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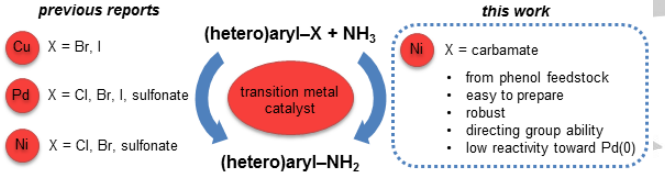
Nickel-catalyzed amination of aryl carbamates with ammonia

Johannes Schranck,*[a] Patrick Furer,[a] Veronika Hartmann[a] and Anis Tlili*[b]

Abstract: Aryl carbamates were employed in the nickel-catalyzed monoarylation of ammonia. The applied, well-defined, single-component nickel(II) precatalyst contains a Josiphos ligand, is air-stable and operates without any ancillary reductant. This catalyst system also promotes the amination of aryl carbamates with ammonium sulfate as well as hydrochloride salts of primary alkyl amines. Their easy preparation, robustness, and directing group ability makes aryl carbamates particularly attractive synthetic intermediates.

The arylation of amines constitutes a persistent and fundamental challenge in modern synthetic chemistry. Various reaction sequences make use of the resulting aniline derivatives as relevant intermediates for the manufacture of industrial products such as agrochemicals, dyes, and pharmaceuticals.[1] Initiated by the groundbreaking work of Buchwald and Hartwig, the transition-metal-catalyzed amination of aryl halides has emerged as one of the most widely applied tools for the construction of aryl amines.[2]



Scheme 1. Monoarylation of ammonia with (hetero)aryl–X electrophiles.

The selective monoarylation of ammonia represents a particular challenge since the resulting monoarylated products are prone to act as contending nucleophiles to ammonia and in turn lead to the formation of polyarylated products. However, continuous efforts taken by the groups of Hartwig[3] Buchwald[4] Beller[5] and Stradiotto[6] have led to the development of several protocols for the selective palladium-catalyzed cross-coupling of aryl (pseudo)halides with ammonia (Scheme 1). Seeking for the employment of cheaper and more abundant metal, first-row transition metals became of interest. Consequently, initiated by the groups of Taillefer[7a,b] and Chang,[7c] a number of copper-catalyzed aminations have been reported to date, albeit most of these protocols are limited to the application of sterically unhindered aryl iodides or activated bromides.[7] More recently, the groups of Stradiotto[8] and Hartwig[9] simultaneously developed the first examples of nickel-catalyzed ammonia monoarylations. This breakthrough was enabled by the employment of relatively electron-rich JosiPhos-type ligands promoting the coupling of aryl chlorides, bromides, and tosylates with ammonia and ammonium salts at elevated temperatures (100-110°C). A subsequent thorough ligand design by the group of Stradiotto led to the development of PAd-DalPhos, a sterically demanding, relatively electron-poor bisphosphine which allows for a room temperature reaction and an extension of the substrate scope towards various sulfonates.[10]

In order to leverage the orthogonality of nickel-catalyzed amination to well-established palladium-catalyzed cross-coupling, we envisioned the application of phenol derivatives which exhibit a low reactivity toward Pd(0) and are derived from an entirely different pool of materials than aryl halides. In this regard, N,N-dialkyl aryl O-carbamates constitute a particularly attractive class of electrophiles. These substrates can be easily prepared from readily available phenol derivatives, are stable under a variety of reaction conditions and allow for a halogen- and sulfonate-free C-N coupling. Furthermore, the carbamate moiety can be utilized in a preceding *ortho* or *para* functionalization via directed ortho-metallation[11], electrophilic aromatic substitution[12], as well as Pd-, Ir- or Rh-catalyzed CH-functionalization.[13] Although the Ni-catalyzed C-O bond cleavage of aryl carbamates has been reported for a number of C-C bond forming protocols,[14] their employment in Buchwald-Hartwig-type C-N coupling has only scarcely been developed.[15] Moreover, the corresponding protocols are limited to the coupling of secondary amines and primary aryl amines. Consequently, a catalyst system capable of activating the C–O bonds of functional groups other than sulfonates and promoting the coupling of ammonia is highly desired.

