Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Altering CO binding on Gold Cluster Cations by Pd-doping

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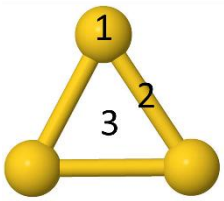
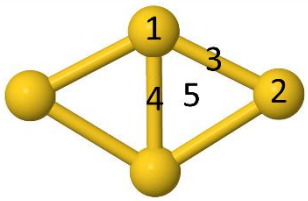
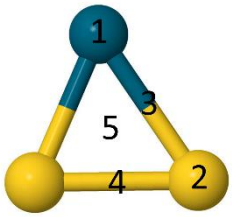
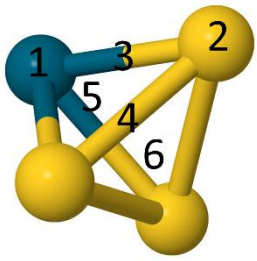
Content

1. Adsorption sites and their relative binding energies ΔE_b and the corresponding calculated frequencies for CO molecule on $Au_N^+(CO)$ and $PdAu_{N-1}^+(CO)$, N=3 and 4, clusters

Table S1: Adsorption sites and their relative binding energies ΔE_b, together with the corresponding calculated frequencies for a CO molecule on $Au_N^+(CO)$ and $PdAu_{N-1}^+(CO)$, N=3 and 4, clusters. The most favourable site for each cluster (having ΔE_b = 0.00 eV and nearest ν_{CO} to the corresponding measured value) is shown in bold.

Model	Site	ΔE_b / eV	ν_{CO} / cm^{-1}
	**1 (atop)**	**0.00**	**2198.77**
	2 (bridge)	0.11	2074.08
	3 (hollow)	0.13	1962.13
	**1 (atop)**	**0.00**	**2184.57**
	2 (atop)	0.18	2192.81
	3 (bridge)	0.19	1961.22
	4 (bridge)	0.21	1893.45
	5 (hollow)	0.18	1969.51
	1 (atop)	0.23	2018.67
	2 (atop)	**0.00**	**2196.14**
	3 (bridge)	0.14	1938.70
	4 (bridge)	0.11	1959.22
	5 (hollow)	0.18	1880.78
	1 (atop)	0.25	1950.11
	2 (atop)	**0.00**	**2180.24**
	3 (bridge)	0.18	1992.02
	4 (bridge)	0.14	2030.27
	5 (hollow)	0.20	1971.10
	6 (hollow)	0.16	1997.76

2. Cluster-CO binding energies, CO stretching frequencies, and average bond lengths

Table S2: Cluster-CO binding energies, CO stretching frequencies, and average bond lengths of putative global minima of $Au_N^+(CO)$ and $PdAu_{N-1}^+(CO)$, N=2-11, clusters.

Species	Average Bond Length (Å)				E_b / eV	ν_{CO} / cm^{-1}
	Au-Au	Au-Pd	M-C	C-O		
$Au_2^+(CO)$	2.61	-----	1.93	1.12	1.93	2215.09
$Au_3^+(CO)$	2.63	------	1.95	1.12	1.76	2198.78
$Au_4^+(CO)$	2.68	-----	1.95	1.12	1.62	2184.57
$Au_5^+(CO)$	2.64	-----	1.94	1.12	1.40	2180.69
$Au_6^+(CO)$	2.66	-----	1.96	1.12	1.46	2189.97
$Au_7^+(CO)$	2.70	-----	1.96	1.12	1.78	2170.97
$Au_8^+(CO)$	2.67	-----	1.96	1.12	1.38	2175.98
$Au_9^+(CO)$	2.74	----	1.98	1.12	1.62	2173.18
$Au_{10}^+(CO)$	2.62	-----	1.96	1.12	1.47	2171.06
$Au_{11}^+(CO)$	2.71	----	1.97	1.12	1.60	2169.51
$PdAu^+(CO)$	-----	2.59	(Au-C=2.0980), (Pd-C=1.8576)	1.14	5.93	2035.40
$PdAu_2^+(CO)$	2.57	2.68	1.95	1.12	1.99	2196.14
$PdAu_3^+(CO)$	2.75	2.61	1.94	1.12	1.66	2180.25
$PdAu_4^+(CO)$	2.75	2.69	1.94	1.12	1.67	2172.35
$PdAu_5^+(CO)$	2.75	2.73	1.89	1.13	1.71	2119.99
$PdAu_6^+(CO)$	2.69	2.77	1.90	1.12	1.81	2132.16
$PdAu_7^+(CO)$	2.72	2.73	1.5	1.2	1.86	2113.70
$PdAu_8^+(CO)$	2.69	2.77	1.90	1.13	1.85	2112.78
$PdAu_9^+(CO)$	2.78	2.70	1.90	1.15	1.80	2114.21
$PdAu_{10}^+(CO)$	2.75	2.70	1.94	1.12	1.78	2150.22

