Immobilization of Dipyridyl Complex to Magnetic Nanoparticle via Click Chemistry as a Recyclable Catalyst for Suzuki Cross-Coupling Reactions

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Abstract: A magnetic nanoparticle (MNP)-supported di(2-pyridyl)methanol palladium dichloride complex was prepared via click chemistry. The MNP-supported catalyst was evaluated in Suzuki coupling reaction in term of activity and recyclability in DMF. It was found to be highly efficient for Suzuki coupling reaction using aryl bromides as substrates and could be easily separated by an external magnet and reused in five consecutive runs without obvious loss of activity.

Key words: Suzuki coupling, supported catalysis, palladium, di(2-pyridyl)methanol, magnetic nanoparticles

The immobilization of homogeneous catalysts to facilitate catalysts separation and recycling is of great importance in catalyst science.[1] Various supports have been explored in the past decades, such as polymers,[2] inorganic solids,[3] fluorous tags,[4] and ionic liquids.[5] However, despite the advantages mentioned above, substantial decrease of activity and selectivity often appeared due to the low solubility of the supported catalysts in the reaction media which resulted in a slow diffusion of reactants and catalysts.[6] In the case of fluorous phase and ionic-liquid-supported catalysts, the preparation of the catalysts was difficult and time-consuming. Nanoparticles have emerged as attractive supports for solid-phase organic transformations[7] due to their high surface areas brought by their nanometer scale. Consequently, the activity of the supported catalysts was greatly improved as compared to catalysts supported on traditional support matrix. But it still came up with the problem of catalyst separation and further recycling due to the colloidal property of the catalyst. This could be solved by using magnetic nanoparticles[8] as catalyst supports, thus the catalyst could be easily separated from the reaction media by the application of an external magnetic field. During the past years, a lot of magnetic-supported catalysts have been reported in organic transformations such as cross-coupling reactions,[9] hydroformylation,[10] olefin hydrogenation,[11] asymmetric hydrogenation,[12] nucleophilic substitution,[13] and esterification.[14]

Recently, the copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction,[15] which was coined as 'click reaction', has been proved to be a powerful tool for conjugation between appropriately functionalized partners of azides and alkynes. It fulfills the advantages of modularity, almost quantative yields, moderate reaction conditions, ease of introduction of both the required azide and alkyne groups, which are compatible with a broad range of functional groups and reaction conditions. These appealing advantages have led CuAAC to wide applications in fields such as drug design,[16] polymer science,[17] biochemistry,[18] molecular biology and solid-phase organic transformations.[19]

Palladium-catalyzed cross-coupling reactions are powerful methods for C–C bond formation. Many supported-catalyst-promoted cross-coupling reactions have been reported to fulfill catalyst separation and recycling using PS, PEG, silica gel as supports with different kinds of ligands such as NHCs,[20] phosphine ligands,[21] and dipyridyl ligands.[22] But only few reports have been seen in literature using magnetic nanoparticles as catalyst supports.[9] Our group has dedicated to the preparation of high efficient catalysts for cross-coupling reactions and their further reuse.[23] Recently, we have reported a PEG-supported dipyridyl catalyst and its application in Suzuki coupling reaction.[23a] Herein we would like to present a simple and efficient preparation of a novel MNP-supported dipyridyl–Pd complex by using click chemistry as a practical tagging method and its application in Suzuki coupling reactions. High activity was observed and the catalyst could be easily isolated from the reaction mixture by simple magnetic decantation and reused several runs without significant loss of activity.

