Electronic Supporting Information

Highly selective Suzuki reaction catalysed by a molecular Pd-P-MOF catalyst under mild conditions: role of ligands and palladium speciation Daniele Cartagenova,^a Stephan Bachmann,^b Kurt Püntener,^b Michelangelo Scalone,^b Mark A. Newton,^c Fabio A. Peixoto Esteves,^a Thomas Rohrbach,^a Patrik P. Zimmermann,^a Jeroen A. van Bokhoven,^{a,c} Marco Ranocchiari^{*a}

^a Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institut, Forschungsstrasse 111,

5232 Villigen PSI, Switzerland.

^b Pharmaceutical Division, Synthetic Molecules Technical Development, Department of Process Chemistry and Catalysis, F. Hoffmann-La Roche Ltd, Grenzacherstrasse 124, 4070 Basel, Switzerland.

^c Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1-5, 8093 Zurich, Switzerland.

*E-mail: marco.ranocchiari@psi.ch

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Experimental

All chemicals and solvents were purchased from commercial suppliers, and used as received unless otherwise specified. Toluene was dried on activated 4 Å molecular sieves. All the liquids used in phosphine-containing reactions were degassed by bubbling argon through them.

Preparative chromatographic purification was performed with a Teledyne ISCO CombiFlash chromatography system, equipped with RediSep silica columns unless otherwise specified.

Characterization techniques

Powder X-ray diffraction (PXRD) measurements were conducted on a Bruker D8 Advance diffractometer working in Bragg-Brentano geometry, with Cu K α_1 radiation wavelength of 1.541 Å. Diffraction was measured in the 20 range between 2° and 25°.

Nitrogen sorption measurements were conducted on a Micromeritics 3Flex Physisorption instrument at 77 K, after activating at 120 °C under vacuum for 16-20 hours. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method by fitting the isotherms in the 0.01 to 0.1 p/p₀ range to meet the consistency criteria described by Gómez-Gualdrón *et al.*¹

For the scanning transmission electron microscopy (STEM) investigation, the solid materials were deposited onto a perforated carbon foil supported on a copper grid. The investigations were performed on an aberration-corrected, dedicated STEM microscope, a HD-2700CS (Hitachi), operated at an acceleration potential of 200 kV (cold field emitter). A probe corrector (CEOS) that is incorporated in the microscope column between the condenser lens and the probe-forming objective lens provides a resolution of about 0.1 nm. Images were obtained with a high-angle annular dark field (HAADF) detector which measures incoherently scattered electrons resulting in a local intensity strongly increasing with the atomic number (Z-contrast). Furthermore, a secondary electron detector is installed inside the column of the HD-2700CS microscope allowing one to study the sample morphology as well. The images (1024 × 1024 pixels) were recorded with frame times between 15 and 30 s. Analytical investigations were done with an energy-dispersive X-ray spectrometer (EDXS, EDAX) attached to the microscope column.

GC was measured on an Agilent 6890 instrument equipped with a DB-1 column and a Flame Ionization Detector (FID). The concentration of 3-bromoanisole (2), 3-methoxy-1,1'-biphenyl (4) and anisole (5) was calibrated using cyclooctane as internal standard. UPLC-MS experiments were performed on a Waters Acquity UPLC H-Class system equipped with a Waters BEH C18 (1.7 μm) column, Acquity PDA UV/VIS and Acquity QDa ESI-MS detectors.

NMR spectra were measured at room temperature on a Bruker AV III-300, or on a Magritek Spinsolve 60. Proton spectra were referenced to the signal of TMS ($\delta = 0$ ppm), carbon spectra were referenced to the signal of the solvent (CDCl₃ $\delta = 77.16$ ppm or DMSO-d₆ $\delta = 39.52$ ppm).

³¹P-MAS-NMR was measured on a Bruker AVANCE AMX-400 spectrometer. The samples were packed in a 4 mm zirconium oxide rotor and the spectra were acquired at a spinning rate of 10 kHz. The spectra were referenced to an external $NH_4H_2PO_4$ reference and chemical shifts are reported relative to 85% H_3PO_4 ($\delta = 0$ ppm).

Elemental analysis was performed on a Horiba Ultima2 ICP-OES spectrometer. The samples were digested with a mixture of 37% HCl, 65% HNO₃ and 30% H_2O_2 (10:3:3) or of 96% H_2SO_4 and 30% H_2O_2 (4:1) and appropriately diluted with 1% HNO₃.

