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Room-Temperature Nickel-Catalysed Suzuki–Miyaura Reactions of Aryl Sulfonates/Halides with Arylboronic Acids

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Room-temperature Suzuki–Miyaura aryl–aryl cross-coupling reactions have been achieved in high yields by using an easily accessible, air-stable Ni^{II}–(σ-aryl) complex as precatalyst without either the pretreatment of organometallic reagents or the presence of external reductants. The Ni^{II} complex, in conjunction with monophosphane ligands such as $PCy_3{\cdot}HBF_4$ or PPh_3, allowed the efficient cross-coupling of aryl sulfonates (OTs, OMs) and/or halides (Cl, Br, I) with arylboronic acids at room temperature in toluene/water in the presence of K_2CO_3 as base.

Introduction

Transition-metal-catalysed Suzuki–Miyaura cross-coupling reactions have become a powerful and indispensable tool in organic synthesis for the construction of biaryl/polyaryl motifs commonly found in biologically active molecules and chemical materials. Palladium-based catalysts have dominated these transformations over the past two decades.[1] On the other hand, efforts to explore more economic metal alternatives have been attracting considerable interest. Since the pioneering work of Percec et al. in 1995,[2] remarkable advances have been made in the nickel-catalysed version of Suzuki–Miyaura aryl–aryl cross-coupling reactions.[3–7] The major advantages of nickel-based systems over palladium lie mainly in their much lower cost and high reactivity, without the need of very special ligands, towards challenging substrates including deactivated aryl chlorides[3a–3g,7d] and sulfonates[4,7a–7c,7e] and even carboxylates,[5a,5b] carbamates,[5c–5f] methyl ether,[5g] nitriles[5h] and sulfamates.[5c,5j,5k]

From a synthetic point of view, room-temperature transformations are highly desirable processes. Indeed, several protocols have been described for the room-temperature nickel-catalysed Suzuki–Miyaura aryl–aryl cross-coupling reactions.[7] Kobayashi and Mizojiri[7a] performed a coupling reaction of electron-deficient aryl mesylates with lithium arylborates that were generated in situ by the pretreatment of arylboronates with *n*BuLi at room temperature in the presence of $[NiCl_2(PPh_3)_2]$ as catalyst. The most successful examples are found in the work of Hu and co-workers[7b–7d] who demonstrated the room-temperature Suzuki–Miyaura reactions of aryl sulfonates/chlorides using $[Ni(cod)_2]$ or a combination of $[NiCl_2(PPh_3)_2]$ and *n*BuLi as the catalytically active nickel(0) source. Very recently, Percec and co-workers[7e] also employed $[Ni(cod)_2]$ as a catalyst precursor in the room-temperature coupling reactions of aryl sulfonates/chlorides with arylboronates. In general, all the systems mentioned above required either the use of a Ni^0 precursor or the pretreatment of Ni^{II} with organometallic reagents.

Ni^0 is generally regarded as the catalytically active species in nickel catalysis. The direct use of Ni^0 complexes such as $[Ni(cod)_2]$ and $[Ni(PPh_3)_4]$ as precatalysts is the simplest method. Such nickel sources, however, are very inconvenient to handle and manipulate due to their high sensitivity to air and moisture and high toxicity. Moreover, they are costly (more expensive than normal Pd sources). In contrast, cheaper and easily handled nickel(II) compounds are more preferred as catalyst precursors. In contrast to Pd^{II}, Ni^{II} is not readily reduced to Ni^0 by the base, solvent and/or ligand in a reaction system. Solutions to this problem have included the use of additional reductants such as Zn[2,3d] and the pretreatment of the Ni^{II} with organometals such as *n*BuLi[3a,3c,7d] to generate in situ Ni^0. Afterwards it was found that Ni^0 can be formed in situ from Ni^{II} at elevated temperatures (80–130 °C) in nickel(II)-catalysed Suzuki–Miyaura reactions by the initial homocoupling of the organoboron reactants,[3b,3e,4a,4b] but this transformation did not seem to occur at room temperature.