3. Electronic distribution

Table S3: Partial charge distributions calculated with both the Mulliken and Löwdin partitioning methods for $Au_N^+(CO)$ and $PdAu_{N-1}^+(CO)$, *N*=2 and 4, clusters and their corresponding free clusters.

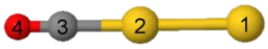
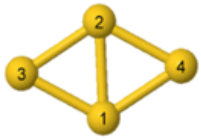
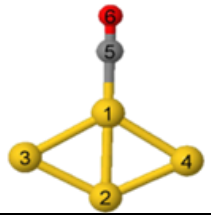
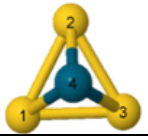
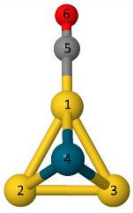
Species	Numbering of the atoms	Type of atom	Charge Population Analysis		Structure
			Mulliken	Löwdin	
Au_2^+	1	Au	0.50	0.50	
	2	Au	0.50	0.50	
$Au_2^+(CO)$	1	Au	0.54	0.45	
	2	Au	0.37	0.43	
	3	C	-0.09	-0.14	
	4	O	0.18	0.26	
$PdAu^+$	1	Au	0.45	0.40	
	2	Pd	0.55	0.60	
$PdAu^+(CO)$	1	Au	0.68	0.62	
	2	Pd	0.36	0.44	
	3	C	-0.16	-0.27	
	4	O	0.12	0.21	
Au_4^+	1	Au	0.23	0.13	
	2	Au	0.23	0.13	
	3	Au	0.27	0.37	
	4	Au	0.27	0.37	
$Au_4^+(CO)$	1	Au	0.03	0.29	
	2	Au	0.23	0.18	
	3	Au	0.34	0.22	
	4	Au	0.34	0.22	
	5	C	-0.09	-0.16	
	6	O	0.15	0.23	
$PdAu_3^+$	1	Au	0.37	0.33	
	2	Au	0.37	0.33	
	3	Au	0.37	0.33	
	4	Pd	-0.12	0.02	
$PdAu_3^+(CO)$	1	Au	0.19	0.41	
	2	Au	0.40	0.22	
	3	Au	0.40	0.25	
	4	Pd	-0.07	0.03	
	5	C	-0.07	-0.15	
	6	O	0.15	0.24	

Table S4: Partial charge distributions calculated with both the Mulliken and Löwdin partitioning methods for $Au_N^+(CO)$ and $PdAu_{N-1}^+(CO)$, *N*=6, clusters and their corresponding free clusters.

