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Functionalized Cellulose-Supported Triphenylphosphine and Its Application in Suzuki Cross-Coupling Reactions

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ABSTRACT: A new heterogeneous cellulose tagged triphenylphosphine (Cell-OPPh$_3$) was synthesized and subsequently coordinated with Pd(OAc)$_2$ to form a cellulose-supported triphenylphosphine palladium complex (Cell-OPPh$_3$-Pd). Cell-OPPh$_3$ and the corresponding palladium complex were fully characterized by TGA, SEM, TEM, and NMR analysis. Results of catalytic activity experiments indicate that the Cell-OPPh$_3$-Pd complex can efficiently catalyze Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids at mild reaction conditions. The coupling products can be obtained in good to excellent yields (up to 98%). The work-up procedure is simple and the catalyst could be easily recovered by filtration, and then reused in next run. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41427.

KEYWORDS: catalysts; cellulose and other wood products; functionalization of polymers

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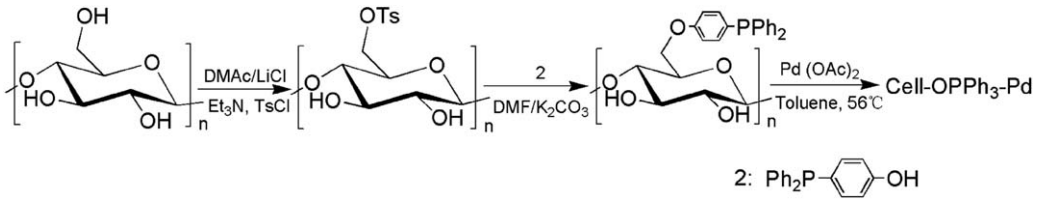
INTRODUCTION

Triphenylphosphine (PPh$_3$) is an important compound that has been widely used in synthetic organic processes such as the Wittig,[1] Mitsunobu,[2] and Appel[3] reactions. But almost without exception, PPh$_3$-triggered reactions result in a stoichiometric amount of a phosphine oxide being generated as a byproduct, thus complicating the purification of the desired product. Because of its high binding affinity toward most transition metals, triphenylphosphine has also been used as a ligand in carbon–carbon bond formation reactions such as Suzuki, Heck, and Negishi.[4] However, during these homogeneous reactions, the desired product is always inevitably contaminated by catalyst residues. These drawbacks greatly limit triphenylphosphine-related organic transformations in industrial applications. Thus, a simple and efficient way to reduce the cost of product purification and minimize the metal content is highly needed, especially in the pharmaceutical industry.

Anchoring triphenylphosphine ligand onto a polymer support is an effective approach to address the aforementioned issues and has attracted great interests in the past years. In 1970s, polystyrene (PS) supported triphenylphosphine was reported. Currently, this reagent and its metal complexes PS-PPh$_3$-M have been commercialized and widely used in various organic transformations.[5–12] Because of the poor swelling properties of PS, other synthetic polymers have been explored as supports to enhance the catalytic activity of phosphine-containing heterogeneous catalysts. For example, PEG-PS resin has been proved to be more active than the usual homogeneous palladium–phosphine complexes such as Pd(PPh$_3$)$_4$ under the same reaction conditions.[13–15] Besides, other polymeric materials such as PIB[16] and PNIPAM[17,18] have been used to make catalysts more active and easily separable. Despite the progresses made in this field, synthetic polymer supports are still expensive to produce and thus to purchase. Moreover, the widely used cross-linked polystyrene supports are susceptible to osmotic shock,[19] making their reuse challenging.

Taking in account all these issues plus the increasing environmental concerns over the efficient utilization of agro-industrial residues, tremendous efforts have been made to develop natural polymers as support materials instead of using petrochemical-based feedstock to create high-performance and environmentally friendly reagents and catalysts. In this regard, cellulose is an attractive candidate to be explored to respond to the current appeal for eco-friendly and sustainable green chemistry. Cellulose is the most abundant naturally occurring biopolymer and available in low price, which are essential for large-scale industrial preparation. Also it can easily be functionalized as soluble or insoluble support by chemical modification of its abundant hydroxyl groups. To date, cellulose and its derivatives have been widely used for coatings, laminates, and optical films; they can also serve as for property-determining additives in building materials, pharmaceuticals, foodstuffs, and cosmetics.[20] In

Additional Supporting Information may be found in the online version of this article.



