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Nickel-Catalyzed Desulfitative Suzuki–Miyaura Cross-Coupling of *N*,*N*-Disulfonylmethylamines and Arylboronic Acids

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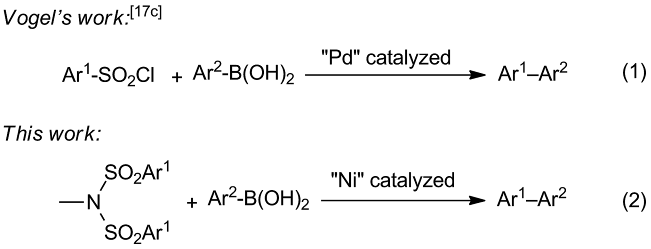
Keywords: Synthetic methods / C–C coupling / Cross-coupling / Biaryls / Nickel

A nickel-catalyzed approach for the synthesis of biaryl compounds from *N*,*N*-disulfonylmethylamines and arylboronic acids has been developed. Instead of arenesulfonyl chlorides, various *N*,*N*-disulfonylmethylamines were used as the aryl source through extrusion of SO_2 to give cross-coupling products in moderate to good yields.

Introduction

Biaryl compounds belong to a privileged class of structures that are prevalent in a large number of natural products, pharmaceuticals, agrochemicals, and functional materials.[1] The study of their synthesis began with the Ullmann coupling[2] more than 100 years ago and has evolved into one of the most-studied transition-metal-catalyzed carbon–carbon bond-forming reactions.[1,3] Over the past decades, palladium-based catalyst systems have been fully developed that allow aryl halides/pseudohalides to be effectively coupled with arylboronic acids under mild reaction conditions.[4] However, the high cost of the frequently used Pd catalysts both for the palladium source and the supporting ligands limits their general use in commercial synthesis. In the evolution of this synthetic methodology, nickel-based catalysts introduced by Percec et al. in 1995[5] have proven to be another milestone. Since then, remarkable advances have been made in the nickel-catalyzed version of the Suzuki reaction.[6–10] The development of efficient, inexpensive nickel-based catalysts has represented an ongoing, central theme of research of this methodology, and $NiCl_2(PCy_3)_2$ (Cy = cyclohexyl), $Ni(cod)_2$ (cod = 1,5-cyclooctadiene), $NiCl_2(PPh_3)_2$, $NiCl_2(dppf)$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene], and nickel/N-heterocyclic carbene (NHC) systems are frequently studied. Very recently, Han et al. demonstrated that the $NiCl_2(dppp)$ complex could be an effective precatalyst for the Suzuki–Miyaura coupling of a broad range of phenol derivatives such as aryl sulfonates,[9i] phosphoramides,[11] and phosphonium salts.[12] Besides, this new catalyst system combined great activity and stability, low catalyst loading and cost, and general applicability, even in the absence of extra supporting ligands, all of which make this catalyst highly desirable.

On the other hand, arenesulfonyl chlorides constitute a large family of inexpensive and widely available organic compounds that have been used for more than a century in materials science and medicinal chemistry.[13] Desulfitative vinylation,[14] carbonylation,[15] and homocoupling[16] of arenesulfonyl chlorides have already been described over the past three decades. Recently, Vogel et al. disclosed a series of palladium-catalyzed cross-coupling reactions (e.g., Stille, carbonylative Stille, Suzuki–Miyaura, Negishi, Sonogashira–Hagihara-type, and Mizoroki–Heck-type arylations).[17] They also reported an iron-catalyzed desulfitative cross-coupling pathway of sulfonyl chlorides with Grignard reagents.[18] Moreover, various palladium-catalyzed desulfitative reactions have been developed by using sodium sulfinates as substrates.[19] To the best of our knowledge, however, examples of the use of nickel-catalyzed systems for these types of desulfitative C–C cross-coupling reactions with sulfonyl chlorides and sodium sulfinates as coupling partners are rare. Herein, we report for the first time that *N*,*N*-disulfonylmethylamines $[CH_3N(SO_2Ar)_2]$ undergo smooth desulfitative Suzuki–Miyaura cross-coupling reactions with arylboronic acids in the presence of catalytic amounts of $[NiCl_2(dppp)]$ [dppp = 1,3-bis(diphenylphosphino)propane] without any extra ligands [Scheme 1, Equation (2)].