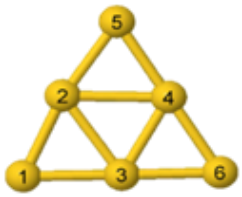
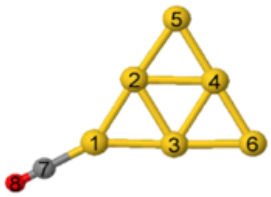
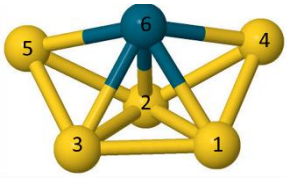
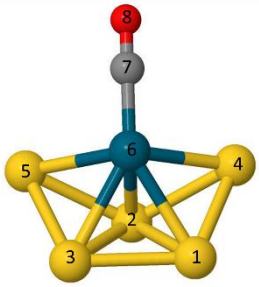
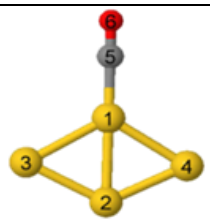
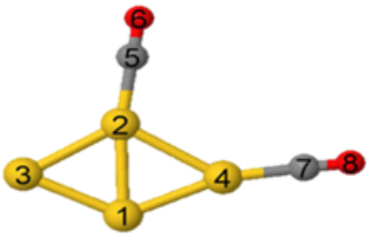
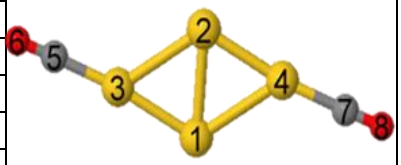
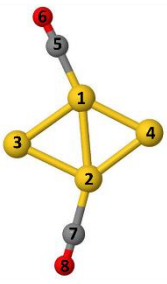
Species	Numbering of the atoms	Type of atom	Charge Population Analysis		Structure
			Mulliken	Löwdin	
Au_6^+	1	Au	0.78	0.24	
	2	Au	-0.35	0.07	
	3	Au	-0.53	0.14	
	4	Au	-0.53	0.14	
	5	Au	0.78	0.24	
	6	Au	0.85	0.17	
$Au_6^+(CO)$	1	Au	0.19	0.32	
	2	Au	-0.15	0.06	
	3	Au	-0.15	0.06	
	4	Au	-0.38	0.13	
	5	Au	0.71	0.17	
	6	Au	0.71	0.17	
	7	C	-0.07	-0.14	
	8	O	0.15	0.24	
$PdAu_5^+$	1	Au	0.30	0.23	
	2	Au	0.31	0.24	
	3	Au	0.29	0.24	
	4	Au	0.28	0.22	
	5	Au	0.29	0.21	
	6	Pd	-0.47	-0.15	
$PdAu_5^+(CO)$	1	Au	0.12	0.16	
	2	Au	0.11	0.15	
	3	Au	0.10	0.17	
	4	Au	0.26	0.19	
	5	Au	0.27	0.19	
	6	Pd	0.12	0.02	
	7	C	-0.07	-0.13	
	8	O	0.15	0.25	

Table S5: Partial charge distributions calculated with both the Mulliken and Löwdin partitioning methods for $Au_4^+(CO)_{1,2}$ clusters and their energetically competitive isomers (labelled by *) and their corresponding free cluster.

Species	Numbering of the atoms	Type of atom	Charge Population Analysis		Structure
			Mulliken	Löwdin	
Au_4^+	1	Au	0.23	0.13	
	2	Au	0.23	0.13	
	3	Au	0.27	0.37	
	4	Au	0.27	0.37	
$Au_4^+(CO)$	1	Au	0.03	0.29	
	2	Au	0.23	0.18	
	3	Au	0.34	0.22	
	4	Au	0.34	0.22	
	5	C	-0.09	-0.16	
	6	O	0.15	0.23	
$Au_4^+(CO)$*	1	Au	0.25	0.23	
	2	Au	0.28	0.18	
	3	Au	0.28	0.18	
	4	Au	0.12	0.32	
	5	C	-0.08	-0.15	
	6	O	0.16	0.24	
$Au_4^+(CO)_2$	1	Au	0.33	0.13	
	2	Au	0.13	0.29	
	3	Au	0.27	0.15	
	4	Au	0.13	0.29	
	5	C	-0.09	-0.17	
	6	O	0.14	0.23	
	7	C	-0.07	-0.15	
	8	O	0.15	0.23	
$Au_4^+(CO)_2$*	1	Au	0.21	0.09	
	2	Au	0.21	0.09	
	3	Au	0.24	0.34	
	4	Au	0.24	0.34	
	5	C	-0.1	-0.16	
	6	O	0.15	0.23	
	7	C	-0.1	-0.16	
	8	O	0.15	0.23	
$Au_4^+(CO)_2$*	1	Au	0.17	0.29	
	2	Au	0.17	0.29	
	3	Au	0.26	0.14	
	4	Au	0.27	0.13	
	5	C	-0.07	-0.15	
	6	O	0.15	0.23	
	7	C	-0.09	-0.16	
	8	O	0.14	0.23	

