Supplementary Information

Real-Time Analysis of $Pd_2(dba)_3$ Activation by Phosphine Ligands

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Experimental Details

$[PPN]^+[TPPMS]^-$, (**1**), was synthesized according to literature procedures.[1,2] $Pd_2(dba)_3$, $Na^+[sSPhos]^-$ (**2**), HPLC grade methanol, and ACS grade DMF, were purchased from Sigma-Aldrich and used as received. UHP200 Argon and HP300 4.8 Nitrogen were purchased from Airgas (Calgary, Canada) and used without further purification.

In a typical reaction, 10.0 mL HPLC grade methanol or ACS grade DMF is transferred to a custom PSI flask (*vide infra*) which is then sparged with nitrogen for 15 minutes before being connected to the instrumentation. Heating was effected with an IKA C-MAG HS 7 stirring hotplate equipped with an ETS-D5 thermocouple and oil bath. All reagent stock solutions were prepared under an inert nitrogen atmosphere in a glovebox. The stock solution was prepared using 0.0020 g $Pd_2(dba)_3$ dissolved in 4.0 mL anhydrous tetrahydrofuran (0.55 mM $Pd_2(dba)_3$, 1.1 mM Pd). (**1**) stock solution was prepared by dissolving 0.0077 g of (**1**) into 4.0 mL of degassed HPLC grade methanol (2.2 mM $[TPPMS]^-$). (**2**) stock was prepared by dissolving 0.0045g of the salt in 4.0 mL degassed HPLC grade methanol (2.2 mM $[sSPhos]^-$). 100 µL of each solution was injected via syringe into 10.0 mL degassed methanol yielding a Pd concentration of 11.0 µM and 2 equivalents of ligand. The PSI flask was charged a stir bar and reagent stock solutions were injected using Hamilton GASTIGHT® syringes when required. The flask is pressurized with 4 psi of argon using a PRAXAIR ProStar Platinum regulator.

The UV-Vis instrument of choice for these experiments was an ASEQ Instruments LR-1 compact spectrometer (version 2.1, Configuration B) equipped with a reflection fiber optic Y-cable probe (F01_R03) fitted with a teflon transflectance dip probe (LQ_R01) and a D2-S1 deuterium/halogen light source. The spectral range of the LR-1 is 200 – 1200 nm with a resolution of < 2 nm. Exposure time was set to 100 ms with a 5 scan average and data was collected from 200 – 1200 nm at a rate of one spectrum per second. Raw spectral data was collected using the ASEQ 16 bits version 1.54 software and chromatographic data was extracted using a custom Python script. A reference scan is collected initially to remove solvent from the background of the UV-Vis spectrum.

The dip probe was fitted with a thermometer adaptor and coupled to the custom PSI flask [3] featuring a built-in condenser, Kontes HI-VAC® extended tip valve with PTFE plug, and two 14/20 size ground glass joints. A 30 cm length of Vici Blue PEEK tubing (inner diameter of .010") was inserted through a rubber

septum fitted to the custom PSI flask and into the solution to be analyzed. The delay time for solution to reach the ESI source was calculated based on replicate trials to be 12.06 s and this is corrected for in all chromatograms. The opposite end of the tubing was connected to the ESI source of a Waters Acquity Triple Quadrupole Detector.

All electrospray ionization mass spectra were recorded using a Waters Acquity Triple Quadrupole Detector equipped with a Z-Spray electrospray ionization source. The capillary voltage was held at 3.1 kV, cone voltage at 10.0 V, and extraction cone at 3.0 V. Importantly, the MS cone voltage was optimized to eliminate in-source fragmentation and guarantee the speciation reported are not artifacts of the ESI process (see section titled "Effect of cone voltage on speciation in ESI-MS"). Source nitrogen gas flow rates and temperatures varied depending on solvent and were set to provide optimal desolvation conditions. For methanol, the desolvation gas flow rate was 200 L/hr, cone gas flow rate 100 L/hr, source temperature 80°C, desolvation temperature 180°C. For DMF, the desolvation gas flow rate was 500 L/hr, cone gas flow rate 100 L/hr, source temperature 130°C, desolvation temperature 230°C. The detector gain was set to an optimal voltage of 470 V. Scan time was set to 5 s, with an inter-scan time of 0.1 s. For all experiments the ESI spray head was left in a position near-perpendicular to the sampling cone with a 7° incline toward the cone. MSMS experiments were performed with a collision energy between 2-20 V with an Argon collision gas flow rate of 0.1 mL/hr.

