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Nickel-Catalyzed Cross-Coupling of Non-Activated or Functionalized Aryl Halides with Aryl Grignard Reagents

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Transition-metal-catalyzed cross-coupling reactions are versatile and powerful tools to construct new C-C bonds.^[1,2] Among the cross-coupling reactions, Suzuki, Negishi, and Stille reactions have been studied in more detail due to the better functional group tolerance.^[1,3] However, Kumada cross-coupling offers a more direct access to the desired products and hence is a more atom-economical reaction.^[4-6] Recently, significant advances have been made for transition-metal-catalyzed Kumada cross-couplings by using functionalized Grignard reagents or functionalized halides.^[6-9] For example, it has been found that functionalized Grignard reagents can undergo efficient cross-coupling with aryl bromides or iodides in the presence of palladium compound and appropriate additives.^[6,7] It was also reported that nickel-catalyzed cross-coupling of aryl or alkyl Grignard reagents with functionalized halides can be carried out at mild conditions.^[8] In these reactions, electrophilic substrates are predominately iodides or bromides. Few functionalized chlorides were used in the Kumada coupling due to low reactivity of the C-Cl bond.^[8c,d,9a,e] However, on the other hand, the use of chlorides would economically benefit a number of industrial processes.^[10] Hence, it is of significance to explore new catalytic systems for chloride substrates although several types of nickel and palladium complexes have been reported to catalyze the coupling of Grignard reagents with chlorides effectively.^[11] In addition, the conversion of aryl fluorides is important for the fundamental understanding of the reactivity of very stable bonds, and the selective synthesis of partially fluorinated compounds.^[12] Herein we wish to report efficient coupling of unactivated and deactivated aryl chlorides and fluorides as well as func-

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tionalized aryl chlorides with aryl Grignard reagents catalyzed by new nickel complexes.

Synthesis and characterization of nickel complexes 1a-1dare presented in the Supporting Information. The catalytic activity of complexes 1a-1d in the Kumada reactions was evaluated through reaction of $p-\text{ClC}_6\text{H}_4\text{OMe}$ with $p-\text{MeC}_6\text{H}_4\text{MgBr}$ and the results are listed in Table 1. Each of complexes 1a-1d is catalytically active for the cross-coupling in THF at room temperature. Both 1c and 1d exhibited higher catalytic activity than 1a and 1b under the same conditions. Solvent effect studies showed that both THF and diethyl ether are suitable solvents for this reaction and toluene is poor.



Table 1. Evaluation of catalytic activity of complexes 1a-1d in the Kumada reaction.^[a]

	MeO He MgBr cat. MeO MeO MeO					
Entry	Cat. [mol%]	Solvent (reaction time [h])	Yield [%] ^[b]			
1	1a	THF (24)	82			
2	1a	toluene (24)	18			
3	1b	THF (24)	78			
4	1c	THF (24)	91			
5	1d	THF (24)	95			
6	1d	Et ₂ O (12)	95			

[a] Reactions were carried out with $1 \mod \%$ catalyst, 0.5 mmol *p*-ClC₆H₄OMe and 0.75 mmol *p*-MeC₆H₄MgBr at 25 °C. [b] Isolated product yields.

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Complexes 1c and 1d also efficiently catalyze reaction of *p*-ClC₆H₄OMe with *o*-MeC₆H₄MgBr or 1-C₁₀H₇MgBr $(C_{10}H_7 = naphthyl)$, giving cross-coupling products in excellent yields (entries 1-4, Table 2). The cross-coupling of PhCl

Table 2. Reaction of ArMgBr with aryl chlorides or fluorides catalyzed by 1c and 1d.^[a] Ar

