Metal–organic gels as functionalisable supports for catalysis†

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Modification of Fe-tricarboxylate based metal–organic gels yielded *tert*-butyl substituted or phosphine-functionalised gels in alcohols or DMF, which were prepared from 5-*tert*-butylisophthalic acid and 5-diphenylphosphanylisophthalic acid, respectively. Owing to their permeability, such phosphine-functionalised metal–organic gels can act as a new type of functionalisable porous scaffold. The phosphorus-containing gel was subsequently functionalised with Pd(II) by immersion in a solution of Pd(COD)Cl_2 (COD = 1,5-cyclooctadiene). The subsequently functionalised Pd(II)-immobilised gel and its xerogel/aerogel showed high activity in the catalysis of Suzuki C–C coupling comparable to unsupported complexes. The gel/xerogels could be reused under ambient atmosphere.

Introduction

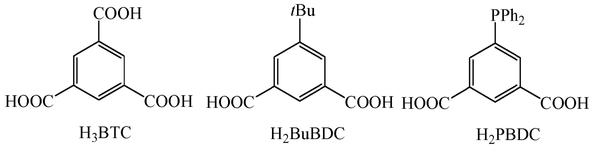
Solid-supported metal catalysts have been actively studied in recent years,[1] and various methods have been developed to synthesise them.[2] Networked structures studied in this regard include zeolites, organic polymers and coordination polymers.[2,3] Supramolecular gels are viscoelastic solid-like materials comprised of a 3D interconnected network which contain a large amount of solvent, usually up to 97%, making them highly permeable. Supramolecular gels are normally formed through solvophobic effects, hydrogen bonding, coordination bonding, van der Waals attraction *etc.*, sometimes by highly organized self-assembly.[4] They behave like soft solids and are of interest for applications in food, cosmetics, medicine, controlled release, optoelectronics, and so on. Although gels could also have some desirable characteristics for heterogeneous catalysis, such as rapid mass transfer or permeability, high surface areas, easy removal, and so on, gels have received limited attention in this area.[5,6] Notably, gels functionalised with free ligand sites which can subsequently be metallated to generate catalytic centres have been rarely described so far.[4i,5a]

Phosphines are widely used in transition metal homogeneous catalysis,[7] for example, palladium catalysed C–C coupling.[8] Palladium complexes bearing phosphines, able to stabilise Pd(0) intermediates, have been found to be particularly active in cross-coupling reactions.[9] However, phosphine-based gels are almost unknown. There are two strategies to synthesise phosphorus-functionalised metallogels. The first is self-assembly through coordination of the phosphines themselves to metal cations. In such a strategy, metal ions interconnect the phosphine ligands to form a 3D gel network. Reported examples include a Ag(I) gel[10] and a Pd(II) gel.[11] The second strategy requires synthesis of a gel network, functionalised with free phosphine groups which are available for coordination. It could then be post-modified with a variety of transition metal ions. Owing to the importance of phosphines in catalysis, this strategy may offer a versatile entry into transition metal gel catalysts.

Although a large number of gels have been discovered in the last decade, phosphine-functionalised gels remain unknown to our knowledge. Herein we show that a previously known coordination polymer gel system can be functionalised with free phosphine groups, further metallated with palladium(II) centres, and employed for catalytic use.

Results and discussion

Metal–organic gels (MOGs) have been shown to be conveniently prepared by mixing solutions of benzene-tricarboxylic acid (H_3BTC, Scheme 1) and $Fe(NO_3)_3$.[12] These gel networks are believed to be connected *via* Fe-carboxylate coordination bonds to form a 3D matrix. Polymeric chains might also form if one of the carboxylate groups were replaced by a different functional group. 5-*tert*-butylisophthalic acid (H_2BuBDC), a dicarboxylic acid, is thus a possible substitute for H_3BTC (although introduction of hydrophobic groups can potentially also affect the formation of gel networks[13]). The phosphine-functionalised diacid, 5-diphenylphosphanylisophthalic acid



Scheme 1

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(H_2PBDC)[14] can be considered similarly. The phosphine group should not interfere with the Fe-carboxylate network due to poor HSAB matching.[15]

