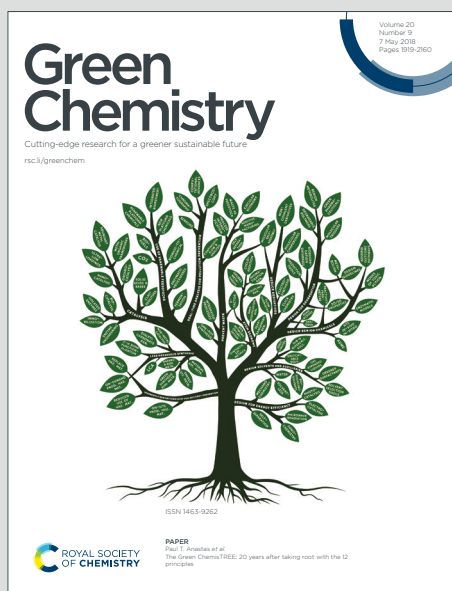


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ARTICLE

A hydrophilic heterogeneous cobalt catalyst for fluoride-free Hiyama, Suzuki, Heck and Hirao cross-coupling reactions in water

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A hydrophilic heterogeneous cobalt catalyst of chitosan, denoted as mTEG-CS-Co-Schiff-base, has been successfully prepared. This newly synthesized catalyst was characterized by different methods such as XRD, FE-SEM, TEM, TGA, FT-IR, ¹³C {¹H} CP/MAS NMR, XPS and ICP analyses. The catalyst displayed excellent activity for the palladium and fluoride-free Hiyama, Suzuki, Heck and Hirao reactions of various aryl iodides, bromides and chlorides (i.e., the most challenging aryl halides which are cheaper and more widely available than aryl iodides and bromides) in water. The presence of triethylene glycol tags with hydrophilic character on the Co-complex supported on chitosan provides dispersion of the catalyst particles in water, which leads to higher catalytic performance and also facile catalyst recovery by successive extraction. It was reused for at least six successive runs without any discernible decrease in its catalytic activity and any remarkable changes in catalyst structure. The use of water as a green solvent, without requiring any additive or organic solvent, as well as low cost and abundant cobalt catalyst instead of expensive Pd catalysts along with the catalyst recovery and scalability, make this method favorable from environmental and economic points of view for the C-C and C(sp²)-P coupling reactions. Notably, this is the first report on the application of a cobalt catalyst in Hiyama reactions.

Introduction

Carbon-carbon and carbon-phosphorus coupling reactions as a powerful synthetic tool and major area in multiple organic transformations have recently been intensively studied in organic synthesis and have been applied to many areas, including the synthesis of natural products, drugs and fine chemicals.¹ The traditional catalysts for cross-coupling reactions are homogeneous palladium complexes, however, they possess some limitations such as toxicity, cost, non-reusability and sensitivity to air.² These problems can be largely overcome by carrying out the reactions using heterogeneous catalysts, and/or using other transition metals such as nickel,³ copper,⁴ iron⁵ and cobalt.⁶ However, in spite of low cost, non-toxicity and availability of cobalt catalysts, the applicability of this metal catalyst in coupling reactions compared to the above mentioned metal catalysts is rare in the literature.⁷

A variety of inorganic and organic materials have already been used for supporting different metal catalysts to produce heterogeneous catalysts.⁸ Within these solid supports, biopolymer supporting

materials such as chitosan (CS) have gained much attention due to the unique characteristics of the biomaterials, which are nontoxic, biodegradable, environmentally friendly, renewable and abundant.⁹ CS is a major naturally occurring biopolymer, which is produced by deacetylation of chitin, the key constituent of the shells of crabs and shrimps.¹⁰ It exhibits high affinity for metal ions due to the amine and hydroxyl functional groups on its chain. These characteristics have made chitosan a desirable material in removal of radioactive elements, waste-water treatment, textile production, medicine, agriculture, cosmetics, photography, biotechnology, food and nutrition.¹¹ More importantly, the presence of these groups provides the possibility of chitosan modifications with new properties or the preparation of heterogeneous catalysts.¹² For example, by amine modification of CS, CS-Schiff-base-cobalt complexes were synthesized and used as heterogeneous catalysts in organic reactions.¹³ Notably, chitosan is only soluble in acidic aqueous media, being insoluble in basic aqueous solutions, which is important for some reactions such as cross-coupling reactions. Remarkably, from environmental and economic perspectives, the interest in catalytic processes by recyclable metal-based catalysts in aqueous media is dramatically increased.¹⁴ Along this line and in continuation of our efforts on the introduction of new heterogeneous catalysts for using in aqueous media,¹⁵ herein, in this paper, a new hydrophilic heterogeneous cobalt catalyst of chitosan (mTEG-CS-Co-Schiff-base, Scheme 1) has been synthesized by modification of both the amine and hydroxyl functional groups on the CS chain. This newly synthesized catalyst was characterized by different methods such as XRD, FE-SEM, TEM, TGA,

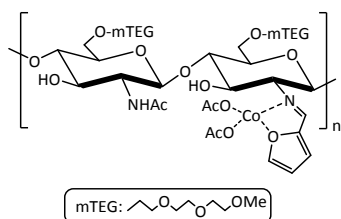
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FT-IR, ^{13}C $\{^1\text{H}\}$ CP/MAS NMR, XPS and ICP analyses and used as a heterogeneous catalyst in some C-C and $\text{C}(\text{sp}^2)$ -P cross-coupling reactions such as Hiyama, Suzuki, Heck and Hirao reactions.

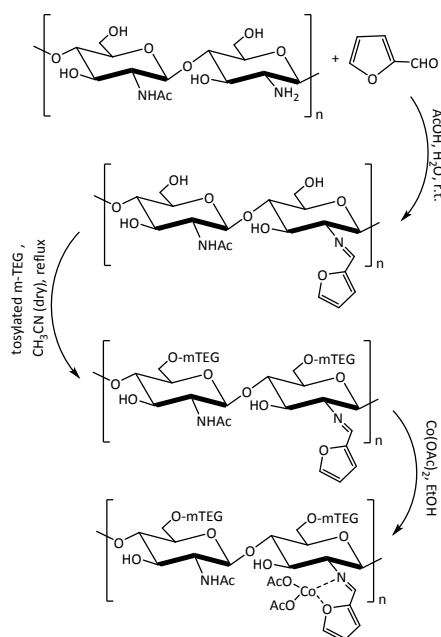
leads to the deformation of hydrogen bonds and lowers the crystallinity of chitosan. DOI: 10.1039/C9GC03455B



Scheme 1. mTEG-CS-Co-Schiff-base

Result and discussion

The catalyst was synthesized by the method outlined in Scheme 2. At first, the amino groups on the chitosan chains were reacted with furfural to form a CS-Schiff-base. The second step involved modification of the hydroxyl group of the CS-Schiff-base with mono-methoxytriethylene glycol (mTEG), as a phase transfer functional group, followed by the reaction with cobalt acetate which produced the mTEG-CS-Co-Schiff-base.