Scheme 1. Desulfitative Suzuki–Miyaura cross-coupling of arylboronic acids.

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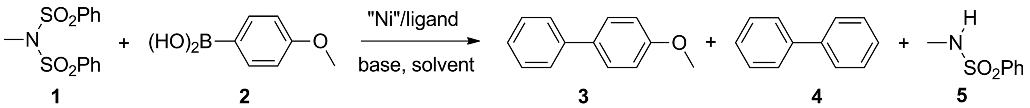
Results and Discussion

Initially, our exploratory experiments started with the coupling of benzenesulfonyl chloride and 4-methoxyphenylboronic acid under different conditions; various nickel catalysts, bases, and solvents were investigated (see the table in the Supporting Information). Much effort was devoted to this task, but low yields (<20%) of the biaryl product were obtained. The starting sulfonyl chloride was totally consumed in all cases, which could be explained by the fact that the sulfonyl chloride was converted into the corresponding sulfonate in boiling solvents in the presence of base. However, the yield could be increased drastically under the same conditions if *N*,*N*-diphenylsulfonylmethylamine [$CH_3N(SO_2Ph)_2$] was used instead of benzenesulfonyl chloride. A systematic study was conducted to optimize the critical reaction conditions (Table 1).

First, a wide variety of nickel catalysts were examined for the model reaction (Table 1, entries 1–18). It was reported that simple $NiCl_2$ without any supporting ligand could catalyze the Suzuki–Miyaura coupling of arylboronic acids to some extent.[7j] However, no product was detected by using 5 mol-% $NiCl_2$ as the catalyst (Table 1, entry 1). $Ni(acac)_2$ (acac = acetylacetonate) also failed to initiate the coupling process, though it efficiently catalyzed cross-coupling reactions between vinyl or aryl *tert*-butyl sulfones and Grignard reagents through desulfonylation (Table 1, entry 2).[20]

Then, we investigated the performance of the most common bidentate ligands in the nickel catalyst system (Table 1, entries 3–9). Among them, $NiCl_2(dppp)$ provided the best yield (72%) with dioxane as the solvent and K_3PO_4 as the base (Table 1, entry 8). Using $Ni(cod)_2/2PCy_3$ or $NiCl_2(PCy_3)_2$ as the catalyst did not give the expected satisfactory result, even though tricyclohexylphosphine (PCy_3) has been often reported to be a good supporting ligand in the Suzuki–Miyaura coupling of arylboronic acids (Table 1, entries 11–13). Further testing showed that the use of larger

Table 1. Screening of the optimal conditions for the desulfitative Suzuki–Miyaura cross-coupling reaction.[a]



