Supporting Information

Theoretical insight into the unique structural stabilization mechanism in actinides-centered boride

Shu-Xian Hu*[1], PengXiang Qiu[2], Haitao Liu*[3]

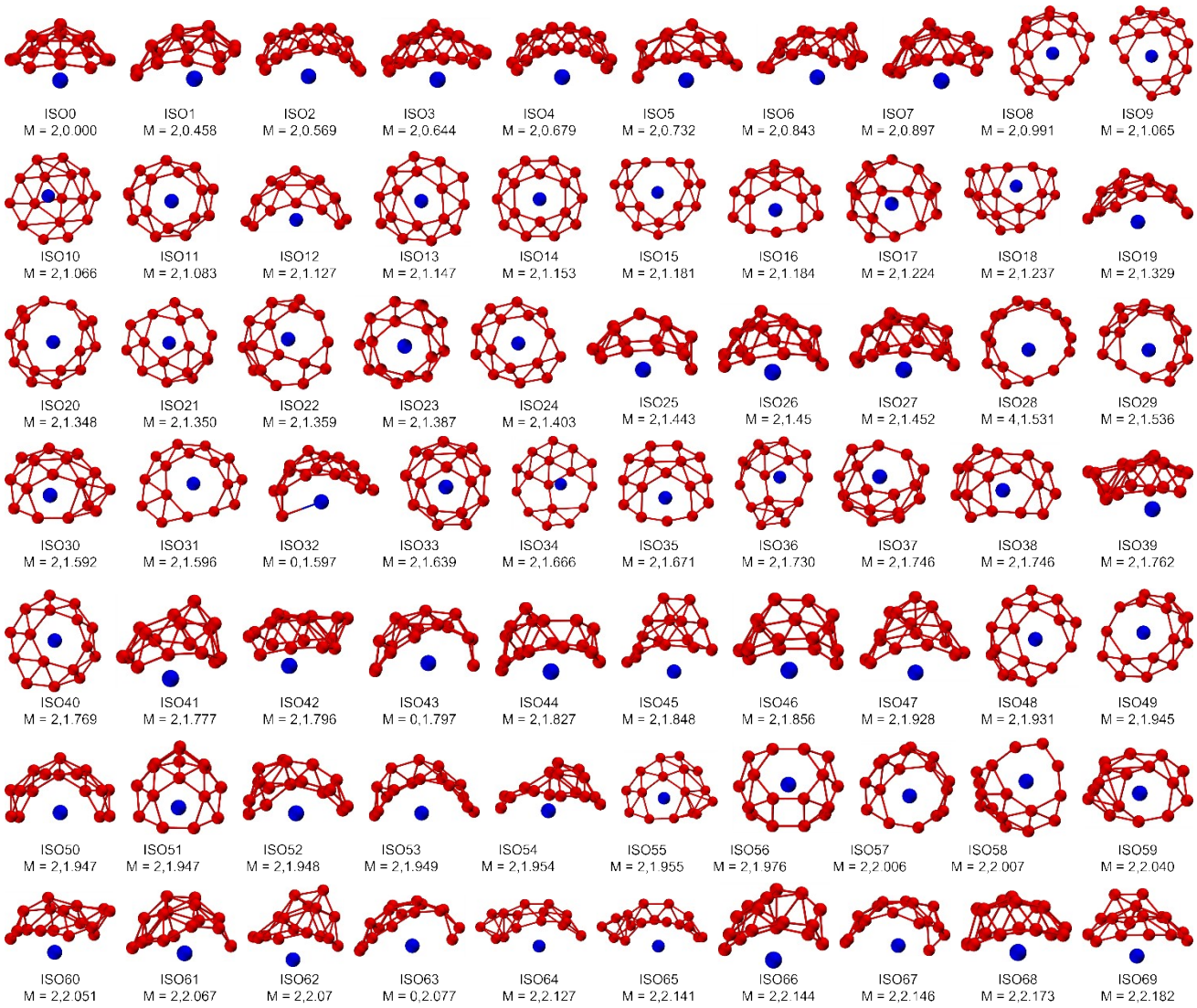
[1] School of mathematics and physics, University of Science and Technology Beijing, Beijing 100083, China

[2] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China

[3] National Key Laboratory of Computational Physics, Institute of Applied Physics and Computational Mathematics, Beijing 100088, China