Scheme 2. Preparation of the mTEG-CS-Co-Schiff-base

The X-ray diffraction (XRD) patterns of the mTEG-CS-Co-Schiff-base, the mTEG-CS-Schiff-base and chitosan are displayed in Figure 1. CS monomers have strong intermolecular hydrogen bonding and thus CS usually exhibits more crystalline character than other carbohydrates. In the XRD pattern of CS, two characteristic peaks at $2\theta = 10$ and 21° were observed. The same peaks are observed in the XRD patterns of the mTEG-CS-Schiff-base and the mTEG-CS-Co-Schiff-base, although with lower peak intensity and peak broadening. This may be related to the lowering of the amount of free amino groups during the condensation with aldehydes. The condensation

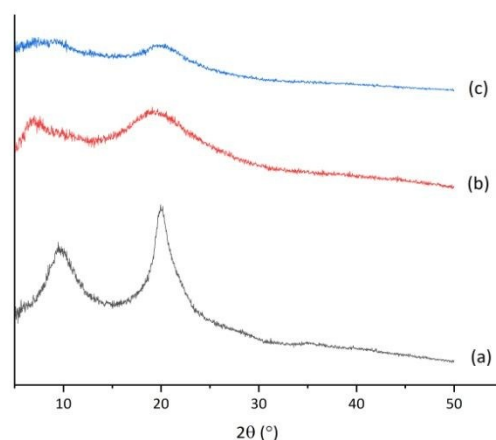
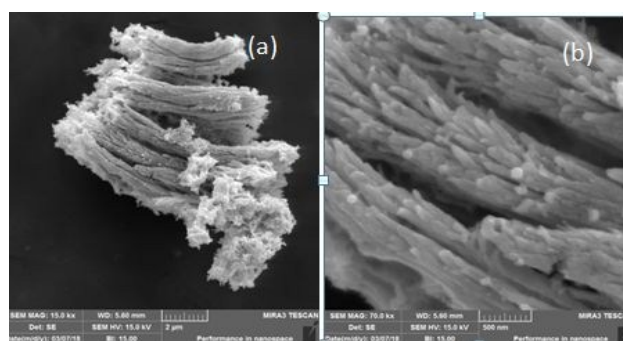


Figure 1. XRD patterns of (a) CS, (b) the mTEG-CS-Schiff-base and (c) the mTEG-CS-Co-Schiff-base

The field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) images of the mTEG-CS-Co-Schiff-base are presented in Figure 2. The roughness observed on the surface of the mTEG-CS-Co-Schiff-base demonstrates the chemical modification of the CS surface (Figure 2a and 2b). The average particle size of the adsorbed cobalt acetate on the surface of oxygen-rich mTEG-CS-Co-Schiff-base was 12 nm based on the TEM image (Figure 2c and 2d).



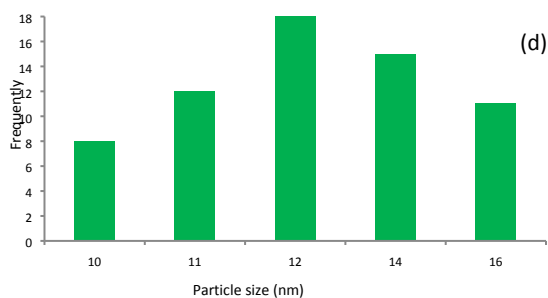


Figure 2. (a, b) FE-SEM images, (c) TEM image of the mTEG-CS-Co-Schiff-base and (d) particle-size distribution of Co in the mTEG-CS-Co-Schiff-base

The thermogravimetric analysis (TGA) of the mTEG-CS-Schiff-base is shown in Figure 3 and illustrates two mass loss stages. The initial mass loss (~6.8%) at around 100 °C is attributed to the evaporation of adsorbed water molecules. A total of 71.8% weight loss in the second stage is due to the decomposition of the polysaccharide chains and also the Schiff-base units. The amount of cobalt in one gram of the catalyst was 0.58 mmol, which was determined by the ICP technique.

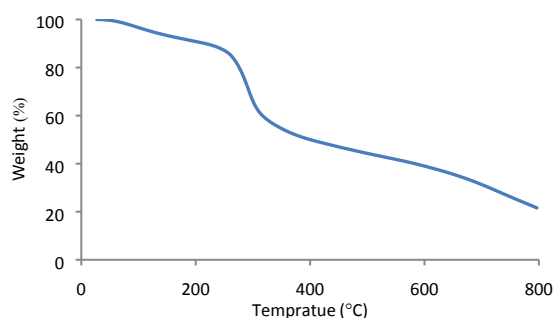


Figure 3. Thermogravimetric (TG) weight-loss curve for the mTEG-CS-Schiff-base

The Fourier-transform infrared (FT-IR) spectra of CS, the CS-Schiff-base and the mTEG-CS-Co-Schiff-base are shown in Figure 4. A comparison of the FT-IR spectra of CS and the CS-Schiff-base indicates the absence of bending-mode frequencies for the -NH_2 group at 1655 cm^{-1} and the presence of two additional bands at 1649 and 1562 cm^{-1} in the FT-IR spectrum of the CS-Schiff base. These two new bands are assigned to the stretching modes of imine (C=N) and C=C groups, respectively. In the FT-IR spectrum of the mTEG-CS-Co-Schiff-base, the shifting ($\sim 7 \text{ cm}^{-1}$) of the stretching vibration of the C=N groups to lower wave number confirms the coordination of Co(II) metal ions to the nitrogen atoms of the Schiff base. The appearance of the band at 1114 cm^{-1} may be attributed to the C-O of TEG.

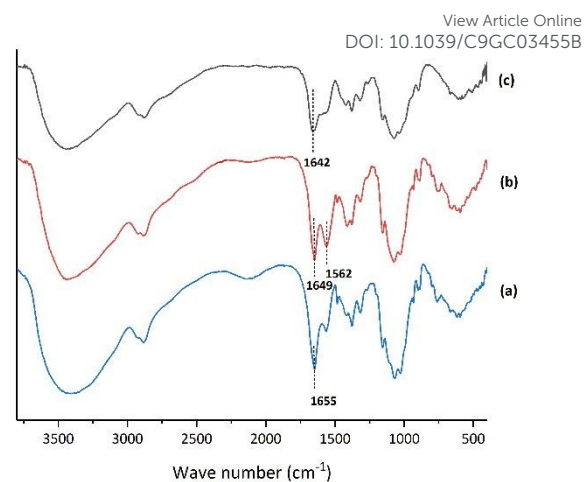


Figure 4. FT-IR spectra of (a) CS, (b) the CS-Schiff base and (c) the mTEG-CS-Co-Schiff-base

Solid-state nuclear magnetic resonance spectra of CS and the mTEG-CS-Co-Schiff-base, obtained with cross-polarization (^{13}C $\{^1\text{H}\}$ CP/MAS NMR), are shown in Figure 5. In the spectrum of CS (Figure 5a), the resonances at around 24, 84, 106 and 174 ppm can be assigned to C_8 , C_3 , C_1 and C_7 , respectively. The broad peaks at around 60 ppm are attributed to C_2 , C_2' and C_6 , where at least two peaks are resolved at 58.1 and 60.9 ppm. The tallest peak at 75.7 ppm is ascribed to C_4 and C_5 . The furan ring with characteristic peaks at 126.6, 129.7, 142.8, 151.3, and 156.5 ppm is observed in the ^{13}C $\{^1\text{H}\}$ CP/MAS NMR spectrum of the mTEG-CS-Co-Schiff-base (Scheme 1, Figure 5b). This observation indicates that the furfural is linked with CS through the Schiff-base linkage. Furthermore, resonances at 49.9 (-OCH_3) and 71.8 ppm ($\text{-OCH}_2\text{CH}_2\text{O-}$) overlap with the C_4 and C_5 sites of the chitosan ring. This confirms the presence of mTEG in the mTEG-CS-Co-Schiff base.

