Supporting Information of:

DFT Global Optimisation of Gas-phase and MgO-supported Sub-nanometre AuPd Clusters

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Tables S1 and S2 contain energies, structures and point group symmetries for all free studied clusters. Table S3 contains total energies for all compositions of MgO(100)-supported clusters. Tables S4 and S5 contain Excess Energies Δ and Binding Energies E_b (gas phase only), Adsorption Energies E_{ads} (surface supported only), and the second difference in energy $\Delta_2 E$ for the studied clusters. Tables S6-S9 contain the energies and structures for homotops of the free monosubstituted clusters and some supported clusters.

Table S1: The energies, structures, and point groups for Au_N and Pd_N clusters, N= 4-10.

Composition	E / eV	Structure	Point Group
Au_4	-6.9261	Rhombic Planar	D_{2h}
Au_5	-9.3888	M-like planar	C_{2v}
Au_6	-12.6879	Planar triangle	D_{3h}
Au_7	-14.4817	Edge-bridged planar triangle	C_s
Au_8	-17.5334	Planar	D_{4h}
Au_9	-19.6323	Planar	C_{2v}
Au_{10}	-22.4613	Planar	C_s
Pd_4	-12.6642	Tetrahedron	T_d
Pd_5	-16.4666	Trigonal bipyramid	D_{3h}
Pd_6	-20.5537	Octahedron	O_h
Pd_7	-24.2169	Capped octahedron	C_{3v}
Pd_8	-28.3425	$\triangle$-Dodecahedron	D_{2d}
Pd_9	-32.7178	Two face sharing octahedron	D_{3h}
Pd_{10}	-36.8133	Icosahedral fragment	C_{3v}

Table S2: The energies, structures, and point groups for all compositions of Au_mPd_n clusters, (m+n)= 4-10.

Composition	E / eV	Structure	Point Group
Au_1Pd_3	-11.2109	Tetrahedron	C_{3v}
Au_2Pd_2	-9.7968	Tetrahedron	C_{2v}
Au_3Pd_1	-8.3892	Planar	C_{2v}
Au_1Pd_4	-15.0785	Trigonal bipyramid	C_{2v}
Au_2Pd_3	-13.8296	Trigonal bipyramid	D_{3h}
Au_3Pd_2	-12.2638	Trigonal bipyramid	C_{2v}
Au_4Pd_1	-10.9688	M-like planar	C_{2v}
Au_1Pd_5	-18.9518	Octahedron	C_{4v}
Au_2Pd_4	-17.6879	Bicapped Tetrahedron	C_{2v}
Au_3Pd_3	-16.1603	Bicapped Tetrahedron	C_s
Au_4Pd_2	-14.8270	Edge-bridged trigonal bipyramid	C_1
Au_5Pd_1	-13.6389	Triangle Planar	C_{2v}
Au_1Pd_6	-23.2010	Capped octahedron	C_{3v}
Au_2Pd_5	-21.8573	Capped octahedron	C_s
Au_3Pd_4	-20.4696	Edge-bridged bicapped Tetrahedron	C_{2v}
Au_4Pd_3	-19.2146	Edge-bridged bicapped Tetrahedron	C_s
Au_5Pd_2	-17.6645	Edge-bridged bicapped Tetrahedron	C_2
Au_6Pd_1	-16.5348	Planar hexagon	D_{3d}
Au_1Pd_7	-27.1492	Bicapped octahedron	C_{3v}
Au_2Pd_6	-25.9037	Bicapped octahedron	D_{3d}
Au_3Pd_5	-24.7344	Meta-bicapped octahedron	C_{2v}
Au_4Pd_4	-23.2697	Meta-bicapped octahedron	C_{2v}
Au_5Pd_3	-21.8577	Edge-bridged pentagonal bipyramid	C_{2v}
Au_6Pd_2	-20.4650	Hexagonal bipyramid	C_{2v}
Au_7Pd_1	-18.8431	Edge-bridged planar hexagon	C_{2v}
Au_1Pd_8	-31.3585	Face-sharing bioctahedra	C_s
Au_2Pd_7	-30.0058	Fused octahedron with trigonal bipyramid	C_s
Au_3Pd_6	-28.8358	Fused octahedron with trigonal bipyramid	C_1
Au_4Pd_5	-27.3847	Fused octahedron with trigonal bipyramid	C_1
Au_5Pd_4	-26.0664	Fused octahedron with trigonal bipyramid	C_2
Au_6Pd_3	-24.5009	Incomplete fragment of centered icosahedra	C_{2v}
Au_7Pd_2	-23.0921	Bicapped pentagonal bipyramid	C_2
Au_8Pd_1	-21.7874	Two edge-capped planar hexagon	D_{2h}
Au_1Pd_9	-35.6073	Capped 2 face-sharing octahedron	C_{2h}
Au_2Pd_8	-34.3625	Capped 2 face-sharing octahedron	C_1
Au_3Pd_7	-33.0843	Capped 2 face-sharing octahedron	C_s
Au_4Pd_6	-31.6600	Tetrahedral tetracapped octahedron	C_1
Au_5Pd_5	-30.3728	Tetrahedral tetracapped octahedron	C_s
Au_6Pd_4	-28.97655	Tetrahedral tetracapped octahedron	D_{2d}
Au_7Pd_3	-27.4580	Tetrahedral tetracapped octahedron	C_{3v}
Au_8Pd_2	-26.0937	Tetrahedral tetracapped octahedron	C_2
Au_9Pd_1	-24.0365	Planar bihexagon	C_{2v}

