EurJIC
European Journal of Inorganic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201800291

Link to VoR: http://dx.doi.org/10.1002/ejic.201800291

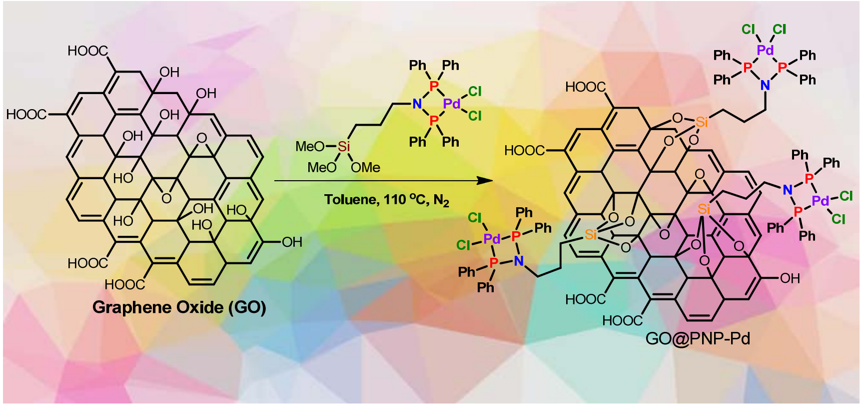
WILEY-VCH

10.1002/ejic.201800291

Immobilization of aminobisphosphine-Pd^{II} complex, [$PdCl_2\{(Ph_2P)_2N(CH_2)_3Si(OMe)_3\}$] over graphene oxide: An efficient and reusable catalyst for Suzuki-Miyaura, Ullmann coupling and cyanation reactions

Debasish Sengupta, Madhusudan K. Pandey, Dipanjan Mondal, Latchupatula Radhakrishna, and Maravanji S. Balakrishna*

This article describes the first example of grafting of a aminobis(phosphine)-Pd^{II} complex on graphene oxide (GO) and its utility in Suzuki-Miyaura, Ullmann coupling and cyanation reactions.



Immobilization of aminobisphosphine-Pd^{II} complex over graphene oxide: An efficient and reusable catalyst for Suzuki-Miyaura, Ullmann coupling and cyanation reactions

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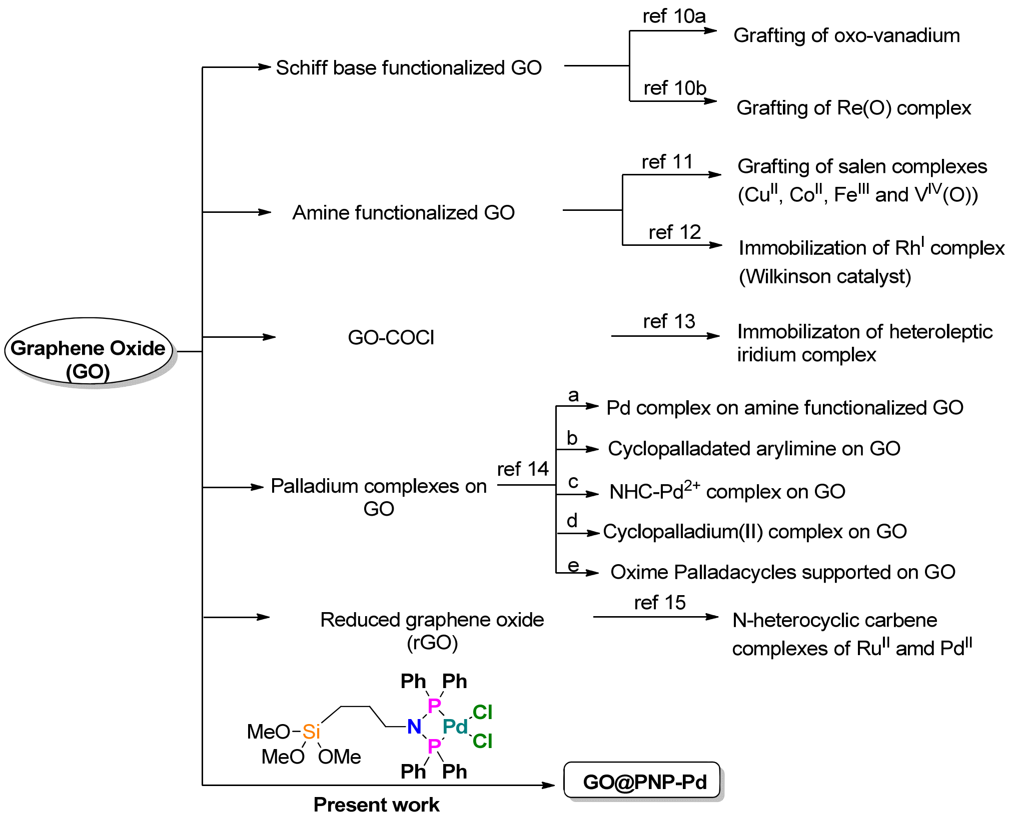
Abstract: The grafting of a aminobis(phosphine)-Pd^{II} complex (PNP-Pd^{II}) $[PdCl_2\{(Ph_2P)_2N(CH_2)_3Si(OMe)_3\}]$ (**2**) on graphene oxide (GO) has been carried out *via* a condensation reaction between methoxysilane groups of **2** and hydroxyl groups of GO. The composite material was characterized by FTIR, solid state ^{31}P NMR, SEM, TEM, XPS and ICP-AES techniques. All these tools support the clean immobilization of compound **2** on GO. The composite material showed high catalytic activity in Suzuki-Miyaura, Ullmann coupling and cyanation reactions. The heterogeneity of the composite was confirmed by hot filtration test. The immobilized PNP-Pd^{II} shows comparable activity as its homogeneous analogue **2**. The recycling ability of the catalyst has been examined for five consecutive runs which showed little or no reduction in its catalytic efficiency.

Introduction

Graphene is the thinnest carbon material made up of sp^2 hybridised carbon atoms, arranged in a honeycomb crystal structure.[1] In recent years graphene has attracted enormous interest owing to its physical, mechanical and thermal properties.[2] Graphene oxide (GO) is an oxidised form of graphene with layered structure containing a range of reactive oxygen functional groups such as epoxide, hydroxyl and carboxyl groups located on basal planes and edges. These are the active sites normally used during functionalization and also for catalysis. Functionalization of graphene oxide has been a subject of numerous studies due to the potential applications in material chemistry,[3] medicinal chemistry[4] and also in catalysis.[5]

The transition-metal phosphine complexes find extensive applications in synthetic organic chemistry as efficient homogeneous catalysts.[6] The immobilization of such systems also attracted much attention since it includes numerous advantages like separation of the catalyst from reaction mixture and reutilization of the material in several cycles. Over the past years a wide range of solid materials like polystyrene, mesoporous silica, alumina, MgO, TiO_2, carbon material etc., have been used for the immobilization of different homogeneous catalysts including phosphines.[7] Although, different immobilization methods such as, encapsulation, coordination and ion interaction are known, the method of covalent attachment is found to be more effective compared to other methods. Different monophosphines and chelated bisphosphines having alkoxysilane groups easily react with silanol groups of silica during immobilization.[8] On the other hand tripodal linker systems have been connected on silica through three silicon atoms.[9] The major drawback of these immobilized catalyst systems is the detachment of active species and the most common way of detachment is the hydrolysis of Si−O−E bond (E = Si, Al or Ti).[8]

Recently Khatri and co-workers have reported the grafting of oxo-vanadium and rhenium-oxo moieties on Schiff base functionalized GO and used as heterogeneous catalysts for alcohol and amine oxidations, respectively.[10] Few salen complexes of Cu^{II}, Co^{II}, Fe^{III} and oxovanadium(IV) have been successfully immobilized on amino-functionalized GO and applied in aerobic epoxidation of styrene.[11] Fan et al. have shown the immobilization of well known Wilkinson catalyst over amine-functionalized GO through coordination interaction and employed in the hydrogenation of cyclohexene.[12] Chemical fixation of carbon dioxide to dimethylformamide has been carried out by using GO grafted heteroleptic iridium complex.[13] Few GO immobilized Pd^{II} complexes have been used for Suzuki-Miyaura cross-coupling reaction.[14] On the other hand, reduced graphene oxide (rGO) has been utilized for the immobilization of N-heterocyclic carbene complexes of palladium and ruthenium by π-stacking.[15] However, the covalent attachment of any phosphine based metal complex over GO is still unknown (Scheme 1). As a part of our continued interest in phosphorus-based ligands and their coordination chemistry and catalytic applications,[16] herein we report for the first time, the covalent attachment of a PNP-Pd^{II} complex on graphene oxide and its catalytic investigations in Suzuki-Miyaura, Ullmann coupling and cyanation reactions.



