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Supporting Information

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Ion-leaching and Atom-leaching Mechanisms from Palladium Nanoparticles in Cross-coupling Reactions

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Experimental Section

Materials and instrumentation. *In situ* UV-visible measurements were performed using a Hewlett Packard 8453 spectrophotometer with a diode array detector. The recorded wavelength range was 190–1100 nm, at 1 nm resolution. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 spectrometer at 300.1 MHz and 75.2 MHz, respectively and on a Varian Inova 500 spectrometer at 499.8 MHz and 125.7 MHz, respectively. TEM images were obtained with a JEOL JEM-1200 EXII instrument, operated at an accelerating voltage of 120 kV. Samples were prepared by placing 150 μL of 1 mM Pd cluster suspension on carbon-coated copper grids. The solvent was then evaporated at 50 $^\circ\text{C}$ and 250 mm Hg. At least four images were taken for each sample. Inductive Coupled Plasma (ICP) measurements were performed on a Perkin Optima 3000 XL ICP instrument. Samples were first dried under vacuum at 65 $^\circ\text{C}$ and then digested using 6 ml of HCl and 2ml of HNO_3 and heated at 220 $^\circ\text{C}$ for 51 min. GC analysis was performed using an Interscience Trace GC-8000 gas chromatograph with a 100% dimethylpolysiloxane capillary column (VB-1, 30 m \times 0.325 mm). GC/MS analysis was performed using a Hewlett-Packard 5890/5971 GC/MS equipped with a ZB-5 (zebron) column (15 m \times 0.25 mm). All products are known compounds and were identified by comparison of their GC retention times to those of authentic samples and by MS analysis. GC conditions: isotherm at 80 $^\circ\text{C}$ (1 min); ramp at 30 $^\circ\text{C min}^{-1}$ to 280 $^\circ\text{C}$; isotherm at 280 $^\circ\text{C}$ (3 min). Fast Atom Bombardment Mass Spectroscopy (FAB-MS) was carried out using JEOL JMS SX/SX 102A four-sector mass spectrometer. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with Xenon atoms with energy of 3 KeV. During the high resolution FAB-MS measurements a resolving power of 10,000 (10 % valley definition) was used. Chemicals were purchased from commercial firms (>99% pure). All solvents were degassed and dried using molecular sieves. Pd clusters were prepared according to the literature procedure.¹

¹J. S. Bradley, B. Tesche, W. Busser, M. Maase, M. T. Reetz, *J. Am. Chem. Soc.* **2000**, *122*, 4631.

Pd Cluster and Pd-iodobenzene oxidative complex transport. The membrane reactor was evacuated and refilled with N₂. 70 ml DMF was placed into both sides (A and B) of membrane reactor. Then 30 ml of Pd clusters (10 mM in DMF) was added in side A and the solution was heated and stirred in the reactor at 100 °C for 144 h. 5 ml of sample was taken from B side after every 24 h. Above experiment was repeated using same amount of Pd clusters on A side and then 100 equivalents of iodobenzene **2** was added on both sides just to prevent the concentration gradients. 5 ml of sample was taken from B side after every 24 h. It is important to keep the reactor always under N₂. All samples were then analyzed using ICP, ¹³C NMR, TEM, UV-Vis spectrophotometer, and ES-MS. The experiments were carried out also in THF. Control experiments showed that the presence of base did not affect the transfer rates.

Heck coupling of *n*-butylacrylate and iodobenzene. A Schlenk-type vessel equipped with a rubber septum and a magnetic stirrer was evacuated and refilled with N₂. Equal 1.5:1 mixtures of **1** (1.5 mmol, 0.19 g) and **2** (1.0 mmol, 0.2 g) in 25 mL DMF were placed into reactor. NaOAc (1.5.0 mmol, 0.21 g) was then added. 7 ml of solution was taken from side B of membrane reactor after 6 days and then added to the same reactor. The reactor was heated at 100 °C and the sample was taken after 72 and analyzed using GC (pentadecane internal standard). After each experiment, the membrane was washed (acetone, 4 × 10 mL) and extracted for 24 h with EtOH.

Suzuki coupling of phenylboronic acid with *p*-iodotoluene. Equal 1.5:1 mixtures of **4** (7.5 mmol, 1.1 g) and **5** (5 mmol, 1.1 g) in 50 mL DMF were placed on both sides of the membrane reactor. NaOAc (15 mmol, 2.07 g) was then added to side **B** and the Pd cluster suspension (10 ml, 10 mM, 2.0 mol%) to side **A**. The reactor was heated at 100 °C and the samples were taken from both the compartments and analyzed using GC (pentadecane internal standard).

