Electronic Supplementary Information

Post-Synthetic Immobilization of Palladium Complexes on Metal-Organic Frameworks – A New Concept for the Design of Heterogeneous Catalysts for Heck Reactions

Meike A. Gotthardt[a], Angela Beilmann[a], Roland Schoch[b], Julia Engelke[a] and Wolfgang Kleist[*a,c]

[a] Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Engesserstr. 20, D-76128 Karlsruhe, Germany.
  Fax: +49 721 608 44820
 Tel: +49 721 608 47989
  E-mail: wolfgang.kleist@kit.edu

[b] TU Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Str. 54, D-67663 Kaiserslautern, Germany.

[c] Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.
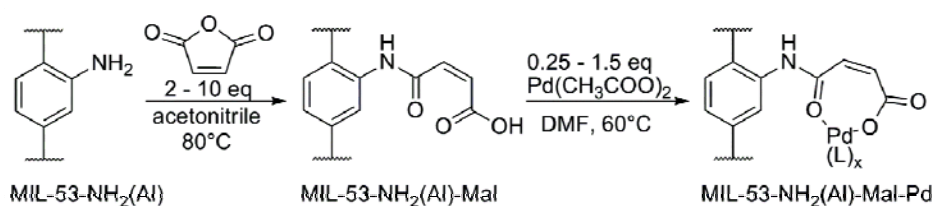
1. Synthesis of MIL-53-NH$_2$(Al)

5.33 mmol (1 eq) 2-aminobenzene-1,4-dicarboxylic acid (H$_2$ABDC) were dissolved in 25 mL H$_2$O and 20 mL DMF at 90 °C under reflux. A solution of 5.33 mmol (1 eq) Al(NO$_3$)$_3$*9H$_2$O in 5 mL H$_2$O was added and the reaction mixture was stirred at 90 °C under reflux for 24 h. After filtration the material was washed with 3 x 10 mL DMF and 1 x 30 mL H$_2$O. The sample was dried over night at room temperature and then for 3 days at 130 °C in air atmosphere.
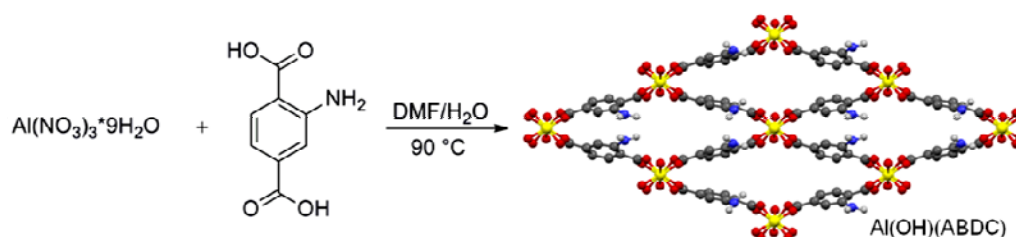
Scheme S1: Synthesis of MIL-53-NH$_2$(Al).

2. Post-synthetic modification (PSM) of MIL-53-NH$_2$(Al)

MIL-53-NH$_2$(Al) was modified in a two step post-synthetic modification reaction (Scheme S2). First, the reaction of maleic anhydride with the amine groups of the organic linker molecules led to the formation of a chelating group which could then in the second step be used to immobilize Pd(II).

Scheme S2: Post-synthetic modification of MIL-53-NH$_2$(Al).

2.1 Modification with maleic anhydride

2 – 10 mmol (2 – 10 eq) maleic anhydride were dissolved in 25 mL acetonitrile. 1 mmol (1 eq) MIL-53-NH$_2$(Al) was suspended in the solution and the reaction mixture was heated under reflux to 80 °C for 24 h. After filtration the resulting material was washed with

5 x 20 mL acetonitrile, 1 x 20 mL DMF and 1 x 20 mL H_2O. The sample was dried over night at room temperature and then for 3 days at 130 °C in air atmosphere.

2.2   Modification with palladium acetate

The amount of Pd precursor was calculated in regard to 40 % of the amino functions being successfully modified with maleic anhydride.[1] 0.1 – 0.6 mmol (0.25 – 1.5 eq) Pd(II) acetate were dissolved in 12 mL *N,N*-dimethylformamide (DMF). 1.0 mmol (1.0 eq) MIL-53-NH_2(Al)-Mal was suspended in the solution and the reaction mixture was heated to 60 °C for 4 h. After filtration the resulting material was washed with 3 x 12 mL DMF and 1 x 12 mL H_2O. The sample was dried over night at room temperature and then for 2 days at 130 °C in air atmosphere.