Corresponding author, E-mail: hushuxian@csrc.ac.cn, liu_haitao@iapcm.ac.cn

SUPPORTING INFORMATION


ISO0 M = 2,0.000
ISO1 M = 2,0.458
ISO2 M = 2,0.569
ISO3 M = 2,0.644
ISO4 M = 2,0.679
ISO5 M = 2,0.732
ISO6 M = 2,0.843
ISO7 M = 2,0.897
ISO8 M = 2,0.991
ISO9 M = 2,1.065
ISO10 M = 2,1.066
ISO11 M = 2,1.083
ISO12 M = 2,1.127
ISO13 M = 2,1.147
ISO14 M = 2,1.153
ISO15 M = 2,1.181
ISO16 M = 2,1.184
ISO17 M = 2,1.224
ISO18 M = 2,1.237
ISO19 M = 2,1.329
ISO20 M = 2,1.348
ISO21 M = 2,1.350
ISO22 M = 2,1.359
ISO23 M = 2,1.387
ISO24 M = 2,1.403
ISO25 M = 2,1.443
ISO26 M = 2,1.45
ISO27 M = 2,1.452
ISO28 M = 4,1.531
ISO29 M = 2,1.536
ISO30 M = 2,1.592
ISO31 M = 2,1.596
ISO32 M = 0,1.597
ISO33 M = 2,1.639
ISO34 M = 2,1.666
ISO35 M = 2,1.671
ISO36 M = 2,1.730
ISO37 M = 2,1.746
ISO38 M = 2,1.746
ISO39 M = 2,1.762
ISO40 M = 2,1.769
ISO41 M = 2,1.777
ISO42 M = 2,1.796
ISO43 M = 0,1.797
ISO44 M = 2,1.827
ISO45 M = 2,1.848
ISO46 M = 2,1.856
ISO47 M = 2,1.928
ISO48 M = 2,1.931
ISO49 M = 2,1.945
ISO50 M = 2,1.947
ISO51 M = 2,1.947
ISO52 M = 2,1.948
ISO53 M = 2,1.949
ISO54 M = 2,1.954
ISO55 M = 2,1.955
ISO56 M = 2,1.976
ISO57 M = 2,2.006
ISO58 M = 2,2.007
ISO59 M = 2,2.040
ISO60 M = 2,2.051
ISO61 M = 2,2.067
ISO62 M = 2,2.07
ISO63 M = 0,2.077
ISO64 M = 2,2.127
ISO65 M = 2,2.141
ISO66 M = 2,2.144
ISO67 M = 2,2.146
ISO68 M = 2,2.173
ISO69 M = 2,2.182

