Electronic Supporting Information

Table S1. Selected geometric parameters of aluminum clusters MAl_{12} with 40 valence electrons (in Å and degrees).[a]

M	Be	Mg	Al	Si	P	Zn	Ga	Ge	As
Structure **1**, I_h									
R(MAl)	2.603	2.716	2.682	2.665	2.675	2.642	2.673	2.655	2.696
Structure **2**, D_{5h}									
$R(MAl_2)$	2.629	2.741	2.699	2.679	2.684	2.659	2.695	2.678	2.715
$R(MAl_5)$	2.666	2.782	2.742	2.724	2.736	2.705	2.735	2.716	2.758
$R(Al_5Al_{10})$	2.554	2.648	2.614	2.595	2.601	2.590	2.614	2.591	2.615
Structure **1i**, C_{5v}									
$R(MAl_3)$	2.502	2.967	2.819	2.707	2.663	2.707	2.844	2.755	2.765
$R(MAl_{13})$	2.323	2.917	2.682	2.485	2.342	2.484	2.672	2.511	2.384
$R(Al_{12}Al_{13})$	2.803	2.781	2.682	2.623	2.612	2.623	2.663	2.609	2.605
$R(Al_3Al_{13})$	2.705	2.693	2.682	2.681	2.704	2.681	2.660	2.669	2.700
Structure **2i**, C_{5v}/C_1									
	C_{5v}	C_{5v}	C_{5v}	C_1	C_1	C_{5v}	C_{5v}	C_1	C_1
$R(MAl_1)$[c]/$R(MAl_2)$[d]	2.371	2.952	2.699	2.786	2.655	2.657	2.704	2.829	2.775
$R(MAl_4)$[c]/$R(MAl_3)$[d]	2.503	2.929	2.784	2.707	2.519	2.680	2.812	2.758	2.750
$R(Al_1Al_4)$[c]/$R(MAl_4)$[d]	2.761	2.748	2.742	2.756	3.662	2.764	2.718	2.801	3.288
$R(Al_4Al_5)$[c]/$R(MAl_5)$[d]	2.746	2.845	2.834	2.641	2.656	2.792	2.833	2.696	2.694
$R(Al_1Al_9)$[c]/$R(MAl_6)$[d]	2.690	2.752	2.742	2.661	2.449	2.709	2.760	2.713	2.577
$R(Al_1Al_3)$[c]/$R(MAl_{13})$[d]	2.847	2.796	2.699	2.491	2.472	2.769	2.667	2.516	2.495
$R(Al_9Al_{10})$[c]/$R(Al_{12}Al_{13})$[d]	2.844	2.833	2.834	2.627	2.720	2.839	2.830	2.614	2.706
Structure **3**, o-C_{3v}									
$R(MAl_2)$	2.484	2.907	2.749	2.654	2.620	2.595	2.709	2.665	2.688
$R(Al_2Al_3)$	4.274	4.620	4.532	4.479	4.497	4.383	4.508	4.498	4.582
$R(Al_{12}Al_{13})$	2.683	2.694	2.718	2.762	2.822	2.681	2.720	2.754	2.809
h(M)[b]	0.303	1.155	0.842	0.599	0.339	0.577	0.753	0.599	0.478
H[b]	4.001	3.753	3.835	3.822	3.892	3.950	3.870	3.852	3.845
Structure **4**, o-C_{2v}									
$R(MAl_2)$	2.317	2.778	2.641	2.552	2.536	2.475	2.560	2.580	2.618
$R(MAl_{12})$	2.328	2.901	2.689	2.508	2.383	2.575	2.605	2.535	2.459
$R(Al_2Al_3)$	4.266	4.350	4.337	4.330	4.379	4.281	4.326	4.374	4.458
Structure **5**, o-C_s									
$R(MAl_2)$	2.290	2.777	2.595	2.446	2.322	2.471	2.509	2.494	2.442
$R(MAl_3)$	2.441	2.932	2.753	2.670	2.397	2.610	2.703	2.707	2.944
$R(MAl_{12})$	2.338	2.840	2.651	2.486	2.362	2.526	2.548	2.505	2.451
$\varphi(Al_2Al_1Al_3)$	130.4	104.4	112.4	119.7	157.3	121.5	119.7	120.9	121.2
$\varphi(Al_{12}Al_1Al_{13})$	95.9	69.6	76.8	85.1	85.2	85.2	83.9	86.1	89.0
Structure **6**, C_{3v}									
$R(MAl_2)$	2.432	2.814	2.636	2.558	2.553	2.572	2.617	2.585	2.618
$R(Al_2Al_3)$	4.111	4.606	4.419	4.424	4.424	4.274	4.515	4.480	4.539
$R(Al_{12}Al_{13})$	2.637	2.592	2.613	2.673	2.779	2.610	2.631	2.677	2.749
h(M)[b]	-0.530	–0.920	–0.663	–0.136	0.040	–0.725	–0.229	–0.027	0.060
H[b]	4.118	4.016	4.119	4.100	4.031	4.071	4.076	4.058	4.038
Structure **7**, ~C_s									
$R(MAl_{10})$				2.681	2.681				
$R(MAl_{11})$				2.529	2.529				
$R(MAl_{12})$				2.676	2.676				