Gelation study

Gelation tests were performed by mixing solutions of $Fe(NO_3)_3$ and H_2BuBDC or H_2PBDC at RT. The gelation ability was evaluated in various solvents. Gel formation is confirmed if the sample does not flow when the test tube is inverted. Both H_2BuBDC and H_2PBDC displayed gelation abilities when reacting with ferrous nitrate (Table 1). Turbid orange–brown gels were obtained when $Fe(NO_3)_3$ solution (0.50 mmol, 5 ml) and H_2BuBDC solution (0.50 mmol, 5 ml) were mixed together. The gels were formed in MeOH (GBu1), EtOH (GBu2) or DMF (GBu3) after 1 min, 2–3 h, 3–5 days, respectively. When THF solutions of $Fe(NO_3)_3$ and H_2BuBDC were mixed together, a precipitate formed immediately, which subsequently formed a gel (GBu4) after 12–24 h. Similar orange–brown gels were also formed when H_2PBDC was used in place of H_2BuBDC. The gels were able to form in a series of solvents, including EtOH (GP1), *n*-BuOH (GP2) and DMF (GP3) after 3–5 days, 3–5 days or 15 days, respectively (Fig. 1). Generally the gelation with H_2PBDC is slower than with H_2BuBDC, and the gelation in DMF is slower than in alcohols.

FT-IR spectra confirmed the presence of carboxylate in the metal coordination sphere (Table 2). The bands due to the coordinated carboxylates are shifted to lower frequencies with respect to the free ligands. The absorption bands characteristic of the carboxylate ligands in the wet gels appear generally around 1651–1624 cm^{-1} for the asymmetric $\nu_{asym}(CO_2)$ vibration and the bands for the symmetric stretch overlap with bands due to the solvents. For the xerogels, strong bands at around 1384 and 1120 cm^{-1} are due to NO_3^- and P–Ar, respectively. The difference between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ of around 180 cm^{-1} suggests that the carboxylate ligands are chelating-bridging.[16] For the xerogels lower P=O stretching frequencies were found at around 1160 cm^{-1}, compared with P=O absorption at around 1176 cm^{-1} due to oxidized H_2PBDC,[17] indicating that some coordinated P=O groups were present.[18] The phosphine may be partially oxidised during formation of these xerogels, which is possibly catalysed by Fe(III).[19] The partial oxidation was also confirmed by MS. However, the P=O presence in the gels could not be proved due to overlapping. The X-ray photoelectron spectroscopy (XPS) analysis exhibited the presence of Fe and P in the xerogel of GP1. A signal at 711.2 eV in the Fe $2p_{3/2}$ region and a signal at 132.5 eV in the P 2p region were evident in the spectrum.

Table 1 Gelation ability in various solvents (1 + 1 ml) for $Fe(NO_3)_3$ (0.05 mmol) and 5-*tert*-butylisophthalic acid/5-diphenylphosphanylisophthalic acid (0.05 mmol)

Solvent	Result[a]	Time	Solvent	Result[a]
5-*tert*-Butylisophthalic acid (H_2BuBDC)				
MeOH	G (GBu1)	1 min	H_2O	P
EtOH	G (GBu2)	2–3 h	CH_3CN	P
DMF	G (GBu3)	3–5 days	DMSO	P
THF	G (GBu4) + P	12–24 h	$HOCH_2CH_2OH$	S
n-BuOH	Weak G	3–5 days		
5-Diphenylphosphanylisophthalic acid (H_2PBDC)				
EtOH	G (GP1)	3–5 days	MeOH	S
n-BuOH	G (GP2)	3–5 days	DMSO	S
DMF	G (GP3)	15 days	DMA	S

[a] S: solution; G: gel; P: precipitate.

Fig. 1 Metal–organic gels formed from solutions of H_2PBDC and $Fe(NO_3)_3$ in ethanol (GP1), left, and *n*-butanol (GP2), right.

Table 2 Comparison of $\Delta\nu$ for the gels/xerogels[a]

	$\nu(OH)/cm^{-1}$	$\nu_{asym}(CO_2)/cm^{-1}$	$\nu_{sym}(CO_2)/cm^{-1}$	$\Delta\nu/cm^{-1}$
H_2PBDC	3413	1635	1432	203
gP1	3427	1616	1432	184
gP2	3413	1614	1434	180
gP3	3428	1610	1437	173
gP1-Pd	3387	1610	1437	173

[a] The xerogels of GP1, GP2, GP3 are referred as gP1, gP2, gP3, respectively.