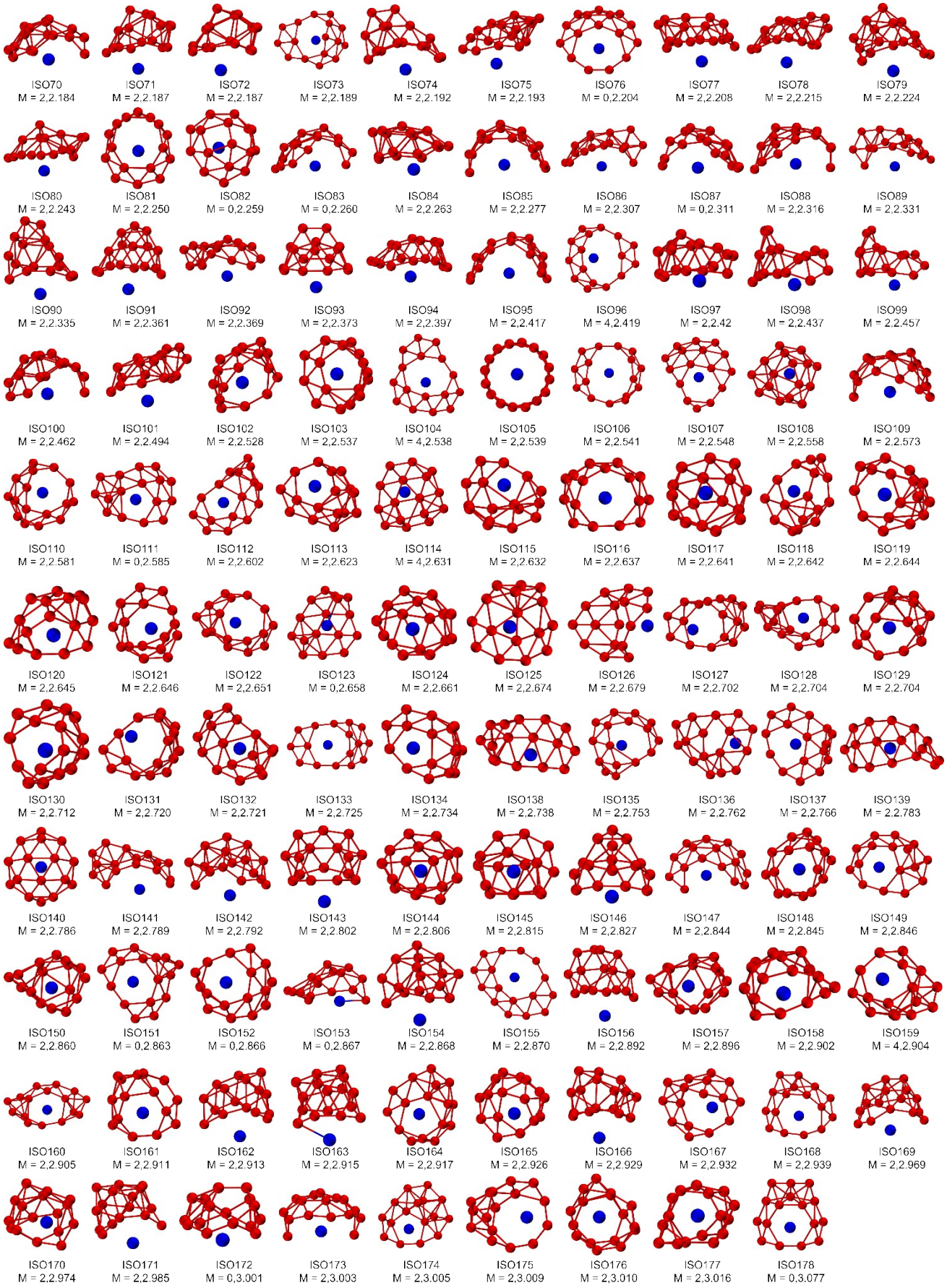
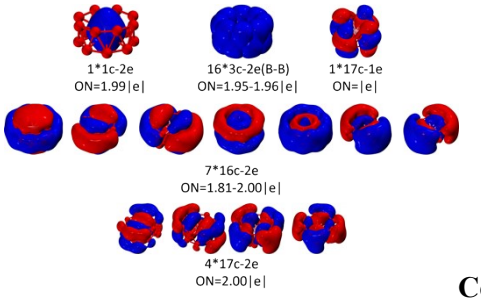
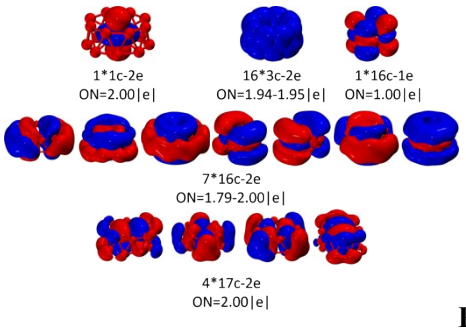


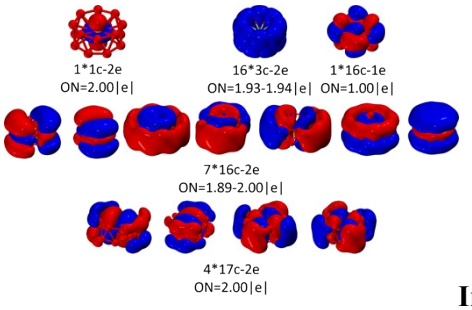
Figure S1. The structures and relative energies in eV for the low-lying isomers of [UB_{16}] at PBE/PLW level.



