

Supporting Information**for the article****Pd₂dba₃ as a Precursor of Soluble Metal Complexes and Nanoparticles:
Determination of Pd Active Species for Catalysis and Synthesis****Sergey S. Zalesskiy, Valentine P. Ananikov ***

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1. Characterization of pure freshly synthesized $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$

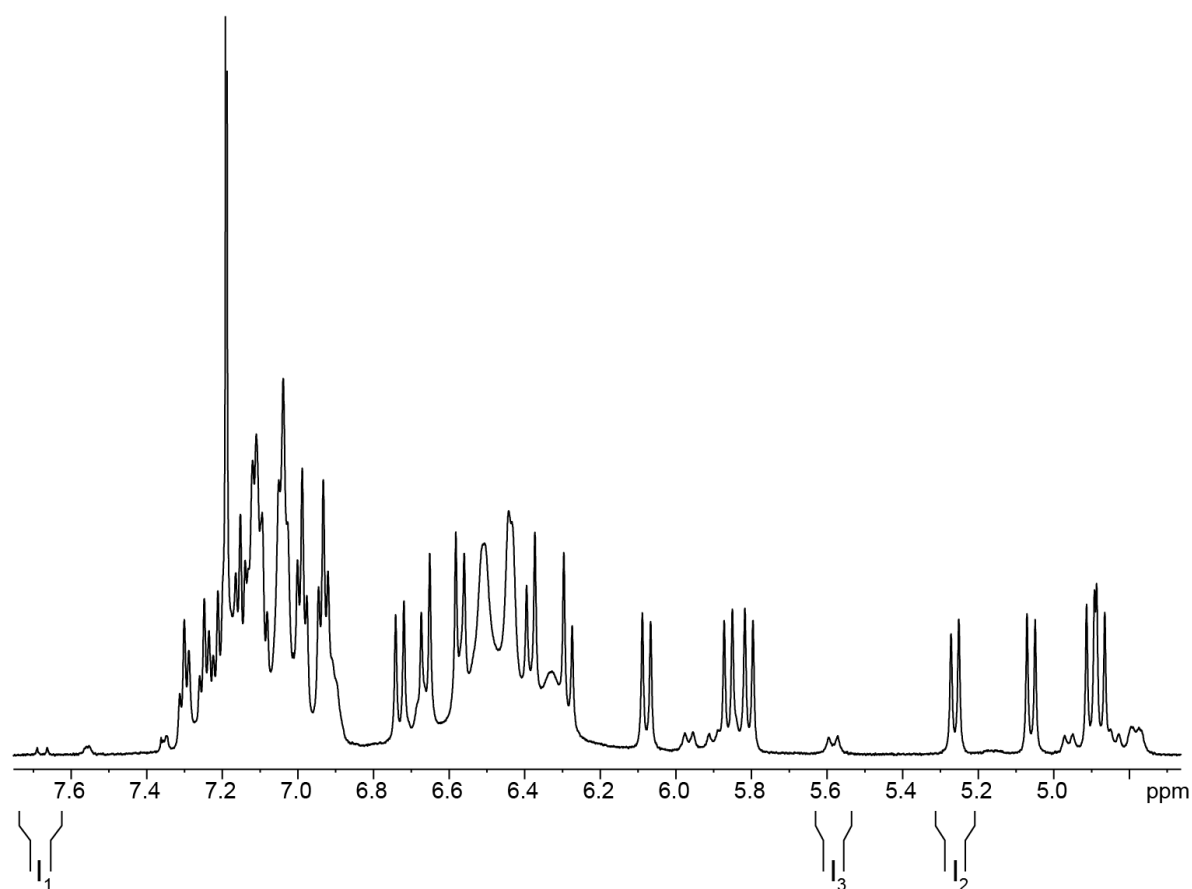


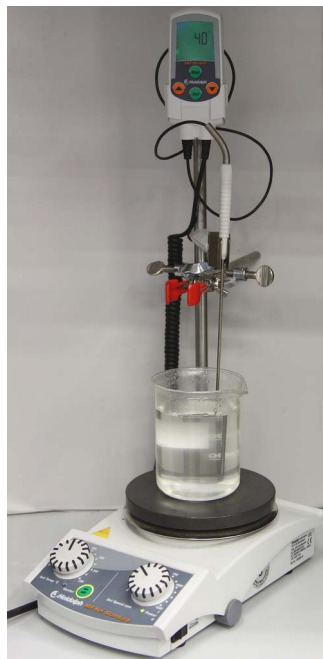
Figure S1. ^1H NMR spectrum of pure $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ in CDCl_3 at 600 MHz: $I_1 = 0.037$, $I_2 = 1.000$, $I_3 = 0.268$; calculated purity – 98.6 % (see section 2.3 for description of integral notations $I_1 - I_3$ and for the equations).

