ChemPubSoc Europe

DOI: 10.1002/chem.201505106

CHEMISTRY
A European Journal
Communication

Homogeneous Catalysis

Nickel-Catalyzed Cross-Coupling of Organolithium Reagents with (Hetero)Aryl Electrophiles

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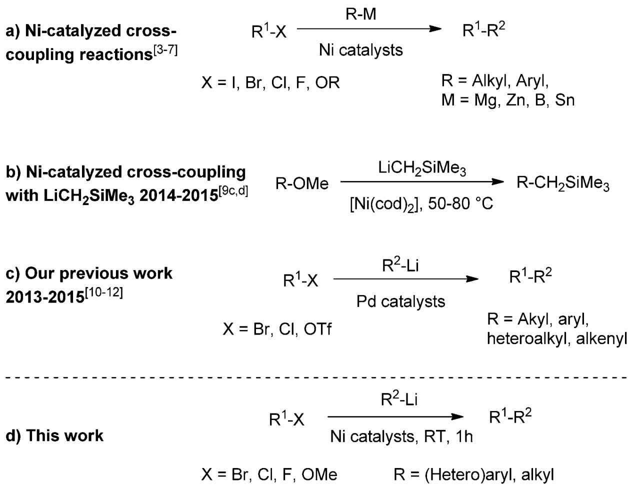
Abstract: Nickel-catalyzed selective cross-coupling of aromatic electrophiles (bromides, chlorides, fluorides and methyl ethers) with organolithium reagents is presented. The use of a commercially available nickel *N*-heterocyclic carbene (NHC) complex allows the reaction with a variety of (hetero)aryllithium compounds, including those prepared via metal-halogen exchange or direct metallation, whereas a commercially available electron-rich nickel-bisphosphine complex smoothly converts alkyllithium species into the corresponding coupled product. These reactions proceed rapidly (1 h) under mild conditions (room temperature) while avoiding the undesired formation of reduced or homocoupled products.

In the ongoing search for more efficient, environmentally benign and economically sustainable processes, current research in cross-coupling methodologies has shown a growing interest in the use of earth-abundant metal-based catalysts.[1] Although palladium is applied in the majority of these processes, catalytic systems based on iron, nickel, or cobalt have proven suitable alternatives in several cases. In particular, the use of nickel has witnessed a rapid growth owing to its low cost and unique properties.[2] Nickel undergoes oxidative addition more readily than palladium although reductive elimination is correspondingly more difficult.[2b,c] Ni^0/Ni^{II} catalytic cycles are well known,[2c] but Ni^I and Ni^{III} oxidation states[2d] can be also accessed, allowing for different modes of reactivity and for radical mechanisms to operate.

Nickel has been extensively used in cross-coupling of organoboron and organozinc reagents with organic halides (Scheme 1 a).[3] For example, a highly efficient nickel-catalyzed method for the synthesis of heterobiaryls at low temperature described by the group of Hartwig highlights the potential of nickel in Suzuki–Miyaura reactions.[4] Since the early reports by Kumada and co-workers in 1972, Grignard reagents in combination with nickel are known to be effective in the cross-coupling with aryl halides,[5] and these organometallic reagents were also the first to be efficiently employed in reactions with the less reactive aromatic ethers.[6a–c] Various groups have further developed the use of Grignard reagents and other nucleophiles, including organozinc and organoboron compounds, in nickel-catalyzed cross-coupling with aryl[6d–f] and benzyl ethers[6g] (Scheme 1 a). Additionally, nickel has also been found to activate very strong C–F bonds.[7] Thus, the coupling of aromatic fluorides with organometallic compounds has been reported, although activated fluoroarenes or polyfluorinated aromatic substrates are usually employed.[7c] Some of these reactions suffer from competing isomerization of the alkyl coupling partners.[7d]



Scheme 1. Nickel-catalyzed cross-coupling methodologies.

