

Electronic Supplementary Information (ESI)

Redox Behavior of Small Metal Clusters with Respect to Hydrogen. The Effect of the Cluster Charge from Density Functional Results

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Table S1. Calculated energy characteristics (in kJ/mol) and interatomic distances (in pm) of optimized structures, obtained by hydrogen adsorption on neutral and charged Ir₄ clusters in the gas phase.

	n^a	ΔE^b	Ns ^c	Ir _b -Ir _b ^d	Ir _b -Ir _t ^d	$\langle \text{Ir}-\text{Ir} \rangle^e$	ΔR^f	Ir-H ^g	
								bridge	terminal
Ir ₄	0		0	247, 248, 248	248, 248, 248	248	1		
[Ir ₄] ⁺	0		1	241, 248, 250	240, 249, 250	246	9		
[Ir ₄] ²⁺	0		2	237, 251, 251	237, 251, 252	247	14		
[Ir ₄] ³⁺	0		3	241, 242, 257	241, 243, 258	247	17		
Ir ₄ H ₃	3	-196	3	244, 245, 245	259, 260, 261	252	17	170/182, 170/185, 181/172	
[Ir ₄ H ₃] ⁺	3	-179	2	246, 247, 247	257, 257, 259	252	14	169/182, 169/184, 178/172	
[Ir ₄ H ₃] ²⁺	3	-201	1	248, 248, 249	251, 252, 260	251	12	168/182, 168/186, 169/181	
[Ir ₄ H ₃] ³⁺	3	-270	0	249, 250, 251	250, 252, 252	251	3	167/184, 167/185, 167/186	
Ir ₄ H ₆	6	-487	0	245, 246, 246	266, 268, 268	256	24	167/197, 169/181, 169/182	159 _t
[Ir ₄ H ₆] ⁺	6	-408	1	243, 244, 246	259, 270, 271	256	28	168/189, 170/181, 187/171	158 _t
[Ir ₄ H ₆] ²⁺	6	-427	0	246, 248, 250	253, 261, 273	255	26	165/195, 166/193, 167/182	160 _t , 170 _t (93)
[Ir ₄ H ₆] ³⁺	6	-475	1	242, 251, 252	257, 267, 280	258	38	165/196, 166/194, 169/178	159 _t , 171 _t (94)
Ir ₄ H ₉	9	-637	1	243, 251, 272	264, 270, 275	262	32	167/193, 169/184, 178/169	158 _t , 162 _b
[Ir ₄ H ₉] ⁺	9	-555	0	240, 249, 273	264, 271, 278	262	38	166/202, 170/181, 179/169	158 _t , 161 _b
[Ir ₄ H ₉] ²⁺	9	-544	1	245, 251, 271	266, 270, 295	261	50	161/226, 167/176, 173/169	157 _t , 161 _b , 169 _t (94)
[Ir ₄ H ₉] ³⁺	9	-727	0	251, 254, 262	248, 272, 308	257 ^h	60	167/182	155 _t , 158 _b , 169 _t (96), 173 _b (91)
Ir ₄ H ₁₂	12	-888	0	264, 266, 271	266, 268, 268	267	7	165/188, 169/182, 172/173	159 _t , 160 _b
[Ir ₄ H ₁₂] ⁺	12	-761	1	270, 272, 276	262, 271, 271	270	14	164/189, 166/189, 173/173	159 _t , 159 _b
[Ir ₄ H ₁₂] ²⁺	12	-809	0	264, 277, 279	251, 264, 271	268	28	159/206, 162/192, 168/299	163 _t , 158 _b , 170 _b (90)
[Ir ₄ H ₁₂] ³⁺	12	-874	1	269, 269, 280	249, 265, 291	266 ^h	42	162/204, 163/193	159 _t , 159 _b , 169 _t (94), 171 _b (92)

^a Number of hydrogen ligands on the metal cluster. ^b Relative stability of the hydrogenated cluster; see text, Eq. (1).

