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

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

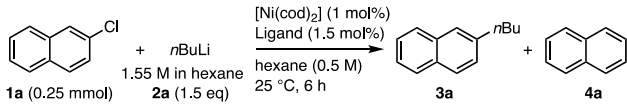
Abstract: A polystyrene-cross-linking bisphosphine ligand PS-DPPBz was used for Ni-catalyzed cross-coupling with organolithiums. A bench-stable precatalyst [NiCl₂(PS-DPPBz)] enabled efficient coupling reactions between aryl chlorides and alkylolithiums. The heterogeneous Ni system showed good reusability.

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 alkylolithiums 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 alkylolithiums with PS-

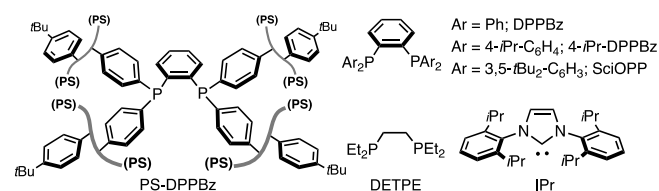
DPPBz. This cross-coupling reaction required neither prior dilution nor slow addition of the alkylolithium. Excellent catalyst reusability was a favorable feature of this heterogeneous system.

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



Entry	Ligand	Time [h]	Conv.		Yield	
			1a [%] ^[b]	3a [%] ^[c]	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>i</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>i</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 ¹H NMR spectroscopy. [d] [NiCl₂(PS-DPPBz)] (1 mol% Ni) was used as catalyst.



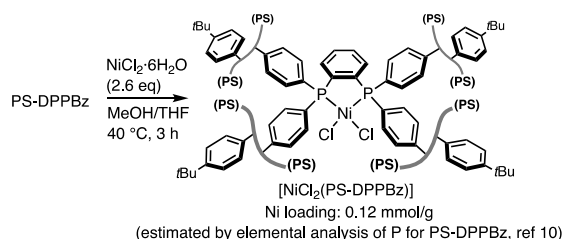
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Initially, we investigated ligand effects for the Ni-catalyzed cross-coupling of aryl chlorides, which are readily accessible and cheaper than the corresponding bromides and iodides, with alkylolithiums.^[11] Specifically, with 1 mol% of a Ni catalyst 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 alkylolithium at 25 °C in hexane (0.5 M based on **1a**) over 6 h, giving 2-butyl-naphthalene (**3a**) in 93%

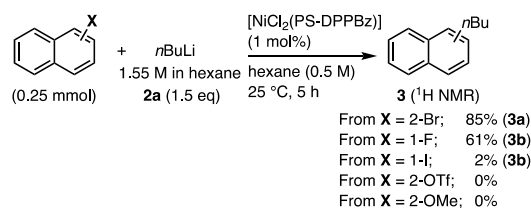
NMR yield (Table 1, entry 1), along with a small amount of a protodehalogenated product (**4a**, 5%). In contrast, DPPBz, which is the parent soluble ligand of PS-DPPBz, induced much lower activity (13%, entry 3). A DPPBz derivative, 4-*i*Pr-DPPBz,^[12] which has *i*Pr groups at the *para* positions 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, PCy₃ 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 [NiCl₂(PS-DPPBz)] (Ni: 0.12 mmol/g),^[14] which was prepared from NiCl₂·6H₂O 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 [NiCl₂(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 [NiCl₂(PS-DPPBz)].

We next examined other aryl electrophiles in the reactions with **2a** and the [NiCl₂(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-butynaphthalene (**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]

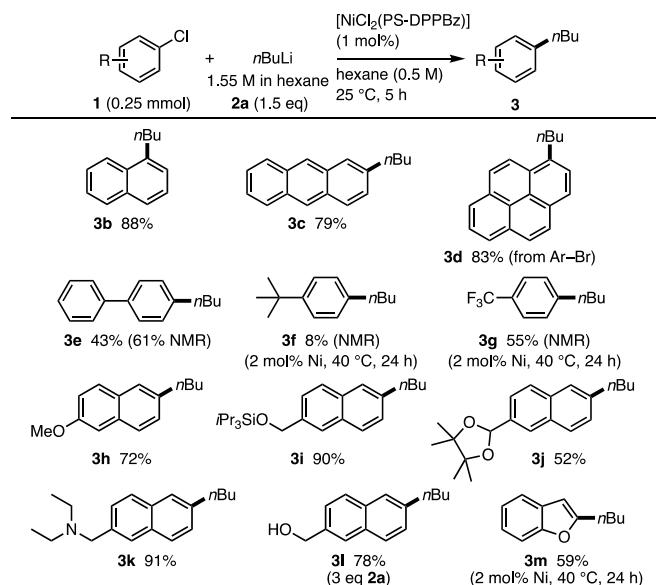


Scheme 2. Screening of aryl electrophiles.

