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A novel and efficient route to diarylmethanes catalyzed by nickel(II) ion on nanoporous carbon

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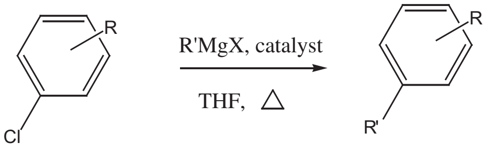
Abstract—Much improved catalytic carbon–carbon bond-forming reactions between aryl chlorides and Grignard reagents has been achieved using nickel(II) ion on nanoporous carbon.

Carbon–carbon bond-forming reactions involving aryl halides have been considered as one of the most important synthetic transformations in synthetic organic chemistry.[1] Since the Grignard cross-coupling reaction (reaction (1)), catalyzed by Group 10 metal-containing species, was discovered by Kumada and co-workers[2] as well as Corriu and Masse[3] in 1972, it has been widely used in modern synthetic organic chemistry.[1a,4]



(1)

This process has been proved as one of the most versatile and powerful approaches for constructing a variety of biaryl compounds.[5] Recent promising catalytic systems 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.[6] Even though many homogeneous systems containing mainly Ni or Pd complexes have been tested, new heterogeneous ones such as polymer-supported ones[7] have continuously been adopted for the application in industry. Recently, Lipshutz reported the efficiency of nickel on charcoal (Ni/C) as a catalyst for Negishi,[8] Kumada couplings,[5f] Suzuki couplings,[9] aminations,[10] and reductive dechlorinations.[11] He summarized his efforts for the development of this new type of catalyst in his recent review.[12] Even though an extensive study has strongly implicated solution-based catalysis within the pores of the charcoal, 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 supporter after filtration.[13]

Since nanostructured carbon materials such as carbon nanotubes have recently attracted much attention due to many possible applications, much effort has been devoted to develop new material. In this regard, new, nanoporous carbon with hexagonally ordered mesostructure developed by Ryoo and co-workers[14] can be an alternative for charcoal as a catalyst supporter.

In this contribution, we now report that Ni/nanoporous carbon (nano C) can be a much improved and active heterogenized catalyst for Kumada couplings.

The Ni catalyst on the nanoporous carbon material is prepared by using CMK-3.[15] Kumada coupling reactions have been carried out using appropriate aryl chlorides and Grignard reagents in the presence of Ni/nano C catalyst (5 mg).[16]

As shown in Table 1, much improved catalytic activities of Ni/nano C towards Kumada coupling reactions

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Keywords: Kumada reaction; Carbon–carbon cross-couplings; Diarylmethanes; Heterogeneous catalysis; Nickel(II) ion on nanoporous carbon.

