Supplementary information

Hydride-containing Ag- and Au-rich 8-electron superatomic icosahedral Cores: A DFT investigation

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Table S1. Selected (averaged) computed data for the 8-electron cores $[(MH)@Ag_{12}]^{x+}$ and $[(MH)@Au_{12}]^{x+}$ (M = Mo-Pd, W-Pt). Interatomic distances are given in Å. WBI = Wiberg bond index; $\Delta E_{H/L}$ = HOMO-LUMO gap; q_M, q_{Ag} and q_{Au} are atomic natural charges.

$[(MH)@Ag_{12}]^{x+}$						$[(MH)@Au_{12}]^{x+}$					
M	Mo	Tc	Ru	Rh	Pd	**M**	Mo	Tc	Ru	Rh[a]	Pd[a]
x	1	2	3	4	5	**x**	1	2	3	4	5
CSM	0.62	0.57	0.52	0.44	0.31	**CSM**	1.03	1.09	1.09	n/a	n/a
$\Delta E_{H/L}$ (eV)	1.56	1.71	1.85	2.20	2.51	**$\Delta E_{H/L}$ (eV)**	1.25	1.26	1.28	1.10	1.25
M-Ag	2.813	2.814	2.829	2.863	2.920	**M-Au**	2.820	2.824	2.837	2.793	2.860
WBI	0.403	0.355	0.300	0.234	0.209	**WBI**	0.436	0.380	0.311	0.249	0.183
Ag-Ag	2.876	2.880	2.790	2.937	3.008	**Au-Au**	2.868	2.868	2.753	2.849	2.867
WBI	0.094	0.092	0.090	0.089	0.083	**WBI**	0.106	0.110	0.116	0.164	0.190
M-H	1.837	1.742	1.679	1.658	1.703	**M-H**	1.821	1.719	1.657	1.637	1.692
WBI	0.471	0.428	0.371	0.297	0.206	**WBI**	0.487	0.460	0.417	0.424	0.344
Ag-H	2.085	2.084	2.090	2.099	2.089	**Au-H**	2.168	2.191	2.211	2.137	1.717
WBI	0.102	0.105	0.109	0.116	0.123	**WBI**	0.099	0.099	0.107	0.171	0.418
q_M	-2.42	-2.13	-1.94	-1.78	-1.38	**q_M**	-1.05	-1.54	-1.80	-2.11	-0.36
q_{Ag}	0.30	0.35	0.43	0.50	0.56	**q_{Au}**	0.27	0.32	0.38	0.42	0.45
q_H	-0.20	-0.20	-0.21	-0.27	-0.38	**q_H**	-0.07	-0.05	-0.05	0.01	0.02
M	W	Re	Os	Ir	Pt	**M**	W	Re	Os	Ir	Pt[a]
x	1	2	3	4	5	**x**	1	2	3	4	5
CSM	0.69	0.67	0.64	0.63	0.66	**CSM**	1.10	1.28	1.39	1.79	n/a
$\Delta E_{H/L}$ (eV)	1.45	1.78	2.01	2.35	2.64	**$\Delta E_{H/L}$ (eV)**	1.25	1.41	1.41	1.57	1.20
M-Ag	2.816	2.820	2.837	2.872	2.934	**M-Au**	2.821	2.830	2.850	2.892	2.839
WBI	0.381	0.332	0.284	0.242	0.209		0.424	0.371	0.307	0.249	0.182
Ag-Ag	2.876	2.880	2.897	2.931	2.993	**Au-Au**	2.866	2.867	2.878	2.899	2.880
WBI	0.091	0.080	0.088	0.087	0.084	**WBI**	0.105	0.108	0.114	0.125	0.200
M-H	1.843	1.754	1.694	1.655	1.651	**M-H**	1.833	1.729	1.665	1.615	1.561
WBI	0.490	0.457	0.403	0.356	0.306	**WBI**	0.504	0.489	0.451	0.438	0.584
Ag-H	2.106	2.114	2.133	2.168	2.234	**Au-H**	2.184	2.233	2.278	2.376	3.085
WBI	0.092	0.092	0.088	0.094	0.090	**WBI**	0.091	0.085	0.087	0.083	0.030
q_M	-3.00	-2.64	-2.36	-1.94	-1.49	**q_M**	-2.59	-2.26	-1.96	-1.51	-0.66
q_{Ag}	0.35	0.40	0.46	0.51	0.57	**q_{Au}**	0.31	0.36	0.42	0.46	0.46
q_H	-0.22	-0.20	-0.21	-0.24	-0.31	**q_H**	-0.11	-0.07	-0.04	-0.02	0.18

(a) Optimized structure having lost its icosahedral parentage

. **Table S2**. Selected (averaged) computed data for the icosahedral 8-electron superatomic cores $[(MH_2)@Ag_{12}]^{x+}$ (M = Mo-Rh, W-Ir) and $[(MH_2)@Au_{12}]^{x+}$ (M = Mo-Ru, W-Os). Interatomic distances are given in Å. WBI = Wiberg bond index; $\Delta E_{H/L}$ = HOMO-LUMO gap; q_M, q_{Ag} and q_{Au} are atomic natural charges.