Table S3: The total energies for all compositions of MgO(100)-supported clusters, N= 4-10.

Cluster	E / eV	Cluster	E / eV	Cluster	E / eV
Pd_4	-426.5281	Au_1Pd_3	-425.3348	Au_2Pd_2	-423.5336
Au_3Pd_1	-422.0454	Au_4	-420.6899		
Pd_5	-430.6890	Au_1Pd_4	-429.3689	Au_2Pd_3	-427.5820
Au_3Pd_2	-426.5624	Au_4Pd_1	-424.8570	Au_5	-422.7648
Pd_6	-434.7030	Au_1Pd_5	-433.2432	Au_2Pd_4	-431.9594
Au_3Pd_3	-430.7069	Au_4Pd_2	-428.8707	Au_5Pd_1	-427.7307
Au_6	-426.1135				
Pd_7	-438.9562	Au_1Pd_6	-437.5350	Au_2Pd_5	-436.2389
Au_3Pd_4	-434.6519	Au_4Pd_3	-433.2087	Au_5Pd_2	-431.6248
Au_6Pd_1	-429.9350	Au_7	-428.1261		
Pd_8	-443.1357	Au_1Pd_7	-441.9092	Au_2Pd_6	-440.6321
Au_3Pd_5	-439.0318	Au_4Pd_4	-437.3377	Au_5Pd_3	-436.4834
Au_6Pd_2	-433.6166	Au_7Pd_1	-432.4803	Au_8	-431.0780
Pd_9	-447.3397	Au_1Pd_8	-445.9536	Au_2Pd_7	-444.1691
Au_3Pd_6	-443.2809	Au_4Pd_5	-441.9145	Au_5Pd_4	-440.3918
Au_6Pd_3	-438.2770	Au_7Pd_2	-436.9025	Au_8Pd_1	-435.7250
Au_9	-433.7606				
Pd_{10}	-451.7787	Au_1Pd_9	-450.4100	Au_2Pd_8	-448.9302
Au_3Pd_7	-447.6585	Au_4Pd_6	-446.3715	Au_5Pd_5	-444.3350
Au_6Pd_4	-442.6103	Au_7Pd_3	-441.1485	Au_8Pd_2	-439.2605
Au_9Pd_1	-437.4065	Au_{10}	-435.6699		

Table S4: Excess Energy Δ and Binding Energy E_b (gas phase only), Adsorption Energy E_{ads} (surface supported only), and the second difference in energy $\Delta_2 E$ for 4 to 8 atoms.