$R(MAl_{13})$				2.629	2.629				
$\theta(MAl_{12}Al_8Al_9)$				4.6	4.6				

[a]Optimized at the B3LYP/6-31G* level. Radius R(MAl) in the $B@Al_{12}^+$ and $C@Al_{12}$ clusters with the structure **1**, I_h, is 2.566 and 2.557 Å, respectively.

[b]h(M) is the distance between heteroatom M and the center of coordinated face (minus indicates that M is located inside the cage) and H is the distance between the coordinated and opposite faces (height of the $[Al_{12}]$ cage).

[c]For C_{5v}-symmetric structures.

[d]For C_1-symmetric structures.

Table S2. Selected geometric parameters (Å) of L[M@Al_{12}] (**11a**, C_{3v}) and L_2[M@Al_{12}] (**16**, D_{3d}) clusters optimized at the B3LYP/6-31G* level.

A. L[M@Al_{12}] (**11a**, C_{3v})[a]

L M	Li^+ Be^{2+}	Na^+ Be^{2+}	Cu^+ Be^{2+}	Be^{2+} Be^{2+}	Mg^{2+} Mg^{2+}	Li^+ Zn^{2+}	Cu^+ Zn^{2+}	Li^+ B^{3+}	Na^+ B^{3+}
R(LM)	4.094	4.461	3.430	3.360	2.996	4.100	3.331	4.104	4.488
R(LAl_a)	2.711	3.022	2.274	2.291	2.839	2.722	2.281	2.742	3.064
R(MAl_a)	2.540	2.540	2.565	2.542	2.857	2.586	2.625	2.482	2.484
R(Al_aAl_a)	2.842	2.861	2.945	3.067	4.195	2.916	3.104	2.791	2.800
R(Al_oAl_o)	2.706	2.712	2.724	2.714	2.692	2.744	2.744	2.676	2.682
L M	Li^+ Al^{3+}	Na^+ Al^{3+}	Al^+ Al^{3+}	Li^+ Ga^{3+}	Li^+ C^{4+}	Na^+ C^{4+}	Li^+ Si^{4+}	Na^+ Si^{4+}	Li^+ Ge^{4+}
R(LM)	4.171	4.552	4.474	4.177	4.124	4.541	4.261	4.668	4.261
R(LAl_a)	2.796	3.105	2.949	2.772	2.808	3.167	2.850	3.196	2.836
R(MAl_a)	2.648	2.648	2.640	2.639	2.421	2.415	2.628	2.626	2.623
R(Al_aAl_a)	3.033	3.039	2.892	2.980	2.770	2.769	2.977	2.990	2.952
R(Al_oAl_o)	2.775	2.777	2.809	2.774	2.685	2.691	2.782	2.777	2.776