	$[(MH_2)@Ag_{12}]^{x+}$				$[(MH_2)@Au_{12}]^{x+}$			
M	W	Re	Os	Ir	**M**	W	Re	Os
x	2	3	4	5	**x**	2	3	4
CSM	1.58	1.55	1.43	1.37	**CSM**	1.67	2.11	2.68
$\Delta E_{H/L}$ (eV)	1.53	1.79	1.72	2.53	**$\Delta E_{H/L}$ (eV)**	1.39	1.27	1.36
M-Ag	2.876	2.889	2.918	2.976	**M-Au**	2.859	2.898	2.940
WBI	0.358	0.311	0.260	0.202	**WBI**	0.404	0.339	0.274
Ag-Ag	2.864	2.877	2.985	2.981	**Au-Au**	2.845	2.839	2.856
WBI	0.096	0.093	0.083	0.083	**WBI**	0.111	0.121	0.128
M-H	1.809	1.718	1.663	1.658	**M-H**	1.990	1.750	1.686
WBI	0.483	0.440	0.377	0.296	**WBI**	0.384	0.432	0.396
Ag-H	2.151	2.164	2.669	2.050	**Au-H**	1.871	2.036	1.890
WBI	0.092	0.093	0.097	0.123	**WBI**	0.198	0.145	0.221
H-M-H (°)	70	71	75	84	**H-M-H (°)**	69	68	70
q_M	-2.36	-2.05	-1.81	-1.53	**q_M**	-2.12	-1.71	-1.36
q_{Ag}	0.39	0.45	0.51	0.59	**q_{Au}**	0.36	0.40	0.45
q_H	-0.16	-0.15	-0.18	-0.26	**q_H**	-0.08	-0.03	-0.02
M	W	Re	Os	Ir	**M**	W	Re	Os
x	2	3	4	5	**x**	2	3	4
CSM	1.71	1.74	1.69	1.72	**CSM**	3.41	2.37	2.83
$\Delta E_{H/L}$ (eV)	1.46	1.79	2.18	2.60	**$\Delta E_{H/L}$ (eV)**	1.28	1.07	1.48
M-Ag	2.881	2.896	2.928	2.987	**M-Au**	2.893	2.927	2.956
WBI	0.345	0.298	0.252	0.211	**WBI**	0.391	0.337	0.271
Ag-Ag	2.861	2.875	2.906	2.971	**Au-Au**	2.837	2.826	2.850
WBI	0.092	0.090	0.086	0.082	**WBI**	0.113	0.124	0.132
M-H	1.818	1.733	1.677	1.651	**M-H**	1.837	1.722	1.677
WBI	0.503	0.469	0.413	0.358	**WBI**	0.463	0.483	0.449
Ag-H	2.175	2.198	2.225	2.138	**Au-H**	1.998	1.957	2.084
WBI	0.082	0.081	0.082	0.095	**WBI**	0.148	0.156	0.137
H-M-H (°)	69	70	73	80	**H-M-H (°)**	51	57	69
q_M	-2.81	-2.45	-2.15	-1.67	**q_M**	-2.42	-2.02	-1.70
q_{Ag}	0.43	0.48	0.54	0.59	**q_{Au}**	0.37	0.42	0.48
q_H	-0.18	-0.16	-0.17	-0.22	**q_H**	-0.03	0.00	0.00

Table S3. Selected (averaged) computed data for the 8-electron superatomic cores $[(MH_3)@Ag_{12}]^{x+}$ (M = Mo-Ru, W-Os). Interatomic distances are given in Å. WBI = Wiberg bond index; $\Delta E_{H/L}$ = HOMO-LUMO gap; ΔE = isomer relative energy; q_M, q_{Ag} and q_{Au} are atomic natural charges.