^c Number of unpaired electrons in the complex. ^d Ir_b – metal atoms at the base of the trigonal pyramid; Ir_t – iridium center at the apex of the cluster, see Figure S1 below.

^e Average nearest-neighbor distance of the metal moiety. ^f Difference between the largest and the smallest nearest-neighbor distances of the optimized structures.

^g Ir-H distances for H adsorption at a distorted bridge site are given as pairs of values, Ir_b-H/Ir_t-H. For terminal hydrogen atoms only average values are provided; subscripts t and b denote distances of H atoms coordinated on-top at Ir_t and Ir_b atoms, respectively. In the structures [Ir₄H_n]^{q+} with high hydrogen loading, for n = 6, 9 or 12, pairs of closely situated hydrogen atoms, i.e. activated H₂ molecules, are indicated their average Ir-H distance and their H-H distances (provided in parentheses, italics). These latter Ir-H distances are larger than average Ir-H distances for terminal bonding and are given as last entries, separately for each pair.

^h Ir-Ir distances exceeding 290 pm (Ir_b-Ir_t = 308 pm in [Ir₄H₉]³⁺; Ir_b-Ir_t = 291 pm in [Ir₄H₁₂]³⁺) are not included in the calculation of the average $\langle \text{Ir}-\text{Ir} \rangle$.

Table S2. Various characteristics calculated for the bare metal clusters $[\text{Ir}_4]^{q+}$ and their hydrogenated congeners $[\text{Ir}_4\text{H}_n]^{q+}$ ($q = 0-3$): HOMO-LUMO gap, in eV; ionization potential, IP in eV; Mulliken charge of the Ir_4 moiety, $\text{MC}(\text{Ir}_4)$ in e; average energy, ε , and the corresponding range, δ , in eV, of Ir 2p, 4f, and 5s levels, and the average shift of all levels, $\langle\Delta\varepsilon\rangle$ in eV.

	gap	IP	MC(Ir_4)	Ir 2p		Ir 4f		Ir 5s		$\langle\Delta\varepsilon\rangle$
				ε	δ	ε	δ	ε	δ	
Ir_4	0.79		0	-11572.9	0.00	-59.74	0.19	-95.09	0.08	
$[\text{Ir}_4]^+$	0.26	6.8	1	-11578.5	0.10	-65.37	0.29	-100.71	0.25	
$[\text{Ir}_4]^{2+}$	0.51	12.2	2	-11584.5	0.04	-71.35	0.29	-106.68	0.33	
$[\text{Ir}_4]^{3+}$	0.59	18.2	3	-11591.0	0.07	-77.79	0.30	-113.10	0.47	
Ir_4H_3	0.55		0.08	-11574.0	0.37	-60.82	0.60	-96.16	0.69	1.07
$[\text{Ir}_4\text{H}_3]^+$	0.38	7.0	0.93	-11578.7	0.21	-65.54	0.42	-100.89	0.52	0.17
$[\text{Ir}_4\text{H}_3]^{2+}$	0.30	12.0	1.71	-11584.4	0.45	-71.20	0.68	-106.54	0.65	-0.14
$[\text{Ir}_4\text{H}_3]^{3+}$	1.03	17.5	2.47	-11590.4	0.58	-77.23	0.81	-112.55	0.59	-0.56
Ir_4H_6	1.12		0.25	-11573.9	0.17	-60.72	0.44	-96.06	0.24	0.97
$[\text{Ir}_4\text{H}_6]^+$	0.40	7.6	0.75	-11579.2	0.37	-66.04	0.60	-101.38	0.52	0.68
$[\text{Ir}_4\text{H}_6]^{2+}$	0.67	12.0	1.38	-11584.2	1.28	-71.02	1.45	-106.35	1.23	-0.32
$[\text{Ir}_4\text{H}_6]^{3+}$	0.49	17.7	1.96	-11590.0	0.37	-76.82	0.57	-112.13	0.38	-0.97
Ir_4H_9	0.83		0.27	-11574.4	0.81	-61.26	1.01	-96.59	1.01	1.52
$[\text{Ir}_4\text{H}_9]^+$	0.76	7.6	0.64	-11579.4	1.26	-66.25	1.56	-101.58	1.26	0.89
$[\text{Ir}_4\text{H}_9]^{2+}$	0.49	12.3	1.16	-11584.3	0.96	-71.12	1.22	-106.44	1.03	-0.23
$[\text{Ir}_4\text{H}_9]^{3+}$	0.97	16.3	1.50	-11589.4	0.84	-76.18	1.10	-111.50	0.83	-1.61
Ir_4H_{12}	2.21		0.44	-11574.6	0.23	-61.41	0.39	-96.74	0.20	1.67
$[\text{Ir}_4\text{H}_{12}]^+$	0.73	8.1	0.61	-11579.4	0.72	-66.25	0.90	-101.58	0.76	0.88
$[\text{Ir}_4\text{H}_{12}]^{2+}$	1.61	11.7	0.82	-11584.0	0.61	-70.84	0.77	-106.17	0.59	-0.50
$[\text{Ir}_4\text{H}_{12}]^{3+}$	0.67	17.5	0.90	-11589.3	0.35	-76.06	0.54	-111.38	0.45	-1.72