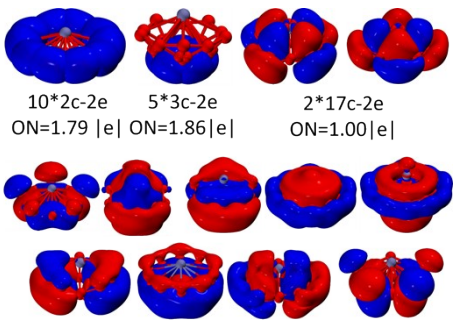
CoB_{16}



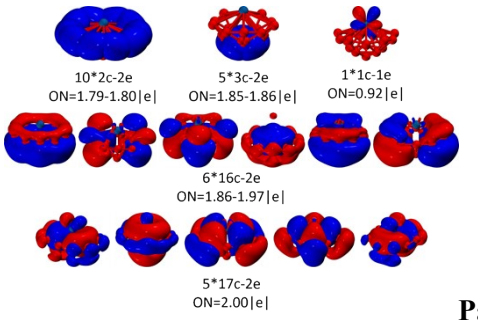
RhB_{16}



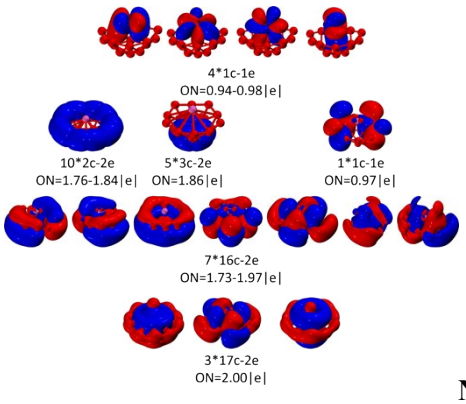
IrB_{16}



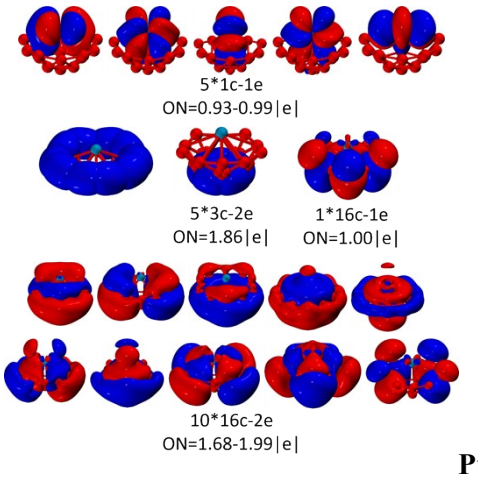
ThB_{16}



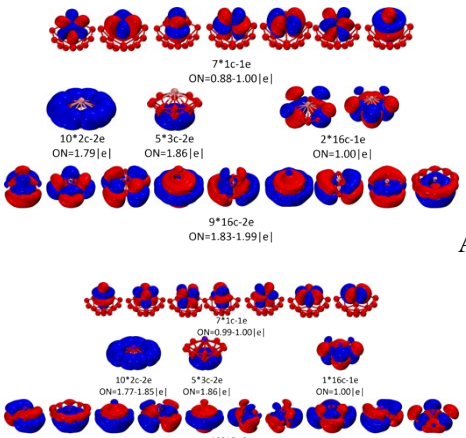
PaB_{16}



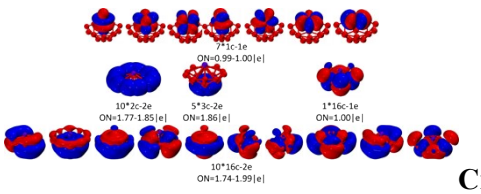
NpB_{16}



PuB_{16}



AmB_{16}



CmB_{16}

Figure S2. Chemical bonding picture for the C_2 CoB_{16}, RhB_{16}, IrB_{16} and C_{5v} AnB_{16} with An = Th, Pa, Np, Pu, Am, Cm, obtained via the UAdNDP analysis. ON (|e|) denotes occupation number.

Table S1. The total energy and relative energy (in kcal/mol) corresponding to the lowest energy spin state of all the [AnB_{16}] species at PBE/TZ2P level of theory.