While investigating the Ni-catalyzed coupling of aryl pivalates with amines, the group of Chatani demonstrated the amination of a N,N-diethylcarbamylphenol with morpholine in a single example in 2010.[15a] Shortly after, the group of Garg reported a Ni-based catalyst system that enables the amination of a broad scope of aryl carbamates albeit the methodology is limited to the employment of secondary amines and primary arylamines.[15] However, the coupling of ammonia poses a more ambitious reaction because of the ability of ammonia to bind to transition metals and deactivate the catalyst via subsequent ligand dissociation.[16] Facing this challenge, we investigated the coupling of 2-naphthyl N,N-diethylcarbamate **1** with ammonia.

Initially, *in situ* catalyst formation from $Ni(cod)_2$ and an ancillary ligand was applied to study the model system. A comprehensive ligand screening was performed by employing a high throughput experimentation platform (Scheme 2).[17] Whereas consistently high conversions occurred in the vast majority of entries the desired 2-naphthylamine **2** was formed

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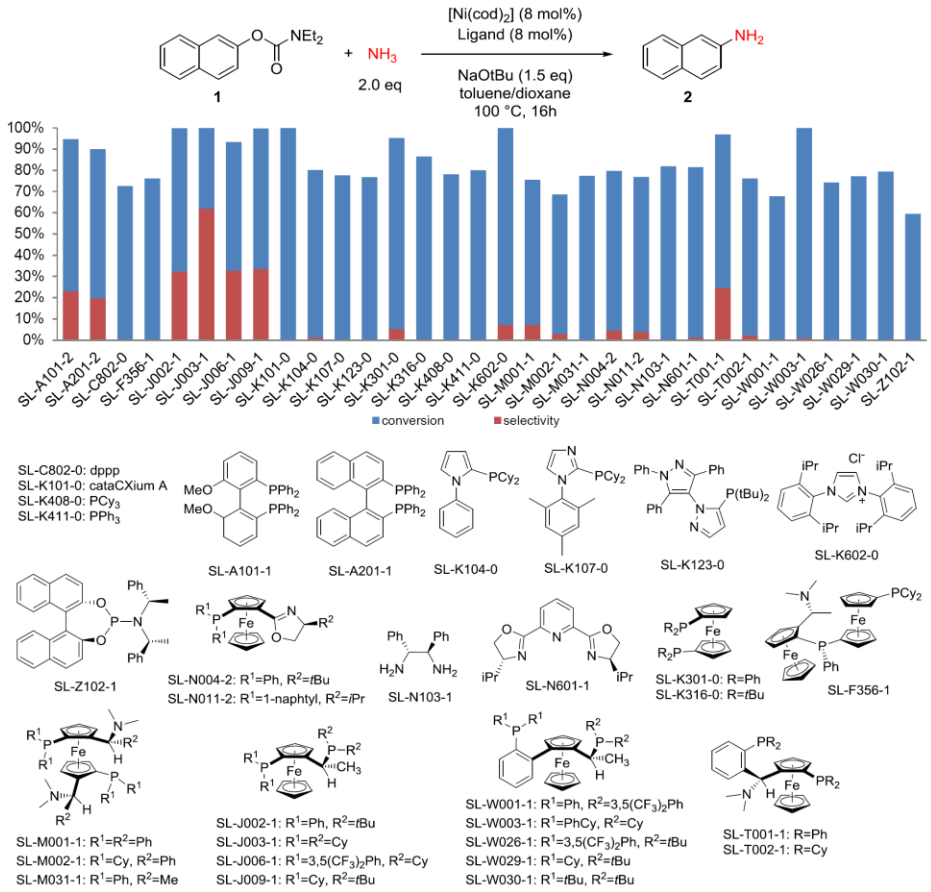


