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# Heterogeneous Nickel-Catalyzed Cross-Coupling between Aryl Chlorides and Alkyllithiums Using a Polystyrene-Cross-Linking Bisphosphine Ligand

Yuki Yamazaki, Nozomi Arima, Tomohiro Iwai,* and Masaya Sawamura*

**Abstract:** A polystyrene-cross-linking bisphosphine ligand PS-DPPBz was used for Ni-catalyzed cross-coupling with organolithiums. A bench-stable precatalyst [$NiCl_2$(PS-DPPBz)] enabled efficient coupling reactions between aryl chlorides and alkyllithiums. The heterogeneous Ni system showed good reusability.

The development of an efficient, green and simple synthetic process for transition metal-catalyzed cross-coupling reactions is important not only for industrial applications but also for fundamental chemistry.[1] Since the pioneering work of Murahashi and co-workers[2] and the later improvement by Feringa *et al.*,[3] organolithiums have been recognized as inexpensive and easily accessible cross-coupling partners (Murahashi coupling), which display attractive features of atom and step efficiency compared to other organometallic reagents.[4] While Pd was originally employed as a catalytic metal,[2,3,5–7] the use of more earth-abundant Ni has recently emerged as an intense area for pursuing environmentally benign organic synthesis.[8,9] However, due to the intrinsic high reactivity of organolithiums, prior dilution and/or slow addition protocols are required for efficient catalysis, as described by Hornillos and Feringa.[8d] Moreover, only a few catalyst systems allow efficient reaction of alkyllithiums having β-hydrogen atoms.[8d,e]

Recently, we developed a polystyrene-fourfold-cross-linking bisphosphine ligand PS-DPPBz (structure shown in Table 1).[10] This ligand allowed spatial isolation of the bisphosphine unit in the polystyrene matrix, resulting in formation of a highly active mononuclear monochelated metal-bisphosphine species. We demonstrated its utility in the Ni-catalyzed amination of aryl chlorides and C–H/C–O cross-coupling between 1,3-azoles and aryl pivalates. Herein, we report heterogeneous Ni catalysis for the cross-coupling of aryl chlorides and alkyllithiums with PS-DPPBz. This cross-coupling reaction required neither prior dilution nor slow addition of the alkyllithium. Excellent catalyst reusability was a favorable feature of this heterogeneous system.

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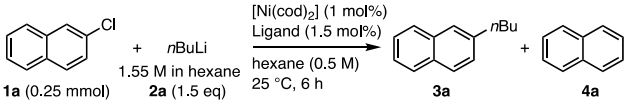
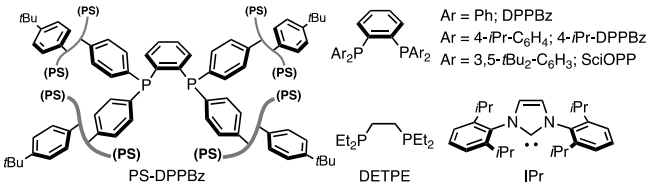
**Table 1.** Ligand effects in the Ni-catalyzed cross-coupling reaction between **1a** and **2a**[a]




**1a** (0.25 mmol) **2a** (1.5 eq) **3a** **4a**

| Entry | Ligand | Time [h] | Conv. **1a** [%][b] | Yield **3a** [%][c] | Yield **4a** [%][b] |
|---|---|---|---|---|---|
| 1 | PS-DPPBz | 6 | 98 | 93 | 5 |
| 2 | PS-DPPBz | 0.5 | 19 | 14 | 1 |
| 3 | DPPBz | 6 | 21 | 13 | 7 |
| 4 | 4-*i*Pr-DPPBz | 6 | 70 | 65 | 5 |
| 5 | SciOPP | 6 | 29 | 24 | 3 |
| 6 | DETPE | 6 | 0 | 0 | 0 |
| 7 | $PCy_3$ (3 mol%) | 6 | 25 | 0 | 8 |
| 8 | IPr (3 mol%) | 6 | 35 | 11 | 15 |
| 9 | none | 6 | 0 | 0 | 0 |
| 10[d] | [$NiCl_2$(PS-DPPBz)] | 6 | >99 | 97 | 3 |
| 11[d] | [$NiCl_2$(PS-DPPBz)] | 0.5 | >99 | 96 | 3 |
| 12[d] | [$NiCl_2$(PS-DPPBz)] + DPPBz (2 mol%) | 5 | 10 | 10 | 0 |
| 13[d] | [$NiCl_2$(PS-DPPBz)] + 4-*i*Pr-DPPBz (2 mol%) | 5 | 66 | 63 | 3 |