3.   Material characterization and analysis

All materials were analyzed using powder X-ray diffraction (PXRD), nitrogen physisorption (BET) and infra-red spectroscopy (FT-IR). The Pd-containing samples were further characterized using atomic absorption spectroscopy (AAS) and X-ray absorption spectroscopy (XAS). To determine conversion and yield of the catalytic tests gas chromatography (GC) was used.

3.1   Powder X-ray diffraction (PXRD)

PXRD measurements were performed using a Bruker D8 Advance. The samples were analyzed in the range 2 Θ = 6 – 50° using Cu K_α radiation. The step width was 2 Θ = 0,0082° with a dwell time of 2 s.

It was shown that the structure of MIL-53-NH_2(Al) is retained throughout the whole modification process.

3.2   Nitrogen physisorption (BET)

The samples were activated for 20 h at 130 °C under vacuum. Nitrogen physisorption was measured using a Belsorp mini II from BEL Japan. The specific surface area was determined using the BET method and the BEL Master software.

As has been described in literature the isotherms of MIL-53-NH$_2$(Al) show a stepwise adsorption which might be because of a change in pore geometry due to the breathing effect. The strong hysteresis that can be seen between adsorption and desorption isotherm is most probably due to measurement settings and apparatus specifications.

Nitrogen physisorption measurements of MIL-53-NH$_2$(Al)-Mal, MIL-53-NH$_2$(Al)-Mal-Pd and Pd@MIL-53-NH$_2$(Al) (Figure S1) show a drastic decrease of the specific surface area (Table S1) after modification of MIL-53-NH$_2$(Al) (Figure S2).
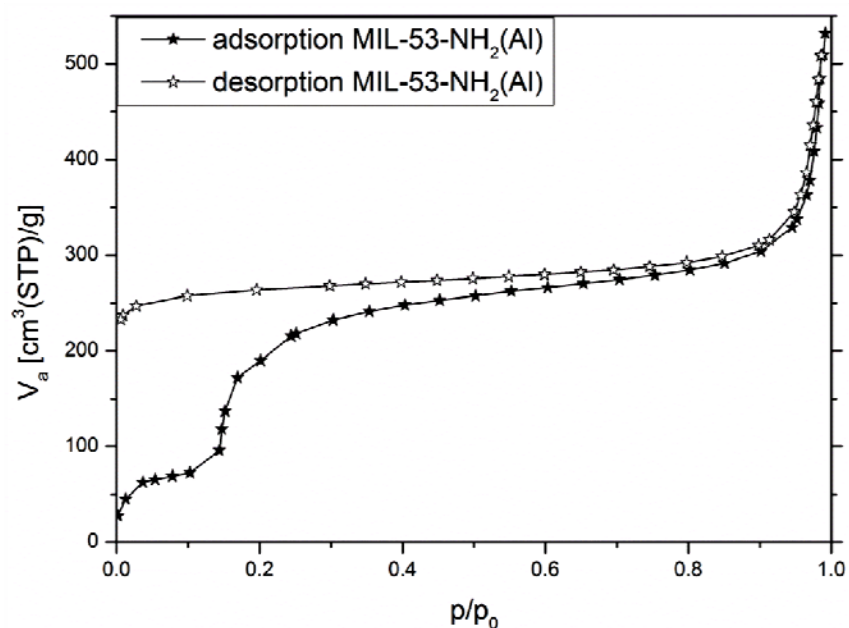

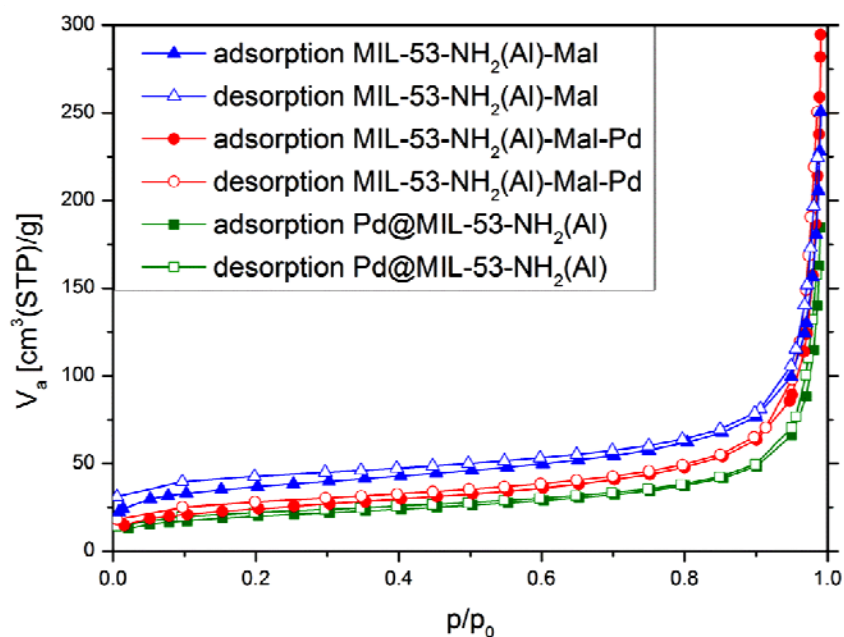**Figure S1:** Adsorption and desorption isotherms of MIL-53-NH$_2$(Al).

