JOC*Note*

Nickel-Catalyzed Amination of Aryl Tosylates

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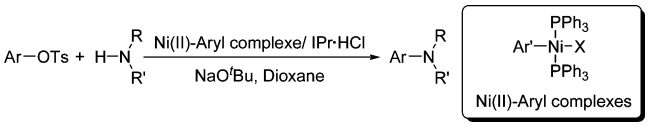

The cross-coupling of aryl tosylates with amines and anilines was accomplished by using a Ni-based catalyst system from the combination of Ni(II)−(σ-aryl) complexes/*N*-heterocyclic carbenes (NHCs). The feature, scope, and limitation of this reaction are disclosed.

Despite remarkable advances in nickel-catalyzed aromatic aminations in recent years, these reactions still have largely been limited to aryl halides as electrophilic substrates.[1−6] On the other hand, aryl sulfonates, a class of synthetic equivalents of aryl halides, are very attractive as coupling partners for the transition metal-catalyzed processes because they are easily accessible from the corresponding phenols.[7] Among them, aryl tosylates are of particular interest due to their ease of preparation and handling, pronounced stability to hydrolysis, and lower cost; at the same time they are also a challenging class of coupling substrates because of their very low activity toward oxidative addition that is a critical initial step in the metal-catalyzed coupling reaction. In contrast, the palladium-catalyzed amination of aryl sulfonates (including aryl tosylates) has been achieved,[8] although Pd catalysts are oftentimes less nucleophilic than Ni species. Furthermore, aryl sulfonates (including aryl tosylates) have also found applications in Ni-catalyzed C−C coupling reactions;[9,10] they, however, have not yet been well established as synthetically useful substrates for the coupling reaction with amines and anilines.[11] We felt that this transformation should be feasible through the proper choice of Ni-based catalyst systems.

We very recently developed a facile, efficient protocol for the Ni-catalyzed cross-couplings based on a type of Ni(II)−(σ-aryl) complexes, *trans*-arylbis(triphenylphosphine)nickel(II) halides, which has successfully been applied to the Suzuki reaction[12] and the amination[4b] of aryl chlorides. As part of our continuing work, we wished to explore the possibility for the amination of aryl tosylates by utilizing such Ni(II)-based catalysts. Herein, we report our findings in this study.

As shown in Table 1, our experiments for the optimal conditions began with the coupling of phenyl tosylate with morpholine catalyzed by a catalytic system consisting of Ni-(II)−(σ-aryl) complexes[13] and NHC ligands that are easily derived in situ from the corresponding imidazolium salts.[14] To our pleasure, a very rapid reaction occurred with 77% yield of the desired product when the reaction was performed under the identical reaction conditions as for the amination of aryl chlorides[4b] (run 1), but the reaction at room temperature gave only a modest 29% yield (run 2). By replacing solvent THF with dioxane (run 3) or toluene (run 4), elevating reaction temperature to 110 °C led to higher isolated yield of 85% or 83%. A 1:1 ratio of IPr·HCl (L-**1**) to Ni(PPh$_3$)$_2$(1-naphthyl)Cl (**1**) seemed to be appropriate because doubling of the IPr·HCl amount did not contribute to the reaction very much (run 5 vs 3). The use of more σ-donating SIPr·HCl (L-**2**), a saturated counterpart of IPr·HCl, as ligand gave a substantially low yield

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(14) Two imidazolium salts used: 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) and 1,3-bis(2,6-diisopropylphenyl)dihydroimidazolium chloride (SIPr·HCl). For their preparation, see: (a) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523−14534. (b) Grasa, G. A.; Viciu, M. S.; Huang, J.; Nolan, S. P. *J. Org. Chem.* **2001**, *66*, 7729−7737.

