# Diarylmethanes catalyzed by nickel(II) ion on nanoporous carbon

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## Abstract

Highly efficient catalytic carbon–carbon bond-forming reactions between aryl chlorides and Grignard reagents have been achieved using nickel (II) ion on nanoporous carbon. The catalytic activities in these reactions were so high that the effects of preparation, reduction, and phosphines could not be observed. No positional effect in the substrates was monitored. Increased formation of homocoupling products with functionalized substrates was also observed and a plausible explanation based on the competitive adsorption between substrates and Grignard reagents was proposed.
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*Keywords:* Kumada reaction; Carbon–carbon cross-couplings; Diarylmethanes; Heterogeneous catalysis; Nickel(II) ion on nanoporous carbon

## 1. Introduction

Carbon–carbon bond-forming reactions with aryl halides such as Kumada, Heck, Stille, Suzuki, and Negishi reactions have been recognized as one of the most important synthetic transformations in modern organic chemistry [1]. With these reactions, Kumada reactions have been widely used in modern synthetic organic chemistry [1,2], especially in constructing a variety of biaryl compounds [3], which have found many applications in the fields of biologically active molecules [4], molecular recognition [5], nonlinear optics and ligands for catalysts [6]. Even though a novel efficient noncatalytic system for biaryls [7] was reported, recent promising catalytic systems have spurred much attention to the new and efficient catalysts for using both more readily available and less expensive aryl chlorides as starting material. Many Ni and Pd complexes have been employed with great success in a wide variety of coupling reactions and well reviewed [8]. While many homogeneous systems containing mainly Ni or Pd complexes have been tested, new heterogeneous ones such as polymer-supported ones [9] have continuously been adopted for the application in industry.

Recent report on the microwave-assisted Kumada reactions [10] is also worth attracting attention.
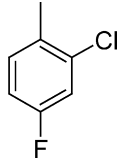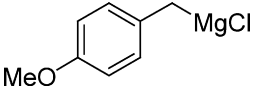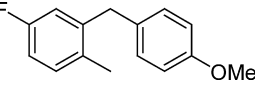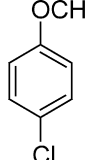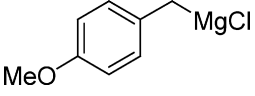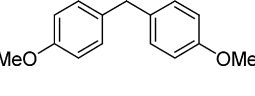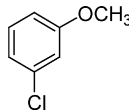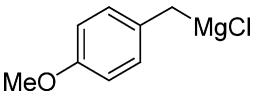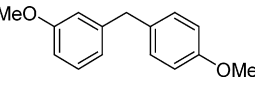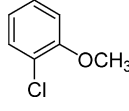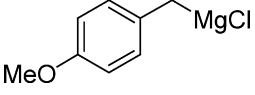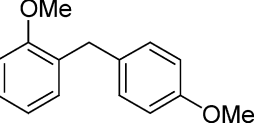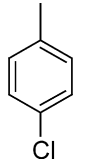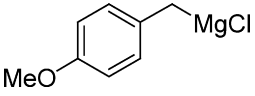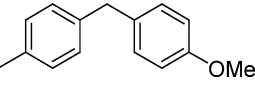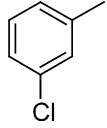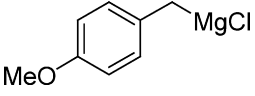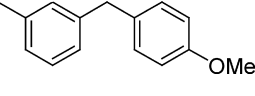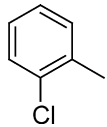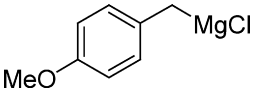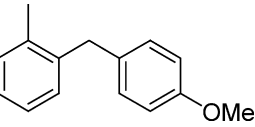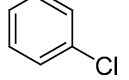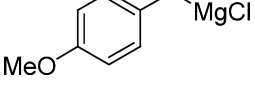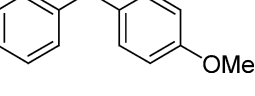
Recent report by Lipshutz and his coworkers on the efficiency of nickel on charcoal (Ni/C) as a catalyst for Negishi coupling [11], Kumada coupling [3f], Suzuki coupling [12], aminations [13], and reductive dechlorinations [14] has attracted much attention. His efforts for the development of this new type of catalyst have been presented in his recent review [15]. Even though an extensive study has strongly implicated solution-based catalysts, it is claimed that Ni/C still can be considered as a heterogeneous catalyst in that essentially complete recovery of the nickel in solution is achieved on the support after filtration [16].
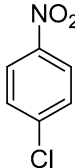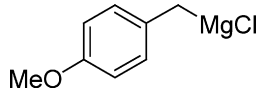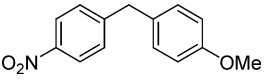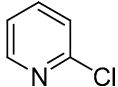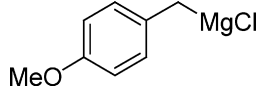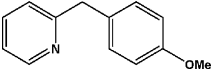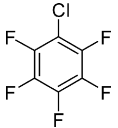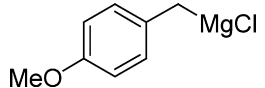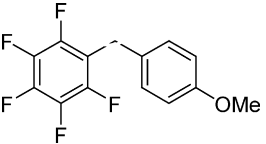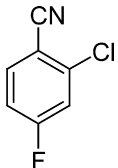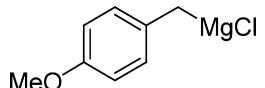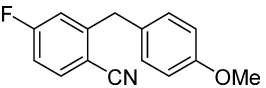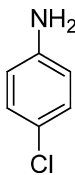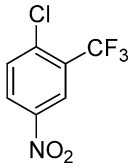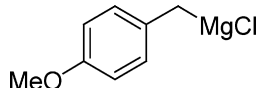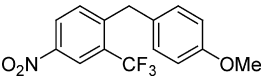
We have reported a preliminary results of diarylmethane formation catalyzed by Ni(II) ion on nanoporous carbon and change of support could induce much improved C–C couplings [17] and many attempts have been made to understand the uncommon nature of this catalytic system. Therefore, new, nanoporous carbon with hexagonally ordered mesostructure developed by Ryoo and his coworkers [18] can be an alternative for charcoal as a catalyst support.