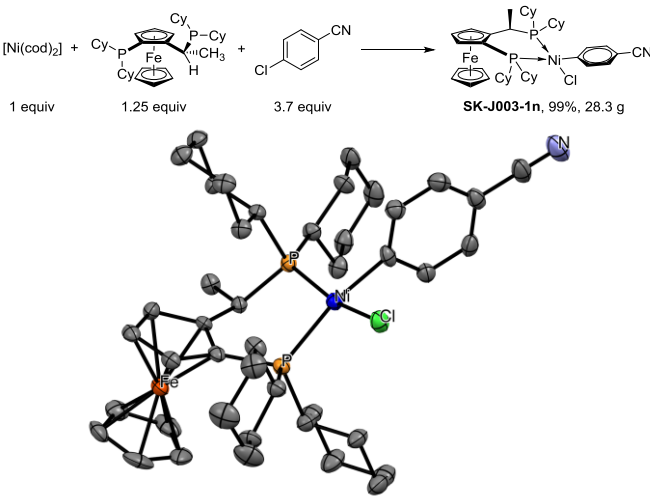
Scheme 2. Coupling of aryl carbamate **1** with ammonia: Ligand screening.

with less than 10% chemoselectivity. The differences in conversion and selectivity can be accounted to the undesired O-C(carbonyl) bond cleavage which led to the formation of significant amounts of 2-naphthol as byproduct. These results reflect the high demand made on the catalyst to be highly active in the challenging oxidative addition of aryl carbamate and likewise selective to avoid both, undesired naphthol formation in addition to further arylation of the formed 2-naphthylamine. Since the monoarylation of ammonia with aryl carbamate has not yet been described and similar nickel-catalyzed transformations have only marginally been investigated[15] a broad variety of ligands was evaluated which have proven useful in Pd- or Ni-catalyzed couplings. Notably, the employment of an N-heterocyclic carbene (SL-K602-0) that promotes the related Ni-catalyzed coupling of aryl carbamates with secondary amines[15] enabled only a low chemoselectivity of 7% in the corresponding ammonia mono arylation. Similarly, the tested monophoshine ligands lacked formation of the desired 2-naphthylamine in significant amounts. Monoarylation of ammonia with >10% chemoselectivity was exclusively observed when bisphosphine ligands with an aromatic backbone where employed. Among this group, ligands of the JosiPhos family proved particularly effective and promoted the formation of 2-naphthylamine with over 30% chemoselectivity. Taking advantage of the high modularity of JosiPhos, SL-J003-1 bearing cyclohexyl groups on both phosphorous moieties was identified most suitable enabling complete conversion and 62% chemoselectivity.

In consideration of the air- and moisture-sensitive nature of $Ni(cod)_2$ we set out to develop a more applicable single component nickel precatalyst. As shown by the group of Hartwig, benzonitrile stabilizes the Ni^0 intermediate and the resulting (PP)Ni(η^2-NC-Ph) complex serves as a resting state in the catalytic cycle.[19] Thus we employed 4-chloro benzonitrile rather than commonly used 2-chloro toluene in the preparation of an air-stable Ni^{II} precatalyst.[20] We envisioned such a precatalyst to eliminate 4-amino benzonitrile under the reaction conditions which then gives rise to a similarly active catalyst. Starting from $Ni(cod)_2$, SL-J003-1 and 4-chloro benzonitrile the formation of the desired complex occurred within 2 h at room temperature and **SK-J003-1n** could be isolated in 99% yield (28.3 g, Scheme 3).[18]

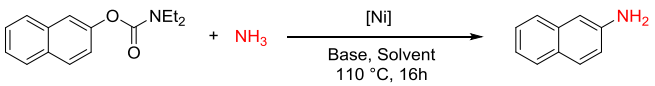
Single-crystal X-ray diffraction analysis of **SK-J003-1n** shows a distorted square-planar coordination geometry at the nickel centre.[23] Ligand SL-J003-1 coordinates in a bidenate fashion and the adjacent chloride arranges in *trans*-position to the phosphorous moiety of the ligand's alkyl sidechain.