Scheme 1. Synthetic pathway of Cell-OPPh$_3$ and Cell-OPPh$_3$-Pd.

recent years, cellulose and its derivatives also have been used as potentially efficient, cheap, renewable, and biodegradable supports for catalysis. For instance, Pd(II) complexes can be stabilized onto cellulose and catalyze the Heck and Sonogashira coupling reactions.[21–24] Elsewhere, methyl cellulose matrix supported silver nanoparticles have been used in the reduction of $AgNO_3$ by sodium borohydride.[25]

Among the numerous methods that have been used to prepare cellulose supported catalysts, deposited Pd particles on cellulose are still the most widely studied ways.[21,23,26] In certain cases, this process was followed by reduction of the thus formed complexes with hydrazine hydrate[27] or potassium borohydride.[28] However, such a coordination of palladium is relatively weak and deactivation often occurs due to leaching of the metal.[29] In 2011, the diphenylphosphinite anchored cellulose was prepared by the reaction of cellulose with diphenylchlorophosphine and then reflux with $PdCl_2$ in ethanol to form Pd particles.[30,31] But this process required a tediously long reaction time. Recently, Palladium nano-particles supported on ethylenediamine-anchored cellulose was used to catalyze Heck and Sonogashira couplings in water and slight decrease in activities was observed after four run cycles. In contrast, the use of immobilized Pd complexes through interaction with ligands functionalized cellulose backbone has not been fully exploited. Further efforts on more highly efficient and successful approaches of functionalization should be made to allow tailoring the surface of cellulose characteristics thereby improving catalytic activities.

With these considerations in mind, in this article, we present the anchoring of triphenylphosphine on cellulose backbone by covalent attachment followed by coordination with $Pd(OAc)_2$ to prepare a cellulose–palladium catalyst. Using the Suzuki–Miyaura coupling reaction as an example, we evaluated the efficiency of this environmentally friendly cellulose–palladium catalytic system.

EXPERIMENTAL

Materials

Avicell PH-101 (Microcrystalline cellulose, degree of polymerization = 180) was purchased from Shandong Liaocheng A Hua Pharmaceutical (Shandong Province, P. R. China). Anhydrous ethanol and CH_2Cl_2 were obtained from KRS Fine Chemical (Tianjin, P. R. China). Other reagents were of analytical grade and were supplied by Tianjin Guangfu Fine Chemical Research Institute (Tianjin, P. R. China). Cellulose, anhydrous lithium chloride, and potassium carbonate were dried under vacuum at 50°C, 40°C, and room temperature (RT) for 24 h, respectively, before use. Dimethylformamide (DMF), dimethylacetamide (DMAc), and CH_2Cl_2 were dried with CaH_2, distilled under reduced pressure and stored over molecular sieves. Other chemicals and reagents, unless otherwise stated, were simply

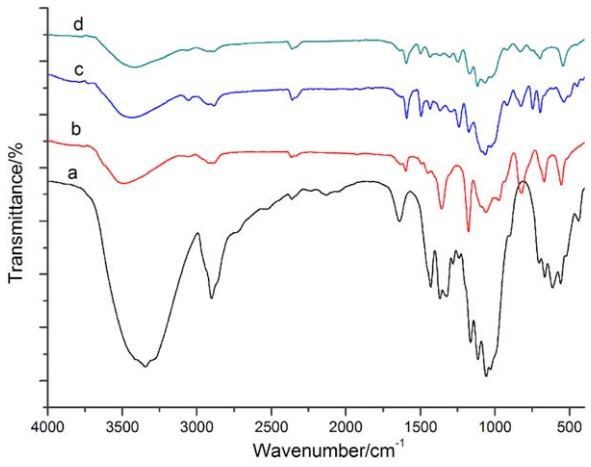


Figure 1. FTIR spectra of Cell (a), Cell-OTs (b), Cell-OPPh$_3$ (c), and Cell-OPPh$_3$-Pd (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

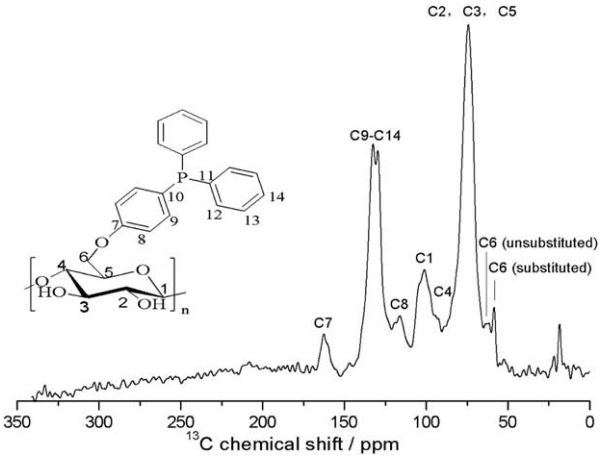


Figure 2. Solid-state CP/MAS ^{13}C-NMR spectra of Cell-OPPh$_3$.

