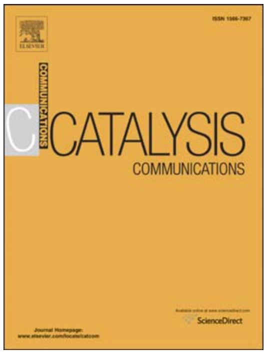

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# *Trans*-Chloro (1-Naphthyl)bis[tris(4-methoxyphenyl)phosphane] nickel(II) Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides with Phenylboronic acid

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## Abstract

A readily accessible trans-chloro-(1-naphthyl)bis-[tris-(4-methoxyphenyl)phosphine]-nickel(II) [NiCl(MOTPP)$_2$(1-naphthyl)] complex was prepared and applied successfully to the Suzuki-Miyaura coupling of aryl chlorides with phenylboronic acid. The pre-catalyst readily forms the catalytically active Ni(0) species in situ under mild conditions without an additional reducing reagent. The electron-rich methoxy moieties on the phosphine ligand may increase the electron density of Ni and thus accelerates the reaction rate of oxidative addition. Single crystal X-ray diffraction revealed the Ni-Cl and Ni-C bonds were lengthened in comparison with those in NiCl(PPh$_3$)$_2$(1-naphthyl), presumably owing to the stronger electron donating ability of MOTPP, which would facilitate the oxidative addition step.

**Keywords**: Suzuki-Miyaura coupling; aryl chlorides; nickel; tris-(4-methoxyphenyl)phosphine

## 1. Introduction

Transition-metal-mediated Suzuki-Miyaura cross-coupling is an extremely efficient strategy for the construction of biaryl compounds, which traditionally involves aryl halides as electrophiles, arylboronic acids as nucleophiles, and a Pd catalyst [1-6]. Bearing relatively strong leaving groups, aryl bromides and iodides readily participate in this cross-coupling. Aryl chlorides, however, are more challenging substrates due to slow oxidative addition of the catalyst into the C-Cl bond [7, 8], thus electron-deficient groups on the aryl chloride will benefit the coupling reaction [7]. The relatively low cost and availability of aryl chlorides adds great value to the pursuit of new cost-effective catalyst systems that allow for their coupling to proceed smoothly [3]. Nickel-catalyzed cross-coupling reactions have gained substantial interest since Percec's first report in 1995 [9-12]. Advantages of Ni over Pd catalysis lie in the low cost and high reactivity toward aryl chlorides and the Ni atom being smaller and more nucleophilic than Pd [10]. In the Ni-catalyzed Suzuki aryl-aryl cross-coupling, the mechanism may follow a Ni(0)-Ni(II) catalytic cycle [11, 13, 14]. $NiCl_2(PPh_3)_2$ [3, 11, 15, 16], $NiCl_2(PCy_3)_2$ [12, 15], $NiCl_2$(dppf) [15, 17], $NiCl_2$(dppe) [15] and $NiCl_2$(dppp) [17] are generally regarded as appropriate Ni(II) sources due to their availability and non-hygroscopicity. Ni(II) may be reduced *in situ* to the active Ni(0) species, and either a reductant (such as Zn [9] or n-BuLi [16]) or elevated reaction temperatures [18, 19] or an external ligand [15, 20] is favorable for the coupling reaction. Recently, a $Ni(COD)_2/PPh_3$ system was found to achieve cross-coupling of aryl chlorides at room temperature [21], suggesting that commercially accessible Ni(COD)$_2$ might be an alternative solution to the activation of Ni(II) to Ni(0). However, this Ni(0) source is expensive and highly air-sensitive [16], and the presence of excess PPh$_3$ is a necessity for the good yields (yield: 80-98%) [21]. Chen and Yang discovered that NiCl(PPh$_3$)$_2$(1-naphthyl) combining with excess of PPh$_3$ (substrate/pre-catalyst/PPh$_3$: 1/0.05/0.1) was highly effective for the Suzuki coupling of aryl chlorides under mild conditions (at 60 °C in THF) [20]. These pioneering works prompted us to develop an easy-to-activate and convenient-to-handle Ni pre-catalyst to carry out the Suzuki coupling of aryl chlorides, including amino-substituted aryl chlorides, which are always regarded as challenging substrates. It is well known that the improvements in Suzuki-Miyaura coupling reactions greatly rely on increasing the reactivity and stability of the metal catalysts by using efficient ligands. Our previous work demonstrated that MOTPP (tris(4-methoxyphenyl)phosphine) was a good ligand for Ru-catalyzed direct arylation of 2-phenylpyridine with aryl chlorides [22]. Being more electron-rich than PPh$_3$ due to the methoxy moieties, MOTPP is expected to increase the electron density of Ni when employed as the ligand to prepare Ni(II) catalyst, and thus should probably facilitate the oxidative addition. In this study, NiCl(MOTPP)$_2$(1-naphthyl) was synthesized and applied to the Suzuki-Miyaura cross-coupling of aryl chlorides with phenylboronic acid. Gratifyingly, this catalytic system appears to be highly effective for various aryl chloride substrates, including those bearing N(CH$_3$)$_2$ or pyridyl groups, in the absence of additional reducing reagents or external ligands.

