

Table S1. Comparison of calculated and experimental results for metal-metal distances (pm) in Mo and W complexes.

molecule	LDA ^[a]	OLYP ^[b]	OPBE ^[c]	PBE ^[d]	BLYP ^[e]	experiment ^[f,g]
Mo₂(CH₃)₆	221	223	221	225	228	217
Mo₂(NH₂)₆	222	225	222	226	229	221
W₂(CH₃)₆	229	231	229	232	235	226
W₂(NH₂)₆	228	231	229	234	234	229
AAD ^[h]	2.25	4.25	2.00	6.00	8.25	

^[a] Local Density Approximation in the Vosko-Wilk-Nusair representation

^[b] Handy-Cohen (exchange) and Lee-Yang-Parr (correlation) functional

^[c] Handy-Cohen (exchange) and Perdew-Burke-Ernzerhof (correlation) functional

^[d] Perdew-Burke-Ernzerhof (exchange and correlation) functional

^[e] Becke 1988 (exchange) and Lee-Yang-Parr (correlation) functional

^[f] Experimental results correspond to Mo-Mo and W-W bond lengths in dinuclear Mo and W species containing C and N donor ligands, and were taken from “Multiple Bonds between Metal Atoms” by FA Cotton and RA Walton (Second Edition, Oxford University Press, New York, 1993)

^[g] The best overall agreement between computational and experimental results is given by the OPBE functional.

^[h] Average Absolute Deviation between calculation and experiment.

Table S2. Comparison of calculated results for the metal-metal distance in U₂Cl₆.

method ^[a]	distance / pm ^[d]
LDA	238
OLYP	238
OPBE	235
PBE	240
BP86 ^[b]	241
BLYP	244
CASPT2 ^[c]	243

^[a] Functional descriptions (for LDA, OLYP, OPBE, PBE, and BLYP) given in Table S1.

^[b] Becke 1988 (exchange) and Perdew 1986 (correlation) functional

^[c] Multiconfigurational perturbative calculations by Gagliardi and Roos (Inorg. Chem. 2006, 45, 803)

^[d] The CASPT2 results are most closely reproduced by the BLYP calculations, but this approach exhibits a rather poor performance when applied to Mo and W complexes and compared to experimental observations (Table S1)

Table S3. Energy decomposition analysis (eV) for Mo_2X_6 complexes ($\text{M}_2\text{X}_6 \leftrightarrow 2 \text{ MX}_3$), performed at various metal-metal distances (M-M) in the vicinity of the potential energy minimum (E_B = Total Bonding Energy, E_P = Pauli Repulsion, E_E = Electrostatic Interaction, E_O = Orbital Mixing).

molecule	M-M / pm	E_B	E_P	E_E	E_O
Mo₂Cl₆	210	-2.97	18.04	-10.79	-10.22
	220	-3.22	13.72	-8.45	-8.50
	230	-3.19	10.47	-6.61	-7.05
	240	-2.98	8.00	-5.17	-5.80
	250	-2.65	6.12	-4.04	-4.73
Mo₂F₆	210	-2.94	19.05	-11.95	-10.04
	220	-3.22	14.48	-9.39	-8.30
	230	-3.19	11.01	-7.37	-6.83
	240	-2.97	8.38	-5.77	-5.58
	250	-2.63	6.38	-4.52	-4.49
Mo₂(OH)₆	210	-2.94	17.80	-10.89	-9.85
	220	-3.18	13.58	-8.60	-8.17
	230	-3.14	10.38	-6.79	-6.73
	240	-2.90	7.95	-5.36	-5.50
	250	-2.56	6.10	-4.23	-4.43
Mo₂(NH₂)₆	210	-2.34	19.60	-12.99	-8.95
	220	-2.56	15.18	-10.47	-7.27
	230	-2.51	11.79	-8.45	-5.86
	240	-2.30	9.18	-6.81	-4.67
	250	-1.99	7.15	-5.50	-3.65
Mo₂(CH₃)₆	210	-2.87	21.50	-14.84	-9.52
	220	-3.08	16.91	-12.15	-7.84
	230	-3.02	13.34	-9.95	-6.41
	240	-2.79	10.55	-8.14	-5.20
	250	-2.46	8.35	-6.66	-4.15