Scheme 1 Grafting of various metal complexes over GO.

Result and Discussion

To begin our study, we synthesized GO from graphite powder using Hummer's method.[17] The reaction of *3*-aminopropyltrimethoxysilane with two equivalent of PPh_2Cl in the presence of triethylamine afforded a short-bite alkoxy functionalized diphosphine ligand $(MeO)_3Si(CH_2)_3N(PPh_2)_2$ (**1**) in good yield.[7j] Compound **1** was characterized by ^1H, ^{13}C, ^{31}P NMR and HRMS data. Reaction of **1** with one equivalent of $Pd(COD)Cl_2$ in dichloromethane at room temperature yielded $[PdCl_2\{(PPh_2)_2N(CH_2)_3Si(OMe)_3\}]$ (**2**). The molecular structure of compound **2** was confirmed by single crystal X-ray diffraction study (Fig. 1). For immobilization, compound **2** was treated with GO in toluene at 110 °C for 24 h under N_2 atmosphere (Scheme 2). After completion of the reaction, the initial yellow colour solution turned colourless. The colourless liquid on evaporation of solvent (toluene) under reduced pressure did not give any residue indicating the complete immobilization of compound **2** on

GO. The composite material was collected as black powder (GO@PNP-Pd) (here after *compound* **2***, i.e. PNP-Pd in GO composite is referred to as* GO@PNP-Pd) and fully characterized using various analytical and spectroscopic methods and employed in Suzuki-Miyaura, Ullmann coupling and cyanation reactions.

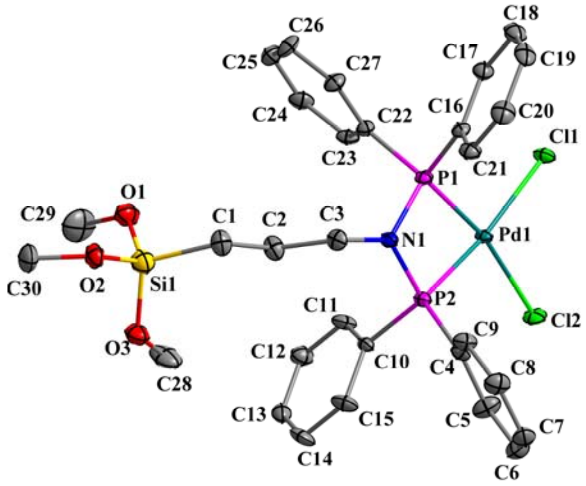
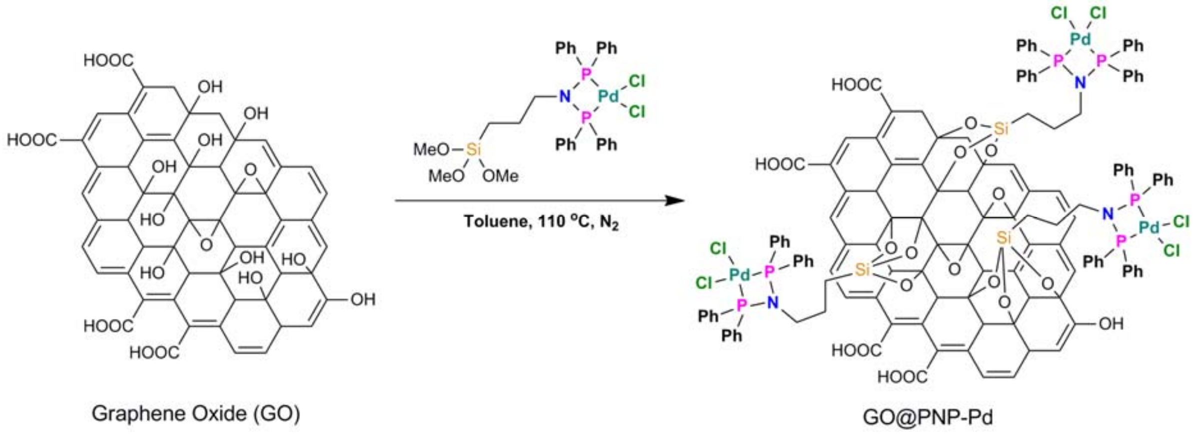


Fig. 1 Molecular structure of compound **2**. All hydrogen atoms were omitted for clarity.



Scheme 2 Immobilization of compound **2** on GO.

Characterization of GO@PNP-Pd

Initially the palladium content in the composite (GO@PNP-Pd) was calculated by ICP-AES analysis. For this purpose 10 mg of the sample was digested with aqua regia (6 mL) and then diluted with water (10 mL), filtered in a 50 mL volumetric flask and used for analysis. The loading of Pd was found to be 2.8 wt%. The BET surface area of the composite (GO@PNP-Pd), calculated by nitrogen physisorption at 77 K was 17.7 $m^2 g^{-1}$.

The FT-IR spectrum of GO@PNP-Pd was recorded and compared with GO and compound **2** (Fig. 2). GO exhibits an intense and broad peak at 3402 cm^{-1}, due to the ν_{O-H} bonds. Apart from this, peaks observed at 1725, 1614, 1240 and 1055 cm^{-1} were assigned to stretching modes of COOH, C=C, C−OH, and C−O−C bonds, respectively. Compound **2** also showed some characteristic peaks in the region 2800-3000 cm^{-1}, attributed to $\nu_{C-H}(sp^2)$ and $\nu_{C-H}(sp^3)$, respectively, and ν_{Si-O} was observed at 1100 cm^{-1}. Although, composite GO@PNP-Pd showed almost all characteristic peaks of GO and compound **2**, considerable decrease in the intensity of O−H peaks was observed as anticipated due to the covalent attachment of PNP-Pd(II) compound on GO *via* condensation reaction.

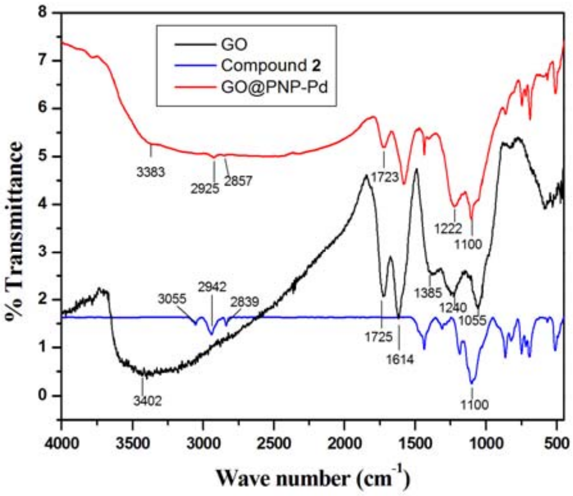


Fig. 2 FT-IR spectra of the GO, compound **2** and GO@PNP-Pd composite.

Solid-state NMR spectroscopy served as a useful analytical tool in the structural investigation of immobilized systems. The solid state ^{31}P NMR spectra of PNP-Pd^{II} complex **2** and GO@PNP-Pd are shown in Fig. 3. Compound **2** showed a major peak at 24 ppm with some side bands, whereas GO@PNP-Pd showed a resonance at 26.8 ppm along with typical side bands. The downfield shift of 2.8 ppm may be due to the inductive effect caused by covalent attachment of **2** on GO surface. These results have clearly indicated the successful immobilization of PNP-Pd^{II} complex keeping the metal coordination sphere intact.