Effect of cone voltage on speciation in ESI-MS

The potential between the capillary and the sampling cone on an ESI-MS instrument is referred to as the cone voltage. Increasing this value has been shown to promote in-source collision-induced dissociation (CID) due to the higher kinetic energy applied to ions generated from the electrospray process. [4] The increased kinetic energy results in CID with the bath gas which is used to promote desolvation. In order to probe the effect cone voltage has on apparent speciation we decided to increase the cone voltage over time and observe changes in the mass spectrum (Figure S1). It was determined that the compounds present above a cone voltage of 10 V are actually fragments formed out of $[Pd(TPPMS)_2(dba)]^{2-}$, therefore, we opted to leave the cone voltage very low at 10 V for all experiments to report the proper speciation because of the delicate nature of the ions of interest.

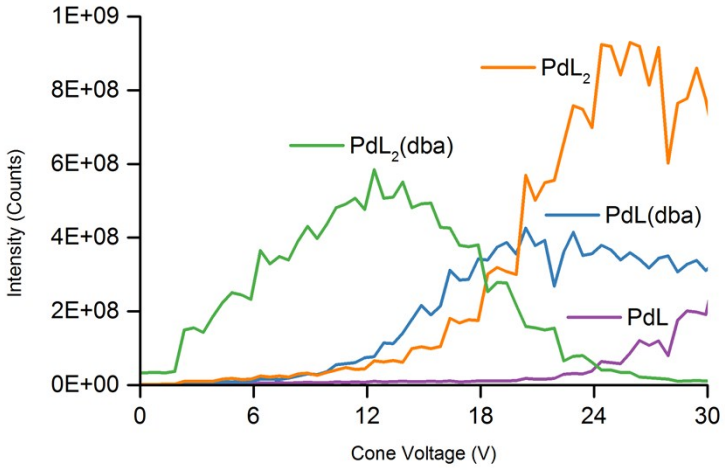

Figure S1. Observed speciation over a range of applied cone voltage following activation of $Pd_2(dba)_3$ with 4eq. $[TPPMS]^-$ in methanol at room temperature (21°C).

ESI-MS Chromatograms

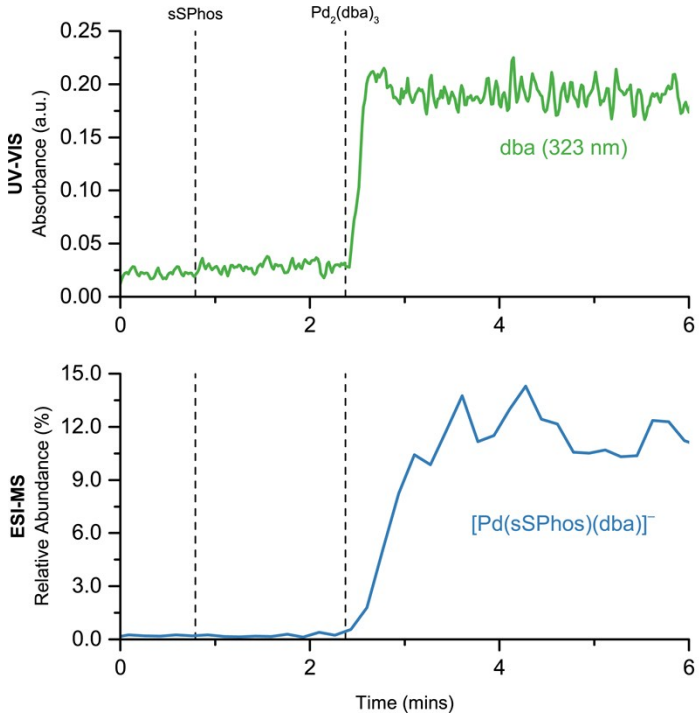

Figure S2. Reaction of $[sSPhos]^-$ with $Pd_2(dba)_3$ in DMF at room temperature (21°C).