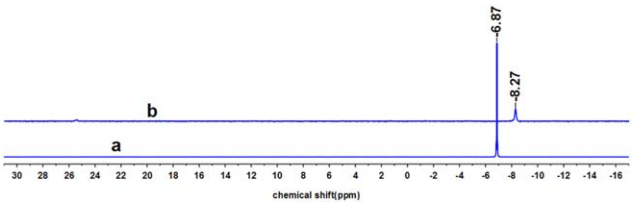


Figure 3. ^{31}P-NMR spectra of $Ph_2PPhOCH_3$ (a) and Cell-OPPh$_3$ (b) in DMSO-d_6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

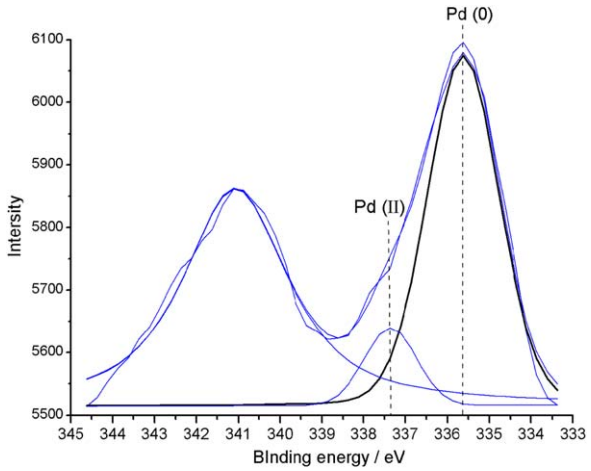


Figure 4. XPS spectrum of fresh Cell-OPPh$_3$-Pd catalyst, Pd 3d regions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

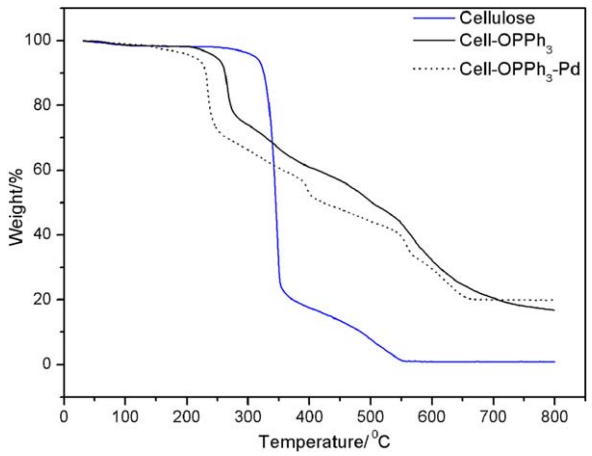


Figure 5. TGA spectra of Cellulose, Cell-OPPh$_3$, and Cell-OPPh$_3$-Pd under air condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

redistilled. 4-Anisyldiphenylphosphine (**1**, $Ph_2PPhOCH_3$)[32,33] and cellulose *p*-toluenesulfonate (Cell-OTs)[34] were prepared according to methods reported in the literature.

Analytical Methods

NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ or d_6-DMSO using TMS as an internal standard. Scanning electron microscopy (SEM) was performed