The magnetic nanoparticles were readily prepared by conventional coprecipitation method with an average diameter of 10 nm. The particles were then coated with a thin layer of silica according to a literature method[24] in order to prevent the aggregation of the nanoparticles. As shown in Scheme 1, further modification of the surface of the silica-capped MNP with excess azide-functionalized silane **3** in refluxed THF afforded **4**.[25] Direct propargylation of **1** give rise to **2** in high yield.[26] Following a typical process developed by Gmeiner,[19a] 6 mol% CuI was found to be optimal for the cycloaddition of **2** and **4** to achieve **5**,[27] and the reaction process was judged by the complete disappearance of the FT-IR absorption of the azide group (2104 cm^{-1}, Figure 1). Then, the MNP-supported dipyridyl–Pd complex **6** was obtained by refluxing **5** with $PdCl_2(MeCN)_2$ in toluene.[28] In each step, the isolation and

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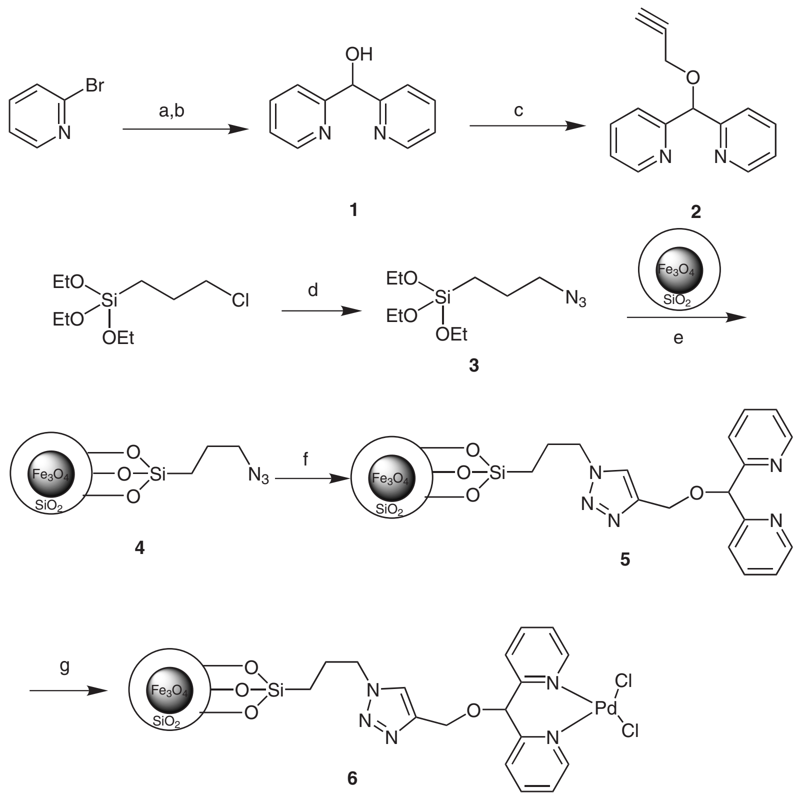


Scheme 1 Preparation of MNP-supported di(2-pyridyl)methanol–Pd complex **6**. *Reaction conditions*: a) –78 °C, *n*-BuLi, then 2-pyridylcarboxaldehyde, –78 °C, 75%; c) NaH, 0 °C, DMF, propargyl bromide, 60%; d) butanone, NaN_3, reflux, 72h, 90%; e) THF, reflux, 24 h; f) CuI, DIPEA, DMF–THF (1:1); g) $PdCl_2(MeCN)_2$, toluene, reflux, 24 h.

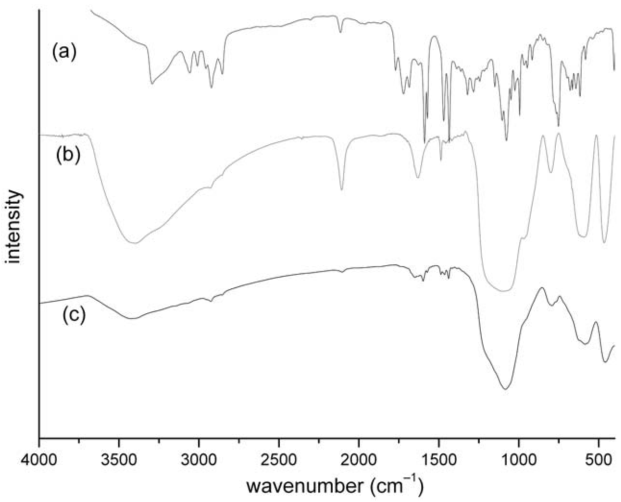


Figure 1 FT-IR Spectra of (a) di(2-pyridyl)methanol propargyl ether (**2**); (b) magnetic nanoparticles **4**, and (c) **5**