As part of our ongoing effort we were interested in developing a new facile protocol for room-temperature nickel-catalysed Suzuki–Miyaura aryl–aryl coupling reactions in which both the use of hard-to-handle nickel(0) sources and the troublesome pretreatment of organometallic reagents would be obviated. For this purpose, we once again considered a special class of Ni^{II} complexes, *trans*-haloarylbis(tri-

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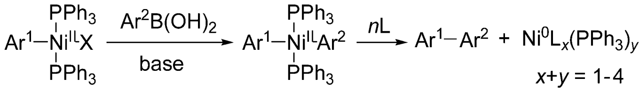
phenylphosphane)nickel(II), as catalyst precursors, which have previously been used in some catalytic C–C or C–N coupling reactions.[8,9] This class of Ni^{II} complexes can be easily prepared from cheap starting materials and are insensitive to air and moisture, making them highly preferred catalyst precursors.[10]

A possible mechanism that has been accepted for the nickel-catalysed Suzuki–Miyaura cross-coupling reaction follows a catalytic cycle of the Ni^0–Ni^{II} shuttle involving sequential oxidative addition, transmetallation and reductive elimination. Thus, the Ni^{II}–(σ-aryl) complex may formally be assumed to be an intermediate (oxidative adduct) in the catalytic cycle. In view of the fact that the Ni^0-catalysed room-temperature Suzuki–Miyaura reaction has been established, the Ni^{II}–(σ-aryl) complex should be able to generate in situ the Ni^0 species at room temperature, if the other conditions are provided properly, by transmetallation of the nucleophilic coupling partner and subsequent reductive elimination prior to a normal catalytic cycle (Scheme 1). Accordingly, we reasoned that it would be feasible to use Ni^{II}–(σ-aryl) complexes as catalysts in room-temperature Suzuki–Miyaura aryl–aryl coupling reactions without the aid of any organometallic reagent or external reductant.

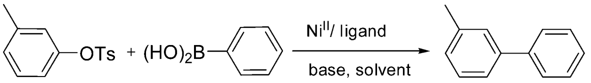


Scheme 1. Possible pathway for the activation of the Ni^{II}–(σ-aryl) complex.

Results and Discussion

Two Ni^{II}–(σ-aryl) complexes, $[Ni(PPh_3)_2(1\text{-naphthyl})Cl]$ (**C-1**) and $[Ni(PPh_3)_2(1\text{-naphthyl})Br]$ (**C-2**), were used in this study because they are very easily prepared from nickel(II) halide, triphenylphosphane, zinc dust, and the corresponding haloarene in ethanol[10] (see the detailed procedures in the Exptl. Sect.). A model reaction of *m*-tolyl tosylate and phenylboronic acid was chosen to screen the reaction conditions and the results are summarized in Table 1. The initial experiment showed that the room-temperature Suzuki–Miyaura reaction can be mediated by using **C-1** as a precatalyst in toluene/H_2O in the presence of the base K_2CO_3, but the conversion level was low (Table 1, entry 1). In this case, a rapid change in colour of the reaction mixture from yellow to red-brown was observed, which suggests that the Ni^{II}–(σ-aryl) complex is very readily activated. The use of an additional PPh_3 ligand did not speed up the reaction significantly (entry 2). Based on the work of Hu and co-workers,[7b–7e] a combination of PCy_3 as ligand and Ni^0 is the most effective system for the room-temperature Suzuki–Miyaura reaction of the tosylate substrate. Thus, we used a system involving **C-1** and PCy_3; this reaction showed promise (entry 3). $PCy_3{\cdot}HBF_4$ was then preferably selected as a ligand because the salt precursor of PCy_3 liberates PCy_3 by deprotonation in the basic reaction system and is more convenient to handle due to its stability in air. Indeed, the $PCy_3{\cdot}HBF_4$ ligand rendered a comparable result to PCy_3 (entry 4). After some experimentation, it was found that a 1:1–1.5 ratio of **C-1** to $PCy_3{\cdot}HBF_4$

Table 1. Screening of the reaction conditions for the Ni-catalysed coupling of *m*-tolyl tosylate and phenylboronic acid at room temperature.[a]