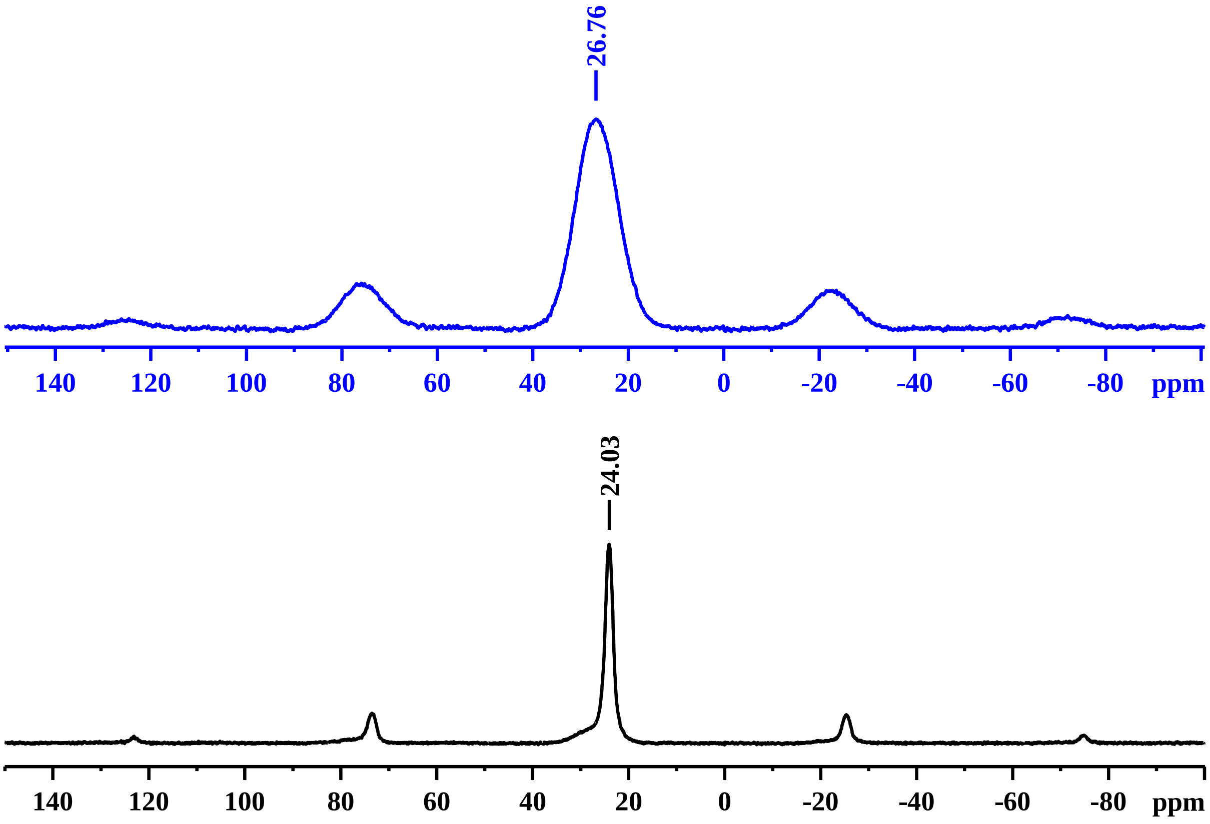


Fig. 3 Solid state ^{31}P NMR of PNP-Pd^{II} complex **2** (black) and GO@PNP-Pd composite (blue).

XPS has been used to determine the oxidation state of palladium in GO@PNP-Pd composite. Full XPS spectra of compound **2** and GO@PNP-Pd contains signature peaks of different elements (Fig. 4). Comparison of Pd 3*d* XPS spectra of compound **2** (336.2 and 341.6 eV) and GO@PNP-Pd (336.2 and 341.5 eV) confirmed the +2 oxidation state of palladium in the composite.

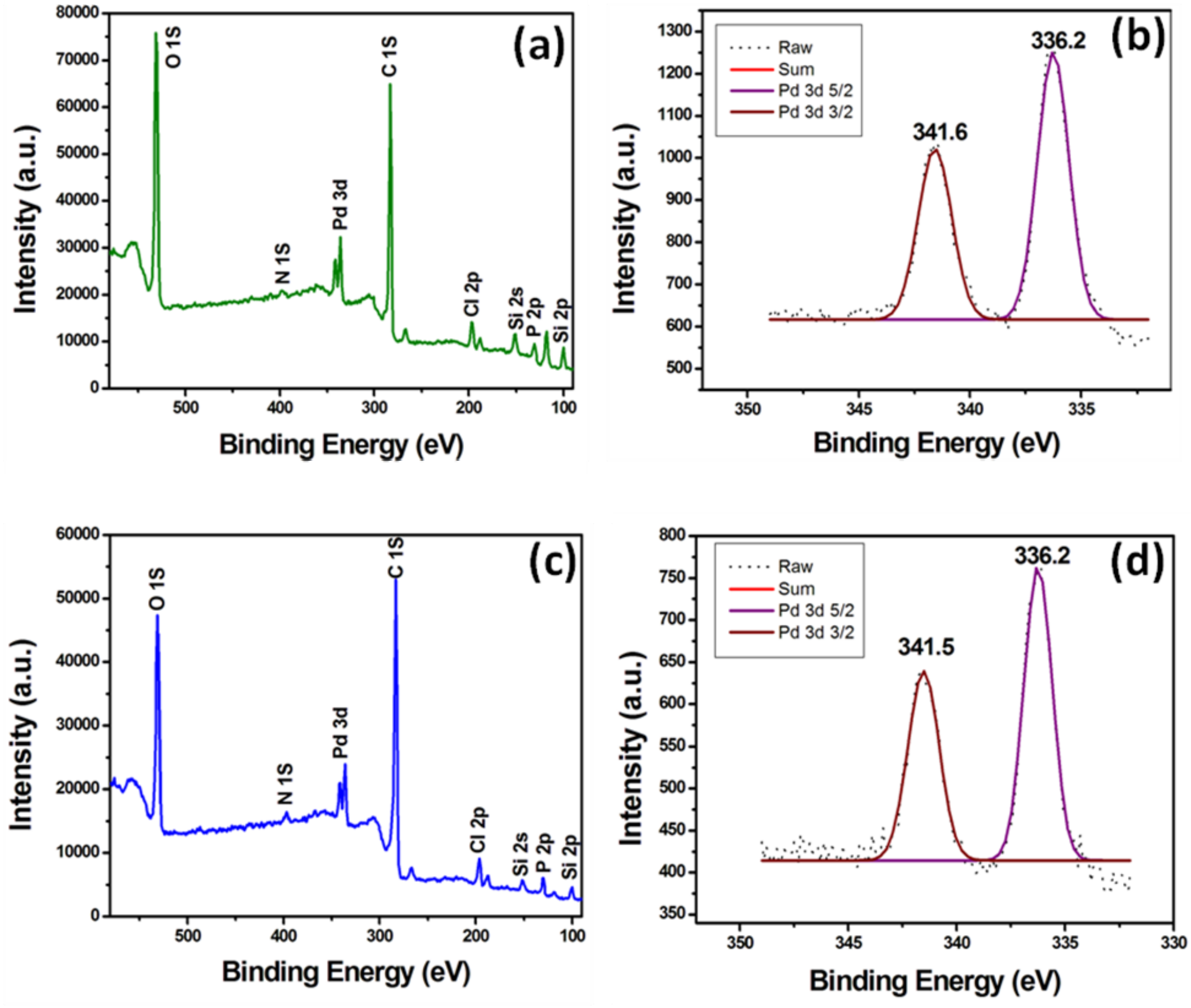


Fig. 4 (a) Full XPS spectra of complex **2,** (b) Pd 3d XPS spectra of complex **2**, (c) Full XPS spectra of GO@PNP-Pd composite, (d) Pd 3d XPS spectra of GO@PNP-Pd.