Gels are generally understood to comprise one-dimensional (1-D) fibrous aggregates,[4,20] which cross-link into 3-D networks, with few exceptions.[11,21] SEM was used to examine the morphology of the xerogels of H_2BuBDC and H_2PBDC (Fig. 2). All the gels have similar globular or block-like morphologies, with characteristic features of 2–10 μm, rather than the more common fibrillar morphologies of gel-phase materials. Such morphologies can be expected however from the random 3-D growth of coordination polymer particles.

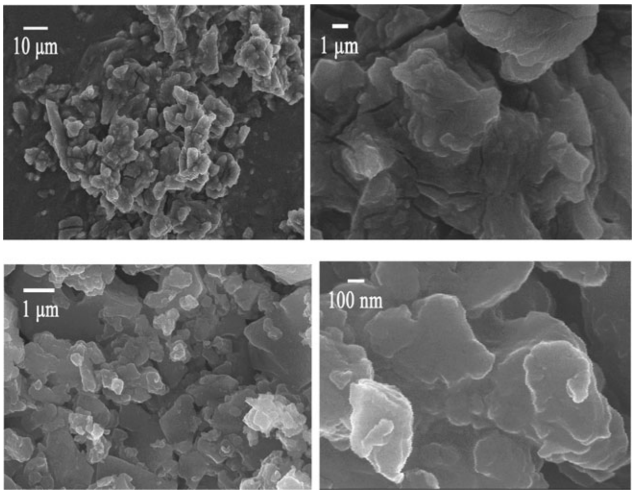


Fig. 2 SEM images of xerogels of GBu2 (top two), and GP2 (bottom two), prepared by slow evaporation of wet gels in air.

The X-ray diffraction diagrams for gels GP1–GP3, and their xerogels confirmed such random growth, showing only an amorphous halo (broad "hump").

The above results with H_2BuBDC/H_2PBDC confirm that gels can form by self assembly of Fe^{3+} with functionalised dicarboxylic acids. Some gels spontaneously fragmented on standing and all were found to fragment if shaken vigorously, suggesting a rigid rather than flexible structure. The gels were not observed to redissolve upon heating, *i.e.* they are thermally irreversible.

Postmodification of metal–organic gel

The phosphine gel is of interest for catalytic studies. The phosphorus centres should be dispersed throughout the whole gel medium, and accessible to molecular reactants. A Pd(II)-functionalised gel was prepared by placing an acetonitrile solution containing excess $Pd(COD)Cl_2$ in on top of the phosphine gel. After diffusion for *ca.* 10 days, the supernatant was decanted and the gel was washed several times with acetonitrile until the washings were colourless. The FT-IR spectrum of the Pd-loaded gel (GP1-Pd) generally displays similar bands to that of GP1 in addition to bands of included acetonitrile. The XPS surface analysis of GP1-Pd confirmed the presence of Fe, P, Pd and Cl in the xerogel of GP1-Pd. The spectrum showed a signal at 711.4 eV in the Fe $2p_{3/2}$ region and a signal at 132.3 eV in the P 2p region. Analysis in the Pd $3d_{5/2}$ region showed a signal at 337.8 eV and a signal at 198.7 eV in the Cl 2p region, confirming attachment of the Pd atoms to the gel network. The P/Pd/Cl ratio was calculated to be about 1 : 1 : 2. The weight percentage of Pd atoms in the GP1-Pd xerogel was determined to be 1.0% by inductively coupled plasma (ICP) spectroscopic analysis. Compared with that in the Fe-BTC gel[12] without phosphorus (0.05%), a much higher content of Pd has been loaded in GP1.