## 2. Experimental

### 2.1 Reagents

Toluene, DMA and dioxane were redistilled from Na/benzophenone prior to use. Distilled water was degassed by nitrogen. NiCl($PPh_3$)$_2$(1-naphthyl) and NiCl(MOTPP)$_2$(1-naphthyl) were synthesized according to the literature procedures [23-25] (see supplementary material).

### 2.2 General Procedure for NiCl(MOTPP)$_2$(1-naphthyl) catalyzed cross-coupling reaction

An oven-dried reaction tube was charged with Ni(MOTPP)$_2$(1-naphthyl)Cl (2 mol %, relative to aryl chloride), $K_3PO_4$ (3 equiv., relative to aryl chloride), phenylboronic acid (1.5 equiv., relative to aryl chloride). Solid aryl chlorides (0.5 mmol) were also added at this time. The tube was evacuated and purged with nitrogen for three times. 1,4-Dioxane (2 mL) and degassed water (0.2 mL) were added via syringe. Liquid aryl chlorides were also added via syringe with the solvents. The mixture was stirred at 100 °C for 1 h under a nitrogen atmosphere, and then was cooled to room temperature. The reaction mixture was extracted with ethyl acetate, and the organic layers were dried over anhydrous $Na_2SO_4$. The organic phase was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel with hexane/ethylacetate as the eluent to afford the desired product. The products were identified by gas chromatograph and NMR spectra.

### 2.3 Characterization

Single crystal X-ray diffraction was conducted on an Oxford Xcalibur, Eos diffractometer. The crystal was kept at 143.00(10) K during data collection. Elemental Analysis was conducted on Italy CARLO ERBA 1106.Gas chromatograph analysis was performed on an Aglient GC 6890 N with an SE-30 column of 30 m × 0.32 mm × 0.25 μm.$^{1}$H and $^{13}$C NMR spectra were recorded on a BrukerAvanceII-400 MHz in $CDCl_3$ with TMS as internal standard.