XAS measurement at the Pd K-edge were performed at the SuperXAS beamline, Swiss light source (SLS), Villigen.² Measurements were made in transmission and using ion chambers for detection of the sample adsorption, normalization to the incident X-ray flux and, through simultaneous measurement of a Pd foil, calibration of the energy scale.

Measurements at the P K-edge were conducted at the Pheonix beamline of SLS.³ Samples were mounted as powders onto a copper backing plate with adhesive carbon tape. Partial fluorescence yield measurements made using a silicon drift diode detector.

The data obtained at the two beamlines was reduced and background subtracted using either the Athena package,⁴ Prestopronto,⁵ or PAXAS.⁶ Subsequent EXAFS analysis for the Pd K-edge data was made using EXCURV.⁷ Principal component analysis (PCA) and Iterative target transformation (ITT) reconstruction of the spectral components was made using the ITFA software due to Rossberg *et al.*⁸

Synthesis of LSK-15



Scheme S1: synthesis of 2-(diphenylphosphaneyl)terephthalic acid

Dimethyl 2-iodoterephthalate

The preparation of dimethyl 2-iodoterephthalate was performed by upscaling a procedure previously reported in literature.⁹ Dimethyl 2-aminoterephthalate (100 g, 478 mmol, 1.00 eq) was mixed with water (160 ml) and ice (320 g) to give a yellow suspension. Sulphuric acid (320 ml, 5.76 mol, 12.1 eq) was added over 10 minutes, while keeping the temperature below 65 °C, to give an orange solution. After cooling back to 0 °C the reaction mixture turned to a pink suspension. Sodium nitrite (40.0 g, 580 mmol, 1.21 eq.) in water (160 ml) was added dropwise over 45 minutes, keeping the temperature below 5 °C, to give a brown solution. The reaction mixture was stirred at 0-5 °C for 1 h. Sodium iodide (71.8 g, 479 mmol, 1.00 eq.) in water (160 ml) was added dropwise over 30 minutes at 0 - 10 °C to give a red-brown suspension with dark crystals (some nitrogen gas was generated). The reaction mixture was stirred at 10 °C for 15 minutes, until almost no gas was evolved, then it was carefully heated up to 60 °C over 45 minutes (significant gas evolution started at 55 °C). The reaction mixture was stirred at 60 - 65 °C for 30 minutes to give a red-violet suspension with dark crystals (after 10 minutes no more gas was evolved). Eventually, it was cooled down to 35 °C and quenched by addition of 10% aqueous sodium thiosulfate (250 ml). The crude was filtered and washed with 10% aqueous sodium thiosulfate and water, then with ethyl acetate until only sulphur was left on the filter. The organic layer was washed with 10% aqueous sodium thiosulfate solution (500 ml), water (500 ml) and brine (500 ml). The water phase was extracted again with ethyl acetate (500 ml). The combined organic layers were dried over sodium sulphate, filtered and dried under vacuum. The crude product (151 g) was dissolved in MeOH (730 ml) and heated to reflux. Active carbon (4.5 g) was added and stirred for 10 minutes at reflux. The hot mixture was filtered over a glass fiber filter, then the filter was washed with boiling MeOH (90 ml). The product was recovered through multiple crystallizations.

Dimethyl 2-iodoterephthalate, yellow solid (114 g, 356 mmol, 75% yield). ¹H-NMR (62 MHz, DMSO-d₆) δ 8.45 (d, J = 1.5 Hz, 1H), 8.05 (dd, J = 8.0, 1.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 3.88 (s, 6H).

Dimethyl 2-(diphenylphosphaneyl)terephthalate

Dimethyl 2-iodoterephthalate (13.0g; 40.6mmol, 1.00 eq), potassium carbonate (12.3 g; 89.0 mmol, 2.20 eq) and acetonitrile (390 ml) were mixed to give a yellow suspension. The reaction mixture was degassed by bubbling argon through the suspension via a long cannula over five minutes. Palladium acetate (390 mg; 1.74 mmol, 0.04 eq) was added and argon was bubbled for five more minutes. Diphenylphosphane (9.35 ml; 53.7 mmol, 1.32 eq) was added and the reaction mixture was stirred at reflux for 24 hours. The reaction mixture turned to an orange suspension. The solvent was removed in vacuum and the residue was purified by column chromatography, solvent gradient of petrol ether:ethyl acetate from 7:3 to 0:1.