AnB_{16}	Symm.	Spin state	SR	ΔE	SO	ΔE
Th	C_{5v}	2	-2325.53	0.0	-2358.96	0.0
		4	-2295.51	30.0	-2357.74	1.2
	C_{8v}	2	-2279.64	45.9	-2311.7	47.3
		4	-2266.05	59.5	-2307.71	51.3
Pa	C_{5v}	1	-2342.64	0.0	-2385.18	0.0
		3	-2327.74	14.9	-2383.66	1.5
	C_{8v}	1	-2298.1	44.5	-2339.57	45.6
		3	-2275.32	67.3	-2339.57	45.6
U	C_{5v}	2	-2332.52	16.5	-2387.54	11.0
		4	-2349.04	0.0	-2398.55	0.0
		6	-2339.76	9.3	-2396.77	1.8
	C_{8v}	2	-2289.9	59.1	-2284.42	114.1
		4	-2296.34	52.7	-2347.53	51.0
		6	-2286.48	62.6	-2347.53	51.0
Np	C_{5v}	1	-2344.95	15.8	-2417.09	0.1
		3	-2360.78	0.0	-2417.24	0.0
		5	-2353.29	7.5	-2416.68	0.6
		7	-2339.39	21.4	/	/
	C_{8v}	1	-2291.52	69.3	-2360.7	56.5
		3	-2307.78	53.0	-2365.49	51.8
		5	-2306.33	54.5	-2364.39	52.8
Pu	C_{5v}	2	-2312.06	27.6	-2399.54	1.2
		4	-2339.65	0.0	-2400.75	0.0
		6	-2334.19	5.5	-2400.59	0.2
	C_{8v}	2	-2274.21	65.4	-2352.46	48.3
		4	-2163.83	175.8	-2354.91	45.8
		6	-2295.9	43.8	-2354.81	45.9
Am	C_{5v}	1	-2296.22	57.8	-2415.77	0.8
		3	-2315.24	38.8	-2414.91	1.7
		5	-2354.03	0.0	-2416.58	0.0
		7	-2344.81	9.2	-2416.52	0.1
	C_{8v}	1	-2257.81	96.2	-2371.5	45.1
		3	-2294.15	59.9	-2373.36	43.2
		5	-2312.49	41.5	-2372.04	44.5
		7	-2314.67	39.4	-2372.08	44.5
Cm	C_{5v}	2	-2370.51	55.0	-2499.61	3.3
		4	-2408.42	17.1	-2496.3	1.2
		6	-2425.55	0.0	-2498.44	0.0
		8	-2424.53	1.0	-2499.12	0.5

		10	-2389.38	36.2	/	/
	C_{8v}	2	-2350.82	74.7	-2446.66	53.0
		4	-2371.1	54.5	-2453.68	45.9
		6	-2386.31	39.2	-2459.47	40.1
		8	-2385.33	40.2	-2459.77	39.8

Table S2. Spin density on M in MB_{16} (M = Sc, Ti, V, Co, Rh, Ir, Eu and Th-Cm) in two competition spin states at PBE/TZ2P level of theory.

Species	Atomic Radius (van der Waals)	Ground Spin state	M spin (|e|) (assg. OS)	*Symm.*	Competing Spin state	M spin (|e|) (assg. OS)	*Symm.*	Relative energy (kcal/mol)
$[ScB_{16}]$	144	2	-0.04 (III)	C_1	4	0.2635 (III)	C_1	19.77
$[TiB_{16}]$	132	3	0.05 (IV)	C_{8v}	1	0.00 (IV)	C_2	4.13
$[VB_{16}]$	122	2	0.01 (V)	C_2	4	0.79 (IV)	C_2	18.23
$[CoB_{16}]$	116	2	0.01 (-1)	C_2	4	0.30 (-1)	C_{8v}	13.70
$[RhB_{16}]$	125	2	-0.02 (-1)	C_2	4	-0.11 (-1)	C_{8v}	9.64
$[IrB_{16}]$	127	2	-0.02 (-1)	C_2	4	0.17 (-1)	C_2	12.46
$[EuB_{16}]$	204	6	6.68 (III)	C_{5v}	8	6.60 (III)	C_{5v}	11.39
$[ThB_{16}]$	237	1	0.00 (IV)	C_{5v}	3	0.29(IV)	C_{5v}	31.13
$[PaB_{16}]$	243	2	0.90 (IV)	C_{5v}	4	0.90 (IV)	C_1	14.41
$[NpB_{16}]$	240	3	2.48 (IV)	C_{5v}	5	2.63 (IV)	C_1	9.06
$[UB_{16}]$	221	4	3.82 (III)	C_{5v}	6	3.82 (III)	C_1	7.47
$[PuB_{16}]$	243	5	5.22 (III)	C_{5v}	7	5.28 (III)	C_1	5.26
$[AmB_{16}]$	244	6	6.57 (II)	C_{5v}	10	6.68 (II)	C_{5v}	9.27
$[CmB_{16}]$	245	7	6.82 (III)	C_{5v}	9	6.77 (III)	C_1	1.02

Table S3. Bond order of MB_{16} species computed using SR/SO-ZORA at PBE/TZ2P level of theory.