The information about the morphology of composite material was extracted from SEM analysis. FEG-SEM images of GO and composite (GO@PNP-Pd) are presented in Fig. 5. GO showed smooth planar surface (Fig. 5a), but composite showed crumpling features due to the chemical modification. The elemental mapping by energy dispersive X-ray absorption spectroscopy (EDS) of the composite revealed the homogeneous distribution of different elements: Pd, Si, P and Cl on the surface (Fig. 6).

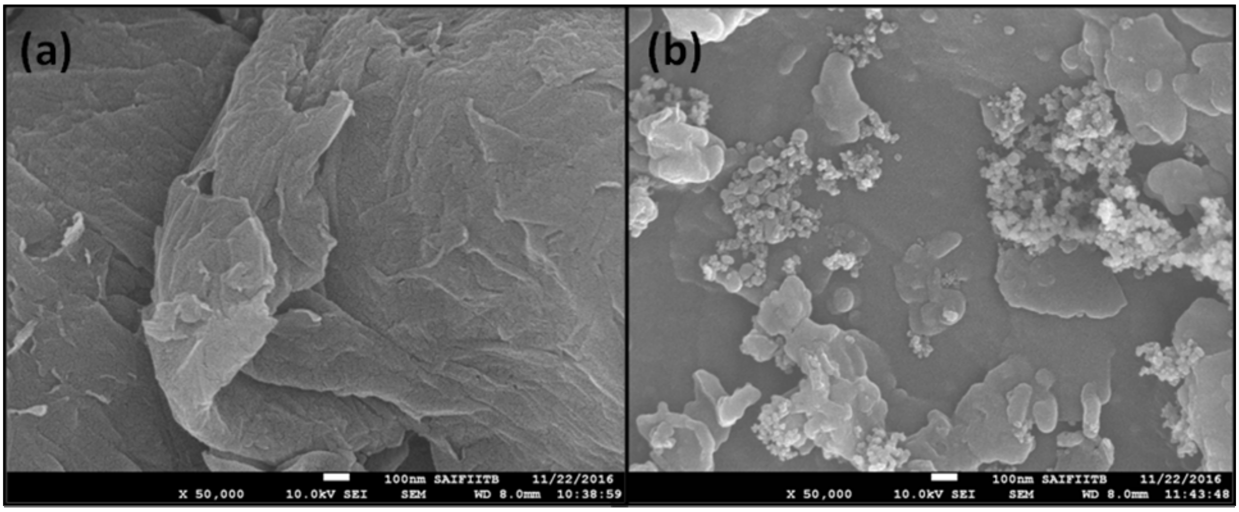


Fig. 5 SEM images of (a) GO and (b) GO@PNP-Pd composite.

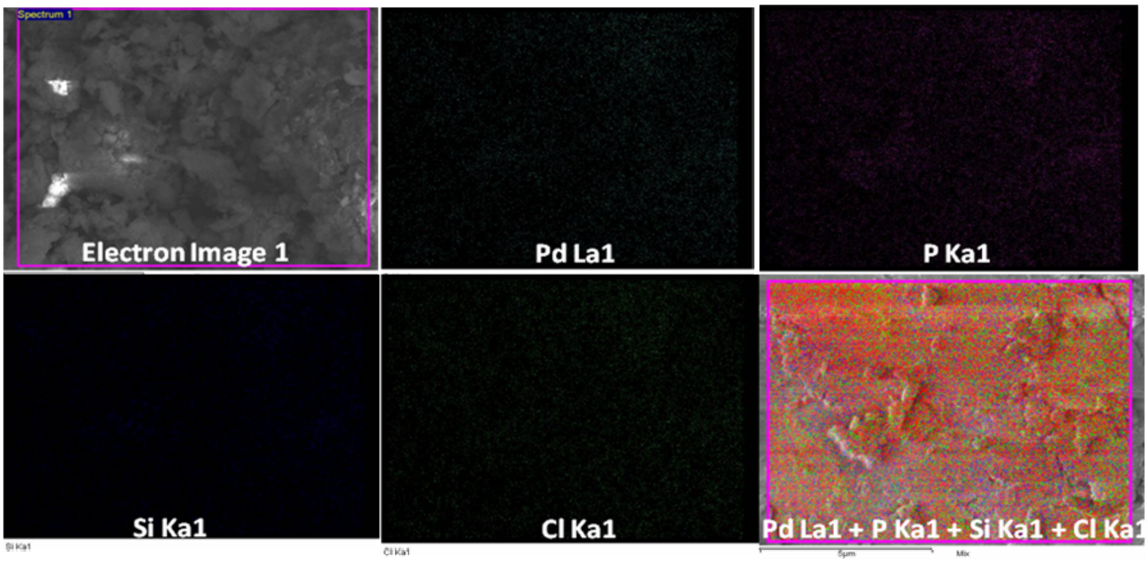


Fig. 6 SEM EDS mapping of GO@PNP-Pd showing elements, Pd, P, Si & Cl.

The TEM images of GO and GO@PNP-Pd composite in different magnification are shown in Fig. 7. GO showed a layer structure (Fig. 7a), whereas the composite (GO@PNP-Pd) displayed different layers decorated with metal stuffs (Fig. 7b & 7c). Energy dispersive X-ray scattering (EDS) analysis (Fig. 7d) of the composite also confirmed the presence of all possible elements such as Pd, P, Si, Cl, N, O and C. Although nitrogen was not identified in SEM analysis, TEM EDS and XPS data confirmed the presence of nitrogen as well.

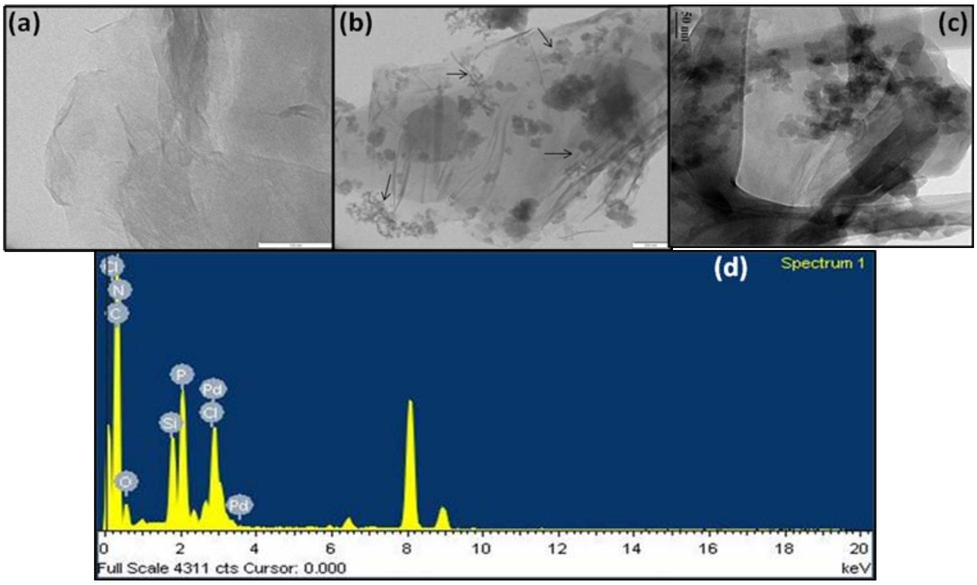


Fig. 7 TEM images in different magnification of (a) GO; (b) & (c) GO@PNP-Pd composite; (d) EDS pattern of the composite GO@PNP-Pd.

