C–N Activation

DOI: 10.1002/anie.201100683

Nickel-Catalyzed Cross-Coupling of Aryltrimethylammonium Iodides with Organozinc Reagents**

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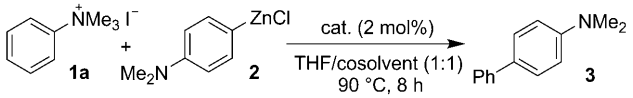
Transition-metal-catalyzed cross-coupling reactions such as Kumada coupling, Negishi coupling, Suzuki coupling, and Stille coupling are reliable and versatile methods to construct carbon–carbon bonds.[1] Among these coupling reactions the Negishi coupling is one of the most powerful owing to the wide-spread availability and high functional-group tolerance of organozinc reagents.[1,2] Electrophiles used in the reaction are predominantly organic halides.[3] Triflates, mesylates/tosylates,[4] and carboxylates[5] are also seen as the alternative coupling partners. However arylamines, whose amino groups can direct the introduction of other functional groups onto the aromatic ring (through *ortho* lithiation and electrophilic aromatic substitution, etc.), have not yet been employed in this context.

Recently, Kakiuchi and co-workers reported ruthenium-catalyzed Suzuki coupling through cleavage of the C–N bond of anilines with a carbonyl group at the *ortho* position to act as the ligating group.[6] Wenkert et al. carried out the nickel-catalyzed Kumada coupling of aryltrimethylammonium iodide salts in 1988.[7] Very recently, Reeves et al. developed the same coupling using aryltrimethylammonium triflates as the electrophiles and palladium as the catalyst.[8] Blakey and MacMillan reported the Suzuki coupling of aryltrimethylammonium triflates with $[Ni(cod)_2]$/IMes as a catalyst in 2003.[9] These successes stimulated us to explore the possibility using arylammonium salts as the electrophilic partners in the Negishi coupling. Herein, we report our initial studies on the nickel-catalyzed coupling of aryltrimethylammonium iodide salts with aryl- and alkylzinc reagents.

We first screened the catalysts and solvents using phenyltrimethylammonium iodide and *p*-$Me_2NC_6H_4ZnCl$ as the substrates (Table 1). On the basis of studies by Wenkert and MacMillan, nickel complexes can activate the aryl–ammonium bond in both Kumada coupling and Suzuki coupling.[7,9] Hence we examined a series of nickel complexes as catalyst precursors. It was found that monodentate and bidentate phosphine coordinated Ni^{II} complexes could drive the reaction to proceed in a 1:1 mixture of THF and NMP (Table 1, entries 1–5). Complex $[Ni(PCy_3)_2Cl_2]$ gave the best result compared with the nickel complexes coordinated by PPh_3, PEt_3, and dppe, and led to the desired cross-coupling product in 99% yield of isolated product. Decreasing the $[Ni(PCy_3)_2Cl_2]$ loading to 1 mol% resulted in diminished yield (Table 1, entry 5). The yield was not remarkably enhanced when an additional 2 mol% of PCy_3 was added to the reaction mixture (Table 1, entry 6). Interestingly, in the absence of phosphine ligands the $[Ni(acac)_2]$ complex also catalyzed the coupling to give 88% yield (Table 1, entry 7). The same reaction substrates were also tested with $PdCl_2/PPh_3$ and $PdCl_2/PCy_3$ as catalyst precursors. However, these palladium complexes were not as effective as the nickel analogues for this transformation (Table 1, entries 8 and 9). Appropriate cosolvents are also critical. The absence of a cosolvent or using toluene, DMA, and dioxane as the cosolvents resulted in much lower yields (Table 1, entries 10–13). The role of NMP is presumably to stabilize the organometallic intermediates formed during the reaction through its coordination with the nickel center.[10] It is also possible that the combination of NMP and THF provides a medium which has the

Table 1: Screening of catalysts and cosolvents.[a]