The scope of aryl chlorides in the catalysis with the [NiCl₂(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 CF₃ 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]

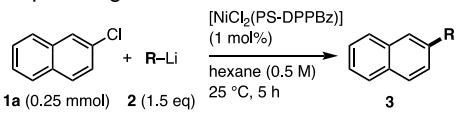
A methoxy group, which is often employed as a directing group in *ortho*-lithiation,^[18] attached on the naphthalene ring was tolerated (**3h**). Silyl ether (**3i**), acetal (**3j**) and amine (**3k**) groups remained untouched. A hydroxy-tethered aryl chloride (**3l**) was a suitable substrate for 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.

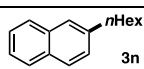
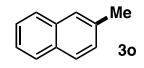
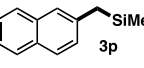
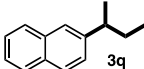
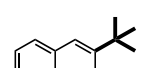


Scheme 3. Scope of aryl chlorides. Conditions: **1** (0.25 mmol), **2a** (1.55 M in hexane, 0.375 mmol), [NiCl₂(PS-DPPBz)] (1 mol%), hexane (0.5 M based on **1**) at 25 °C for 5 h. Yields of isolated products are shown. In some cases, small amounts of protodehalogenated byproducts of **1** were formed.

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 methylolithium proceeded smoothly at 40 °C to afford **3o** in 83% yield (entry 2). (Trimethylsilyl)methylolithium 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 ¹H NMR and GC-MS analysis of the crude product.^[20]

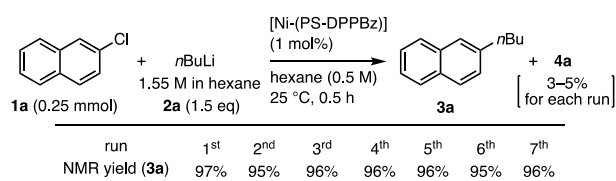
Table 2. Scope of organolithiums^[a]



entry	R	State of RLi	Conditions	Products (3)	Yield [%] ^[b]
1	<i>n</i> Hex	2.3 M in hexane	25 °C, 5 h		96
2	Me	1.11 M in Et ₂ O	40 °C, 24 h		83
3 ^[c]	Me ₃ SiCH ₂	1.0 M in pentane	25 °C, 24 h		87
4	<i>s</i> -Bu	1.05 M in cyclohexane-hexane	25 °C, 5 h		86 ^[d]
5	<i>t</i> -Bu	1.52 M in pentane	25 °C, 5 h		22 ^[e,f]

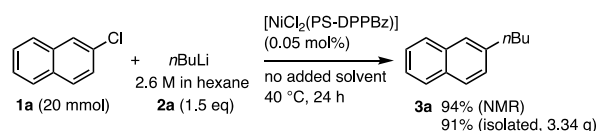
[a] Conditions: **1a** (0.25 mmol), **2** (0.375 mmol), [NiCl₂(PS-DPPBz)] (1 mol%), hexane (0.5 M based on **1a**), 25 °C, 6 h. [b] Isolated yields. [c] 2 equiv of Me₃SiCH₂Li. [d] The isolated product contains 11% of **3a**. [e] Determined by ¹H NMR spectroscopy. [f] 2-Isobutylnaphthalene (6%, an isomerization 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 [NiCl₂(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).



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 [NiCl₂(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, [NiCl₂(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 Et₂O). 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 ¹H 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**)).

Acknowledgements

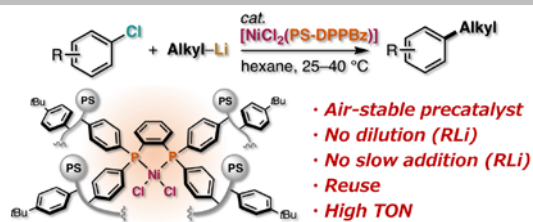
This work was supported by JSPS KAKENHI Grant Number JP 17H04877 in Young Scientists (A) to T.I., and by JSPS KAKENHI Grant Number JP15H05801 in Precisely Designed Catalysts with Customized Scaffolding to M.S. Support from the Tosoh Finechem Corporation is gratefully acknowledged.

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

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COMMUNICATION

A polystyrene-cross-linking bisphosphine ligand PS-DPPBz was used for Ni-catalyzed cross-coupling with organolithiums. A bench-stable precatalyst $[\text{NiCl}_2(\text{PS-DPPBz})]$ enabled efficient coupling reactions between aryl chlorides and alkyllithiums. The heterogeneous Ni system showed good reusability.



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