Catalytic activity of GO@PNP-Pd

Initially, the catalytic activity of the newly synthesized GO@PNP-Pd composite was evaluated in Suzuki-Miyaura cross-coupling reaction due to its wide application in the pharmaceutical and fine chemical industries.[18] Various palladium catalysts with ancillary phosphine ligands have been used for Suzuki-Miyaura reaction.[19] Different reusable heterogeneous palladium systems are also equally efficient for Suzuki-Miyaura reaction.[20] Very recently several research groups have studied the Suzuki-Miyaura coupling by developing some mono- and bimetallic heterogeneous systems.[14, 21] In spite of their potentiality, these systems suffered from various disadvantages such as prolonged reaction time, high catalyst concentration and low substrate scope. Herein, we report a convenient route to perform Suzuki-Miyaura coupling by using low catalyst concentration with broad range of substrates including benzylic systems. We optimized the reaction conditions with 4-bromoacetophenone and phenylboronic acid as coupling partner using the newly developed

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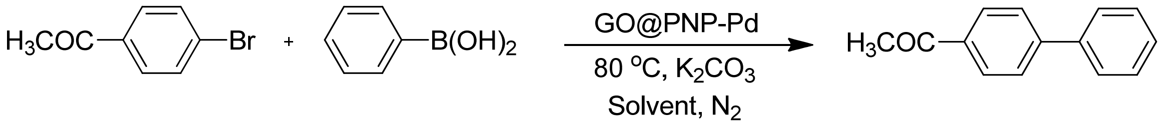
GO@PNP-Pd as an immobilized homogeneous catalyst and K_2CO_3 as a base (Table 1) at 80 ^{o}C. Solvent plays a vital role in Suzuki-Miyaura cross-coupling reaction.[22] In DMF 1 mol% catalyst (with respect to palladium) was required to achieve 100 % conversation after 10 h, whereas in DMF:H_2O (1:1) the reaction was completed within 1 h with 0.01 mol% of catalyst (entries 1 & 2). In water, reaction needs more time for the completion (entry 3). However in methanol the reaction was completed within 30 min using the same amount of catalyst (entry 4). Further the conversion has been decreased when the reaction was performed at lower temperature (entry 5). Reactions without the catalyst or only with GO did not show any conversion (entries 6 & 7). Therefore, the entry 4 in Table 1 represents the optimized reaction condition.

Table 1 Optimization of Suzuki-Miyaura reaction using GO@PNP-Pd.[a]



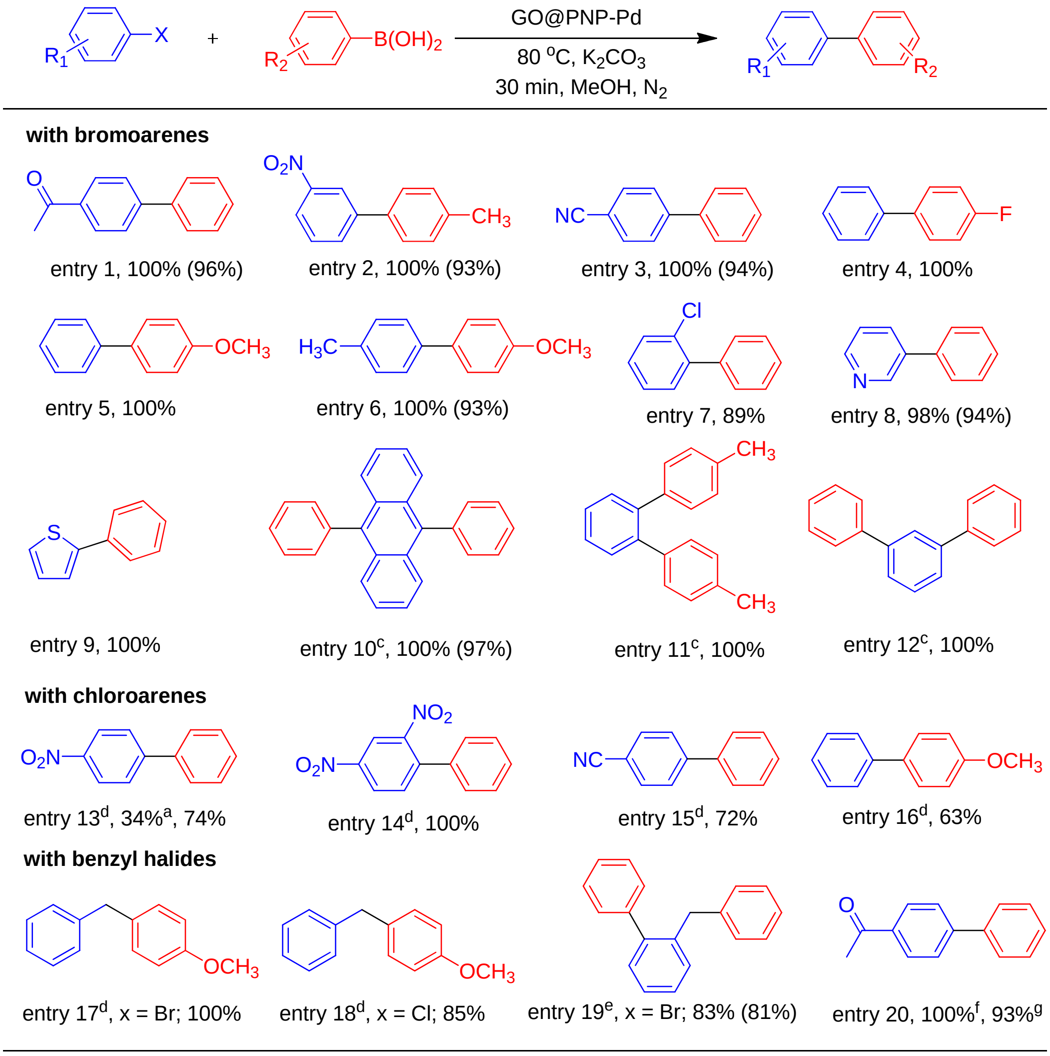
Sl. No.	Catalyst Pd content (mol%)	Solvent	Time (h)	Conversion (%)[b]
1	1	DMF	10	100
2	0.01	DMF:H_2O (1:1)	1	100
3	0.01	H_2O	2.5	100
4	**0.01**	**MeOH**	**0.5**	**100**
5[c]	0.01	MeOH	0.5	59
6	none	MeOH	3	0
7[d]	Graphene oxide	MeOH	3	0

[a] 4-Bromo acetophenone (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.2 mmol) and solvent (2.5 mL), 80 ^{o}C under N_2. [b] GC-MS conversion. [c] Reaction performed at 60 ^{o}C. [d] Graphene oxide (1 mg).

To explore the scope and limitations of the catalyst, a range of substituted bromoarenes were employed with different boronic acids (Table 2, entries 1-7) which resulted in desired products in excellent yields. Heteroaryl bromides were equally effective for the reaction and afforded corresponding cross-coupling products in excellent yield (Table 2, entries 8 and 9). Di-bromo compounds such as *9,10*-Dibromoanthracene, *1,2*-dibromobenzene and *1,3*-dibromobenzene efficiently reacted with boronic acid derivatives (Table 2, entries 10-12). On the other hand, reaction of 4-nitrochlorobenzene with phenylboronic acid gave only 34% of the cross-couple product (Table 2, entry 13). Since aryl chlorides are less reactive compared to aryl bromides in cross-coupling reactions, the catalyst loading was increased to 1 mol% that resulted in better conversions. Several aryl chlorides were reacted with various boronic acids and the cross-coupling products were obtained in moderate to good yields (Table 2, entries 13-16). Reactions between aliphatic halides and boronic acids have been carried out by employing 1 mol% of the catalyst GO@PNP-Pd (with respect to palladium). Benzyl bromide, benzyl chloride and 2-bromobenzyl bromide afforded corresponding cross-coupled products in good to excellent yield (Table 2, entries 17-19). The catalytic efficiency of PNP-Pd(II) compound before (**2**) and after immobilization (GO@PNP-Pd) were comparable (Table 2, entries 1 & 20), however, GO@PNP-Pd showed better durability and did not show any reduction in the catalytic efficiency even after five consecutive catalytic cycles (see Fig. 8) and also in scaled up reactions (Table 2, entry 20).