Figure S2: Adsorption and desorption isotherms of the modified frameworks based on MIL-53-NH$_2$(Al).

Table S1: Specific surface areas of MIL-53-NH$_2$(Al) and the modified samples.

material	specific surface area [m²/g]
MIL-53-NH$_2$(Al)	980
MIL-53-NH$_2$(Al)-Mal	155
MIL-53-NH$_2$(Al)-Mal-Pd	90
Pd@MIL-53-NH$_2$(Al)	65

3.3 Infrared spectroscopy (FT-IR)

IR data were acquired using a FT-IR spectrometer Vertex 70 from Bruker Optics equipped with a Golden Gate Single Reflection ATR sample cell from Specac. The data were collected from 4500 to 600 cm^{-1} and for each spectrum the arithmetic average of 400 measurements was taken.
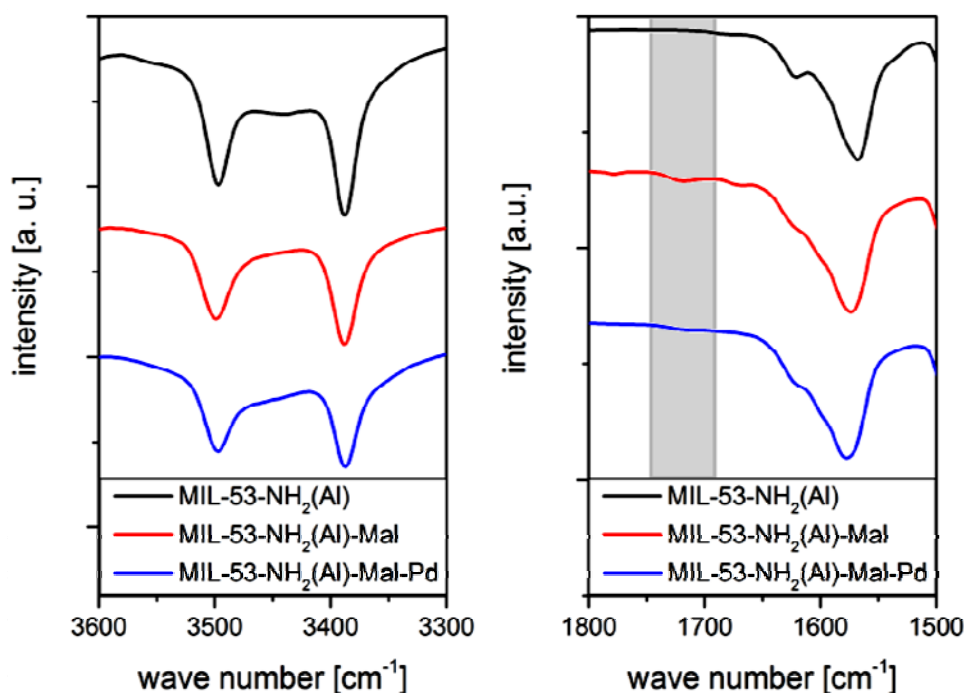
Figure S3: IR-spectra of MIL-53-NH$_2$(Al) (black), MIL-53-NH$_2$(Al)-Mal (red) and MIL-53-NH$_2$(Al)-Mal-Pd (blue); 3550-3300 cm^{-1}: NH stretching vibration; red curve, around 1700 cm^{-1}: additional CO stretching vibration due to the modification of the amine group.

3.4 Atomic absorption spectroscopy (AAS)

For AAS measurements a Z-6100 Polarized Zeeman atomic absorption spectrometer from Hitachi was used. The Pd-containing solid frameworks were digested in 7 mL aqua regia and diluted with 93 mL distilled water.