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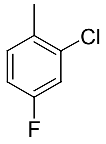
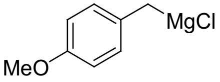
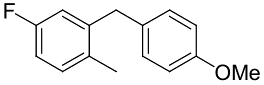
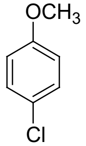
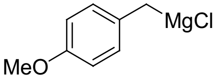
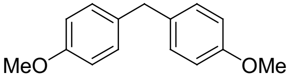
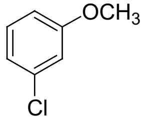
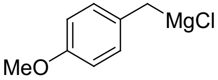
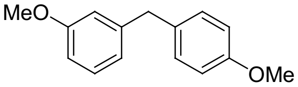
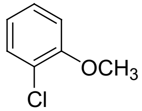
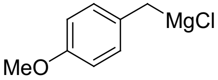
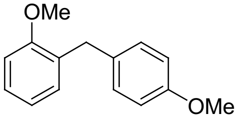
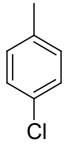
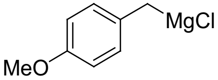
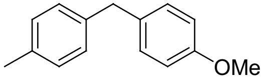
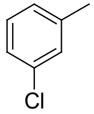
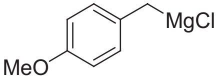
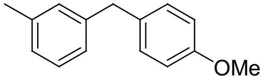
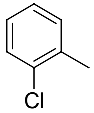
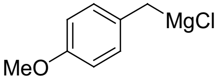
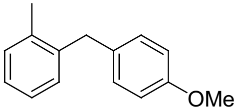
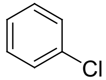
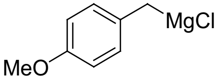
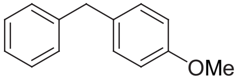
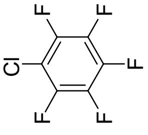
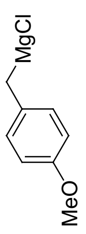
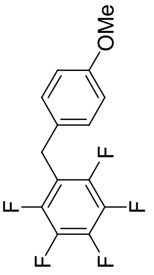
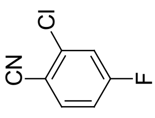
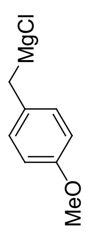
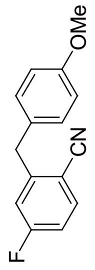
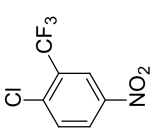
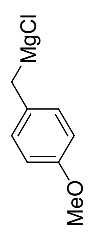
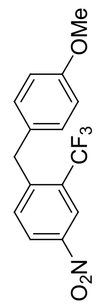
Table 1. Results of the Kumada reaction catalyzed by Ni/Mesoporous C

No.	Aryl chloride	Grignard reagent	Product	Ni catalyst	Reaction time (min)	Crosscoupling versus homo-coupling	Isolated yield (%)	Conversion (%)	Reaction time yield in Ref. 5f
1				Ni/nano C	10	Cross	95	99	9 h, 76%
2				Ni/nano C $Ni(NO_3)_2$; 1 mg $Ni(NO_3)_2$; 3 mg $Ni(NO_3)_2$; 5 mg	10 10 10 10	Cross 1:1 1:1 1:1	83 40 41 42	96 45 47 49	9 h, 83%
3				Ni/nano C	10	Cross	88	98	
4				Ni/nano C	10	Cross	85	94	
5				Ni/nano C	10	Cross	82	93	9 h, 81%
6				Ni/nano C	10	Cross	85	99	
7				Ni/nano C	10	Cross	84	92	
8				Ni/nano C	10	Cross	88	99	16 h, 93%

9				Ni/nano C	10	4.2:1	77	80
10				Ni/nano C	10	3.8:1	76	80
11				Ni/nano C	10	4:1	71	80

are clearly observed than those of Ni/charcoal.[5f] Lipshutz 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 or reduction with *n*-BuLi for the in situ formation of Ni(0). It is reported that *n*-BuLi in the presence of PPh_3 is the most efficient reagent for the reduction of Ni(II) on charcoal[12] but later excess of Grignard reagent can accomplish the same results.[17] Even though only 20% excess Grignard reagents are used and no reduction was carried out before use in this study, much faster reaction rates have been observed (run nos. 1, 2, 5 in Table 1).

Nickel contents in Ni/nano C before and after the reaction were analyzed by atomic absorption (AA) spectroscopy to be 6.28 and 3.04 wt %, respectively. This indicates that maximum 0.2 mg of Ni is leached out from the catalysts during the reaction. Even though this value before the reaction is roughly two times as large as that in the Lipshutz's catalyst (3.82%), the amount of catalyst is much less (5–50 mg) and so is the active species in the reaction system. Therefore, much faster reaction rates cannot be attributed to the amount of active species.

In order to check the possibility of homogeneous catalysis by bleeding Ni species, catalysis by $Ni(NO_3)_2$ 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 was detected, while only cross-coupling products were monitored in the reaction with heterogenized catalyst. The ratio of homo and cross-coupling products in the homogeneous catalysis does not change with the amount of $Ni(NO_3)_2$.