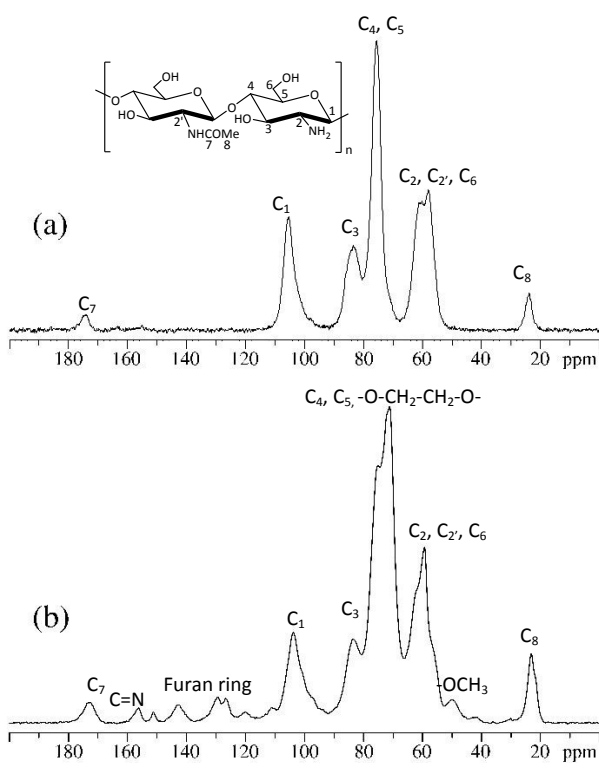
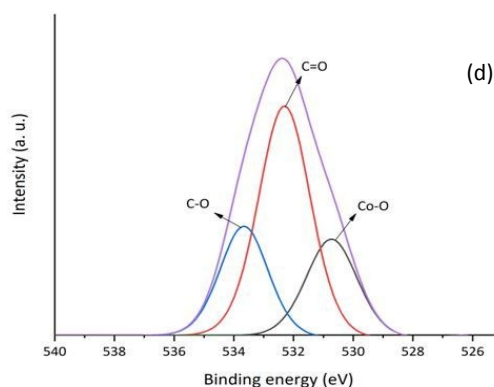
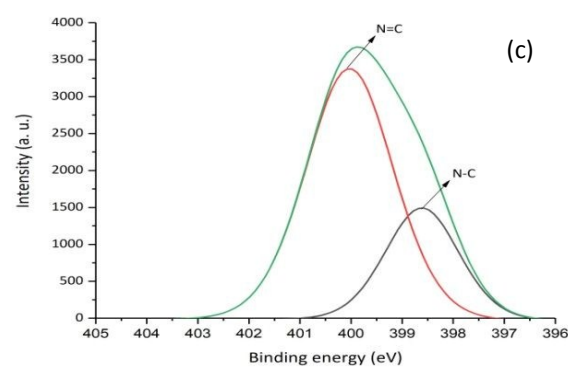
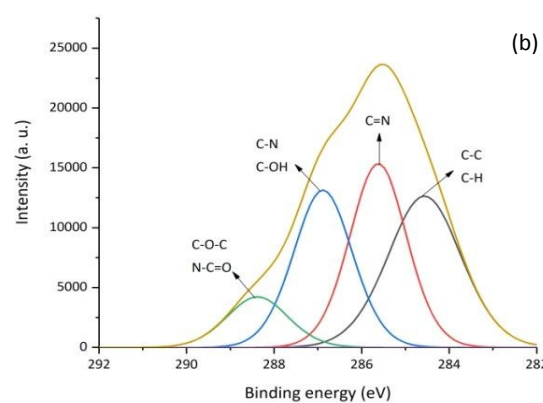
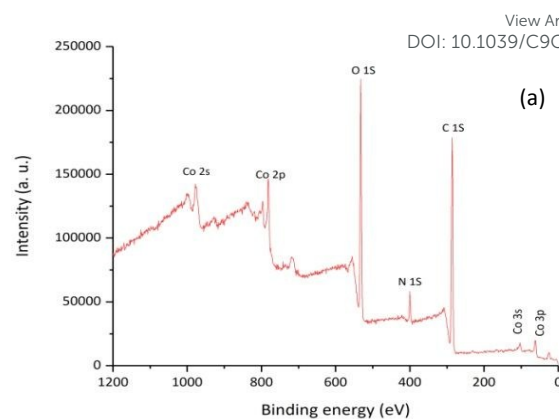


Figure 5. ^{13}C $\{^1\text{H}\}$ CP/MAS NMR spectra (9.4 T) of (a) CS and (b) the mTEG-CS-Co-Schiff-base

The catalyst was also analyzed by XPS spectroscopy (Figure 6). The observed characteristic peaks in the XPS elemental survey are attributed to carbon (C 1s), nitrogen (N 1s), oxygen (O 1s) and cobalt (Figure 6a).¹⁶ The C 1s spectrum (Figure 6b) showed binding energies of 284.2 (C-C and C-H), 285.6 (-C=N-), 286.8 (C-N and C-OH) and 288.4 eV (-C-O-C- and N-C=O).¹⁷ Furthermore, high resolution XPS results of the N 1s region confirmed the presence of -N-H and imine (-N=C-) by revealing two peaks at 398.5 and 400.0 eV, respectively (Figure 6c).¹⁷ Three distinct peaks at 530.8, 532.2 and 533.6 eV in the O 1s spectrum (Figure 6d) represented the incorporation of Co-O, C=O and C-O.^{16,17} The spectrum of cobalt matches well with the reported binding energy values of cobalt signals for immobilized Co-Schiff-base complexes (Figure 6e).¹⁸ The typical peaks at 781.1 and 796.7 eV for $2p_{3/2}$ and $2p_{1/2}$, respectively, indicate the presence of Co^{2+} in the catalyst. Cobalt nanospecies which are observed in the TEM image (Figure 2c), might be cobalt acetate that are adsorbed on the surface of oxygen-rich mTEG-CS-Co-Schiff-base catalyst. The peaks of adsorbed cobalt acetate overlapped with those of the Co-complex in the Co-XPS spectrum at 783.1, 786.5, 798.7 and 802.4 eV.¹⁸



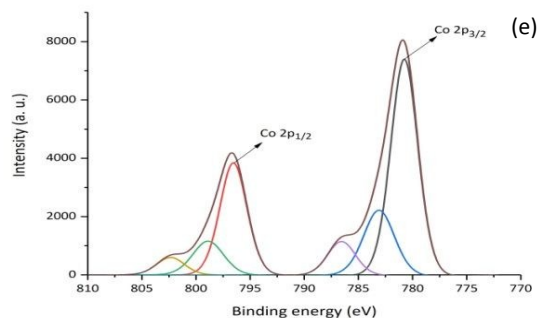


Figure 6. (a) XPS patterns of the mTEG-CS-Co-Schiff-base, (b) C (1s), (c) N (1s), (d) O (1s), (e) Co

Catalytic activity of mTEG-CS-Co-Schiff-base in the C-C cross-coupling reactions in water

Among the C–C cross-coupling reactions, Hiyama and Suzuki reactions are efficient tools in organic chemistry for the synthesis of symmetrical and unsymmetrical biphenyl derivatives.¹⁹ Organosilicon compounds are used in Hiyama cross-coupling reactions.²⁰ These compounds are the best alternative to the other reagents, such as organozinc or organomagnesium compounds and tin reagents, from an environmental point of view, ease of preparation, stability, low cost and accessibility.²¹ They are also preferred to organoboron compounds, which are used in Suzuki reactions,²² since organoboron compounds are either unstable or difficult to purify and frequently lose boron to give undesirable homocoupling products. Meanwhile, due to the weak polarization of the carbon–silicon bond in organosilicon derivatives, they act as poor cross-coupling partners. Therefore, the nucleophilicity of the organosilicon reagents needs to be enhanced. Fluoride anions are the most commonly activators employed for this purpose. However, the fluoride ion is a strong base, so base-sensitive protecting groups, acidic protons and functional groups may be affected by the addition of this activator. This limitation has been overcome by replacement of fluoride ions with inorganic bases in water.²³ The reported procedures in water suffered from one or more of the following drawbacks such as using organic co-solvents, phase transfer catalyst, surfactant or large amount of the catalyst. Following our research on the development of new catalytic systems to perform cross-coupling reactions by environmentally friendly procedures,²⁴ herein, we have studied the catalytic activity of the mTEG-CS-Co-Schiff-base in fluoride-free Hiyama coupling reactions in water. Based on our literature survey, this is the first report on the application of a cobalt catalyst in the Hiyama cross-coupling reaction. To probe the catalytic activity of the mTEG-CS-Co-Schiff-base toward the Hiyama cross-coupling reactions, the cross-coupling reaction of iodobenzene with triethoxyphenylsilane in aqueous media was taken as a model reaction. Various reaction parameters such as temperature, base and the amount of the catalyst were screened for the reaction model, and the results are summarized in Table 1. As indicated in Table 1, NaOH was found to

be the most effective base (entry 4) presumably due to its better water solubility than the other bases (entries 2–4). In an effort to optimize the amount of the catalyst, the best yield of the product was obtained in the presence of 0.5 mol% of the catalyst (entry 5). The reaction proceeded with lower yields at lower temperatures (entries 7 and 8). To show the role of the hydrophilic group on the catalyst, the reaction was performed in the presence of the CS-Co-Schiff-base. The product was obtained after a longer reaction time (entry 9) compared with the mTEG-CS-Co-Schiff-base (entry 5). The model reaction was also studied in the presence of Co(OAc)₂. It was found that the desired product was obtained in low yield after 24 h (entry 10).