## 3. Results and discussion

### 3.1 Optimization of reaction conditions

$NiCl(PPh_3)_2$(1-naphthyl) and $NiCl(MOTPP)_2$(1-naphthyl) were synthesized and applied to catalyze the cross-coupling reaction. From the outset, the effects of the solvent, base and temperature on the cross-coupling reaction were investigated using a model reaction between 4-chlorobenzotrifluoride and phenylboronic acid. 1,4-Dioxane was chosen as a candidate solvent since it is an aprotic solvent and miscible with water. More importantly, it was shown to be a good solvent for other Ni-catalyzed Suzuki-Miyaura coupling reactions [16]. As demonstrated in Table 1, moderate yield was observed in 1,4-dioxane (70%, Entry 1). Interestingly, the yield was dramatically increased to 97% when little amounts of $H_2O$ was added (Entry 2, $V_{dioxane}/V_{water} = 10/1$). In an attempt to implement more environmentally friendly coupling reactions [12], water alone was investigated as the solvent, but only a low yield of 35% was obtained. From Entries 1-3 in Table 1, it can be seen that moisture had no negative influence on the catalytic activity. Rather, the coupling reaction could be accelerated by adding a small amount of $H_2O$, matching the general assumption that the added water increased the solubility of the inorganic base $K_3PO_4$ [20]. Other organic solvents (i.e., toluene or DMA) mixed with water were tested, but the results were inferior to that observed for the dioxane-water mixture (Entries 4 and 5 vs 2, Table 1), possibly due to their immiscibility with water. Subsequently, the influence of the base was evaluated in dioxane/$H_2O$ at 100 °C. Apart from the strong base NaOH and the weak base $CH_3COONa$ (Entries 6 and 9), all other bases tested, including $K_2CO_3$, $NaHCO_3$ and $K_3PO_4$, gave good yields (Entries 7, 8 and 2). In particular, the moderately basic $K_3PO_4$ led to the best result (Entry 2), agreeing with previous reports that the base can decrease the activation barrier for transmetalation by forming a potassium aryl boronate salt with phenylboronic acid [26, 27]. A decrease in the quantity of $K_3PO_4$ resulted in a slight decrease in yield (Entries 10, 11 and 2). Based on these results, $K_3PO_4$ was chosen as the base in the following investigation. $NiCl(PPh_3)_2$(1-naphthyl) was also effective for the cross-couplings of aryl chlorides with phenylboronic acid but slightly inferior to $NiCl(MOTPP)_2$(1-naphthyl) (Entries 12 vs 2, yield: 83% vs 97%). However, $NiCl(PPh_3)_2$(1-naphthyl) combing with an excess of $PPh_3$ was ineffective for catalyzing the model cross-coupling reaction at room temperature (Entry 13), which as previously reported by Chen [20]. Referring to $NiCl(MOTPP)_2$(1-naphthyl), there was very little reactivity at either room temperature or 50 °C (Entries 14 and 15); the elevated temperature is one of the key factors required for generating the catalytically active Ni(0) species in situ [16, 18, 19]. Fortunately, $NiCl(MOTPP)_2$(1-naphthyl) did afford an 85% yield of the biaryl when the reaction was heated to 75 °C (Entry 16). $NiCl(PPh_3)_2$(1-naphthyl), in comparison, only led to an yield of 22% under 75 °C (Entry 17), which suggests that the

$NiCl(MOTPP)_2$(1-naphthyl) catalytic system is capable of generating the catalytically active Ni(0) species in situ at lower temperatures without the need of additional reducing reagents or excess ligands [18, 19].

### 3.2 Expand on different substrates

Under our established reaction conditions ($NiCl(MOTPP)_2$(1-naphthyl) as the catalyst, S/C molar ratio 50:1, 10:1 dioxane/$H_2O$ as the solvent and $K_3PO_4$ as the base), electron-rich or electron-deficient aryl chlorides coupled efficiently with phenylboronic acid in comparable yields without the need of an additional reducing reagent. For aryl chlorides bearing electron-withdrawing groups at the para-, meta- or ortho- position, excellent yields (92-98%) could be obtained within 1 h as shown in Table 2 (Entries 1-9), indicating that the steric hindrance of electron-deficient substrate had less influence on this coupling reaction. The yields were comparable to those achieved by using 4% ($Ni(COD)_2$/8% $PPh_3$) [16] (room temperature, 30 h) or ($NiCl(Ph_2PCH_2CH_2OH)_2(H_2O))Cl$ [28] (80 °C, 4-12 h). Although longer reaction times (around 20 h) were required, it is interesting to note that good yields (around 78-88%) were observed for aryl chlorides with electron-donating substituents (Entries 10-14), hinting that the catalyst has a good stability even in the absence of additional ligands [15, 20]. Sterically hindered electron-rich aryl chlorides inhibited the reaction more obviously than electron-deficient substrates (Entry 15 vs 13 vs 11, Entry 16 vs 14 vs 10), and only trace amount of coupling product was obtained for more bulky substrate 2,6-dimethylchlorobenzene (Entry 16). Gratifyingly, pyridyl chloride and amino-substituted aryl chlorides also successfully coupled with phenylboronic acid in this system (Table 2, Entries 7, 12). The Suzuki-Miyaura coupling between amino-substituted aryl chlorides and phenylboronic acid is always regarded to be tough given that the electron-rich $NR_2$ group might coordinate with and deactivate the metal (i.e., Ni) [29, 30]. To our delight, moderate yield (80%) was obtained for 4-chloro-N,N-dimethylaniline (Entry 12). In addition, upon decreasing the catalyst loading from 2 mol% to 1 mol% or further to 0.5 mol%, yields remained relatively steady for electron-deficient aryl chlorides (Entries 3 vs 17 vs 19, yield: 97% vs 95% vs 88%), but were greatly influenced with respect to the electron-rich aryl chlorides (Entries 10 vs 18 vs 20, yield: 88% vs 70% vs 32%). A substrate substituted by electron-withdrawing group might facilitate the oxidative addition of Ni into aryl chloride [28], which presumably because the electron-drawing groups may help polarize the C-Cl bond, in turn, electron-donating substituted aryl chloride is unfavorable for the oxidative addition.