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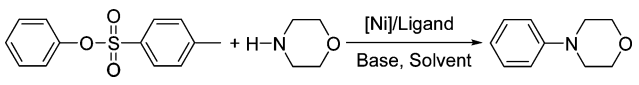
TABLE 1. Screening of Conditions for Ni(II)-Catalyzed Amination of Phenyl Tosylate[a]



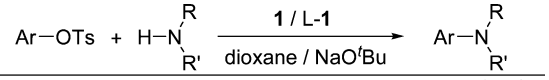
run	[Ni][b] (mol %)	ligand[c] (mol %)	base	solvent	*T* (°C)	yield (%)[d]
1	**1** (5)	L-**1** (5)	NaO^{t}Bu	THF	70	77
2	**1** (5)	L-**1** (5)	NaO^{t}Bu	THF	rt	29
3	**1** (5)	L-**1** (5)	NaO^{t}Bu	dioxane	110	85
4	**1** (5)	L-**1** (5)	NaO^{t}Bu	toluene	110	83
5	**1** (5)	L-**1** (10)	NaO^{t}Bu	dioxane	110	80
6	**1** (5)	L-**2** (5)	NaO^{t}Bu	dioxane	110	10
7	**1** (5)	L-**1** (5)	KO^{t}Bu	dioxane	110	*e*
8	**1** (5)	L-**1** (5)	$NaOCH_3$	dioxane	110	NR[f]
9	**1** (5)	L-**1** (5)	Cs_2CO_3	dioxane	110	NR[f]
10	**2** (5)	L-**1** (5)	NaO^{t}Bu	dioxane	110	84
11	**3** (5)	L-**1** (5)	NaO^{t}Bu	dioxane	110	76
12	**4** (5)	L-**1** (5)	NaO^{t}Bu	dioxane	110	76
13	**5** (5)	L-**1** (5)	NaO^{t}Bu	dioxane	110	80
14	**1** (5)	PPh_3 (10)	NaO^{t}Bu	dioxane	110	NR[f]
15	**1** (3)	L-**1** (3)	NaO^{t}Bu	dioxane	110	25

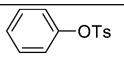
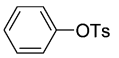
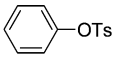
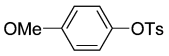
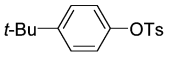
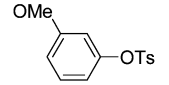
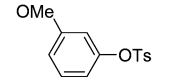
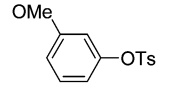
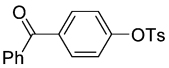
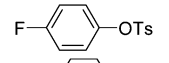
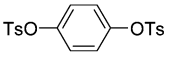
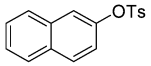
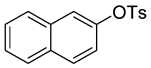
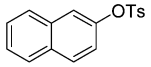
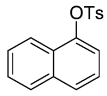
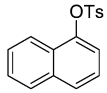
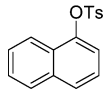
[a] Reaction conditions: aryl tosylate (1.0 equiv), morpholine (1.5 equiv), base (1.6 equiv), 15 min. [b] **1**: Ni(PPh$_3$)$_2$(1-naphthyl)Cl. **2**: Ni(PPh$_3$)$_2$(1-naphthyl)Br. **3**: Ni(PPh$_3$)$_2$(phenyl)Cl. **4**: Ni(PPh$_3$)$_2$(phenyl)Br. **5**: Ni(PPh$_3$)$_2$[1-(4-acetylnaphthyl)]Cl. [c] L-**1**: IPr·HCl. L-**2**: SIPr·HCl. [d] Isolated yield. [e] Phenol was predominant with a trace of the coupled product. [f] NR: no reaction.

(run 6); the catalyst system was ineffective for the reaction without the use of NHC as ligand (run 14). For the bases used, strongly basic KO^{t}Bu promoted decomposition of phenyl tosylate into phenol (i.e., the cleavage of the O−S bonds of tosylates) rather than the desired coupling reaction (run 7); weaker bases $NaOCH_3$ (run 8) and Cs_2CO_3 (run 9) were ineffective for this transformation. Several other Ni(II)−(σ-aryl) complexes, including Ni(PPh$_3$)$_2$(1-naphthyl)Br (**2**) (run 10), Ni(PPh$_3$)$_2$(phenyl)Cl (**3**) (run 11), Ni(PPh$_3$)$_2$(phenyl)Br (**4**) (run 12), and Ni(PPh$_3$)$_2$[1-(4-acetylnaphthyl)]Cl (**5**) (run 13), did not seem to be superior to Ni(PPh$_3$)$_2$(1-naphthyl)Cl (**1**) under the same conditions. An attempt to reduce catalyst loadings led to a significantly decreased yield (run 15). Finally, the optimal reaction conditions were set as run 3 in Table 1.

