

Supplementary Information

The Geometric Effect in Palladium-Gold Catalysis. Is the Coupling the Rate-Determining Step in the Vinyl-Acetate Synthesis?

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Methodology and Computational Details

Figure S1.

Cartesian coordinates of all intermediates and transition states

Imaginary frequencies of transition states

Methodology and computational details

In order to model the second neighbor Pd pair ensemble on PdAu(100) and PdAu(111) surfaces we have built-up the clusters starting with a group of two non-contiguous Pd atoms and two Au atoms bonded to both of them. Then, the first neighbors of those four atoms have been added both in the first and in the second layer. In this way, the active sites are represented by Pd₂Au₁₉ and Pd₂Au₂₀ cluster models, or Pd₂Au₁₉(12,9) and Pd₂Au₂₀(14,8) to indicate the number of atoms in each cluster layer, for Au(100) and Au(111) surfaces, respectively.

Initially, the atomic positions have been assigned as in bulk gold, with the experimental lattice parameter of 4.08 Å, yielding an Au-Au (initially equal to Pd-Au) distance of 2.885 Å.

With these models a good description of the coordination of the two non-contiguous Pd monomers involved in the chemisorption sites for both low-index gold surfaces is obtained.

First, the size of the Pd₂Au₁₉(12,9) model has been increased by adding a third layer in such a way as to obtain for the PdAu(100) surface the Pd₂Au₂₃(12,9,4) cluster including in the third layer four gold atoms which lie in the positions corresponding to that of the four central atoms in the first layer, because of the ABAB packing of the fcc(100) surface. For the less open fcc(111) gold surface with the ABCABC packing, eight atoms have been added in the third layer to the Pd₂Au₂₀(14,8) model in correspondence to the atomic positions defining the fcc-hollow adsorption sites, giving rise to the larger Pd₂Au₂₈(14,8,8) cluster.

Starting from these three-layer models, other two more extended clusters have been constructed completing the set of the first neighbor atoms for all the peripheral atoms of the first and the second layer. The resulting Pd₂Au₅₅(24,21,12) and Pd₂Au₆₂(30,21,13) large models for the Pd/Au(100) and the Pd/Au(111) systems, respectively, would prevent any indirect insaturation effect for the two non-contiguous Pd and the two Au atoms of the active sites. Moreover, these large models have been used to take into account local relaxation effects due to the substitution of two non-contiguous surface gold atoms with two Pd monomers. The positions of the atoms defining the Pd₂Au₁₉(12,9) and Pd₂Au₂₀(14,8) models have been fully optimized, in fact, within the Pd₂Au₅₅(24,21,12) and Pd₂Au₆₂(30,21,13) clusters freezing the positions of the remaining atoms (see Figure S1).

Due to relaxation effects in the surface plane the neighboring gold atoms move towards the palladium monomers (see Figure S1 (a)) whereas, on the axis perpendicular to the surface, the Pd atoms move inward (of 0.16-0.20 Å) with respect to the surface gold layer (see Figure S1 (b)). As a result of these local relaxations, the Pd-Au distances in the active sites become shorter with respect to the Au-Au distances in the pure gold surfaces. In particular, Pd-Au distances are equal to 2.840 and 2.861 Å for the

PdAu(100) and (111) surfaces, respectively. These values differ by 0.017-0.026 Å from the Au-Au distances found with the locally relaxed pure gold clusters.

The calculations have been performed with the Turbomole package (version 5.9)¹ at the DF level, using the BP86 functional² within the resolution of the identity approximation for computing the electronic Coulomb interaction (RI-J). This approach expands the molecular electron density in a set of atom-centered auxiliary functions improving the computational efficiency of large-scale calculations.^{3,4}

The Stuttgart effective core potential⁵ has been used to model the scalar relativistic effects replacing the 28 and 60 core electrons of palladium and gold atoms, respectively. The valence electrons of metal atoms, 18 for Pd and 19 for Au, and all electrons for C, O and H atoms have been explicitly considered by use of the Turbomole's TZVP basis set⁶ along with the corresponding TZVP auxiliary basis set.⁷