In contrast, with the presence of 0.5 mol% $NiCl(PPh_3)_2$(1-naphthyl) under the similar conditions with 0.5 mol% $NiCl(MOTPP)_2$(1-naphthyl), the yields were only 14% and 1.6% for the coupling between phenylboronic acid and 4-chlorobenzotrifluoride (Entry 21) or 4-chlorotoluene (Entry 22), respectively, thus demonstrating the superiority of $NiCl(MOTPP)_2$(1-naphthyl) over $NiCl(PPh_3)_2$(1-naphthyl) in regards to catalytic efficiency. We also performed $NiCl(MOTPP)_2$(1-naphthyl) catalyzed Suzuki-Miyaura coupling between 4-chlorotrifluorotoluene and various arylboronic acids, such as 4-methoxyphenylboronic acid, pyridine-3-boronic acid, 2,6-dimethylphenylboronic acid and thiophene-3-boronic acid (see Entries 23-26, Table 2). Unfortunately, except the former two could give the isolated yield of 38% and 16%, respectively, nearly no desired products were observed for the latter two.

### 3.3 Proposed reason for the superiority of NiCl(MOTPP)$_2$(1-naphthyl)

In this study, NiCl(MOTPP)$_2$(1-naphthyl) (**CI**) showed much better performance than NiCl(PPh$_3$)$_2$(1-naphthyl) (**CII**). It is well known that increasing the electron density of central metal can accelerate the oxidation addition [29]. MOTPP is more electron-rich than PPh$_3$, the electron density of Ni in **CI** may be higher than that in **CII**, hence, the oxidative addition of aryl chloride was expected to proceed more smoothly on species **A** which was derived from **CI** than on the corresponding species derived from **CII** (Scheme 1). In addition, the characteristic of more electron-rich MOTPP may in turn influence the Ni-Cl or Ni-C (1-naphthyl) bonds in **CI**. So, we expected to seek some supporting information from the structures of **CI** and **CII**. Fortunately, the single crystal X-ray diffraction of **CI** and **CII** were obtained successfully and the data evidenced that the average length of Ni-P bond in **CI** was little shorter than that in **CII** (Figure 1), the Ni-Cl bond in **CI** is elongated to 2.2280 Å compared to 2.2238 Å in **CII**, and accordingly, the Ni-C bond between the Ni atom and naphthyl moiety is lengthened from 1.899 Å to 1.929 Å, which hint the more electron-rich MOTPP might increase the electron density of Ni, weaken the Ni-Cl and Ni-C bonds in **CI** and make them more prone to dissociate than those in **CII**. Although the structure of nickel complex in solution will not be identical to the crystal state, the information of the crystal structure still clearly revealed the influence from electronic effect of phosphine. Based on the above study, it is reasonable to infer that **CI** is more likely to generate the catalytically active Ni(0) species (compound **A**, Scheme 1), and then proceed into the requisite catalytic cycle (proposed in Scheme 1). It is also reasonable to suggest that the coordination bonds between Ni and carbon atoms in species **B** and **C** might be weaker due to the electron-rich phosphines MOTPP (Scheme 1), and the reductive elimination was probably easier to occur with the presence of **CI** than **CII**.