In sharp contrast, the direct use of organolithium reagents, among the most versatile and widely used reagents in organic synthesis,[8] in nickel-catalyzed cross-couplings reactions has been limited to the polymerization of lithiated (hetero)-arenes,[9a,b] the coupling of (trimethylsilyl)methyllithium with aromatic ethers (Scheme 1 b),[9c,d] and the homo-coupling of arylbromides although the scope of the latter is limited so far.[9e] Despite these important advances, a general method for the nickel-catalyzed cross-coupling of alkyl and (hetero)aryllithium reagents with aryl(pseudo)halides remains elusive.

Organolithium compounds[8] are commercially available or readily accessible by lithium–halogen exchange and they are often employed as precursors for other organometallic compounds (Mg, B, Zn, Sn) used in cross-coupling reactions. Their direct use drastically reduces the amount of byproducts with the light lithium halide being the only stoichiometric reaction waste. Our group recently described the direct use of these re-

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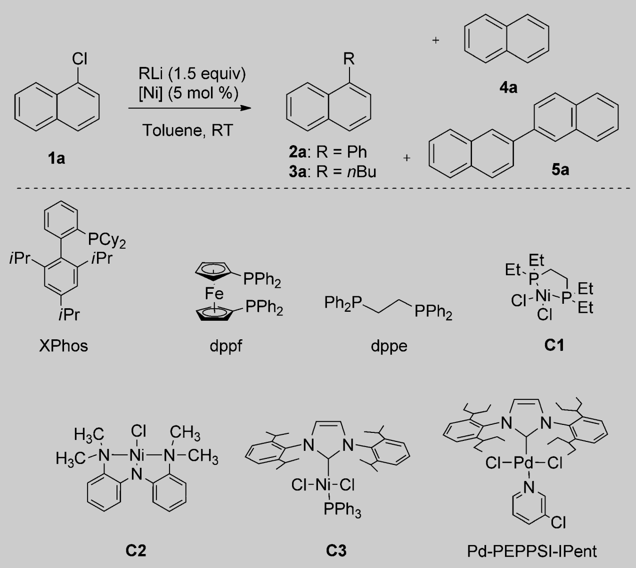
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201505106.

agents in palladium-catalyzed cross-coupling under mild conditions of a wide variety of organic bromides,[10] chlorides,[11] and triflates,[12] providing high yields and selectivities (Scheme 1 c).[13] Considering the advantages associated with the use of nickel-based catalytic systems, the development of a general nickel-catalyzed cross-coupling with easily accessible organolithium reagents will provide a highly desirable alternative to existing methodologies. Moreover, since the palladium-catalyzed methods with these reagents are based on the use of aryl bromides, chlorides, and triflates, we were interested in exploring the coupling of less reactive fluorides and aromatic ethers, the latter being obtained from a pool of materials entirely distinct from aryl halides.

Herein, we report that the use of a commercially available nickel *N*-heterocyclic carbene (NHC) or bisphosphine complex allows for the selective cross-coupling of organolithium compounds with aryl bromides, chlorides, fluorides, and methyl ethers in high selectivity under mild conditions (RT) and within short reaction times (1 h; Scheme 1 d).