Table 1. Optimization of the Hiyama cross-coupling reaction of iodobenzene with triethoxyphenylsilane.

^aReaction conditions: iodobenzene (1 mmol), triethoxyphenylsilane

Entry	Catalyst (mol%)	Base	T (°C)	Time (h)	Isolated Yield ^a (%)
1	1	Et ₃ N	90	45 min	61
2	1	KF	90	1.5	39
3	1	NaF	90	2.5	60
4	1	NaOH	90	0.5	98
5	0.5	NaOH	90	1	98
6	0.35	NaOH	90	1	80
7	0.5	NaOH	50	1.5	72
8	0.5	NaOH	r.t.	1	61
9 ^b	0.5	NaOH	90	8 (24)	88 (88)
10 ^c	0.5	NaOH	90	24	30

(1.5 mmol), base (2 mmol), H₂O (3 mL).

^bCatalyst without hydrophilic group

^cCo(OAc)₂

Under the optimized reaction conditions (0.5 mol% of the catalyst, NaOH and 90 °C), the substrate scope of the reaction was examined and the results are shown in Table 2. As it is depicted in Table 2, reactions of both electron-deficient and electron-rich aryl halides (iodides, bromides and chlorides) gave the corresponding biaryl derivatives in good to excellent yields, irrespective of the electronic nature of the substituent.

Table 2. Hiyama reaction of aryl halides with triethoxyphenylsilane catalyzed by mTEG-CS-Co-Schiff-base in water.

Entry	X	R	Time (h)	Isolated Yield ^a (%)
1	I	H	1	98

2	I	OMe	3.5	90
3	I	Cl	2	90
4	I	I	6	93
5	Br	H	3	90
6	Br	OMe	5	80
7	Br	NO ₂	2.5	95
8	Br	CN	2.5	90
9	Br	Cl	3	87
10	Cl	H	4	90
11	Cl	NO ₂	3	90
12	Cl	CN	3.5	80

^aReaction conditions: catalyst (0.5 mol%), triethoxyphenylsilane (1.5 equiv.), NaOH (2 equiv.).

To examine the reusability of the catalyst, a recycling experiment was performed with iodobenzene and triethoxyphenylsilane under the optimized reaction conditions. Due to the presence of hydrophilic TEG tag in the catalyst, the mTEG-CS-Co-Schiff-base dispersed in the aqueous phase without any affinity to the organic phase (Figure 7). Considering this property, after the first use of the catalyst, the product was simply extracted by EtOAc, while the catalyst remained in the aqueous phase (Figure 7b). Without any isolation of the catalyst, the aqueous phase was recharged with iodobenzene, triethoxyphenylsilane and NaOH for the next run. After six runs, the catalyst was simply isolated from the aqueous layer by filtration. By this method, no significant loss of catalytic activity or loss of the catalyst (3%) were observed after six runs (Figure 8). FT-IR, FE-SEM and XRD of the catalyst after six times reuse showed that the structure and morphology of the catalyst maintained unchanged during the recycling process (Figure 9). Hot filtration test was performed to check if the active catalyst is indeed heterogeneous. After completion of 65% of the coupling reaction, the solid was separated at the reaction temperature and the liquid phase was allowed to react for 24 h. No further conversion showed that the observed catalysis was heterogeneous in nature. The heterogeneous nature of the catalyst was also examined by a poisoning test using S₈ (0.05 g) as a metal scavenger in the model reaction. Any considerable change in the progress of the reaction was not observed (Figure 10c).

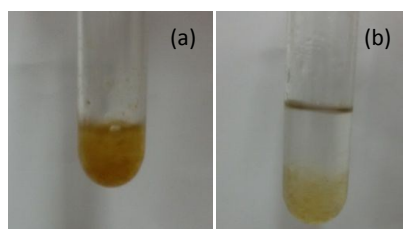


Figure 7. (a) Dispersion of the mTEG-CS-Co-Schiff-base in water, (b) distribution of the mTEG-CS-Co-Schiff-base in a biphasic water/EtOAc mixture.

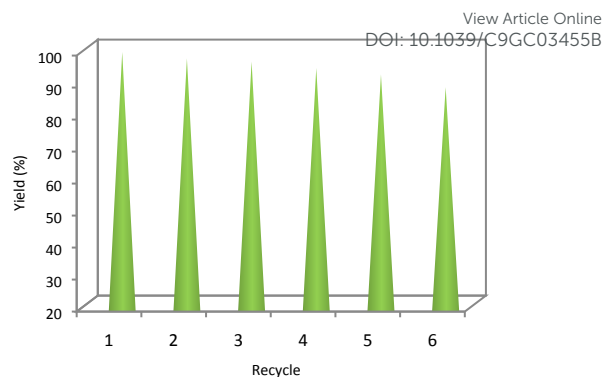


Figure 8. Reusability of the mTEG-CS-Co-Schiff-base in the reaction of iodobenzene and triethoxyphenylsilane in aqueous media for 1 h.

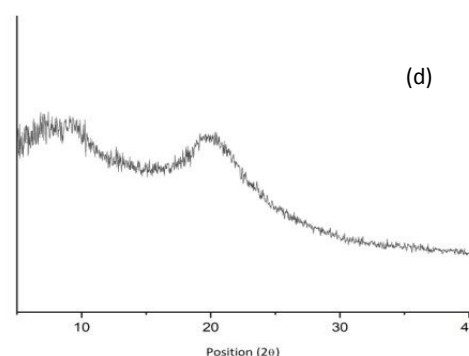
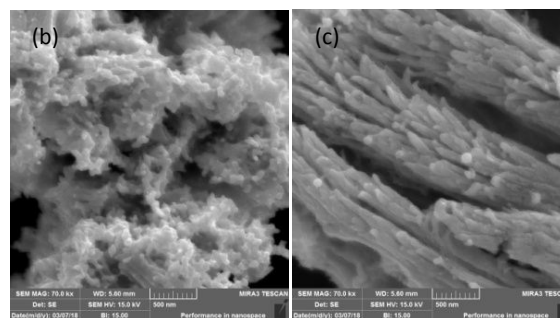
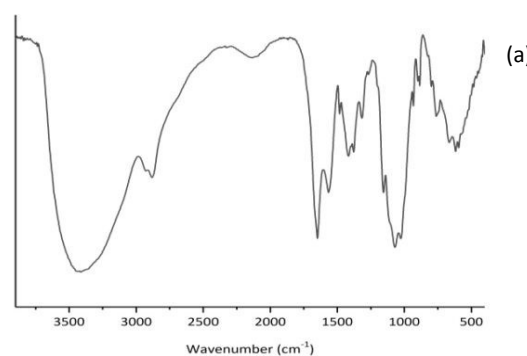


Figure 9. (a) FT-IR, (b, c) FE-SEM images and (d) XRD analysis of the mTEG-CS-Co-Schiff-base after six times reuse.