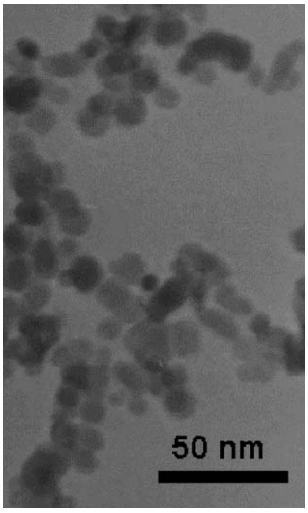
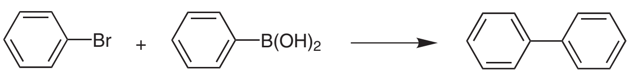


Figure 2 TEM image of **5** (scale bar 50 nm)

purification of the MNP was achieved via an external magnetic field. The TEM image of **5** is illustrated in Figure 2, which showed the core-shell structure of the silica-caped MNP (the long strips in Figure 2 were considered as the margin of the copper grids). The loading capacity of **4**, **5**, and **6**, calculated from elemental analysis data of N are 0.684 mmol/g, 0.628 mmol/g, and 0.60 mmol/g, further showed the high efficiency of the click chemistry for the immobilization of ligand. ICP-OES revealed **6** containing 0.58 mmol/g Pd, which was quite near to the value of the ligand suggesting the almost complete coordination of the ligand with Pd.

Initial studies of reaction conditions for Suzuki coupling were performed with bromobenzene and phenylboronic acid as the model reaction with different solvents, bases, and catalyst loadings (Table 1). Using K_2CO_3 as base and **6** as catalyst, the reaction proceeded much slower in toluene, water, and DMF–water than in DMF (Table 1, entries

Table 1 Suzuki–Miyaura Coupling of $PhB(OH)_2$ with Bromobenzene[a]



Entry	Pd (%)	Base	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	0.2	K_2CO_3	toluene	110	5	60
2	0.2	K_2CO_3	H_2O	100	5	83
3	0.2	K_2CO_3	DMF	100	5	92
4	0.2	K_2CO_3	DMF–H_2O[c]	100	5	86
5	0.2	Cs_2CO_3	DMF	100	5	85
6	0.2	Na_2CO_3	DMF	100	5	75
7	0.2	NaOAc	DMF	100	5	60
8	0.1	K_2CO_3	DMF	100	8	85

[a] Reaction conditions: bromobenzene (2 mmol), $PhB(OH)_2$ (2.6 mmol), base (4 mmol), solvent (5 mL).

[b] Isolated yield.

[c] DMF–H_2O = 3:2.

1–4). When Cs_2CO_3, Na_2CO_3, or NaOAc was used as base, an obvious decrease in yield was observed (Table 1, entries 5–7). Reducing the amount of **6** resulted in a direct decrease in yield even with longer reaction time (Table 1, entry 8).

With the optimized reaction conditions in hand, cross-coupling reactions of different aryl halides with aryl boronic acids were performed and the results are summarized in Table 2. Under standard conditions, which use DMF as solvent, K_2CO_3 as base, and with 0.2% catalyst loading, good to excellent yields were obtained with bromoarenes bearing both electron-withdrawing groups and releasing groups (Table 2, entries 1–4). But for the substrate with an *ortho* substituent, the yield of the coupling products dropped slightly even using more catalyst loading (Table 2, entry 5). Two other kinds of aryl boronic acids were also tested and they all reacted smoothly with aryl bromides with high product yields (Table 2, entries 6–10). Unfortunately, the catalytic system was less effective with substrates such as aryl chloride and heterocyclic bromide even using 1% of **6** and prolonged reaction time (Table 2, entries 11 and 12). It was worthy to note that magnetic nanoparticle **6** was air and moisture stable, and the coupling reactions could be carried out under air directly.