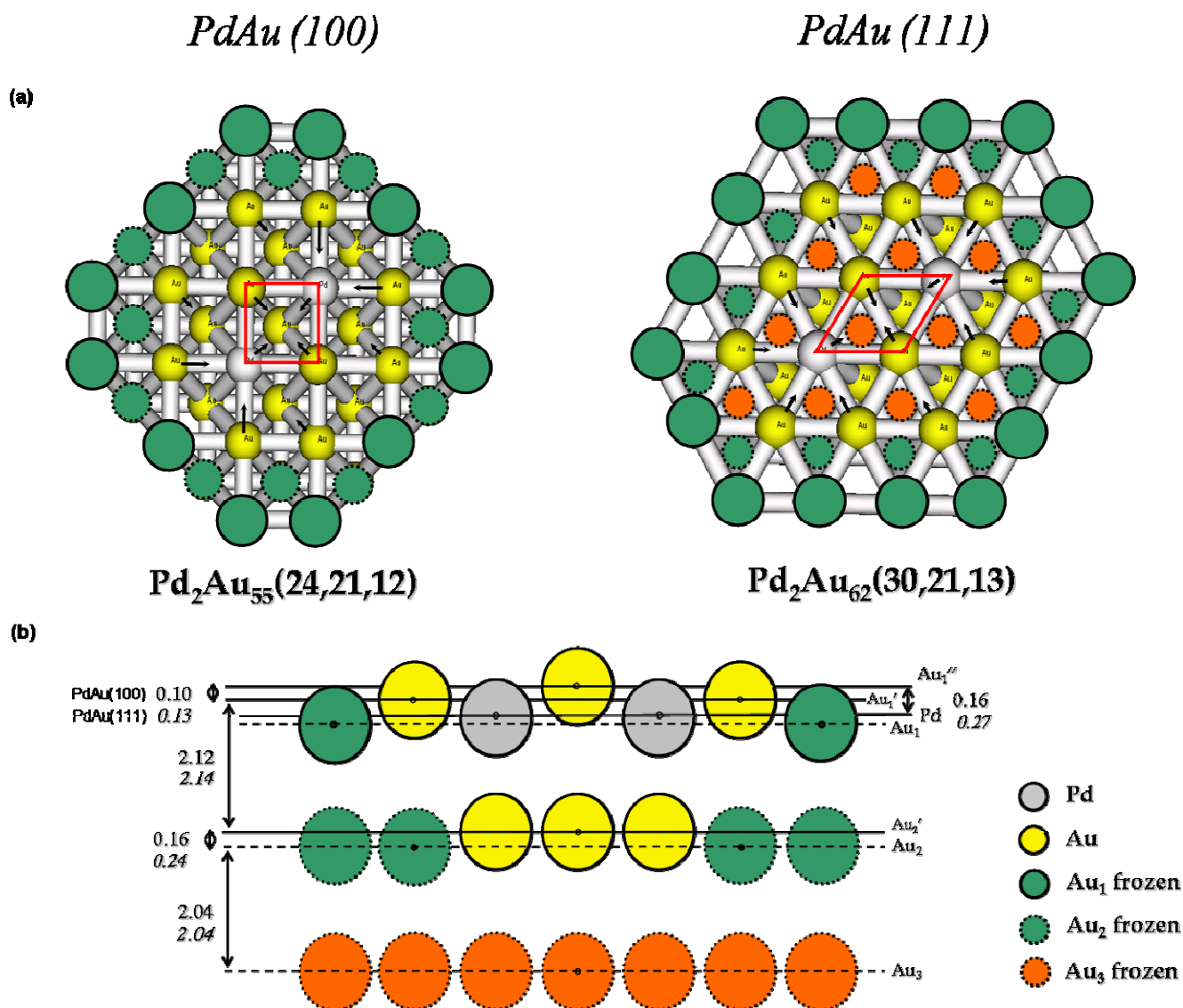


Figure S1. Schematic representation of the Pd_2Au_n clusters used to model the critical ensemble of two non-contiguous Pd monomers on the PdAu(100) and PdAu(111) surface alloys. Top view (a) shows unit cells of the Au(100) and Au(111) pure surfaces in red and changes in the atomic positions due to the local relaxation by arrows. Side view (b) indicates surface layers relaxation with respect to bulk gold interlayer distances.

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Supplementary Material (ESI) for Chemical Communications
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Cartesian Coordinates of all minima and transition states