In this contribution, we now summarize our recent efforts to rationalize the Kumada coupling reaction results with Ni/nanoporous carbon (nano C) and to optimize the catalytic system.

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Table 1
Results of the Kumada reaction catalyzed by Ni/mesoporous C

| No. | Aryl chloride | Grignard reagent | Product | Ni catalyst | Reaction time (min) | Cross-coupling vs. homo-coupling | Isolated yield (%) | Conversion (%) | Reaction time yield in ref. [3f] |
|---|---|---|---|---|---|---|---|---|---|
| 1 |  |  |  | 1 | 10 | Cross | 90 | 98 | 9 h, 76% |
|  |  |  |  | 2 | 10 | 2:1 | 62 | 65 |  |
|  |  |  |  | 3 | 10 | Cross | 95 | 99 |  |
| 2 |  |  |  | 1 | 10 | Cross | 91 | 96 | 9 h, 83% |
|  |  |  |  | 2 | 10 | Cross | 86 | 97 |  |
|  |  |  |  | 3 | 10 | Cross | 83 | 96 |  |
|  |  |  |  | Ni(NO$_3$)$_2$ 1 mg | 10 | 1:1 | 40 | 45 |  |
|  |  |  |  | Ni(NO$_3$)$_2$ 3 mg | 10 | 1:1 | 41 | 45 |  |
|  |  |  |  | Ni(NO$_3$)$_2$ 5 mg | 10 | 1:1 | 42 | 49 |  |
| 3 |  |  |  | 1 | 10 | Cross | 85 | 99 |  |
|  |  |  |  | 2 | 10 | Cross | 91 | 99 |  |
|  |  |  |  | 3 | 10 | Cross | 88 | 98 |  |
| 4 |  |  |  | 1 | 10 | Cross | 90 | 97 |  |
|  |  |  |  | 2 | 10 | Cross | 89 | 98 |  |
|  |  |  |  | 3 | 10 | Cross | 85 | 94 |  |
| 5 |  |  |  | 1 | 10 | Cross | 82 | 96 | 9 h, 81% |
|  |  |  |  | 2 | 10 | Cross | 80 | 97 |  |
|  |  |  |  | 3 | 10 | Cross | 82 | 93 |  |
| 6 |  |  |  | 1 | 10 | Cross | 88 | 97 |  |
|  |  |  |  | 2 | 10 | Cross | 90 | 97 |  |
|  |  |  |  | 3 | 10 | Cross | 85 | 99 |  |
| 7 |  |  |  | 1 | 10 | Cross | 86 | 96 |  |
|  |  |  |  | 2 | 10 | Cross | 89 | 97 |  |
|  |  |  |  | 3 | 10 | Cross | 84 | 92 |  |
| 8 |  |  |  | 1 | 10 | Cross | 90 | 99 | 16 h, 93% |
|  |  |  |  | 2 | 10 | 2:1 | 60 | 67 |  |
|  |  |  |  | 3 | 10 | Cross | 88 | 99 |  |