Entry	Cat. (mol-%)[b]	Ligand (mol-%)	Base	Solvent	*T* [°C]	% Yield of **3**[c]
1	$NiCl_2$ (5)		K_3PO_4	dioxane	110	n.r.
2	$Ni(acac)_2$ (5)		K_3PO_4	dioxane	110	n.r.
3	$NiCl_2$(bpy) (5)		K_3PO_4	dioxane	110	11
4	$NiCl_2$(phen) (5)		K_3PO_4	dioxane	110	13
5	$NiCl_2$(dppf) (5)		K_3PO_4	dioxane	110	25
6	$NiCl_2$(dppm) (5)		K_3PO_4	dioxane	110	19
7	$NiCl_2$(dppe) (5)		K_3PO_4	dioxane	110	53
8	$NiCl_2$(dppp) (5)		K_3PO_4	dioxane	110	72
9	$NiCl_2$(dppb) (5)		K_3PO_4	dioxane	110	31
10	$NiCl_2(PPh_3)_2$ (5)		K_3PO_4	dioxane	110	32
11	$NiCl_2(PCy_3)_2$ (5)		K_3PO_4	dioxane	110	47
12	$NiCl_2(PCy_3)_2$ (5)	PCy_3 (10)	K_3PO_4	dioxane	110	29
13	$Ni(cod)_2$ (5)	PCy_3 (10)	K_3PO_4	dioxane	110	7
14	$Ni(cod)_2$ (5)	IPr·HCl[d] (10)	K_3PO_4	dioxane	110	17
15	$Ni(PPh_3)_2$(1-naphthyl)Cl (5)		K_3PO_4	dioxane	110	26
16	$Ni(PCy_3)_2$(1-naphthyl)Cl (5)		K_3PO_4	dioxane	110	50
17	$Ni(PPh_3)_2$ (cinnamyl)Cl (5)		K_3PO_4	dioxane	110	18
18	Ni(dppf) (cinnamyl)Cl (5)		K_3PO_4	dioxane	110	13
19	$NiCl_2$(dppp) (5)	dppp (5)	K_3PO_4	dioxane	110	45
20	$NiCl_2$(dppp) (5)		K_3PO_4	dioxane	110	41[e]
21	$NiCl_2$(dppp) (5)		K_3PO_4	dioxane	110	74[f]
22	$NiCl_2$(dppp) (5)		K_2CO_3	dioxane	110	37
23	$NiCl_2$(dppp) (5)		Na_2CO_3	dioxane	110	31
24	$NiCl_2$(dppp) (5)		Cs_2CO_3	dioxane	110	15
25	$NiCl_2$(dppp) (5)		*t*BuOK	dioxane	110	13
26	$NiCl_2$(dppp) (5)		NaOH	dioxane	110	35
27	$NiCl_2$(dppp) (5)		KOH	dioxane	110	38
28	$NiCl_2$(dppp) (5)		K_3PO_4	toluene	110	25
29	$NiCl_2$(dppp) (5)		K_3PO_4	THF	70	28
30	$NiCl_2$(dppp) (5)		K_3PO_4	CH_3CN	80	trace
31	$NiCl_2$(dppp) (5)		K_3PO_4	*i*PrOH	80	11
32	$NiCl_2$(dppp) (5)		K_3PO_4	DMF	130	33
33	$NiCl_2$(dppp) (5)		K_3PO_4	diglyme	130	45

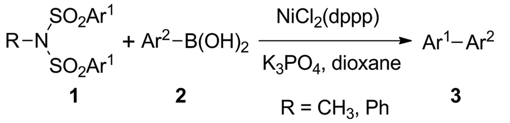
[a] Reaction conditions: **1** (0.25 mmol), **2** (0.63 mmol, 2.5 equiv.), base (1.00 mmol, 4.0 equiv.), solvent (3.00 mL), 24 h, under N_2. [b] bpy = 2,2′′-bipyridyl, phen = 1,10-phenanthroline, dppm = 1,1-bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppb = 1,4-bis(diphenylphosphino)butane. [c] Yield of isolated product. [d] IPr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride. [e] 12 h. [f] 36 h; n.r.: no reaction.

amounts of the ligand was not necessary (Table 1, entries 12 and 19). The Ni^{II}–(σ-aryl) or Ni^{II}–(σ-cinnamyl) complexes, which were efficient for some C–C/C–N bond-forming coupling reactions,[9g,10c,21] could not afford better yields (Table 1, entries 15–18). Additionally, lengthening the reaction time from 24 to 36 h did not favor the reaction much, whereas reducing the time caused a substantial decrease in the yield (Table 1, entries 20 and 21 vs. entry 8). Efforts to enhance the yield by replacing K_3PO_4 with K_2CO_3, Na_2CO_3, Cs_2CO_3, *t*BuOK, NaOH, or KOH proved fruitless (Table 1, entries 22–27). Additionally, as K_3PO_4 is an inorganic base that is insoluble in dioxane, it was ground (by using a porcelain mortar for 10 min) into a fine powder in all of our trials. Dioxane was irreplaceable because all the other solvents resulted in a negative effect (Table 1, entries 28–33). Of particular note is that commercially available arylboronic acids can contain small amounts of phenol and water, and therefore, this reagent was washed with hexanes and dried under vacuum to remove all traces of phenol and water beforehand. Further variation of the reaction conditions (temperature, additives, phase-transfer reagents[22]) disclosed that this desulfitative cross-coupling procedure was the most efficient if it proceeded in dioxane for 24 h at 110 °C in the presence of K_3PO_4 (4 equiv.) with a 5 mol-% loading of $NiCl_2$(dppp) (Table 1, entry 8).