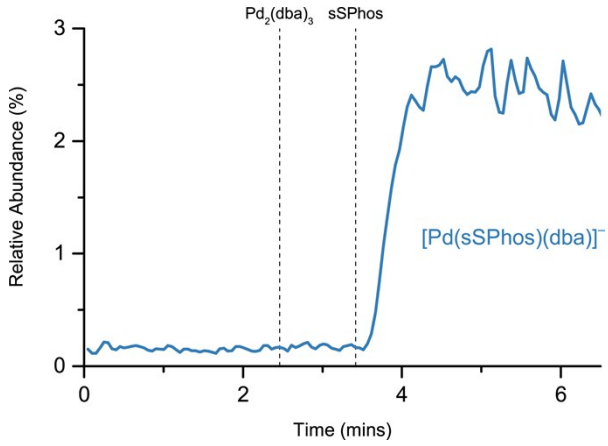

Figure S3. Reaction of $[sSPhos]^-$ with $Pd_2(dba)_3$ in MeOH at reflux (65°C).

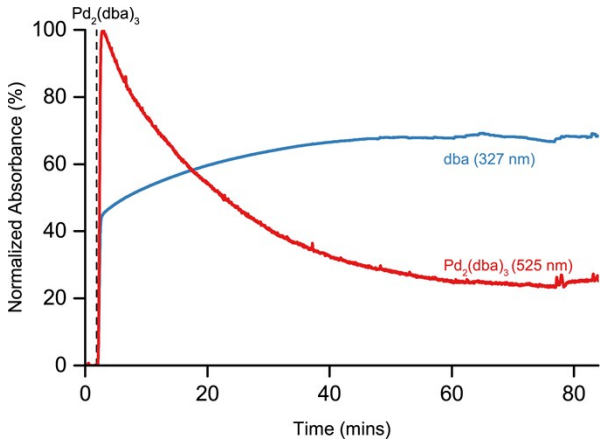

Figure S4. Loss of $Pd_2(dba)_3$ in DMF at room temperature (21°C).

ESI-MS Mass Spectra

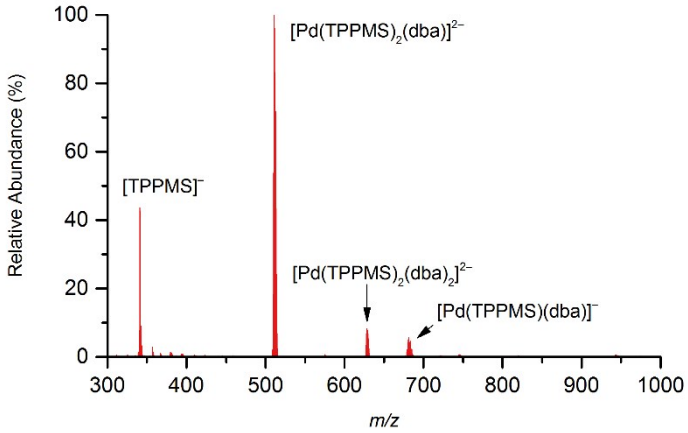

Figure S5. Mass spectrum of the mixture of 4 eq. $[TPPMS]^-$ with 1 eq. $Pd_2(dba)_3$ in MeOH.

