# **Supplementary Information**

# The Role of Trinuclear Species in Palladium Acetate/Trifluoroacetic Acid Catalytic System

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### **Exchange experiments**

The NMR spectra were recorded on a 400 MHz and 500 MHz Bruker Avance spectrometers.

In NMR tube 50 mg of palladium(II)acetate (recrystallized, purchased from Sigma-Aldrich) was dissolved in 0.6 ml of  $CD_2Cl_2$ . Trifluoromethyl benzene (2 µL) was added into the solution as a standard for measurement of <sup>19</sup>F NMR and mesitylene for <sup>1</sup>H NMR. Trifluoroacetic acid was then added in small portions and <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded. Equilibration is fast process and there was no change in spectra measured 5 minutes after the mixing and after 15 and 30 minutes, respectively. After one day the solution with higher amount of TFA turns black and black precipitate was formed. To obtain integral values of overlapping signals the gaussian-lorentzian deconvolution implemented in Topspin was used.



Figure S1. Differences in <sup>1</sup>H NMR spectra caused by sequential addition of TFA to the  $CD_2Cl_2$  solution of palladium(II) acetate.



**Figure S2**. Detailed view and assignment of the individual signals in <sup>1</sup>H NMR.



**Figure S3**. Detailed view and assignment of the individual signals in <sup>19</sup>F NMR. Note that signal of free trifluoroacetic acid is not depicted.



**Figure S4**. Differences in <sup>13</sup>C NMR spectra caused by sequential addition of TFA to the  $CD_2Cl_2$  solution of palladium(II) acetate. Region of carbonyl groups of trifluoroacetates coordinated to the palladium.



**Figure S5**. Differences in <sup>13</sup>C NMR spectra caused by sequential addition of TFA to the  $CD_2Cl_2$  solution of palladium(II) acetate. Region of trifluoromethyl groups of trifluoroacetates coordinated to the palladium. Note that only central parts of quadruplets are depicted (central two peaks).



**Figure S6.** Sums of the <sup>19</sup>F NMR signals of trifluoroacetate methyl groups of species **2-7** plotted in dependence on OTFA/OAc ratios.

Detailed analysis of signal patterns

Signal set	<sup>1</sup> H NMR	<sup>19</sup> F NMR
1		
2		
3		
4		1 k 1 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
5	1	2 2 2 2 2 k m n o 1 p
6		
7		

**Figure S7.** Signal patterns for individual signal groups 1,2,3,4,5,6,7 obtained from <sup>1</sup>H and <sup>19</sup>F NMR. The numbers above signals show integrals of appropriate signals.

**DOSY experiments** The <sup>1</sup>H and <sup>19</sup>F DOSY experiments were measured for solutions with the OTFA/OAc ratios of 0, 0.19, 1.58, 6.3 and 15.8 using stimulated echo pulse sequence with sine-shaped gradient pulses of duration of 2 ms increased from 0.49 to 49 Gauss/cm in 16 linearly spaced steps and with diffusion time set to 50 ms.

<sup>1</sup> H NMR									
V(TFA) µL	0 µL	6 µL	50 µL	200 µL					
OTFA/OAc		0.19	1.58	6.3					
specie	diffusion coefficient ·10 <sup>9</sup> m <sup>2</sup> s <sup>-1</sup>								
toulene	3.01	2.70	2.79	3.03					
AcOH	2.54	2.40	2.22	2.19					
1	1.52	1.15							
2		1.16							
3		1.16	1.24						
4			1.25						
5			1.23	1.42					
6			1.23	1.44					
7									

Table	<b>S1</b> .	Values	of	diffusion	coeffic	ient	obtained	from	$^{1}$ H	and	<sup>19</sup> F	DOSY	NMR	spectra	by	the	addition	n of
approp	riate	amoun	t of	TFA do	the solut	ion	of 50 mg	pallad	liun	n(II) a	acet	ate in C	$^{c}D_{2}Cl_{2}.$					