Some representative aryl tosylates and secondary cyclic amines were examined under the standard conditions (Table 2). As we can see, the nature of substituents on the aryl fragment of aryl tosylates was closely responsible for this reaction. Electron-neutral tosylates (entries 1−3, and 12−17) appeared to be suitable substrates and could be aminated in moderate to excellent yields, while aryl tosylates with electron-donating groups, such as *p*-methoxy (entry 4) and *p*-*tert*-butyl (entry 5), afforded mainly the recovered starting tosylates. Likewise, for the reason of the electron-donating effect bis-tosylate was doubly aminated only with a low yield (entry 11). Different from haloarenes, electron-drawing groups displayed variable effects on the amination of arenetosylates. The weakly electron-drawing *m*-methoxy group was favorable for the reaction (entry 6−8), and strongly electron-withdrawing groups could promote both the C−O cleavage (the desired reaction) and the O−S cleavage (side reaction). For example, in the case of the *p*-benzoyl group a good yield of the desired product was afforded with small amounts of the phenol byproduct (entry 9), while *p*-fluorophenyl tosylate gave the dominant byproduct *p*-fluorophenol with a trace of the coupled product (entry 10). It was found that the

TABLE 2. Ni(II)-Catalyzed Amination of Aryl Tosylates with Secondary Cyclic Amines[a]



Entry	ArOTs	Amine	Isolated Yield (%)
1			85
2			73
3			60
4			trace
5			trace
6			95
7			74
8			52
9			67[b]
10			*c*
11			24
12			96
13			79
14			58
15			76
16			57
17			45

[a] Reaction conditions: aryl tosylate (1.0 equiv), amine (1.5 equiv), base (1.6 equiv), **1** (5 mol %), L-**1** (5 mol %), dioxane, 110 °C, 15 min. [b] **1** (15 mol %), L-**1** (15 mol %). [c] 4-Fluorophenol was obtained predominantly.

carbonyl group, somehow, might negatively affect the activity of the Ni catalyst and therefore much higher catalyst loadings were required to ensure a complete conversion of the starting tosylate (entry 9). Additionally, the reaction was slightly sensitive to the steric effects of the starting tosylates. For instance, the reaction of 1-naphthyl tosylate furnished lower yields than the corresponding reaction of 2-naphthyl tosylate (entries 12−14 vs 15−17, respectively). Noticeably, we found that this catalytic amination required a very short period of time, and generally went to the end within 15 min. Control experiments suggested that prolonged reaction times were helpless for the enhancement of yields and hence unnecessary.

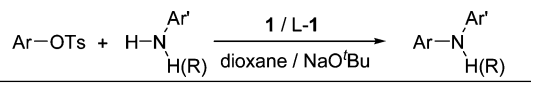
Under the above-mentioned standard conditions, aniline reacted with phenyl tosylate to give 55% yield of the desired product. When the molar ratio of Ni(II) to IPr·HCl was adjusted to 1:2, an improved yield of 68% was obtained (Table 3, entry 1). Then, the cross-couplings of various anilines and aryl tosylates were carried out under the modified reaction conditions (Table 3). As in the reaction with amines, the amination reactions were strongly influenced by the electronic properties of the starting aryl tosylates. Phenyl tosylate could be aminated with acceptable to good yields (entries 1−5); electron-rich aryl tosylates, such as *p*-methoxy and *p*-*tert*-butyl tosylates, did not undergo the amination reaction (unlisted in Table 3); and electron-deficient 4-tosylbenzophenone was consumed rapidly, although yields were not very high due to partial decomposition of the tosylate into phenol (entries 17−19). Particularly, electron-neutral naphthyl tosylates performed very well and good-to-excellent yields were generally afforded regardless of both the steric and electronic natures of anilines (entries 6−10 and 12−16) except in the case of *N*-methylaniline (entry 11), which is a more bulky secondary aromatic amine. Likewise, a rapid reaction with anilines was observed (completed within 30 min), albeit a bit longer than that with secondary cyclic amines.