	R	X + ArMgBr E = CH or N	Cat. R	
Entry	Aryl halide	Ar	Catalyst (mol%)	Yield [%] ^[b]
1	<i>p</i> -MeOC ₆ H ₄ Cl	o-MeC ₆ H ₄	1c (1)	86
2	p-MeOC ₆ H ₄ Cl	o-MeC ₆ H ₄	1d (1)	90
3	<i>p</i> -MeOC ₆ H ₄ Cl	1-naphthyl	1c (1)	86
4	p-MeOC ₆ H ₄ Cl	1-naphthyl	1d (1)	87
5	PhCl	p-MeC ₆ H ₄	1c (0.5)	97
6	PhCl	p-MeC ₆ H ₄	1d (0.5)	99
7	PhCl	<i>p</i> -MeOC ₆ H ₄	1c (0.5)	87
8	PhCl	<i>p</i> -MeOC ₆ H ₄	1c (1)	96
9	PhCl	<i>p</i> -MeOC ₆ H ₄	1d (0.5)	93
10	2-ClC ₅ H ₄ N	p-MeC ₆ H ₄	1d (0.5)	98
11	2-ClC ₅ H ₄ N	o-MeC ₆ H ₄	1d (0.5)	90
12	o-MeOC ₆ H ₄ Cl	p-MeC ₆ H ₄	1c (2)	53
13	PhF	p-MeC ₆ H ₄	1c (2)	99
14	PhF	<i>p</i> -MeC ₆ H ₄	1d (2)	99
15	PhF	<i>p</i> -MeOC ₆ H ₄	1c (2)	88
16	PhF	<i>p</i> -MeOC ₆ H ₄	1c (3)	87
17	PhF	<i>p</i> -MeOC ₆ H ₄	1d (2)	94
18	<i>p</i> -MeOC ₆ H ₄ F	p-MeC ₆ H ₄	1c (2)	96
19	<i>p</i> -MeOC ₆ H ₄ F	<i>p</i> -MeC ₆ H ₄	1d (2)	99
20	<i>p</i> -MeOC ₆ H ₄ F	o-MeC ₆ H ₄	1c (2)	90
21	p-MeOC ₆ H ₄ F	$o-MeC_6H_4$	1d (2)	92

[a] Reactions were carried out on a 0.5 mmol scale in Et₂O at 25 °C for 12 h, 1.5 equiv ArMgBr were used. [b] Isolated product yields.

with p-MeC₆H₄MgBr requires less catalyst loading, only 0.5 mol% of complexes 1c and 1d driving the reaction to go to completion (entries 5 and 6,

Table 2). However, reactivity of p-MeOC₆H₄MgBr appears to be lower, as 1 mol% of 1c is necessary to complete the reaction between p-MeOC₆H₄MgBr and PhCl (entries 7 and 8, Table 2). 2-Chloropyridine showed similar reactivity to PhCl, its reaction with p-MeC₆H₄MgBr or 0-MeC₆H₄MgBr can be completed in the presence of 0.5 mol% of **1d** (entries 10 and 11, Table 2). For sterically hindered reactants the catalysts led to poor results. Reaction of pwith 2,4,6-ClC₆H₄Me Me₃C₆H₂MgBr using 1 mol % of 1c as catalyst formed trace cross-coupling product, and o-ClC₆H₄OMe with р-MeC₆H₄MgBr under the same

Table 3. Optimization of reaction conditions.^[a,b]

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conditions produced 1-methoxy-2-(p-tolyl)benzene in 53% yield (entry 12, Table 2). Both 1c and 1d can also activate C-F bonds in unactivated and deactivated aryl fluorides (entries 13-21, Table 2). These reactions of C-F bond activation require more catalyst loading due to low reactivity of C-F bond. 2 mol% of 1c or 1d led to cross-coupling of PhF or *p*-MeOC₆H₄F with *p*-MeC₆H₄MgBr in almost quantitative yields. The reaction of p-MeOC₆H₄MgBr with PhF or o-MeC₆H₄MgBr with *p*-MeOC₆H₄F also gave satisfactory results in the presence of 2 mol% of 1c or 1d. In addition, it should be indicated that each reaction gave homocoupling product of Grignard reagent besides cross-coupling product. For example, reaction of p-ClC₆H₄OMe with p- MeC_6H_4MgBr catalyzed by 1 mol% 1c yielded 9% (p- MeC_6H_4)₂ (calculated based on the amount of Grignard reagent added) besides the cross-coupling product.

With the purpose of understanding the catalytic mechanism, we tried to isolate the catalyst intermediates. In a reaction of p-MeC₆H₄MgBr with excess p-ClC₆H₄OMe in the presence of 20 mol% of 1c, we obtained a nickel species after removing the coupling products and magnesium halide by washing with toluene and water, respectively. ¹H NMR spectrum showed that the nickel species contains the phosphine ligand and C₆H₄OMe part in about 1:1 ratio. The presence of C₆H₄OMe may be through oxidative addition of p-ClC₆H₄OMe to the low-valence nickel. Only one phosphine ligand in the complex implies that the nitrogen atoms of the ligand coordinate to the nickel center for stabilizing the complex.