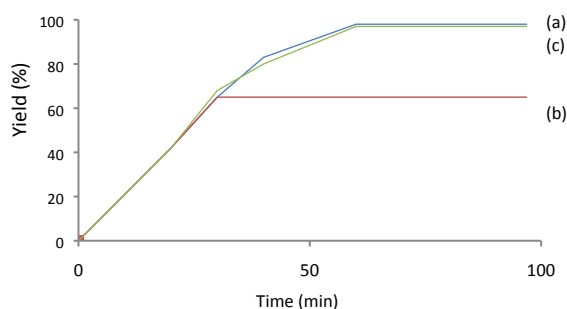


Figure 10. Hiyama coupling reaction of iodobenzene with triethoxyphenylsilane catalyzed by the mTEG-CS-Co-Schiff-base in water in (a) normal reaction, (b) hot filtration test and (c) poisoning test.

To test the potential synthetic applications of this method, the reaction of iodobenzene (50 mmol) and triethoxyphenylsilane (75 mmol) on a larger scale was examined under the optimized reaction conditions. The desired product was obtained in 97% yield after 3 h. Encouraged by the results from the Hiyama reaction, the coupling reaction leading to biaryl compounds was investigated *via* the Suzuki cross-coupling reaction. At first, the reaction conditions were optimized for the reaction of iodobenzene with phenylboronic acid in aqueous media (Table 3). As shown in Table 3, among the bases examined (entries 1-5), K_2CO_3 was found to be the best choice (entry 2). The model reaction was performed at different temperatures (entries 2, 6-8) and the best result was obtained at 90 °C (entry 2). The effect of the amount of the catalyst (entries 2, 9-12) was also investigated and it was found that the reaction proceeded well in the presence of 0.5 mol% of the catalyst (entry 9).

Table 3. Suzuki coupling reaction of iodobenzene with phenylboronic acid catalyzed by the mTEG-CS-Co-Schiff-base in water under different conditions

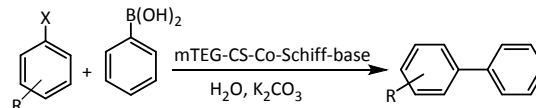
Entry	Catalyst (mol%)	Base	T (°C)	Time (min)	Isolated Yield ^a (%)
1	1	Et_3N	90	30	58
2	1	K_2CO_3	90	45	93
3	1	CS_2CO_3	90	30	81
4	1	KOH	90	45	52
5	1	NaOH	90	55	29
6	1	K_2CO_3	r.t	30	60
7	1	K_2CO_3	50	30	71
8	1	K_2CO_3	70	35	82
9	0.5	K_2CO_3	90	60	93
10	0.75	K_2CO_3	90	50	90
11	0.25	K_2CO_3	90	50	61
12	0.35	K_2CO_3	90	55	79

^aReaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.1 mmol), base (2 mmol), H_2O (3 mL).

With the optimized reaction conditions in hand, we then studied the general usefulness of our new catalytic system in the Suzuki reaction of some aryl halides with phenylboronic acid (Table 4). Under the

optimized reaction conditions, different aryl halides (iodides, bromides and chlorides) were successfully converted to the corresponding biaryl products.

Table 4. Suzuki coupling reaction of various aryl halides with phenylboronic acid catalyzed by the mTEG-CS-Co-Schiff-base in water.



Entry	x	R	Time (h)	Isolated Yield ^a (%)
1	I	H	1	93
2	I	OMe	3	85
3	I	Cl	1.5	90
4	I	I	5	91
5	Br	H	2	90
6	Br	OMe	4	82
7	Br	NO_2	1.5	90
8	Br	CN	2	91
9	Br	Cl	2.5	86
10	Cl	H	3	90
11	Cl	NO_2	2.5	89
12	Cl	CN	2.5	82

^a Reaction conditions: catalyst (0.5 mol%), aryl halide (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2 mmol), H_2O (3 mL), 90 °C.

Metal catalyzed carbon-carbon bond forming reactions between aryl halides and olefins in the presence of a base (Heck reaction) is a powerful method for the synthesis of various organic molecules.²⁵ Generally, this reaction is promoted by palladium catalysts, however, some cobalt based catalysts have recently been reported for the Heck reaction.^{7a-f} The reported synthetic routes have certain limitations such as requiring high temperature and/or large amount of the catalyst, and most importantly, the use of organic solvents. Moreover, most of the reported methods suffer from lack of generality for the coupling reactions of arylchlorides. Thus, in our studies on the C-C coupling reactions, we decided to expand the catalytic application of the mTEG-CS-Co-Schiff-base in the Heck reaction. For this reason, various factors including base, temperature and catalyst loading were screened to optimize the Heck reaction conditions of iodobenzene and *n*-butyl acrylate in aqueous media (Table 5). Amongst the bases tested (entries 1-5), highest catalytic activity was observed in the presence of Et_3N (entry 1). The effect of various amounts of the catalyst and temperature on the model reaction was also investigated in depth (entries 6-11). The results of these experiments revealed that 0.35 mol% of the catalyst and 90 °C are the optimal reaction conditions (entry 10).

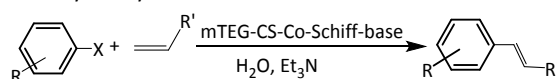
Table 5. Heck cross-coupling reaction of iodobenzene with *n*-butyl acrylate catalyzed by the mTEG-CS-Co-Schiff-base in water under different reaction conditions

Entry	Catalyst (mol %)	Base	T (°C)	Time (min)	Isolated Yield ^a (%)
1	0.5	Et ₃ N	90	20	90
2	0.5	K ₂ CO ₃	90	30	91
3	0.5	KOH	90	60	83
4	0.5	CH ₃ COOK	90	30	58
5	0.5	Cs ₂ CO ₃	90	40	75
6	0.5	Et ₃ N	70	45	80
7	0.5	Et ₃ N	50	30	60
8	0.5	Et ₃ N	r.t.	45	45
9	0.25	Et ₃ N	90	30	84
10	0.35	Et ₃ N	90	30	98
11	-	Et ₃ N	90	24h	10

^a Reaction conditions: iodobenzene (1 mmol), olefin (1.1 mmol), base (2 mmol), H₂O (3 mL).

Then the scope and limitation of this catalytic system for different substrates were explored and the results were summarized in Table 6. A variety of aryl iodides were coupled with different alkenes such as *n*-butyl/methyl/ethyl acrylate and methyl methacrylate in the presence of the catalyst under optimized reaction conditions and the desired products were obtained in 65-98% yields (Table 6, entries 1-6). The coupling reaction of aryl bromides and chlorides (much cheaper and more widely available than aryl iodides and bromides) with *n*-butyl acrylate proceeded well and the corresponding products produced in good to high yields (entries 7-12). The applicability of this method for the coupling reaction of aryl halides with styrene was also investigated. The examined aryl halides underwent the coupling reactions and gave the desired products in relatively good yields (entries 13-19).

Table 6. Heck cross-coupling reaction of different arylhalides with olefins catalyzed by the mTEG-CS-Co-Schiff-base in water.



