Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Selected $AB_4^{2-/-}$ (A = C, Si, Ge; B = Al, Ga, In) Ions: A Battle between Covalency and Aromaticity, and Prediction of Square Planar Si in $SiIn_4^{2-/-}$.

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Supporting Information

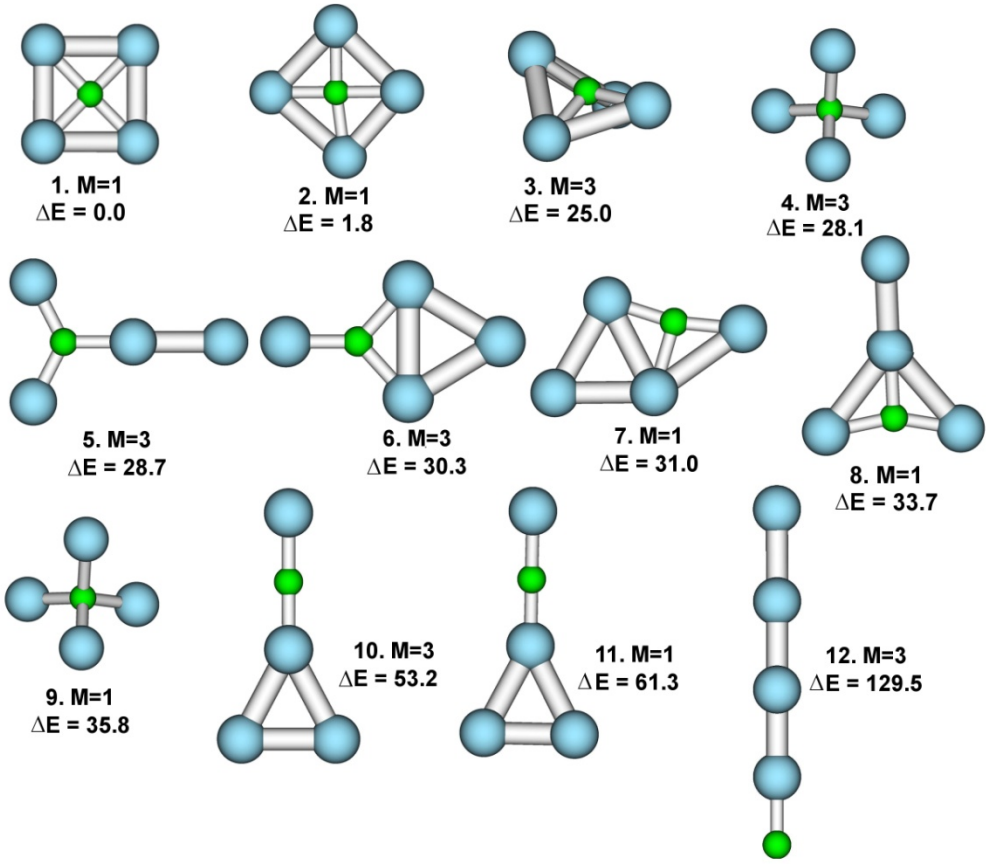

Figure S1. The lowest energy isomers of the CAl_4^{2-} cluster found by GEGA at the B3LYP/3-21G level of theory (Al – blue, C – green). M is multiplicity. Energy differences are in kcal/mol.