	Gas Phase			Surface Supported	
	Δ/eV	Δ_2E/eV	E_b/eV	Δ_2E/eV	E_{ads}/eV
Pd_4	0.0000	—	1.6952	—	-2.0092
Au_1Pd_3	0.0187	—	1.6969	—	-2.0963
Au_2Pd_2	-0.0016	—	1.7084	—	-1.9783
Au_3Pd_1	-0.0285	—	1.7215	—	-1.9191
Au_4	0.0000	—	1.7208	—	-1.8889
Pd_5	0.0000	-0.2846	1.8225	0.0734	-2.4288
Au_1Pd_4	-0.0274	—	1.8369	—	-2.4178
Au_2Pd_3	-0.1941	—	1.8791	—	-2.2299
Au_3Pd_2	-0.0438	—	1.8601	—	-3.8606
Au_4Pd_1	-0.1644	—	1.8910	—	-2.5606
Au_5	0.0000	-0.8363	1.8670	-0.6368	-1.5048
Pd_6	0.0000	0.4238	1.9548	-0.1196	-2.5392
Au_1Pd_5	0.2909	—	1.9312	—	-2.5511
Au_2Pd_4	0.2550	—	1.9620	—	-2.4559
Au_3Pd_3	0.4604	—	1.9526	—	-4.7531
Au_4Pd_2	0.4828	—	1.9737	—	-3.2158
Au_5Pd_1	0.3599	—	2.0191	—	-2.0625
Au_6	0.0000	1.5052	2.1039	0.6680	-1.5551
Pd_7	0.0000	-0.4624	1.9887	0.0369	-2.8856
Au_1Pd_6	-0.3748	—	2.0522	—	-2.6424
Au_2Pd_5	-0.4219	—	2.0688	—	-3.7557
Au_3Pd_4	-0.4249	—	2.0791	—	-2.8437
Au_4Pd_3	-0.5607	—	2.1084	—	-1.7859
Au_5Pd_2	-0.4013	—	2.0971	—	-2.0666
Au_6Pd_1	-0.6623	—	2.1428	—	-2.3772
Au_7	0.0000	-1.2579	2.0581	-0.4697	-1.3326
Pd_8	0.0000	-0.24974	2.07199	-0.0122	-2.9827
Au_1Pd_7	-0.1578	—	2.1053	—	-3.1149
Au_2Pd_6	-0.2634	—	2.1321	—	-4.0233
Au_3Pd_5	-0.4453	—	2.1685	—	-4.7494
Au_4Pd_4	-0.3317	—	2.1679	—	-3.4934
Au_5Pd_3	-0.2708	—	2.1739	—	-2.7661
Au_6Pd_2	-0.2293	—	2.1823	—	-2.5308
Au_7Pd_1	0.0414	—	2.1621	—	-2.6648
Au_8	0.0000	0.95281	2.1809	0.1347	-2.3324

Table S5: Excess Energy Δ and Binding Energy E_b (gas phase only), Adsorption Energy E_{ads} (surface supported only), and the second difference in energy $\Delta_2 E$ for 9 and 10 atoms.

	Gas Phase			Surface Supported	
	Δ/eV	Δ_2E/eV	E_b/eV	Δ_2E/eV	E_{ads}/eV
Pd_9	0.0000	0.2797	2.1645	-0.1175	-2.7822
Au_1Pd_8	-0.0946	—	2.1757	—	-3.4869
Au_2Pd_7	-0.1958	—	2.1876	—	-2.6532
Au_3Pd_6	-0.4798	—	2.2198	—	-3.2611
Au_4Pd_5	-0.4827	—	2.2208	—	-2.9025
Au_5Pd_4	-0.6183	—	2.2366	—	-2.6899
Au_6Pd_3	-0.5519	—	2.2249	—	-3.0183
Au_7Pd_2	-0.5519	—	2.2306	—	-2.4475
Au_8Pd_1	-0.7011	—	2.2478	—	-5.4071
Au_9	0.0000	-0.7300	2.1706	0.3865	-2.2012
Pd_{10}	0.0000	—	2.2105	—	-3.4407
Au_1Pd_9	-0.2291	—	2.2359	—	-4.2517
Au_2Pd_8	-0.4196	—	2.2574	—	-3.6512
Au_3Pd_7	-0.5766	—	2.2756	—	-3.1747
Au_4Pd_6	-0.5801	—	2.2784	—	-3.0033
Au_5Pd_5	-0.7355	—	2.2965	—	-3.4862
Au_6Pd_4	-0.8743	—	2.3128	—	-2.5966
Au_7Pd_3	-0.6911	—	2.2970	—	-2.7252
Au_8Pd_2	-0.7620	—	2.3066	—	-1.6295
Au_9Pd_1	-0.1399	—	2.2469	—	-2.3352
Au_{10}	0.0000	—	2.2354	—	-1.5802

Table S6: The energies and structures for homotops of the free monosubstituted clusters, N=4-7.