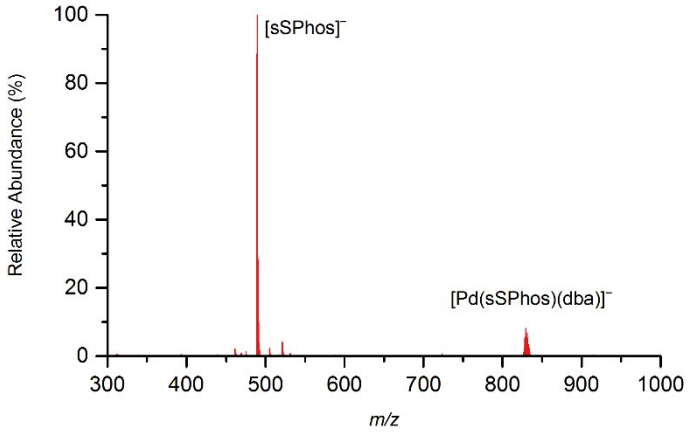

Figure S6. Mass spectrum of the mixture of 4 eq. $[sSPhos]^-$ with 1 eq. $Pd_2(dba)_3$ in MeOH.

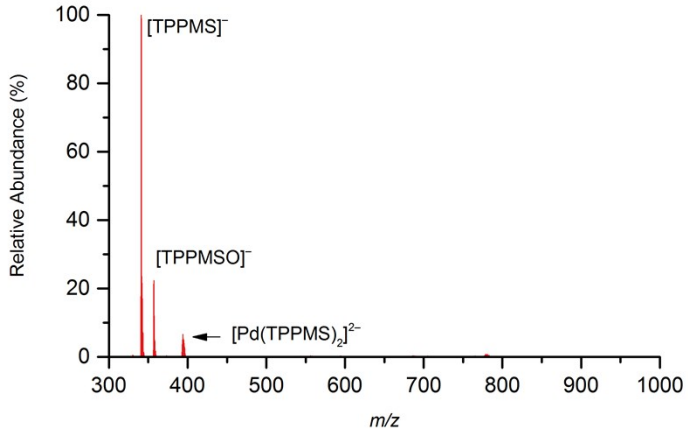

Figure S7. Mass spectrum of the mixture of 4 eq. $[TPPMS]^-$ with 1 eq. $Pd_2(dba)_3$ in DMF.

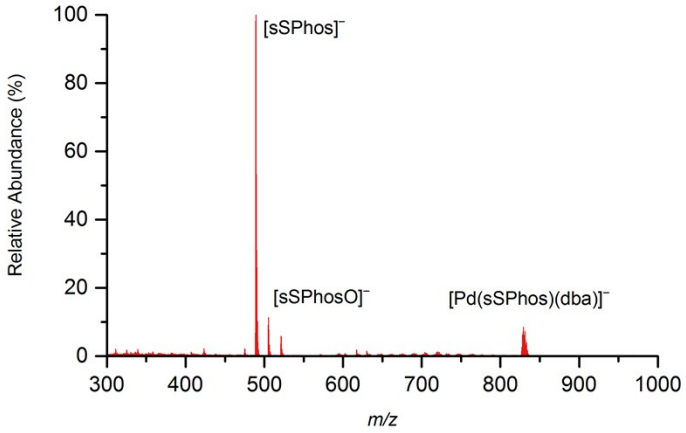

Figure S8. Mass spectrum of the mixture of 4 eq. $[sSPhos]^-$ with 1 eq. $Pd_2(dba)_3$ in DMF.