Entry	$[Ni^{II}]$[b] (quatity [mol-%])	Ligand (quatity [mol-%])	Base	Solvent[c] (5 mL)	Water [mL]	Yield [%][d]
1	**C-1** (5)	None	K_2CO_3	toluene	0.25	46
2	**C-1** (5)	PPh_3 (10)	K_2CO_3	toluene	0.25	48
3	**C-1** (5)	PCy_3 (10)	K_2CO_3	toluene	0.25	83
4	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (10)	K_2CO_3	toluene	0.25	80
5	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (5)	K_2CO_3	toluene	0.25	88
6	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0.25	91
7	**C-2** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0.25	89
8	$NiCl_2{\cdot}6H_2O$ (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0.25	n.r.
9	$Ni(acac)_2$ (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0.25	n.r.
10	$[Ni(PPh_3)_2Cl_2]$ (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0.25	n.r.
11	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0	40
12	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	toluene	0.5	57
13	**C-1** (5)	IPr·HCl[e] (5)	K_2CO_3	toluene	0.25	35
14	**C-1** (5)	Bipy[f] (5)	K_2CO_3	toluene	0.25	<5
15	**C-1** (5)	Phena[g] (5)	K_2CO_3	toluene	0.25	<5
16	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_3PO_4	toluene	0.25	89
17	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	Na_2CO_3	toluene	0.25	68
18	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	KOH	toluene	0.25	trace
19	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	dioxane	0.25	49
20	**C-1** (5)	$PCy_3{\cdot}HBF_4$ (7.5)	K_2CO_3	THF	0.25	40
21	**C-1** (3)	$PCy_3{\cdot}HBF_4$ (4.5)	K_2CO_3	toluene	0.25	52

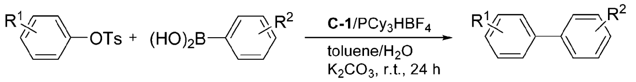
[a] Reaction conditions: *m*-tolyl tosylate (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (3 mmol), room temperature (ca. 23 °C), 24 h. [b] **C-1**: $[Ni(PPh_3)_2(1\text{-naphthyl})Cl]$; **C-2**: $[Ni(PPh_3)_2(1\text{-naphthyl})Br]$. [c] 5 mL of solvent. [d] Isolated yields. n.r.: No reaction. [e] IPr·HCl: 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride. [f] Bipy: 2,2′-bipyridine. [g] Phena: 1,10-phenanthroline.