Oxidative complex formation in THF. The oxidative complex forms and can catalyze the Heck reaction in other solvents also. To study this we repeated the experiment in THF, using a 1:1 PhI: Pd ratio. The typical black color of Pd colloids

changed to brownish yellow. Figure S1 shows the UV-visible spectra of the sample in THF on side **B** after 144 h. We see an absorption peak around 450 nm, which can be attributed to the $(\text{Ph})\text{Pd}(\text{I})_2^-$ complex. The oxidative complex with Pd is stable in both THF and DMF. To check the activity of this complex we ran Heck reaction using same sample in both solvents. In DMF this complex was active but in THF we didn't observe any reaction in the presence of NaOAc. In presence of triethylamine as a base the conversion was 70%.

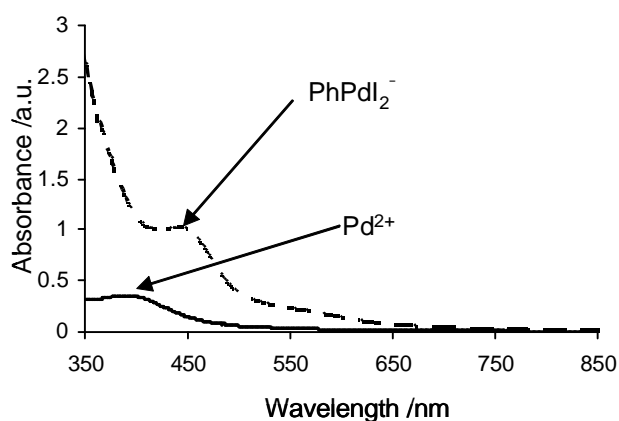


Figure S1. UV-Visible absorption spectra of $\text{Pd}(\text{OAc})_2$ in THF (continuous curve) and oxidative arylpalladium complex on side B (dotted curve). Reaction conditions: 10 mM of 30 mL Pd clusters suspension on side **A**, 1 equivalents of iodobenzene on both sides, 100 °C, N_2 atmosphere.

^{13}C NMR and FAB-MS studies of the clusters and complexes in DMF. Figure S2 shows the ^{13}C NMR spectrum of a mixture of Pd clusters and PhI in DMF (bottom), and the corresponding control sample without Pd (inset). The peaks reported by Reetz and Westermann² (indicated by arrows) are clearly observed. Comparing this with the ^{13}C NMR spectra of the reaction mixture from side **B** of the membrane reactor (Figure S3), we observe the same peaks as in the Pd-containing solution.

² M. T. Reetz, E. Westermann, *Angew. Chem.* **2000**, *112*, 170; *Angew. Chem. Int. Ed.* **2000**, *39*, 165.