Entry	Catalyst	Cosolvent	Yield [%][b]
1	$[Ni(dppe)Cl_2]$	NMP	91
2	$[Ni(PPh_3)_2Cl_2]$	NMP	85
3	$[Ni(PEt_3)_2Cl_2]$	NMP	94
4	$[Ni(PCy_3)_2Cl_2]$	NMP	99
5[c]	$[Ni(PCy_3)_2Cl_2]$	NMP	87
6[c]	$[Ni(PCy_3)_2Cl_2] + 2\,PCy_3$	NMP	89
7	$[Ni(acac)_2]$	NMP	88
8	$PdCl_2 + 2\,PPh_3$	NMP	37
9	$PdCl_2 + 2\,PCy_3$	NMP	37
10	$[Ni(PCy_3)_2Cl_2]$	–	57
11	$[Ni(PCy_3)_2Cl_2]$	toluene	trace
12	$[Ni(PCy_3)_2Cl_2]$	DMA	trace
13	$[Ni(PCy_3)_2Cl_2]$	dioxane	25

[a] The reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation unless otherwise specified; 1.5 equivalents of *p*-$Me_2NC_6H_4ZnCl$ was employed. [b] A mixture of the cross-coupling product and $PhNMe_2$ (formed by hydrolysis of unreacted *p*-$Me_2NC_6H_4ZnCl$) was isolated by column chromatography and the yield was calculated based on the integratal ratio of ^1H NMR spectrum of the mixture. [c] 1 mol% of catalyst was employed. acac = acetylacetonate, Cy = cyclohexyl, DMA = *N*,*N*-dimethylacetamide, dppe = 1,2-bis(diphenylphosphanyl)ethane, NMP = *N*-methylpyrrolidine, THF = tetrahydrofuran.

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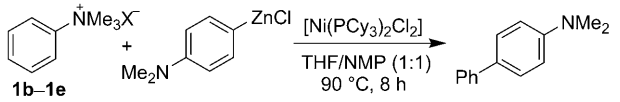
[**] This research was supported by the National Basic Research Program of China (grant no. 2009CB825300) and the National Natural Science Foundation of China (grant no. 20772119).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100683.

suitable polarity for the reaction of an ammonium salt with the active catalyst in the catalytic cycle.[11]

The counterion effect was also investigated by reaction of the same nucleophile as above with phenyltrimethylammonium salts with Br^-, Cl^-, BF_4^-, and OTf^-, respectively, as a counterion in a 1:1 mixture of NMP and THF at 90 °C (Table 2). In the presence of 2 mol % of $[Ni(PCy_3)_2Cl_2]$ the tetrafluoroborate salt exhibited the lowest reactivity (Table 2, entry 1). The bromide and chloride salts showed higher

Table 2: Counterion screening with $[Ni(PCy_3)_2Cl_2]$.[a]



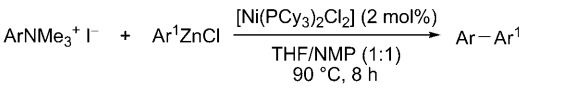
Entry	X	Amount of catalyst [mol %]	Yield [%][b]
1	BF_4 (**1b**)	2	64
2	Br (**1c**)	2	84
3	Cl (**1d**)	2	90
4	OTf (**1e**)	2	99
5	OTf (**1e**)	1	73

[a] The reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation; 1.5 equivalents of *p*-$Me_2NC_6H_4ZnCl$ was employed. [b] Yield of isolated product. Tf = trifluoromethanesulfonyl.

reactivity than the tetrafluoroborate (Table 2, entries 2 and 3). The triflate salt was the most reactive among the four compounds. It led to 99 % yield of cross-coupling product (Table 2, entry 4), being identical with the corresponding iodide salt. However, when catalyst loading was decreased to 1 mol %, the triflate salt gave a lower yield compared with the iodide salt (Table 2, entry 5). More examples using arylammonium triflates as the electrophilic partners are summarized in Table S1 in the Supporting Information.