<sup>19</sup> F NMR									
	6 µL	50 µL	200 µL	500 μL					
OTFA/OAc	0.19	1.58	6.3	15.8					
specie	diffusion coefficient ·10 <sup>9</sup> m <sup>2</sup> s <sup>-1</sup>								
TFA	2.05	2.32	2.34	2.01					
1									
2	1.14								
3	1.15	1.22							
4	1.14	1.24							
5		1.25	1.33						
6		1.24	1.33	0.97					
7			1.33	0.98					



**Figure S8.** Illustration of reversibility of ligand exchange. Blue line corresponds to the <sup>1</sup>H NMR spectrum of mixture containing 20 mg of palladium(II) acetate and 15  $\mu$ L of TFA in CD<sub>2</sub>Cl<sub>2</sub>. Red spectrum represents spectrum after addition of 15  $\mu$ L of acetic acid to the upper mentioned solution. There is clearly visible shift in spectral pattern to one with lower OTFA/OAc ratio.



**Figure S9.** Illustration of reversibility of ligand exchange. Blue line corresponds to the <sup>19</sup>F NMR spectrum of mixture containing 20 mg of palladium(II) acetate and 15  $\mu$ L of TFA in CD<sub>2</sub>Cl<sub>2</sub>. Red spectrum represents spectrum after addition of 15  $\mu$ L of acetic acid to the upper mentioned solution. There is clearly visible shift in spectral pattern to one with lower OTFA/OAc ratio.

#### **Kinetics experiments**

The reactions were initiated by addition of TFA in amounts corresponding to the OTFA/OAc ratios 1.65 and 2.9 to the  $CD_2Cl_2$  solution of palladium(II) acetate in NMR tube. The <sup>1</sup>H NMR spectra were measured immediately after insertion of the sample into the spectrometer without shimming.



**Figure S10.** Time dependent spectral changes in <sup>1</sup>H NMR spectra caused by addition of 10  $\mu$ L TFA to solution containing 10 mg of palladium(II) acetate in 0.5 ml CD<sub>2</sub>Cl<sub>2</sub>. First spectrum (blue) was measured 50 seconds after addition, the last one 7 minutes.



**Figure S11.** Time dependent spectral changes in <sup>1</sup>H NMR spectra caused by addition of 17  $\mu$ L TFA to solution containing 10 mg of palladium(II) acetate in 0.5 ml CD<sub>2</sub>Cl<sub>2</sub>. First spectrum (blue) was measured 50 seconds after addition, the last one 7 minutes.

#### Kinetic experiments - C-H activation of acetanilides

Various amount of TFA was added to the solution containing 10 mg (0.045 mmol) of palladium(II) acetate and 2  $\mu$ L of trifluoromethylbenzene in 0.45 ml CD<sub>2</sub>Cl<sub>2</sub>. After ten minutes, the appropriate amount of 3-bromoacetanilide was dissolved in 0.1 ml of CD<sub>2</sub>Cl<sub>2</sub> and added to the solution. The NMR spectra were measured as soon as possible after the mixing.



**Figure S12.** <sup>1</sup>H NMR spectra of the mixture containing 10 mg of palladium(II) acetate and 10 mg 4-bromoacetanilide in  $CD_2Cl_2$  collected within 4 hours.



**Figure S13.** Time dependent <sup>19</sup>F NMR spectral changes caused by addition of 10 mg 3-bromoacetanilide to the  $CD_2Cl_2$  solution of 10 mg palladium(II) acetate preactivated by 15  $\mu$ L TFA. The reaction was monitored within 90 minutes.



**Figure S14.** Time dependent <sup>1</sup>H NMR spectral changes in area of aromatic hydrogens of trinuclear (**T**) and binuclear (**D**) complexes caused by addition of 20 mg 3-bromoacetanilide to the  $CD_2Cl_2$  solution of 10 mg palladium(II) acetate preactivated by 23 µL TFA.