In order to prove the heterogeneous nature of the catalyst, hot filtration test has been performed. Fig. 9 shows that the Suzuki-Miyaura reaction between 4-bromoacetophenone and phenylboronic acid was very fast and completed within 30 min. Therefore, in order to perform the hot filtration test, the catalyst was filtered off after 1.5 min and the remaining liquid part (without catalyst) was heated again at 80 °C for another 30 min. After separation of the catalyst from the reaction, catalytic process was quenched (see hot filtration graph in Fig. 9) suggesting that Pd was not leached out from GO surface during initial course of the reaction and GO@PNP-Pd catalyst was of heterogeneous in nature.

Table 2 Suzuki-Miyaura reaction of aryl halides with boronic acids using GO@PNP-Pd.[a,b]



[a]Reaction condition: ArBr (1 mmol), boronic acid (1.2 mmol), K$_2$CO$_3$ (1.2 mmol), GO@PNP-Pd (0.6 mg, 0.01 mol% Pd), MeOH (2.5 mL), heating the reaction mixture at 80 °C under N$_2$ for 30 min. [b]GC-MS Conversion & yield in bracket represents isolated yield. [c]ArBr$_2$ (0.5 mmol), boronic acid (1.2 mmol), K$_2$CO$_3$ (1.2 mmol), GO@PNP-Pd (0.6 mg, 0.02 mol% Pd), MeOH (2.5 mL), heating the reaction mixture at 80 °C for 30 min. [d]ArCl or benzyl halide (0.25 mmol), boronic acid (0.3 mmol), K$_2$CO$_3$ (0.3 mmol), GO@PNP-Pd (9.5 mg, 1 mol% Pd) heating the reaction mixture at 80 °C under N$_2$ for 8 h. [e]2-Bromobenzyl bromide (0.25 mmol), boronic acid (0.6 mmol), K$_2$CO$_3$ (0.6 mmol), GO@PNP-Pd (9.5 mg, 1 mol% Pd) heating the reaction mixture at 80 °C under N$_2$ for 8 h. [f]Using 0.01 mol% of compound **2**. [g]Scaled up reaction: 4-bromoacetophenone (995 mg, 5 mmol), phenylboronic acid (731.6 mg, 6 mmol), potassium carbonate (829.3 mg, 6 mmol) and GO@PNP-Pd (3 mg, 0.01 mol% Pd), MeOH (7 mL), heating the reaction mixture at 80 °C under N$_2$ for 1 h.

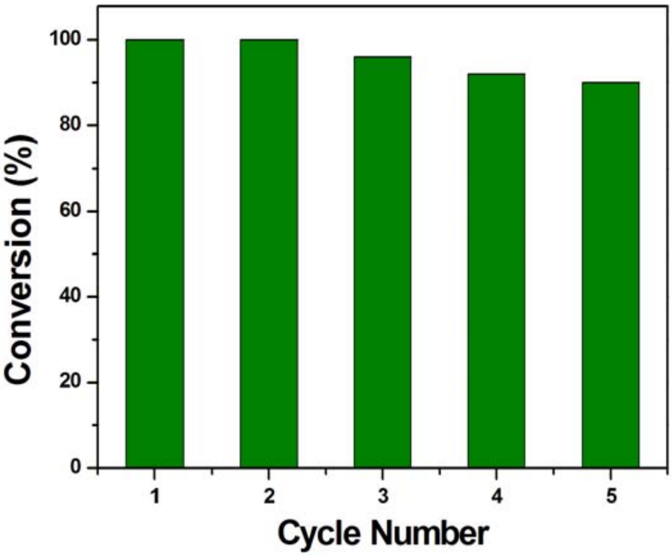


Fig. 8 Recycling experiments of GO@PNP-Pd catalyst in Suzuki-Miyaura reaction between 4-bromoacetophenone and phenylboronic acid.

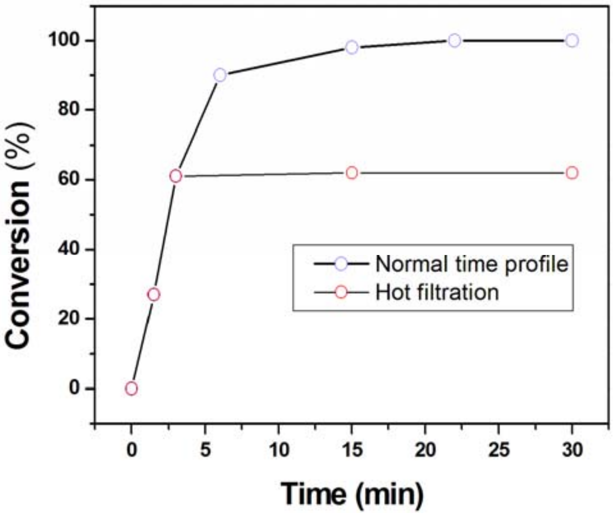
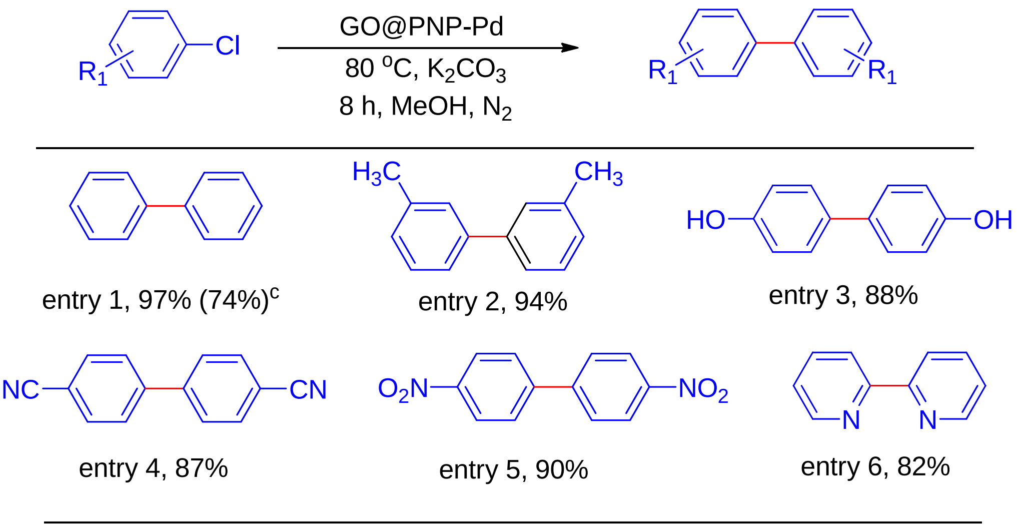


Fig. 9 Comparison of normal time profile verses hot filtration test.

Ullmann coupling is one of the cost-effective method for the synthesis of biaryls since it eliminates the use of arylmetals, like arylboronic acids, arylstannanes, arylzinc, aryl Grignard regents etc. On the other hand, use of chloro arenes in Ullmann coupling reaction is more economical compared to bromo and iodo arenes as aryl chlorides are inexpensive and environmentally benign. Limited number of heterogeneous palladium catalysts have been reported for the Ullmann coupling of aryl chlorides and the major drawbacks are high catalyst loading, hazardous solvents and prolong reaction time.[23] Herein, the newly developed catalyst (GO@PNP-Pd) has been used as a heterogeneous catalyst for Ullmann coupling reaction of chloro arenes with a high efficacy. The reaction has been performed in methanol at 80 °C using 1 mol% (with respect to palladium) of the catalyst, GO@PNP-Pd. However, the yield of the product decreases with the lowering of temperature. Different chloro arenes having electron donating and withdrawing groups such as –CH_3, –OH, –NO_2, and –CN undergo Ullmann reaction efficiently and produce corresponding biaryl compounds in high yields (Table 3, entries 1-6). The catalyst has been used for five consecutive cycles with appreciable conversion (see ESI S1).