In preliminary studies, we focused on reactions between either *n*BuLi or PhLi and 1-chloronaphthalene (**1 a**) in toluene at RT (Table 1). Surprisingly, the use of $[\mathrm{Ni(cod)_2}]$ (cod = 1,5-cyclooctadiene), which has previously been shown to be effective for the cross-coupling of (trimethylsilyl)methyllithium with aryl ethers,[9c,d] gave no conversion into the desired products **2 a** or **3 a**. (Table 1, entries 1 a,b). Adding a phosphine ligand such as 1,2-bis(diphenylphosphino)ethane (dppe) to the nickel catalyst gave the same disappointing result for *n*BuLi (Table 1, entry 2 a) and 51 % conversion, along with dehalogenated side product **4 a**, for PhLi (entry 2 b). Considering these results and the fact that $[\mathrm{Ni(cod)_2}]$ requires rigorous air-free conditions, hampering both large-scale applications and optimization efforts, we turned our attention to nickel(II) catalysts. Low to moderate conversions and selectivities were observed when $[\mathrm{NiCl_2(dme)}]$ (dme = dimethoxyethane) or $[\mathrm{NiCl_2(PPh_3)_2}]$ were used (Table 1, entries 3 a–4 b). Using more electron rich and bulky phosphines ($\mathrm{PCy_3}$[14] or XPhos[15]) resulted in higher conversion, but the selectivity for **2 a** or **3 a** remained unsatisfactory (Table 1, entries 5 a–6 b). Subsequently, we investigated the effect of common bidentate phosphines, which have been reported to impart high activity in related nickel-catalyzed cross-coupling reactions with other organometallics. The use of $[\mathrm{NiCl_2(dppe)}]$[16] and $[\mathrm{NiCl_2(dppf)}]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene)[4] resulted in even higher conversions but dehalogenation remained substantial (Table 1, entries 7 a–8 b). Encouraged by these results, we studied variations in the ligand structure and we found that the use of commercial nickel complex $[\mathrm{NiCl_2(depe)}]$ (**C1**; depe = bis(diethylphosphino)ethane)[17] bearing a bidentate alkylphosphine, led to full conversion in the reaction with both *n*BuLi and PhLi with excellent selectivity toward the cross-coupled products **2 a** or **3 a** (Table 1, entries 9 a,b). The nitrogen-based tridentate ligand **C2** (Table 1, entries 10 a,b)[18] was not efficient for this transformation. Remarkably, the use of Pd-PEPPSI-IPent (Table 1, entry 12), as well as other palladium-based catalysts (not shown) in the reaction of *n*BuLi gave rise to lower selectivity than that observed with the nickel catalyst **C1**.

Table 1. different ligands.



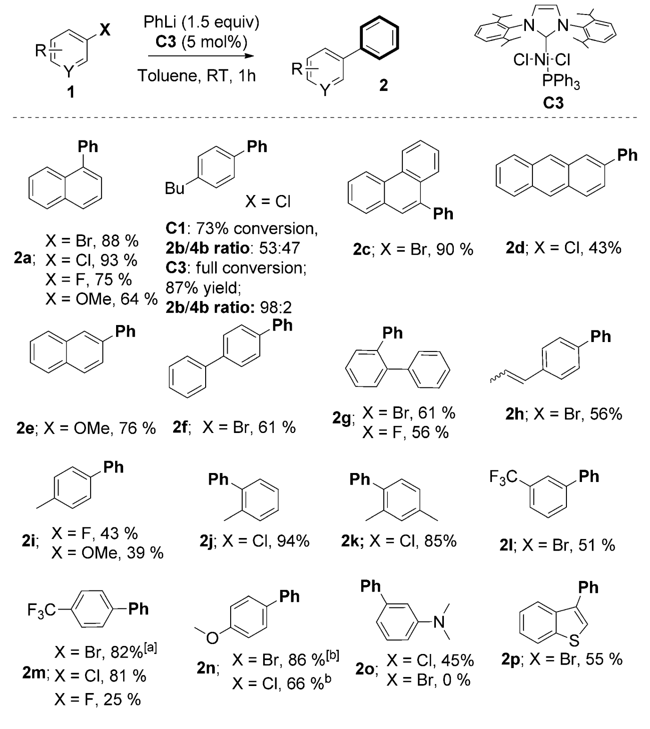
Entry[a]	R	Catalyst	Conv. [%][b]	**2 a/3 a:4 a:5 a**[b]
1 a	*n*Bu	$[\mathrm{Ni(cod)_2}]$	2	–
1 b	Ph		0	–
2 a	*n*Bu	$[\mathrm{Ni(cod)_2}]$/dppe	3	–
2 b	Ph		51	53:47:0
3 a	*n*Bu	$[\mathrm{NiCl_2(dme)}]$	5	–
3 b	Ph		39	85:15:0
4 a	*n*Bu	$[\mathrm{NiCl_2(PPh_3)_2}]$	40	42:40:18
4 b	Ph		30	90:10:0
5 a	*n*Bu	$[\mathrm{NiCl_2(PCy_3)_2}]$	68	25:60:15
5 b	Ph		> 99	68:30:2
6 a	*n*Bu	$[\mathrm{NiCl_2(dme)}]$/Xphos	69	15:46:23
6 b	Ph		33	67:33:0
7 a	*n*Bu	$[\mathrm{NiCl_2(dppe)}]$	> 99	93::7:0
7 b	Ph		86	73:25:2
8 a	*n*Bu	$[\mathrm{NiCl_2(dppf)}]$	85	52:35:8
8 b	Ph		92	79:15:6
9 a	*n*Bu	**C1**	> 99	94:6:0
9 b	Ph		> 99	95:1:4
10 a	*n*Bu	**C2**	36	11:89:0
10 b	Ph		98	58:42:0
11 a	*n*Bu	**C3**	72	57:43:0
11 b	Ph		> 99	> 99:0:0
11 c[c]	Ph		> 99	> 99:0:0
11 d[d]	Ph		> 99	> 99:0:0 (98 % yield)
11 e[e]	Ph		30	> 99:0:0
12	*n*Bu	Pd-PEPPSI-Ipent	> 99	86:14:0