Species	PBE-SR				PBE-SO			
	An-B(1)	An-B(2)	An-B(3)	An-B(4)	An-B(1)	An-B(2)	An-B(3)	An-B(4)
ScB_{16}	0.233	0.234*5	0.231*5	0.234*5	0.195	0.216	0.265	0.280
ThB_{16}	0.188	0.281*5	0.414*5	0.352*5	0.188	0.282	0.413	0.353
PaB_{16}	0.197	0.330*5	0.489*5	0.383*5	0.195	0.327	0.485	0.382
UB_{16}	0.145	0.314*5	0.501*5	0.367*5	0.146	0.314	0.500	0.368
NpB_{16}	0.146	0.297*5	0.467*5	0.359*5	0.146	0.297	0.468	0.360
PuB_{16}	0.149	0.268*5	0.409*5	0.334*5	0.149	0.269	0.410	0.334
AmB_{16}	0.092	0.224*5	0.331*5	0.275*5	0.094	0.227	0.333	0.277
CmB_{16}	0.120	0.215*5	0.296*5	0.271*5	0.122	0.216	0.295	0.272
EuB_{16}	0.125	0.183*5	0.281*5	0.241*5	0.126	0.184	0.282	0.241
CoB_{16}	0.344				0.344			
RhB_{16}	0.185				0.185			
IrB_{16}	0.213				0.301			
VB_{16}	0.366				0.366			
TiB_{16}	0.211		0.434		0.211		0.434	

Table S4. Mulliken Charge on M and B of MB16 species computed using SR/SO-ZORA at PBE/TZ2P level of theory.

Species	PBE-SR					PBE-SO				
	An	B(1)	B(2)	B(3)	B(4)	An	B(1)	B(2)	B(3)	B(4)
ScB_{16}	0.482	-0.037	-0.030	-0.031	-0.028	0.542	-0.041	0.057	-0.187	0.030
ThB_{16}	0.299	-0.064	0.112	-0.178	0.019	0.293	-0.073	0.118	-0.188	0.026
PaB_{16}	0.217	-0.055	0.114	-0.180	0.033	0.223	-0.055	0.114	-0.180	0.033
UB_{16}	0.172	-0.058	0.102	-0.163	0.038	0.172	-0.058	0.102	-0.163	0.039
NpB_{16}	0.144	-0.071	0.100	-0.167	0.052	0.140	-0.072	0.100	-0.165	0.051
PuB_{16}	0.257	-0.071	0.092	-0.182	0.052	0.255	-0.072	0.094	-0.180	0.050
AmB_{16}	0.303	-0.077	0.090	-0.187	0.052	0.289	-0.076	0.090	-0.185	0.053
CmB_{16}	0.388	-0.073	0.087	-0.186	0.036	0.378	-0.074	0.088	-0.186	0.038
EuB_{16}	0.742	-0.107	0.088	-0.219	0.004	0.740	-0.107	0.088	-0.218	0.004
CoB_{16}	-0.277	0.016				-0.263	0.016			
RhB_{16}	0.876	-0.055				0.874	-0.055			
IrB_{16}	0.313	-0.020				0.370	-0.023			
VB_{16}	0.083	-0.005				0.083	-0.005			
TiB_{16}	0.333	0.017		-0.058		0.333	0.017		-0.058	
C_{2h} B_{16}	/	-0.12	0.17	-0.19	0.04	/				

Table S5. Spin density on M and B of MB_{16} species computed using SR/SO-ZORA at PBE/TZ2P level of theory.