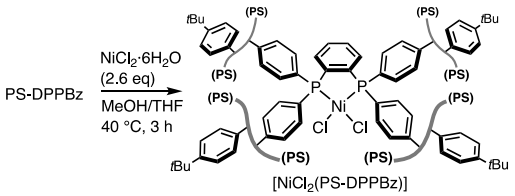
[a] Conditions: **1a** (0.25 mmol), **2a** (1.55 M in hexane, 0.375 mmol), [$Ni(cod)_2$] (1 mol%), ligand (1.5 mol%), hexane (0.5 M based on **1a**), 25 °C. [b] Determined by GC spectroscopy. [c] Determined by $^1$H NMR spectroscopy. [d] [$NiCl_2$(PS-DPPBz)] (1 mol% Ni) was used as catalyst.




Initially, we investigated ligand effects for the Ni-catalyzed cross-coupling of aryl chlorides, which are readily accessible and cheaper than the corresponding bromides and iodides, with alkyllithiums.[11] Specifically, with 1 mol% of a Ni catalyst prepared *in situ* from [$Ni(cod)_2$] and PS-DPPBz (Ni/L 1:1.5), the reaction between 2-chloronaphthalene (**1a**, 0.25 mmol) and *n*-butyllithium (**2a**, 1.55 M in hexane, 1.5 eq) proceeded smoothly without prior dilution or slow addition of the alkyllithium at 25 °C in hexane (0.5 M based on **1a**) over 6 h, giving 2-butylnaphthalene (**3a**) in 93%

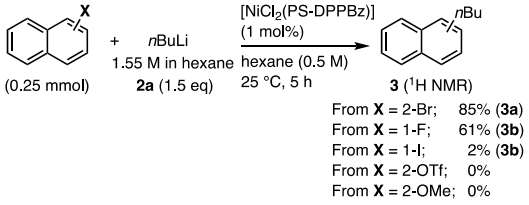
NMR yield (Table 1, entry 1), along with a small amount of a protodehalogenated product (**4a**, 5%). In contrast, DPPBz, which is the parent soluble ligand of PS-DPPBz, induced much lower activity (13%, entry 3). A DPPBz derivative, 4-*i*Pr-DPPBz,[12] which has *i*Pr groups at the *para* positions of the four *P*-Ph groups as a model for the polystyrene chain, gave a moderate yield (65%, entry 4), while the yield was reduced with SciOPP, the 3,5-di-*t*Bu-substituted derivative of DPPBz (24%, entry 5).[13] These results indicated the polymer effect is crucial, and that *para*-substituents on the *P*-Ph groups of DPPBz-type ligands are effective for increasing the catalytic activity. Other soluble ligands such as DETPE, $PCy_3$ and IPr, which had been employed as effective ligands for Ni-catalyzed cross-coupling with organolithiums,[8] were also much less effective than PS-DPPBz (entries 6–8). No reaction occurred in the absence of an added ligand (entry 9).

Next, we examined the use of a bench-stable Ni(II) salt as a Ni source instead of the air-sensitive Ni(0) complex [Ni(cod)$_2$]. A polymer-bound Ni(II) precatalyst [$NiCl_2$(PS-DPPBz)] (Ni: 0.12 mmol/g),[14] which was prepared from $NiCl_2 \cdot 6H_2O$ and PS-DPPBz in MeOH/THF (Scheme 1), showed much higher activity than the [Ni(cod)$_2$]/PS-DPPBz system (93% *vs.* 97% for 6 h, Table 1, entries 1 and 10; 14% *vs.* 96% for 0.5 h; entries 2 and 11). Notably, complete substrate consumption was observed within 0.5 h (entry 11). Addition of a soluble DPPBz derivative, DPPBz or 4-*i*Pr-DPPBz (2 mol%), to the [$NiCl_2$(PS-DPPBz)] system led to a decrease in the yield (entries 12 and 13), offering support for the importance of the controlled bisphosphine monochelation to the Ni center.[15]