[a] Conditions: *n*-Butyllithium (0.45 mmol, 1,6 M in hexanes diluted with toluene to a final concentration of 0.45 M) or phenyllithium (0.45 mmol, 1.8 M solution in dibutyl ether diluted with toluene to a final concentration of 0.5 M) was added to a solution of 2-chloronaphthalene (0.3 mmol) in toluene (1,5 mL) over 1 h. [b] Conversion and **2 a/3 a:4:5** ratios determined by GC analysis. [c] Using 0.5 mol % of catalyst. [d] 10 mmol (1.63 g) scale reaction using 1.5 mol % of catalyst. [e] Using 0.25 mol % of catalyst.

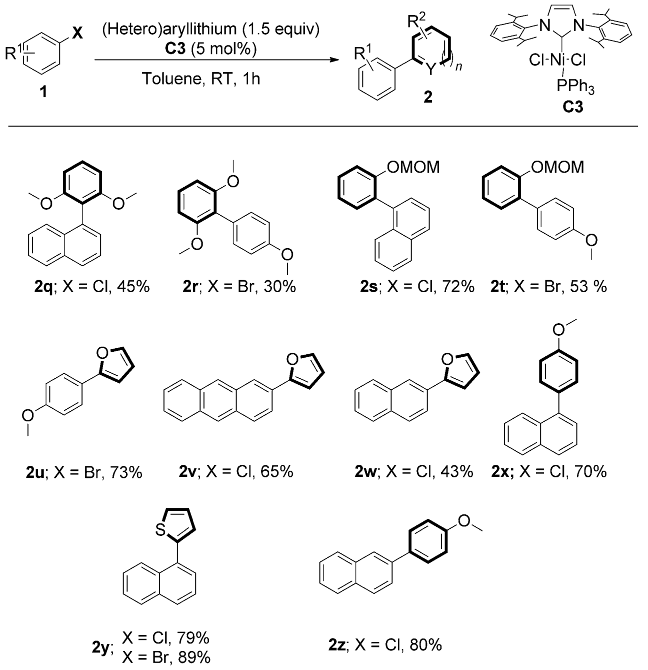
We then explored the effectiveness of catalyst **C1** with respect to a less reactive, non-π-extended aryl chloride, such as 1-butyl-4-chlorobenzene **1 b** (Scheme 2), but incomplete conversion was observed in the case of PhLi, alongside a large amount of *n*-butylbenzene **4 b** (Scheme 2). As neither elevated nor lower temperatures improved this result, further screening of nickel catalysts was carried out. We found that the use of commercially available nickel(II) complex **C3**,[9a] bearing a *N*-heterocyclic carbene, was key to restoring the conversion (87 % yield of isolated product) and selectivity (98:2) toward **2 b** (Scheme 2). Catalyst **C3** also gave full conversion with high selectivity in the reaction of **1 a** with PhLi (Table 1, entry 11 b), allowing a decrease in the catalyst loading to 0.5 mol % (entry 11c). Moreover, when this reaction was performed on a larger scale (10 mmol, 1.63 g) in the presence of 1.5 mol % of catalyst **C3**, **2 a** was still obtained as the exclusive product in excellent yield (98 % isolated product). The use of **C3** in the reaction of **1 a** with *n*BuLi afforded the desired compound **3 a**, albeit with decreased conversion and selectivity compared to **C1** ((Table 1, entry 11 a).