B. L_2[M@Al_{12}] (**16**, D_{3d})[b]

2L M	$2Li^+$ Be^{2+}	$2Li^+$ Mg^{2+}	$2Li^+$ Zn^{2+}	$2Na^+$ Be^{2+}	$2Li^+$ Li^+	$2Li^+$ Cu^+	$2Li^+$ Al^{3+}	$2Li^+$ B^{3+}	$2Li^+$ Ga^{3+}
R(LM)	4.204	4.260	4.221	4.571	4.175	4.151	4.337	4.251	4.335
R(LAl_a)	2.774	2.809	2.782	3.077	2.744	2.727	2.873	2.823	2.859
R(MAl_a)	2.531	2.666	2.580	2.539	2.572	2.533	2.641	2.496	2.634
R(Al_aAl_a)	2.797	2.977	2.861	2.807	2.848	2.794	2.994	2.759	2.917
R(Al_aAl_e)	2.645	2.750	2.684	2.653	2.681	2.649	2.729	2.618	2.725

[a]Indexes “a” and “o” in the structure **11a** denote atoms Al located at the “active” and “opposite” faces, respectively.

[b]Indexes “a” and “e” in the structure **16** denote Al atoms located at the active faces and in the equatorial region, respectively.

Table S3. Selected geometric parameters of the exohedral isomer **3'**, C_{3v}, of *closo*-alanes, boranes and gallanes $MA_{12}H_{12}^-$ (in Å and degrees).[a]

A. Alanes $MAl_{12}H_{12}$

Ln^+	Li^+	Be^{2+}	Na^+	Mg^{2+}	Al^{3+}	Cu^+	Ga^+
$R(MA_2)$	2.654	2.299	2.985	2.689	2.546	2.322	2.977
$R(A_2A_3)$	2.695	2.730	2.706	2.746	2.822	2.797	2.727
$R(MH_{14})$	1.984	1.471	2.538	1.904	1.659	1.723	2.547
$R(A2H_{14})$	1.648	1.756	1.746	1.726	1.932	1.719	1.619
$R(A_2A_7)$	2.677	2.679	2.681	2.673	2.688	2.672	2.693
$R(A_2A_8)$	2.630	2.611	2.640	2.609	2.610	2.608	2.670
$R(A_7A_8)$	2.753	2.802	2.742	2.793	2.845	2.768	2.732
$R(A_{12}A_{13})$	2.718	2.742	2.711	2.730	2.756	2.729	2.721
$\varphi(H_{14}MH_{15})$	112.9[b]	119.7[c]	103.3[b]	114.2[b]	120.0	120.0	103.2[b]
$\varphi(MH_{14}A_2)$	93.5	90.4	94.5	95.5	90.0	84.9	88.3
$\varphi(A_2A_7A_3)$	59.6	59.2	59.7	59.2	63.3	61.6	60.8

B. Boranes $MB_{12}H_{12}$ and gallanes $MGa_{12}H_{12}$

M	Li^+	Be^{2+}	Na^+	Mg^{2+}	Al^+	Cu^+	Zn^{2+}	Ga^+	Al^{3+}
$R(MA_2)$	2.137	1.797	2.518	2.217	2.417	2.179	2.158	2.498	2.158
$R(A_2A_3)$	1.789	1.808	1.794	1.813	1.781	1.812	1.836	1.788	1.817
$R(MH_{14})$	1.900	1.545	2.203	1.956	2.107	1.973	1.973	2.197	1.889
$R(A_2H_{14})$	1.226	1.288	1.223	1.260	1.220	1.243	1.257	1.221	1.269
$R(A_2A_7)$	1.779	1.776	1.779	1.772	1.779	1.777	1.765	1.779	1.750
$R(A_2A_8)$	1.761	1.730	1.766	1.742	1.768	1.760	1.748	1.771	1.744
$R(A_7A_8)$	1.796	1.813	1.794	1.811	1.798	1.801	1.822	1.798	1.837
$\varphi(H_{14}MH_{15})$	101.8[b]	117.1[b]	88.0[b]	100.4[b]	91.1[b]	101.1[b]	102.8[b]	88.5[b]	103.3[b]
$\varphi(MH_{14}A_2)$	83.3	78.2	89.9	84.0	89.1	81.9	80.5	89.2	83.8