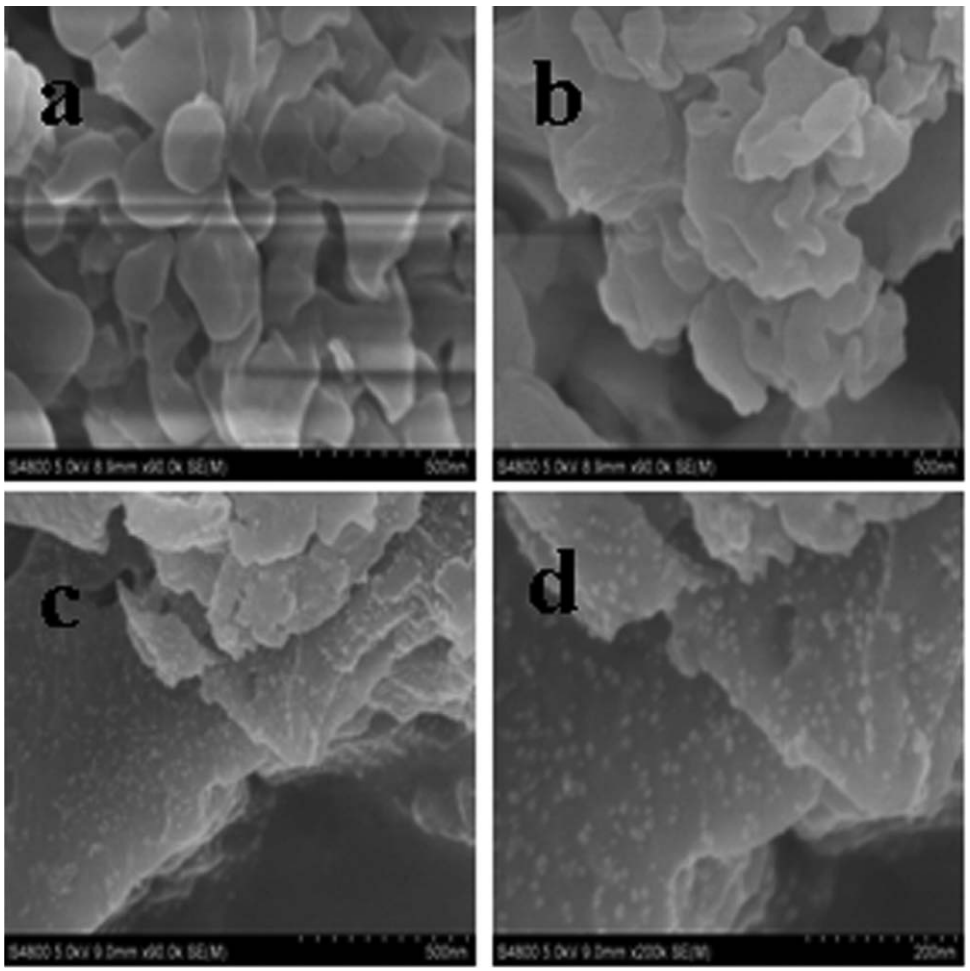


Figure 6. SEM images of the Cell-OTs (a), Cell-OPPh$_3$ (b), and Cell-OPPh$_3$-Pd (c and d).