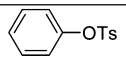
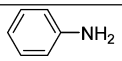
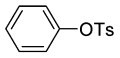
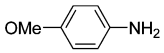
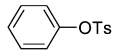
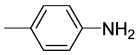
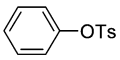
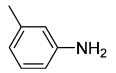
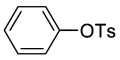
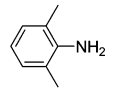
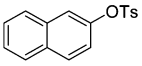
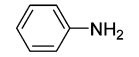
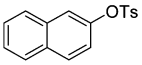
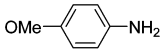
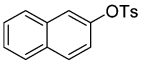
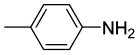
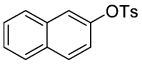
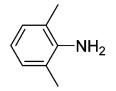
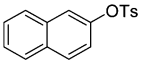
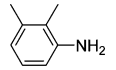
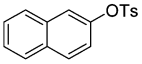
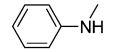
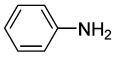
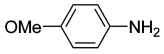
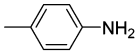
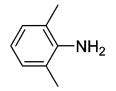
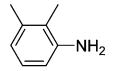
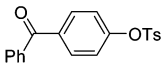
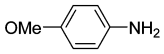
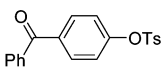
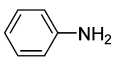
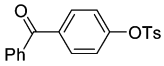
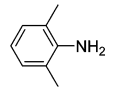
Under the current conditions, byproduct biaryls from the self-coupling of aryl tosylates were not detected in this amination reaction, but another side reaction, decomposition of the starting tosylate into phenoxide arising from the O−S cleavage of the tosylate by attack of NaO^{t}Bu or/and amines on electrophilic sulfur atom,[8b,15] occurred to less or more extent in all cases examined. Apparently, strongly electron-withdrawing groups would promote the side reaction. The electron-rich aryl tosylates cannot be aminated under the present conditions due presumably to their extremely poor activity toward oxidative addition.

The catalytically active species may be the Ni(0) species that could be formed in situ from the reaction of Ni(II)−(*σ*-aryl) complex with the amine (i.e., by transmetalation of the nucleophilic reactant and subsequent reductive elimination prior to the normal reaction). Indirect evidence is that a small amount of 1-naphthyl amination byproduct was usually observed,[16] and a previous stoichiometric reaction of Ni(II)−(*σ*-aryl) complexes and morpholine[4b] supported the activation mode of the Ni(II) pre-catalyst as well. Combining previous studies[17] with our experimental results, we presumed that the mechanism might follow a catalytic cycle of the Ni(0)−Ni(II) shuttle involving sequential oxidative addition, transmetalation, and reductive elimination (Scheme 1). The rate-determining step of the amination reaction is unclear at present.

It is noteworthy that this reaction was unusually fast compared to the other reported Ni-[1−5] and Pd-catalyzed[8] amination processes. We speculated that two major factors might be responsible for the acceleration phenomenon. First, in our protocol the formed Ni(0) specie might be coligated with IPr and PPh_3. The existence of the strong *σ*-donating IPr ligand would substantially enhance the electron density of the Ni metal center to facilitate the oxidative addition step; the hemilabile ligand PPh_3 might dissociate readily from the metal center to

TABLE 3. Ni(II)-Catalyzed Amination of Aryl Tosylates with Anilines[a]



Entry	ArOTs	Amine	Isolated Yield (%)
1			68
2			69
3			46
4			50
5			37
6			92
7			95
8			83
9			88
10			92
11			52
12			82
13			89
14			88
15			90
16			72
17			66[b]
18			73[b]
19			65[b]

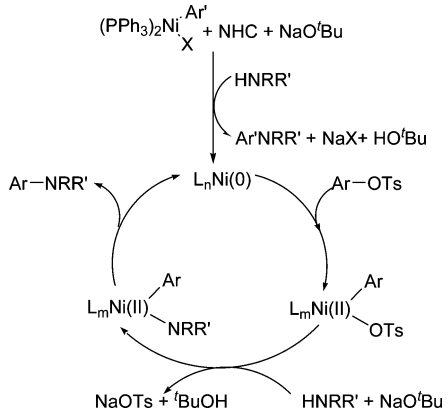
[a] Reaction conditions: aryl tosylate (1.0 equiv), aryl amine (1.5 equiv), base (1.6 equiv), **1** (5 mol %), L-**1** (10 mol %), dioxane, 110 °C, 30 min. [b] **1** (15 mol %), L-**1** (30 mol %).

(15) Ahman, J.; Buchwald, S. L. *Tetrahedron Lett.* **1997**, *38*, 6363−6366.