With the optimized conditions in hand, the applicability of the reaction was examined on a series of *N*,*N*-disulfonylmethylamines **1** and arylboronic acids **2**. The results are summarized in Table 2; moderate to good yields were observed. The reaction was found to be significantly affected by substituents on the aromatic rings of both the *N*,*N*-disulfonylmethylamines and the arylboronic acids. For the scope of the *N*,*N*-disulfonylmethylamines, substrates bearing electron-withdrawing substituents were coupled smoothly in high yields, whereas sharply diminished yields were found for reagents bearing electron-donating groups (see **3fa**, **3ga**, **3gd** vs. **3ba**, **3aa**; Table 2). On the contrary, arylboronic acids with electron-donating substituents on the phenyl ring proved to be more efficient than those with electron-withdrawing groups (see **3da**, **3db** vs. **3dc**, **3dd** and **3ga**, **3gb** vs. **3ge**; Table 2). The unsuitability of 4-nitro-substituted **1h** might be attributed to its high electron deficiency. However, a NO_2 group often inhibits low-valent metal catalysis owing to its high oxidation state (see **3ha**, Table 2). The reaction was not noticeably affected by the position of substituents on the aromatic ring (see **3fa**, **3fb**, **3fc** vs. **3gb**, **3gc**; Table 2), but this methodology did not fit well with multisubstituted substrates (see **3ca**, Table 2). Halogen substituents such as fluoro and chloro were tolerated under the optimal reaction conditions, and the desired products were obtained in acceptable to moderate yields.

Reagents bearing a naphthyl group seemed to be the most effective, which thereby resulted in the formation of **3de**, **3gh**, **3ia**, and **3ja** in 68, 85, 75, and 70% yield, respectively. In addition, heteroaromatic derivatives were also applicable to this method, but they delivered the corresponding heterobiaryls in lower yields (see **3df** and **3ka**, Table 2). For comparison, *N*,*N*-disulfonylanilines were employed as coupling partners under identical conditions, but no differences were observed, except for slightly diminished yields (see **3aa**, **3ba**, **3da**, **3ha**; Table 2).

Table 2. Desulfitative Suzuki–Miyaura cross-coupling of *N*,*N*-disulfonylmethylamines **1** and arylboronic acids **2**.[a]



Entry	1	Ar^1	Ar^2	3	% Yield[b]
1	**1a**	4-MeOC$_6$H$_4$	Ph	**3aa**	31 (28)[c]
2	**1b**	4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$	**3ba**	53 (51)[c]
3	**1b**	4-MeC$_6$H$_4$	Ph	**3bb**	46[d]
4	**1c**	mesityl	4-MeOC$_6$H$_4$	**3ca**	28
5	**1d**	Ph	4-MeOC$_6$H$_4$	**3da**	72 (65)[c]
6	**1d**	Ph	4-MeC$_6$H$_4$	**3db**	51[d]
7	**1d**	Ph	4-AcC$_6$H$_4$	**3dc**	28
8	**1d**	Ph	4-NCC$_6$H$_4$	**3dd**	31
9	**1d**	Ph	1-C$_{10}$H$_7$	**3de**	68[d]
10	**1d**	Ph	2-thienyl	**3df**	25
11	**1e**	4-FC$_6$H$_4$	4-MeOC$_6$H$_4$	**3ea**	51
12	**1f**	4-F$_3$CC$_6$H$_4$	4-MeOC$_6$H$_4$	**3fa**	76
13	**1f**	4-F$_3$CC$_6$H$_4$	3-MeOC$_6$H$_4$	**3fb**	82
14	**1f**	4-F$_3$CC$_6$H$_4$	2-MeOC$_6$H$_4$	**3fc**	47
15	**1g**	4-NCC$_6$H$_4$	4-MeOC$_6$H$_4$	**3ga**	70
16	**1g**	4-NCC$_6$H$_4$	4-MeC$_6$H$_4$	**3gb**	61
17	**1g**	4-NCC$_6$H$_4$	2-MeC$_6$H$_4$	**3gc**	53
18	**1g**	4-NCC$_6$H$_4$	Ph	**3gd**	80
19	**1g**	4-NCC$_6$H$_4$	4-AcC$_6$H$_4$	**3ge**	31
20	**1g**	4-NCC$_6$H$_4$	4-FC$_6$H$_4$	**3gf**	51
21	**1g**	4-NCC$_6$H$_4$	4-ClC$_6$H$_4$	**3gg**	34
22	**1g**	4-NCC$_6$H$_4$	1-C$_{10}$H$_7$	**3gh**	85
23	**1h**	4-O$_2$NC$_6$H$_4$	Ph	**3ha**	34 (28)[c]
24	**1i**	1-C$_{10}$H$_7$	4-MeOC$_6$H$_4$	**3ia**	75
25	**1i**	1-C$_{10}$H$_7$	Ph	**3ib**	82[d]
26	**1j**	2-C$_{10}$H$_7$	4-MeOC$_6$H$_4$	**3ja**	70
27	**1k**	2-thienyl	Ph	**3ka**	34

