proved to be the most effective solvent, yielding a TON of 243 (Entry 7). Therefore, DMSO was used to further optimize the C–N coupling reaction conditions.

One of the requirements for many cross-coupling reactions, and particularly for aminations, is the use of a base [28, 29]. None of cesium carbonate ( $Cs_2CO_3$ ), potassium carbonate ( $K_2CO_3$ ), 4-dimethylaminopyridine (DMAP) or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) yielded any product (Entries 8–11), while relatively stronger bases such as KOH gave high yields (Entry 12). Results showed that KO<sup>t</sup>Bu was most effective (Entry 7) and was thus used for all subsequent reactions.

#### 3.2 Optimizing Reaction Temperature and Aryl Halide Comparison

In reactions run at temperatures ranging from 70 to 120  $^{\circ}$ C, increasing the temperature resulted in higher yields and TONs (Fig. 3). The TON of the reaction increased slightly from 70 to 100  $^{\circ}$ C with values of 169, 174, 181 and 195, respectively. Similar trends were observed at 110 and

#### Table 1 Amination of chlorobenzene using varies of solvents and bases



Entry	Solvent	Base	TON
1	DMF	KO <sup>t</sup> Bu	NR
2	MTBE	KO <sup>t</sup> Bu	$3\pm 1$
3	Dioxane	KO'Bu	$25 \pm 2$
4	THF	KO <sup>t</sup> Bu	36±7
5	Toluene	KO <sup>t</sup> Bu	$68 \pm 14$
6	DMA	KO <sup>t</sup> Bu	$69 \pm 5$
7	DMSO	KO <sup>t</sup> Bu	$243 \pm 29$
8	DMSO	$Cs_2CO_3$	NR
9	DMSO	K <sub>2</sub> CO <sub>3</sub>	NR
10	DMSO	DMAP	NR
11	DMSO	DBU	NR
12	DMSO	КОН	20

Yields represents an average of two runs. TON was measured in GC by using decane as an internal standard *MTBE* methyl tert-butyl ether

120 °C, with values of 212 and 219, respectively, with maximum TON observed at 120 °C.

After identifying the optimal amination conditions using **2**, we investigated the amination of chloro-, bromoand iodobenzene with morpholine in DMSO with KO<sup>t</sup>Bu. In order to focus on low catalyst loadings and short



Fig. 3 Effect of temperature (70 °C to 120 °C) on the amination reaction using 2 and KO<sup>t</sup>Bu in DMSO. Yields represent an average of two runs after 3 h

reaction times, all reactions were heated at 110 °C for 3 h under argon (Table 2). Bromobenzene yielded the desired product with highest TON of 484 (Entry 3) compared to chlorobenzene (361, Entry 2) and iodobenzene (317, Entry 1). Note that 484 turnovers amount to 97% conversion of the bromobenzene limiting reagent with a selectivity of 95% due to a small amount of biphenyl formation. None-theless, aryl chlorides were chosen as the major focus of this work as they are less expensive and more widely available than their bromo and iodo analogs.

 Table 2
 Evaluation of various electrophiles

×+	HN O 6a	2 (0.2 mol %) DMSO KO <sup>1</sup> Bu 110 °C, 3 h, Ar	5ab = Cl 5ac = Br 5ad = l
Entry		Х	TON
1		Ι	316.9±3.8
2		Cl	$361.3 \pm 0.07$
3		Br	$484.1 \pm 1.1$

Yields represent an average of two runs. TON was measured in GC by using decane as an internal standard

Scheme 1 Pincer nickel catalyzed amination of chlorobenzene with 1° amines. Yields represents an average of two runs. TON was measured in GC by using decane as an internal standard. The GC–MS spectra of the products are given in the Supporting Information