**Scheme 1.** Synthesis of [$NiCl_2$(PS-DPPBz)].

We next examined other aryl electrophiles in the reactions with **2a** and the [$NiCl_2$(PS-DPPBz)] catalyst system (in hexane at 25 °C, Scheme 2). The coupling reaction of 2-bromonaphthalene occurred smoothly to give **3a** in 85% yield. 1-Fluoronaphthalene also participated in the reaction, affording 1-butylnaphthalene (**3b**) in 61% yield, while the corresponding iodide was not suitable due to rapid Li/I exchange (2%). Although aryl triflates were applicable substrates in the Pd-catalyzed cross-coupling with organolithiums,[3e] 2-naphthyl trifluoromethanesulfonate did not provide **3a** but formed 2-naphthol (~20% conv. by GC analysis) instead. The corresponding methyl ether was also inactive.[16]

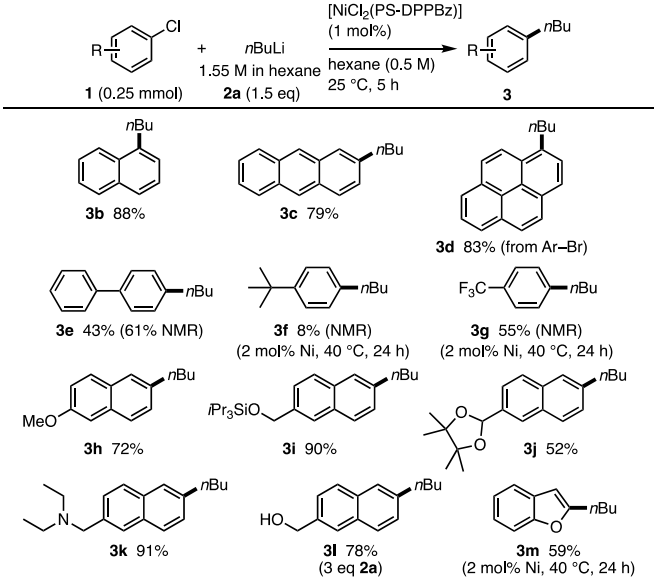



**Scheme 2.** Screening of aryl electrophiles.

The scope of aryl chlorides in the catalysis with the [$NiCl_2$(PS-DPPBz)] system was investigated using **2a** as a representative organolithium reagent (Scheme 3). The reaction of 1-chloronaphthalene with **2a** occurred at 25 °C, giving **3b** in high yield. The more π-extended 2-chloroanthracene was a suitable substrate (**3c**). A commercially available 1-bromopyrene gave **3d** in good yield.

Compared to polyaromatic aryl chlorides, monocyclic substrates showed lower reactivities. Specifically, the reaction of 4-chlorobiphenyl gave **3e** in moderate yield. The reaction of 4-*t*-butylchlorobenzene with 2 mol% Ni loading at 40 °C for 24 h afforded **3f** in only 8% NMR yield. Introduction of a $CF_3$ group instead of the *t*Bu group increased the yield to 55% (**3g**). This trend suggests that C–Cl oxidative addition of aryl chlorides to Ni(0) may be a rate-determining step.[17]

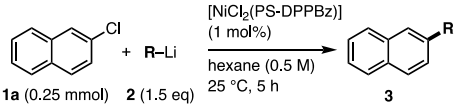
A methoxy group, which is often employed as a directing group in *ortho*-lithiation,[18] attached on the naphthalene ring was tolerated (**3h**). Silyl ether (**3i**), acetal (**3j**) and amine (**3k**) groups remained untouched. A hydroxy-tethered aryl chloride (**3l**) was a suitable substrate for the C–Cl cross-coupling reaction with 3 equiv of **2a**. With 2 mol% Ni catalyst at 40 °C for 24 h, 2-chlorobenzofuran was converted to the corresponding coupling product **3m** in an acceptable yield.