When tested in the ammonia monoarylation with 2-naphthyl carbamate **1**, **SK-J003-1n** indeed enabled an improved yield of 76% which could be further increased to 87% by extending the reaction time (Table 1, entry 1). Among the examined bases, NaO*t*Bu was found to be the optimal choice. Reactions in the presence of other alcoholate bases (LiO*t*Bu, KO*t*Bu) gave lower yields, whereas with inorganic bases (Cs_2CO_3, K_2CO_3, K_3PO_4) no product formation occurred (entries 1-6). In the absence of any toluene, with dioxane from the ammonia solution as sole solvent, a diminished yield of 38% was observed (entry 7).



Scheme 3. Synthesis and single-crystal X-ray structure of the air-stable Nickel Josiphos precatalyst complex **SK-J003-1n** (CCDC 1533232). Ellipsoids shown at 50% probability, hydrogen atoms omitted for clarity.

Table 1. Coupling of 2-naphthyl carbamate **1** with ammonia: Variation of reaction conditions.[a]

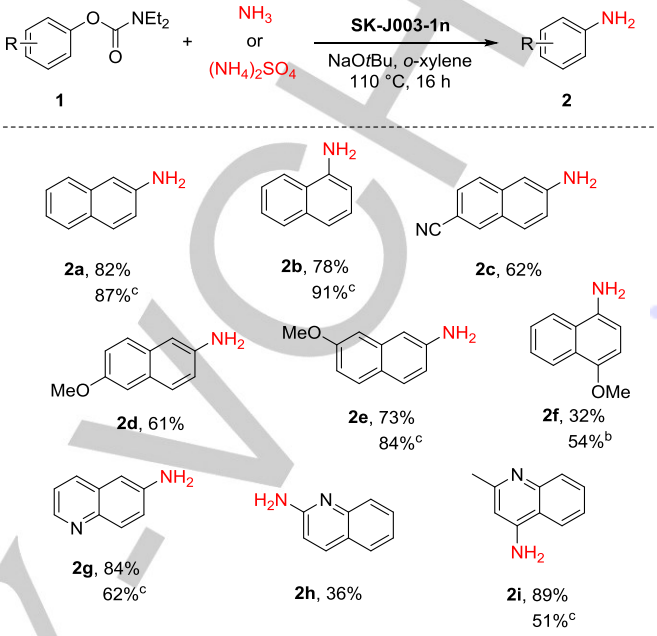


Entry	[Ni]	Solvent	Base	Yield [%][b]
1	SK-J003-1n	toluene	NaOtBu	76, 87[c]
2	SK-J003-1n	toluene	LiOtBu	41
3	SK-J003-1n	toluene	KOtBu	45
4	SK-J003-1n	toluene	K_2CO_3	0
5	SK-J003-1n	toluene	Cs_2CO_3	0
6	SK-J003-1n	toluene	K_3PO_4	0
7	SK-J003-1n	-	NaOtBu	38
8	SK-J003-1n	toluene	NaOtBu	42[d]
9	SK-J003-1n	DMSO	NaOtBu	<5
10	SK-J003-1n	DMF	NaOtBu	41
11	SK-J003-1n	H_2O	NaOtBu	0
12	SK-J003-1n	diglyme	NaOtBu	52
13	SK-J003-1n	o-xylene	NaOtBu	86, 82[e]
14	SK-J003-1n	o-xylene	-	0
15	-	o-xylene	NaOtBu	0

[a] Reactions were performed with 0.5 mmol of 2-naphthylcarbamate, [Ni] (8 mol%, NH_3 (2.0 equiv, 0.5 M in dioxane), solvent (2 ml), base (1.5 equiv), t = 16 h, T = 110 °C unless otherwise noted. [b] Calibrated GC yield using 1,3-dimethoxybenzene as internal standard, average of two runs. [c] Reaction performed at 110 °C for 72 hours. [d] Reaction performed with 8 mol% of PhCN as additive. [e] Isolated yield. DMSO = dimethyl sulfoxide, DMF = *N*,*N*-dimethylformamide.