Table 3 GO@PNP-Pd catalyzed Ullmann coupling of aryl chlorides.[a,b]

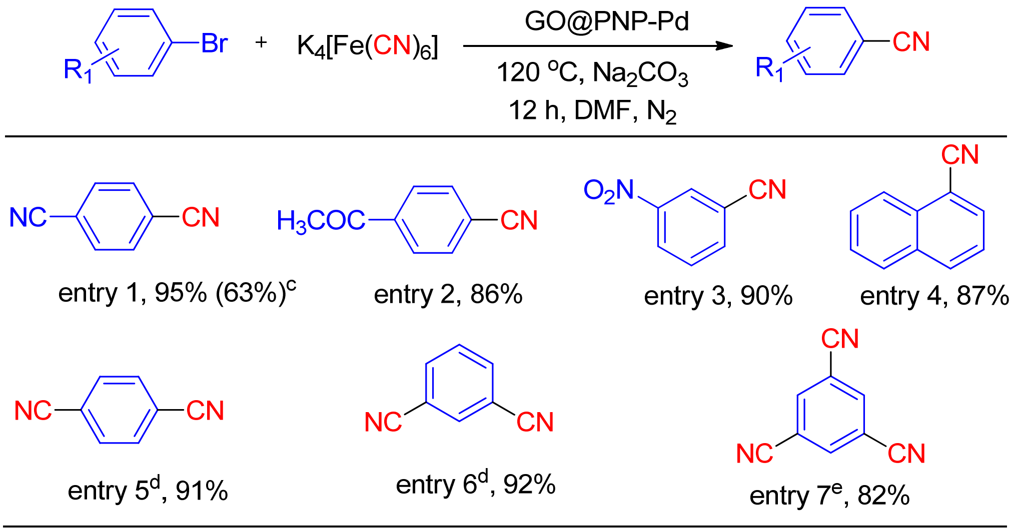


[a]Reaction condition: ArCl (0.25 mmol), K_2CO_3 (0.3 mmol), GO@PNP-Pd (9.5 mg, 1 mol% Pd), MeOH (2 mL) heating the reaction mixture at 80 °C under N_2 for 8 h; [b]Isolated Yield. [c]Reaction was performed at 60 °C.

After successful completion of Suzuki-Miyaura and Ullmann coupling reaction, the GO@PNP-Pd catalyst has been employed in the cyanation reaction. Aryl nitriles represent an important class of organic compounds used as intermediates in the synthesis of many pharmaceuticals, agrochemicals and dyes.[24] In recent times, transition metal catalysed cyanation reaction of aryl halides has become more attractive as it eliminates the use of elevated temperature (150-200 ^{o}C) and stoichiometric amount of toxic cyanating reagents.[24b] Many homogeneous and heterogeneous palladium catalysts are known for cyanation reactions but most of the methods suffer from the limitation such as high reaction temperature, use of additives and poor reusability factors.[25] Several phosphine ligands are well-known for performing the cyanation reaction under mild condition.[26] Herein, the GO immobilized phosphine complex (GO@PNP-Pd) has been used as a reusable heterogeneous catalyst for the cyanation reaction of aryl bromides. The reaction was performed with 1 mol% of the catalyst (with respect to palladium) in DMF at an optimized temperature of 120 ^{o}C with $K_4[Fe(CN)_6]\cdot 3H_2O$ as a cyanating reagent. On decreasing the temperature below 120 ^{o}C, the yield was lowered considerably. Aryl bromides having different substituents efficiently react with $K_4[Fe(CN)_6]\cdot 3H_2O$ to afford corresponding nitrile derivatives (Table 4, entries 1-7). Finally the recyclability of the catalyst GO@PNP-Pd has been examined for five consecutive runs (see ESI S1) with an average yield 96% of terephthalonitrile.

To compare the morphological nature of the catalyst before and after the reaction, TEM images of the catalyst have been taken after 1st and 2nd runs of Suzuki-Miyaura reaction (see ESI S2). TEM images indicate the agglomeration of the palladium catalyst occurred over GO surface during the reaction. On the other hand, Pd 3*d* line in XPS spectra (see ESI S3) indicates the partial reduction of Pd^{II} species to Pd^{0}, however, the catalytic activity remains unaltered.

Table 4 GO@PNP-Pd catalyzed cyanation of aryl bromides.[a,b]



entry 1, 95% (63%)[c]

entry 2, 86%

entry 3, 90%

entry 4, 87%

entry 5[d], 91%

entry 6[d], 92%

entry 7[e], 82%

[a] Reaction condition: ArBr (0.25 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.045 mmol), Na_2CO_3 (0.37 mmol), GO@PNP-Pd (9.5 mg, 1 mol% Pd), DMF (2 mL), heating the reaction mixture at 120 °C under N_2 for 12 h. [b] Isolated yield. [c] Reaction was performed at 100 °C. [d] $ArBr_2$ (0.125 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.045 mmol), Na_2CO_3 (0.37 mmol), GO@PNP-Pd (9.5 mg, 2 mol% Pd). [e] $ArBr_3$ (0.125 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.068 mmol), Na_2CO_3 (0.55 mmol), GO@PNP-Pd (14.25 mg, 3 mol% Pd).

Conclusions

In summary, we have demonstrated a facile and efficient method to immobilize PNP-Pd(II) complex on graphene oxide. The supported PNP-Pd(II) material (GO@PNP-Pd) has been well characterized by different spectroscopic and microscopic techniques and applied as a heterogeneous catalyst in Suzuki-Miyaura, Ullmann coupling and cyanation reaction. Aryl bromides and chlorides were efficiently reacted with boronic acids to produce the cross-coupling products in good to excellent yield. Aliphatic bromides are equally effective for the Suzuki-Miyaura reaction. On the other hand aryl chlorides have been utilized in Ullmann coupling reaction for the synthesis of symmetrical biaryls. The heterogeneous nature of the catalyst has been examined by hot filtration test. Further investigation on grafting of other metal systems (ruthenium, copper etc) and their catalytic application in other cross-coupling reactions, hydrogenation and transfer-hydrogenation reactions is in progress.

Experimental Section

General Information

All phosphine based works were performed using standard vacuum-line and Schlenk techniques under nitrogen atmosphere. All solvents were purified by conventional procedures and distilled prior to use. Chemicals were purchased and used directly. [Pd(COD)Cl_2] was prepared according to the published procedure.[27]

Instrumental Methods

FTIR spectra of the samples were recorded using Perkin-Elmer, Spectrum One FTIR instrument by KBr pellet method. The Field Emission Gun-Scanning Electron Microscope (FEG-SEM) measurements of the samples were carried out using a JSM-7600F. Transmission electron microscopy (TEM) of the samples were carried out with a Tecnai G2, F30 (Make- FEI) operating at 300 kV and CM 200 (Make-PHLIPS) operating voltages: 20-200 kv. The concentration of Pd in the composite has been estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using ARCOS, simultaneous ICP Spectrometer, Germany. X-ray photoelectron spectroscopic (XPS) measurements were recorded on AXIS Supra, Make**:** Kratos Analytical, UK (SHIMADZU group). The ^{1}H and ^{31}P NMR (δ in ppm) spectra were obtained from either Bruker Avance-400 MHz or Bruker Avance- 500 MHz spectrometer. The spectra were recorded in $CDCl_3$ solutions with $CDCl_3$ as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^{1}H and $^{31}P\{^{1}H\}$ NMR, respectively. The solid state ^{31}P NMR spectra were recorded in Bruker Avance- 500 MHz spectrometer. All GC-MS analyses were carried out in Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD.

Preparation of GO

To an ice-cold concentrated sulfuric acid (46 mL) was slowly added sodium nitrate (100 mg) and then graphite powder (2 g) with vigorous magnetic stirring. After that potassium permanganate (6 g) was added slowly to the reaction mixture keeping the temperature within 0–5 ^{o}C to avoid any possible explosion. The mixture was allowed to stir at room temperature for 6 h forming a thick paste. It was diluted with millipore water (92 mL) under stirred condition. The temperature of the solution was raised to about 90 ^{o}C and the mixture was allowed to stir for 30 min. Finally, 280 mL millipore water was added followed by slow addition of 3 mL H_2O_2 (30%). The colour of the solution changes from dark brown to yellowish brown. The overall solution was centrifuged at 10000 rpm to collect the solid mass at bottom and the supernatant liquid was thrown out. The solid mass was washed with 1 (N) HCl followed by water to remove the acid and metal ions. Finally, the brown mass was collected and dried at 60 ^{o}C under vacuum to obtain solid graphene oxide.