| 9 | | | | 1 | 10 | 1:1 | 43 | 49 |
| | | | | 2 | 10 | 6:1 | 83 | 85 |
| | | | | 3 | 10 | 10:1 | 88 | 90 |
| 10 | | | | 1 | 10 | 2.3:1 | 60 | 69 |
| | | | | 2 | 10 | 4.4:1 | 76 | 80 |
| | | | | 3 | 10 | 2.5:1 | 69 | 71 |
| 11 | | | | 1 | 10 | 1.7:1 | 57 | 60 |
| | | | | 2 | 10 | 3.4:1 | 74 | 76 |
| | | | | 3 | 10 | 4.2:1 | 77 | 80 |
| 12 | | | | 1 | 10 | 3:1 | 71 | 74 |
| | | | | 2 | 10 | 3.7:1 | 73 | 78 |
| | | | | 3 | 10 | 3.8:1 | 76 | 80 |
| 13 | | | | 1 | 20 | 2.4:1 | 66 | 70 |
| | | | | 2 | 10 | 3.7:1 | 74 | 79 |
| | | | | 3 | 10 | 4:1 | 74 | 80 |
| 14 | | | | 1 | 10 | 2.5:1 | 69 | 71 |
| | | | | 2 | 10 | 3.7:1 | 72 | 80 |
| | | | | 3 | 10 | 4:1 | 71 | 80 |

## 2. Experimental

All reagents, purchased from Aldrich Chemical Co., were used as supplied commercially without further purification. ^{1}H and ^{13}C NMR spectra were recorded by using a 5 mm tube on a Varian Unity Inova 400 (400.265 and 100.657 MHz, respectively) or a Varian Gemini 2000 (199.976 and 50.289 MHz, respectively) spectrometer and were referenced to tetramethylsilane (TMS). All manipulations were conducted under an inert atmosphere. Grignard reagents were formed from the precursor halides by following the standard procedures. All products were chromatographed on 200–425 mesh Fisher Brand silica gel. Elemental analyses were performed with EA-1110 (CE Instruments) in Inha University.

### 2.1. General procedure for preparing Ni/nano C

The synthesis of mesoporous silica template, SBA-15 [18] and CMK-3 [17,18] was performed following the procedures described elsewhere.

Three kinds of CMK-3 materials containing Ni species were prepared. First sample was prepared by wetness impregnation of CMK-3 with $Ni(NO_3)_2$. Typically, 5 g of the CMK-3 was slurried in the aqueous solution containing 2.49 g of $Ni(NO_3)_2 \cdot 6H_2O$ for about 30 min at room temperature. Subsequently, the water was completely evaporated at 333 K by using a rotary evaporator and dried in an oven for 24 h at 373 K. The sample thus obtained are denoted by Ni/CMK-3-imp (abbreviated by Ni(3)), where the imp means the impregnation method. Second Ni/CMK-3 material was obtained with the following procedure. 2.49 g of $Ni(NO_3)_2 \cdot 6H_2O$ was first supported on 10 g of the calcined SBA-15. After drying for 24 h at 373 K, the Ni/SBA-15 was directly used as the template for CMK-3 materials. The preparation method for the CMK-3 was the same as the above procedure. This sample is referred to as Ni/CMK-3-pre (abbreviated as Ni(1)), where the pre means the pre-impregnation with Ni species. The procedure for the synthesis of the third Ni/CMK-3 sample was very similar to that of CMK-3 materials, except that the $Ni(NO_3)_2 \cdot 6H_2O$ was mixed with the carbon source. The mesopores of the SBA-15 were filled with a mixture of the sucrose, sulphuric acid and $Ni(NO_3)_2 \cdot 6H_2O$ by the impregnation method. Remaining procedure for the carbon materials was the same as the above method. The third sample is designated as Ni/CMK-3-com (abbreviated as Ni(2)), where the com indicates composite material of mesoporous carbon and Ni species.