The catalyst materials as well as the solutions of the hot filtration test were analyzed. The results were used to calculate the amount of Pd-leaching (in %) during the reaction.

3.5   X-ray absorption spectroscopy (XAS)

The XAS experiments were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY) at DORIS III (4.45 GeV, 120 mA current) using beam line X1 (energy range: $7 - 100$ keV). For the measurement at the Pd K edge (24.35 keV) a Si(311) double-crystal monochromator was used. All spectra were recorded using boron nitride pellets at ambient temperature.

For data evaluation a Victoreen-type polynomial was subtracted from the spectrum to remove the background.[2] Afterwards the first inflection point was taken as energy E_0. A piecewise polynomial was used to determine the smooth part of the spectrum. It was adjusted in a way that the low-R components of the resulting Fourier transform were minimal. The background subtracted spectrum was divided by its smoothed part and the photon energy was converted to photoelectron wave number k. For evaluation of the EXAFS spectra the resulting functions were weighted with k^3 and calculated with EXCURVE98, which works based on the EXAFS function and according to a formulation in terms of radial distribution functions:[3]

$$\chi(k) = \sum_j S_0^2(k) F_j(k) \int P_j(r_j) \frac{e^{\frac{-2r_j}{\lambda}}}{kr_j^2} \sin\left[2kr_j + \delta_j(k)\right] dr_j$$

For analysis, no Fourier filtering was necessary due to the high signal-to-noise ratio. The number of independent points N_{ind} was calculated for every fit to prevent overinterpretation by using too many parameters:[3a]

$$N_{ind} = \frac{2\Delta k \Delta R}{\pi}$$

In which Δk is the used range in k-space and ΔR the range in which distances were fitted. The accuracy of the determined distances is 1%, of the Debye-Waller factor 10%[4] and of the coordination numbers (depending on the distance) 5-15%.
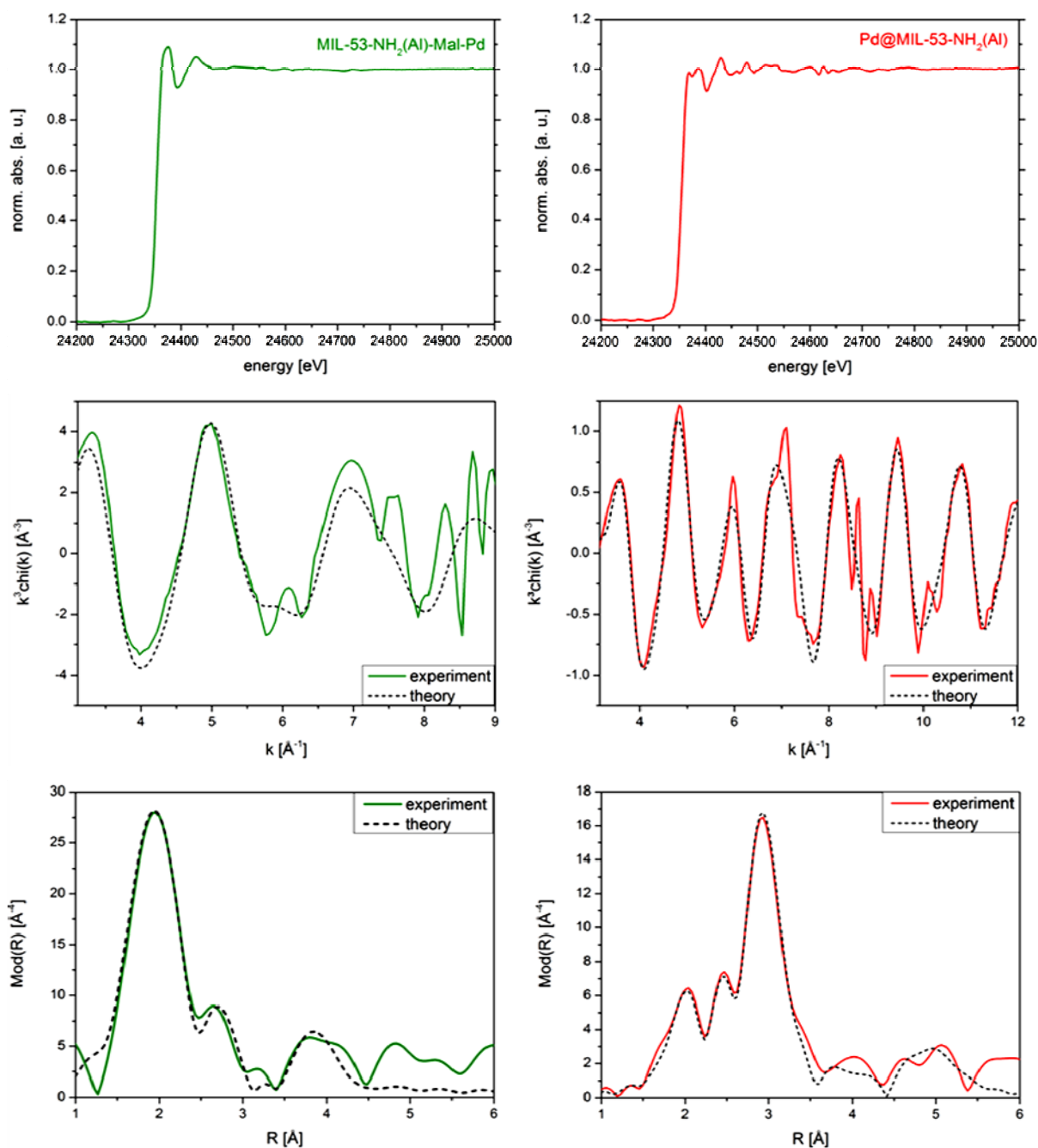
Figure S4: EXAFS spectra (top), k^3chi(k) (middle) and Fourier transform (bottom) of MIL-53-NH$_2$(Al)-Mal-Pd (green) and Pd@MIL-53-NH$_2$(Al) (red).