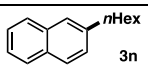
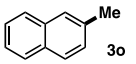
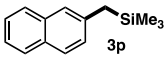
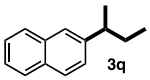
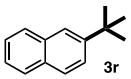



**Scheme 3.** Scope of aryl chlorides. Conditions: **1** (0.25 mmol), **2a** (1.55 M in hexane, 0.375 mmol), [$NiCl_2$(PS-DPPBz)] (1 mol%), hexane (0.5 M based on **1**) at 25 °C for 5 h. Yields of isolated products are shown. In some cases, small amounts of protodehalogenated byproducts of **1** were formed.

The applicability of commercially available alkyllithiums is summarized in Table 2. *n*-Hexyllithium reacted with **1a**, giving **3n** in 96% yield (entry 1). The reaction with methyllithium proceeded smoothly at 40 °C to afford **3o** in 83% yield (entry 2). (Trimethylsilyl)methyllithium also participated in the coupling reaction (**3p**, entry 3).[19] The reaction of *s*-Butyllithium gave the corresponding coupling product (**3q**) in high yield (86%), while 2-*n*-butylnaphthalene (**3a**) was also produced in 11%, suggesting isomerization of a putative alkyl-Ni(II) intermediate through β-hydride elimination (entry 4). *t*-Butyllithium underwent less efficient coupling reaction. In addition to the formation of the desired product **3r** (22%), an isomerized product (2-isobutylnaphthalene, 6%) and a homocoupling product (2,2'-binaphthalene, 26% based on **1a**) were observed by $^1$H NMR and GC-MS analysis of the crude product.[20]

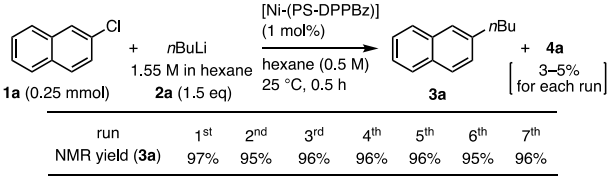
**Table 2.** Scope of organolithiums[a]




| entry | R | State of RLi | Conditions | Products (**3**) | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | *n*Hex | 2.3 M in hexane | 25 °C, 5 h |  **3n** | 96 |
| 2 | Me | 1.11 M in $Et_2O$ | 40 °C, 24 h |  **3o** | 83 |
| 3[c] | $Me_3SiCH_2$ | 1.0 M in pentane | 25 °C, 24 h |  **3p** | 87 |
| 4 | *s*-Bu | 1.05 M in cyclohexane-hexane | 25 °C, 5 h |  **3q** | 86[d] |
| 5 | *t*-Bu | 1.52 M in pentane | 25 °C, 5 h |  **3r** | 22[e,f] |

[a] Conditions: **1a** (0.25 mmol), **2** (0.375 mmol), [$NiCl_2$(PS-DPPBz)] (1 mol%), hexane (0.5 M based on **1a**), 25 °C, 6 h. [b] Isolated yields. [c] 2 equiv of $Me_3SiCH_2Li$. [d] The isolated product contains 11% of **3a**. [e] Determined by $^1$H NMR spectroscopy. [f] 2-Isobutylnaphthalene (6%, an isomerization product) and 2,2'-binaphthalene (26%, a homocoupling product, based on **1a**) were also detected in the crude product.

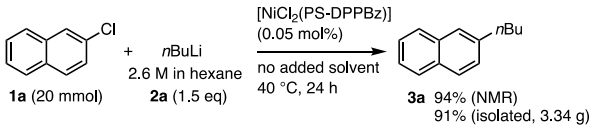
The heterogeneous [Ni-(PS-DPPBz)] catalyst was examined for reusability. After the reaction between **1a** and **2a** with [$NiCl_2$(PS-DPPBz)] (1 mol% Ni in hexane, 25 °C, 0.5 h), the polymer-bound Ni catalyst was separated in a glove box and reused at least six times with high yields retained (>95%, Scheme 4).




| run | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th |
|---|---|---|---|---|---|---|---|
| NMR yield (**3a**) | 97% | 95% | 96% | 96% | 96% | 95% | 96% |

**Scheme 4.** Reuse of the [Ni-(PS-DPPBz)] catalyst system.

A catalyst turnover number (TON) as high as 1880 was achieved in a larger scale reaction with 20 mmol of **1a** and 2.6 M **2a** in hexane without an additional solvent at 40 °C over 24 h (0.05 mol% Ni, 94% yield of **3a**, NMR) (Scheme 5). To our knowledge, this is the highest TON achieved to date for cross-coupling of organolithiums using Ni catalysts.