Samanos-type mechanism

PdAu(100) – Pd₂Au₅₅ cluster model

	R			TS(S)			P		
	x	y	z	x	y	z	x	y	z
Au	4,0800	-2,0400	-2,4695	4,0800	-2,0400	-2,4695	4,0800	-2,0400	-2,4695
Au	2,0400	-4,0800	-2,4695	2,0400	-4,0800	-2,4695	2,0400	-4,0800	-2,4695
Au	4,0800	2,0400	-2,4695	4,0800	2,0400	-2,4695	4,0800	2,0400	-2,4695
Au	2,0400	0,0000	-2,4695	2,0400	0,0000	-2,4695	2,0400	0,0000	-2,4695
Au	0,0000	-2,0400	-2,4695	0,0000	-2,0400	-2,4695	0,0000	-2,0400	-2,4695
Au	-2,0400	-4,0800	-2,4695	-2,0400	-4,0800	-2,4695	-2,0400	-4,0800	-2,4695
Au	2,0400	4,0800	-2,4695	2,0400	4,0800	-2,4695	2,0400	4,0800	-2,4695
Au	0,0000	2,0400	-2,4695	0,0000	2,0400	-2,4695	0,0000	2,0400	-2,4695
Au	-2,0400	0,0000	-2,4695	-2,0400	0,0000	-2,4695	-2,0400	0,0000	-2,4695
Au	-4,0800	-2,0400	-2,4695	-4,0800	-2,0400	-2,4695	-4,0800	-2,0400	-2,4695
Au	-2,0400	4,0800	-2,4695	-2,0400	4,0800	-2,4695	-2,0400	4,0800	-2,4695
Au	-4,0800	2,0400	-2,4695	-4,0800	2,0400	-2,4695	-4,0800	2,0400	-2,4695
Au	6,1200	-2,0400	-0,4295	6,1200	-2,0400	-0,4295	6,1200	-2,0400	-0,4295
Au	4,0800	-4,0800	-0,4295	4,0800	-4,0800	-0,4295	4,0800	-4,0800	-0,4295
Au	2,0400	-6,1200	-0,4295	2,0400	-6,1200	-0,4295	2,0400	-6,1200	-0,4295
Au	6,1200	2,0400	-0,4295	6,1200	2,0400	-0,4295	6,1200	2,0400	-0,4295
Au	4,1303	0,0000	-0,4335	4,1303	0,0000	-0,4335	4,1303	0,0000	-0,4335
Au	2,0104	-2,0092	-0,2598	2,0104	-2,0092	-0,2598	2,0104	-2,0092	-0,2598
Au	-0,0005	-4,1513	-0,4582	-0,0005	-4,1513	-0,4582	-0,0005	-4,1513	-0,4582
Au	-2,0400	-6,1200	-0,4295	-2,0400	-6,1200	-0,4295	-2,0400	-6,1200	-0,4295
Au	4,0800	4,0800	-0,4295	4,0800	4,0800	-0,4295	4,0800	4,0800	-0,4295
Au	2,0105	2,0093	-0,2596	2,0105	2,0093	-0,2596	2,0105	2,0093	-0,2596
Au	-0,0001	0,0000	-0,2763	-0,0001	0,0000	-0,2763	-0,0001	0,0000	-0,2763
Au	-2,0115	-2,0087	-0,2588	-2,0115	-2,0087	-0,2588	-2,0115	-2,0087	-0,2588
Au	-4,0800	-4,0800	-0,4295	-4,0800	-4,0800	-0,4295	-4,0800	-4,0800	-0,4295
Au	2,0400	6,1200	-0,4295	2,0400	6,1200	-0,4295	2,0400	6,1200	-0,4295
Au	-0,0005	4,1509	-0,4580	-0,0005	4,1509	-0,4580	-0,0005	4,1509	-0,4580
Au	-2,0116	2,0087	-0,2587	-2,0116	2,0087	-0,2587	-2,0116	2,0087	-0,2587
Au	-4,1298	0,0000	-0,4334	-4,1298	0,0000	-0,4334	-4,1298	0,0000	-0,4334
Au	-6,1200	-2,0400	-0,4295	-6,1200	-2,0400	-0,4295	-6,1200	-2,0400	-0,4295
Au	-2,0400	6,1200	-0,4295	-2,0400	6,1200	-0,4295	-2,0400	6,1200	-0,4295
Au	-4,0800	4,0800	-0,4295	-4,0800	4,0800	-0,4295	-4,0800	4,0800	-0,4295
Au	-6,1200	2,0400	-0,4295	-6,1200	2,0400	-0,4295	-6,1200	2,0400	-0,4295