The spectrum was recorded immediately after the synthesis of $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ as described in section 4.2 of the article using experimental setup showed below in the supporting information (p. S3 – S10). Sample preparation for NMR is described in section 4.3 of the article.

2. Experimental setup used for the synthesis of $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$

Synthesis of $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ is shown on Pictures 1 – 17 (see Section 4.2 for description). The synthesis was carried out on air and we found the yield and purity of the complex well reproducible after several runs (synthesis under Ar is another possible option).

For re-purification of Pd_2dba_3 (as described in Section 4.5) the procedure shown on Pictures 12 – 17 should be utilized after removing insoluble part and evaporation of chloroform. The volumes of solvents used may be corrected depending on the amount of Pd_2dba_3 to be purified.



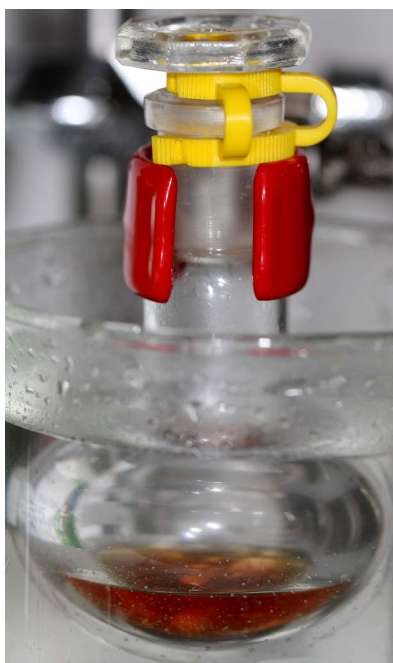
Picture 1.
Temperature stabilized magnetic stirrer used for the synthesis.



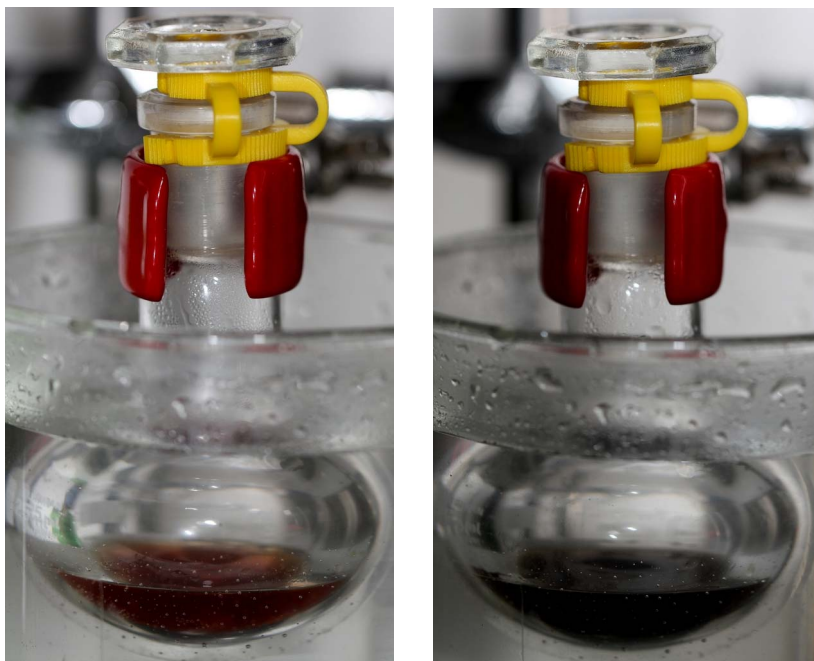
Picture 2.
All solid reagents ($\text{Pd}(\text{OAc})_2$, AcONa , and dba) were loaded into the flask.