M			Mo					Tc			Ru
x			3					4			5
Structure type	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**	**B**
CSM	2.32	2.41	1.88	6.40	4.91	2.55	2.37	1.93	6.49	6.95	2.25
$\Delta E_{H/L}$ (eV)	1.36	2.22	2.13	2.01	2.04	2.18	2.20	2.14	2.04	1.89	2.24
ΔE (kcal/mol)	0.0	2.9	3.1	7.4	11.5	0.0	2.1	2.1	8.0	10.5	
M-Ag	2.950	2.946	2.946	2.960	2.937	2.980	2.975	2.985	2.973	2.972	3.025
WBI	0.318	0.315	0.314	0.317	0.309	0.278	0.268	0.276	0.268	0.271	0.469
Ag-Ag	2.853	2.850	2.858	2.840	2.855	2.874	2.881	2.864	2.891	2.876	2.931
WBI	0.100	0.100	0.953	0.102	0.098	0.096	0.092	0.096	0.096	0.095	0.295
M-H	1.791	1.798	1.797	1.794	1.808	1.703	1.707	1.717	1.733	1.711	1.659
WBI	0.492	0.481	0.481	0.494	0.489	0.442	0.436	0.446	0.435	0.434	0.615
Ag-H	2.074	2.085	2.153	2.055	2.168	2.065	2.214	2.167	2.148	2.067	2.138
WBI	0.097	0.098	0.091	0.113	0.091	0.098	0.082	0.096	0.100	0.093	0.301
q_M	-2.27	-2.30	-2.18	-2.30	-2.27	-1.97	-1.99	-1.93	-1.92	-1.97	-1.70
q_{Ag}	0.47	0.48	0.48	0.46	0.48	0.52	0.53	0.52	0.54	0.53	0.60
q_H	-0.12	-0.15	-0.15	-0.13	-0.16	-0.10	-0.13	-0.13	-0.17	-0.13	-0.15
M			W					Re			Os
x			3					4			5
Structure type	**A**	**B**	**C**	**D**	**E**	**A**	**B**	**C**	**D**	**E**	**B**
CSM	2.43	2.66	2.17	6.49	5.28	2.54	2.75	2.44	6.64	5.27	2.98
$\Delta E_{H/L}$ (eV)	2.29	2.21	2.04	2.12	1.59	1.32	2.40	2.24	2.06	2.17	2.43
ΔE (kcal/mol)	0.0	2.8	3.3	7.2	11.3	0.0	1.9	2.1	7.7	10.4	
M-Ag	2.954	2.954	2.964	2.954	2.953	2.984	2.992	2.992	2.970	2.985	3.047
WBI	0.312	0.308	0.311	0.308	0.308	0.270	0.263	0.269	0.259	0.265	0.222
Ag-Ag	2.836	2.713	2.839	2.845	2.844	2.869	2.873	2.864	2.887	2.869	2.907
WBI	0.100	0.918	0.097	0.096	0.096	0.093	0.089	0.091	0.087	0.092	0.092
M-H	1.804	1.801	1.807	1.809	1.809	1.724	1.718	1.734	1.739	1.726	1.671
WBI	0.516	0.508	0.519	0.508	0.508	0.473	0.477	0.478	0.481	0.471	0.420
Ag-H	2.063	2.103	2.146	2.060	2.103	2.121	2.203	2.196	2.194	2.225	2.220
WBI	0.091	0.085	0.086	0.089	0.086	0.085	0.085	0.097	0.085	0.071	0.074
q_M	-2.61	-2.59	-2.51	-2.59	-2.59	-2.27	-2.27	-2.18	-2.23	-2.26	-1.94
q_{Ag}	0.50	0.51	0.50	0.51	0.51	0.55	0.55	0.55	0.56	0.56	0.61
q_H	-0.14	-0.17	-0.16	-0.17	-0.17	-0.12	-0.13	-0.14	-0.18	-0.14	-0.12

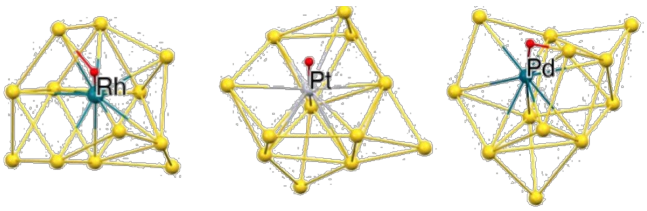

Figure S1. The non-icosahedral optimized geometries of $[RhHAu_{12}]^{4+}$ and $[PtHAu_{12}]^{5+}$, $[PdHAu_{12}]^{5+}$.