Entry	Aryl halide	Olefin	Time (h)	Isolated ^a yield (%)
1	PhI	CH ₂ =CH-CO ₂ Bu ⁿ	0.5	98
2	PhI	CH ₂ =CH-CO ₂ Me	0.5	92
3	PhI	CH ₂ =CH-CO ₂ Et	0.5	95
4	PhI	CH ₂ =C(Me)-CO ₂ Me	45 min	92
5	4-MeOC ₆ H ₄ I	CH ₂ =CH-CO ₂ Bu ⁿ	4	65
6	4-ClC ₆ H ₄ I	CH ₂ =CH-CO ₂ Bu ⁿ	1.5	83

7	PhBr	CH ₂ =CH-CO ₂ Bu ⁿ	1	90
8	4-O ₂ NC ₆ H ₄ Br	CH ₂ =CH-CO ₂ Bu ⁿ	1	80
9	4-NCC ₆ H ₄ Br	CH ₂ =CH-CO ₂ Bu ⁿ	1	85
10	PhCl	CH ₂ =CH-CO ₂ Bu ⁿ	2.5	82
11	4-O ₂ NC ₆ H ₄ Cl	CH ₂ =CH-CO ₂ Bu ⁿ	2	80
12	4-NCC ₆ H ₄ Cl	CH ₂ =CH-CO ₂ Bu ⁿ	2	92
13	PhI	Ph CH=CH ₂	1.5	90
14	4-MeOC ₆ H ₄ I	Ph CH=CH ₂	3	73
15	4-ClC ₆ H ₄ I	Ph CH=CH ₂	2	94
16	PhBr	Ph CH=CH ₂	2	85
17	4-NCC ₆ H ₄ Br	Ph CH=CH ₂	1.5	72
18	4-O ₂ NC ₆ H ₄ Br	Ph CH=CH ₂	1.5	80
19	PhCl	Ph CH=CH ₂	4	82

^aReaction conditions: catalyst (0.35 mol%), aryl halide (1 mmol), olefin (1.1 mmol), Et₃N (2 mmol), H₂O (3 mL), 90 °C. *Trans* isomer of the products were obtained based on ³J_{H-H} value of 16.0-16.4 Hz for vinylic hydrogens in ¹H NMR.

Catalytic activity of mTEG-CS-Co-Schiff-base in C(sp²)-P cross-coupling reactions in water

Arylphosphonates are valuable intermediates in organic synthesis²⁶ and versatile ligands in catalytic reactions.²⁷ They find numerous practical applications in medicinal and polymer chemistry,²⁸ the design of fuel cell membranes²⁹ and building blocks in construction of metal-organic frameworks (MOFs).³⁰ They were also used in the design of new materials with special optical properties,³¹ which have been employed in solar cells.³² In the 1980s, Hirao and co-workers described the first examples of coupling of aryl and vinyl halides with dialkylphosphites using a Pd catalyst.³³ This method has later been successfully extended to other coupling partners such as aryl triflates, tosylates, diazonium salts, triaryl bismuth, aryl hydrazine and arylboronic acid.³⁴ The transition metals used so far for C(sp²)-P bond formation by the cross-coupling reaction are palladium,³⁵ copper,³⁶ manganese,³⁷ nickel,³⁸ gold³⁹ and silver.⁴⁰ Surprisingly, there is only one report on the use of cobalt for C(sp²)-P bond formation,⁷¹ although cobalt is a low cost, easily available and relatively environmentally benign metal. However, this reported method suffers from severe problems related to the separation and recovery of the homogeneous catalyst, the use of toxic organic solvent, high temperature, and requiring copper iodide and argon atmosphere.⁷¹ To address these limitations, we have studied the cross-coupling reaction of aryl halides with triethylphosphite catalyzed by the mTEG-CS-Co-Schiff-base in water. For this purpose, the coupling reaction of iodobenzene (1 mmol) with

triethylphosphite (2 mmol) in the presence of the mTEG-CS-Co-Schiff-base in water (4 mL) was chosen as a model reaction to find the best suitable reaction conditions. The effect of some parameters such as base, temperature and amount of the catalyst on the reaction yield and time was investigated (Table 7). The best results were obtained in the presence of Et₃N as the base and 2 mol% of the catalyst at 80 °C (Table 7, entry 1).

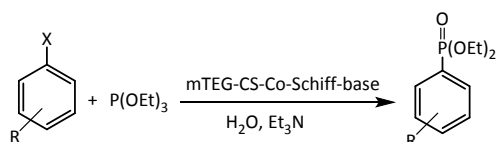
Table 7. The effect of different parameters on the cross-coupling reaction of iodobenzene and triethylphosphite catalyzed by the mTEG-CS-Co-Schiff-base

Entry	Catalyst (mol%)	Base	T (°C)	Time (h)	Isolated Yield ^a (%)
1	2	Et ₃ N	80	5	92
2	2	K ₂ CO ₃	80	4	63
3	2	CS ₂ CO ₃	80	3	41
4	2	NaOH	80	6	45
5	2	Et ₃ N	r.t.	9	39
6	2	Et ₃ N	50	3	64
7	1	Et ₃ N	80	6	72
8	0.5	Et ₃ N	80	8	55
9	-	Et ₃ N	80	24	-

^a Reaction conditions: iodobenzene (1 mmol), triethylphosphite (2 mmol), base (3 mmol), H₂O (4 mL).

To examine the scope of this method, the C(sp²)-P cross-coupling reaction of various halobenzenes with triethylphosphite was studied under optimal reaction conditions (Table 8). As indicated in Table 8, the reaction of triethylphosphite with different aryl iodides, bromides and chlorides containing electron-withdrawing or electron-releasing groups proceeded well and the desired products were isolated in 75–92% yields. Both halogens in 1,4-diiodo and 1,4-dibromobenzene were replaced by twice amount of triethylphosphite under the present reaction conditions (Table 8, entries 13 and 14).

Table 8. C(sp²)-P cross-coupling reaction of different halobenzenes and triethylphosphite catalyzed by the mTEG-CS-Co-Schiff-base



Entry	Aryl halide	Time (h)	Isolated ^a Yield (%)
1	C ₆ H ₅ I	5	92
2	4-ClC ₆ H ₄ I	4.5	91
3	4-IC ₆ H ₄ I	6	90
4	C ₆ H ₅ Br	6	84
5	4-MeOC ₆ H ₄ Br	7	79
6	4-NO ₂ C ₆ H ₄ Br	5	86
7	4-MeC ₆ H ₄ Br	6	87

8	4-BrC ₆ H ₄ Br	5	82
9	C ₆ H ₅ CH=CHBr	9.5	75
10	C ₆ H ₅ Cl	9	83
11	4-NO ₂ C ₆ H ₄ Cl	8	86
12	4-MeC ₆ H ₄ Cl	10	78
13 ^b	IC ₆ H ₄ I	9	89
14 ^b	BrC ₆ H ₄ Br	10	86

^aReaction conditions: catalyst (1 mol%), iodobenzene (1 mmol), triethylphosphite (2 mmol), base (3 mmol), H₂O (4 mL).

^b triethylphosphite (4 mmol)

The recyclability of the mTEG-CS-Co-Schiff-base was investigated in a model reaction of iodobenzene in Suzuki, Heck and Hirao cross-coupling reactions with phenylboronic acid, *n*-butyl acrylate, triethylphosphite, respectively, under optimized reaction conditions. EtOAc was added to the reaction mixtures after 1, 0.5 and 5 h, respectively. The products were simply extracted by EtOAc, while the catalyst remained in the aqueous phase. The aqueous phase was recharged with the starting material and reagents. As shown in Figure 11, the catalyst could be reused for six consecutive runs without any significant loss of its activity.

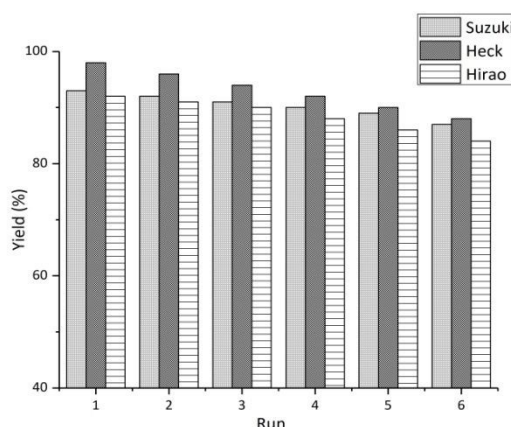


Figure 11. Reusability of the mTEG-CS-Co-Schiff-base in Suzuki, Heck and Hirao reactions.

