Rutile-deposited PtPd clusters: a hypothesis regarding the stability at 50/50 ratio

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Supporting Information

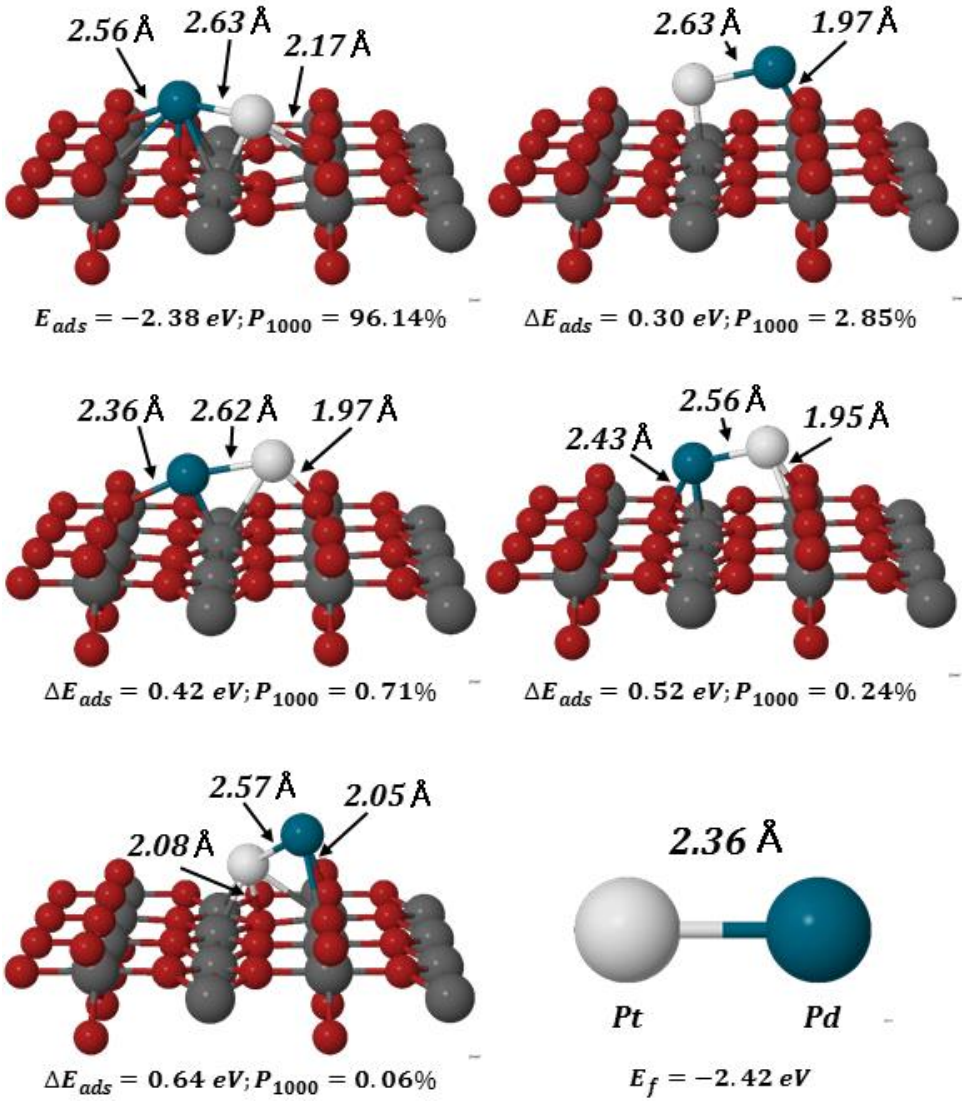

Figure S1. Structures of the gas phase and surface-deposited dimers: both the global and low-energy local minima are shown, with their relative energies and Boltzmann populations at 1,000 K. The absolute adsorption energy is displayed for the global minimum, all adsorption energies following the global minimum are relative adsorption energies.