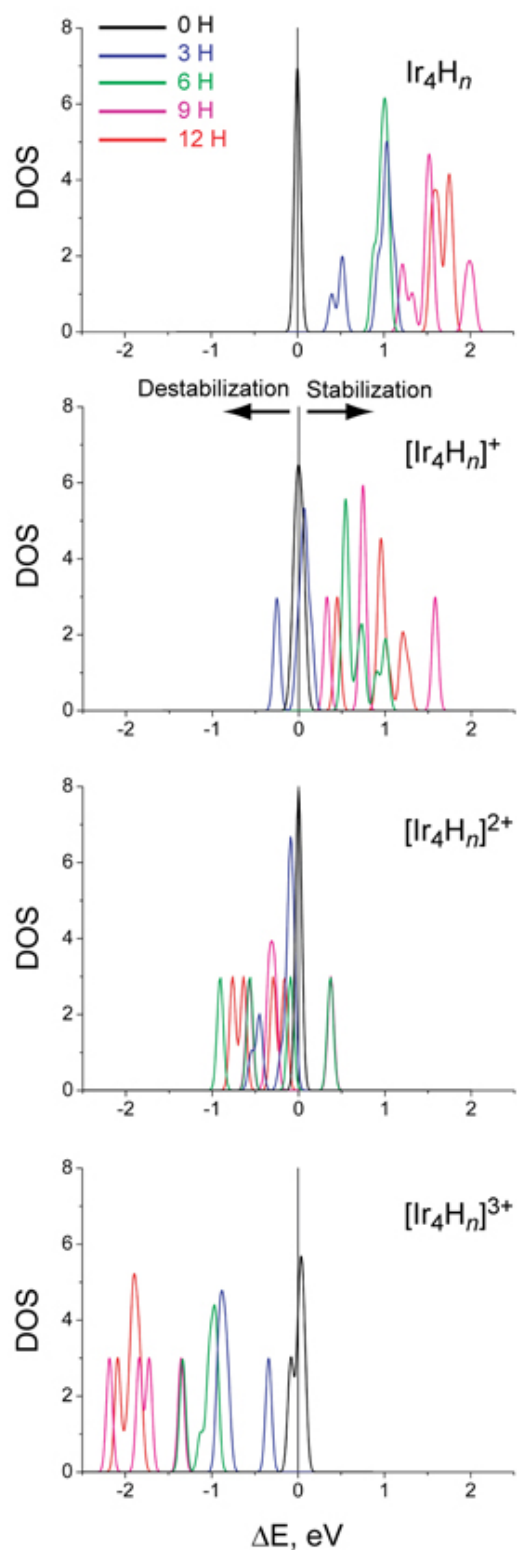


Figure S1. DOS plots for Ir 2p core levels of Ir centers of the bare clusters $[\text{Ir}_4]^{q+}$ and the hydrogenated clusters $[\text{Ir}_4\text{H}_n]^{q+}$ ($q = 0-3$), relative to the energy of the Ir 2p level of the Ir_4 cluster with corresponding charge q . The 2p levels of $[\text{Ir}_4]^{3+}$ form two groups of different energies; therefore an average value is used to estimate of the energy shifts of the hydrogenated species. The energies of the Ir 2p levels of the bare clusters are -11572.9 eV in Ir_4 , -11578.5 eV in $[\text{Ir}_4]^+$, -11584.5 eV in $[\text{Ir}_4]^{2+}$, and -11591.0 eV in $[\text{Ir}_4]^{3+}$.