### 2.2. General procedures for coupling of aryl chlorides with RMgX

To a flame-dried 100 ml of round bottomed flask under nitrogen at room temperature was added Ni(II)/nano C (5 mg). Dry THF (20 ml) was added via a syringe and the slurry was stirred for 20 min. An aryl chloride (1.0 mmol) was added dropwise with stirring and then excess Grignard reagent (1.1 mmol) in 20 ml of THF was slowly added at room temperature. The mixture was heated to reflux for the appropriate time. The reaction was monitored by ^{1}H NMR after sampling 1 ml of solution every 5 min. After completion of the reaction, methanol (5 ml) was then added and the slurry was stirred so as to quench excess Grignard reagent. The crude mixture was filtered through a short silica column (1 cm) on the glass frit and the filter cake was further washed with methanol and THF. Solvents were then removed under reduced pressure and column chromatography on silica gel gave the purified product.

### 2.3. Reduction of Ni(II)/nano C

To a flame-dried 100 ml round bottomed flask under nitrogen at room temperature was added Ni(II)/nano C (200 mg). Hydrogen was introduced to flush over the catalysts for 4 h at room temperature under atmospheric pressure with stirring magnetically. After treatment with $H_2$, the catalysts were stored under nitrogen atmosphere.

### 2.4. Reactions with PPh3

The procedure was the same as described above except that five equivalents of $PPh_3$ (to the substrate) was added to the solution.

### 2.5. Determination of metal contents by atomic absorption (AA) spectroscopy

About 10 mg of sample was completely dissolved in 10 ml of aqua regia with stirring vigorously at 70 °C. Then the solution was used to determine the metal content by AA spectroscopy (Spectra AA 220FS, Varian).

## 3. Results and discussion

As shown in Table 1, much improved catalytic activities of Ni/nano C towards Kumada coupling reactions are clearly observed than those of Ni/charcoal [3f] but contrary to our expectation, the activities of the catalysts are so high that the dependence of catalytic activity on the preparation procedures cannot be established. Further reduction of catalyst amount (less than 5 mg) cannot be tried due to possible increase in uncertainty in experimental results. As described in detail in the experimental section, catalytically active species, Ni(II) ions are introduced to nanostructured carbon before, during, and after the carbonization and it is expected that the last one has more catalytic active species on the surface of supports than the other ones and shows the highest activity.

Lipshutz et al. already pointed out the advantages of Ni/C such as simplicity of use and low price but his catalytic system requires 40–70% excess Grignard reagents for the *in situ* formation of Ni(0) [3f]. They also reduced Ni(II) ion by *n*-BuLi before use, which resulted in the formation of more active Ni(0) more efficiently. They also claimed that without LiBr, which was originally used to avoid homocoupling, the reaction was slower but cleaner. They showed that addition of LiBr actually led to the increase in homocoupling [14]. Even though only 20% excess Grignard reagents are used and no reduction is carried out before use except in some cases in Table 2 in this study,

Table 2
Results of the Kumada reaction catalyzed by Ni/mesoporous C after hydrogen or *n*-BuLi treatment

| No. | Aryl chloride | Grignard reagent | Product | Ni Catalyst | Reaction time (min) | Cross-coupling vs. homo-coupling | Isolated yield (%) | Conversion (%) |
|-----|---------------|------------------|---------|-------------|---------------------|----------------------------------|--------------------|----------------|
| 1 |  |  |  | 1 | 10 | Cross | 90 | 96 |
| | | | | 2 | 10 | Cross | 89 | 95 |
| | | | | 3 | 10 | Cross | 93 | 99 |
| | | | | 3[a] | 10 | Cross | 89 | 94 |

[a] Reduction with *n*-BuLi.

Table 3
Ni contents in catalysts determined by atomic absorption spectroscopy

| No. | Ni | | | Mg |
|-----|-----|-----|-----|-----|
| | Type | wt% | Modified wt%[a] | wt% |
| As prepared | Ni(1) | 6.00 | 6.12 | 2 |
| | Ni(2) | 6.11 | 6.22 | 1.72 |
| | Ni(3) | 6.28 | 6.42 | 2.22 |
| After reaction (entry 1) | Ni(1) | 2.05 | 2.15 | 4.50 |
| | Ni(2) | 2.39 | 2.67 | 10.35 |
| | Ni(3) | 2.66 | 3.04 | 12.41 |

[a] Modified wt%: Ni contents after removal of Mg.

much faster reaction rates have been observed (runs 1, 2, and 5 in Table 1). Addition of LiBr (1.0 equiv. relative to aryl chloride) or reduction of catalysts with *n*-BuLi or $H_2$ does not change the rates and conversions significantly (Table 2). Lipshutz and Bromgren pointed out that *n*-BuLi in the presence of $PPh_3$ was the most efficient reagent for the reduction of Ni(II) on charcoal [11] but later that excess of Grignard reagent accomplished the same results [14].