For MIL-53-NH$_2$(Al)-Mal-Pd 3.9 oxygen atoms could be fitted in the first shell at a distance of 2.008 Å, which is in good agreement with Pd(II) complexes in a fourfold coordination. In addition no palladium shells could be fitted. In contrast, Pd@MIL-53-NH$_2$(Al) shows only 1.3 oxygen atoms in the first shell at a distance of 2.035 Å. Three palladium shells could be fitted at 2.740, 3.794 and 4.750 Å which corresponds well to distances in metallic palladium. Obviously Pd@MIL-53-NH$_2$(Al) mainly contains metallic Pd nanoparticles with only minor contributions of immobilized Pd(II) complexes.

Table S2: Results of the XAS data analysis.

sample	Abs-Bs	N(Bs)	R(Abs-Bs) [Å]	σ [Å^{-1}]	R [%] χ^2_{red} E_f [eV] Afac
MIL-53-NH$_2$(Al)-Mal-Pd	Pd-O	3.9±0.3	2.008±0.020	0.107±0.010	35.48
	Pd-C	2.6±0.2	2.842±0.028	0.112±0.011	18.9086x10^{-6}
	Pd-C	6.2±0.6	3.959±0.039	0.112±0.011	7.108
					0.800
Pd@MIL-53-NH$_2$(Al)	Pd-O	1.7±0.1	2.031±0.020	0.055±0.005	25.27
	Pd-Pd	5.0±0.5	2.741±0.027	0.074±0.007	7.1680x10^{-6}
	Pd-C	8.4±0.8	2.898±0.028	0.112±0.011	4.045
	Pd-Pd	3.6±0.3	3.803±0.038	0.112±0.011	0.547
	Pd-Pd	5.3±0.8	4.745±0.047	0.084±0.008	

For Pd@MIL-53-NH$_2$(Al) the size of the Pd particles was determined. Due to a strong correlation between the measured first nearest neighbor metal coordination number and the disorder of their bond length, it is possible to ascertain the size of metal particles via EXAFS.[5] The correlation can be modeled with a hyperbolic equation[6]:

$$N_i = \frac{aN_{at}}{b+N_{at}} + \frac{cN_{at}}{d+N_{at}}$$

N_i: Average number of neighbor atoms for each coordination shell

N_{at}: Number of atoms present in cluster

a, b, c, d: Modeling parameters

The calculation was carried out with the parameters listed in Table S3, which can generally be used for all metals with fcc structure.[6]

Table S3: Parameters used to fit the coordination number for each shell.[6]

Parameter	N$_1$	N$_2$
a	8.981	3.922
b	9.640	7.368
c	3.026	2.192
d	1462.61	989.28

Pd@MIL-53-NH$_2$(Al) shows a coordination number of 5.0±0.5 in the first Pd-contribution, which leads with the mentioned modeling to a cluster size of 10-15 atoms. At 3.803 Å and 4.745 Å two further Pd-shells could be fitted with coordination numbers of 3.6±0.3 and 5.3±0.8 atoms. For the second shell this indicates clusters of 36-111 atoms. The results for

cluster sizes from the second shell and even more from the third shell are strongly influenced by multiple scattering effects, whereby the sizes of cluster atoms are falsified. This supports the conclusion, that a distribution of various cluster sizes is present.