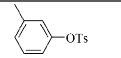
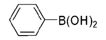
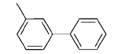
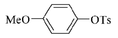
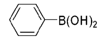
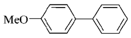
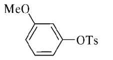
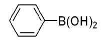
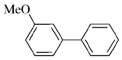
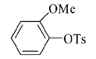
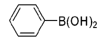
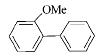
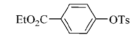
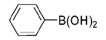
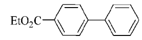
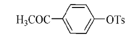
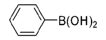
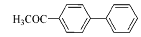
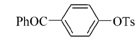
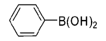
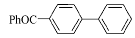
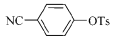
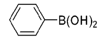
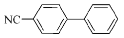
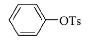
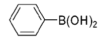
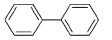
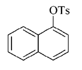
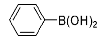
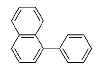
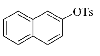
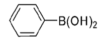
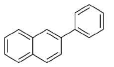
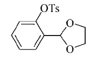
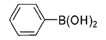
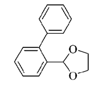
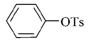
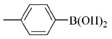
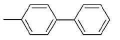
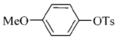
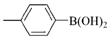
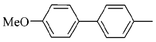
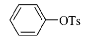
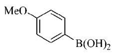
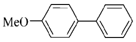
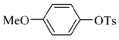
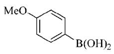
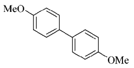
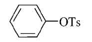
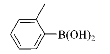
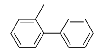
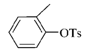
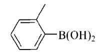
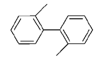
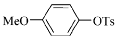
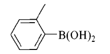
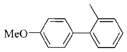
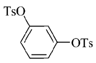
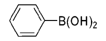
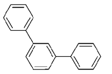
seemed to be suitable for gaining excellent yields of the desired product (entries 5 and 6). Under the same conditions, the **C-2** complex was also effective for the reaction (entry 7). The significance of the nickel(II) source in this reaction was established by control experiments. Common Ni^{II} complexes like $NiCl_2·6H_2O$, $Ni(acac)_2$ and $[Ni(PPh_3)_2Cl_2]$ did not mediate the reaction at all (entries 8–10), which indicates that the active Ni^0 was not produced from these Ni^{II} precursors under the mild conditions. Small amounts of water as additive accelerates the reaction probably because the added water helps to activate K_2CO_3 towards phenylboronic acid (entry 6 vs. 11), but excess water would disfavour the reaction (entry 12 vs. 6). Several other commonly used ligands were surveyed and the results suggest that IPr·HCl (entry 13) is an ineffective ligand and 2,2′-bipyridine (entry 14) and 1,10-phenanthroline (entry 15) are detrimental to the reaction. Among the bases screened, K_3PO_4, the most commonly used in nickel-catalysed Suzuki–Miyaura reactions,[2–5,7] worked as well as K_2CO_3 (entry 16), the weaker base Na_2CO_3 (entry 17) gave a mediocre yield and strongly basic KOH (entry 18) was far inferior to both K_2CO_3 and K_3PO_4. Toluene appeared to be the solvent of choice and was far superior to ether-type solvents like dioxane (entry 19) and THF (entry 20). Unfortunately, an attempt to lower the loadings of the catalyst caused a substantially reduced yield (entry 21). Finally, our standard reaction conditions were established as entry 6 of Table 1.

With the optimal conditions in hand, we next examined the room-temperature Suzuki–Miyaura reactions of aryl tosylates as electrophilic coupling partners. A wide range of aryl tosylates were tested with several representative arylboronic acids (Table 2). In general, activated (entries 1, 3 and 5–8), nonactivated (entries 9–11, 13, 15 and 17) and deactivated (entries 2, 14, 16 and 19) aryl tosylates smoothly underwent the coupling reaction to afford high yields of the desired products; *ortho* substituents on the tosylate did not produce a substantial influence on the reaction (entries 4, 10 and 18) unless the substituent was particularly large (entry 12). The reaction was also insensitive to the electron-donating (entries 13–16) and steric effects (entries 17–19) of arylboronic acids. Furthermore, the mild reaction conditions tolerated some sensitive functional groups such as ester (entry 5), carbonyl (entry 7) and enolizable carbonyl (entry 6), cyano (entry 8) and acetal (entry 12) functionalities. The phenylene-ditosylate underwent a double cross-coupling reaction, but needed to be accelerated by appropriate heating (entry 20).

To examine the catalytic efficacy of the Ni^{II}–(1-naphthyl) complex/$PCy_3·HBF_4$ system, we applied this protocol to other types of electrophilic substrates involving aryl mesylates, chlorides, bromides and iodides. The results are shown in Table 3. The electrophiles, whether activated (entries 2, 6 and 11) or deactivated (entries 1, 3–5, 7, 9, 10, 12, 14 and 15), gave good-to-excellent yields of the desired products except for the special case of *o*-dichlorobenzene (entry 8). In particular, with aryl halides as electrophiles, quantitative yields were obtained in most cases (entries 5–7 and 9–15).