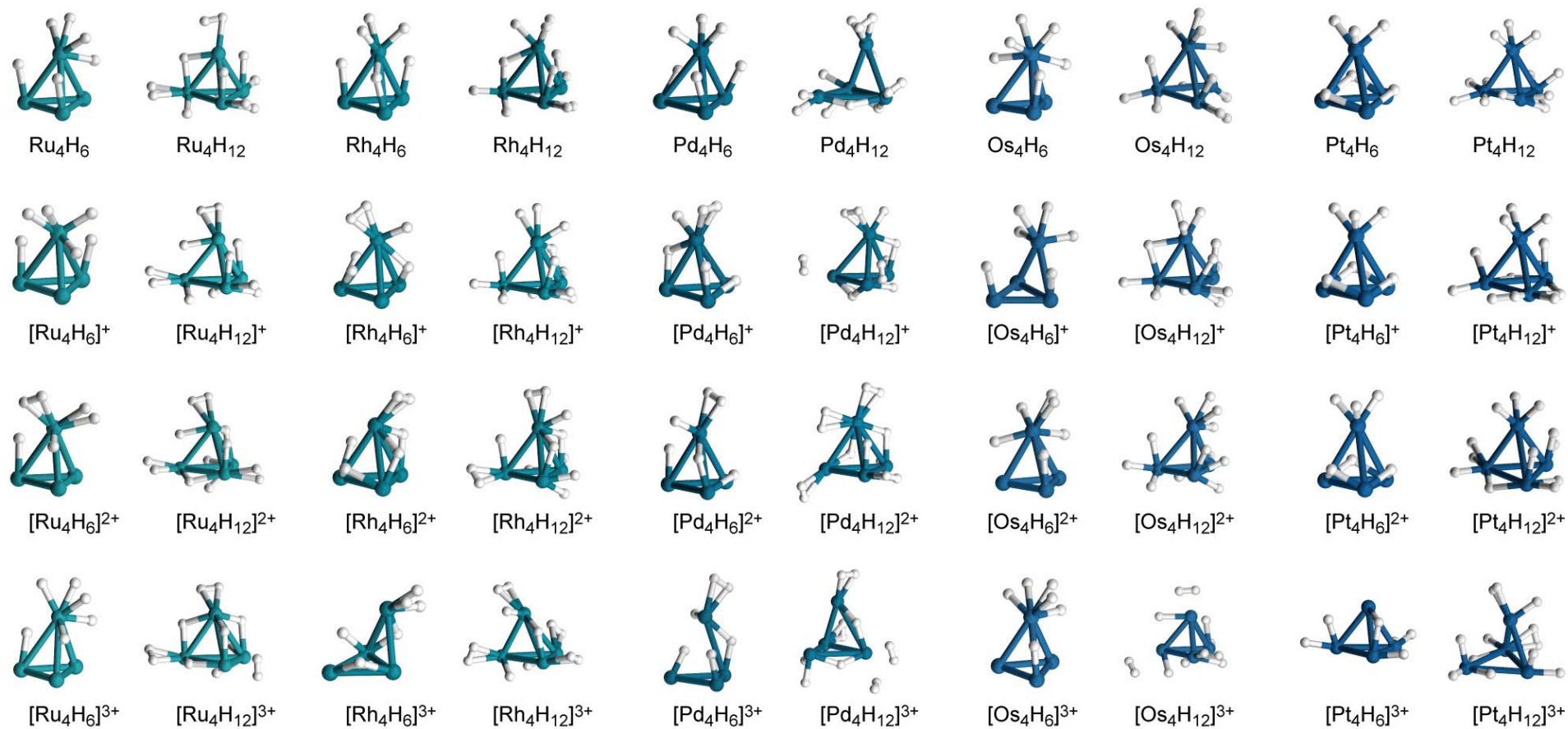


Figure S2. Optimized structures of $[\text{M}_4\text{H}_n]^{q+}$ species for $q = 0, 1, 2, 3$ and $n = 6, 12$.

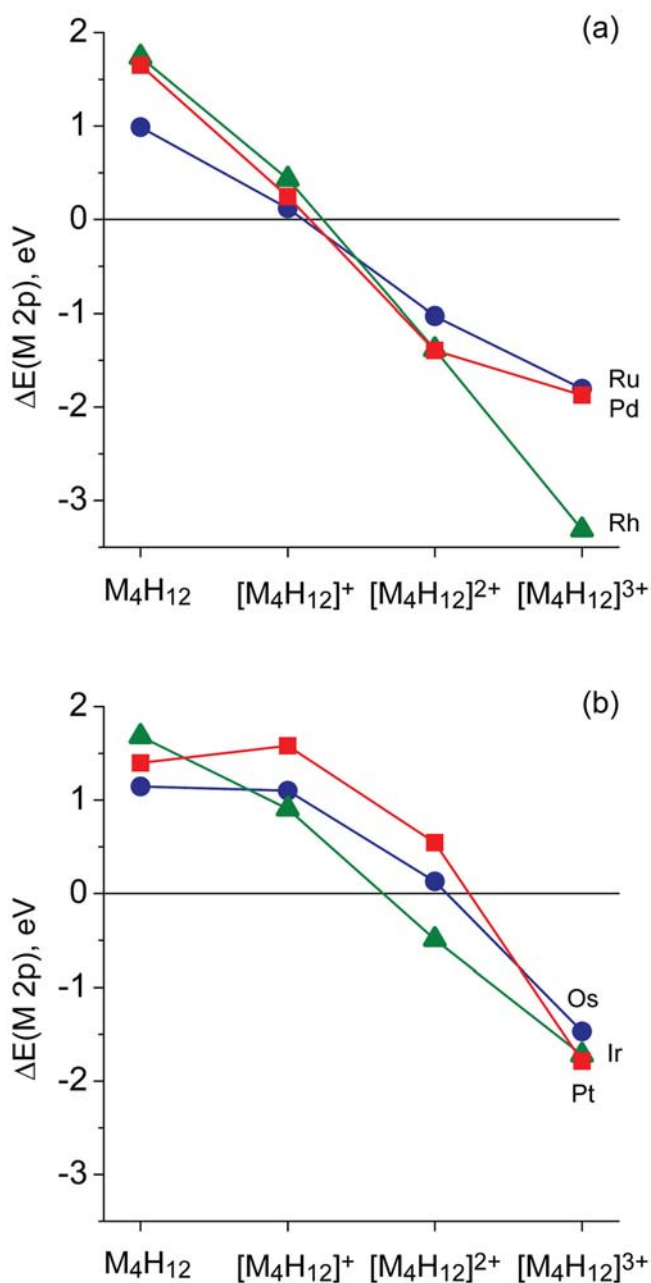


Figure S3. Variations of the average shifts of the M 2p levels in $[M_4H_{12}]^{q+}$ clusters with the total charge of the complexes of the (a) 4d and (b) 5d transition metals.