The high catalytic activity of complexes 1c and 1d in the C-Cl- and C-F-bond activation inspirited us to try reactions with functionalized aryl chlorides. Preliminary experiments showed that only trace cross-coupling product was formed in the reaction of *p*-ClC₆H₄COOEt with *p*-MeC₆H₄MgBr in

	EtOOC		
Entry	Additive	Solvent	Yield [%] ^[e]
1	LiBr (1.2 equiv)	THF	28
2	LiCl (1.2 equiv)	THF	8
3	LiCl (1.2 equiv)	THF+NMP 2:1	33
4	LiCl (4 equiv)	THF+NMP 2:1	62
5	LiBr (1.2 equiv), ZnCl ₂ (10 mol %)	THF+NMP 2:1	trace
6	LiBr (1.2 equiv), H ₂ O (10 mol%)	THF+NMP 2:1	trace
7	LiBr (1.2 equiv), ZnCl ₂ (10 mol %), H ₂ O (10 mol %)	THF	25
8	$ZnCl_2$ (10 mol %), H ₂ O (10 mol %)	THF+NMP 2:1	70
9	LiBr (1.2 equiv), ZnCl ₂ (10 mol %), H ₂ O (10 mol %)	THF+NMP 2:1	74
10	LiCl(1.2 equiv), ZnCl ₂ (10 mol %), H ₂ O (10 mol %)	THF+NMP 2:1	77
11	LiCl(1.2 equiv), ZnCl ₂ (10 mol %), NaOH (10 mol %)	THF+NMP 2:1	74
12 ^[c]	LiCl (1.2 equiv), ZnCl ₂ (10 mol %), H ₂ O (10 mol %)	THF+NMP 2:1	87
13 ^[d]	LiCl (1.2 equiv), ZnCl ₂ (10 mol%), H ₂ O (10 mol%)	THF+NMP 2:1	92

[a] Reactions were performed with 0.5 mmol p-ClC₆H₄CO₂Et and 0.66 mmol p-MeC₆H₄MgBr according to the conditions indicated by the above equation unless otherwise stated. [b] After the reaction mixtures were stirred for 2 h, 0.66 additional equiv of p-MeC₆H₄MgBr were added, and stirring was continued for 2 h. [c] Reactions were run at 55 °C. [d] 5 mol% of 1c was used and the reaction was run at 55 °C. [e] A mixture of the coupling product and unreacted ethyl 4-chlorobenzonate was obtained by column chromatography. The yields were calculated on the basis of weight and integration ratio of the ¹H NMR spectral signals of the mixtures.

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Table 4. Cross-coupling of ArMgBr with functionalized aryl halides catalyzed by 1c and 1d.^[a]

$\begin{array}{c} ArX + \begin{array}{c} & \\ R \end{array} \end{array} \xrightarrow{25 \circ C, 4h} \begin{array}{c} \\ R \end{array}$						
Entry	ArX	R	Catalyst (mol%)	Additive	Solvent	Yield [%] ^[d]
1	EtOOC Br	<i>p</i> -Me	1c (5)	-	THF+NMP 4:3	99
2	EtOOC-	<i>p</i> -Me	1c (5)	-	THF+NMP 4:3	96
3 ^[b]	EtOOC -CI	<i>p</i> -Me	1d (2.5)	$ZnCl_2$ (10 mol %), H_2O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	90
4 ^[b]	EtOOC -CI	<i>p</i> -Me	1d (5)	$ZnCl_2$ (10 mol %), H_2O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	95
5 ^[b]	EtOOC -CI	o-Me	1d (5)	$ZnCl_2$ (10 mol %), H_2O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	99
6 ^[b]	EtOOC -CI	p-MeO	1d (5)	$ZnCl_2$ (10 mol %), H_2O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	89
7 ^[b,c]	Ph Cl	<i>p</i> -Me	1c (5)	ZnCl ₂ (10 mol %), H ₂ O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	85
8 ^[b,c]	Ph	<i>p</i> -Me	1c (5)	$ZnCl_2$ (10 mol %), H ₂ O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	92
9 ^[b,c]	Ph CI	<i>p</i> -Me	1d (5)	ZnCl ₂ (10 mol %), H ₂ O (10 mol %), LiCl (1.2 equiv)	THF+NMP 2:1	88
10 ^[b,c]		<i>p</i> -Me	1d (5)	ZnCl ₂ (10 mol %), H ₂ O (10 mol %), LiCl (1.2 equiv)	THF $+$ NMP (2:1)	91
11		<i>p</i> -Me	1c (5)	ZnCl ₂ (30 mol %), LiCl (1.2 equiv)	THF+NMP 4:3	87
12		<i>p</i> -Me	1d (5)	ZnCl ₂ (30 mol %), LiCl (1.2 equiv)	THF+NMP 4:3	91
13	p-MeC ₆ H ₄ N	<i>p</i> -Me	1c (5)	ZnCl ₂ (30 mol %), LiCl (1.2 equiv)	THF+NMP 4:3	81
14	<i>p</i> -MeC ₆ H₄N CI	p-Me	1d (5)	ZnCl ₂ (30 mol %), LiCl (1.2 equiv)	THF+NMP 4:3	86
15	O Et ₂ N	<i>p</i> -Me	1c (2.5)	-	THF	91
16	O Et ₂ N	<i>p</i> -Me	1d (2.5)	-	THF	96
17	Br	<i>p</i> -Me	1c (2.5)	-	THF	97
18	tBuOOC CI	<i>p</i> -Me	1c (2.5)	LiCl (1.2 equiv)	THF $+$ NMP (2:1)	85