## Conclusions

Satisfactory to excellent yields were achieved in NiCl(MOTPP)$_2$(1-naphthyl) catalyzed Suzuki-Miyaura cross-coupling of aryl chlorides with phenylboronic acids, under relatively mild conditions. This catalyst provides a convenient, relatively efficient and less expensive alternative for the synthesis of biaryls. Owing to MOTPP ligand, the Ni-Cl and Ni-C bonds in NiCl(MOTPP)$_2$(1-naphthyl) were weakened, which play a vital role in improving the whole catalytic cross-coupling process.

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**The list of Table, Figure, and Scheme captions**

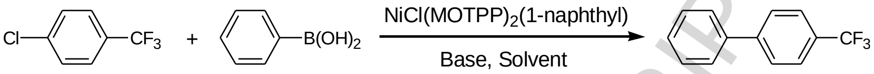
**Table 1.** The optimum of reaction conditions for NiCl(MOTPP)$_2$(1-naphthyl) catalyzed Suzuki cross-coupling between 4-chlorobenzotrifluoride and phenylboronic acid.[a]

**Table 2.** Suzuki coupling of a variety of aryl chlorides with arylboronic acids.[a]

**Figure 1.** ORTEP view of the molecular structure of the two complexes.

**Scheme 1.** Synthesis of NiCl(MOTPP)$_2$(1-naphthyl) and proposed mechanism for the cross coupling of aryl chlorides with phenylboronic acid.

**Table 1.** The optimum of reaction conditions for NiCl(MOTPP)$_2$(1-naphthyl) catalyzed Suzuki cross-coupling between 4-chlorobenzotrifluoride and phenylboronic acid.[a]



| Entry | Solvent | Base | Temp. (°C) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 1,4-Dioxane | $K_3PO_4$ | 100 | 1 | 70 |
| 2 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 100 | 1 | 97 |
| 3 | $H_2O$ | $K_3PO_4$ | 100 | 1 | 35 |
| 4 | Toluene-$H_2O$ | $K_3PO_4$ | 100 | 1 | 63 |
| 5 | DMA- $H_2O$ | $K_3PO_4$ | 100 | 1 | 35 |
| 6 | 1,4-Dioxane-$H_2O$ | NaOH | 100 | 1 | Trace |
| 7 | 1,4-Dioxane-$H_2O$ | $K_2CO_3$ | 100 | 1 | 70 |
| 8 | 1,4-Dioxane-$H_2O$ | $NaHCO_3$ | 100 | 1 | 50 |
| 9 | 1,4-Dioxane-$H_2O$ | $CH_3COONa$ | 100 | 1 | Trace |
| 10 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 100 | 1 | 80[c] |
| 11 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 100 | 1 | 88[d] |
| 12 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 100 | 1 | 83[e] |
| 13 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 25 | 1 | NR[f] |
| 14 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 25 | 1 | NR |
| 15 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 50 | 1 | NR |
| 16 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 75 | 1 | 85 |
| 17 | 1,4-Dioxane-$H_2O$ | $K_3PO_4$ | 75 | 1 | 22[e] |

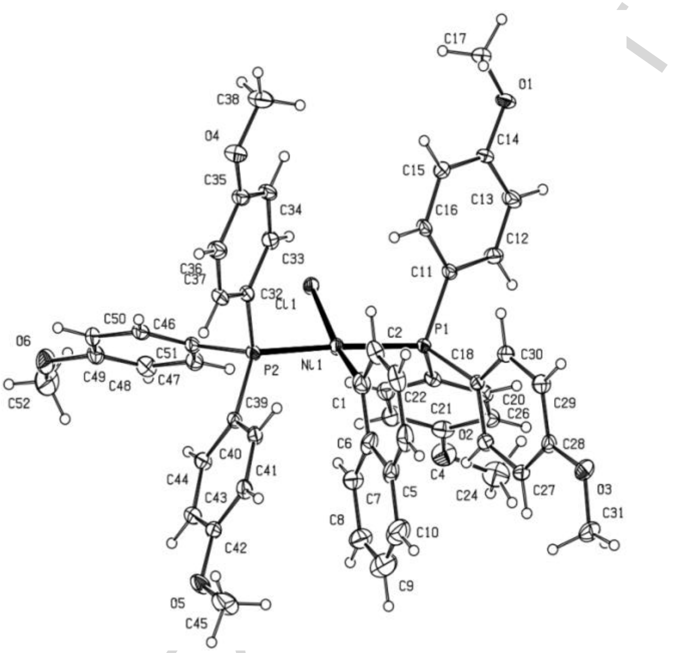
[a] Reaction conditions: 4-chlorobenzotrifluoride (0.5 mmol), phenylboronic acid (0.75 mmol), NiCl(MOTPP)$_2$(1-naphthyl) (0.01 mmol), $K_3PO_4$, NaOH, $K_2CO_3$, $NaHCO_3$ and $CH_3COONa$ (1.5 mmol), dioxane (2 mL), $H_2O$ (0.2 mL). [b] Isolated yields (average of two runs). [c] $K_3PO_4$ (0.5 mmol).[d] $K_3PO_4$ (1.0 mmol).[e] the catalyst was NiCl(PPh$_3$)$_2$(1-naphthyl) (0.01 mmol). [f] the catalyst was NiCl(PPh$_3$)$_2$(1-naphthyl)/PPh$_3$ (0.01 mmol/0.025 mmol).