ESI-MSMS product ion scan spectra

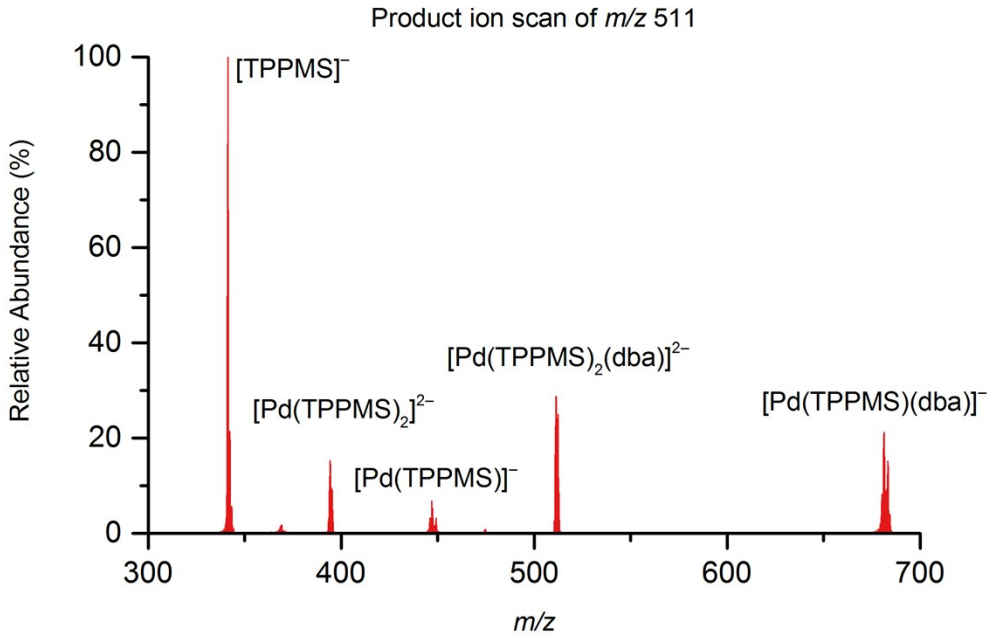

Figure S9. Product ion scan of $[Pd(TPPMS)_2(dba)]^{2-}$ (m/z 511).

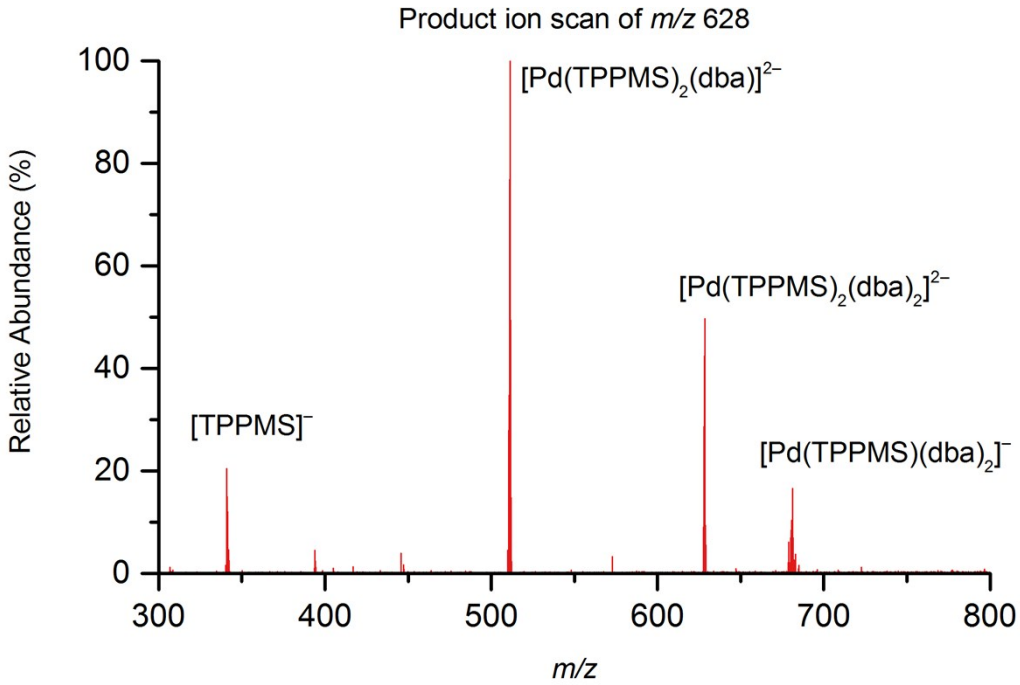

Figure S10. Product ion scan of $[Pd(TPPMS)_2(dba)_2]^{2-}$ (m/z 628).