With the optimized conditions in hand, we next tested the scope of the cross-coupling reaction (Table 3). Besides *p*-$Me_2NC_6H_4ZnCl$, each of *p*-MeC_6H_4ZnCl, *o*-MeC_6H_4ZnCl, *p*-$MeOC_6H_4ZnCl$, and 2-C_4H_3OZnCl (C_4H_3O = furyl) coupled efficiently with $PhNMe_3^+I^-$ (Table 3, entries 1–5). The hindrance of *o*-MeC_6H_4ZnCl seems not to affect the coupling very much. However, increasing the catalyst loading did significantly enhance the yield (Table 3, entry 3). Bulkier zinc reagent such as 2,6-$(MeO)_2C_6H_3ZnCl$ did not efficiently couple with arylammonium salts. Its reaction with $PhNMe_3^+I^-$ generated only a trace quantity of product. Reaction of *o*-$MeC_6H_4NMe_3^+I^-$ with *p*-$MeOC_6H_4ZnCl$ gave similar yield to $PhNMe_3^+I^-$ (Table 3, entry 6). However, bulkier ammonium salt led to unusual result. A reaction between 2,4,6-$Me_3C_6H_2NMe_3^+OTf^-$ (the corresponding iodide cannot be obtained) and *p*-$MeOC_6H_4ZnCl$ under the same conditions generated 2,4,6-$Me_3C_6H_2NMe_2$ in low yield. Arylammonium iodide salts with electron-donating substituents were highly reactive in the coupling. Both *p*-$MeOC_6H_4NMe_3^+I^-$ and *m*-$MeOC_6H_4NMe_3^+I^-$ reacted efficiently with *p*-MeC_6H_4ZnCl, and afforded the coupling products in excellent yields (Table 3, entries 8 and 9). These

Table 3: Nickel-catalyzed coupling of aryltrimethylammonium iodide salts with arylzinc reagents.[a]



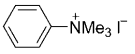
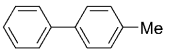
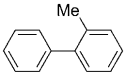
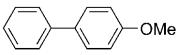
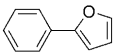
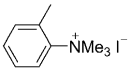
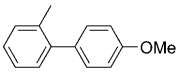
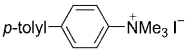
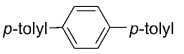
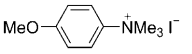
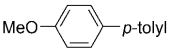
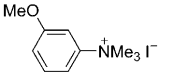
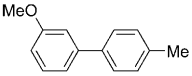
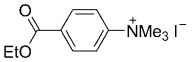
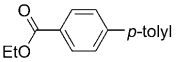
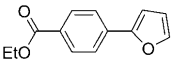
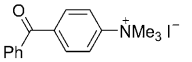
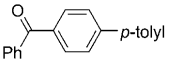
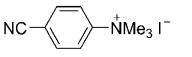
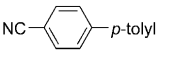
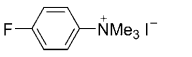
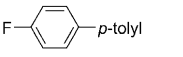
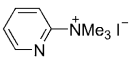
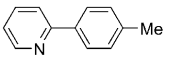
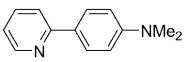
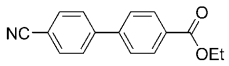
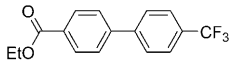
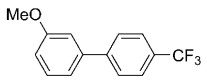
Entry	$ArNMe_3^+I^-$	Product	Yield [%][b]
1	 **1a**	 **4**	91
2	**1a**	 **5**	88
3[c]	**1a**	**5**	95
4	**1a**	 **6**	84
5	**1a**	 **7**	83
6	 **8**	 **9**	83
7	 **10**	 **11**	89
8	 **12**	 **13**	92
9	 **14**	 **15**	96
10	 **16**	 **17**	96
11[d]	**16**	**17**	85
12	**16**	 **18**	92
13	 **19**	 **20**	87
14	 **21**	 **22**	99
15	 **23**	 **24**	34
16	 **25**	 **26**	87
17	**25**	 **27**	81