## 3.3 Amination Scope of Chlorobenzene with Aliphatic/Aromatic Amines

A series of 1° amines were tested for cross-coupling reactions using chlorobenzene under the same conditions as previously stated (Scheme 1). Good TONs were obtained for most 1° amines tested. Among the series of linear aliphatic amines (**7a–h**), there was no clear-cut trend for the smaller compounds (**7a–c**). However, as the amine chain lenth increased, a rise in TON (from 173 to 365) was observed (**7d–h**). All linear aliphatic amines were found to react with chlorobenzene to produce the desired products (143–365) TON). Octyl- and decyl-amines yielded high TONs of 331 and 365, respectively (**7f**, **h**). The steric bulk of the amines was found to negatively influence the outcome of the desired products, as *t*-butylamine produced low TON of 55 (**7i**). Similarly, other sterically bulky amines also showed dimished activities (**7j**, **k**). Two of the amine products (**7l**, **m**) were isolated from the reaction mixture for the purpose of <sup>1</sup>H and <sup>13</sup>C NMR analysis and these characterizations are included in supplementary information (Fig. S1).

Reactions of chlorobenzene with alkyl and aromatic  $2^{\circ}$  amines with varying degrees of steric bulk and nucleophilicity were also investigated (Scheme 2). Alkyl amines Scheme 2 Pincer nickel catalyzed amination of chlorobenzene with 2° amines. Yields represent an average of two runs. TON was measured in GC by using decane as an internal standard. The GC–MS spectra of the products are provided in the Supporting Information



with relatively less steric hindrance furnished the desired products with TONs in the range of 156–215 (**8a–d**, **f**), while more hindered amines showed lower activity, as in the case of diisopropylamine (**8e**).

#### 3.4 Amination Scope of Substituted Aryl Halides with Aliphatic/Aromatic Amines

Establishing optimal conditions for nickel-catalyzed amination of substituted aryl bromides has proved challenging, generally requiring complicated catalyst systems and often giving low yields [28, 29]. Indeed, using complex **2** with varying ratios of KO<sup>t</sup>Bu gave insignificant conversions. However, using 1 eq. of LiHMDS as a base, the desired coupling products were obtained from aniline and several substituted aryl bromides in poor to fair yields (3–30% **9a–c**, Scheme 3).

Applying a similar protocol (but using 2 eq. of LiHMDS) to the amination of several substituted aryl chlorides catalyzed by **2** gave fair to moderate yields of the coupled products (7, 21% **10a**, **b**).

#### 3.5 Kinetic Study of Aryl Chloride Amination Using Nickel Pincer Catalyst 2

Initial rates of chlorobenzene amination using aniline and KOtBu in DMSO at 110 °C were measured with respect to catalyst, aryl chloride, amine and base. Plots of concentrations of diphenylamine versus time at various concentrations of amine, catalyst, base, and aryl chloride along with their reaction schemes are shown in the Supporting Information (Figs. S2–S5 and Tables S1–S4). The first observation of note was that no reaction was observed for the first 20-30 min depending on the ratio of base to catalyst precursor, suggesting that the active catalyst is slow to form, even at 110 °C. Plots of the initial amination rate versus time at various concentrations of amine, catalyst, base, and aryl chloride are shown in the supporting information (Fig. S6). The results are consistent with a first order rate dependence on the concentrations of catalyst and aryl chloride and zero order for the bae and amine. Similar observations have been reported previously with other Ni catalysts [17]. At high concentrations of aryl chloride using 2, however, the rate is suppressed, likely due to catalyst deactivation.

Scheme 3 Pincer nickel-catalyzed amination of substituted aryl bromides and chlorides with 1° amine. Yields represents an average of two runs. TON was measured in GC by using decane as an internal standard. **10a** and **10b**, LiHMDS (0.66 mL, 2 equiv. to substrate). The GC–MS spectra of the products are given in the Supporting Information



(7.3% GC yield)

# (21% GC yield)

#### 3.6 Proposed Reaction Pathway of Pincer Nickel Complex-Catalyzed Amination of Aryl Halides with Amines

the long induction period whereas rate-limiting oxidative addition of the aryl halide is consistent with the first order rate dependence on both catalyst and aryl halide.

As mentioned in the literature for different Ni- and Pdcomplexes, reactions usually occur via oxidative addition of aryl halides followed by reductive elimination from a metal-amido intermediate [16]. While catalysts have been designed to accomplish these steps exclusively through Ni(0–II) intermediates [17], many Ni(II) catalysts are proposed instead to involve paramagnetic Ni(I–III) intermediates in which the base serves as the initial reductant [30, 31]. We propose a similar scheme using anionic catalyst **2**.