Dimethyl 2-(diphenylphosphaneyl)terephthalate, yellow solid (9.9 g; contaminated by phosphine oxide). ¹H NMR (62 MHz, DMSO-d₆) δ 8.43 – 6.92 (m, 13H), 3.73 (d, J = 5.1 Hz, 6H). ³¹P NMR (25 MHz, DMSO-d₆) δ 27.78, -5.95. UPLC-MS: 379.2 (M+H⁺) retention time 1.53 min.

2-(diphenylphosphaneyl)terephthalic acid

Dimethyl 2-(diphenylphosphaneyl)terephthalate (9.9 g (contaminated by phosphine oxide); 22 mmol; 1.0 eq), THF (90 ml) and MeOH (45 ml) were mixed to give a yellow solution. The solution was degassed by bubbling argon through the reaction mixture via a long cannula over five minutes. Degassed aqueous 2 M LiOH solution (45 ml; 90 mmol, 4.1 eq) was added. The reaction mixture was stirred at room temperature for five hours and turned to a colourless cloudy solution. This solution was then concentrated in vacuum and the aqueous residue was filtered. More solid was precipitated from the mother liquor by addition of concentrated aqueous HCl (10 ml). The yellow solid was filtered, washed with water and dried in vacuum. The residue was purified by column chromatography on a C18 column, solvent gradient of water (+0.1% TFA):EtOH (+0.1% TFA) from 9:1 to 0:1. The product fractions were combined and reduced to a small volume; a yellow solid precipitated. The residue was extracted with ethyl acetate (200 ml) and aqueous 2 M HCl solution (200 ml). The aqueous phase was extracted once more with ethyl acetate (200 ml). The combined organic layers were washed with brine (200 ml) and dried over sodium sulphate. UPLC analysis revealed the presence of phosphine oxide, so the product was further purified via trituration with dichloromethane:ethyl acetate (19:1) in an ultrasonic bath for 20 minutes. The resulting solid was filtered, washed with dichloromethane and dried in vacuum.

2-(diphenylphosphaneyl)terephthalic acid, yellow solid (3.9 g, 11 mmol, yield 47%). ¹H NMR (300 MHz, DMSO-d₆) δ 13.24 (broad s, 2H), 8.08 (dd, *J* = 8.0, 3.6 Hz, 1H), 8.00 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.50 (dd, *J* = 3.8, 1.6 Hz, 1H), 7.42 – 7.35 (m, 6H), 7.25 – 7.14 (m, 4H). ¹³C NMR (76 MHz, DMSO-d₆) δ 167.30 (d, *J* = 2.2 Hz), 166.34, 140.09 (d, *J* = 28.8 Hz), 138.61 (d, *J* = 19.1 Hz), 137.60 (d, *J* = 12.1 Hz), 134.33, 133.40 (d, *J* = 21.0 Hz), 133.26, 130.48 (d, *J* = 2.3 Hz), 129.35, 128.83, 128.68 (d, *J* = 7.1 Hz). ³¹P NMR (122 MHz, DMSO-d₆) δ -5.62. UPLC-MS: 351.25 (M+H⁺) retention time 1.14 min.

LSK-15

Aluminium chloride hexahydrate (2.89 g, 12.0 mmol, 3.00 eq) was weighed in a flask, then dimethylformammide (DMF) (160 ml) and a stir bar were added. The mixture was stirred and sonicated until complete dissolution, then argon was bubbled through the solution to degas it. 2-(diphenylphosphaneyl)terephthalic acid (1.40 g, 4.00 mmol, 1.0 eq) and 2-aminoterephthalic acid (1.45 g, 8.00 mmol, 2.0 eq) were weighed in a one litre three-necked round bottomed flaks and a stir bar was added. Degassed DMF (320 ml) was added, the mixture was stirred until complete dissolution and heated to 110 °C. The metal precursor solution was transferred to the dropping funnel under inert atmosphere and it was added to the flask over one hour. A precipitate started to form upon addition. The mixture was stirred and heated for three additional hours, then the stirring was stopped and it was kept at 110 °C overnight. The following morning, the mixture was cooled to room temperature

and the solid was recovered by filtration. It was washed with degassed DMF (100 ml), degassed methanol (100 ml) and degassed *tert*-butylmethylether (100 ml), then dried under vacuum overnight.