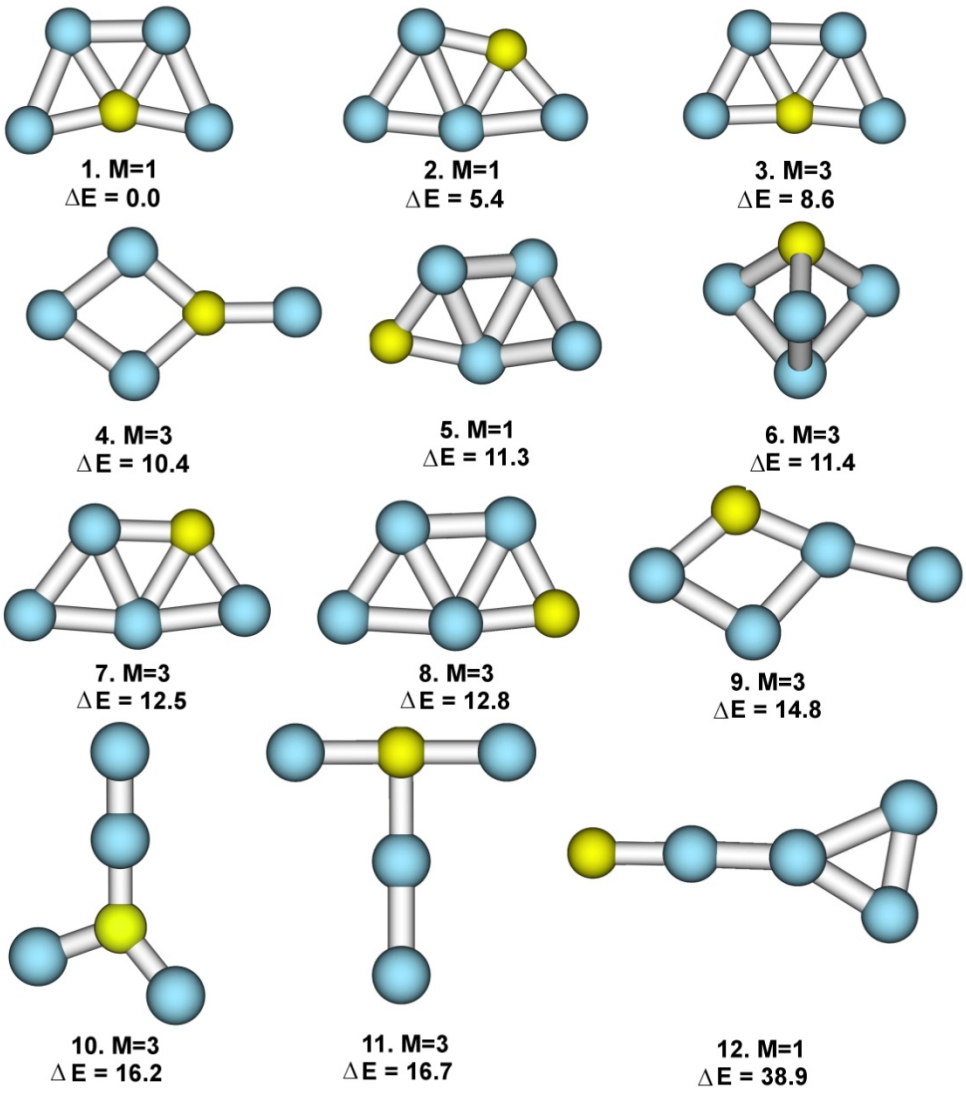

Figure S2. The lowest energy isomers of the $SiAl_4^{2-}$ cluster found by GEGA at the B3LYP/3-21G level of theory (Al – blue, Si – yellow). M is multiplicity. Energy differences are in kcal/mol.

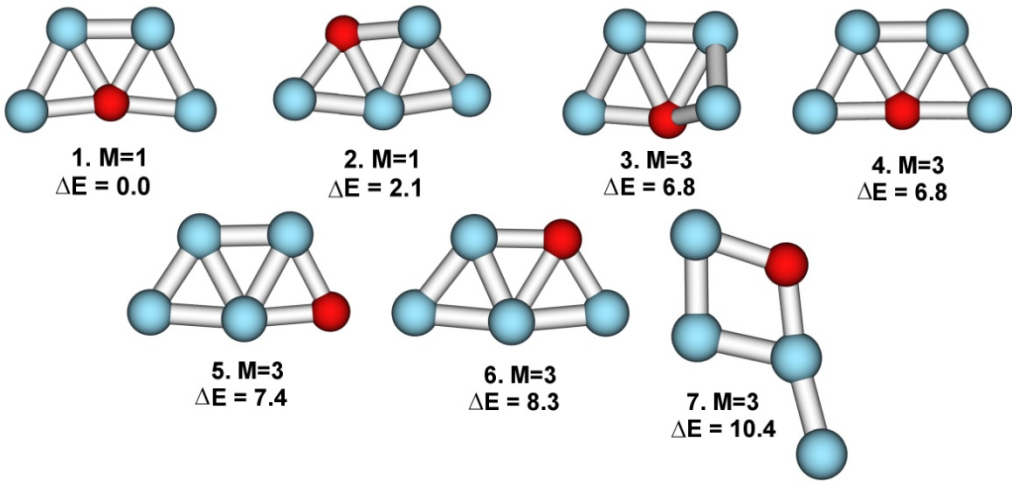

Figure S3. The lowest energy isomers of the $GeAl_4^{2-}$ cluster found by GEGA at the B3LYP/3-21G level of theory (Al – blue, Ge – red). M is multiplicity. Energy differences are in kcal/mol.