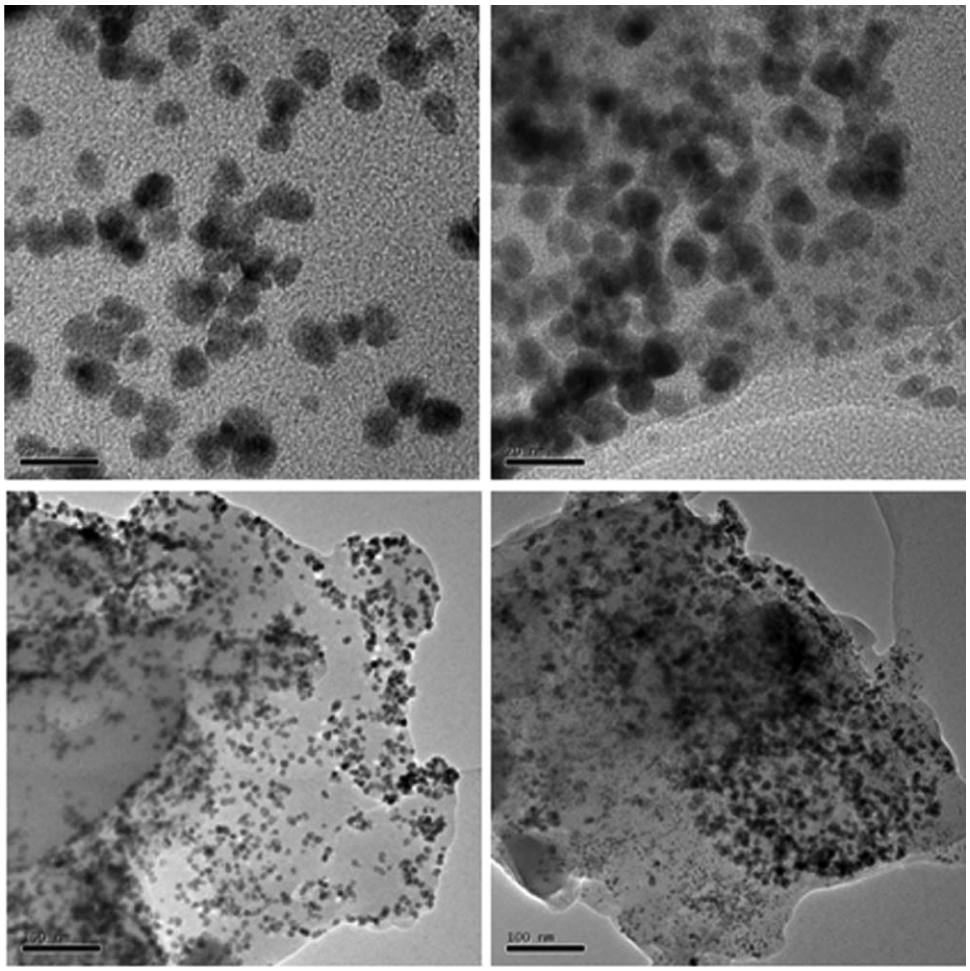


Figure 7. TEM images of fresh Cell-$OPPh_3$-Pd catalyst (left) and recovered catalyst (right).

with a Hitachi S-4800 instrument. The particle sizes of the samples were observed on a Tecnai G2 F20 transmission electron microscopy (TEM). The elemental contents of sulfur, phosphorus, and palladium were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash corporation, ICP-9000 (N+M) instrument. Thermogravimetric analysis (TGA) was measured with a STA 409 PC thermal analyzer (NETZSCH, Germany). X-ray photoelectron spectrometer (XPS) was conducted with a PHI1600 ESCA System (Perkin-Elmer). Fourier transform infrared spectroscopy (FTIR) analysis was performed on a BIO-RAD FTS3000 IR Spectrum Scanner. The CP/MAS ^{13}C-NMR measurement was performed at Varian Infinityplus-400MHz spectrometer. Preparative TLC (20 cm × 20 cm) was performed on Silica Gel 60 F254.

Preparation of 4-Hydroxyphenyldiphenylphosphine (2, Ph_2PPhOH)

$Ph_2PPhOCH_3$ (11.7 g, 40.0 mmol) was dissolved in 110 mL of distilled CH_2Cl_2 under a nitrogen atmosphere followed by addition of $AlCl_3$ (26.7 g, 200 mmol). After 2 days of refluxing, the mixture was filtered to remove the solid residue and slowly poured into a dilute HCl solution to consume residual $AlCl_3$. The solution was then extracted with ethyl acetate, washed with brine, and dried over Na_2SO_4. Evaporation of the solvent followed by silica gel chromatography (petroleum ether/ethyl acetate = 10 : 1) gave 6.06 g (55%) of **2** as a white solid (NMR characterization data shown in the Supporting Information).

Table I. Effect of Solvent on the Suzuki–Miyaura Cross-Coupling Reaction

Entry	Solvent	Time (h)	Yield[a] (%)
1	Toluene	3.5	4
2	DMSO	3.5	6
3	DMF	3.5	12
4	Dimethoxyethane	3.5	22
5	CH_3CN/H_2O (1 : 1)	3.5	7
6	2-Propanol	3.5	62
7	95% C_2H_5OH	3.5	62
8	C_2H_5OH	3.5	92

Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), Cell-$OPPh_3$-Pd (0.80 mol %), K_2CO_3 (1 mmol), solvent (5 mL), 80°C, in air.
[a] Yield determined by TLC analysis.

Table II. Effect of the Amount of Cell-$OPPh_3$-Pd Catalyst on the Cross-Coupling Reaction

Entry	Amount of catalyst (mol)	Time (h)	Yield[a] (%)
1	0.10%	3.5	12
2	0.26%	3.5	75
3	0.52%	3.5	82
4	0.80%	3.5	92
5	1.06%	3.5	93

Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), Cell-$OPPh_3$-Pd, K_2CO_3 (1 mmol), anhydrous EtOH (5 mL), 80°C, in air.
[a] Yield determined by TLC analysis.

Preparation of Cell-$OPPh_3$

To a 100 mL flask containing 26 mL of DMF was added Cell-OTs with degree of substitution (DS) of 0.25 (1.39 g, 6.93 mmol) under nitrogen atmosphere, and the solution was stirred at 80°C for 12 h followed by overnight stirring at room temperature to ensure complete dissolution of Cell-OTs. Ph_2PPhOH (2.23 g, 8.00 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) were then added to the solution under nitrogen and the mixture was stirred for 2 days at 80°C. After cooling to room temperature, the reaction mixture was filtered and slowly poured into a stirring diethyl ether solution. The precipitate was collected via centrifugation and washed sequentially with 95% ethanol, ethanol/water (8 : 2, v/v), water, and ethanol. The purified product was dried under vacuum at room temperature (0.70 g, Yield 46%) (^{31}P NMR spectrum data of Cell-OPPh3 can be seen in Supporting Information S2). The DS of Cell-$OPPh_3$ was 0.17 determined on the basis of phosphorus content as described previously.[34]

Preparation of Cell-$OPPh_3$-Pd

To a 50 mL flask containing 15 mL of toluene was added Cell-$OPPh_3$ (0.50 g, 2.27 mmol) and palladium acetate (0.13 g, 0.58 mmol) under nitrogen atmosphere. The reaction mixture was stirred at 56°C for 20 h. After cooling to room temperature, the mixture was stirred for another 10 h. The precipitate was filtered off and washed carefully with toluene, acetone, and diethyl ether. The collected solid product was vacuum dried at room temperature.