Nickel contents in Ni(1), Ni(2), and Ni(3) analyzed by atomic absorption (AA) spectroscopy are 6.0, 6.11, and 6.28 wt%, respectively (Table 3). Since these values are roughly two times as large as that in the Lipshutz's catalyst (3.82%), much

faster reaction rates cannot be attributed only to the amount of active species. After the reaction, the remaining nickel contents in Ni(1), Ni(2), and Ni(3) are found to be 2.15, 2.67, and 3.04 wt%, respectively. This indicates that maximum 0.2 mg of Ni is leached out from the catalysts during the reaction.

In order to check the possibility of homogeneous catalysis by bleeding Ni species, catalysis by addition of $Ni(NO_3)_2$ has been tested (entry 2). To our surprise, even 1 mg of $Ni(NO_3)_2$ is enough to complete the reaction in 10 min. However, a distinct difference between homogeneous and heterogenized catalysts has been found in the selectivity of the product; in the homogeneous catalysis, 1:1 mixture of homo and cross-coupling products is detected, while only cross-coupling products are formed in the case of heterogenized catalyst. The ratio of homo and cross-coupling products in the homogeneous catalysis does not change with the amount of $Ni(NO_3)_2$.

Tasler and Lipshutz proposed the mechanism where homocoupling occurred with the involvement of charge transfer π-complex (Scheme 1) [19]. As reported by them, adoption of *n*-BuMgCl instead of aryl Grignard reagents failed to produce coupling products up to 10 h in both reactions. Therefore, it may be tentatively concluded that the nanoporous carbon support effectively blocks the catalytic cycle involving the charge transfer π-complex to suppress the homocoupling. At this point, it is not clear how the support plays a key role but single electron transfer (SET) step is the most possible one.



Scheme 1. Possible mechanistic pathway for ligandless cross- and homocouplings of aryl chlorides proposed by Lipshutz [15].

It is also interesting that coupling reactions proceed very rapidly irrespective of the nature of substituents onto the arene ring. Even the slowest reaction (entry 13 with catalyst 1) has completed in 20 min. Much improved tolerance towards various functional groups shown in this system is quite different from the results reported by Lipshutz et al., where the extent of functional group tolerance is governed by the reactivity of the Grignards in general, and hence, an electrophilic center present in the educt or RMgX is not tolerated [3f]. Again the nature of carbon support greatly affects the efficiency of Kumada coupling reaction, even though the reasons of difference cannot be proposed yet.

It appears that the selectivity of the reaction product depends on the nature of substituents. Generally, the presence of electron donating group (Me or MeO) in the aromatic ring induces the clean cross-coupling but electron withdrawing groups (F, $NO_2$, CN) induce a mixture of homo- and cross-coupling products. The aryl chloride with amino group and chloropyridine produced the mixture. In general, more cross-coupling products are formed in the following order except chloropyridine (entry 10); Ni(3) > Ni(2) > Ni(1). This order is appeared to be inversely correlated with the leaching amount of nickel species. Considering the facts that the ligandless reaction with the Ni/C system of Lipshutz leads to more homocoupling product [19] and reactions with $Ni(NO_3)_2$ produce mixtures of homo- and cross-coupling products (vide supra), this order can be rationalized.

Since alkyl Grignard reagents are more powerful reducing agent than aryl ones, no reaction with alkyl Grignard reagents cannot be rationalized in a simple way. As mentioned above, much faster reaction rates than those with Ni/C cannot be understood only on the basis of different nature of support and more active species in the catalysts. Therefore, the following equilibrium, known as Schlenk equilibrium, is considered to explain the experimental results:
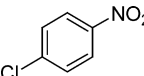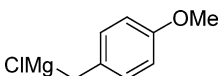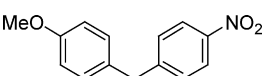
$$2\,RMgX \rightleftharpoons MgR_2 + MgX_2$$

This equilibrium is generally endothermic, favoring the Grignard reagent and substitution of alkyl groups for Ph further depresses the disproportionation reaction [20]. This trend is also supported by an experiment in $Et_2O$ [21]. However, reaction enthalpies of these equilibria for EtMgBr and PhMgBr in THF were estimated as 25.5 and 11.8 kJ/mol, respectively [22] and this difference was attributed to increased coordination number of magnesium halides [23].