**Table 2.** Suzuki coupling of a variety of aryl chlorides with arylboronic acids.[a]

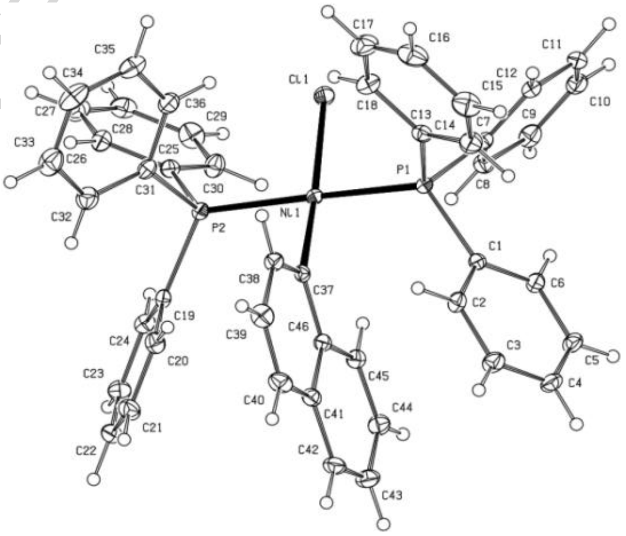
| Entry | aryl chloride | arylboronic acid | t (h) | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | 4-Chlorobenzaldehyde | phenylboronic acid | 1 | **a** | 98 |
| 2 | 4-Chlorobenzonitrile | phenylboronic acid | 1 | **b** | 97 |
| 3 | 4-Chlorotrifluorotoluene | phenylboronic acid | 1 | **c** | 97 |
| 4 | 4-Chloroacetophenone | phenylboronic acid | 1 | **d** | 97 |
| 5 | 3-Chlorotrifluorotoluene | phenylboronic acid | 1 | **e** | 97 |
| 6 | 3-Chloroacetophenone | phenylboronic acid | 1 | **f** | 95 |
| 7 | 3-Chloropyridine | phenylboronic acid | 1 | **g** | 92 |
| 8 | 2-Chlorobenzonitrile | phenylboronic acid | 1 | **h** | 98 |
| 9 | 2-Fluorochlorobenzene | phenylboronic acid | 1 | **i** | 93 |
| 10 | 4-Chlorotoluene | phenylboronic acid | 20 | **j** | 88 |
| 11 | 4-Chloroanisole | phenylboronic acid | 20 | **k** | 87 |
| 12 | 4-Chloro-N,N-dimethylaniline | phenylboronic acid | 20 | **l** | 80 |
| 13 | 3-Chloroanisole | phenylboronic acid | 20 | **m** | 85 |
| 14 | 2-Chlorotoluene | phenylboronic acid | 20 | **n** | 78 |
| 15 | 2-Chloroanisole | phenylboronic acid | 20 | **o** | trace |
| 16 | 2,6-Dimethylchlorobenzene | phenylboronic acid | 20 | **p** | trace |
| 17 | 4-Chlorotrifluorotoluene | phenylboronic acid | 1 | **c** | 95[b] |
| 18 | 4-Chlorotoluene | phenylboronic acid | 20 | **j** | 70[b] |
| 19 | 4-Chlorotrifluorotoluene | phenylboronic acid | 20 | **c** | 88[c] |
| 20 | 4-Chlorotoluene | phenylboronic acid | 20 | **j** | 32[c] |
| 21 | 4-Chlorotrifluorotoluene | phenylboronic acid | 20 | **c** | 14[d] |
| 22 | 4-Chlorotoluene | phenylboronic acid | 20 | **j** | 1.6[d] |
| 23 | 4-Chlorotrifluorotoluene | 4-methoxyphenylboronic acid | 20 | **q** | 38 |
| 24 | 4-Chlorotrifluorotoluene | pyridine-3-boronic acid | 20 | **r** | 16 |
| 25 | 4-Chlorotrifluorotoluene | 2,6-dimethylphenylboronic acid | 20 | **s** | trace |
| 26 | 4-Chlorotrifluorotoluene | Thiophene-3-boronic acid | 20 | **t** | trace |