Species	PBE-SR					PBE-SO				
	An	B(1)	B(2)	B(3)	B(4)	An	B(1)	B(2)	B(3)	B(4)
ScB_{16}	0.747	-0.041	0.027	-0.006	0.038	-0.041	-0.028	0.037	0.219	-0.042
ThB_{16}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
PaB_{16}	0.903	-0.032	0.022	-0.002	0.006	0.920	-0.031	0.020	-0.004	0.006
UB_{16}	2.481	-0.038	0.003	-0.131	0.040	2.484	-0.038	0.002	-0.132	0.040
NpB_{16}	3.819	-0.034	-0.020	-0.181	0.044	3.815	-0.035	-0.020	-0.180	0.044
PuB_{16}	5.224	-0.037	-0.039	-0.284	0.086	5.223	-0.038	-0.039	-0.283	0.085
AmB_{16}	6.571	0.007	-0.053	-0.354	0.092	6.561	0.006	-0.053	-0.352	0.092
CmB_{16}	6.821	0.002	-0.055	-0.165	0.055	6.822	0.001	-0.056	-0.165	0.056
EuB_{16}	6.682	0.023	-0.044	-0.384	0.087	6.680	0.023	-0.044	-0.384	0.087
CoB_{16}	0.011	0.060				0.009	0.062			
RhB_{16}	-0.019	0.064				-0.019	0.064			
IrB_{16}	-0.020	0.064				-0.021	0.064			
VB_{16}	0.011	0.06				0.011	0.062			
TiB_{16}	0.052	0.157		0.087		0.053	0.157		0.087	

Table S6. The energy decomposition analysis (EDA, kcal/mol) of $[MB_{16}]$ species at PBE/TZ2P level.

Species	ΔE_{els}	ΔE_{Pauli}	ΔE_{orb}	ΔE_{steric}	ΔE_{total}	$\Delta E_{els}/\Delta E_{orb}$
$[ScB_{16}]$	-14.55	25.88	-20.02	11.33	-8.68	0.73
$[TiB_{16}]$	-23.08	46.88	-29.30	23.81	-5.50	0.79
$[VB_{16}]$	-27.66	57.51	-38.33	29.85	-8.47	0.72
$[CoB_{16}]$	-20.71	34.69	-22.16	13.98	-8.18	0.93
$[RhB_{16}]$	-21.92	36.76	-19.11	14.84	-4.27	1.15
$[IrB_{16}]$	-36.19	67.22	-39.17	31.03	-8.14	0.92
$[EuB_{16}]$	-13.24	22.58	-13.29	9.34	-3.95	1.00
$[ThB_{16}]$	-20.18	38.18	-25.77	18.00	-7.76	0.78
$[PaB_{16}]$	-19.76	38.70	-28.40	18.94	-9.46	0.70
$[NpB_{16}]$	-19.33	35.59	-27.93	16.26	-11.67	0.69
$[UB_{16}]$	-16.99	31.55	-25.16	14.57	-10.59	0.68
$[PuB_{16}]$	-16.66	29.71	-22.12	13.05	-9.07	0.75
$[AmB_{16}]$	-15.04	26.44	-16.97	11.41	-5.56	0.89
$[CmB_{16}]$	-14.96	26.19	-20.56	11.23	-9.33	0.73

Table S7. The electron density and energy density parameters computed at the BCPs of $[MB_{16}]$ species.

Parameters at BCP	ρ	$\nabla^2\rho$	ε	Total energy density H(r) = V(r) + G(r)
$[ScB_{16}]$	0.037	0.115	1.083	-0.002
$[TiB_{16}]$	0.060	0.108	5.923	-0.018
$[VB_{16}]$	0.071	0.118	3.324	-0.025
$[CoB_{16}]$	0.070	0.099	2.276	-0.026
$[RhB_{16}]$	0.078	0.103	2.571	-0.033
$[IrB_{16}]$	0.081	0.081	5.027	-0.037
$[EuB_{16}]$	0.032	0.088	3.251	-0.002
$[ThB_{16}]$	0.046	0.211	3.994	-0.010
$[PaB_{16}]$	0.050	0.090	2.421	-0.012
$[NpB_{16}]$	0.048	0.102	2.255	-0.010
$[UB_{16}]$	0.050	0.098	1.430	-0.011
$[PuB_{16}]$	0.046	0.102	1.150	-0.008
$[AmB_{16}]$	0.053	0.066	0.973	-0.020
$[CmB_{16}]$	0.042	0.100	2.600	-0.006