Table S4. Energy decomposition analysis (eV) for W_2X_6 complexes ($M_2X_6 \leftrightarrow 2 MX_3$), performed at various metal-metal distances (M-M) in the vicinity of the potential energy minimum (E_B = Total Bonding Energy, E_P = Pauli Repulsion, E_E = Electrostatic Interaction, E_O = Orbital Mixing).

molecule	M-M / pm	E_B	E_P	E_E	E_O
W_2Cl_6	210	-3.56	26.78	-18.58	-11.76
	220	-4.18	20.42	-14.64	-9.96
	230	-4.36	15.58	-11.53	-8.41
	240	-4.25	11.88	-9.06	-7.07
	250	-3.95	9.06	-7.11	-5.90
W_2F_6	210	-3.61	27.07	-19.16	-11.51
	220	-4.27	20.53	-15.06	-9.73
	230	-4.46	15.56	-11.82	-8.19
	240	-4.34	11.78	-9.26	-6.86
	250	-4.03	8.91	-7.25	-5.69
$W_2(OH)_6$	210	-3.43	24.82	-16.93	-11.32
	220	-4.03	18.90	-13.35	-9.59
	230	-4.20	14.41	-10.52	-8.08
	240	-4.07	10.99	-8.29	-6.76
	250	-3.75	8.38	-6.53	-5.60
$W_2(NH_2)_6$	210	-2.78	27.38	-19.55	-10.60
	220	-3.32	21.16	-15.69	-8.80
	230	-3.46	16.38	-12.57	-7.26
	240	-3.33	12.69	-10.08	-5.94
	250	-3.04	9.83	-8.07	-4.80
$W_2(CH_3)_6$	210	-3.27	30.12	-22.32	-11.07
	220	-3.82	23.59	-18.12	-9.29
	230	-3.97	18.50	-14.70	-7.77
	240	-3.84	14.53	-11.91	-6.45
	250	-3.54	11.41	-9.65	-5.31

Table S5. Energy decomposition analysis (eV) for U_2X_6 complexes ($\text{M}_2\text{X}_6 \leftrightarrow 2 \text{ MX}_3$), performed at various metal-metal distances (M-M) in the vicinity of the potential energy minimum (E_B = Total Bonding Energy, E_P = Pauli Repulsion, E_E = Electrostatic Interaction, E_O = Orbital Mixing).

molecule	M-M / pm	E_B	E_P	E_E	E_O
U_2Cl_6	210	1.34	25.89	-5.52	-19.03
	220	0.25	18.39	-3.05	-15.09
	230	-0.16	13.19	-1.47	-11.89
	240	-0.17	9.57	-0.47	-9.27
	250	0.09	7.04	0.16	-7.11
U_2F_6	210	0.66	29.78	-9.10	-20.02
	220	-0.60	21.62	-5.99	-16.22
	230	-1.14	15.89	-3.92	-13.11
	240	-1.19	11.85	-2.53	-10.51
	250	-0.91	8.97	-1.59	-8.28
$\text{U}_2(\text{OH})_6$	210	0.91	34.94	-14.69	-19.34
	220	-0.41	26.23	-11.17	-15.47
	230	-0.94	19.98	-8.66	-12.26
	240	-0.99	15.45	-6.85	-9.59
	250	-0.81	12.13	-5.50	-7.43
$\text{U}_2(\text{NH}_2)_6$	210	0.45	29.46	-9.99	-19.02
	220	-0.61	21.76	-7.27	-15.11
	230	-1.03	16.34	-5.42	-11.96
	240	-1.05	12.47	-4.13	-9.39
	250	-0.82	9.69	-3.22	-7.29
$\text{U}_2(\text{CH}_3)_6$	220	-0.85	29.05	-13.06	-16.84
	230	-1.34	22.60	-10.47	-13.46
	240	-1.37	17.84	-8.52	-10.68
	250	-1.16	14.26	-7.02	-8.39