In our reaction system, loss of chloride from 2 is likely required before the complex can be reduced to the Ni(I) anion, where either amines or KO<sup>t</sup>Bu can reduce the metal by singlet electron transfer process [30, 31], likely present as the amine complex **A** (Fig. 4). Following aryl halide oxidative addition, halide elimination would again be required to recoordinate the amine in intermediate **B**. Deprotonation of the coordinated amine will also be favored from the neutral Ni(III) intermediate **B** and subsequent reductive elimination of the product and recoordination of the amine regenerates the active Ni(I) catalyst **A**. The slow reduction of **2** to **A** presumably gives rise to

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The reaction was also performed in the presence of a radical quencher, namely 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) assess its effect on the rate. The rate of reaction was found to be unaffected in the presence of TEMPO. Therefore, it can be inferred that organic radicals are not involved in the catalyst cycle.

### **4** Conclusion

Nickel pincer-based catalyst **2** was used for the first time in C–N cross coupling amination of aryl halides with amines. The catalyst is stable and relatively easy to handle under atmospheric conditions and after an induction period, low catalyst loading (0.2 mol%) and short reaction times afford significant product yields for both 1° and 2° amines with a variety of substituted aryl halides. Various amines and aryl halides were examined, and the catalyst demonstrated moderate to high TONs (up to 400). Kinetic studies revealed that the reaction proceeds with first-order kinetics with respect to catalyst and aryl halide concentrations while amine and base concentrations did not affect the overall reaction rate.



Fig. 4 Proposed mechanism for the nickel catalyzed amination of aryl halides with amines using catalyst  ${\bf 2}$ 

The proposed reaction pathway involves the oxidative addition of aryl halides to the anionic Ni(I) catalyst **A** and loss of halide to give a neutral Ni(III) amine intermediate **B**. Deprotonation of the coordinated amine in **B** is followed by reductive elimination of the N-arylamine product. The reaction does not proceed through organic radical intermediates as revealed by radical quencher studies. In future studies, generation, isolation and reactivity of the reduced version of **2** will likely be informative.

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#### References

- 1. Ricci A (2000) Modern amination methods. Wiley, Weinheim
- Garella D, Borretto E, Di Stilo A et al (2013) (2013) Microwaveassisted synthesis of N-heterocycles in medicinal chemistry. Med-ChemComm. 4(10):1323–1343