Au	6,1200	-4,0800	1,6105	6,1200	-4,0800	1,6105	6,1200	-4,0800	1,6105
Au	4,0800	-6,1200	1,6105	4,0800	-6,1200	1,6105	4,0800	-6,1200	1,6105
Au	6,1200	0,0000	1,6105	6,1200	0,0000	1,6105	6,1200	0,0000	1,6105
Au	4,0420	-2,0081	1,8525	4,0420	-2,0081	1,8525	4,0420	-2,0081	1,8525
Au	2,0068	-4,0368	1,8579	2,0068	-4,0368	1,8579	2,0068	-4,0368	1,8579
Au	0,0000	-6,1200	1,6105	0,0000	-6,1200	1,6105	0,0000	-6,1200	1,6105
Au	6,1200	4,0800	1,6105	6,1200	4,0800	1,6105	6,1200	4,0800	1,6105
Au	4,0419	2,0082	1,8523	4,0419	2,0082	1,8523	4,0419	2,0082	1,8523
Pd	2,0426	0,0000	1,7918	2,0426	0,0000	1,7918	2,0426	0,0000	1,7918
Au	0,0000	-1,9640	1,9533	0,0000	-1,9640	1,9533	0,0000	-1,9640	1,9533
Au	-2,0073	-4,0364	1,8578	-2,0073	-4,0364	1,8578	-2,0073	-4,0364	1,8578
Au	-4,0800	-6,1200	1,6105	-4,0800	-6,1200	1,6105	-4,0800	-6,1200	1,6105
Au	4,0800	6,1200	1,6105	4,0800	6,1200	1,6105	4,0800	6,1200	1,6105
Au	2,0068	4,0367	1,8576	2,0068	4,0367	1,8576	2,0068	4,0367	1,8576
Au	0,0001	1,9640	1,9530	0,0001	1,9640	1,9530	0,0001	1,9640	1,9530
Pd	-2,0432	0,0000	1,7922	-2,0432	0,0000	1,7922	-2,0432	0,0000	1,7922
Au	-4,0427	-2,0083	1,8524	-4,0427	-2,0083	1,8524	-4,0427	-2,0083	1,8524
Au	-6,1200	-4,0800	1,6105	-6,1200	-4,0800	1,6105	-6,1200	-4,0800	1,6105
Au	0,0000	6,1200	1,6105	0,0000	6,1200	1,6105	0,0000	6,1200	1,6105
Au	-2,0073	4,0363	1,8574	-2,0073	4,0363	1,8574	-2,0073	4,0363	1,8574
Au	-4,0426	2,0084	1,8521	-4,0426	2,0084	1,8521	-4,0426	2,0084	1,8521
Au	-6,1200	0,0000	1,6105	-6,1200	0,0000	1,6105	-6,1200	0,0000	1,6105
Au	-4,0800	6,1200	1,6105	-4,0800	6,1200	1,6105	-4,0800	6,1200	1,6105
Au	-6,1200	4,0800	1,6105	-6,1200	4,0800	1,6105	-6,1200	4,0800	1,6105
O	2,0482	0,2169	3,9392	2,1767	0,1743	4,0046	2,3952	0,1957	4,2118
C	1,4128	1,0862	4,6271	1,2029	0,5038	4,7243	1,3703	0,4066	4,8573
O	0,5516	1,9202	4,2166	0,1284	1,0698	4,2487	0,2125	-0,0836	4,3738
C	1,7177	1,0798	6,1200	1,2991	0,2220	6,2103	1,3640	1,1859	6,1456
H	2,7816	0,8767	6,2893	2,3537	0,1438	6,4950	2,3956	1,3242	6,4826
H	1,1424	0,2685	6,5898	0,8215	-0,7457	6,4292	0,7736	0,6828	6,9233
H	1,4251	2,0318	6,5756	0,8029	1,0000	6,8029	0,9139	2,1764	5,9735
C	-1,9637	0,0061	4,0879	-1,5953	0,6641	4,9477	-1,0983	0,4125	4,8009
C	-3,0516	-0,8361	4,1531	-2,3587	-0,1195	4,0503	-2,1704	-0,1874	3,9273
H	-0,9623	-0,3908	4,2601	-1,1832	0,1863	5,8367	-3,1240	0,3126	4,1436
H	-2,0863	1,0828	4,2172	-1,8593	1,7144	5,0740	-2,2790	-1,2611	4,1172
H	-2,9178	-1,9051	4,3291	-2,3648	-1,1952	4,2361	-1,2511	0,0944	5,8494
H	-4,0625	-0,4408	4,2566	-3,3506	0,3119	3,8485	-1,0999	1,5102	4,7482