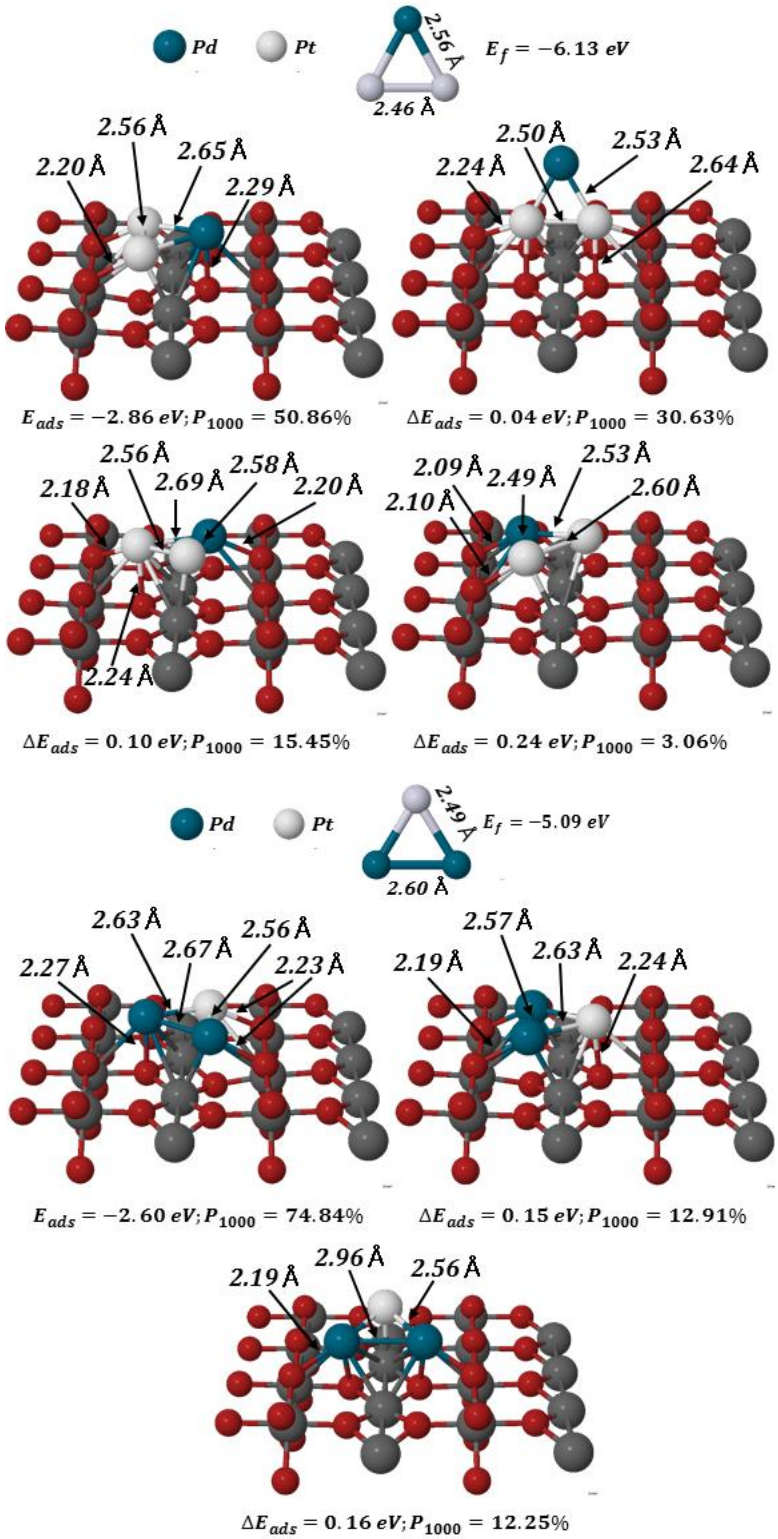

Figure S2. Structures of the gas phase and surface-deposited Pt_2Pd (left) and Pd_2Pt (right) trimers: both the global and low-energy local minima are shown, with their relative energies and Boltzmann populations at 1,000 K.