With two optimized catalyst systems (**C3** for (hetero)aryllithium and **C1** for alkyllithium, respectively) we examined the generality of this reaction. A broad range of aryl bromides, chlorides, fluorides, and methoxyarenes could be coupled with PhLi, using **C3** as catalyst (Scheme 2). Polyaromatic compounds showed high reactivity and could be transformed into the coupled products in good to high yields with excellent selectivity (**2 a**, **2 c**–**e**). Substrates containing two aromatic groups can also be transformed selectively (**2 f**, X = Br, and **2 g**, X = Br, F). It is important to note that high reactivity was also found for simple phenyl halides or methyl ethers, regardless of the electronic nature or the leaving group employed (**2 i**–**o)**. As shown for **2 g**, **2 j**, and **2 k**, the presence of an *ortho* substituent did not significantly hamper the cross-coupling. A substrate containing an olefin (**1 h**) was also readily converted into the corresponding product **2 h** with high selectivity (Scheme 2). Trifluoromethylated compounds, which are very important in the agrochemical and pharmaceutical industries,[19] were also suitable substrates, furnishing the corresponding products **2 l** and **2 m** in moderate to good yield. As expected, C–Br and C–Cl bonds are more reactive than a C–O bond, allowing the selective coupling of 4-bromo- or 4-chloroanisole at 0 °C, leaving the methoxy group untouched (**2 n**). Only dehalogenation was observed in the reaction of 3-bromo-*N*,*N*-dimethylaniline **1 o** with PhLi. However, the corresponding chloride provided biaryl **2 o** in 45 % yield. A sulfur-containing heterocycle was also coupled, affording compound **2 p** with high selectivity.

We next examined the compatibility of our catalytic system with the most efficient procedures to access (hetero)aryllithium species, which include direct metalation[20] and halogen–lithium exchange[8] (Scheme 3). Hindered bis-*ortho*-substituted (2,6-dimethoxyphenyl)lithium, prepared by directed lithiation, undergoes cross-coupling with 1-chloronaphthalene and electron-rich 4-bromoanisole providing biaryls **2 q** and **2 r**, without the need to increase the temperature or reaction time. More-



Scheme 2. Nickel-catalyzed cross-coupling of phenyllithium with (hetero)aryl (pseudo)halides. [a] Conditions: Phenyllithium (0.75 mmol, 1.8 M solution in dibutyl ether diluted with toluene to a final concentration of 0.6 M) was added to a solution of organic (pseudo)halide (0.5 mmol) in toluene (1.5 mL) over 1 h; yields refer to product isolated by column chromatography; [b] reaction performed at 0 °C.

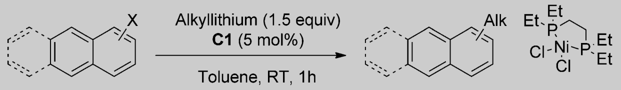


Scheme 3. Nickel-catalyzed cross-coupling of (hetero)aryllithium reagents with aryl halides. Conditions: Aryllithium (0.75 mmol, diluted with toluene to a final concentration of 0.45 M) was added to a solution of organic halide (0.5 mmol) in toluene (1.5 mL) over 1 h; >90 % selectivity to **2** vs. dehalogenated + homocoupled products; yields refer to product isolated by column chromatography.

over a methoxymethyl (MOM) protecting group could be tolerated at the *ortho* position of the organolithium reagent, allowing for an easy *ortho*-lithiation/cross-coupling sequence to afford the corresponding MOM-protected phenol (**2s**, **2t**). Furyllithium, obtained by direct lithiation of furan, smoothly couples to provide compounds **2u–w** with good yields and high selectivities. Organolithium compounds, obtained through halogen–lithium exchange, could also be used as exemplified in the preparation of **2x** and **2z**. Importantly, commercially available 2-thienyllithium, which, according to our previous study,[10a] requires the addition of stoichiometric amounts of tetramethylethylenediamine (TMEDA) as activating agent and elevated temperatures, reacted with 1-chloro- and 1-bromonaphthalene at room temperature without the use of any additive (**2y**).