To obtain its more precise microstructure, the gel GP1-Pd was dried by supercritical CO_2 extraction so that the solvent in the network of the gel was removed and an aerogel was formed. The XRD pattern showed that the aerogel was amorphous. The SEM images show that the aerogel was composed of interconnected macroporous networks of globular or block-like nanometer-sized particles of diameter *ca.* 100–300 nm (Fig. 3). The microstructure is similar to the xerogels without loading of Pd, although the component particles are significantly smaller. An adsorption isotherm of the solid was performed using N_2 gas as the adsorbate at liquid nitrogen temperature. BET analyses show that the solid, which was dried in vacuum for 20 h at RT before analysis, exhibits a N_2-physisorption isotherm of type III, indicative of macroporous solids (Fig. 4).[22] No hysteresis is observed between the desorption and adsorption isotherms of the aerogel, indicating that there is little irreversible interaction between N_2 and the pores. The BET surface area is 22.1 $m^2\ g^{-1}$ and total pore volume is 0.074 mL g^{-1}. The low BET surface area of the aerogel may result from the closure of micropores in the drying process. The results of the adsorption isotherm are consistent with SEM microscopy. The aerogel may thus exhibit a colloidal microstructure rather than a polymeric one.[23]

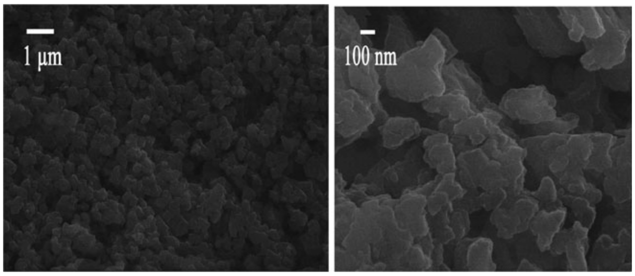


Fig. 3 SEM images of the GP1-Pd supercritical aerogel.

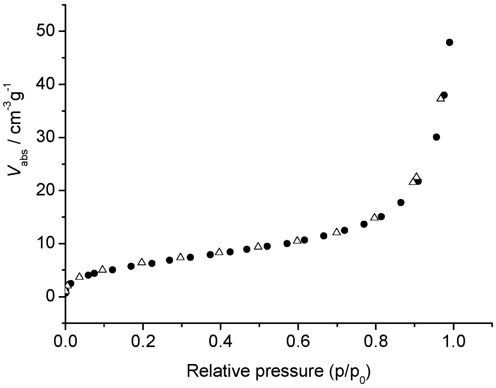


Fig. 4 N_2 adsorption–desorption isotherm of GP1-Pd (circle, adsorption; triangle, desorption).

The thermostability of the GP1-Pd aerogel was studied by thermogravimetric analyses (TGA) as depicted in Fig. 5. The TG curve exhibits two types of weight losses from RT to 600 °C. The weight losses of 7.3 and 6.9% in the temperature range of RT–140 and 140–240 °C, respectively, are attributed to the loss of water and organics absorbed on the particle surface and those physisorbed and chemisorbed in the pores. The coordination network may be anticipated to collapse from 240 to 590 °C shown by the weight loss of 52.9%.

Catalytic activity

GP1-Pd was found to be an active catalyst for the Suzuki C–C cross-coupling of aryl halides/bromopyridines with arylboronic acids. Catalytic reactions were performed under slow stirring with the gel catalyst packed in a filter paper bag to avoid mechanical degradation, and the results are given in Table 3 and 4. The reaction of iodobenzene with phenylboronic acid

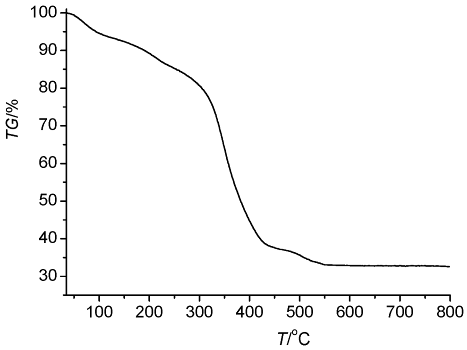
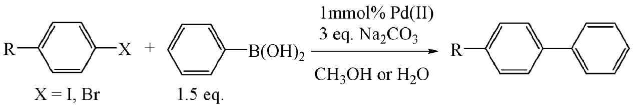


Fig. 5 TG curve for the GP1-Pd aerogel.