Table 2 MNP-Supported Catalyst **6** in Suzuki Coupling of Aryl Halides and Aryl Boronic Acid[a,29]

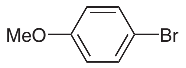
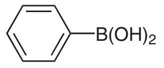
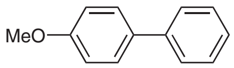
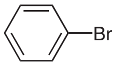
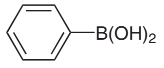
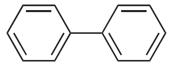
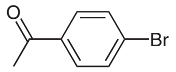
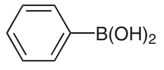
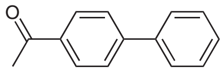
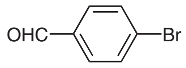
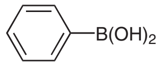
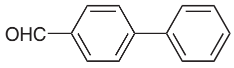
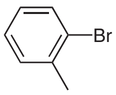
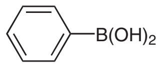
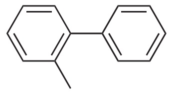
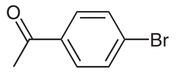
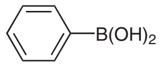
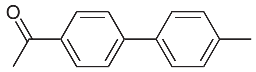
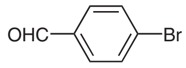
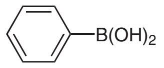
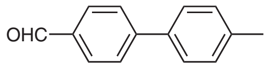
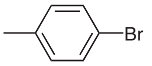
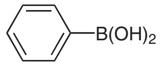
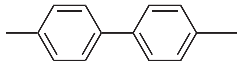
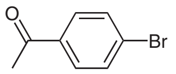
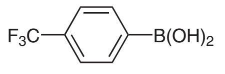
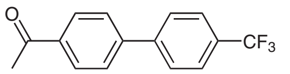
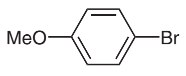
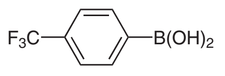
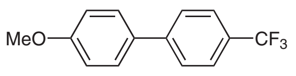
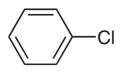
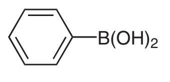
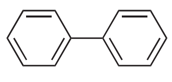
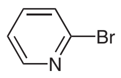
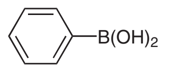
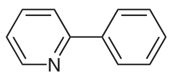
Entry	Aryl halides	Aryl boronic acids	Time (h)	Product	Yield (%)[b]
1			9	 **7a**	92
2			5	 **7b**	92
3			3	 **7c**	99
4			3	 **7d**	99
5			12	 **7e**	83
6			3	 **7f**	99
7			3	 **7g**	97
8			5	 **7h**	92

Table 2 MNP-Supported Catalyst **6** in Suzuki Coupling of Aryl Halides and Aryl Boronic Acid[a,29] (continued)

Entry	Aryl halides	Aryl boronic acids	Time (h)	Product	Yield (%)[b]
9			6	 **7i**	91
10			6	 **7j**	90
11			20	 **7b**	<20
12			20	 **7k**	46

[a] Reaction conditions: aryl halide (2 mmol), aryl boronic acid (2.6 mmol), **6** (0.004 mmol), K_2CO_3 (4 mmol), DMF (5 mL), 100 °C.
[b] Isolated yield.
[c] The amount of 0.4 mol% of Pd were used.
[d] The amount of 1 mol% of Pd was used.

Having established the scope of the new reaction system, we then turned our attention to the recovery and reuse of the catalyst **6**. We chose the cross-coupling of 4-bromoacetophenone and phenylboronic acid as the model reaction. After the completion of the reaction, the reaction mixture was diluted with diethyl ether and the catalyst was easily separated by an external magnet, washed with diethyl ether, water, dried under vacuum, and then used directly in the next run. No obvious loss in catalytic activity was observed in five recycling runs under the same reaction conditions (Table 3).

Table 3 Reuse of **6** in Suzuki Coupling of 4-Bromoacetophenone and Phenylboronic Acid

Run	1	2	3	4	5
[a]Yield (%)	[a]99	[a]99	[a]99	[a]96	[a]95

In summary, we have described a novel MNP-supported di(2-pyridyl)methanol-derived palladium chloride **6** prepared via click chemistry. The catalyst was proved to be highly efficient in Suzuki reactions with a variety of aryl bromoarenes as substrates. Furthermore, the MNP-supported catalyst could be easily separated from the reaction system by magnetic decantation and reused for several runs with little loss in activity. Due to the wide application of dipyridyl ligand, further effort to extend the use of **6** in other reactions is still in progress.