(16) The small amount of 1-naphthyl amination byproduct generated from $Ni(PPh_3)_2$(1-naphthyl)Cl is proportional to the amount of the complex used and usually does not interfere with the separation of the desired amination product. In the case of 1-naphthyl tosylate as substrate, the reported yields have subtracted the contribution from the catalyst used according to an estimation that $Ni(PPh_3)_2$(1-naphthyl)Cl would be completely converted.

(17) (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374−4376. (b) See refs 9a and 3e.

SCHEME 1. Plausible Mechanism for the Amination of Aryl Tosylates Catalyzed by Ni(II)−(*σ*-Aryl) Complex/NHC Systems



supply the vacant coordination site required for oxidative addition and might re-ligate to the metal center, associated with the steric effect of bulky IPr, to accelerate the reductive elimination step. The analogous effects of mixed ligands have been observed in Pd-[18] and Ni-catalyzed[19] couplings. Second, the tosylate anion, like other sulfonates, is weakly coordinating and so its metal complexes may have an ionic structure.[9a,20] That implies that the leaving group might not be bound very closely to the Ni(II) center in the oxidative adduct intermediate. Thus such a Ni(II) complex would readily undergo the transmetalation step.

In conclusion, we have for the first time demonstrated the Ni-catalyzed amination of aryl tosylates with amines and anilines. This protocol further enhances the utility of the methodology employing Ni(II)−(*σ*-aryl) complexes as the Ni-based catalyst. Studies are underway in our laboratory to overcome the limitation of aryl tosylate substrates as well as to detail information about the mechanism of this reaction.

Experimental Section

General Procedure for the Amination of Aryl Tosylate. An oven-dried 100-mL three-necked flask was charged with NaO^{t}Bu (1.6 mmol), Ni(PPh$_3$)$_2$(1-naphthyl)Cl (5 mol %), and IPr·HCl (5 mol % for amine or 10 mol % for aniline). The aryl tosylate (1.0 mmol) and the amine (1.5 mmol, if solid) were added at this time. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The amine (1.5 mmol, if liquid) was added via syringe at this time, followed by dried dioxane (5 mL). The reaction mixture was heated at 110 °C for 15−30 min and then allowed to cool to room temperature, and filtered through a silica gel pad that was washed with ethyl acetate (3 × 20 mL). The combined organic phases were evaporated under reduced pressure and the residue purified by silica gel column chromatography to give the desired product.

***N*-Phenylmorpholine**[21] **(Table 2, entry 1).** According to the general procedure, phenyl tosylate (248 mg, 1.0 mmol) and morpholine (131 mg, 1.5 mmol) were coupled and the product purified by column chromatography with petroleum/ethyl acetate (6:1, v/v) to give a colorless solid (138 mg, 85%): mp 49−51 °C (lit.[21] mp 52−53 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.13−3.25 (m, 4H), 3.80−4.00 (m, 4H), 6.86−7.05 (m, 3H), 7.28−7.37 (m, 2H); MS (EI) *m*/*z* 163 (M$^+$).

Diphenylamine[22] **(Table 3, entry 1).** According to the general procedure, phenyl tosylate (248 mg, 1.0 mmol) and aniline (140 mg, 1.5 mmol) were coupled and the product purified by column chromatography with petroleum/ethyl acetate (12/1, v/v) to give a pale yellow solid (115 mg, 68%): mp 48−50 °C (lit.[22] mp 50−52 °C). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.97 (t, J = 7.2 Hz, 2H), 7.13 (d, J = 7.9 Hz, 4H), 7.27 (t, J = 7.9 Hz, 4H); MS (EI) *m*/*z* 169 (M$^+$).

Acknowledgment. The authors thank the National Natural Science Foundation of China (Project No. 20672116) for financial support of this work.

Supporting Information Available: Experimental procedures, characterization data, and references to the known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO7022558

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(19) (a) Lee, C. C.; Ke, W. C.; Chan, K. T.; Lai, C. L.; Hu, C. H.; Lee, H. M. *Chem. Eur. J.* **2006**, *13*, 582−591. (b) Ho, C. Y.; Jamison, T. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 782−785.

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(21) Kang, S. K.; Lee, H. W.; Choi, W. K.; Hong, R. K.; Kim, J. S. *Synth. Commun.* **1996**, *26*, 4219−4224.

(22) Aubrey, D. W.; Lappert, M. F.; Majumdar, M. K. *J. Chem. Soc.* **1962**, 4088−4094.