LSK-15, yellow solid (3.83 g, 3.65 mmol, yield 91%). The PXRD pattern (Figure S4, black line) is comparable to that of MIL-101-NH₂ (Al). The BET surface area measured was of 2100 m²/g. A small amount of material (10 mg) was digested with DCl in D₂O (0.2 ml) and diluted with DMSO-d6 (1 ml). ¹H-NMR analysis of the resulting solution revealed a ratio between 2-(diphenylphosphaneyl)terephthalic acid and 2-aminoterephthalic acid of approximately 2:8.

Synthesis of Pd-LSK-15 catalysts

Palladium acetate (60 or 120 mg, 267 or 534 µmol, 0.5 or 1 eq) and LSK-15 (1.00 g, 533 µmol P, 1 eq) were weighed in a Schlenk tube under inert atmosphere. Dry and degassed toluene (45 or 90 ml) and a stir bar were added, and the mixture was stirred at room temperature for one hour. The liquid was decanted and the solid was dried in vacuum. The crystalline structure was retained upon palladium functionalization (Figure S4). The BET surface area measured was of 1900 m²/g (Pd:P 1:2) and 1100 m²/g (Pd:P 1:1).

Procedure for catalytic reactions

Pd precursor (30 µmol Pd, 0.03 eq) and ligand (when needed, in the desired amount) were weighed in a 20 ml headspace glass vial under inert atmosphere. Dry and degassed toluene (5 ml) and a stir bar were added, then the vial was sealed with a PTFE crimp cap. The mixture was stirred at room temperature for 30 minutes. 3-Bromoanisole (**2**, 127 µl, 1.00 mmol, 1.00 eq), cyclooctane (135 µl, 1.00 mmol, 1.00 eq), phenylboronic acid (**3**, 183 mg, 1.50 mmol, 1.50 eq) and triethylamine (279 µl, 2.00 mmol, 2.00 eq) were added under inert atmosphere. Water (36 µl, 2.0 mmol, 2.0 eq) was added and the mixture was stirred for some minutes. The reaction was monitored via GC-FID: the reaction mixture (*ca.* 100 µl) was sampled and filtered, then diluted with methanol (50 µl diluted to 1 ml). A first sample was taken and the reaction mixture was heated to 90 °C. The reaction was monitored with regular sampling throughout its progress. The substrate conversion was calculated as ratio between the concentration of **2** over the sum of the concentrations of **2**, **4** and **5** in the first sample. The selectivity towards Suzuki reaction was calculated as ratio between the concentration of **4** over the sum of the concentrations of **4** and **5**.

Procedure for hot filtration test

Palladium acetate (6.7 mg, 0.03 mmol, 0.03 eq) and LSK-15 (120 mg, 0.06 mmol P, 0.06 eq) were weighed in a 10 ml Schlenk tube under inert atmosphere. Dry and degassed toluene (5 ml) and a stir bar were added, and the mixture was stirred at room temperature for 30 minutes. 3-Bromoanisole (**2**, 127 μ l, 1.00 mmol, 1.00 eq), cyclooctane (135 μ l, 1.00 mmol, 1.00 eq), phenylboronic acid (**3**, 183 mg, 1.50 mmol, 1.50 eq) and triethylamine (279 μ l, 2.00 mmol, 2.00 eq) were added under inert atmosphere. Water (36 μ l, 2.0 mmol, 2.0 eq) was added and the mixture was stirred for some minutes. The reaction was monitored via GC-FID: the reaction mixture (*ca*. 100 μ l) was sampled and filtered, then diluted with methanol (50 μ l diluted to 1 ml). A first sample was taken and the reaction mixture was heated to 90 °C. When *ca*. 30% of the substrate was converted, the reaction solution was filtered through a PTFE cannula in a second Schlenk tube containing a stir bar. The entire apparatus was heated at reaction temperature, to avoid affecting the catalyst speciation by temperature swings. The liquid phase was further heated and its composition was monitored via GC-FID (Figure S1).



Figure S1: relative concentration of species **2**, **4** and **5** in the reaction mixture. The hot filtration is indicated by a dashed vertical line.