PdAu(111) – Pd₂Au₆₂ cluster model

	R			TS(S)			P		
	x	y	z	x	y	z	x	y	z
Au	7,2125	7,4954	0,0000	7,2125	7,4954	0,0000	7,2125	7,4954	0,0000
Au	8,6550	9,9939	0,0000	8,6550	9,9939	0,0000	8,6550	9,9939	0,0000
Au	10,0975	12,4924	0,0000	10,0975	12,4924	0,0000	10,0975	12,4924	0,0000
Au	11,5400	14,9909	0,0000	11,5400	14,9909	0,0000	11,5400	14,9909	0,0000
Au	10,0975	7,4954	0,0000	10,0975	7,4954	0,0000	10,0975	7,4954	0,0000
Au	11,5400	9,9939	0,0000	11,5400	9,9939	0,0000	11,5400	9,9939	0,0000
Au	12,9825	12,4924	0,0000	12,9825	12,4924	0,0000	12,9825	12,4924	0,0000
Au	14,4250	14,9909	0,0000	14,4250	14,9909	0,0000	14,4250	14,9909	0,0000
Au	12,9825	7,4954	0,0000	12,9825	7,4954	0,0000	12,9825	7,4954	0,0000
Au	14,4250	9,9939	0,0000	14,4250	9,9939	0,0000	14,4250	9,9939	0,0000
Au	15,8675	12,4924	0,0000	15,8675	12,4924	0,0000	15,8675	12,4924	0,0000
Au	15,8675	7,4954	0,0000	15,8675	7,4954	0,0000	15,8675	7,4954	0,0000
Au	17,3100	9,9939	0,0000	17,3100	9,9939	0,0000	17,3100	9,9939	0,0000
Au	5,7700	8,3283	2,3556	5,7700	8,3283	2,3556	5,7700	8,3283	2,3556
Au	7,2125	10,8267	2,3556	7,2125	10,8267	2,3556	7,2125	10,8267	2,3556
Au	8,6550	13,3252	2,3556	8,6550	13,3252	2,3556	8,6550	13,3252	2,3556
Au	10,0975	15,8237	2,3556	10,0975	15,8237	2,3556	10,0975	15,8237	2,3556
Au	7,2125	5,8298	2,3556	7,2125	5,8298	2,3556	7,2125	5,8298	2,3556
Au	8,6470	8,3235	2,5240	8,6470	8,3235	2,5240	8,6470	8,3235	2,5240
Au	10,0773	10,8180	2,5362	10,0773	10,8180	2,5362	10,0773	10,8180	2,5362
Au	11,5300	13,3021	2,5347	11,5300	13,3021	2,5347	11,5300	13,3021	2,5347
Au	12,9825	15,8237	2,3556	12,9825	15,8237	2,3556	12,9825	15,8237	2,3556
Au	10,0975	5,8298	2,3556	10,0975	5,8298	2,3556	10,0975	5,8298	2,3556
Au	11,5223	8,3153	2,5359	11,5223	8,3153	2,5359	11,5223	8,3153	2,5359
Au	12,9630	10,8161	2,5315	12,9630	10,8161	2,5315	12,9630	10,8161	2,5315
Au	14,4360	13,3114	2,5370	14,4360	13,3114	2,5370	14,4360	13,3114	2,5370
Au	15,8675	15,8237	2,3556	15,8675	15,8237	2,3556	15,8675	15,8237	2,3556
Au	12,9825	5,8298	2,3556	12,9825	5,8298	2,3556	12,9825	5,8298	2,3556
Au	14,4000	8,3317	2,5355	14,4000	8,3317	2,5355	14,4000	8,3317	2,5355
Au	15,8602	10,8439	2,5366	15,8602	10,8439	2,5366	15,8602	10,8439	2,5366
Au	17,3100	13,3252	2,3556	17,3100	13,3252	2,3556	17,3100	13,3252	2,3556
Au	15,8675	5,8298	2,3556	15,8675	5,8298	2,3556	15,8675	5,8298	2,3556
Au	17,3100	8,3283	2,3556	17,3100	8,3283	2,3556	17,3100	8,3283	2,3556
Au	18,7525	10,8267	2,3556	18,7525	10,8267	2,3556	18,7525	10,8267	2,3556
Au	4,3275	9,1611	4,7112	4,3275	9,1611	4,7112	4,3275	9,1611	4,7112
Au	5,7700	11,6596	4,7112	5,7700	11,6596	4,7112	5,7700	11,6596	4,7112
Au	7,2125	14,1581	4,7112	7,2125	14,1581	4,7112	7,2125	14,1581	4,7112
Au	8,6550	16,6565	4,7112	8,6550	16,6565	4,7112	8,6550	16,6565	4,7112
Au	5,7700	6,6626	4,7112	5,7700	6,6626	4,7112	5,7700	6,6626	4,7112
Au	7,2418	9,1521	5,1036	7,2418	9,1521	5,1036	7,2418	9,1521	5,1036
Au	8,6544	11,6193	5,0736	8,6544	11,6193	5,0736	8,6544	11,6193	5,0736
Au	10,0998	14,1188	5,0136	10,0998	14,1188	5,0136	10,0998	14,1188	5,0136
Au	11,5400	16,6565	4,7112	11,5400	16,6565	4,7112	11,5400	16,6565	4,7112
Au	7,2125	4,1641	4,7112	7,2125	4,1641	4,7112	7,2125	4,1641	4,7112
Au	8,6623	6,6923	5,1047	8,6623	6,6923	5,1047	8,6623	6,6923	5,1047
Pd	10,1032	9,1645	4,9167	10,1032	9,1645	4,9167	10,1032	9,1645	4,9167
Au	11,5442	11,6202	5,1198	11,5442	11,6202	5,1198	11,5442	11,6202	5,1198
Au	13,0014	14,1110	5,0369	13,0014	14,1110	5,0369	13,0014	14,1110	5,0369
Au	14,4250	16,6565	4,7112	14,4250	16,6565	4,7112	14,4250	16,6565	4,7112
Au	10,0975	4,1641	4,7112	10,0975	4,1641	4,7112	10,0975	4,1641	4,7112
Au	11,5045	6,6819	5,0731	11,5045	6,6819	5,0731	11,5045	6,6819	5,0731
Au	12,9509	9,1839	5,1197	12,9509	9,1839	5,1197	12,9509	9,1839	5,1197
Pd	14,4040	11,6472	4,9093	14,4040	11,6472	4,9093	14,4040	11,6472	4,9093
Au	15,8672	14,1271	5,0513	15,8672	14,1271	5,0513	15,8672	14,1271	5,0513
Au	17,3100	16,6565	4,7112	17,3100	16,6565	4,7112	17,3100	16,6565	4,7112
Au	12,9825	4,1641	4,7112	12,9825	4,1641	4,7112	12,9825	4,1641	4,7112
Au	14,3912	6,6835	5,0142	14,3912	6,6835	5,0142	14,3912	6,6835	5,0142
Au	15,8357	9,1997	5,0366	15,8357	9,1997	5,0366	15,8357	9,1997	5,0366
Au	17,2831	11,6733	5,0509	17,2831	11,6733	5,0509	17,2831	11,6733	5,0509
Au	18,7525	14,1581	4,7112	18,7525	14,1581	4,7112	18,7525	14,1581	4,7112
Au	15,8675	4,1641	4,7112	15,8675	4,1641	4,7112	15,8675	4,1641	4,7112
Au	17,3100	6,6626	4,7112	17,3100	6,6626	4,7112	17,3100	6,6626	4,7112
Au	18,7525	9,1611	4,7112	18,7525	9,1611	4,7112	18,7525	9,1611	4,7112
Au	20,1950	11,6596	4,7112	20,1950	11,6596	4,7112	20,1950	11,6596	4,7112
C	13,8947	10,6144	7,8198	13,4884	11,0884	7,9005	14,4547	9,8996	8,3801
C	14,0609	10,8042	9,3241	13,5652	11,1625	9,4091	12,3230	9,5917	7,8370
O	14,3512	11,5600	7,0989	14,3835	11,6235	7,2096	13,3183	10,3083	8,4737
O	13,3225	9,5488	7,4308	12,4762	10,4702	7,3446	12,9204	11,5633	9,2154
H	13,5076	11,7007	9,6370	12,7271	11,7617	9,7946	12,5357	12,3154	8,5095
H	15,1208	10,9767	9,5519	14,5086	11,6285	9,7095	13,8081	11,9642	9,7128
H	13,6947	9,9297	9,8707	13,4889	10,1588	9,8493	12,1338	11,3707	9,9585
C	9,8827	9,7766	7,4469	10,9989	9,6167	8,2182	10,9347	10,0013	7,9176
C	10,2919	8,4799	7,4717	10,0283	9,1483	7,3011	10,0662	9,0965	7,0829
H	9,5710	7,6635	7,5386	9,0891	9,7043	7,2897	9,01521	9,3284	7,2895
H	8,8263	10,0430	7,5003	11,6411	8,8838	8,7081	10,25584	8,0441	7,3187
H	10,6051	10,5875	7,5507	10,7686	10,5067	8,8052	10,82371	11,0603	7,6353