With an efficient procedure for aryl–aryl cross-coupling in hand, we turned our attention to the use of alkyllithium compounds (Table 2).[21] A range of polyaromatic chlorides and fluorides were regioselectively alkylated at position 1 or 2, indicating that benzyne intermediates, formed through 1,2-elimination, are not involved. No isomerization of the alkyl moiety and less than 5% of reduced product were observed when primary alkyllithium reagents were employed, demonstrating that competing β-hydride elimination/dissociation was almost completely inhibited. Importantly, the use of EtLi, which was unreactive in our previous palladium-based systems, afforded the corresponding products (**3a**, **3e**, **3g**) in good yields and nearly perfect selectivities. These results highlight how alternative metals such as nickel, besides being inexpensive, can also display complementary reactivity to palladium. The reaction using *i*PrLi, which contains an increased number of β-hydrogen atoms, proceeds without isomerization, although a minor amount of the reduced product was formed (Table 2, entries 4 and 14).[22] Cyclopropyllithium,[23] prepared from cyclopropyl bromide and lithium metal, also provided the coupled product with high selectivity without any ring-opened side products (Table 2, entry 11).[24]

Table 2. catalyzed cross-coupling of alkyllithium compounds



1 3 C1

Entry[a]	Aryl halide	Alkyllithium	Yield [%][b]
1 (**3a**)	1-chloronaphthalene	EtLi	65
2 (**3b**)		*n*BuLi	78
3 (**3c**)		*n*-HexLi	87
4 (**3d**)		*i*PrLi[c]	63
5 (**3e**)	2-chloroanthracene	EtLi	67
6 (**3f**)		*n*-HexLi	39
7 (**3g**)	1-chloroanthracene	EtLi	94
8 (**3h**)		*n*BuLi	84
9 (**3i**)		*n*-HexLi	85
10 (**3j**)		*i*PrLi[c]	44
11 (**3k**)		cycloPrLi	66
12 (**3b**)	1-fluoronaphthalene	*n*BuLi	76
13 (**3a**)		EtLi	66
14 (**3d**)		*i*PrLi	63

[a] Conditions: Alkyllithium (0.45 mmol, diluted with toluene to a final concentration of 0.45 M) was added to a solution of organic halide (0.3 mmol) in toluene (2 mL) over 1 h; GC selectivity >95%. [b] Yields refer to product isolated by column chromatography. [c] GC selectivity >80%.

In summary, we have described for the first time how a range of (hetero)aryl and alkyllithium compounds can be employed in cross-coupling reactions with aryl bromides, chlorides, fluorides, and aromatic ethers, by using nickel as catalyst. The reaction takes place under mild conditions (RT) with a broad scope of organolithium compounds and substrates, enabling transformations that were proven difficult with palladium catalysts, such as the cross-coupling of alkyllithium reagents bearing β-hydrogen with aryl chlorides and the use of EtLi as a coupling partner. The low cost and availability of both organolithium reagents and nickel catalysts, together with the selectivity of the novel method presented herein, make it a valuable alternative with lower environmental impact for atom-economic formation of C–C bonds.

Acknowledgements

The Netherlands Organization for Scientific Research (NWO-CW), the National Research School Catalysis (NRSC-C), the European Research Council (ERC advanced grant 227897 to B.L.F.), the Royal Netherlands Academy of Arts and Sciences (KNAW), the Ministry of Education Culture and Science (Gravitation program 024.601035) and the Swiss National Science Foundation (SNSF) are acknowledged for financial support.

Keywords: biaryl synthesis · cross-coupling · homogeneous catalysis · nickel · organolithium compounds

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[24] Full conversion was also obtained using aryl bromides although the presence of reduced starting material was also observed in the reaction mixture.

Received: December 21, 2016