Procedure for recycling tests of Pd-LSK-15 (1:2)

Palladium acetate (6.7 mg, 0.03 mmol, 0.03 eq) and LSK-15 (120 mg, 0.06 mmol P, 0.06 eq) were weighed in a 10 ml Schlenk tube under inert atmosphere. Dry and degassed toluene (5 ml) and a stirring bar were added, and the mixture was stirred at room temperature for 30 minutes. 3-Bromoanisole (**2**, 127 μ l, 1.00 mmol, 1.00 eq), cyclooctane (135 μ l, 1.00 mmol, 1.00 eq, internal standard), phenylboronic acid (**3**, 183 mg, 1.50 mmol, 1.50 eq) and triethylamine (279 μ l, 2.00 mmol, 2.00 eq) were added under inert atmosphere. Water (36 μ l, 2.0 mmol, 2.0 eq) was added and the mixture was stirred for some minutes. The reaction was monitored via GC-FID: the reaction mixture (*ca*. 100 μ l) was sampled and filtered, then diluted with methanol (50 μ l diluted to 1 ml). A first sample was taken and the reaction mixture was heated to 90 °C. When *ca*. 30% of the substrate was

converted, the solid was decanted and the solution was removed with a syringe. Dry and degassed toluene (5 ml), 3-bromoanisole (**2**, 127 μ l, 1.00 mmol, 1.00 eq), cyclooctane (135 μ l, 1.00 mmol, 1.00 eq), phenylboronic acid (**3**, 183 mg, 1.50 mmol, 1.50 eq), triethylamine (279 μ l, 2.00 mmol, 2.00 eq) and water (36 μ l, 2.0 mmol, 2.0 eq) were added to the Schlenk tube containing the solid. The mixture was stirred for some minutes, a first GC sample was taken and the reaction mixture was heated to 90 °C. This procedure was repeated for a third catalytic run.

Table S1: catalytic performance of Pd-LSK-15 (1:2) in multiple reaction runs.^a



Entry	Reaction run	Reaction time (h)	2 conversion (%) ^b	Suzuki selectivity (%) ^{b,c}
1	1 st	3	25	96
2	2 nd	24	39	96
3	3 rd	23	12	>99

^{*a*}Standard conditions: **2** (1.0 mmol), **3** (1.5 mmol), Et₃N (2.0 mmol), H₂O (2.0 mmol), Pd(OAc)2 (0.03 mmol), LSK-15 (0.06 mmol P), toluene (5.0 ml), 90 °C. ^{*b*}Calculated via GC-FID.

'The main byproduct observed was anisole.

Procedure for substrate scope reactions with Pd-LSK-15 (1:2)

Palladium acetate (6.7 mg, 0.03 mmol, 0.03 eq) and LSK-15 (120 mg, 0.06 mmol P, 0.06 eq) were weighed in a 20 ml headspace vial under inert atmosphere, dry and degassed toluene (5 ml) and a stir bar were added. The mixture was stirred for 30 minutes at room temperature, then substrate (1.00 mmol, 1.00 eq), phenylboronic acid (**3**, 183 mg, 1.50 mmol, 1.50 eq) and triethylamine (279 µl, 2.00 mmol, 2.00 eq) were added under inert atmosphere. Water (36 µl, 2.0 mmol, 2.0 eq) was added and the mixture was heated to 90 °C. After 90 hours, the mixture was allowed to cool to room temperature, then filtered on a pad of silica gel and washed with diethyl ether (25 ml) and ethyl acetate (25 ml). The reaction crude was purified by column chromatography on silica gel.

Procedure for substrate scope reactions with Pd(PPh₃)₄

Tetrakis(triphenylphosphine)palladium(0) (35 mg, 30 μ mol, 0.03 eq), substrate (1.00 mmol, 1.00 eq), phenylboronic acid (**3**, 183 mg, 1.50 mmol, 1.50 eq) and triethylamine (279 μ l, 2.00 mmol, 2.00 eq) were mixed in a 20 ml headspace vial under inert atmosphere. Dry and degassed toluene (5 ml) and a stir bar were added. Water (36 μ l, 2.0 mmol, 2.0 eq) was added and the mixture was heated to 90 °C. The reaction progress was monitored by comparing the area of the UV absorption signals of the substrate with those of the product. After 90 hours, the mixture was allowed to cool to room temperature, then filtered on a pad of silica gel and washed with diethyl ether (25 ml) and ethyl acetate (25 ml). The reaction crude was purified by column chromatography on silica gel.