MgBr

cat

[a] Reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation, 1.32 equiv of p-MeC₆H₄MgBr were used unless otherwise stated. [b] After the reaction mixtures were stirred for 2 h, additional 0.66 equiv of p-MeC₆H₄MgBr was added, and stirring was continued for 2 h. [c] Reactions were carried out at 55 °C. [d] Isolated product yields.

the presence of 2.5 mol % **1c** in THF or toluene at room temperature. We also found that no addition reaction of *p*-MeC₆H₄MgBr to COOEt group occurred in the course of the reaction, *p*-ClC₆H₄COOEt being recovered almost quantitatively. This makes it possible to improve the reaction through changes of reaction conditions such as additives, solvents and reaction temperature. The results are listed in Table 3. Each of the **1c**-catalyzed reaction of *p*-ClC₆H₄COOEt with *p*-MeC₆H₄MgBr in THF in the presence of additives such as Et₃N, TMEDA, MgBr₂ and ZnCl₂ gave trace cross-coupling products. However, in the presence of 1.2 equiv of LiBr or LiCl the reaction afforded the crosscoupling product in 8–33% yields. Further experiments

showed that 4 equiv of LiCl can lead to 62% yield of product in a mixture of THF and NMP (entries 1–4, Table 3). These results encouraged us to explore other additives or additive combinations. The combinations of LiBr/ZnCl₂ and LiBr/H₂O are noneffective, and the combination of 10% ZnCl₂ and 10% H₂O showed good results in THF/NMP solvent mixtures (entries 5–8, Table 3). Further investigations indicated that a combination of 10% ZnCl₂, 10% H₂O and 1.2 equiv of LiBr or LiCl in a mixture of THF and NMP gave the best results (entries 9 and 10, Table 3). NaOH can be used to replace H₂O as an additive, which led to similar results as with H₂O (entry 11, Table 3). Elevated reaction temperature can further promote the reaction. For example, at 55 °C 2.5 mol% of 1c can lead to 87% yield of cross-coupling product, and 5 mol% of 1c gave 92% yield of crosscoupling product. In addition, after reaction of p-ClC₆H₄COOEt with 1.32 equiv of p-MeC₆H₄MgBr in the presence of catalyst and additives for 2 h, injection of 0.66 additional equivalents of p-MeC₆H₄MgBr resulted in better cross-coupling results. A minor part of the excess Grignard reagent was transformed into the homocoupling product (7.5% based the amount of the Grignard reagent added in the reaction p-ClC₆H₄COOEt with p-MeC₆H₄MgBr catalyzed by the adduct of 1c, ZnCl₂ and H₂O), and most of them were hydrolyzed after the reaction. Only if in the presence of excess Grignard reagent in the reaction system, can the aryl chloride be completely consumed. In other words, enough concentrations of Grignard reagent must be maintained during the whole reaction process to ensure for the reaction to go to completion.