**Figure S15.** Time dependent <sup>1</sup>H NMR spectral changes in area of aliphatic hydrogens of trinuclear (**T**) and binuclear (**D**) complexes caused by addition of 20 mg 3-bromoacetanilide to the  $CD_2Cl_2$  solution of 10 mg palladium(II) acetate preactivated by 23 µL TFA.



**Figure S16.** Time dependent <sup>1</sup>H NMR spectral changes in area of amidic hydrogens of trinuclear (**T**) and binuclear (**D**) complexes caused by addition of 20 mg 3-bromoacetanilide to the  $CD_2Cl_2$  solution of 10 mg palladium(II) acetate preactivated by 23 µL TFA.



**Figure S17.** Differences in <sup>1</sup>H NMR spectra in area of aromatic hydrogens of trinuclear (**T**) and binuclear (**D**) complexes measured at the beginning (10 minutes) and after 90 minutes for the reaction mixtures with different stoichiometry. First five pairs from bottom correspond to the different amounts of TFA added to the equimolar mixture of 3-bromoacatanilide and palladium acetate. Next pair corresponds to two molar excess of acetanilide compared to palladium. The last pair corresponds to half amount of acetanilide compared to palladium.

#### Influence of acetanilide concentration

Time dependent changes of abundances of trinuclear complex **T** (blue), binuclear complex **D** (red), 3bromoacetanilide (purple), sum of **T**+**D** complexes (black) and precatalyst (green) caused by addition of various amount of 3-bromoacetanilide to the  $CD_2Cl_2$  solution of 10 mg (0.045 mmol) palladium(II) acetate preactivated by 23 µL (0.3 mmol) TFA.



Figure S18. anilide vs. palladium molar ratio 0.5:1



Figure S19. anilide vs. palladium molar ratio 1:1



Figure S20. anilide vs. palladium molar ratio 2:1



Figure S21. anilide vs. palladium molar ratio 5:1

#### Trinuclear complexes (T) with mixed ligand sphere

As an indirect proof of existence trinuclear complexes congaing both trifluoroacetate and acetate ligands could serve region between 1.8 and 2.0 ppm in <sup>1</sup>H NMR spectra. In case of reaction mixtures containing smaller amount of TFA, a small set of signals appears. This set could correspond to the acetates coordinated to palladium in atoms in trinuclear complexes **T**. The rich signal pattern is caused by presence of more possible isomers and various ratios of acetate and trifluoroacetate ligands present in individual complexes.



**Figure S22.** Time dependent <sup>1</sup>H NMR spectral changes in area of alyphatic hydrogens caused by addition of 2 mg 3-bromoacetanilide to the  $CD_2Cl_2$  solution of 10 mg palladium(II) acetate preactivated by 3  $\mu$ L TFA.

## Characterization of the compound Binuclear complex (D)



yellow solid

**m. p.** 165-167 °C

<sup>1</sup>**H NMR** (500 MHz, DMSO-d6): ppm 12.09 (s, 1H, NH); 7.54 (s, 1H, ArH); 7.51 (s, 2H, ArH); 2.35 (s, 3H, CH<sub>3</sub>)

<sup>13</sup>C NMR (125 MHz, DMSO-d6): ppm 169.5; 156.6; 137.8; 134.0; 127.2; 119.8; 21.7

<sup>19</sup>**F NMR** (376 MHz, DMSO-d6): -73.57 ppm

**IR** (ATR) *v*<sub>max</sub> (cm<sup>-1</sup>): 3312, 3187, 1663, 1637, 1605, 1532, 1456, 1367, 1190, 1152, 857, 733



<sup>1</sup>H NMR (DMSO-d6) spectrum of binuclear complex D.



<sup>13</sup>C NMR (DMSO-d6) spectrum of binuclear complex D.