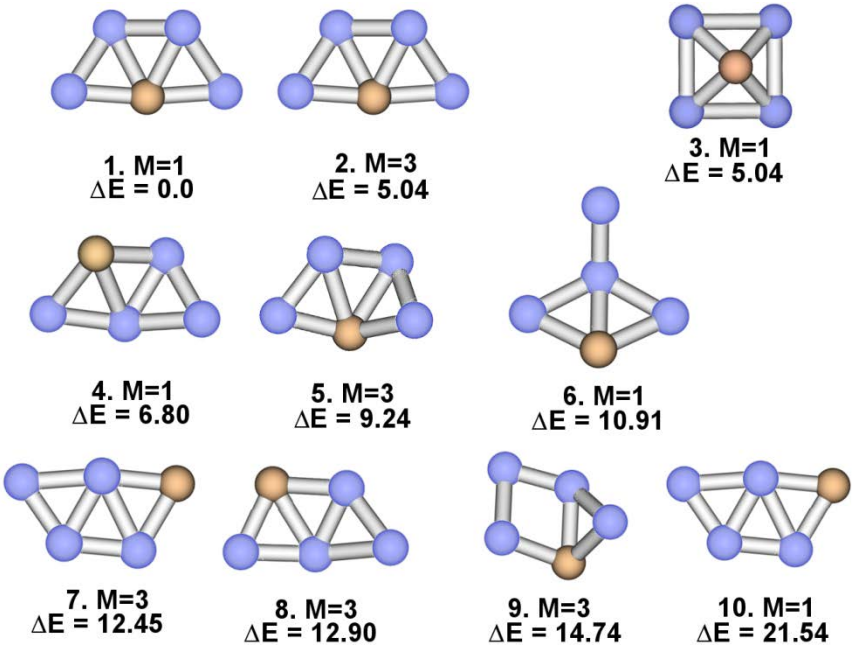

Figure S4. The lowest energy isomers of the $SiGa_4^{2-}$ cluster found by GEGA at the B3LYP/3-21G level of theory (Ga – blue, Si – orange). M is multiplicity. Energy differences are in kcal/mol.