$MgR_2$ has been widely used as an efficient transalkylating agent in polymer chemistry but Grignard reagents have been hardly exploited. It is reported that the Mg–C bond strength in $MgR_2$ is weaker than that in Grignard reagents and Mg–C bond in PhMgX is stronger than those in RMgX [24]. With this in mind, it can be considered that $MgR_2$ is a much powerful transalkylating agent or a reducing agent than Grignard reagents. Actually much slower reaction rates with Grignard reagents prepared after only 4 h reflux in THF are observed. In these cases, the Grignard reagents still showed characteristic purple color due to small amount of iodine added for activation of Mg. However, Grignard reagents formed after 24 h reflux in THF show typical dark brown color and some white solids, which might indicate the formation of $MgR_2$ and $MgCl_2$. Reaction between bleeding Ni(II) and $MgR_2$ would resulted in faster formation of Ni(0), active species for catalysis and faster rates of cross-coupling reaction. However, no coupling products with n-BuMgCl obtained after 24 h reflux in THF were found even after 10 h reflux and this cannot be rationalized in this manner. Commerically available n-$Bu_2$Mg also did not produce coupling products with any kind of chloride compounds either. At this point, no rational explanation can be proposed.

Increased formation of homocoupling products with functionalized substrates may be rationalized by assuming the competitive adsorption of aryl Grignard reagents and substrates. In other words, aryl Grignard reagents are initially adsorbed on the surface of nano carbon material and slowly bleeding into the solution with the process of coupling reactions. Therefore, limited solution concentration of aryl Grignard reagents resulted in effective prevention of homocoupling (vide supra). On the other hand, substrates with functional groups showing considerable coordinating abilities such as $NO_2$, amine, and CN may prevent aryl Grignard reagents from adsorption by preferential adsorption on the surface of support and this results in increased solution concentration of aryl Grignard reagents which lead to more homocoupling via the charge transfer π-complex mechanism. Methyl, methoxy and F do not have good coordinating abilities and adsorption of aryl Grignard reagents cannot be effectively blocked and only cross-coupling products are formed. However, presence of five F's onto the arene ring (entry 11) appears to block the adsorption of aryl Grignard reagents. This assumption is confirmed by the formation of homocoupling products only with the addition of $NEt_3$ ($NEt_3$:substrate:Grignard reagent = 320:1:1.1) in entry 2 conditions. Formation of cross-coupling product is observed with decrease in amine (the ratio of cross to homocoupling product is 2 with $NEt_3$:substrate:Grignard reagent = 160:1:1.1). However, no further change of the ratio is observed with less $NEt_3$ (the ratio of cross to homocoupling product is 2 with $NEt_3$:substrate:Grignard reagent = 32:1:1.1).

Table 4
Results of the Kumada reaction catalyzed by Ni/nanoporous C with $PPh_3$ (5 equiv.).

| Aryl chloride | Grignard reagent | Product | Ni catalyst | Reaction time (min) | Cross-coupling vs. homo-coupling | Isolated YIELD (%) | Conversion (%) |
|---|---|---|---|---|---|---|---|
|  |  |  | 3 | 10 | Cross | 90 | 99 |

It is worth mentioning that in runs 1 and 8, only Ni(2) produces the mixture of homo- and cross-coupling products. No rational explanation can be deduced yet.

No positional effect of the substituents on the reaction rate is observed (runs 2–4 and 5–7). This represents that no size discrimination can be made by this system and this may be due to the solution-based catalysis of this system.

Addition of five equivalents of PPh₃ also does not induce significant increase in the reaction rate (Table 4) possibly due to the fast reaction rate of this system.

## 4. Conclusion

Facile carbon–carbon bond formation between aryl chlorides and Grignard reagents was achieved using nickel on nanoporous carbon. This reaction proceeds essentially in a homogeneous manner but the ratio of cross to homocoupling is different from the pure homogeneous system. Catalytic activity is too high to discriminate the preparative methods and to observe the effect of reduction or addition of phosphine. Increased formation of homocoupling products with functionalized substrates may be rationalized by assuming the competitive adsorption of aryl Grignard reagents and substrates, which was confirmed by base addition experiments. No positional effect of the substituents on the reaction rate was also observed.

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