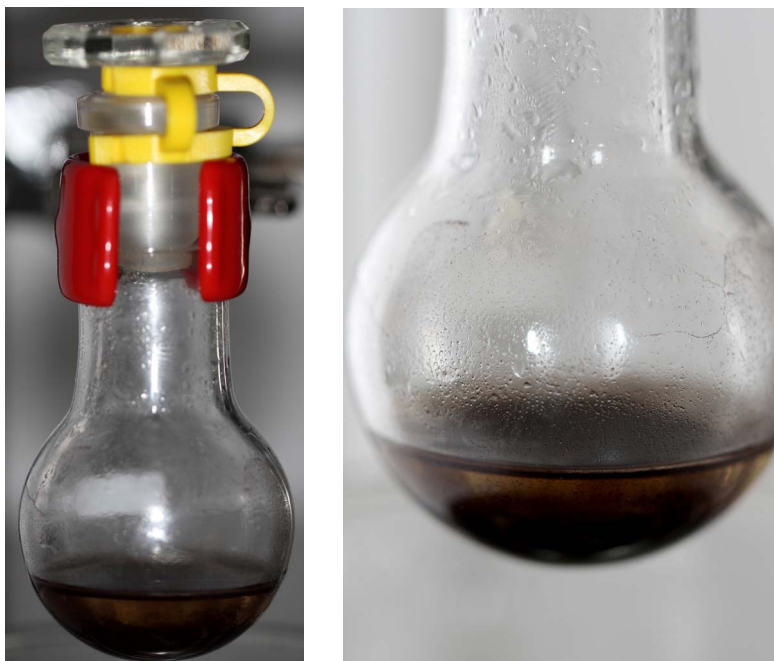
Picture 3.
Solvent (MeOH, 10 mL)
was added to the flask.



Picture 4.
Heating started with
stirring (temperature
stabilized bath, 40°C).



Picture 5.
Heating proceeded under continuous stirring.
Solution color changed to brown-black in 5 min.



Picture 6.
Heating finished after 3 h at 40°C. The reaction mixture consisted of black precipitate and yellow liquid phase.



Picture 7.
Assembly used for vacuum-filtration. Right arm of the three-way adapter was connected to vacuum (water-jet pump).



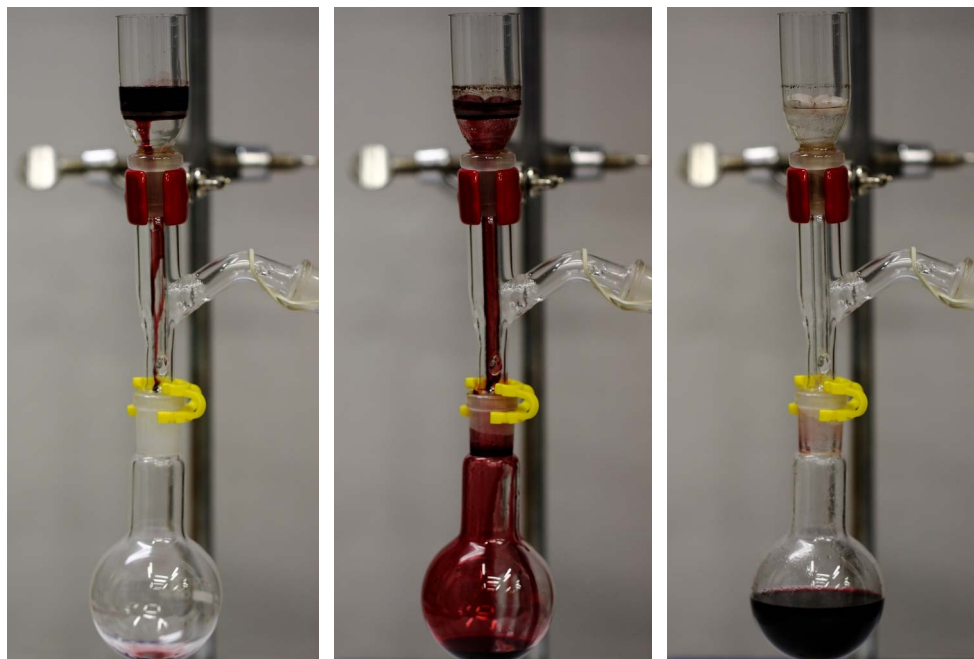
Picture 8.
Reaction mixture was filtered and washed with methanol (2×3 mL).



Picture 9.
Residue was washed with water (3×3 mL) to remove unreacted AcONa. Blue arrow indicates solid Pd_2dba_3 remained on the filter.



Picture 10.
Solid Pd_2dba_3 on the filter after washing.



Picture 11.
Solid being washed off
the filter with CHCl_3 (~25
mL). Dark solution of
 Pd_2dba_3 was collected
into the flask.



Picture 12.
 CHCl_3 was removed on
rotary evaporator (40°C,
20 mbar), reddish-brown
solid of Pd_2dba_3 was
obtained.



Picture 13.
Solid was redissolved in a minimal amount of chloroform (~ 5 mL) and gave dark purple solution.



Picture 14.
Acetone (20 mL) was added to the chloroform solution of Pd_2dba_3 . The mixture was kept overnight at -18°C .



Picture 15.
After overnight storing at -18°C . $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ was crystallized as a black precipitate at the bottom of the flask, the solution became pale red and transparent.



Picture 16.
 $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ was filtered and washed with cold acetone (5°C , 2×5 mL).



Picture 17.
The $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ product on the filter. ^1H NMR spectrum is shown on Figure S1.