Table 3 Suzuki cross-coupling of aryl halides with phenylboronic acid catalysed by gel GP1-Pd[a]



Entry	X, R	T/°C	Solvent	Yield[b] (%) (t/h)
1	X = I, R = H	60	MeOH	99 (0.5), 100 (1.0)
2	X = I, R = H	60	H_2O	39 (0.5), 51 (1.0), 66 (1.5), 81 (2.0)
3	X = I, R = H	RT	MeOH	69 (0.5), 74 (1.0), 82 (2.0), 91 (3.0), 98 (3.5)
4	X = Br, R = H	60	MeOH	71 (0.5), 74 (3.0)
5	X = Br, R = OMe	60	MeOH	26 (0.5), 35 (1.0), 39 (3.0)
6	X = Br, R = COMe	60	MeOH	97 (0.5), 99 (1.0)

[a] *Reaction conditions*: 0.67 mmol of aryl halide, 1.5 mol equiv. of $PhB(OH)_2$, 0.2 mmol% of Pd(II) of the catalyst, 3 mol equiv. of Na_2CO_3, in 8 ml of CH_3OH or H_2O under air. [b] GC yield.

Table 4 Suzuki cross-coupling of bromopyridines with boronic acids catalysed by gel GP1-Pd in methanol at 60 °C[a]

Entry	Ar′X	$ArB(OH)_2$	Yield[a] (%) (t/h)
1	4-Bromopyridine	3,5-Difluorophenylboronic acid	68 (0.5), 87 (1.0), 92 (1.5), 95 (2.0)
2	4-Bromopyridine	Phenylboronic acid	79 (0.25), 98 (0.5), >99 (1.0)
3	3-Bromopyridine	3,5-Difluorophenylboronic acid	38 (0.5), 42 (1.0), 53 (2.0), 71 (3.0)
4	2-Bromopyridine	3,5-Difluorophenylboronic acid	32 (0.5), 35 (1.0), 52 (2.0), 53(3.0)

[a] Determined by GC.

(1.5 mol equiv.) in the presence of 0.2 mmol% of Pd(II) of GP1-Pd under air, proceeded efficiently in methanol to give biphenyl in 99% yield at 60 °C after 0.5 h, and in 98% yield at RT after 3.5 h, while use of water as solvent at 60 °C also gave a good yield (81%) after 2.0 h. As expected, bromobenzene was less reactive, and its coupling with phenylboronic acid gave a yield of 74% at 60 °C after 3.0 h in methanol, while a relatively modest yield (39%) was achieved in the coupling between phenylboronic acid and 4-bromoanisole, a deactivated electron-rich aryl bromide, and the use of 4-bromoacetophenone, an activated electron-poor one, resulted in a near quantitative yield after 1.0 h. The catalyst is also effective towards the coupling of bromopyridines with boronic acids. 4-Bromopyridine could be coupled with phenylboronic acid easily giving near-quantitative yields after 1.0 h. The coupling of different isomers of bromopyridine with 3,5-difluorophenylboronic acid gave 4-(3,5-difluorophenyl)-anisole, 3-(3,5-difluorophenyl)anisole and 2-(3,5-difluorophenyl)anisole in 95% (after 2.0 h), 71% (3.0 h) and 53% (3.0 h) yield, respectively.

As control experiments, we examined the catalytic activity of $Pd(COD)Cl_2$ towards iodobenzene, and the yield of biphenyl at 60 °C was 97% after 0.5 h in the presence of 1 mmol% of Pd(II). A yield of 26% was obtained from the reaction of 4-bromoanisole and phenylboronic acid after 3.0 h. The coupling of 4-bromopyridine with phenylboronic acid gave 4-phenylpyridine in 55% yield after 0.5 h, and 70% after 1.0 h. Comparison of the results of GP1-Pd and $Pd(COD)Cl_2$ shows that the gel has higher catalytic activity than the unsupported homogeneous catalyst.