As reported by Lipshutz, the Kumada reactions with alkyl Grignard reagents proceed much more slowly than those with aryl ones.[5f] In this study, the result became worse; *n*-BuMgCl failed to produce coupling products up to 10 h under the same conditions.

It is also interesting that coupling reactions proceed very rapidly despite of the nature of substituents onto the arene ring even though only limited substituents are tested. Much improved tolerance towards various functional groups shown in this system is quite different from the results reported by Lipshutz, where the extent of functional group tolerance is governed by the reactivity of the Grignards. In general, an electrophilic center present in the educt or RMgX is not tolerated.[5f] The nature of carbon supporter seems to greatly affect 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 mixture of homo- and cross-coupling products.

No positional effect of the substituents on the reaction rate was observed (runs 2, 3, 4 and 5, 6, 7). This represents that no size discrimination can be done by this system and this may be due to solution-based catalysis of this system.

Further study is on progress to understand the unusual nature of this catalytic system.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.02.114.

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15. Procedure for preparing Ni/nano C: The synthesis of mesoporous silica template, SBA-15, was performed following the procedures described elsewhere.[14] In case of CMK-3, the calcined SBA-15 and sucrose were used as the template and the carbon source, respectively. The mesopores of the SBA-15 (10 g) were filled with the mixture of the sucrose (12.5 g), sulfuric acid (1.4 g) and water (50 g) by impregnation method. The mixtures were dried at 373 K and subsequently at 433 K, and then impregnation/drying step was repeated once more. The carbonization was carried out with heating to 1173 K under nitrogen flow, and finally, the silica templates were dissolved at room temperature in water/ethanol solution of NaOH.

    Ni/nano C was prepared by wetness impregnation of $Ni(NO_3)_2$ into the CMK-3. 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.
16. General procedures for coupling of aryl chlorides with RMgX: To a flame-dried 100 ml of round bottomed flask under nitrogen at room temperature were added Ni(II)/nano C (5 mg). Dry THF (20 ml) was added via 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 ^1H NMR after sampling 1 ml of solution every 5 min. After completion of 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 further washed with methanol and THF. Solvents were then removed under reduced pressure and column chromatography on silica gel gave the purified product.

    2,3,4,5,6-Pentafluoro-4′-methoxydiphenylmethane: ^1H NMR (199.976 MHz, $CDCl_3$) δ 7.32 (d, 2H), 6.85 (d, 2H), 3.81 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (50.289 MHz, $CDCl_3$) δ 163.2, 142.3, 137.5, 132.4, 129.3, 113.5, 113.1, 58.2, 24.9; Anal. Calcd for $C_{14}H_9F_5O$: C, 58.34; H, 3.15. Found: C, 58.25; H, 2.92.

    2-Cyano-5-fluoro-4′-methoxydiphenylmethane: ^1H NMR (199.976 MHz, $CDCl_3$) δ 7.65 (q, 1H), 7.27 (d, 2H), 7.04 (m, 2H), 6.80 (d, 2H), 3.78 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (50.289 MHz, $CDCl_3$) δ 167.5, 163.2, 140.1, 135.3, 132.4, 129.3, 115.4, 113.9, 113.1, 110.6, 58.2, 38.8; Anal. Calcd for $C_{15}H_{12}FNO$: C, 74.67; H, 5.01; N, 5.81. Found: C, 75.19; H, 4.95; N, 5.55.

    2-Trifluoromethyl-4-nitro-4′-methoxydiphenylmethane: ^1H NMR (199.976 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.67 (d, 1H), 7.23 (d, 2H), 7.05 (d, 1H), 6.83 (d, 2H), 3.78 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (50.289 MHz, $CDCl_3$) δ 163.2, 143.7, 139.3, 132.4, 129.8, 129.3, 127.7, 124.1, 121.1, 117.4, 113.1, 58.2, 38.9; Anal. Calcd for $C_{15}H_{12}F_3NO_3$: C, 57.88; H, 3.89; N, 4.50. Found: C, 58.13; H, 3.76; N, 4.49.
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