Table 2. Room-temperature Ni-catalysed Suzuki–Miyaura cross-coupling reactions of aryl tosylates with arylboronic acids.[a]

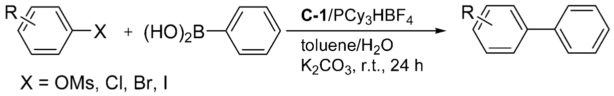


Entry	Ar–OTs	Ar'–B(OH)$_2$	Product	Yield (%)[b]
1				91
2				74
3				93
4				81
5				99
6				99
7				90
8				99
9				90
10				99
11				99
12				33 (95[c])
13				92
14				75
15				86
16				75
17				83
18				71
19				76
20				58[d] (93[c,d])

[a] Reagents: aryl tosylate (1 mmol), arylboronic acid (1.5 mmol), **C-1** (0.05 mmol), $PCy_3·HBF_4$ (0.075 mmol), K_2CO_3 (3 mmol), toluene/H_2O (5 mL/0.25 mL). [b] Isolated yields. [c] At 60 °C, 12 h. [d] Phenylboronic acids (3 mmol).

In view of the fact that the Ni^{II}–(σ-aryl)-based catalyst possesses high activity and that aryl halides differ from aryl sulfonates (i.e., the C_{aryl}–halogen bond is weaker than the C_{aryl}–oxygen bond), we continued our investigations into the room-temperature Suzuki–Miyaura coupling of haloarenes by replacing $PCy_3·HBF_4$ with the much cheaper PPh_3 as ligand (Table 4). The PPh_3/**C-1** system was found to catalyse the coupling of deactivated aryl bromides and iodides with phenylboronic acid at room temperature to give almost

Table 3. Room-temperature Ni-catalysed Suzuki–Miyaura cross-coupling reactions of aryl mesylates/halides as electrophilic substrates.[a]



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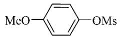
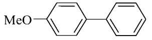
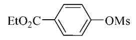
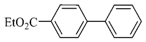
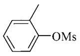
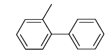
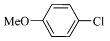
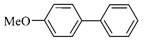
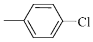
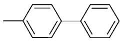
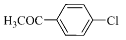
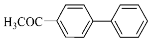
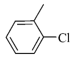
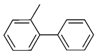
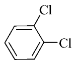
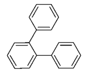
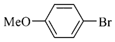
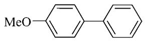
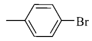
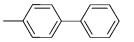
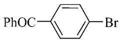
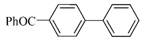
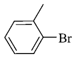
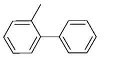
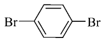
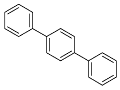
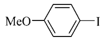
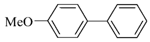
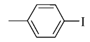
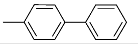
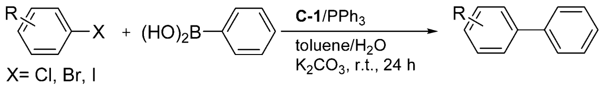
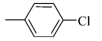
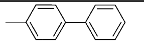
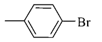
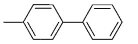
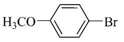
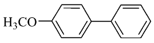
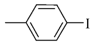
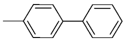
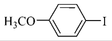
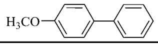
1			93
2			99
3			79
4			86
5			99
6			97
7			99
8			38[c] (66[c,d])
9			97
10			99
11			99
12			92
13			99
14			99
15			99

[a] Reagents: aryl mesylate/halide (1 mmol), phenylboronic acid (1.5 mmol), **C-1** (0.05 mmol), $PCy_3 \cdot HBF_4$ (0.075 mmol), K_2CO_3 (3 mmol), toluene/H_2O (5 mL/0.25 mL). [b] Isolated yields. [c] Phenylboronic acids (3.0 mmol). [d] At 60 °C, 12 h.

quantitative yields (Table 4, entries 2–5). The reaction of the deactivated chloride was slightly slower but still gave a satisfactory yield (Table 4, entry 1).

Table 4. Room-temperature Suzuki–Miyaura cross-coupling reactions of aryl halides catalysed by the Ni^{II}/PPh_3 system.[a]



Entry	Ar–X	Product	Yield (%)[b]
1			80
2			99
3			95
4			99
5			99

[a] Reagents: aryl halide (1 mmol), phenylboronic acid (1.5 mmol), **C-1** (0.05 mmol), PPh_3 (0.1 mmol), K_2CO_3 (3 mmol), toluene/H_2O (5 mL/0.25 mL). [b] Isolated yields.