Synthesis of Compounds 3a-3r (Table V); General Procedure

A mixture of aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), and K_2CO_3 (1 mmol) was stirred in ethanol (5 mL) at 80°C in aerobic conditions for 1–4.5 h. After reaction completion, the mixture was extracted with ethyl acetate, washed with brine, and dried over anhydrous $MgSO_4$. The $MgSO_4$ was then filtered off. After removal of the solvent, the crude product was purified by preparative TLC (eluent: petroleum ether/ethyl acetate, 20 : 1) to give the product.

Table III. Effect of Base on the Cross-Coupling Reaction

Entry	Base	Time (h)	Yield[a] (%)
1	K_2CO_3	3.5	93
2	K_3PO_4	3.5	86
3	Cs_2CO_3	3.5	78
4	*t*-BuOK	3.5	75
5	Et_3N	3.5	8

Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.6 mmol), Cell-$OPPh_3$-Pd (0.80 mol %), base (1 mmol), anhydrous EtOH (5 mL), 80°C, in air.
[a] Yield determined by TLC analysis.

Table IV. Effect of Mole Ratio (Phenylboronic Acid/4-Bromoanisole) on the Cross-Coupling Reaction

Entry	Mole ratio (phenylboronic acid/ 4-bromoanisole)	Time (h)	Yield[a] (%)
1	1.0	3.5	83
2	1.2	3.5	91
3	1.5	3.5	94

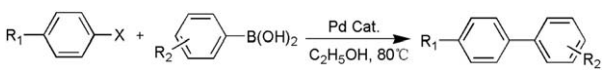
Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid, Cell-$OPPh_3$-Pd (0.80 mol %), K_2CO_3 (1 mmol), anhydrous EtOH (5 mL), 80°C, in air.
[a] Yield determined by TLC analysis.

RESULTS AND DISCUSSION

Synthesis and Characterization of Covalently Bonded Phosphine-Cellulose and Its Corresponding Palladium Complex

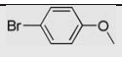
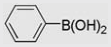
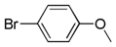
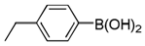
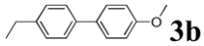
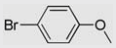
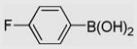
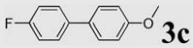
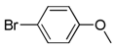
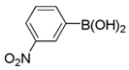
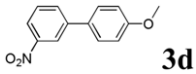
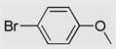
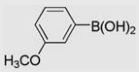
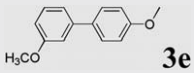
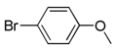
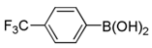
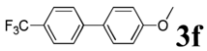
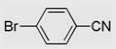
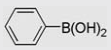
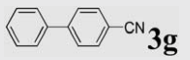
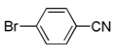
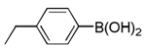
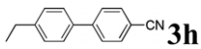
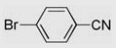
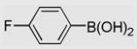
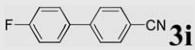
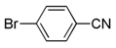
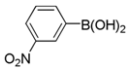
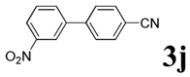
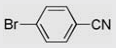
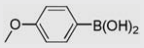
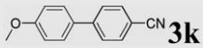
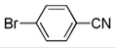
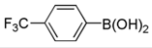
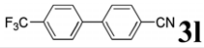
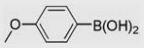
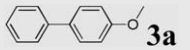
Cellulose-tagged triphenylphosphine (Cell-$OPPh_3$) was synthesized via nucleophilic substitution of Cell-OTs with 4-hydroxyphenyldiphenylphosphine (Ph_2PPhOH) (Scheme 1). First, Cell-OTs were obtained by converting the active hydroxyl groups of cellulose to tosylate groups by *p*-toluenesulfonyl chloride in a completely homogeneous DMAc/LiCl system. The efficiency of such a transformation has been demonstrated before.[34] The tosylates then acted as good leaving groups to allow the S_N2 reaction with Ph_2PPhOH as previously reported.[35,36] Compared with the route using the direct reaction of cellulose with diphenylchlorophosphine in pyridine,[30,31] which required a 5-day duration, our synthesis pathway using cellulose tosylate is much less time consuming. More importantly, the amount of palladium loaded in our final cellulose-supported triphenylphosphine palladium complex (Cell-$OPPh_3$-Pd) was 0.50 mmol/g as determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), which was much higher than that of Cell-$OPPh_2$-Pd catalyst (0.33 mmol/g) reported in previous literature[30] and commercial PS-PPh_3-Pd complex. This suggests a high metal coordination capacity of Cell-$OPPh_3$ as expected. It was attributed to strong electron donating ability of three benzene rings together with interactions between palladium and hydroxyl groups on the cellulose backbone.