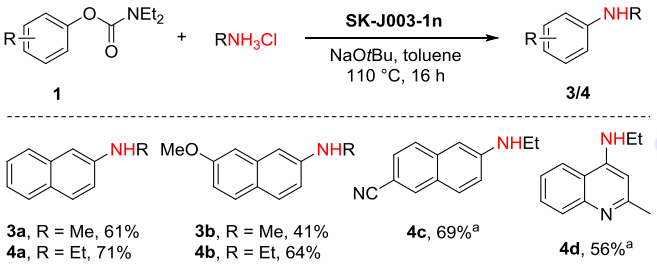
Attempts to improve the catalyst performance by adding benzonitrile did not prove successful (entry 8). Changing the solvent revealed nonpolar aromatic solvents to be beneficial with *o*-xylene being particularly suitable (entries 9-13). Control experiments showed that no desired product is formed in the absence of either base or catalyst (entries 14-15).

With the optimized conditions in hand, we turned our focus to the scope and limitations of the reaction (Scheme 4). 1- and 2-naphthyl amine (**2a**, **2b**) were obtained in high yields. Naphthyl N-diethylcarbamates containing electron-withdrawing groups (**2c**), and electron-donating groups (**2d**, **2e**) on the naphthyl ring, underwent the transformation in moderate to good yields. Methoxy substitution in *para*-position to the carbamate moiety (**2f**) was tolerated with moderate yield. Our catalytic system was found to tolerate methoxy substituents in contrast to the Ni/NHC-catalyst reported by Chatani which promotes the amination of N-heteroaryl methyl ethers via cleavage of carbon–oxygen bonds.[21] Heterocyclic quinolines were coupled with moderate (**2h**) to high yields (**2g**, **2i**). In general, excellent selectivities were observed since only less than 10% of the reduced starting materials or traces of the corresponding phenols were detected by GC/MS. In cases of moderate yields, incomplete conversions of the starting material were observed. For example, besides the isolation of **2f** in 54% yield, 35% of the carbamate **1f** was recovered from the corresponding reaction mixture after 36 h. Unfortunately, the employment of non-fused aryl carbamates proved much more challenging as low conversions occurred and the desired anilines were not formed in significant amounts.



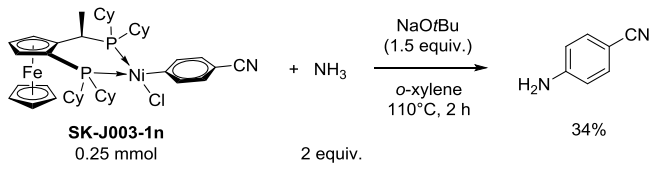
Scheme 4. Nickel-catalyzed amination of aryl carbamates with ammonia or ammonium sulfate. Reactions were performed with 0.5 mmol of (hetero)aryl carbamate, SK-J003-1n (8 mol%), NH_3 (2 equiv., 0.5 M in dioxane), *o*-xylene (2 ml), NaO*t*Bu (1.5 equiv), t = 16 h, T = 110 °C; isolated yields; [b] t = 36 h; [c] $(NH_4)_2SO_4$ (2 equiv), NaO*t*Bu (4.0 equiv) were used.

Pursuing a more practical source of ammonia than diluted solutions, we evaluated cheap and abundant ammonium salts in the Nickel-catalyzed amination of aryl carbamates.[22] As a result we found our catalytic system to promote the employment of ammonium sulfate in conjunction with an increased loading of NaO*t*Bu (4 equiv.). These conditions enable the formation of the desired primary aryl amines in comparable yields to those obtained with ammonia solution (Scheme 4).



Scheme 5. Nickel-catalyzed amination of aryl carbamates with alkyl ammonium chlorides. Reactions were performed with 0.5 mmol of (hetero)aryl carbamate, SK-J003-1n (8 mol%), RNH_3Cl (3 equiv.), toluene (3 ml), NaO*t*Bu (4 equiv), t = 16 h, T = 110 °C; isolated yields; [a] t = 2 h.