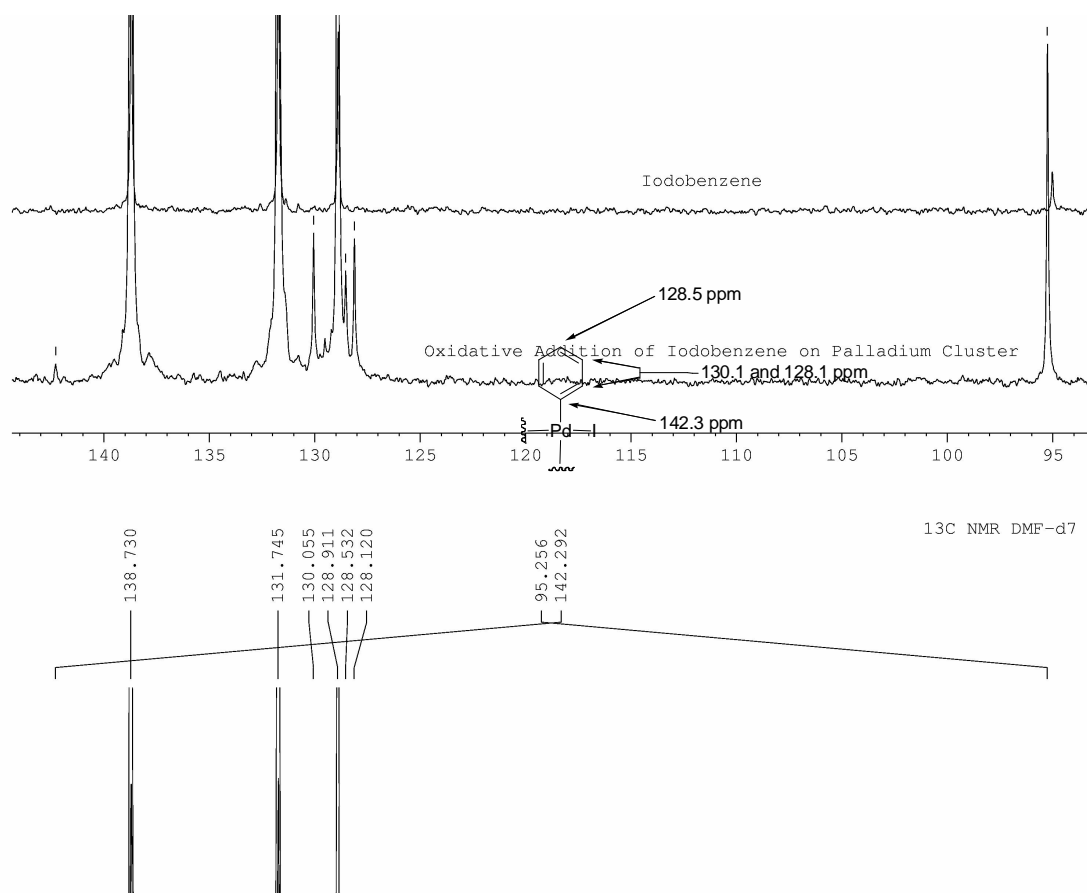


Figure S2. ^{13}C NMR spectrum of a mixture of Pd clusters and PhI in DMF. The inset shows the corresponding control sample without Pd.

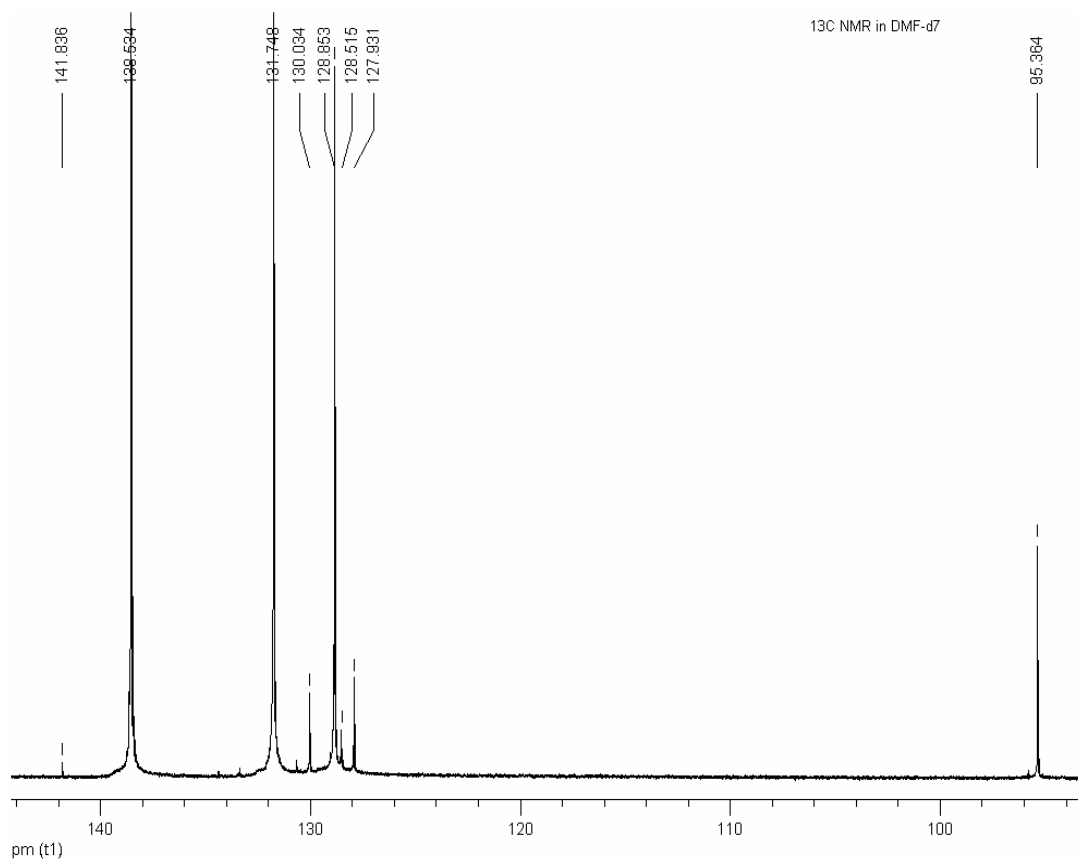


Figure S3. ^{13}C NMR spectrum of the mixture from side **B** of the membrane reactor.