The FTIR spectra of cellulose, cellulose derivatives Cell-OTs, Cell-$OPPh_3$, and Cell-$OPPh_3$-Pd are shown in Figure 1. The band at 1359 cm^{-1} and 1179 cm^{-1} corresponded to the υ_{as}(O═S) and υ_s(O═S) stretch of Cell-OTs, respectively, which were greatly



Scheme 2. Reaction of aryl halides with arylboronic acids.

Table V. The Coupling Reactions of Aryl Halides with Various Arylboronic Acids

Entry	Aryl halide	Arylboronic acid	Product	Time (h)	Yield[a] (%)
1			 **3a**	1	95
2			 **3b**	3	95
3			 **3c**	1	95
4			 **3d**	4	34
5			 **3e**	1	97
6			 **3f**	1.5	66
7			 **3g**	2	97
8			 **3h**	2	97
9			 **3i**	1.5	98
10			 **3j**	2.5	85
11			 **3k**	2	98
12			 **3l**	1.3	96
13			 **3a**	3	10
14			**3m**	2	85
15			**3n**	2	97
16			**3o**	4.5	10
17			**3p**	4.5	40
18			**3q**	4.5	4
19			**3r**	4.5	21

Reaction conditions: aryl halide (0.5 mmol), arylboronic acids (0.75 mmol), supported palladium catalyst (0.80 mol %), K_2CO_3 (1 mmol), anhydrous EtOH (5 mL), 80°C.
[a] Yield determined by TLC analysis.

weakened after substitution with Ph_2PPhOH as shown in Figure 1(b,c). Correspondingly, an absorption band at 1242 cm^{-1} recorded in Figure 1(c) was assigned to the new C—O bond of Cell-$OPPh_3$. In Figure 1(d) for Cell-$OPPh_3$-Pd, this band slightly shifted to higher wave number because of the chelation of palladium with the phosphorus atom. The success of grafting triphenylphosphine onto the cellulose backbone was also confirmed by CP/MAS ^{13}C-NMR and ^{31}P-NMR spectroscopy as indicated in Figures 2 and 3, respectively. However, the resonance observed at 18.4 ppm was attributed to CH_3 of Cell-OTs residue as shown in Figure 2. In addition, a peak was observed at chemical shift −8.27 ppm for Cell-$OPPh_3$ (Figure 3).

Table VI. Reusability of the Cell-$OPPh_3$-Pd in Suzuki Cross-Coupling Reaction

Recycle	First	Second	Third	Fourth
Time (h)	2.6	3	3	3
Yield (%)[a]	95	94	62	56

[a] Yield determined by TLC analysis.

XPS was used to investigate the valence state of the surface region of the fresh catalyst. As shown in Figure 4, the binding energies of $Pd3d_{5/2}$ in the cellulose–palladium catalyst are 335.6 and 337.4 eV, respectively, indicating the existence of two different chemical states of Pd (0) and Pd (II).[21]

Thermogravimetric analysis was performed to evaluate the stability of the cellulose-supported catalyst in air and high temperature, because the following Suzuki reaction requires heating in an aerobic condition. As shown in Figure 5, TGA of the catalyst system showed high thermal stability with decomposition at around 225°C in air. These results demonstrated that Cell-$OPPh_3$ support was considerably stable in an oxygen-containing atmosphere as a catalyst support in experimental conditions.

Surface Morphology of Cellulose After Modification

Surface morphology of the cellulose fibers was investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM results showed no obvious change of surface morphology between Cell-OTs and Cell-$OPPh_3$ [Figure 6(a,b)]. However, different morphology was observed on the surface of Cell-$OPPh_3$-Pd [Figure 6(c,d)], which showed evenly distributed small particles. Also, TEM images (Figure 7) revealed the presence of palladium nanoparticles of about 10 nm in size, which proved the excellent dispersion of palladium sites on the surface of cellulose.