It is worth to note that a few papers, which suggest a mechanism for the cobalt-catalyzed cross-coupling reactions, are available in the literature.^{7k,f,l,j,g,h,41} Following these reports, a plausible mechanism for the cross-coupling reactions catalyzed by the mTEG-CS-Co-Schiff-base is postulated in Scheme 3. At first, the reaction was supposed to be started by in-situ reduction of Co(II) in the catalyst to Co(I) or Co(0) species under basic conditions.^{7h} Then, upon the oxidative addition of aryl halides to the reduced Co species, aryl cobalt intermediate (I) was formed. In the Hiyama and Suzuki cross-coupling reactions, transmetalation of aryl cobalt intermediate (I) with triethoxyphenylsilane or phenylboronic acid afforded intermediate II, which underwent reductive elimination to produce the biaryl products. In the Heck cross-coupling reaction, a π -complex was formed by the olefin coordination to the aryl cobalt intermediate (I). A migratory insertion of the olefin

followed by β -hydride elimination afforded the Heck products. To check a possible radical mechanism for the Heck reaction,^{41a} the reaction of iodobenzene with *n*-butyl acrylate under optimized reaction conditions was studied in the presence of an electron trap. For this purpose, hydroquinone was added to the reaction mixture after 15 min. No changes in the progress of the reaction compared with the normal conditions, confirmed that no radicals were formed during the coupling process (Figure 12). In the Hirao cross-coupling reaction, aryl cobalt intermediate (I) reacted with triethylphosphite to afford intermediate III. Arylphosphonates were produced from intermediate III by ethyl halide elimination through an Arbuzov-type reaction followed by reductive elimination. Subsequently, in each cycle, the active cobalt species were regenerated in the presence of the base

and returned to the catalytic cycle. Finally, aerobic oxidation furnished the Co (II) catalyst. DOI: 10.1039/C9GC03455B

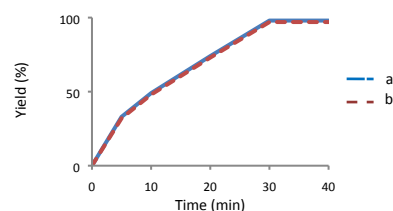
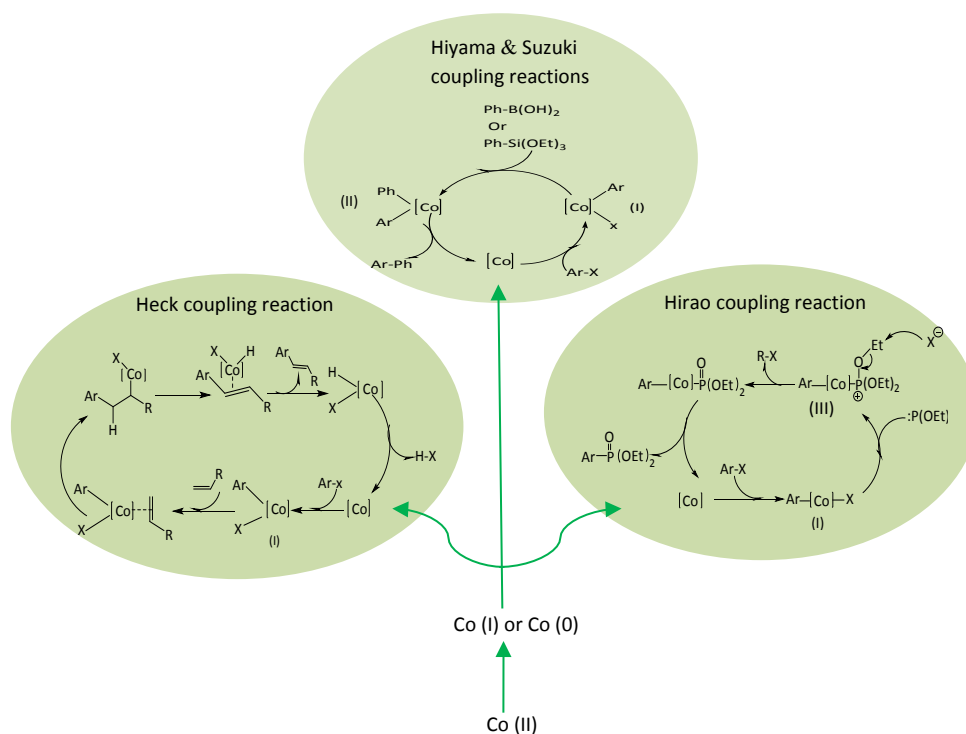


Figure 12. Heck coupling reaction of iodobenzene with *n*-butyl acrylate catalyzed by the mTEG-CS-Co-Schiff-base in water (a) under normal reaction conditions and (b) in the presence of an electron trap.



Scheme 3. A plausible mechanism for the Hiyama, Suzuki, Heck and Hirao cross-coupling reactions catalyzed by the mTEG-CS-Co-Schiff-base

In the last part of our studies, the activity of the mTEG-CS-Co-Schiff-base was compared with those of some reported Co catalysts in the Heck, Suzuki and Hirao reactions (Table 9).⁷ As depicted in Table 9, the mTEG-CS-Co-Schiff-base is the most effective catalyst for the C-C and C(sp²)-P coupling reactions of aryl iodides, bromides and chlorides (the most challenging arylhalides which are much cheaper and more widely available than aryl iodides and bromides). Notably, most of the reported methods suffer from lack of generality for the coupling reactions of aryl chlorides. Moreover, the reported

synthetic routes have certain limitations such as requiring high temperature and/or large amounts of the catalyst and most importantly the use of organic solvents. Promising results obtained in the presence of the mTEG-CS-Co-Schiff-base should be attributed to the water dispersibility of the catalyst. The water-dispersibility ensures the better contact between the catalyst and the reactants, thus significantly enhancing the catalytic activity and stability of the catalyst.

Table 9. Comparison of catalytic activity of mTEG-CS-Co-Schiff-base catalyst with some reported cobalt catalysts for Heck, Suzuki and Hirao cross-coupling reactions

DOI: 10.1039/C9GC03455B

Entry ^{ref}	Catalyst (mol%)	Reaction	Reaction conditions	X	Time (h)	Yield (%)
1 ^{7a}	Co-B amorphous alloy (5)	Heck	H ₂ O/DMF, 130 °C	I	12-24	95-100
2 ^{7b}	Nano Co (2)	Heck	NMP, 130 °C	I	12-24	67-85
				Br	20-30	40-73
				Cl	30	Trace
3 ^{7c}	Co-NHC@MWCNT (0.35)	Heck	PEG, 80 °C	I	5-8	74-92
				Br	6-10	58-80
4 ^{7d}	Co-MS@MNPs/CS (1.1)	Heck	PEG, 80 °C	I	1	69-92
				Br	1	15-87
				Cl	1	30-71
5 ^{7e}	Co/Al ₂ O ₃ (10)	Heck	NMP, 150 °C	I	24	21-85
6 ^{7f}	Fe ₃ O ₄ @Boehmite-NH ₂ -Co (0.44)	Heck	H ₂ O, 80 °C	I	0.4-3	25-98
				Br	0.8-5	40-90
				Cl	3-7	15-40
7 ^{This work}	mTEG-CS-Co-Schiff-base (0.35)	Heck	H ₂ O, 90 °C	I	0.5-3	65-98
				Br	1-2	72-90
				Cl	2-4	80-92
8 ^{7g}	Co@ GO/Fe ₃ O ₄ /L-dopa ^a (1.84)	Suzuki	H ₂ O, 100 °C	Br	4-8	65-82
				Cl	5-7.25	62-72
9 ^{7h}	Cobalt pincer complex (0.5)	Suzuki	CH ₃ CN, 80 °C	I	16	71-90
				Br	16	40-83
				Cl	16	68
10 ⁷ⁱ	Cobalt Schiff-base complex ^b (2)	Suzuki	CH ₃ CN, 80 °C	I	16	58-79 ^c
				Br	16	40-83 ^c
11 ^{7j}	CoASGO ^d (0.32)	Suzuki	EtOH, 80 °C	I	8	97.1 ^c
				Br	12, 24	45-89
				Cl	24	18, 23
12 ^{7k}	Cobalt salen complex ^e (2)	Suzuki	Refluxing 1,4-dioxane	I	8	68,85
				Br	8	35-80
13 ^{7f}	Fe ₃ O ₄ @Boehmite-NH ₂ -Co (0.33)	Suzuki	H ₂ O, 80 °C	I	0.4-3	60-98
				Br	0.5-4	50-95
				Cl	2-9	15-65
14 ^{This work}	mTEG-CS-Co-Schiff-base (0.5)	Suzuki	H ₂ O, 90 °C	I	1-3	85-93
				Br	1.5-4	82-91
				Cl	2-3	82-90
15 ^{7l}	Co (acac) ₂ (5) /CuI (5)	Hirao	NMP, 110 °C	I	10	76-89
				Br	10	73-83
16 ^{This work}	mTEG-CS-Co-Schiff-base (2)	Hirao	H ₂ O, 80 °C	I	4.5-5	91-92
				Br	5-9.5	75-86
				Cl	8-10	78-86