Following the success of the reaction of p-ClC₆H₄COOEt with p-MeC₆H₄MgBr, we tested reactions of different functionalized aryl halides with aryl Grignard reagents catalyzed by complexes 1c and 1d. The 1c-catalyzed reaction of more active halides, such as *p*-BrC₆H₄COOEt and *p*- IC_6H_4COOEt , with *p*-MeC₆H₄MgBr in a THF/NMP solvent mixture does not require any additives, affording cross-coupling products in excellent yields (entries 1 and 2, Table 4). Complex 1d showed higher catalytic activity than complex **1c.** The former can efficiently catalyze reactions of *p*-ClC₆H₄COOEt with *p*-MeC₆H₄MgBr, *o*-MeC₆H₄MgBr and p-MeOC₆H₄MgBr, respectively, in the presence of ZnCl₂, H_2O and LiCl at room temperature (entries 3–6, Table 4). Both 1c and 1d also catalyze cross-coupling of (2-chlorophenyl)phenylmethanone and (4-chlorophenyl)phenylmethanone with p-MeC₆H₄MgBr in the presence of ZnCl₂, H₂O and LiCl at 55°C, giving 85-92% yields of coupling products (entries 7-10, Table 4). Both p-ClC₆H₄CN and p-ClC₆H₄CH=NC₆H₄Me-4 exhibited a little different reactivity from p-ClC₆H₄COOEt and p-ClC₆H₄COPh. The reactions of p-ClC₆H₄CN and p-ClC₆H₄CH=N(p-MeC₆H₄) with p-MeC₆H₄MgBr catalyzed by 1c and 1d require the presence of 30% of ZnCl₂ and 1.2 equiv of LiCl in THF/NMP. The yields of the cross-coupling product range from 81 to 91% depending on the substrates and catalysts (entries 11-14, Table 4). It is surprising that the reaction of p- $ClC_6H_4CONEt_2$ with *p*-MeC₆H₄MgBr catalyzed by 1c or 1d does not require any additives and proceeded smoothly in THF at room temperature, giving N,N-diethyl-4-(p-tolyl)benzamide in excellent yields (entries 15 and 16, Table 4).

Nakamura and co-workers corroborated that in the Kumada cross-coupling catalyzed by a nickel complex bearing a P,O-ligand Ni/Mg bimetallic cooperation promotes the C–X-bond activation.^[11d,e] In our catalytic reaction a Ni/Mg adduct may be similarly formed during the reaction process. However, in the reaction of functionalized aryl chlorides with a Grignard reagent the functional groups appear to combine with the Ni/Mg adduct through coordination, which leads to a decrease in the catalytic activity of the Ni/Mg adduct. The difference of coordination power of the

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functional groups to the Ni/Mg center results in a decrease of the catalytic activity of the Ni/Mg adduct in different extent. This can be verified through comparison of the reaction of p-ClC₆H₄COOEt and p-ClC₆H₄COOtBu with p-ClC₆H₄MgBr under the same conditions, the former giving 33% yield of cross-coupling product (entry 3, Table 3), while the latter giving 85% yield of product due to steric hindrance which prevents combination of COOtBu with the Ni/Mg center (entry 18, Table 4). The use of LiX may partly prevent coordination of the functional groups in the aryl chlorides to the Ni/Mg adduct through complexation of the Li⁺ with the functional groups. The addition of ZnCl₂ and H₂O could lead to formation of a Zn-O-Ni bridged complex,^[8c] which is a better catalyst for the reaction of functionalized aryl chlorides. In order to find evidences for Zn-O-Ni complex formation, we mixed red-brown complex 1c, 1 equiv of ZnCl₂ and 1 equiv of H₂O in THF. After stirring for 6 h and then removing THF, a yellow-orange powder was obtained. This solid species is soluble in toluene and showed different ¹H NMR spectrum from complex **1c**. More importantly, this species exhibited close activity to in situ formed those as shown in Table 3 in catalyzing the reaction of ethyl 4-chlorobenzoate with p-MeC₆H₄MgBr (74% yield was achieved when we used the solid adduct of 1c, ZnCl₂ and H₂O as catalyst). Attempts to recrystallize the compound for X-ray diffraction analysis were unsuccessful.

In summary, we have developed new nickel catalysts for the Kumada reaction. The nickel complexes can efficiently catalyze cross-coupling of unactivated and deactivated aryl chlorides and fluorides as well as functionalized aryl chlorides with aryl Grignard reagents under mild conditions, giving cross-coupling products in excellent yields. The work significantly expands the substrate scopes of Kumada crosscoupling reactions. Studies on alkyl–aryl coupling of functionalized substrates using these catalysts are in progress.

Experimental Section

A representative procedure for the coupling of functionalized aryl chlorides: A Schlenk tube was charged with nickel complex (required amount), NMP (1.5 mL), aryl chloride (0.5 mmol) and additives successively. To the mixture was slowly added a solution of ArMgBr (2 mL, 0.33 m in THF, 0.66 mmol) at 25 °C with stirring. After stirring at this temperature for 2 h, additional ArMgBr (1 mL, 0.33 m in THF, 0.33 mmol) was slowly added. The resulting solution was stirred at 25 °C for 2 h and then quenched with water. The mixture was extracted with diethyl ether (3×5 mL). The combined organic phases were dried over MgSO₄, concentrated by rotary evaporation and purified by column chromatography on silica gel.

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