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Active Pd species in the formation of polysubstituted olefins and naphthalenes in the reaction between arylboronic acid and diphenylacetylene

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S1. Experimental

S1.1. General

All reactants and solvents were obtained from Sigma-Aldrich or Acros (grade p.a.) and were used as received without further purification or drying.

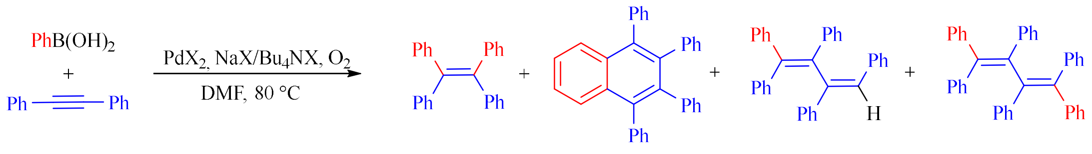
Qualitative analysis of the products formed in the catalytic reactions was performed by GC-MS (Shimadzu QP2010 Ultra, ionization energy of 70 eV, 0.25 μm × 0.25 mm × 30 m GsBP-5MS column, He as the carrier gas) using "SCAN" mode with scanning the m/z range from 18 to 999. For all the substances presented the match with the spectra from the libraries (Wiley, NIST, and NIST05) was no less than 90%. One exception was 1,2,3,4,5-pentaphenylbuta-1,3-diene for which there was no the authentic spectrum in the libraries used, and the conclusion about its formation was drawn based on the analysis of mass-spectra obtained experimentally (see below). The proposals about the identity of phenyl rings from either arylboronic acid or diphenylacetylene in the products **1-4** depicted in Scheme 1 were definitely confirmed by the analysis of the mass spectra of the reaction products obtained by varying the *para*-substituent in the benzene ring of arylboronic acid.

The quantitative compositions of the samples were determined using gas chromatography (GC) (Chromatec Crystal 5000.2 instrument fitted with a flame ionization detector [FID] and 15 m HP-5 methyl phenyl siloxane capillary column) at a 1:10 split ratio. The values of the analytical yields of the products **1-4** (Scheme 1) were calculated by the internal standard (naphthalene) method using experimental and calculated response factors determined with authentic samples and by solving the systems of material balance equations of the reactions, respectively. The material balance was calculated in each reaction mixture sample taking into account the amounts of consumed diarylacetylene and the products formed in the reaction. A deviation did not exceed 5%. Triphenylethylene (<0.5%) and biphenyl (0.5-3%) were formed as side products. To estimate the reproducibility of the data, each experiment was performed three times.

S1.2. Pd-catalyzed reaction between phenylboronic acid and diphenylacetylene

All catalytic reactions were carried out by mixing phenylboronic acid (2.5 mmol), diphenylacetylene (2.5 mmol), and naphthalene (GC internal standard, 0.5 mmol) in DMF (5 ml). Oxygen was bubbled through the resulted solution, and it was placed in a 25 ml two-necked round bottom flask equipped with a magnetic stirring bar and a septum inlet containing Pd precursor (0.04 mmol), NaOAc (0.8 mmol, if used) as the base, and Bu_4NBr (0.8 - 1.6 mmol, if used) under oxygen (balloon). The reaction was initiated by placing the reactor in a pre-heated oil bath (80ºC) with stirring (480 rpm). The reaction was continued for 30 h. The samples of the reaction mixture were collected using a syringe with a steel needle at different reaction time points. 100 µl of each sample was preliminary treated with 100 µl of toluene/water mixture (1:1) for subsequent analysis by GC.

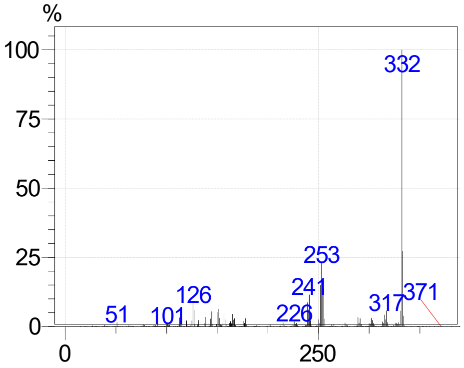
S2. Mass-spectra of the reaction products



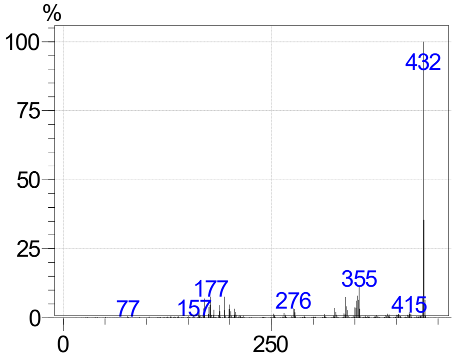
1, 1-22% **2,** 2-80% **3,** 1-9% **4,** 1-63%

X= Cl, Br, OAc **[2+1]** **[1+2-H]** **[1+2+H]** **[2+2]**

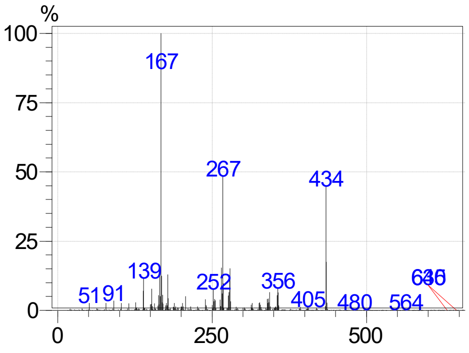
Scheme S1 Ligand-free Pd-catalyzed reaction between phenylboronic acid and diphenylacetylene.



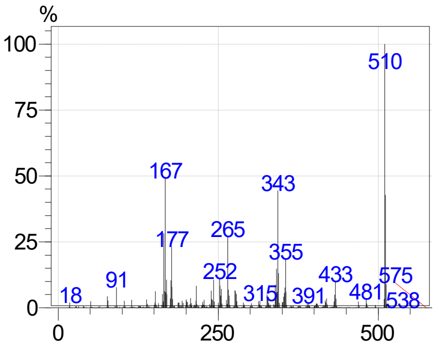
Mass-spectrum of tetraphenylethylene (product **1**, [2+1])



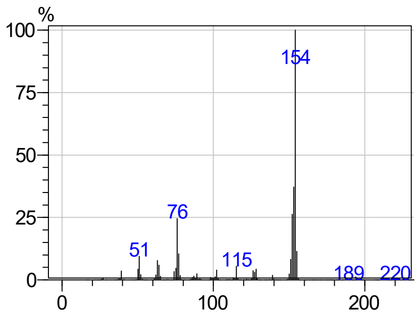
Mass-spectrum of 1,2,3,4-tetraphenylnaphthalene (product **2**, [1+2-H])



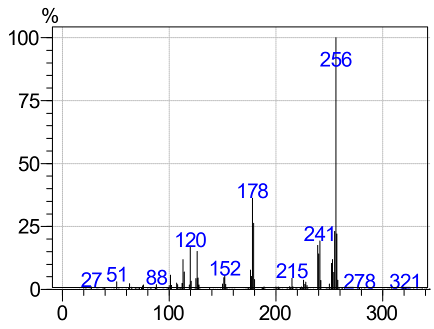
Mass-spectrum of 1,2,3,4,5-pentaphenylbuta-1,3-diene (product **3**, [1+2+H])



Mass-spectrum of hexaphenylbuta-1,3-diene (product **4**, [2+2]).



Mass-spectrum of biphenyl (side product)



Mass-spectrum of triphenylethylene (side product)