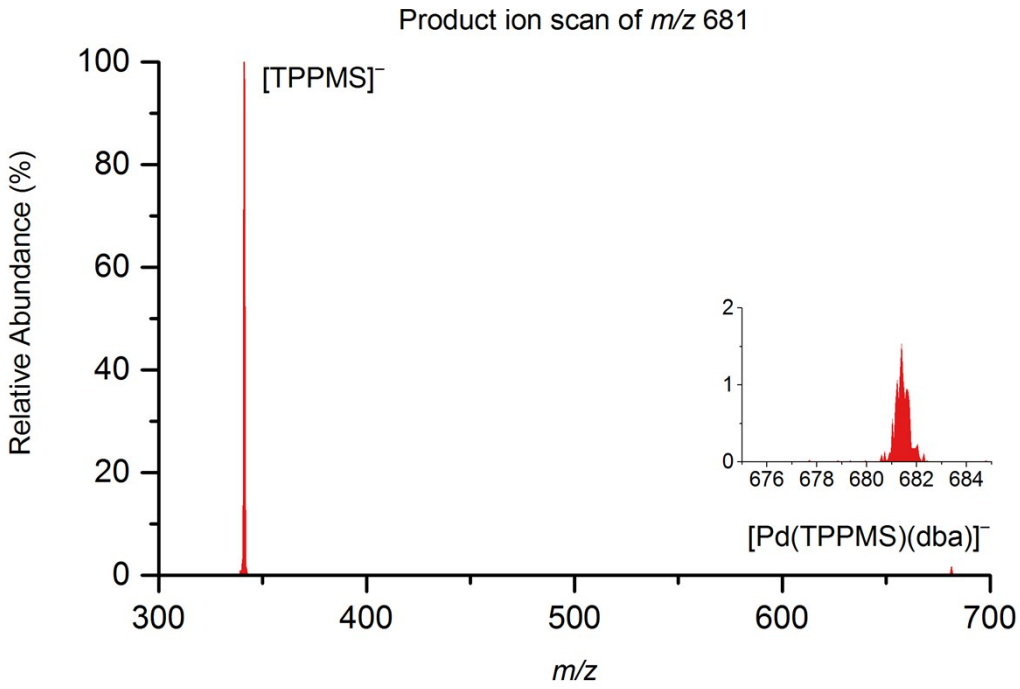

Figure S11. Product ion scan of $[Pd(TPPMS)(dba)]^-$ (m/z 681).