**Scheme 5.** The reaction of **1a** and **2a** with low catalyst loading (S/C = 2000).

In summary, a polystyrene-cross-linking bisphosphine PS-DPPBz enabled the efficient Ni-catalyzed cross-coupling of aryl chlorides with alkyllithiums. The bench-stable polymer-bound Ni(II) precatalyst [$NiCl_2$(PS-DPPBz)] showed improved performance over previously reported Ni systems. The utility of the heterogeneous Ni catalyst was demonstrated in catalyst reuse and on a larger scale reaction. Further applications of the polystyrene-cross-linking bisphosphine as a ligand are currently being investigated in our laboratory.

## Experimental Section

**General Procedure for Ni-catalyzed Cross-Coupling between Aryl Chlorides and Alkyllithiums (Table, 1, entry 11).**

In a nitrogen-filled glove box, [$NiCl_2$(PS-DPPBz)] (0.12 mmol/g, 20.8 mg, 0.0025 mmol, 1.0 mol%), 2-chloronaphthalene (**1a**, 40.6 mg, 0.25 mmol) and hexane (0.255 mL) were successively placed in a 10-mL glass tube containing a magnetic stirring bar. The tube was sealed with a screw cap and removed from the glove box. *n*BuLi (**2a**, 1.55 M in hexane, 0.245 mL, 0.375 mmol, 1.5 eq) was added by a syringe at once. The reaction mixture was stirred at 25 °C for 0.5 h. After quenching with MeOH, the mixture was filtered with a silica gel pad (eluting with $Et_2O$). The solvent was removed under reduced pressure. Internal standard (*p*-dimethoxybenzene) was added to the residue. The yield of the coupling product **3a** was determined by $^1$H NMR (96%). The crude material was then purified by silica gel chromatography with hexane for isolation (44.9 mg, 96% yield, contaminated with a trace amount of naphthalene (**4a**)).

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**Keywords:** nickel • cross-coupling • organolithium • bisphosphine • heterogeneous catalyst


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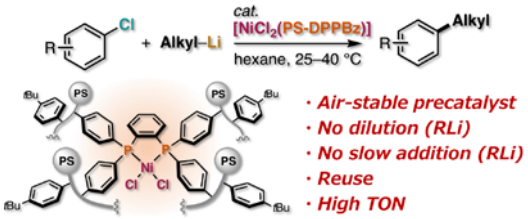
[20] The [$NiCl_2$(PS-DPPBz)] catalyst system was applicable to the reactions of aryllithiums. Specifically, the reaction between **1a** and PhLi (1.09 M in cyclohexane/$Et_2O$, 1.5 eq) with 1 mol% of [$NiCl_2$(PS-DPPBz)] in hexane (0.5 M) at 40 °C for 24 h without slow addition produced the corresponding biaryl compound (2-phenylnaphthalene, **3s**) in 48% NMR yield (68% conv. of **1a**), which was comparable to that with the Feringa's catalyst [$NiCl_2$(IPr)($PPh_3$)] (ref 8d) under otherwise the same conditions (69% conv., 53% yield). The reaction using 2-thienyllithium (1.0 M in THF/hexane, 1 mol% Ni, 25 °C, 5 h) gave 2-(2-naphthyl)thiophene (**3t**) in 32% isolated yield.

# COMMUNICATION

A polystyrene-cross-linking bisphosphine ligand PS-DPPBz was used for Ni-catalyzed cross-coupling with organolithiums. A bench-stable precatalyst [$NiCl_2$(PS-DPPBz)] enabled efficient coupling reactions between aryl chlorides and alkyllithiums. The heterogeneous Ni system showed good reusability.

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***Page No. – Page No.***

***Heterogeneous Nickel-Catalyzed Cross-Coupling between Aryl Chlorides and Alkyllithiums Using a Polystyrene-Cross-Linking Bisphosphine Ligand***