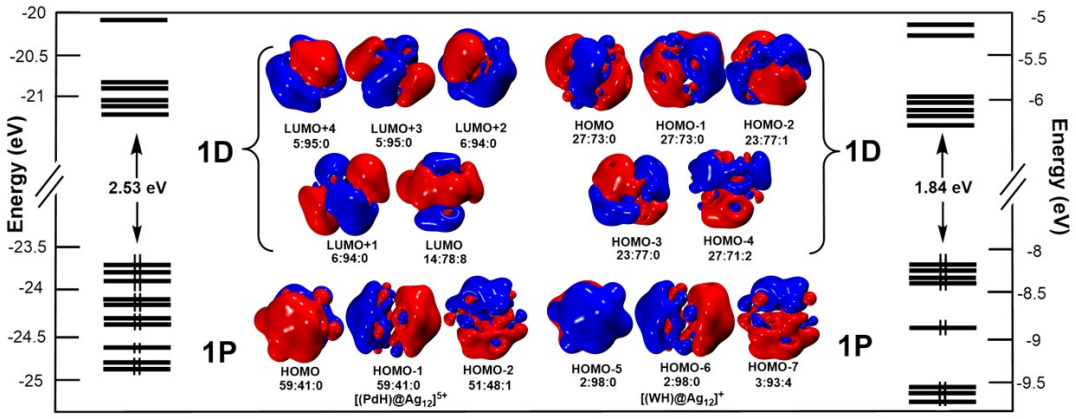

Figure S2. The Kohn-Sham orbital diagram of $[(PdH)@Ag_{12}]^{5+}$ and $[(WH)@Ag_{12}]^{+}$. Orbital localization (%) is given in the order Pd/Ag/H and W/Ag/H, respectively.

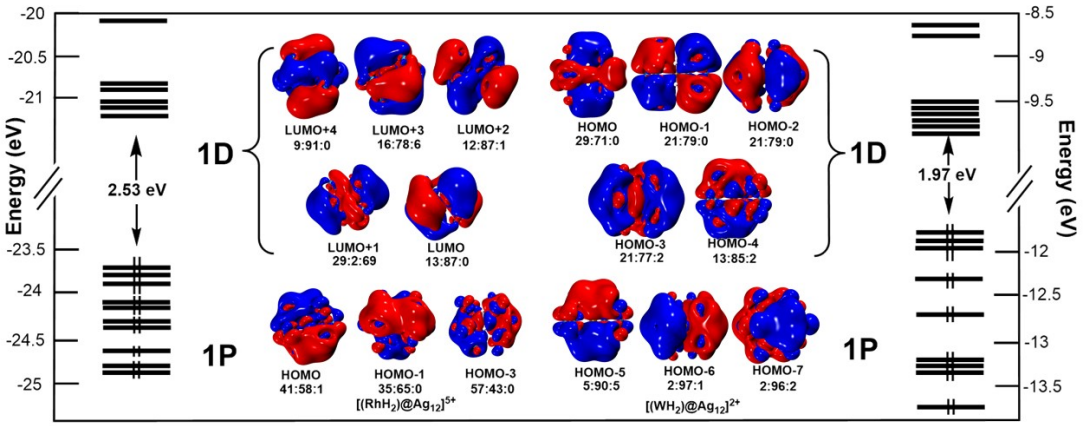

Figure S3. The Kohn-Sham orbital diagram of $[(RhH_2)@Ag_{12}]^{5+}$ and $[(WH_2)@Ag_{12}]^{2+}$. Orbital localization (%) is given in the order Rh/Ag/H and W/Ag/H, respectively.

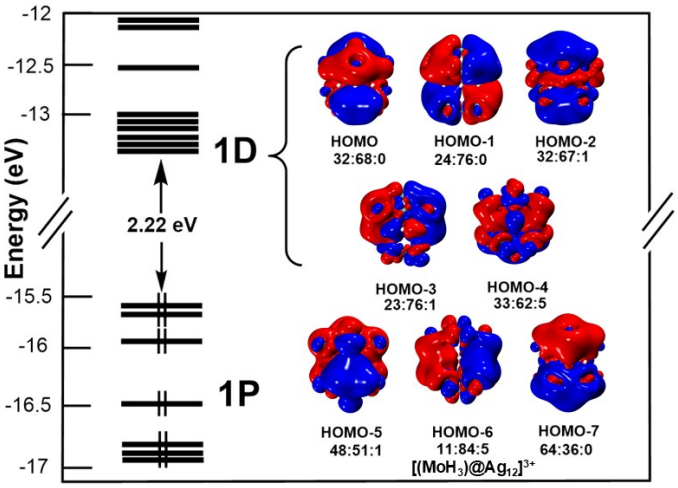

Figure S4. The Kohn-Sham orbital diagram of $[(MoH_3)@Ag_{12}]^{3+}$. Orbital localization (%) is given in the order Mo/Ag/H.