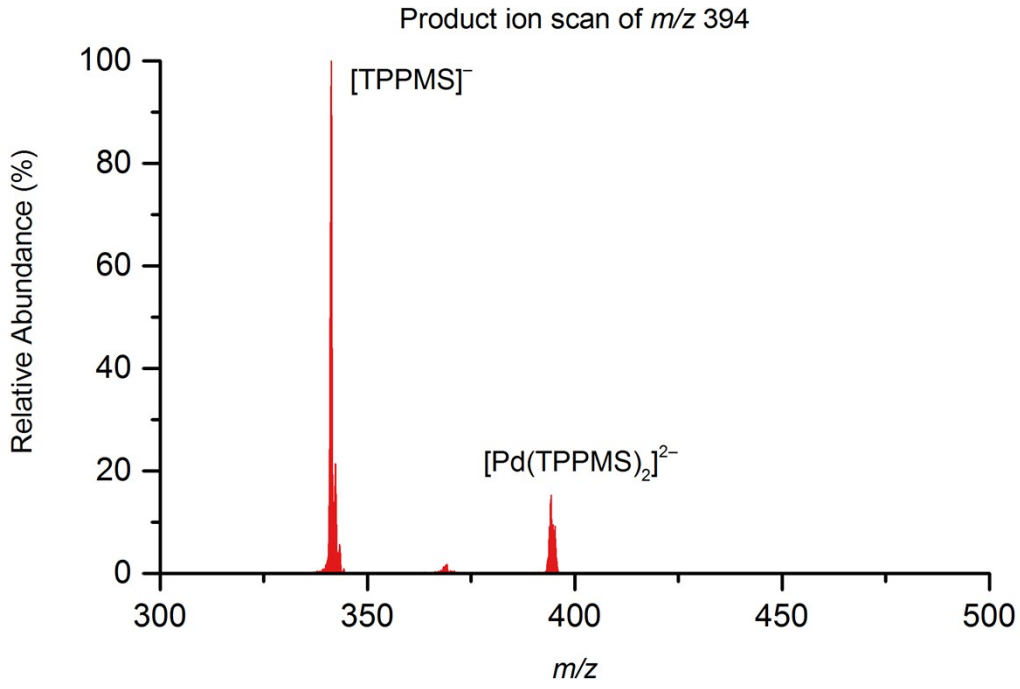

Figure S12. Product ion scan of $[Pd(TPPMS)_2]^{2-}$ (m/z 394).

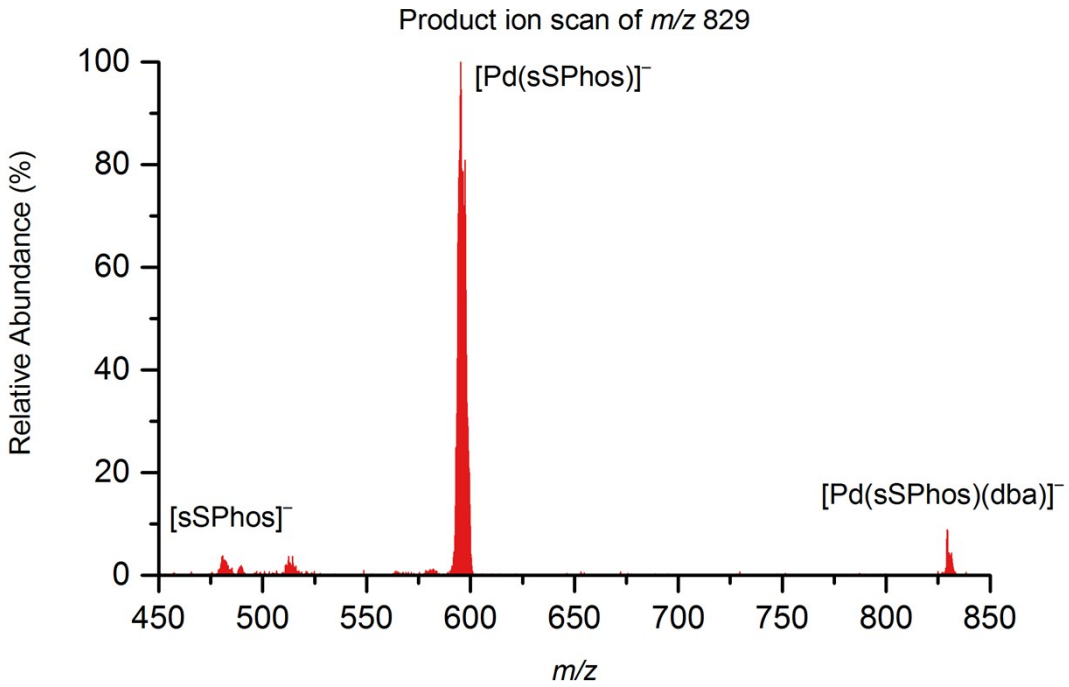

Figure S13. Product ion scan of $[Pd(sSPhos)(dba)]^-$ (m/z 829).

References

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2 M. R. Barton, Y. Zhang and J. D. Atwood, *J. Coord. Chem.*, 2002, **55**, 969.
3 K. L. Vikse, M. P. Woods and J. S. McIndoe, *Organometallics*, 2010, **29**, 6615.
4 V. A. Pashynska, M. V. Kosevich, H. Van Den Heuvel and M. Claeys, *Rapid Commun. Mass Spectrom.*, 2006, **20**, 755.