In order to enlarge the scope of application of our nickel catalyst, we encompassed the challenging coupling of primary aliphatic amines as a particularly significant class of amines for such cross coupling. To avoid the difficult handling of gaseous methyl- and ethylamine, the corresponding ammonium chloride salts were used. Under our standard catalytic conditions, the monoarylation of methyl- as well as ethylamine occurred with moderate to good yields and excellent selectivities (Scheme 5). It should be mentioned that toluene turned out to be a slightly better solvent for this type of substrates. The reaction was tolerant to both electron-withdrawing as well as electron-donating groups. More interestingly, the heterocyclic compound **4d** could be obtained in good isolated yield (56%) after 2 h reaction time.



Scheme 6. Stoichiometric reaction of **SK-J003-1n** with ammonia.

Whereas the mechanism for the palladium-catalyzed amination of aryl electrophiles has been studied in detail, the mechanism for the corresponding nickel-catalyzed coupling has been studied to a much lesser extent. However, investigations by the group of Hartwig are consistent with a Ni(0)/Ni(II) catalytic cycle for the coupling of aryl halides with amines.[19] To demonstrate the introduction of our single component precatalyst into a similar catalytic cycle **SK-J003-1n** was reacted with ammonia in the presence of NaO*t*Bu (Scheme 6). As a result, 4-aminobenzonitrile was formed via reductive elimination from an intermediate arylnickel(II) amido complex. Preliminary in-situ ^{31}P-NMR studies indicate the formation of (SL-J003-1)Ni(η^2-NC-Ph-4-NH_2) which can readily initiate the catalytic cycle via subsequent oxidative addition of an aryl electrophile.

In summary, we have identified a Nickel/JosiPhos catalyst system that has enabled the first examples of ammonia monoarylation with aryl carbamates. Furthermore, the synthesis and application of the air-stable single component nickel precatalyst **SK-J003-1n** has been described. The efficacy of this complex has been demonstrated in the coupling of ammonia from solution or ammonium sulfate. The scope of primary alkyl amines, employed as their hydrochloride salts, is unprecedented in amination reactions of aryl carbamates. These findings provide a meaningful extension of applicable electrophiles in catalytic amination reactions which not only allows avoiding the use of halides and sulfonates but also gives access to an orthogonal functionalization strategy of aromatic compounds. Additional mechanistic investigation as well as the applicability of (JosiPhos)Ni(Ph-4-CN)Cl complexes in different cross coupling processes are ongoing.

Acknowledgements

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Keywords: amination • ammonia • arylation • cross-coupling • nickel

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[17] For details of the applied high throughput experimentation and the corresponding reaction parameters see supporting information.

[18] The cost-efficient synthesis of SK-J003-1 from Ni^{II} sources is currently being developed.

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[22] For examples on the employment of ammonium salts in nickel-catalyzed amine arylations see ref. 9 and 10a.

[23] **SK-J003-1n** is commercially available from STREM and Sigma Aldrich. The supplementary crystallographic data for **SK-J003-1n** can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif under CCDC 1533232.

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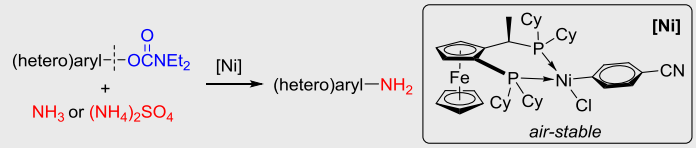

The title reaction, is catalyzed by an air-stable single-component nickel(II) precatalysts containing a Josiphos ligand. This catalyst system also promotes the amination of aryl carbamates with ammonium sulfate as well as hydrochloride salts of primary alkyl amines. Their easy preparation, robustness, and directing group ability makes aryl carbamates particularly attractive synthetic intermediates.

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Nickel-catalyzed amination of aryl carbamates with ammonia