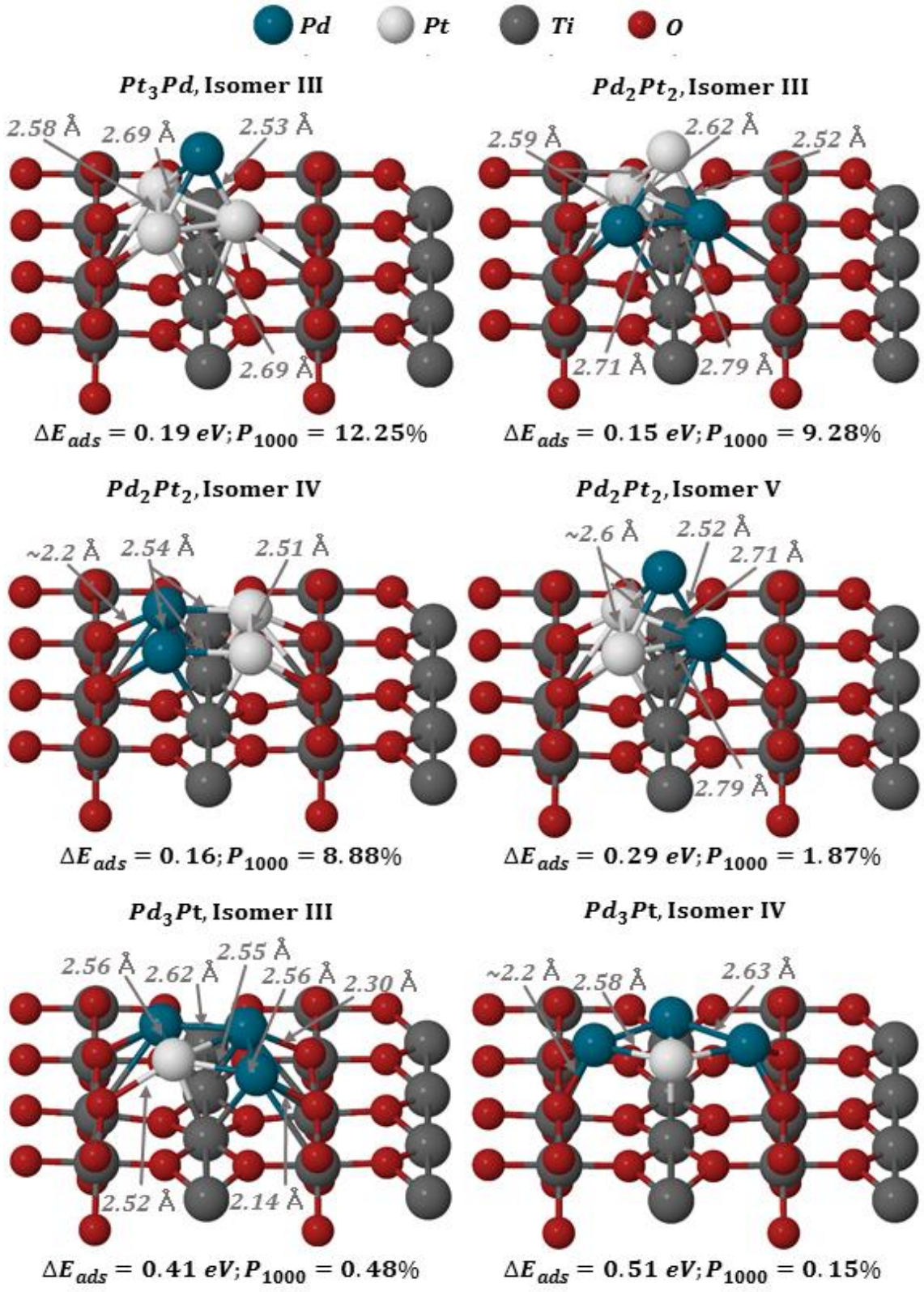

Figure S3. Less probable structures of the surface-deposited tetramers, with their relative energies and Boltzmann populations at 1,000 K. Pd_3Pt Isomers III and IV are structures,

which minimize coordination to surface oxygen due to their distortion into a rhombus or a diamond.

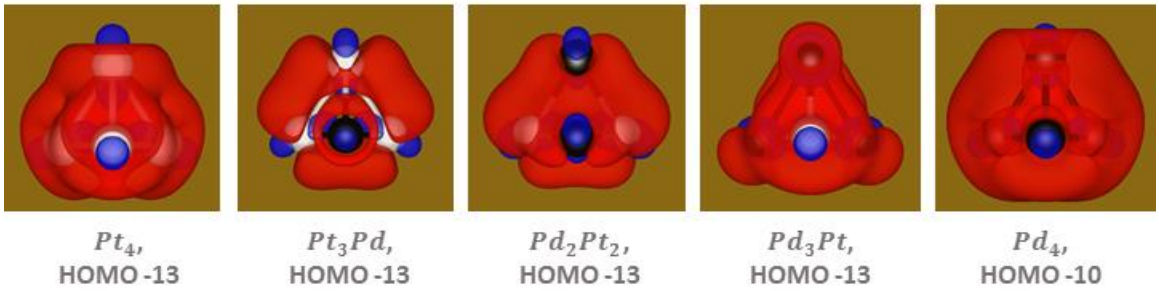

Figure S4. σ- aromaticity of gas-phase global minima clusters; for clarity, Pt is white and Pd is black.