The xerogel, obtained after the solvent in GP1-Pd was allowed to evaporate slowly in air at RT, was also examined for its activity. The reaction of iodobenzene with phenylboronic acid (1.5 mol equiv.) in the presence of 0.2 mmol% of Pd(II) of the xerogel (without filter paper bag) under air at 60 °C gave biphenyl in 88% yield after 0.5 h, and in 93% yield after 1.0 h. When the xerogel was subjected to the reaction of 4-bromopyridine with 3,5-difluorophenylboronic acid under similar conditions, 4-(3,5-difluorophenyl)anisole was obtained in 32% (after 0.25 h), 58% (0.5 h), 70% (1.0 h), 78% (1.5 h), 81% (2.0 h) and 87% (2.5 h) yield. These results indicate that the xerogel showed poorer catalytic activity than the GP1-Pd gel.

The catalytic activity of the supercritical aerogel was also studied (Table 5, entry 1). The aerogel exhibited slightly lower activity than the wet gel (36% *vs.* 40% after 1.0 h) in the reaction of bromobenzene with phenylboronic acid. The aerogel was observed to show increasing activity at higher temperature (153 °C) in refluxing DMF. Higher yields was obtained, 58% after 20 min and 62% after 0.5 h for the reaction of 4-bromoanisole and phenylboronic acid, and >98% within 0.5 h for the coupling of 3,5-difluorophenylboronic acid and 3- or 4-bromopyridine.

Table 5 Suzuki cross-coupling of bromobenzene with phenylboronic acid using GP1-Pd and the aerogel as recovered catalysts[a]

Entry	Run	Yield[b] (%) (Cat.: wet gel)	Yield[b] (%) (Cat.: aerogel)
1	1st	40	36
2	2nd	20	13
3	3rd	9	2

[a] 0.5 mmol of bromobenzene, 0.75 mmol of $PhB(OH)_2$, 1.5 mmol of Na_2CO_3, 0.2 mmol% of Pd(II) of wet gel/aerogel in a filter paper bag, in 6 mL of methanol (60 °C) under ambient atmosphere for 1 h. [b] Determined by GC.

Encouraged by the good catalytic activity of GP1-Pd, we examined its recyclability in the reaction of bromobenzene/bromopyridine with phenylboronic acid. The gels/xerogels/aerogels packed in filter bags were readily separated after catalysis. In the reactions of aryl halides, the recovered catalyst could be subjected to the next reactions after the first reaction. There was no leaching into solution observed for the xerogels, while a small amount of leaching was observed for the gels/aerogels. Palladium black was observed within the filter paper bags, and the catalytic activity of wet gel/aerogel was diminished in the following reuse, as shown in the reaction of bromobenzene with phenylboronic acid (Table 5).

It is noteworthy, however, that no palladium black was visually seen in the reactions of bromopyridines with boronic acids. The gel or xerogel maintains its catalytic activity under similar conditions after five reuses at least, as shown in the reaction of 4-bromopyridine with 3,5-difluorophenylboronic acid (Table 6). The reactions in the 1st and 5th cycled run gave 4-(3,5-difluorophenyl)anisole in 85% and 80% yield, respectively, catalysed by the wet gel, and in 41 and 55% yield, respectively, catalysed by the xerogel. In addition, the results show again that the xerogel has poorer catalytic activity than the GP1-Pd gel under similar conditions.

Conclusions

In conclusion, we have demonstrated that a known Fe–H_3BTC gel system can be readily modified to give new phosphine-functionalised gels. These are novel metal–organic gels with free phosphorus donors[24] available for further coordination. The subsequently functionalised Pd(II)-immobilised gel and its xerogel/aerogel showed high activity in the catalysis of Suzuki C–C coupling comparable to unsupported complexes. The gel/xerogel could be reused in the reactions of bromopyridines under ambient atmosphere as shown in the reaction of 4-bromopyridine with 3,5-difluorophenylboronic acid. These show that metal–organic gels can act as a new type of functionalisable porous scaffold despite their potential complexity in some aspects, for example, sensitivity to mechanical stress, which however may be overcome by specific postmodification.[25] Due to the large range of metal ions and organic ligands available, metal–organic gels have much further chemistry to explore. MOG-supported catalysts may have tailored properties compared with conventional organic polymer supports, or silica/alumina supports, which are usually prepared by sol–gel processes.[23,26] Such gel networks may also be further readily modified by loading with other metals, such as Pt, Rh, Ir and so on. It would also be interesting to explore combining the catalytic abilities of both the supporting and supported metal ions. Studies along these lines are currently in progress in our lab.