ARTICLE

^a L-3,4-Dihydroxyphenylalanine^b A complex between 4-aminoacetophenone, salicylaldehyde and cobalt acetate^c GC yield^d Cobalt Schiff-base immobilized on graphene nanosheet^e A salen of *o*-phenylenediamine and salicylaldehyde

Experimental

Synthesis of mTEG-CS-Schiff-base

Tosylated mono-methoxytriethylene glycol⁴² (20 mmol) was added to the stirring mixture of CS-Schiff-base⁴³ and K₂CO₃ (20 mmol) in dry CH₃CN (50 mL) and stirred at 60 °C for 24 h. The reaction was allowed to be cooled to room temperature. The solid material was separated by filtration and washed with EtOH (3 × 20 mL) and H₂O (3 × 20 mL) and dried in a vacuum oven at 50 °C for 24 h to give the mTEG-CS-Schiff-base.

Synthesis of mTEG-CS-Co-Schiff-base

Cobalt acetate (4 mmol) was added to the mixture of the mTEG-CS-Schiff-base (1 g) in EtOH (15 mL) and stirred at 80 °C for 24 h. Then the reaction was allowed to be cooled to room temperature. The mixture was filtered off and washed with EtOH (3 × 20 mL) and dried in an oven at 60 °C for 24 h.

General procedure for Hiyama cross-coupling reaction

mTEG-CS-Co-Schiff-base (0.008 g, 0.5 mol%) was added to the stirring mixture of aryl halide (1 mmol), NaOH (2 mmol), triethoxyphenylsilane (1.5 mmol) in H₂O (3 mL). The above mixture was heated at 90 °C in an oil bath. The reaction progress was monitored by TLC. After passing the time mentioned in Table 2, the reaction mixture was allowed to be cooled to ambient temperature. The organic compound was extracted with EtOAc (3 × 5 mL) from the aqueous layer. The separated organic layer was dried by anhydrous MgSO₄ and filtered. The organic solvent was evaporated in vacuum to produce the crude product. The pure products were isolated by chromatography on silica gel (*n*-hexane:EtOAc = 50:1). The aqueous phase which contains the catalyst was used for another run.

General procedure for Suzuki cross-coupling reaction

mTEG-CS-Co-Schiff-base (0.008 g, 0.5 mol%) was added to the stirring mixture of aryl halide (1 mmol), K₂CO₃ (2 mmol), phenylboronic acid (1.1 mmol) in H₂O (3 mL). The above mixture was heated at 90 °C in

an oil bath. The reaction progress was monitored by TLC. After passing the time mentioned in Table 4, the reaction mixture was allowed to be cooled to ambient temperature. The organic compound was extracted with EtOAc (3 × 5 mL) from aqueous layer. The separated organic layer was dried by anhydrous MgSO₄ and filtered. The organic solvent was evaporated in vacuum to produce the crude product. The pure products were isolated by chromatography on silica gel (*n*-hexane:EtOAc = 50:1). The aqueous phase, which contains the catalyst, was used for another run.

General procedure for the Heck cross-coupling reaction

mTEG-CS-Co-Schiff-base (0.005 g, 0.35 mol%) was added to the stirring mixture of aryl halide (1 mmol), Et₃N (2 mmol), olefin (1.1 mmol) in H₂O (3 mL). The above mixture was heated at 90 °C in an oil bath. The reaction progress was monitored by TLC. After passing the time mentioned in Table 6, the reaction mixture was allowed to be cooled to ambient temperature. The organic compound was extracted with EtOAc (3 × 5 mL) from aqueous layer. The separated organic layer was dried by anhydrous MgSO₄ and filtered. The organic solvent was evaporated in vacuum to produce the crude product. The pure products were isolated by chromatography on silica gel (*n*-hexane:EtOAc = 50:1). The aqueous phase, which contains the catalyst, was used for another run.

General procedure for the Hirao cross-coupling reaction

mTEG-CS-Co-Schiff-base (0.032 g, 2 mol%) was added to the stirring mixture of aryl halide (1 mmol), Et₃N (3 mmol), triethylphosphite (2 mmol) in H₂O (4 mL). The above mixture was heated at 80 °C in an oil bath. The reaction progress was monitored by TLC. After passing the time mentioned in Table 8, the reaction mixture was allowed to be cooled to ambient temperature. The organic compound was extracted with EtOAc (3 × 5 mL) from aqueous layer. The separated organic layer was dried by anhydrous MgSO₄ and filtered. The organic solvent was evaporated in vacuum to produce the crude product. The pure products were isolated by chromatography on silica gel (*n*-hexane:EtOAc = 2:1). The aqueous phase, which contains the catalyst, was used for another run.

Conclusion

In this paper, a new hydrophilic heterogeneous cobalt catalyst of chitosan-Schiff base, containing mono-methoxytriethylene glycol (mTEG) as a phase transfer functional group, was introduced. This newly synthesized catalyst was characterized by different methods such as XRD, FE-SEM, TEM, TGA, FT-IR, $^{13}\text{C}\{^1\text{H}\}$ CP/MAS NMR, XPS and ICP analysis and used efficiently as a heterogeneous catalyst in C-C and $\text{C}(\text{sp}^2)\text{-P}$ cross-coupling reactions such as palladium and fluoride-free Hiyama, Suzuki, Heck and Hirao reactions in water. A wide range of aryl iodides, bromides and chlorides (the most challenging aryl halides which are much cheaper and more widely available than aryl iodides and bromides) was coupled successfully with triethoxyphenylsilane, phenylboronic acid, alkyl acrylates, styrene and triethylphosphite to generate the corresponding products. By this method, good to high yields of the products were achieved in water as a benign solvent without the need of any additive or organic solvents. Notably, this is the first report on the application of a cobalt catalyst in the Hiyama reaction. Any further conversion in the remaining solution after separation of the catalyst in the hot filtration test and poisoning test using S_8 showed that the observed catalysis was heterogeneous in nature. Due to the extremely low solubility of the catalyst in organic solvents, the separated aqueous phase which contains the catalyst can be readily recycled for six sequential runs without a noteworthy loss in activity. Finally, the catalyst can be simply isolated from the aqueous layer by filtration. Using water as a green solvent without requiring any additive or organic solvent, low cost and abundant cobalt catalyst instead of expensive Pd catalysts, facile catalyst recovery and scalability make this method favourable from the environmental and economic point of view for the C-C and $\text{C}(\text{sp}^2)\text{-P}$ cross-coupling reactions.

Conflicts of interest

There are no conflicts to declare.

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