Characterization of products

3-methoxy-1,1'-biphenyl, pale yellow oil. δ_{H} (300 MHz, CDCl₃) 7.63 – 7.53 (2 H, m), 7.49 – 7.37 (2 H, m), 7.38 – 7.31 (2 H, m), 7.18 (1 H, ddd, *J* = 7.6, 1.7, 1.0 Hz), 7.13 (1 H, dd, *J* = 2.6, 1.6 Hz), 6.89 (1 H, ddd, *J* = 8.2, 2.6, 1.0 Hz), 3.86 (3 H, s). The spectroscopic data correspond to previously published ones.¹⁰

3-methyl-1,1'-biphenyl, colourless oil. $\delta_{\rm H}$ (300 MHz, CDCl₃) 7.64 – 7.53 (2 H, m), 7.48 – 7.37 (4 H, m), 7.37 – 7.28 (2 H, m), 7.20 – 7.12 (1 H, m), 2.42 (3 H, s). The product is contaminated by ca. 4% of 1,1'-biphenyl. The spectroscopic data correspond to previously published ones.¹¹

3,5-bis(trifluoromethyl)-1,1'-biphenyl, colourless oil. $\delta_{\rm H}$ (300 MHz, CDCl₃) δ 8.01 (2 H, s), 7.86 (1 H, s), 7.64 – 7.56 (2 H, m), 7.55 – 7.40 (3 H, m). The product is contaminated by ca. 7% of 1,1'-biphenyl. The spectroscopic data correspond to previously published ones.¹²

2-([1,1'-biphenyl]-3-yl)acetonitrile, colourless oil. $\delta_{\rm H}$ (300 MHz, CDCl₃) δ 7.60 – 7.52 (4 H, m), 7.50 – 7.41 (3 H, m), 7.40 – 7.33 (1 H, m), 7.33 – 7.28 (1 H, m), 3.80 (2 H, s). $\delta_{\rm c}$ (76 MHz, CDCl₃) 142.36, 140.35, 130.53, 129.66, 128.98, 127.84, 127.24, 126.96, 126.81, 117.93, 23.75. The product is contaminated by ca. 11% of 2-(3-bromophenyl)acetonitrile

3-phenylpyridine, yellow oil. $\delta_{\rm H}$ (300 MHz, CDCl₃) δ 8.90 (1 H, d, *J* = 1.5 Hz), 8.65 (1 H, dd, *J* = 4.9, 1.6 Hz), 7.91 (1 H, ddd, *J* = 7.9, 2.3, 1.6 Hz), 7.62 – 7.53 (2 H, m), 7.53 – 7.36 (4 H, m). The spectroscopic data correspond to previously published ones.¹³

4-phenylpyridine, white solid. δ_{H} (300 MHz, CDCl₃) δ 8.77 – 8.69 (2 H, m), 7.69 – 7.59 (2 H, m), 7.59 – 7.37 (5 H, m). The spectroscopic data correspond to previously published ones.¹³

Stability of MIL-101-NH₂ (AI) to acids and bases in toluene

MIL-101-NH₂ was synthesized to an analogous procedure to LSK-15, using only 2-aminoterephthalic acid as a linker. The obtained MOF featured the expected PXRD pattern and a BET surface area of 2900 m²/g. The MOF (100 mg) was treated with toluene (10 ml) and an acid or base (sulphuric acid, trifluoroacetic acid (TFA), acetic acid (AcOH), potassium carbonate, 1,1,3,3-tetramethylguanidine (TMG) and trimethylamine (Et₃N), 0.1 mmol) for 24 hours at room temperature. The solid was then recovered via centrifugation, washed twice with toluene (2 x 10 ml) and dried under vacuum at room temperature. The obtained material was characterized by means of PXRD, the recorded patterns are shown in Figure S2.



Figure S2: PXRD patterns of pristine MIL-101-NH₂ (Al) (black) and of the solids recovered upon treatment of this MOF with toluene and H₂SO₄ (red), TFA (blue), AcOH (light green), K₂CO₃ (purple), TMG (dark green) or Et₃N (orange).