- Xu S, Kim EH, Wei A et al (2014) Pd-and Ni-catalyzed crosscoupling reactions in the synthesis of organic electronic materials. Sci Technol Adv Mater 15(4):044201
- Hili R, Yudin AK (2006) Making carbon-nitrogen bonds in biological and chemical synthesis. Nat Chem Biol 2(6):284
- Taylor RD, MacCoss M, Lawson ADG (2014) Rings in drugs: miniperspective. J Med Chem 57(14):5845–5859
- Ullmann F (1903) Ueber eine neue bildungsweise von diphenylaminderivaten. Ber Dtsch Chem Ges 36(2):2382–2384
- Goldberg I (1906) Ueber phenylirungen bei gegenwart von kupfer als katalysator. Ber Dtsch Chem Ges 39(2):1691–1692
- Wolfe JP, Wagaw S, Marcoux J-F et al (1998) Rational development of practical catalysts for aromatic carbon–nitrogen bond formation. Acc Chem Res 31(12):805–818
- Yang BH, Buchwald SL (1999) Palladium-catalyzed amination of aryl halides and sulfonates. J Organomet Chem 576(1-2):125-146
- Hartwig JF (2002) In: Negishi EI (ed.) Handbook of organopalladium chemistry for organic synthesis. Wiley, Hoboken
- Hartwig JF (1998) Transition metal catalyzed synthesis of arylamines and aryl ethers from aryl halides and triflates: scope and mechanism. Angew Chem Int Ed 37(15):2046–2067
- Heravi MM, Kheilkordi Z, Zadsirjan V et al (2018) Buchwald– Hartwig reaction: an overview. J Organomet Chem 861:17–104
- Forero-Cortés PA, Haydl AM (2019) The 25th anniversary of the Buchwald–Hartwig amination: development, applications, and outlook. Org Proc Res Dev 23(8):1478–1483
- Balcells D, Nova A (2018) Designing Pd and Ni catalysts for cross-coupling reactions by minimizing off-cycle species. ACS Catal 8(4):3499–3515
- Yang K, Qiu Y, Li Z et al (2011) Ligands for copper-catalyzed C-N bond forming reactions with 1 Mol% CuBr as catalyst. J Org Chem 76(9):3151–3159
- Desmarets C, Schneider R, Fort Y (2002) Nickel (0)/dihydroimidazol-2-ylidene complex catalyzed coupling of aryl chlorides and amines. J Org Chem 67(9):3029–3036
- Ge S, Green RA, Hartwig JF (2014) Controlling first-row catalysts: Amination of aryl and heteroaryl chlorides and bromides with primary aliphatic amines catalyzed by a BINAPligated single-component Ni (0) complex. J Am Chem Soc 136(4):1617–1627
- Park NH, Teverovskiy G, Buchwald SL (2014) Development of an air-stable nickel precatalyst for the amination of aryl chlorides, sulfamates, mesylates, and triflates. Org Lett 16(1):220–223
- Hidai M, Kashiwagi T, Ikeuchi T et al (1971) Oxidative additions to nickel (0): preparation and properties of a new series of arylnickel(II) complexes. J Organomet Chem 30(2):279–282
- Wolfe JP, Buchwald SL (1997) Nickel-catalyzed amination of aryl chlorides. J Am Chem Soc 119(26):6054–6058
- Brenner E, Fort Y (1998) New efficient nickel(0) catalysed amination of aryl chlorides. Tetrahedron Lett 39(30):5359–5362
- 22. Tasker SZ, Standley EA, Jamison TF (2014) Recent advances in homogeneous nickel catalysis. Nature 509(7500):299
- Li C, Kawamata Y, Nakamura H et al (2017) Electrochemically enabled, nickel-catalyzed amination. Angew Chem Int Ed 56(42):13088–13093
- Kawamata Y, Vantourout JC, Hickey DP et al (2019) Electrochemically driven, Ni-catalyzed aryl amination: scope, mechanism, and applications. J Am Chem Soc 141(15):6392–6402
- Rull SG, Funes-Ardoiz I, Maya C et al (2018) Elucidating the mechanism of aryl aminations mediated by NHC-supported nickel complexes: evidence for a nonradical Ni(0)/Ni(II) pathway. ACS Catal 8(5):3733–3742
- 26. Gartia Y, Biswas A, Stadler M et al (2012) Cross coupling reactions of multiple CCl bonds of polychlorinated solvents with

Grignard reagent using a pincer nickel complex. J Mol Catal A 363–364:322–327

- 27. Gartia Y, Ramidi P, Jones DE et al (2014) Nickel complex catalyzed efficient activation of sp<sup>3</sup> and sp<sup>2</sup> C–H bonds for alkylation and arylation of oxygen containing heterocyclic molecules. Catal Lett 144(3):507–515
- Lavoie CM, MacQueen PM, Rotta-Loria NL et al (2016) Challenging nickel-catalysed amine arylations enabled by tailored ancillary ligand design. Nat Commun 7:1–11073
- 29. Tassone JP, England EV, MacQueen PM et al (2019) PhPAd-Dal-Phos: ligand-enabled, nickel-catalyzed cross-coupling of (hetero) aryl electrophiles with bulky primary alkylamines. Angew Chem Int Ed 58(8):2485–2489
- Zheng B, Tang F, Luo J et al (2014) Organometallic nickel(III) complexes relevant to cross-coupling and carbon-heteroatom bond formation reactions. J Am Chem Soc 136(17):6499–6504
- Barham JP, Coulthard G, Emery KJ et al (2016) KO'Bu: a privileged reagent for electron transfer reactions? J Am Chem Soc 138(23):7402–7410

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