<sup>19</sup>F NMR (DMSO-d6) spectrum of binuclear complex D.



IR (ATR) spectrum of binuclear complex D.

## Crystallography

The yellow crystals of complex **D** were collected from reaction mixture containing 10 mg 3bromoacetanilide, 10 mg of palladium(II) acetate and 3  $\mu$ L of TFA dissolved in 0.5 ml of dichloromethane after 3 hours.

The greenish crystals of complex **T** were collected from reaction mixture containing 10 mg 3bromoacetanilide, 20 mg of palladium(II) acetate and 23  $\mu$ L of TFA dissolved in 0.5 ml of dichloromethane after 2 hours.

Full sets of diffraction data for complex **D** and **T**, respectively, were collected at 150(2) K with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K<sub> $\alpha$ </sub> radiation;  $\lambda = 0.71073$  Å) microfocus X-ray (IµS) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection.

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2014/7 software implemented in APEX3 v2016.5-0 (Bruker AXS) system.<sup>1</sup> Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors  $H_{iso}(H) = 1.2 U_{eq}$  (pivot atom) or of  $1.5U_{eq}$  (methyl). H atoms in methyl moieties and hydrogen atoms in aromatic rings were placed with C–H distances of 0.96 and 0.93 Å and 0.86 Å for N–H bonds.

 $R_{\text{int}} = \sum |F_{o}^{2} - F_{o,\text{mean}}^{2}| / \sum F_{o}^{2}, \ S = [\sum (w(F_{o}^{2} - F_{c}^{2})^{2}) / (N_{\text{diffrs}} - N_{\text{params}})]^{\frac{1}{2}} \text{ for all data, } R(F) = \sum |F_{o}| - |F_{c}| |/\sum |F_{o}| \text{ for observed data, } wR(F^{2}) = [\sum (w(F_{o}^{2} - F_{c}^{2})^{2}) / (\sum w(F_{o}^{2})^{2})]^{\frac{1}{2}} \text{ for all data.}$ 

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1561485 for **T** and 1561486 for **D**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Both crystals of **D** and **T** contain disordered solvent molecules. Attempts were made to model these disorders or split it into two positions, but were unsuccessful. PLATON/SQUEZZE<sup>2</sup> was used to correct the data for the presence of disordered solvent. In the crystal of **T**, a potential solvent volume of 825 Å<sup>3</sup> was found. 235 electrons per unit cell worth of scattering were located in the void which corresponds the composition **T**'(CH<sub>3</sub>COOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>. For crystal of **D**, the composition was estimated to be **D**'(CH<sub>3</sub>COOH)<sub>2</sub>(H<sub>2</sub>O)<sub>1.5</sub> based on identified voids of 5925 Å<sup>3</sup> corresponding to 1368 electrons. Crystals of **T** are instable and as such not suitable for a long time measurements, where a presence of small particles presumably of elemental palladium were observable inside the crystal after an overnight experiment. Crystallographic data and structural refinement parameters for yellow single crystal of **D**:  $C_{24}H_{25}Br_{2}F_{6}N_{2}O_{11.5}Pd_{2}$ , M = 1012.08, trigonal, *R*-3c, *a* = 26.0800(17), *b*=26.0800(17), *c*=28.279(2) Å, Z = 18, V = 16657(2) Å^{3}, D<sub>c</sub> = 1.816 g.cm<sup>-3</sup>,  $\mu = 3.213$  mm<sup>-1</sup>, T<sub>min</sub>/T<sub>max</sub> = 0.4095/0.7454; -32 ≤ h ≤ 32, -29 ≤ k ≤ 31, -35 ≤ 1 ≤ 35; 67607 reflections measured ( $\theta_{max} = 26.35^{\circ}$ ), 3762 independent (R<sub>int</sub> = 0.0337), 2764 with  $I > 2\sigma(I)$ , 173 parameters, S = 1.033, *R1*(obs. data) = 0.0473, *wR2*(all data) = 0.1071; max., min. residual electron density = 1.068, - -0.923 eÅ<sup>-3</sup>.