The MOF partially retained its crystalline structure upon treatment with AcOH and Et_3N , and to a smaller extent with TFA. The treatment with H_2SO_4 , K_2CO_3 and TMG resulted in the destruction of the framework.

Catalyst characterization

STEM



Figure S3: HAADF-STEM image of LSK-15 treated with $Pd_2(dba)_3$ (Pd:P ratio 1:1).





Figure S4: PXRD patterns of LSK-15 (black), Pd-LSK-15 (1:1) (red) and Pd-LSK-15 (1:2) (blue).



Figure S5: PXRD patterns of Pd-LSK-15 (1:2) after synthesis (black) and after its use in catalysis (red).



Figure S6: ³¹P-MAS-NMR spectra of LSK-15 (black), Pd-LSK-15 (1:1) (red) and Pd-LSK-15 (1:2) (blue).





Figure S7: Pd K-edge XANES of Pd-LSK-15 (1:2) as synthesized (black) and of reference materials: Pd(PPh₃)₄ (red), Pd(PPh₃)₂Cl₂ (dark blue), Pd₂(dba)₃xCHCl₃ (green) and PdO (light blue).



Figure S8: P K-edge spectra of Pd-LSK-15 (1:2) as synthesized (black) and after use in catalysis (red). The spectrum of Pd(PPh₃)₂Cl₂ is added as a reference (blue).



Figure S9: P K-edge spectra of Pd-LSK-15 (1:1) as synthesized (black) and after use in catalysis (red). The spectrum of Pd(PPh₃)₂Cl₂ is added as a reference (blue).



Figure S10: P K-edge spectra of LSK-15 (black), 2-(diphenylphosphaneyl)terephthalic acid (red), 2-(diphenylphosphoryl)terephthalic acid (blue) and Pd(PPh₃)₄ (green).

EXAFS and fits

Samples



Figure S11: k³-weighed Pd K-edge EXAFS (left) and the corresponding Fourier transform (right) of Pd-LSK-15 (1:1) as synthesized (black) and relative fit (red)



Figure S12: k³-weighed Pd K-edge EXAFS (left) and the corresponding Fourier transform (right) of Pd-LSK-15 (1:1) after use in catalysis (black) and relative fit (red)



Figure S13: k³-weighed Pd K-edge EXAFS (left) and the corresponding Fourier transform (right) of Pd-LSK-15 (1:2) as synthesized (black) and relative fit (red)



Figure S14: k³-weighed Pd K-edge EXAFS (left) and the corresponding Fourier transform (right) of Pd-LSK-15 (1:2) after use in catalysis (black) and relative fit (red)

Reconstructed components



Figure S15: k³-weighed Pd K-edge EXAFS (left) and the corresponding Fourier transform (right) of reconstructed component A (black) and relative fit (red)



Figure S16: k³-weighed Pd K-edge EXAFS (left) and the corresponding Fourier transform (right) of reconstructed component B (black) and relative fit (red)

Spectrum	Shell	Na	r (Å)⁵	DW (2σ²) ^c	E _F (eV) ^d	R % ^e
Component A	0	2.0	2.06	0.011	-8.9	22.88
	Р	1.6	2.32	0.011		
Component B ^g	0	0.7	2.02	0.003	-4.2	14.90
	Р	1.0	2.20	0.018		

Table S2: EXAFS fits for the components A and B reconstructed from PCA^f

Pd	4.6	2.75	0.018
Pd	2.3	3.83	0.019
Pd	2.0	4.78	0.018
Pd	4.0	5.37	0.021

^aCoordination number (±10% of stated value).

^bDistance of the scattering atom from the central atom (±1.5% of stated value).

^cDebye–Waller factor; σ is the root mean square internuclear separation (Å).

^{*d*}Edge position relative to the vacuum zero (Fermi energy, eV).

^{*e*}*R* % = ($\int [c^T - c^E]k^3 dk/[c^E]k^3 dk$) × 100 where c^T and c^E are the theoretical and experimental EXAFS and *k* is the photoelectron wave vector.

^{*f*}Other parameters: AFAC = 0.9, related to the proportion of electron undergoing scattering post absorption that contribute to the EXAFS. The fitting range is 3.0-13.0k (Å⁻¹).

^gThe inclusion of four palladium shells is indicative and only done to show consistency with the expected *fcc* structure for palladium NPs.

References

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