Table 6 Suzuki cross-coupling of 4-bromopyridine with 3,5-difluorophenylboronic acid using recovered GP1-Pd as catalyst[a]

Entry	Run	Yield[b] (%) (Cat.: wet gel)	Yield[b] (%) (Cat.: xerogel)
1	1st	85	41
2	2nd	83	43
3	3rd	80	45
4	4th	82	49
5	5th	80	55[c]

[a] 0.5 mmol of 4-bromopyridine hydrochloride, 0.55 mmol of 3,5-difluorophenylboronic acid, 2.0 mmol of Na_2CO_3, 0.2 mmol% of Pd(II) of wet gel/xerogel in a filter paper bag, in 6 mL methanol (60 °C) under ambient atmosphere for 1 h. [b] Determined by GC. [c] The yield increased due to catalyst's smaller size.

Experimental

All starting materials and solvents were obtained from commercial sources and used without further purification. 5-Diphenylphosphanylisophthalic acid was synthesised following the literature method.[14] Infrared spectra were measured on a Nicolet Avatar 330 FT-IR spectrometer with KBr pellets except that those of gels were measured with liquid film on KBr plates. Scanning electron micrographs were recorded by using a Jeol JSM-6330F instrument. Gel samples were evaporated slowly to dryness in air, dried in vacuum, and applied to aluminium stubs. Prior to examination the gels were coated with a thin layer of gold. X-Ray photoelectron spectroscopy was measured on a Thermo-VG Scientific ESCALAB 250 spectrometer, under a pressure of $\sim 2 \times 10^{-9}$ mbar, fitted with X-ray monochromated Al-Kα radiation (photo-energy = 1486.6 eV, 15 kV, 150 W, spot size = 500 μm). Pd elemental analyses were performed by inductively coupled plasma–atomic emission spectroscopy using a TJA IRIS HR ICP instrument.

Synthesis of metal–organic gels

(a) $Fe(NO_3)_3$ (303 mg, 0.75 mmol) and 5-*tert*-butylisophthalic acid (111 mg, 0.50 mmol) were each dissolved in ethanol (5 ml each), and the two solutions were rapidly mixed together, then left to stand. An turbid orange gel (GBu2) was formed after 1 min. Similar gels were also obtained in MeOH or DMF.

(b) 5-Diphenylphosphanylisophthalic acid (0.05 mmol) and $Fe(NO_3)_3$ (0.05 mmol) in ethanol (1 ml each) were mixed together, and then left to stand. An turbid orange gel (GP1) was formed after 3–5 days. Similar gels were obtained in *n*-BuOH or DMF.

Post-modification of metal–organic gel

An acetonitrile solution containing an excess of Pd(COD)Cl_2 was allowed to stand above a sample of gel GP1. After slow diffusion for *ca.* 10 days, the supernatant was decanted and the gel was washed several times with acetonitrile until the washings were colourless, yielding a gel, GP1-Pd.

Formation of aerogel

The wet gel GP1-Pd was extracted with liquid CO_2 (*ca.* 270 g) in a supercritical high pressure Soxhlet extractor (0.75 L) for 3 h to remove solvent from the gel. The extraction temperature were kept at 35.0 °C. When the autoclave was depressurized slowly for 1 h, a supercritical aerogel was obtained.

General procedure for the coupling reactions of aryl halides with boronic acids catalysed by gel/xerogel

A typical procedure is given for the reaction shown in entry 1 of Table 3. Iodobenzene (136.7 mg, 0.67 mmol), phenylboronic acid (121.9 mg, 1.0 mmol), Na_2CO_3 (212.0 mg, 2.0 mmol), MeOH (8 ml) and GP1-Pd (0.2 mmol% of Pd(II)) were introduced to a flask under ambient atmosphere. The mixture was slowly stirred at 60 °C. H_2O (10 ml) was added into the resultant mixture and extracted three times with Et_2O (10 ml). The ethereal extract was evaporated to dryness and analyzed by GC/MS and NMR spectroscopy. For recovering, the gel was packed in a filter paper bag, and the xerogel/aerogel was either centrifuged after reaction or packed in a filter paper bag.

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