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(25) **Preparation of 4**
Silica-capped MNP (1 g; prepared exactly according to the literature method[30]) and 3-azidopropyltriethoxysilane **3** (0.5 g, 2.02 mmol) was refluxed in anhyd toluene for 24 h, then the mixture was submitted to external magnetic field, and washed sequentially with toluene (3 × 10 mL), Et_2O (3 × 10 mL). The loading was determined to be 0.684 mmol g^{-1} by elemental analysis. FT-IR: 2104, 1635, 1487, 1101, 969, 798, 585 cm^{-1}.

(26) **Synthesis of Di(2-pyridyl)methyl Propargyl Ether (2)**
To a stirred solution of **1** (0.93 g, 5 mmol) in anhyd DMF (10 mL) at 0 °C under Ar was added NaH (0.24 g, 6 mmol) in batches, the mixture was stirred at 0 °C for 1 h. After the dropwise addition of propargyl bromide (0.65 mL, 6 mmol) over 10 min, the reaction mixture was raised to r.t., and stirred for another 10 h. Then the system was quenched with MeOH (10 mL) and submitted to flash chromatography on silica gel (PE–EtOAc, 1:1) to afford **2** as dark brown solid (0.6 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.57 (d, 2 H, J = 4.8 Hz), 7.72 (t, 2 H), 7.62 (d, 2 H, J = 7.8), 7.19 (t, 2 H), 5.93 (s, 1 H), 4.28 (d, 2 H, J = 2.4), 2.45 (t, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 149.3, 136.8, 122.8, 121.9, 83.8, 75.1, 56.6, 29.7. Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.96; H, 5.36; N, 12.39.

(27) **Preparation of Di(2-Pyridyl)methanol-Functionalized MNP 5 via Click Reaction**
Compounds **2** (0.25 g, 1.12 mmol) and **4** (1 g) were mixed with CuI (0.008 g, 3.77×10^{-2} mmol) in DMF–THF (1:1, 10 mL) under Ar atmosphere, to this was injected DIPEA (1 mL), and the reaction mixture was stirred with a mechanic stirring at r.t. The reaction was monitored by FT-IR as was indicated by the almost complete disappearance of IR signal of 2104 cm^{-1} which stands for the azide group. Then the reaction mixture was submitted to magnetic separation, and the MNP were washed sequentially with Et_2O (3 × 20 mL), H_2O (3 × 20 mL), then acetone (3 × 20 mL), finally dried under vacuum. FT-IR: 1646, 1597, 1475, 1434, 1091, 794, 588, 463 cm^{-1}.

(28) **Preparation of 6**
To the freshly prepared $PdCl_2(MeCN)_2$ (0.16 g, 0.62 mmol) solution in toluene (10 mL) was added **5** (1 g), the mixture was mechanically stirred and refluxed for 12 h, the reaction system was magnetically separated, the MNP were washed with H_2O (3 × 20 mL) and MeOH (5 × 20 mL) then dried in vacuo.

(29) **Typical Procedure for Suzuki Coupling**
A mixture of aryl halide (2 mmol), arylboronic acid (2.6 mmol), **6** (0.004 mmol), K_2CO_3 (4 mmol), and DMF (5 mL) was added to a flask and stirred at 100 °C, open to the air, for the desired time until complete consumption of the starting substrates as judged by TLC. After completion of the reaction, the reaction mixture was cooled to r.t., and to the solution was added Et_2O (30 mL), then a magnet was used to separate the catalyst, washed with H_2O (3 × 10 mL), then the organic phase was evaporated and the residue was purified by flash chromatography to afford the desired coupling products. The MNP-supported catalyst **6** was washed with Et_2O, H_2O, dried, and reused directly in the next run. All the coupling products could be found in literature.

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