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

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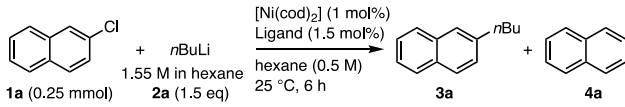
Abstract: A polystyrene-cross-linking bisphosphine ligand PS-DPPBz was used for Ni-catalyzed cross-coupling with organolithiums. A bench-stable precatalyst [NiCl₂(PS-DPPBz)] enabled efficient coupling reactions between aryl chlorides and alkylolithiums. The heterogeneous Ni system showed good reusability.

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-

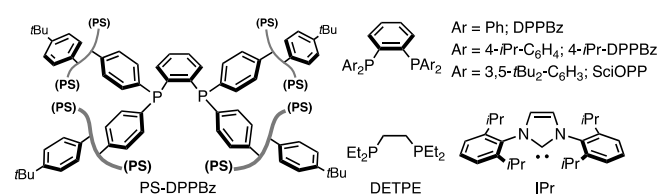
DPPBz. This cross-coupling reaction required neither prior dilution nor slow addition of the alkylolithium. Excellent catalyst reusability was a favorable feature of this heterogeneous system.

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



Entry	Ligand	Time [h]	Conv. 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>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.



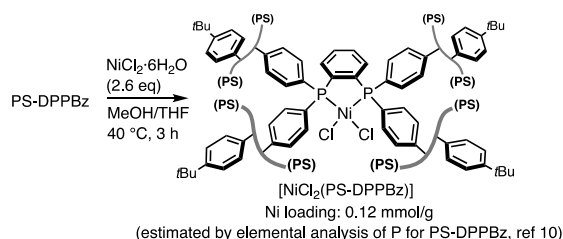
Initially, we investigated ligand effects for the Ni-catalyzed cross-coupling of aryl chlorides, which are readily accessible and cheaper than the corresponding bromides and iodides, with alkylolithiums.^[11] Specifically, with 1 mol% of a Ni catalyst prepared *in situ* from [Ni(cod)₂] and PS-DPPBz (Ni/L 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%

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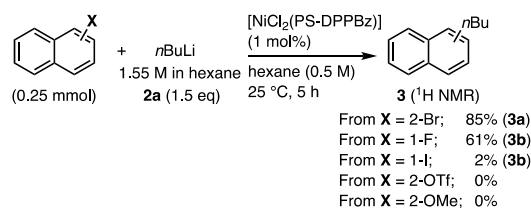
NMR yield (Table 1, entry 1), along with a small amount of a protodehalogenated product (**4a**, 5%). In contrast, DPPBz, which is the parent soluble ligand of PS-DPPBz, induced much lower activity (13%, entry 3). A DPPBz derivative, 4-*i*Pr-DPPBz,^[12] which has *i*Pr groups at the *para* positions 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-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]

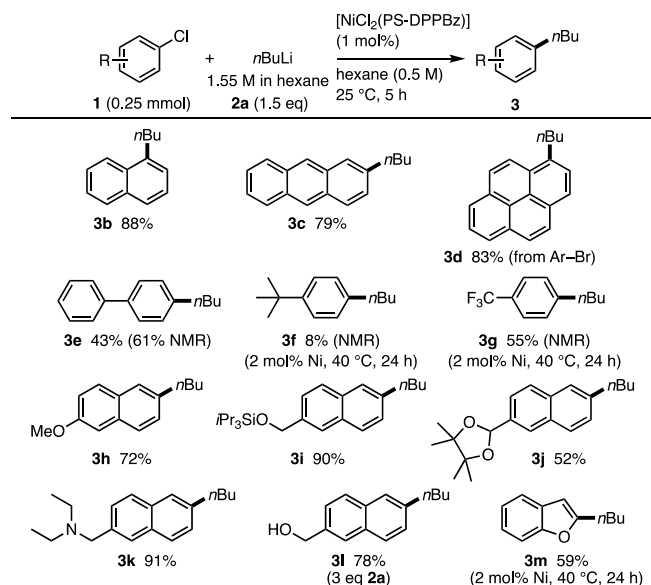


Scheme 2. Screening of aryl electrophiles.

The scope of aryl chlorides in the catalysis with the [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.

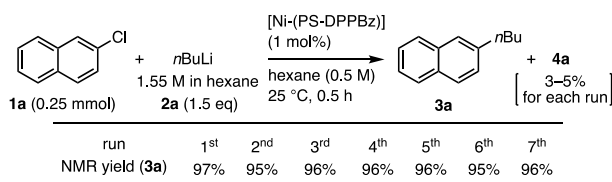
The applicability of commercially available alkyllithiums is summarized in Table 2. *n*-Hexyllithium reacted with **1a**, giving **3n** in 96% yield (entry 1). The reaction with methylolithium proceeded smoothly at 40 °C to afford **3o** in 83% yield (entry 2). (Trimethylsilyl)methylolithium also participated 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]

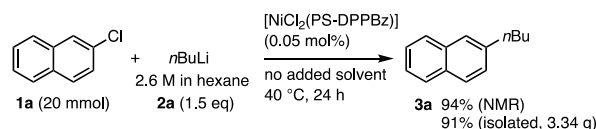
[a] Conditions: **1a** (0.25 mmol), **2** (0.375 mmol), [NiCl₂(PS-DPPBz)] (1 mol%), hexane (0.5 M based on **1a**), 25 °C, 6 h. [b] Isolated yields. [c] 2 equiv of Me₃SiCH₂Li. [d] The isolated product contains 11% of **3a**. [e] Determined by ¹H NMR spectroscopy. [f] 2-Isobutylnaphthalene (6%, an isomerization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

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**)).

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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 alkylolithiums. The heterogeneous Ni system showed good reusability.



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