Applications in Suzuki–Miyaura Coupling Reaction

Evaluation of Its Catalytic Activity. The Suzuki–Miyaura coupling reaction of 4-bromoanisole with phenylboronic acid was selected as a model reaction to evaluate our newly synthesized cellulose-supported catalyst. A wide variety of solvents, the amount of catalyst, the type of base, and the molar ratio of phenylboronic acid to 4-bromoanisole were screened (Tables I–IV).

Among the different solvents screened, alcohols were found to be the most favorable (Table I, entries 6–8), likely due to the solvent swelling effect on the cellulose matrix. Ethanol proved to be the best solvent. Results in Table II showed that the quantity of catalyst has an important effect on the reaction yield (Table II, entries 1–3). The yield increased with the increase of the amount of catalyst. However, no drastic improvement of the yield was observed when the amount of catalyst increased from 0.80 to 1.06 mol %. Therefore, 0.80 mol % of the catalyst (Table II, entry 4) was considered sufficient to catalyze the reaction.

To explore the influence of the base, we examined both organic and inorganic alkalis. Results indicated that the inorganic alkalis have a better catalytic effect than the organic alkalis. Among the screened bases, K_2CO_3 proved to be the best (Table III, entry 1) and thus, was the base of choice. Finally, we investigated the effect of the molar ratio between phenylboronic acid and 4-bromoanisole. The yield increased when the molar ratio increased with the highest yield obtained at a molar ratio of 1.5 (Table IV).

Overall, these screening studies have led us to conclude that the optimized reaction conditions should be: phenylboronic acid (0.75 mmol), 4-bromoanisole (0.50 mmol), catalyst (0.80 mol %), and K_2CO_3 (1.00 mmol) in anhydrous EtOH (5.00 mL) at 80°C under aerobic conditions.

Under the optimal conditions, various aryl halides and arylboronic acid derivatives were examined (Scheme 2) to evaluate the scope of the reaction and the results were summarized in Table V. The cellulose-supported catalyst was effective toward most of the substrates (Characterization data were shown in the Supporting Information). When aryl bromides were used, both electron-rich (Table V, entries 1, 2, 3 and 5) and electron-deficient substrates (entries 7–12) reacting with various arylboronic acids proceeded well and gave the corresponding products with high yields. An exception was observed for arylboronic acids substituted with strong electron-withdrawing groups (entries 4 and 6). As expected, the reactivity of aryl chloride was lower than that of the corresponding aryl bromides and iodides (Table V, entries 13–15). However, the reaction between aryl bromides and heterocyclic boronic acids was sluggish and gave only small amounts of products even under prolonged reaction times (entries 16–19).

Separation of the Catalyst and Recycling Tests. After completion of the Suzuki–Miyaura reaction, the liquid phase was removed by centrifugation. The solid catalyst was simply recovered by filtration and washing. Without drying, the recovered catalyst was directly used in next reaction with new portions of reactants. As shown in Table VI, the catalytic activity stayed constant after two successive uses (95% and 94%) while it decreased greatly after the third usage (62%). We have also examined the catalytic activity of the solid catalyst recovered by washing and drying. The same results were obtained as above. The total amount of palladium leaching after the third cycle was 12% as detected by ICP-AES analysis (the amount of palladium is 3.74% before reaction and 3.28% after three cycles). Therefore, the decrease of catalytic activity may be the result of the aggregation of palladium nanoparticles as shown in TEM images of the recovered catalysts.[37–39]

CONCLUSIONS

Cellulose-tagged triphenylphosphine was synthesized by the nucleophilic reaction of 4-hydroxyphenyldiphenylphosphine with cellulose tosylate. The cellulose-based triphenylphosphine ligand was then coordinated with $Pd(OAc)_2$ in toluene to give the final cellulose-supported triphenylphosphine palladium complex. The catalyst's efficiency in the Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids was evaluated. Most of the cross-coupling reactions gave excellent yields, with a few exceptions: arylboronic acids containing strong electron-withdrawing groups and heterocyclic boronic acids. Further applications of cellulose-based triphenylphosphine in other organic reactions are currently being investigated in our laboratory.

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AUTHOR CONTRIBUTIONS

Xiaoxia Wang performed the experiments, analyzed the data and wrote the manuscript; Yanjun Xu helped perform the

experiments and analyze the data; Fang Wang contributed analysis tools; Yuping Wei conceived and designed the experiments.

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