M	Li^+	Be^{2+}(b)	Be^{2+}(s)[d]	Na^+	Mg^{2+}	Ga^+	Ga^{3+}(b)	Ga^{3+}(s)	Al^{3+}(s)
$R(MA_2)$	2.601	2.254	2.176	2.928	2.643	2.828	2.829	2.430	2.474
$R(A_2A_3)$	2.592	2.644	3.757	2.606	2.633	2.615	2.757	4.055	4.037
$R(MH_{14})$	2.038	1.476	3.202	2.391	1.931	2.501	2.480	3.530	3.536
$R(A_2H_{14})$	1.617	1.746	1.542	1.608	1.708	1.580	1.575	1.540	1.540
$R(A_2A_7)$	2.567	2.557	2.612	2.566	2.556	2.569	2.488	2.750	2.726
$R(A_2A_8)$	2.505	2.484	2.444	2.515	2.479	2.533	2.567	2.492	2.501
R(A7A8)	2.646	2.719	2.663	2.634	2.703	2.620	2.766	2.650	2.649
$R(A_{12}A_{13})$	2.594	2.627	2.597	2.589	2.611	2.596	2.988	2.546	2.548
$\varphi(H_{14}MH_{15})$[c]	112.3[b]	119.7[c]	108.3[c]	102.5[b]	113.8[b]	104.7[b]	106.8[b]	119.0[c]	119.9[c]
$\varphi(MH_{14}A_2)$	90.0	68.4	36.9	92.0	93.0	84.5	25.4	34.9	36.5
$\varphi(A_2A_7A_3)$	60.7	62.3	92.0	61.0	62.0	61.2	67.3	95.2	95.5
$\varphi(A_{12}A_8A_{13})$	60.4	61.8	60.9	60.3	61.1	60.8	72.6	59.7	59.8

[a]B3LYP calculations with the 6-311+G* basis set for boranes and 6-31G* for alanes and gallanes.
[b]Atom M is located above hydrogen atoms H_{14}, H_{15}, and H_{16}. [c]Atom M is located below hydrogen atoms H_{14}, H_{15}, and H_{16}. [d]N_{im}=2.

Table S4. Calculated geometric parameters (Å) of the endo-isomer **1'**, I_h, of *closo*-alanes, boranes, and gallanes $M@A_{12}H_{12}$.

	Boranes $M@B_{12}H_{12}$						
M	–[a]	Li^+	Na^+	Be^{2+}	Mg^{2+}	Al^{3+}	Ga^{3+}
R(MA)	(1.700)	1.784	1.922	1.780	1.923	1.912	1.961
R(AA)	1.787	1.876	2.021	1.872	2.022	2.010	2.062
R(AH)	1.205	1.186	1.186	1.177	1.176	1.172	1.179

	Alanes $M@Al_{12}H_{12}$					Gallanes $M@Ga_{12}H_{12}$				
M	–[a]	Li^+	Na^+	Al^+	Mg^{2+}	–[a]	Li^+	Na^+	Mg^{2+}	Ga^{3+}
R(MA)	(2.571)	2.612	2.671	2.656	2.665	(2.453)	2.489	2.530	2.579	2.498
R(AA)	2.703	2.746	2.809	2.793	2.803	2.579	2.616	2.659	2.712	2.626
R(AH)	1.605	1.586	1.587	1.598	1.574	1.568	1.554	1.552	1.542	1.531

[a]Data for isolated (empty) $A_{12}H_{12}^{2-}$ dianions.