Crystallographic data and structural refinement parameters for greenish single crystal of **T**:  $C_{28}H_{24}Br_{2}F_{12}N_{2}O_{16}Pd_{3}$ , M = 1351.51, triclinic, *P*-1, *a* = 11.5323(14), *b* = 17.832(2), *c* = 18.105(2) Å,  $\alpha$ = 112.321(6),  $\beta$  = 96.629(6),  $\gamma$  = 105.443(5) °, Z = 3, V = 3220.4(7) Å<sup>3</sup>, D<sub>c</sub> = 2.091 g.cm<sup>-3</sup>,  $\mu$  = 3.223 mm<sup>-1</sup>, T<sub>min</sub>/T<sub>max</sub> = 0.472/0.745; -14 ≤ h ≤ 14, -22 ≤ k ≤ 22, -22 ≤ 1 ≤ 22; 43887 reflections measured ( $\theta_{max}$  = 26.85°), 13330 independent (R<sub>int</sub> = 0.0697), 8562 with *I* > 2 $\sigma$ (*I*), 732 parameters, S = 1.124, *R1*(obs. data) = 0.0755, *wR2*(all data) = 0.1942; max., min. residual electron density = 2.223, -1.847 eÅ<sup>-3</sup>.

#### Discussion

Both crystallized complexes **D** and **T** were subjected to sc-XRD analysis which confirmed its composition. The binuclear species of **D** is made of two palladium atoms separated by 2.893(3) Å (for all the parameters see attached Crystallographic Information Files) which is approaching the sum of covalent radii of 2.4 Å.<sup>3</sup> These atoms are interconnected by two trifluoroacetate units revealing the isobidentate bridging bonding fashion and the *cis*-coordination to each palladium. Distances between the oxygen and palladium atoms are in the range of ~ 2.05-2.20 Å which is slightly elongated when compared to the sum of covalent radii of both atoms being 1.83 Å. On the other hand, purely donor-acceptor bonds of the carbonyl groups of *otho*-metallated ligand is a bit shorter (1.991(3) Å) revealing thus a strong coordination. Both ligands are situated in a *syn*-arrangement with rather sharp interplanar angle of 25.73(12)° caused by the constraints of trifluoroacetyl groups. Similar binuclear arrangement of palladium complexes is already reported by Dong and others<sup>4</sup> who isolated them mainly during the palladium catallyzed *ortho*-arylation of phenylacetamides, benzamides, and anilides. From the point of view of a supramolecular architecture, the neighboring molecules are interconnected by the H-bridges from the NH groups to the one of the oxygen atoms of the trifluoracetate groups to the three dimensional network.

Two types of a trinuclear palladium acetate complexes were identified in the literature whereas the first are a triangular-like simple acetates<sup>5</sup> and the second, the linear-like type isolated mainly from the *ortho*-metallation of different aryl species containing a donor group in a convenient position.<sup>6</sup>

These three structures significantly resemble the arrangement of the complex **T** where three palladium atoms are linearly bound by four trifluoroacetate units revealing the same Pd-Pd distances and the bonding fashion as in **D**. In the crystal of **T**, three crystallographically independent molecules with rather similar interatomic distances and angles were found. Much closer separations between Pd–O atoms from the trifluoroacetate were determined in **T** (~2.0 Å) than in **D** while the rest of the separations of atoms found in the palladium coordination spheres are the same. The coplanar and mutual *anti*-orientation of the chelating aryl ligand bound to the terminal palladium atoms is caused by the electronic repulsion of these ligands and trifluoroacetate groups. The carbonyl groups are slightly deviated from the planar arrangement of the ligands most probably by the same reason. Again the supramolecular network of the molecules of **T** is made by the same type of the H-bonds.

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