Table 3: (Continued)

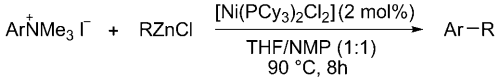
Entry	$ArNMe_3^+I^-$	Product	Yield [%][b]
18[e]	**21**		37
		28	
19[c,e]	**21**	**28**	58
20[f]	**16**	**28**	trace
21	**16**		90
		29	
22	**14**		25
		30	
23[g]	**16**	**17**	92
24[g]	**14**	**15**	93

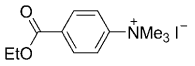
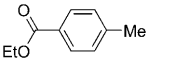
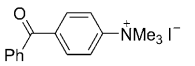
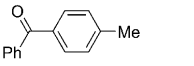
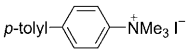
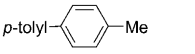
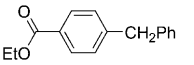
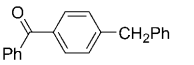
[a] The reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation unless otherwise specified; 1.5 equivalents of arylzinc reagent was employed. [b] Yield of isolated product. [c] 5 mol% of catalyst was employed. [d] Reaction was performed at room temperature. [e] *p*-$EtO_2CC_6H_4ZnI$ was employed. [f] *p*-NCC_6H_4ZnBr was employed. [g] The reaction was carried out on a 5 mmol scale.

results are consistent with those reported in arylammonium Suzuki reaction.[9] The arylammonium salts with an electron-withdrawing group such as COOEt, PhC(O), and CN each showed superior reactivity (Table 3, entries 10–14). Reaction of *p*-$EtO_2CC_6H_4NMe_3^+I^-$ with *p*-MeC_6H_4ZnCl could even be carried out at room temperature although the yield was lower than that at 90 °C (Table 3, entries 10 and 11). We and the Knochel research group previously observed that nitriles are less active as substrates in the coupling with an arylzinc reagent.[3f–h] However, the reaction of *p*-$NCC_6H_4NMe_3^+I^-$ proceeded in a normal fashion when using the present catalyst system (Table 3, entry 14), however, *p*-$FC_6H_4NMe_3^+I^-$ was an exception. Its reaction with *p*-MeC_6H_4ZnCl gave only 34% yield of the cross-coupling product (Table 3, entry 15), along with 1,4-di(*p*-tolyl)benzene (18%) as a side product. This outcome is attributed to the cleavage of the aryl–F bond under the current reaction conditions. If *p*-$ClC_6H_4NMe_3^+I^-$ is employed as an electophilic partner, no simple cross-coupling product can be isolated. Instead, a disubstituted product of *p*-$ClC_6H_4NMe_3^+I^-$ was obtained (Table S2 in the Supporting Information). Pyridyltrimenthylammonium iodide is also a good electrophile for the coupling reaction. Its reaction with *p*- MeC_6H_4ZnCl and *p*-$Me_2NC_6H_4ZnCl$ proceeded in 87% and 81% yield, respectively (Table 3, entries 16 and 17). Arylzinc reagents with an electron-withdrawing group showed lower reactivity. Reaction of *p*-$EtO_2CC_6H_4ZnI$ with either $PhNMe_3^+I^-$ or *p*-$MeOC_6H_4NMe_3^+I^-$ using 2 mol% of $[Ni(PCy_3)_2Cl_2]$ as a catalyst gave only a trace amount of products, and with *p*-$NCC_6H_4NMe_3^+I^-$ only 37% of cross-coupling product was formed (Table 3, entry 18). Increasing catalyst loading to 5 mol% resulted in 58% yield of the product (Table 3, entry 19). Reaction of *p*-NCC_6H_4ZnBr with *p*-$EtO_2CC_6H_4NMe_3^+I^-$ was also unsuccessful. Reaction of *p*-$F_3CC_6H_4ZnCl$ with an activated ammonium such as *p*-$EtO_2CC_6H_4NMe_3^+I^-$ afforded the product in excellent yield, but with a deactivated ammonium salt, *m*-$MeOC_6H_4NMe_3^+I^-$, led to low product yield (Table 3, entries 21 and 22). In addition, the reaction can be carried out on a bigger scale. Treatment of 5 mmol of *p*-$EtO_2CC_6H_4NMe_3^+I^-$ or *m*-$MeOC_6H_4NMe_3^+I^-$ with *p*-MeC_6H_4ZnCl resulted in cross-coupling products in 92% and 93% yields, respectively (Table 3, entries 23 and 24).