[a] Reaction conditions: aryl chloride (0.5 mmol), arylboronic acid (0.75 mmol), NiCl(MOTPP)$_2$(1-naphthyl) (0.01mmol), $K_3PO_4$ (1.5 mmol), dioxane (2 mL), $H_2O$

(0.2 mL), 100 °C. [b] the catalyst was 1 mol%. [c] the catalyst was 0.5 mol%. [d] the catalyst was 0.5 mol% $NiCl(PPh_3)_2$(1-naphthyl).

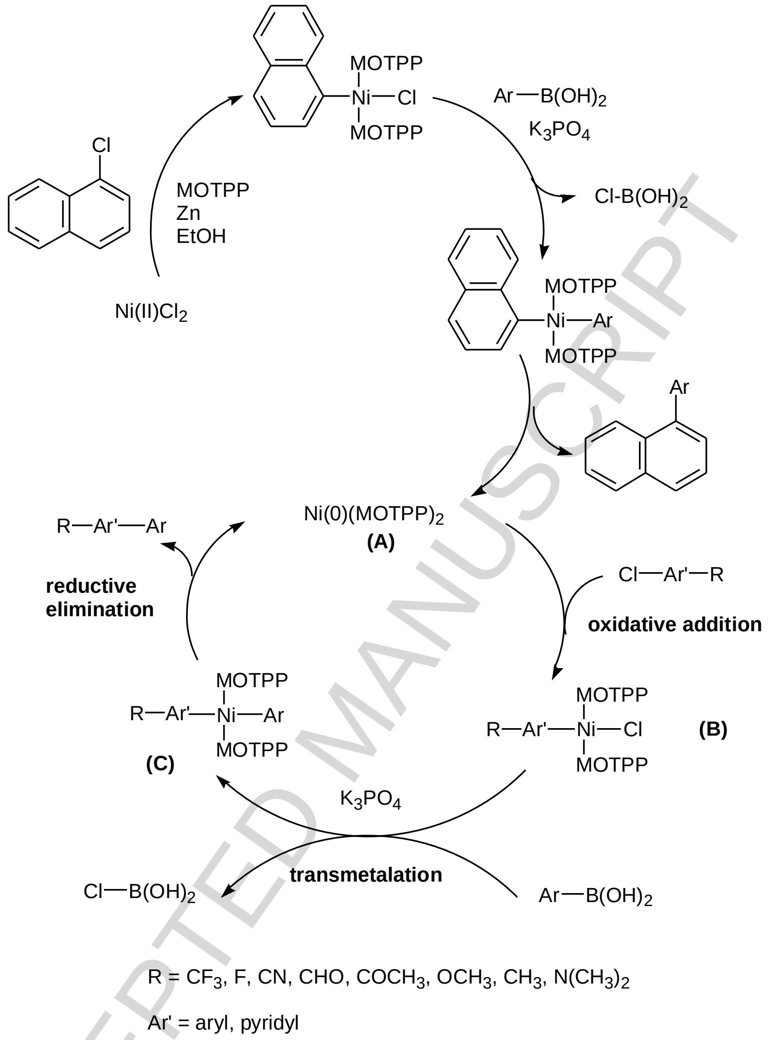


(**CI**): $NiCl(MOTPP)_2$(1-naphthyl), Ni1-Cl1: 2.2280(8) Å, Ni1-C1: 1.929(4) Å, Ni1-P1: 2.2263(9) Å, Ni1-P2: 2.2114(9) Å