The FAB-MS data for a sample from side **B** is shown in Figure S4, top. Zooming in (Figure S4, bottom), we observe several polymeric iodopalladium species, in agreement with the results reported by de Vries *et al.*³

³ A. H. M. de Vries, F. J. Parlevliet, L. Schmieler-van de Vondervoort, J. H. M. Mommers, H. J. W. Henderickx, M. A. M. Walet, J. G. de Vries, *Adv. Synth. Catal.* **2002**, *344*, 996.

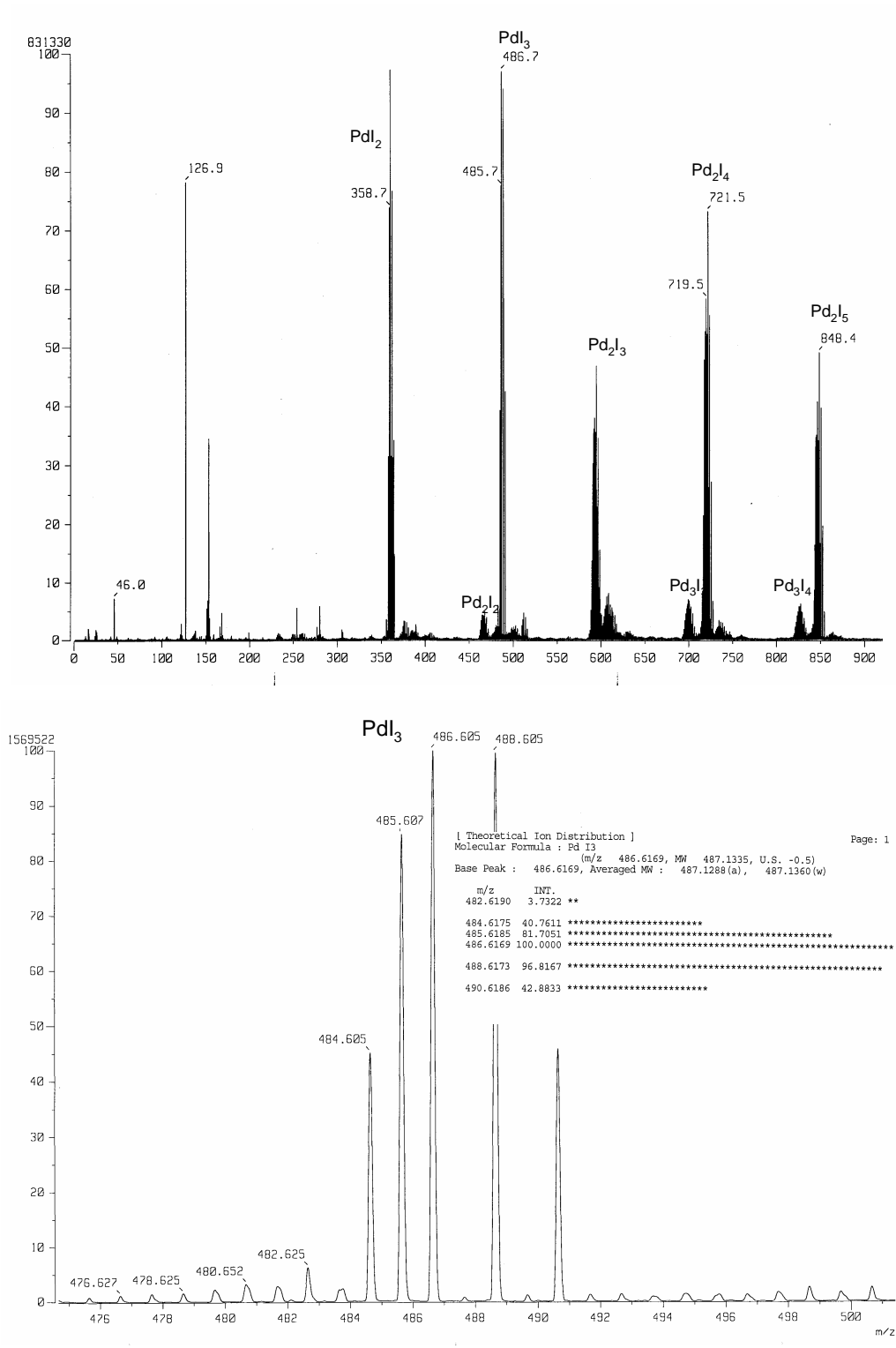


Figure S4. FAB-MS spectrum of the mixture from side **B** of the membrane reactor (top) and zoom-in view on the polymeric iodopalladium species (bottom).