4. Determination of optimal spin states

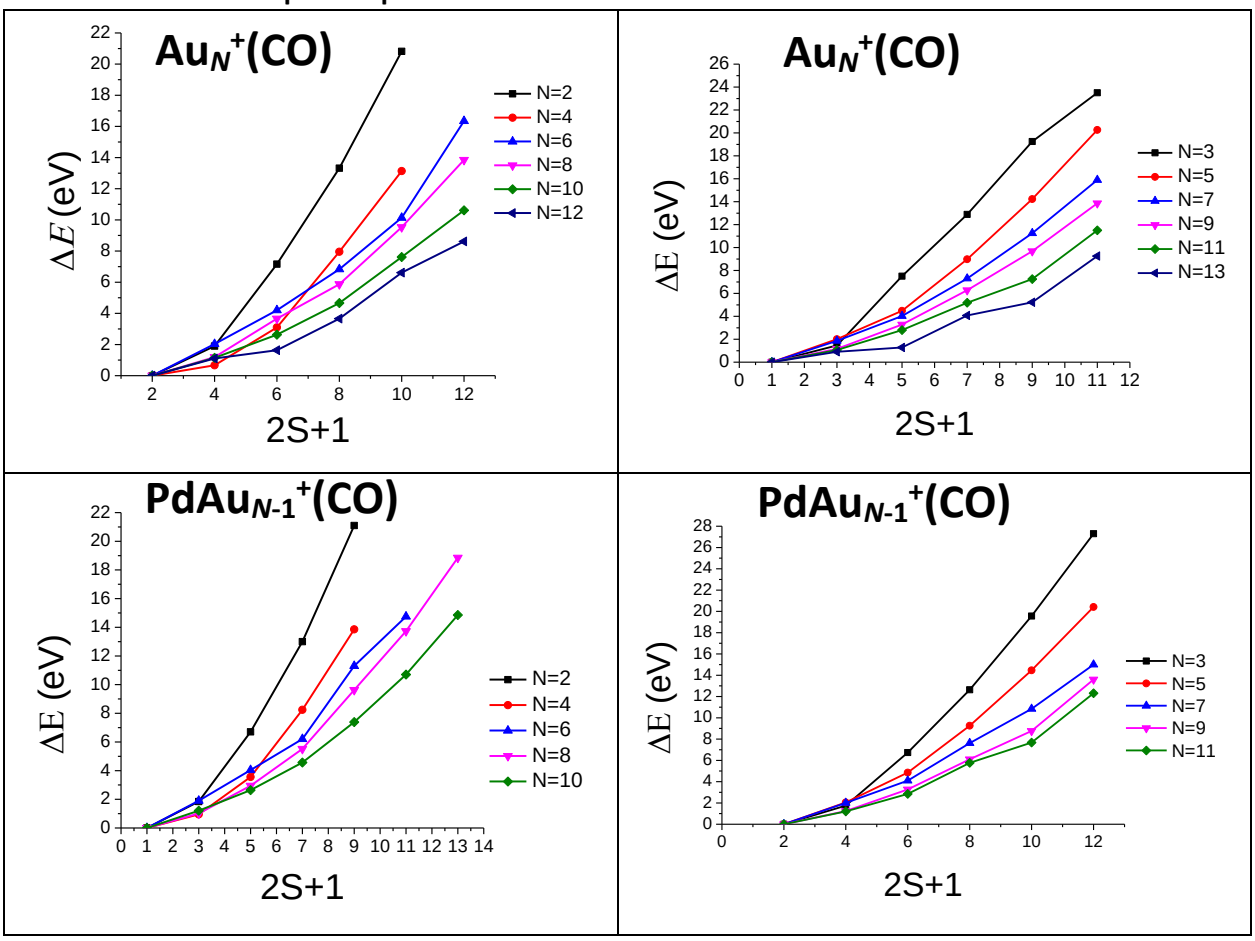


Fig S1. Relative energies as a function of spin state for $Au_N^+(CO)$ (N=2-13) and $PdAu_{N-1}^+(CO)$ (N=2-11) clusters.

5. PBE calculations

Table S6: Cluster-CO binding energies for putative global minima of $Au_N^+(CO)$ and $PdAu_{N-1}^+(CO)$, N=3-6, clusters.

Species	E_b / eV
$Au_3^+(CO)$	1.94
$Au_4^+(CO)$	1.72
$Au_5^+(CO)$	1.80
$Au_6^+(CO)$	1.48
$PdAu_2^+(CO)$	1.93
$PdAu_3^+(CO)$	1.84
$PdAu_4^+(CO)$	1.86
$PdAu_5^+(CO)$	1.96