Moiseev -type mechanism

PdAu(100) – Pd₂Au₅₅ cluster model

	R'			TS(M)			P'		
	x	y	z	x	y	z	x	y	z
Au	4,0800	-2,0400	-2,4695	4,0800	-2,0400	-2,4695	4,0800	-2,0400	-2,4695
Au	2,0400	-4,0800	-2,4695	2,0400	-4,0800	-2,4695	2,0400	-4,0800	-2,4695
Au	4,0800	2,0400	-2,4695	4,0800	2,0400	-2,4695	4,0800	2,0400	-2,4695
Au	2,0400	0,0000	-2,4695	2,0400	0,0000	-2,4695	2,0400	0,0000	-2,4695
Au	0,0000	-2,0400	-2,4695	0,0000	-2,0400	-2,4695	0,0000	-2,0400	-2,4695
Au	-2,0400	-4,0800	-2,4695	-2,0400	-4,0800	-2,4695	-2,0400	-4,0800	-2,4695
Au	2,0400	4,0800	-2,4695	2,0400	4,0800	-2,4695	2,0400	4,0800	-2,4695
Au	0,0000	2,0400	-2,4695	0,0000	2,0400	-2,4695	0,0000	2,0400	-2,4695
Au	-2,0400	0,0000	-2,4695	-2,0400	0,0000	-2,4695	-2,0400	0,0000	-2,4695
Au	-4,0800	-2,0400	-2,4695	-4,0800	-2,0400	-2,4695	-4,0800	-2,0400	-2,4695
Au	-2,0400	4,0800	-2,4695	-2,0400	4,0800	-2,4695	-2,0400	4,0800	-2,4695
Au	-4,0800	2,0400	-2,4695	-4,0800	2,0400	-2,4695	-4,0800	2,0400	-2,4695
Au	6,1200	-2,0400	-0,4295	6,1200	-2,0400	-0,4295	6,1200	-2,0400	-0,4295
Au	4,0800	-4,0800	-0,4295	4,0800	-4,0800	-0,4295	4,0800	-4,0800	-0,4295
Au	2,0400	-6,1200	-0,4295	2,0400	-6,1200	-0,4295	2,0400	-6,1200	-0,4295
Au	6,1200	2,0400	-0,4295	6,1200	2,0400	-0,4295	6,1200	2,0400	-0,4295
Au	4,1303	0,0000	-0,4335	4,1303	0,0000	-0,4335	4,1303	0,0000	-0,4335
Au	2,0104	-2,0092	-0,2598	2,0104	-2,0092	-0,2598	2,0104	-2,0092	-0,2598
Au	-0,0005	-4,1513	-0,4582	-0,0005	-4,1513	-0,4582	-0,0005	-4,1513	-0,4582
Au	-2,0400	-6,1200	-0,4295	-2,0400	-6,1200	-0,4295	-2,0400	-6,1200	-0,4295
Au	4,0800	4,0800	-0,4295	4,0800	4,0800	-0,4295	4,0800	4,0800	-0,4295
Au	2,0105	2,0093	-0,2596	2,0105	2,0093	-0,2596	2,0105	2,0093	-0,2596
Au	-0,0001	0,0000	-0,2763	-0,0001	0,0000	-0,2763	-0,0001	0,0000	-0,2763
Au	-2,0115	-2,0087	-0,2588	-2,0115	-2,0087	-0,2588	-2,0115	-2,0087	-0,2588
Au	-4,0800	-4,0800	-0,4295	-4,0800	-4,0800	-0,4295	-4,0800	-4,0800	-0,4295
Au	2,0400	6,1200	-0,4295	2,0400	6,1200	-0,4295	2,0400	6,1200	-0,4295
Au	-0,0005	4,1509	-0,4580	-0,0005	4,1509	-0,4580	-0,0005	4,1509	-0,4580
Au	-2,0116	2,0087	-0,2587	-2,0116	2,0087	-0,2587	-2,0116	2,0087	-0,2587
Au	-4,1298	0,0000	-0,4334	-4,1298	0,0000	-0,4334	-4,1298	0,0000	-0,4334
Au	-6,1200	-2,0400	-0,4295	-6,1200	-2,0400	-0,4295	-6,1200	-2,0400	-0,4295
Au	-2,0400	6,1200	-0,4295	-2,0400	6,1200	-0,4295	-2,0400	6,1200	-0,4295
Au	-4,0800	4,0800	-0,4295	-4,0800	4,0800	-0,4295	-4,0800	4,0800	-0,4295
Au	-6,1200	2,0400	-0,4295	-6,1200	2,0400	-0,4295	-6,1200	2,0400	-0,4295
Au	6,1200	-4,0800	1,6105	6,1200	-4,0800	1,6105	6,1200	-4,0800	1,6105
Au	4,0800	-6,1200	1,6105	4,0800	-6,1200	1,6105	4,0800	-6,1200	1,6105
Au	6,1200	0,0000	1,6105	6,1200	0,0000	1,6105	6,1200	0,0000	1,6105
Au	4,0420	-2,0081	1,8525	4,0420	-2,0081	1,8525	4,0420	-2,0081	1,8525
Au	2,0068	-4,0368	1,8579	2,0068	-4,0368	1,8579	2,0068	-4,0368	1,8579
Au	0,0000	-6,1200	1,6105	0,0000	-6,1200	1,6105	0,0000	-6,1200	1,6105
Au	6,1200	4,0800	1,6105	6,1200	4,0800	1,6105	6,1200	4,0800	1,6105
Au	4,0419	2,0082	1,8523	4,0419	2,0082	1,8523	4,0419	2,0082	1,8523
Pd	2,0426	0,0000	1,7918	2,0426	0,0000	1,7918	2,0426	0,0000	1,7918
Au	0,0000	-1,9640	1,9533	0,0000	-1,9640	1,9533	0,0000	-1,9640	1,9533
Au	-2,0073	-4,0364	1,8578	-2,0073	-4,0364	1,8578	-2,0073	-4,0364	1,8578
Au	-4,0800	-6,1200	1,6105	-4,0800	-6,1200	1,6105	-4,0800	-6,1200	1,6105
Au	4,0800	6,1200	1,6105	4,0800	6,1200	1,6105	4,0800	6,1200	1,6105
Au	2,0068	4,0367	1,8576	2,0068	4,0367	1,8576	2,0068	4,0367	1,8576
Au	0,0001	1,9640	1,9530	0,0001	1,9640	1,9530	0,0001	1,9640	1,9530
Pd	-2,0432	0,0000	1,7922	-2,0432	0,0000	1,7922	-2,0432	0,0000	1,7922
Au	-4,0427	-2,0083	1,8524	-4,0427	-2,0083	1,8524	-4,0427	-2,0083	1,8524
Au	-6,1200	-4,0800	1,6105	-6,1200	-4,0800	1,6105	-6,1200	-4,0800	1,6105
Au	0,0000	6,1200	1,6105	0,0000	6,1200	1,6105	0,0000	6,1200	1,6105
Au	-2,0073	4,0363	1,8574	-2,0073	4,0363	1,8574	-2,0073	4,0363	1,8574
Au	-4,0426	2,0084	1,8521	-4,0426	2,0084	1,8521	-4,0426	2,0084	1,8521
Au	-6,1200	0,0000	1,6105	-6,1200	0,0000	1,6105	-6,1200	0,0000	1,6105
Au	-4,0800	6,1200	1,6105	-4,0800	6,1200	1,6105	-4,0800	6,1200	1,6105
Au	-6,1200	4,0800	1,6105	-6,1200	4,0800	1,6105	-6,1200	4,0800	1,6105
O	1,9943	0,1730	3,9465	1,8061	-0,0823	4,0403	2,3925	0,0665	4,1375
C	1,2993	0,9907	4,6347	0,7239	0,1371	4,6377	1,6364	0,0558	5,1009
O	0,4899	1,8729	4,2127	-0,2403	0,8609	4,1319	0,3198	-0,1998	4,8830
C	1,4432	0,8635	6,1461	0,5272	-0,4067	6,0342	2,1147	0,3036	6,5062
H	2,4717	0,5947	6,4127	1,2655	-1,1843	6,2550	3,2084	0,2949	6,5066
H	0,7815	0,0505	6,4806	-0,4942	-0,7945	6,1508	1,7287	-0,4543	7,2022
H	1,1410	1,7921	6,6416	0,6461	0,4198	6,7506	1,7716	1,2894	6,8566
C	-2,0745	-0,0636	3,8204	-2,0765	0,2416	3,8583	-0,6348	-0,1102	5,9011
C	-2,2808	-1,0913	4,6483	-2,5023	-0,9312	4,4059	-1,7462	-0,8361	5,8239
H	-1,8653	0,9414	4,1992	-2,4610	1,2178	4,1473	-0,4306	0,6271	6,6781
H	-2,2749	-0,9140	5,7323	-3,4216	-0,9319	5,0031	-2,5193	-0,7177	6,5807
H	-2,4632	-2,1175	4,3254	-1,9743	-1,8785	4,3004	-1,9121	-1,5389	5,0076