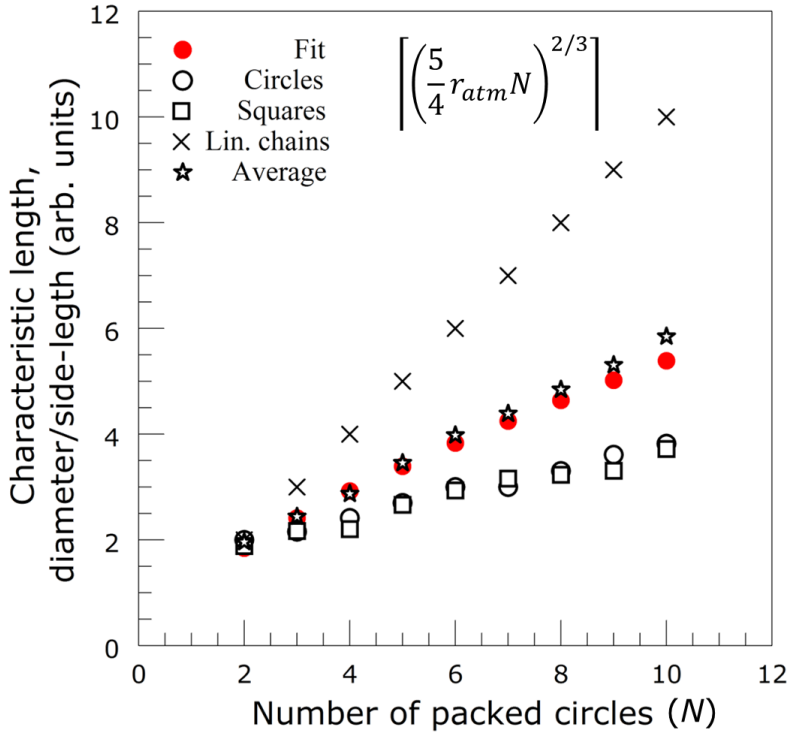

Figure S5. Analytical fit to the average size of a particle formed by optimally packing unit-circles into circles, squares, and linear chains. Used to ensure that a monomer properly dissociates from a filamentary-like *N*-mer; relevant due to the finer grid-spacing in the new sintering model.

Table S1. Calculated relative energies of the gas phase Pt_4 tetramers. Comparison of TPSS(h)/aug-cc-pVTZ and PW-DFT results.

Method	Isomer I (eV), Tetrahedral	Isomer II (eV), Planar
TPSS/aug-cc-pVTZ-PP	-10.75, C_{3v}, 3 [1]	-10.45, D_{2h}, 3 [2]
TPSSh/aug-cc-pVTZ-PP	-9.86, T_d, 3 [3]	-9.57, D_{4h}, 1 [4]

[1] The T_d structure is slightly higher in energy (~1 kcal/mol) and has two imaginary frequencies.
[2] The quintet is slightly lower in energy (~1 kcal/mol), but is a transition state; both D_{2h} structures are favored over D_{4h} ones.
[3] The quintet differs by ~2 kcal/mol, but contains two imaginary frequencies.
[4] The quintet differs by ~4 kcal/mol; both the singlet and quintet are transition states.

Table S2. Calculated relative energies of the gas phase Pd_1Pt_3 tetramers. Comparison of TPSS(h)/aug-cc-pVTZ and PW-DFT results.

Method	Isomer I (eV), Tetrahedral	Isomer II (eV), Planar
TPSS/aug-cc-pVTZ-PP	-9.75, C_{3v}, 3	-9.48, C_{2v}, 5 [1]
TPSSh/aug-cc-pVTZ-PP	-9.26, C_1, 3	-8.55, C_{2v}, 1 [2]

[1] The triplet is degenerate, differing by < 1 kcal/mol; both are local minima with no imaginary frequencies.
[2] The triplet is degenerate, differing only by half a kcal/mol; the singlet is a transition state, while the triplet is a local minimum.

Table S3. Calculated relative energies of the gas phase Pd_2Pt_2 tetramers. Comparison of TPSS(h)/aug-cc-pVTZ and PW-DFT results.

Method	Isomer I (eV), Tetrahedral	Isomer II (eV), PdPdPtPt (planar)	Isomer III (eV), PdPtPdPt (planar)
TPSS/aug-cc-pVTZ-PP	-8.75, C_{2v}, 3	-8.48, C_{2v}, 3 [1]	-8.39, D_{2h}, 3 [1, 2]
TPSSh/aug-cc-pVTZ-PP	-8.52, C_{2v}, 3	-7.59, C_{2v}, 3 [1]	-7.50, D_{2h}, 1 [1]

[1] Transition-state.
[2] The singlet is degenerate, slightly higher in energy by ~ 1 kcal/mol.