Conclusions

We have developed a new protocol for room-temperature Ni-catalysed Suzuki–Miyaura aryl–aryl cross-coupling reactions employing a Ni^{II}–(σ-aryl) complex as precatalyst. The key advantages of the method lie in both avoiding the use of hard-to-handle expensive nickel(0) sources and not requiring the presence of additional reducing agents. Furthermore, the reaction offers a broad scope, being suitable for aryl halides (I, Br, Cl) and sulfonates (OTs, OMs) as well as activated and deactivated electrophilic substrates. To the best of our knowledge, this reaction performed with Ni^{II} precatalysts without the aid of any organometallic reagent or external reductant has not yet been reported. This facile, mild and general protocol represents, to a certain extent, a new advance in Suzuki–Miyaura cross-coupling reactions.

Experimental Section

Synthesis of Ni^{II}–(σ-Aryl) Complexes[10]

[$Ni(PPh_3)_2$(1-naphthyl)Cl] (C-1): A stirred mixture of $NiCl_2 \cdot 6H_2O$ (4.8 g, 0.02 mol), triphenylphosphane (11.53 g, 0.044 mol) and 95% ethanol (90 mL) was heated until gentle boiling at reflux started. 1-Chloronaphthalene (6.5 g, 0.04 mol, excess) was then added, followed by zinc dust (1.3 g, 0.02 mol) over 5 min. The dark-green mixture very soon turned yellow. After stirring and heating at reflux for 1.5 h (under nitrogen), the mixture was cooled to room temperature. Four 2 mL portions of 30% aqueous hydrochloric acid were added over 15 min. After stirring for 1.5 h, the solid was filtered off on a sintered-glass funnel and successively washed with ethanol (20 mL), 1 M aqueous hydrochloric acid (2 × 20 mL), ethanol (2 × 20 mL) and petroleum (30–60 °C; 20 mL). The yellow solid was dried in vacuo at a bath temperature of not higher than 45 °C. The yield was above 80%.

[$Ni(PPh_3)_2$(1-naphthyl)Br] (C-2): Orange, air-stable powder. Prepared by a procedure similar to the synthesis of the Ni^{II} complex **C-1** from $NiBr_2 \cdot 3H_2O$, PPh_3 and 1-bromonaphthalene.

General Procedure for the Ni^{II}–(σ-Aryl)-Catalysed Room-Temperature Reaction of Aryl Sulfonates/Halides with Arylboronic Acids: An oven-dried 25-mL three-necked flask was charged with K_2CO_3 (3 mmol), [$Ni(PPh_3)_2$(1-naphthyl)Cl] (0.05 mmol) and $PCy_3 \cdot HBF_4$ (0.075 mmol). Then the aryl sulfonates/halides (1 mmol) (if solid) and arylboronic acid (1.5 mmol) were added. The flask was evacuated and back-filled with nitrogen, with the operation being repeated twice. The halides (if liquid), dried toluene (5 mL) and degassed water (0.25 mL) were added through a syringe at this time. The reaction mixture was stirred at room temperature for 24 h and filtered through a pad of silica gel that was washed with ethyl acetate. The combined organic phases were evaporated under reduced pressure and the residue purified by silica gel column chromatography to give the desired products.[11]

Supporting Information (see footnote on the first page of this article): General considerations and characterization data for all compounds prepared.

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[11] Note: In all experiments there always exists a small amount of the 1-arylnaphthalene byproduct generated from the precatalyst $\mathrm{Ni^{II}}$–(1-naphthyl) complex. In most cases, the byproduct does not cause any difficulty in the separation of the desired products due to pronounced differences in their R_f values in chromatography. In a few cases, the byproduct may be removed easily by recrystallization because of its low content. In the case of the 1-naphthyl substrate, the yield reported was determined after subtracting the contribution from the $\mathrm{Ni^{II}}$–(1-naphthyl) complex used, based on an estimate that $[(1\text{-naphthyl})\mathrm{Ni(PPh_3)_2Cl}]$ would be completely converted.

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