3.6 Gas chromatography (GC)

For GC measurements a GC-2010 Plus from Shimadzu with a non-polar column (Rxi®-5Sil MS, length: 30 m, diameter: 0.25 mm, film thickness: 0.25 µm) and a FID detector was used. 1 µL of the sample was injected and vaporized at 250 °C. The column was heated from 50 °C to 280 °C at a rate of 10 K/min.

GC measurements were used to calculate conversion and yield of the Heck-type CC coupling reactions.

4. Catalytic test reactions

A Heck-type CC coupling reaction was chosen to probe the catalytic activity of the new materials MIL-53-NH$_2$(Al)-Mal-Pd and Pd@MIL-53-NH$_2$(Al). Non-activated aryl halides (namely bromo- and chlorobenzene) were chosen as substrates.
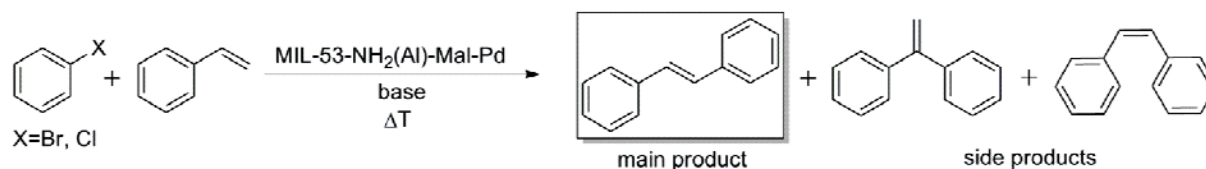
Scheme S3: Heck-type CC coupling reaction of aryl halides and styrene.

4.1 Heck reaction of bromobenzene and styrene

In a typical experiment 10 mmol bromobenzene, 15 mmol styrene, 12 mmol sodium acetate and diethylen-glycol-dibutyl-ether as internal GC standard were dissolved in 10 mL *N*-methyl-2-pyrrolidone (NMP) in a sealed glass tube. 0.01 mol% of the catalyst (based on Pd) were suspended in the reaction mixture and the mixture was then heated to 140 °C for 3 h. To optimize conversion and yield, the reaction temperature and reaction time were varied.

For the hot filtration test the catalyst was filled into a paper filter which was removed from the reaction mixture after 0.5 h. The reaction was then resumed for another 2.5 h. Samples for GC analysis were taken after 0.5 h and (0.5 + 2.5) h.

4.2 Heck reaction of chlorobenzene and styrene

In a typical experiment 10 mmol chlorobenzene, 15 mmol styrene, 12 mmol potassium hydroxide, 6 mmol tetrabutylammonium bromide (TBAB) and 2.3 mmol diethylen-glycol-dibutyl-ether as internal GC standard were dissolved in 10 mL N-methyl-2-pyrrolidone (NMP) in a sealed glass tube. 0.01 mol% of the catalyst (based on Pd) were suspended in the reaction mixture and the mixture was then heated to 160 °C for 6 h.

To optimize conversion and yield the reaction temperature, reaction time, base and amount of TBAB were varied.

References

1. S. J. Garibay, Z. Wang and S. M. Cohen, *Inorg. Chem.*, 2010, **49**, 8086.
2. (a) T. S. Ertel, H. Bertagnolli, S. Hückmann, U. Kolb and D. Peter, *Appl. Spectrosc.*, 1992, **46**, 690; (b) M. Newville, P. Livins, Y. Yacoby, J. J. Rehr and E. A. Stern, *Phys. Rev. B*, 1993, **47**, 14126.
3. (a) N. Binsted and F. Mosselmans, *EXCURV98 Manual*, Daresbury, UK; (b) N. Binsted and S. S. Hasnain, *J. Synchrotron. Radiat.*, 1996, **3**, 185.
4. D. C. Koningsberger, B. L. Mojet, G. E. van Dorssen and D. E. Ramaker, *Top. Catal.*, 2000, **10**, 143.
5. A. I. Frenkel, C. W. Hills and R. G. Nuzzo, *J. Phys. Chem. B*, 2001, **105**, 12689.
6. A. Jentys, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4059.