PdAu(111) – Pd₂Au₆₂ cluster model

	R'			TS(M)			P'		
	x	y	z	x	y	z	x	y	z
Au	7,2125	7,4954	0,0000	7,2125	7,4954	0,0000	7,2125	7,4954	0,0000
Au	8,6550	9,9939	0,0000	8,6550	9,9939	0,0000	8,6550	9,9939	0,0000
Au	10,0975	12,4924	0,0000	10,0975	12,4924	0,0000	10,0975	12,4924	0,0000
Au	11,5400	14,9909	0,0000	11,5400	14,9909	0,0000	11,5400	14,9909	0,0000
Au	10,0975	7,4954	0,0000	10,0975	7,4954	0,0000	10,0975	7,4954	0,0000
Au	11,5400	9,9939	0,0000	11,5400	9,9939	0,0000	11,5400	9,9939	0,0000
Au	12,9825	12,4924	0,0000	12,9825	12,4924	0,0000	12,9825	12,4924	0,0000
Au	14,4250	14,9909	0,0000	14,4250	14,9909	0,0000	14,4250	14,9909	0,0000
Au	12,9825	7,4954	0,0000	12,9825	7,4954	0,0000	12,9825	7,4954	0,0000
Au	14,4250	9,9939	0,0000	14,4250	9,9939	0,0000	14,4250	9,9939	0,0000
Au	15,8675	12,4924	0,0000	15,8675	12,4924	0,0000	15,8675	12,4924	0,0000
Au	15,8675	7,4954	0,0000	15,8675	7,4954	0,0000	15,8675	7,4954	0,0000
Au	17,3100	9,9939	0,0000	17,3100	9,9939	0,0000	17,3100	9,9939	0,0000
Au	5,7700	8,3283	2,3556	5,7700	8,3283	2,3556	5,7700	8,3283	2,3556
Au	7,2125	10,8267	2,3556	7,2125	10,8267	2,3556	7,2125	10,8267	2,3556
Au	8,6550	13,3252	2,3556	8,6550	13,3252	2,3556	8,6550	13,3252	2,3556
Au	10,0975	15,8237	2,3556	10,0975	15,8237	2,3556	10,0975	15,8237	2,3556
Au	7,2125	5,8298	2,3556	7,2125	5,8298	2,3556	7,2125	5,8298	2,3556
Au	8,6470	8,3235	2,5240	8,6470	8,3235	2,5240	8,6470	8,3235	2,5240
Au	10,0773	10,8180	2,5362	10,0773	10,8180	2,5362	10,0773	10,8180	2,5362
Au	11,5300	13,3021	2,5347	11,5300	13,3021	2,5347	11,5300	13,3021	2,5347
Au	12,9825	15,8237	2,3556	12,9825	15,8237	2,3556	12,9825	15,8237	2,3556
Au	10,0975	5,8298	2,3556	10,0975	5,8298	2,3556	10,0975	5,8298	2,3556
Au	11,5223	8,3153	2,5359	11,5223	8,3153	2,5359	11,5223	8,3153	2,5359
Au	12,9630	10,8161	2,5315	12,9630	10,8161	2,5315	12,9630	10,8161	2,5315
Au	14,4360	13,3114	2,5370	14,4360	13,3114	2,5370	14,4360	13,3114	2,5370
Au	15,8675	15,8237	2,3556	15,8675	15,8237	2,3556	15,8675	15,8237	2,3556
Au	12,9825	5,8298	2,3556	12,9825	5,8298	2,3556	12,9825	5,8298	2,3556
Au	14,4000	8,3317	2,5355	14,4000	8,3317	2,5355	14,4000	8,3317	2,5355
Au	15,8602	10,8439	2,5366	15,8602	10,8439	2,5366	15,8602	10,8439	2,5366
Au	17,3100	13,3252	2,3556	17,3100	13,3252	2,3556	17,3100	13,3252	2,3556
Au	15,8675	5,8298	2,3556	15,8675	5,8298	2,3556	15,8675	5,8298	2,3556
Au	17,3100	8,3283	2,3556	17,3100	8,3283	2,3556	17,3100	8,3283	2,3556
Au	18,7525	10,8267	2,3556	18,7525	10,8267	2,3556	18,7525	10,8267	2,3556
Au	4,3275	9,1611	4,7112	4,3275	9,1611	4,7112	4,3275	9,1611	4,7112
Au	5,7700	11,6596	4,7112	5,7700	11,6596	4,7112	5,7700	11,6596	4,7112
Au	7,2125	14,1581	4,7112	7,2125	14,1581	4,7112	7,2125	14,1581	4,7112
Au	8,6550	16,6565	4,7112	8,6550	16,6565	4,7112	8,6550	16,6565	4,7112
Au	5,7700	6,6626	4,7112	5,7700	6,6626	4,7112	5,7700	6,6626	4,7112