Table S4. Calculated relative energies of the gas phase Pd_3Pt tetramers. Comparison of TPSS(h)/aug-cc-pVTZ and PW-DFT results.

Method	Isomer I (eV), Tetrahedral	Isomer II (eV), Planar
TPSS/aug-cc-pVTZ-PP	-8.40, C_{3v}, 3	-7.40, C_{2v}, 1 [1]
TPSSh/aug-cc-pVTZ-PP	-7.67, C_{3v}, 3	-6.55, C_{2v}, 1 [1]

[1] Transition-state.

Table S5. Calculated relative energies of the gas phase Pd_4 tetramers. Comparison of TPSS(h)/aug-cc-pVTZ and PW-DFT results.

Method	Isomer I (eV), Tetrahedral	Isomer II (eV), Planar
TPSS/aug-cc-pVTZ-PP	-7.32, C_1, 3 [1]	-6.36, D_{4h}, 1 [2]
TPSSh/aug-cc-pVTZ-PP	-6.56, C_1, 3 [3]	-5.49, D_{4h}, 1 [2]

[1] The T_d structure is slightly higher in energy (< 1 kcal/mol) and has two imaginary frequencies.
[2] Transition-state.
[3] The T_d and C_{3v} structures are slightly higher in energy (< 1 kcal/mol) and have two imaginary frequencies

Table S6. NBO Population Analysis of Charges at higher levels of theory compared to Quantum Espresso of Planar Structures of Mixed Gas Phase Clusters[1]

	TPSSh/NBO				**QE/Bader**
Config.	Spin	Atom	Natural Charge[2]	Valence Charge	Valence Charge
Pt_3Pd	1	Pd	0.20990	0.21	0.21
		Pt	-0.03374	-0.04	0.02
		Pt	-0.08808	-0.08	-0.11
		Pt	-0.08808	-0.08	-0.11
Pd_2Pt_2	3	Pd	0.10776	0.11	0.12
(PdPdPtPt)		Pt	-0.10776	-0.10	0.00
		Pd	0.10776	0.11	0.02
		Pt	-0.10776	-0.10	-0.15
Pd_2Pt_2	1	Pt	-0.18063	-0.18	-0.13
(PdPtPdPt)		Pt	-0.18063	-0.18	-0.13
		Pd	0.18063	0.19	0.13
		Pd	0.18063	0.19	0.13
Pd_3Pt	1	Pt	-0.25211	-0.26	-0.12
		Pd	0.06741	0.06	-0.07
		Pd	0.09235	0.09	0.09
		Pd	0.09235	0.09	0.09

[1] Pure Pd and Pt planar structures demonstrated charges of 0.00 in the singlet and triplet state. Only in the quintet state did the atoms attain a charge, Pt_4 alternated a natural charge of -/+ 0.13621 e/Pt and Pd_4 alternated -/+ 0.18843 e/Pd for a summation of 0.00 natural charge.
[2] The natural charge in Gaussian 09 considers shifts in electronic population between the core, valence, and Rydberg states.

Table S7. NBO Population Analysis of Charges at higher levels of theory compared to Quantum Espresso of Tetrahedral Structures of Mixed Gas Phase Clusters[1]

	TPSSh/NBO				QE/Bader
Config.	Spin	Atom	Natural Charge[2]	Valence Charge	Valence Charge
Pt_3Pd	3	Pd	0.17514	0.19	0.15
		Pt	-0.10488	-0.11	-0.10
		Pt	-0.03510	-0.05	-0.05
		Pt	-0.03510	-0.05	0.00
Pd_2Pt_2	3	Pt	-0.12715	-0.13	-0.16
		Pt	-0.12715	-0.13	-0.05
		Pd	0.12715	0.13	0.11
		Pd	0.12715	0.13	0.10
Pd_3Pt	3	Pt	-0.19381	-0.19	-0.17
		Pd	0.06459	0.07	0.09
		Pd	0.06461	0.07	0.05
		Pd	0.06461	0.07	0.02

[1] Pure Pd and Pt tetrahedral structures demonstrated charges of 0.00.

[2] The natural charge in Gaussian 09 considers shifts in electronic population between the core, valence, and Rydberg states.