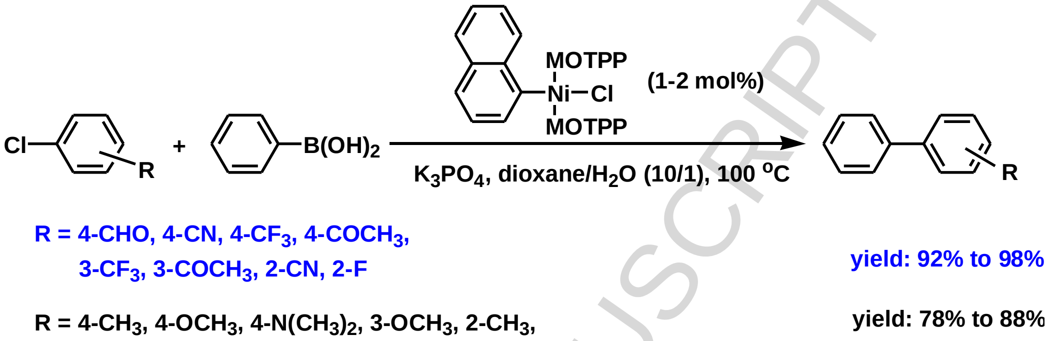
(**CII**): $NiCl(PPh_3)_2$(1-naphthyl), Ni1-Cl1: 2.2238(7) Å, Ni1-C37: 1.899(2) Å, Ni1-P1: 2.2179(7) Å, Ni1-P2: 2.2236(7) Å

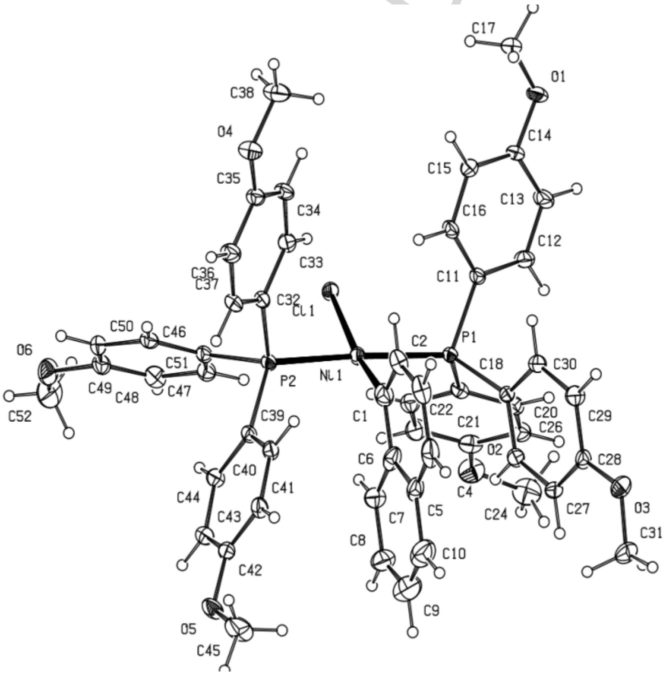
**Figure 1.** ORTEP view of the molecular structure of the two complexes.



**Scheme 1.** Synthesis of NiCl(MOTPP)$_2$(1-naphthyl) and proposed mechanism for the cross coupling of aryl chlorides with phenylboronic acid.

NiCl(MOTPP)$_2$(1-naphthyl) could afford excellent yields (92-98%) within 1 h for the coupling of aryl chlorides bearing electron-withdrawing groups. Around 78-88% yields were observed for aryl chlorides with electron-donating or amino-substituents.





NiCl(MOTPP)$_2$(1-naphthyl)

Graphical abstract

Highlights

- NiCl(MOTPP)$_2$(1-naphthyl) was prepared and applied successfully.
- Excellent yields were achieved for the coupling of various aryl chlorides.
- The impact of MOTPP was studied by single crystal X-ray diffraction.
- The Ni-C and Ni-Cl bonds in NiCl(MOTPP)$_2$(1-naphthyl) were somewhat lengthened.
- MOTPP increased the electron density of Ni compared to TPP.