[a] Reaction conditions: **1** (0.25 mmol), **2** (0.63 mmol), $NiCl_2$(dppp) (5.00 mol-%), K_3PO_4 (1.00 mmol), dioxane (3.00 mL), 110 °C, 24–36 h, under N_2. [b] Yield of isolated product. [c] Yield obtained by using *N*,*N*-disulfonylaniline instead of *N*,*N*-disulfonylmethylamine. [d] Yield was determined by ^{1}H NMR spectroscopy.

Unsymmetrical biaryl compounds were not the sole products of this nickel-catalyzed desulfitative cross-coupling approach. Symmetric biaryls were also detected in most cases. This byproduct can be explained by the desulfitative homocoupling of the sulfonyl group. Surprisingly, diaryl sulfides, which appear frequently in palladium-based catalyst systems,[17a,17c,23] were not observed.

Conclusions

In summary, we have demonstrated the $NiCl_2$(dppp)-catalyzed desulfitative Suzuki–Miyaura cross-coupling reaction between *N*,*N*-disulfonylmethylamines and arylboronic acids. *N*,*N*-Disulfonylmethylamines proved to be superior to sulfonyl chlorides, and the crossing-coupling products were obtained in moderate to good yields. The easy availability, high activity, and great stability of the $NiCl_2$(dppp) complex make this catalyst system much more appealing in organic synthesis. As the nickel-catalyzed desulfitative cross-coupling reaction with arylboronic acids is disclosed for the first time, studies on other nickel-catalyzed desulfitative reactions are currently underway in our laboratory.

Experimental Section

General Procedure for the Desulfitative Suzuki–Miyaura Cross-Coupling Reactions of *N,N*-Disulfonylmethylamines and Arylboronic Acids: A 25 mL Schlenk tube equipped with a magnetic bar was charged with $NiCl_2$(dppp) (0.0125 mmol, 6.8 mg), the *N,N*-disulfonylmethylamine (0.25 mmol), the arylboronic acid (0.63 mmol), and anhydrous K_3PO_4 (1.00 mmol, 212.3 mg). The tube was then evacuated (3 × 10 min) under vacuum and backfilled with N_2. Dry dioxane (3.0 mL) was injected by syringe, and the mixture was stirred at 110 °C until the *N,N*-disulfonylmethylamine had disappeared, as monitored by TLC. The mixture was then poured into water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude material was purified by flash chromatography (silica gel, hexane/ethyl acetate or hexane/CH_2Cl_2) to give the desired cross-coupled products.

General Procedure for the Synthesis of *N,N*-Disulfonylmethylamines: The sulfonyl chloride (1 mmol) was added at room temperature to a solution of methylamine (1.1 mol, 25% aq. soln) in distilled water (2 mL), and vigorous stirring was continued until the reaction was complete (monitored by TLC). Sometimes, NaOH (1 mmol) was added to promote the conversion of the sulfonyl chloride. The mixture was then extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated to dryness. The crude residue was then dissolved in dry CH_2Cl_2 (50 mL), and another portion of the sulfonyl chloride (1.1 mmol) and Et_3N (3 mmol) was added with stirring. The mixture was then slowly heated to a gentle reflux. Upon completion of the reaction (monitored by TLC), water (ca. 50 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried with anhydrous Na_2SO_4, filtered, and concentrated to dryness again. The crude material was purified by column chromatography (cyclohexane/dichloromethane, 5:1 to 1:1).

Supporting Information (see footnote on the first page of this article): Experimental details and copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgments

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