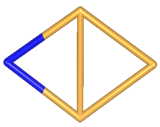
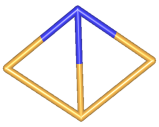
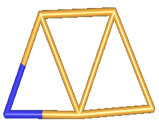
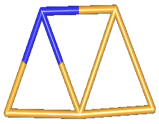
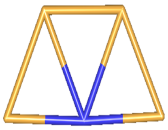
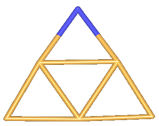
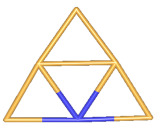
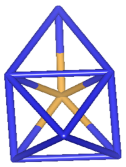
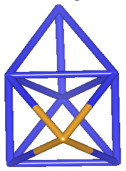
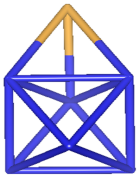
Size, N	Composition	Homotop, E/eV	GM, E/eV
4	Au_3Pd_1	 -7.8866	 -8.3892
5	Au_1Pd_4	 -14.0342	 -15.0785
5	Au_4Pd_1	 -10.0001  -10.0477	 -10.9688
6	Au_5Pd_1	 -10.7715	 -13.6389
7	Au_1Pd_6	 -21.2622  -23.0893	 -23.2010

Table S7: The energies and structures for homotops of the free monosubstituted clusters, N=7-9.

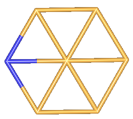
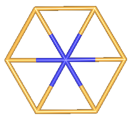
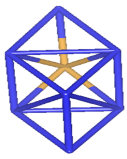
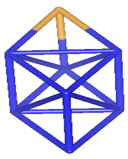
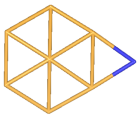
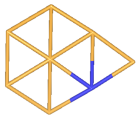
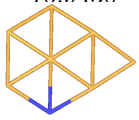
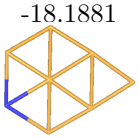
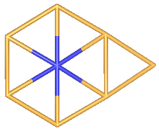
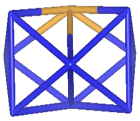
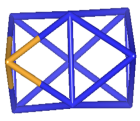
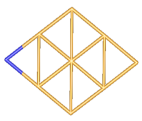
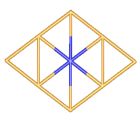
Size, N	Composition	Homotop, E/eV	GM, E/eV
7	Au_6Pd_1	 -16.2542	 -16.5348
8	Au_1Pd_7	 -26.7958	 -27.1492
8	Au_7Pd_1	 -18.1356  -16.9430  -18.1881  -18.4109	 -18.8431
9	Au_1Pd_8	 -31.2069	 -31.3585
9	Au_8Pd_1	 -21.5006	 -21.7874

Table S8: The energies and structures for homotops of the free monosubstituted clusters, N=9 and10.

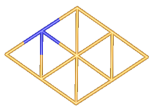
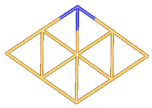
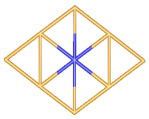
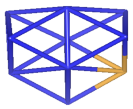
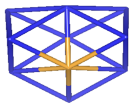
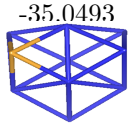
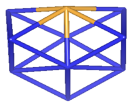
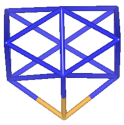
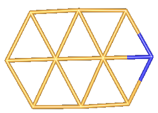
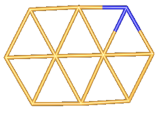
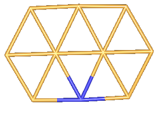
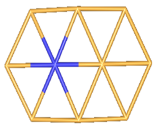
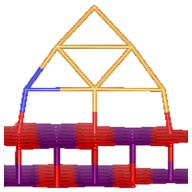
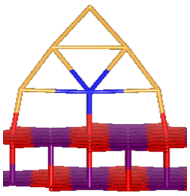
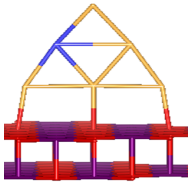
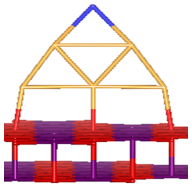
Size, N	Composition	Homotop, E/eV	GM, E/eV
9	Au_8Pd_1	 -21.4551  -21.0059	 -21.7874
10	Au_1Pd_9	 -35.2896  -35.0493  -35.2830  -35.0497	 -35.6073
10	Au_9Pd_1	 -23.4507  -23.5524  -23.5525	 -24.0365

Table S9: The energies and structures for homotops of the MgO(100)-supported Au_5Pd_1 cluster

Size, N	Composition	Homotop, E/eV	GM, E/eV
6	MgO(100)-Au_5Pd_1	 -427.1217	 -427.7307
		 -427.1341	
		 -426.7215	