Au	7,2418	9,1521	5,1036	7,2418	9,1521	5,1036	7,2418	9,1521	5,1036
Au	8,6544	11,6193	5,0736	8,6544	11,6193	5,0736	8,6544	11,6193	5,0736
Au	10,0998	14,1188	5,0136	10,0998	14,1188	5,0136	10,0998	14,1188	5,0136
Au	11,5400	16,6565	4,7112	11,5400	16,6565	4,7112	11,5400	16,6565	4,7112
Au	7,2125	4,1641	4,7112	7,2125	4,1641	4,7112	7,2125	4,1641	4,7112
Au	8,6623	6,6923	5,1047	8,6623	6,6923	5,1047	8,6623	6,6923	5,1047
Pd	10,1032	9,1645	4,9167	10,1032	9,1645	4,9167	10,1032	9,1645	4,9167
Au	11,5442	11,6202	5,1198	11,5442	11,6202	5,1198	11,5442	11,6202	5,1198
Au	13,0014	14,1110	5,0369	13,0014	14,1110	5,0369	13,0014	14,1110	5,0369
Au	14,4250	16,6565	4,7112	14,4250	16,6565	4,7112	14,4250	16,6565	4,7112
Au	10,0975	4,1641	4,7112	10,0975	4,1641	4,7112	10,0975	4,1641	4,7112
Au	11,5045	6,6819	5,0731	11,5045	6,6819	5,0731	11,5045	6,6819	5,0731
Au	12,9509	9,1839	5,1197	12,9509	9,1839	5,1197	12,9509	9,1839	5,1197
Pd	14,4040	11,6472	4,9093	14,4040	11,6472	4,9093	14,4040	11,6472	4,9093
Au	15,8672	14,1271	5,0513	15,8672	14,1271	5,0513	15,8672	14,1271	5,0513
Au	17,3100	16,6565	4,7112	17,3100	16,6565	4,7112	17,3100	16,6565	4,7112
Au	12,9825	4,1641	4,7112	12,9825	4,1641	4,7112	12,9825	4,1641	4,7112
Au	14,3912	6,6835	5,0142	14,3912	6,6835	5,0142	14,3912	6,6835	5,0142
Au	15,8357	9,1997	5,0366	15,8357	9,1997	5,0366	15,8357	9,1997	5,0366
Au	17,2831	11,6733	5,0509	17,2831	11,6733	5,0509	17,2831	11,6733	5,0509
Au	18,7525	14,1581	4,7112	18,7525	14,1581	4,7112	18,7525	14,1581	4,7112
Au	15,8675	4,1641	4,7112	15,8675	4,1641	4,7112	15,8675	4,1641	4,7112
Au	17,3100	6,6626	4,7112	17,3100	6,6626	4,7112	17,3100	6,6626	4,7112
Au	18,7525	9,1611	4,7112	18,7525	9,1611	4,7112	18,7525	9,1611	4,7112
Au	20,1950	11,6596	4,7112	20,1950	11,6596	4,7112	20,1950	11,6596	4,7112
C	13,9166	10,6294	7,8188	12,8452	10,5401	7,9393	14,5682	11,7148	7,4422
C	14,0854	10,8391	9,3199	12,3936	10,8330	9,3517	13,8868	11,3631	8,3925
O	14,3513	11,5814	7,08927	13,7705	11,1878	7,4161	12,6624	10,8158	8,1374
O	13,3652	9,5516	7,43933	12,2559	9,5217	7,3255	14,3445	11,4903	9,8231
H	13,4459	11,6757	9,63485	12,7423	11,8224	9,6647	11,7663	10,4669	9,1516
H	15,1245	11,1179	9,5373	12,8250	10,0710	10,0181	10,8462	9,5342	8,9228
H	13,8090	9,9352	9,87184	11,3003	10,7569	9,4324	13,7416	12,2371	10,3613
C	10,1859	9,0967	6,96885	9,5312	10,1726	7,7151	15,3883	11,8168	9,8181
C	9,1934	9,0290	7,8589	10,2917	9,2338	7,1122	14,2509	10,5338	10,3568
H	8,1320	8,9641	7,61655	10,3526	8,1960	7,4274	11,8406	11,0470	10,0721
H	11,2271	9,1447	7,29921	8,7168	9,8414	8,3707	10,1075	9,3068	9,6886
H	9,4509	9,0412	8,92656	9,6379	11,2473	7,5592	10,7987	8,9995	7,9732

Imaginary frequencies (cm^{-1}) of transition states

	PdAu(100)	PdAu(111)
TS(S) Samanos-type	$-357i$	$-428i$
TS(M) Moiseev-type	$-396i$	$-454i$