Synthesis of $(Ph_2P)_2N(CH_2)_3Si(OMe)_3$ (1)

A solution of chlorodiphenylphosphine (2.46 g, 11.158 mmol) in toluene (10 mL) was added dropwise to the mixture of 3-aminopropyltrimethoxysilane (1 g, 5.579 mmol) and NEt_3 (1.7 mL, 12.27 mmol) in toluene (30 mL) at -60 ^{o}C. The white colour solution thus obtained was stirred at room temperature for 24 h. The reaction mixture was filtered to separate the ammonium salt and the filtrate was evaporated under reduced pressure to afford compound **1** (2.63 g, Yield: 86 %) as light yellow oil.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) δ: 62.2 (s); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.23 (t, J = 8.5 Hz, 2H, $CH_2{-}Si$), 1.21-1.24 (m, 2H, $-CH_2{-}CH_2Si$), 3.24 (t, J = 8.5 Hz, 2H, $-CH_2N$), 3.39 (s, 9H, OCH_3), 7.31-7.41 (m, 20H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 6.1, 24.3, 50.3, 55.7, 128.0, 128.7, 132.7 (t, J = 11.1 Hz), 139.6 (t, J = 6.3 Hz). $C_{30}H_{36}NO_3P_2Si$ $[M+H]^+$: 548.1940; Found: 548.1637.

Synthesis of [$PdCl_2\{(Ph_2P)_2N(CH_2)_3Si(OMe)_3\}$] (2)

A solution of Pd(COD)Cl_2 (141 mg, 0.494 mmol) in CH_2Cl_2 (20 mL) was added slowly to a solution of **1** (270.4 mg, 0.494 mmol) in CH_2Cl_2 (15 mL) and stirred the mixture for 6 h. The solvent was evaporated under reduced pressure and the residue was washed with petroleum ether to afford analytically pure product of **2** as a yellow solid. Yield: 87 % (0.312 g). Mp: 250 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) δ: 30.96; ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.20 (t, *J* = 8.0 Hz, 2H, $-\underline{CH_2}-Si$), 1.22-1.26 (m, 2H, $-\underline{CH_2}-CH_2Si$), 2.99-3.05 (m, 2H, $-\underline{CH_2}N$), 3.33 (s, 9H, OCH_3), 7.55 (t, *J* = 7.0 Hz, 8H, ArH), 7.66 (t, *J* = 7.0 Hz, 4H, ArH), 7.86-7.90 (m, 8H, ArH). Anal. Calcd. for $C_{30}H_{35}Cl_2NO_3P_2PdSi$: C, 49.70; H, 4.87; N, 1.93 %. Found: C, 49.15; H, 4.73; N, 2.26 %.

The crystal of compound **2** suitable for the X-ray diffraction study was obtained by slow diffusion of petroleum ether into a dichloromethane solution of **2**.

Synthesis of GO@PNP-Pd composite

400 mg GO was dispersed in 50 mL toluene by sonication (30 min) under nitrogen atmosphere. Then 100 mg of compound **2** in toluene (20 mL) was added slowly to the stirred solution of GO and heated the reaction mixture at 110 °C, for 24 h under N_2. After completion of reaction the mixture was cooled to room temperate and stands for 30 min. The colourless supernatant liquid was decanted in another flask and the black residue was wash with toluene (3 x 10 mL) and diethyl ether (3 x 10 mL). The resulting black powder was dried under vacuum and used for analysis and reactions.

Sample preparation for ICP-AES analysis

10 mg of GO@PNP-Pd composite was heated in aqua regia (6 mL) at 150 °C for 1 h. After cooling, the mixture was diluted with water (10 mL), filtered into a 50 mL volumetric flask and used for analysis. The loading of Pd was found to be 2.8 wt%.

Representative procedure for Suzuki-Miyaura reaction with GO@PNP-Pd composite

A mixture of 4-bromoacetophenone (199 mg, 1 mmol), phenylboronic acid (146.3 mg, 1.2 mmol), potassium carbonate (165.8 mg, 1.2 mmol) and GO@PNP-Pd (0.6 mg) in MeOH (2.5 mL) was taken in a 15 mL screw cap reaction tube, flashed with N_2 and heated the reaction mixture at 80 ^oC for 30 min under gentle magnetic starring. After completion of reaction the mixture was allowed to cool and diluted with ethyl acetate (3 mL), stirred and then allowed to stand for 15 min. The supernatant liquid was decanted into another flask and this process was repeated three times more. The organic part was washed with water, dried over anhydrous Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography over a short column of silica gel and eluting with 3% ethyl acetate-light petroleum to obtain the pure product (189 mg, Yield: 96%). The product was characterized by ^1H and ^{13}C NMR data (See ESI S5 & S6).

Catalyst Recovery

After completion of the reaction, the reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate (3 mL) and stirred for 15 min. This process was repeated three times and the supernatant liquid was separated by decantation. The residue (composite GO@PNP-Pd) was further washed with methanol (3 x 3 mL) followed by diethyl ether (3 x 3 mL) and dried under vacuum to give free–flowing black powder which was used in subsequent catalytic cycles.

Representative procedure for Ullmann coupling with GO@PNP-Pd composite

A mixture of 3-chlorotoluene (31.6 mg, 0.25 mmol), potassium carbonate (41.46 mg, 0.3 mmol) and GO@PNP-Pd (9.5 mg) in MeOH (2 mL) was taken in a 15 mL screw cap reaction tube, flashed with N_2 and heated the reaction mixture at 80 ^oC for 8 h under gentle magnetic starring. After completion of reaction the mixture was allowed to cool and diluted with ethyl acetate (3 mL), stirred and then allowed to stand for 15 min. The supernatant liquid was decanted into another flask and this process was repeated three times more. The organic part was washed with water, dried over anhydrous Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography over a short column of silica gel and eluting with light petroleum to obtain the pure product (21.4 mg, Yield: 94%). The product was characterized by ^1H and ^{13}C NMR data (See ESI S5 & S6).

Representative procedure for cynation reaction with GO@PNP-Pd composite

A mixture of 4-bromobenzonitrile (45.5 mg, 0.25 mmol), $K_4[Fe(CN)_6]\cdot3H_2O$ (19 mg, 0.045 mmol), sodium carbonate (39.2 mg, 0.37 mmol) and GO@PNP-Pd (9.5 mg) in DMF (2 mL) was taken in a 15 mL screw cap reaction tube, flashed with N_2 and heated the reaction mixture at 120 ºC for 12 h under gentle magnetic starring. After completion of reaction the mixture was allowed to cool and diluted with ethyl acetate (3 mL), stirred and then allowed to stand for 15 min. The supernatant liquid was decanted into another flask and this process was repeated three times more. The organic part was washed with water, dried over anhydrous Na_2SO_4, concentrated under vacuum. The residue was purified by column chromatography over a short column of silica gel and eluting with 7% ethyl acetate-light petroleum to obtain the pure product (48.5 mg, Yield: 95%). The product was characterized by ^1H and ^{13}C NMR data (See ESI S5 & S6).

X-ray Crystallography

Single crystal X-ray data collection was performed in Rigaku Saturn724 Diffractometer. Data collected at 150 K using graphite monochromated Mo-Kα radiation source. The structure was solved by direct method and refined by full-matrix least-squares procedures using the SHELXTL program package.[28] Crystal data and summary of data collection for compound **2** was given in electronic supplementary information S4.

Electronic Supplementary Information

Crystallographic information, XPS, TEM images of GO@PNP-Pd after Suzuki-Miyaura reaction, NMR spectral data and spectra for isolated compounds.

Accession Codes

CCDC 1563182 (Compound **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

DS thanks IIT Bombay for postdoctoral fellowship. MP, LR thanks UGC and DM thanks DST, New Delhi for providing fellowships. MSB thanks the Science & Engineering Research Board (SERB), New Delhi, India, for funding through grant SB/S1/IC-108/2014. We thank SAIF & ESCA lab of IIT Bombay for providing the instrumental facilities.

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