We also examined the reactivity of aryltrimethylammonium iodide salts with primary alkylzinc reagents catalyzed by $[Ni(PCy_3)_2Cl_2]$ (Table 4). Reaction of methylzinc chloride

Table 4: Nickel-catalyzed coupling of aryltrimethylammonium iodide salts with alkylzinc reagents.[a]



Entry	$ArNMe_3^+I^-$	Product	Yield [%][b]
1			96
	16	**31**	
2			92
	19	**32**	
3			68
	10	**33**	
4[c]	**10**	**33**	78
5	**16**		89
		34	
6	**19**		76
		35	
7[c]	**19**	**35**	82

[a] The reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation unless otherwise specified; 1.5 equivalents of alkylzinc reagent was employed. [b] Yield of isolated product. [c] 5 mol% of catalyst was employed.

with aryltrimethylammonium iodide salts that incorporate electron-withdrawing substituents proceeded smoothly in the presence of 2 mol% of $[Ni(PCy_3)_2Cl_2]$ and gave the coupling products in excellent yields (Table 4, entries 1 and 2). Reaction of *p*-(*p*-$MeC_6H_4)C_6H_4NMe_3^+I^-$ under the same conditions resulted in lower yield (Table 4, entry 3). This outcome is ascribed to an electronic effect exerted by the substituent on the phenyl ring. Increasing the catalyst loading improved the yield of the product (Table 4, entry 4). Benzylzinc chloride also reacted smoothly with the activated arylammonium iodide salts such as *p*-$EtO_2CC_6H_4NMe_3^+I^-$ and *p*-$PhC(O)C_6H_4NMe_3^+I^-$ (Table 4, entries 5–7). However, the yields are lower than those corresponding with MeZnCl. In addition, reaction of *p*-$PhC(O)C_6H_4NMe_3^+I^-$ with either

*n*BuZnCl or EtZnCl resulted in a mixture of the cross-coupling product and benzophenone. A similar result was obtained in the nickel-catalyzed cross-coupling reaction of *p*-*n*Bu$C_6H_4NMe_3^+I^-$ with *i*PrMgBr.[7]

In summary, a highly efficient process for the nickel-catalyzed cross-coupling of aryltrimethylammonium iodide salts with arylzinc or alkylzinc reagents has been developed. The coupling reaction using arylzinc reagents as nucleophiles displays a broad substrate scope and good functional group tolerance. Meanwhile methyl and benzylzinc reagents were applicable to the coupling with arylammonium iodide salts containing electron-withdrawing substituents.

Experimental Section

A representative procedure (Table 2): Aryltrimethylammonium iodide (0.5 mmol), [Ni(PCy_3)$_2$$Cl_2$] (0.0069 g, 0.01 mmol), and NMP (1.5 mL) were added to a Schlenk tube. To the stirring mixture was added ArZnCl solution (1.5 mL, 0.5 M solution in THF, 0.75 mmol) by syringe. The reaction mixture was stirred at 90 °C (bath temperature) for 8 h and then cooled to room temperature. Water (10 mL) and several drops of acetic acid were successively added. The resulting mixture was extracted with Et_2O (3 × 10 mL) and the extract was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on sillca gel (eluent: petroleum ether or petroleum ether/ethyl acetate 60:1).

Received: January 27, 2011
Revised: March 23, 2011
Published online: April 26, 2011

Keywords: C–N activation · cross-coupling · homogeneous catalysis · nickel · organozinc reagents

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