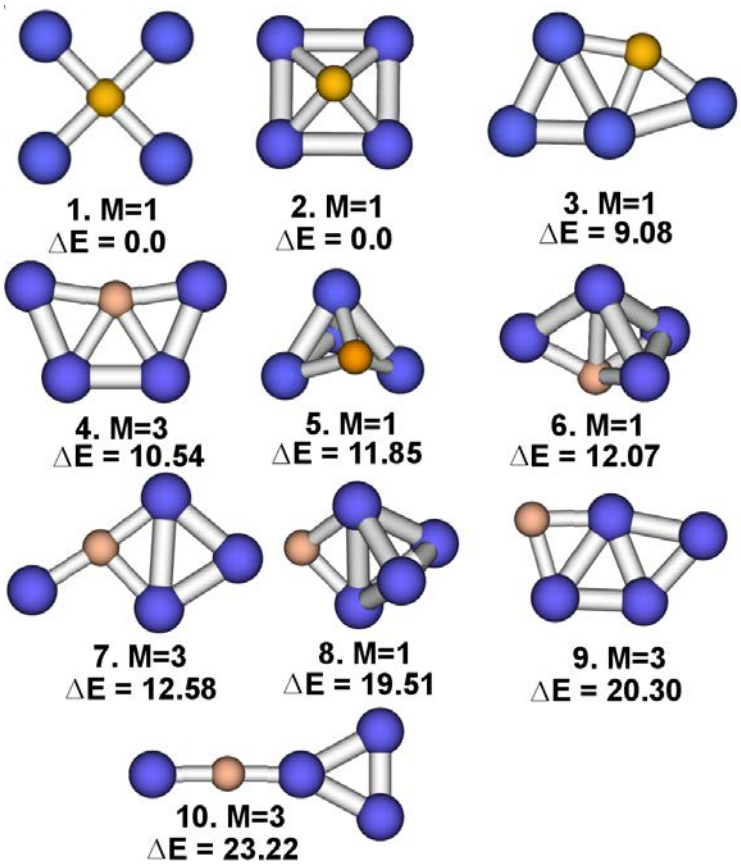

Figure S5. The lowest energy isomers of the $SiIn_4^{2-}$ cluster found by GEGA at the B3LYP/3-21G level of theory (In – blue, Si – orange). M is multiplicity. Energy differences are in kcal/mol.

Table S1. Calculated molecular properties of the CAl_4^{2-} and CAl_4^{-} clusters, isomer **I** (Figure S1).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{2-}	E_{total} (a.u.)	-1007.87227	-1005.44239	-1005.44254510 (-1005.45099783)
	ZPE (kcal/mol)	4.384781888	4.36539186	N/A
	NImag	0	1	N/A
	$Q(Al_4)$	0.63479	N/A	N/A
	Q(C)	-2.63479	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{-}	E_{total} (a.u.)	-1007.941848	-1005.905390	-1005.9712823 (-1006.0398107)
	ZPE (kcal/mol)	3.43740	4.3582	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	1.80952	N/A	N/A
	Q(C)	-2.80954	N/A	N/A

Table S2. Calculated molecular properties of the CAl_4^{2-} and CAl_4^{-} clusters, isomer **II** (Figure S1).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{2-}	E_{total} (a.u.)	-1007.86529	-1005.84513	-1005.9021585 (-1005.9787038)
	ZPE (kcal/mol)	4.39323	4.55404	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	0.63464	N/A	N/A
	Q(C)	-2.63464	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{-}	E_{total} (a.u.)	-1007.9308919	-1005.5340441	-1005.9714426 (-1006.001402)
	ZPE (kcal/mol)	3.43739	4.36090	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	1.80952	N/A	N/A
	Q(C)	-2.80952	N/A	N/A

Table S3. Calculated molecular properties of the CAl_4^{2-} and CAl_4^{-} clusters, isomer **III** (Figure S1).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{2-}	E_{total} (a.u.)	-1007.8269622	-1005.7948815	-1005.8627943 (-1005.9356969)
	ZPE (kcal/mol)	3.65625	4.20730	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	0.71216	N/A	N/A
	Q(C)	-2.71215	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{-}	E_{total} (a.u.)	-1007.9308916	-1005.5340528	-1005.9712822 (-1006.0398106)
	ZPE (kcal/mol)	3.43747	4.36150	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	1.80948	N/A	N/A
	Q(C)	-2.80948	N/A	N/A

Table S4. Calculated molecular properties of the CAl_4^{2-} and CAl_4^{-} clusters, isomer **IV** (Figure S1).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{2-}	E_{total} (a.u.)	-1007.82773033	-1005.42375872	-1005.8452939 (-1005.9206296)
	ZPE (kcal/mol)	3.91754248	4.10642287	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	0.66740	N/A	N/A
	Q(C)	-2.66740	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
CAl_4^{-}	E_{total} (a.u.)	-1007.8959212	-1005.855948	-1005.9263626 (-1005.9962728)
	ZPE (kcal/mol)	4.09063	3.92532	N/A
	NImag	0	1	N/A
	$Q(Al_4)$	1.72756	N/A	N/A
	Q(C)	-2.72757	N/A	N/A

Table S5. Calculated molecular properties of the $SiAl_4^{2-}$ and $SiAl_4^-$ clusters, isomer **I** (Figure S2).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$SiAl_4^{2-}$	E_{total} (a.u.)	-1259.28188029	-1256.49673847	-1256.49714221 (-1256.50669493)
	ZPE (kcal/mol)	2.748363918	2.885474635	N/A
	NImag	0	1	N/A
	Q(Al_4)	-0.64574	N/A	N/A
	Q(Si)	-1.35427	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$SiAl_4^-$	E_{total} (a.u.)	-1259.3447913	-1256.9172923	-1256.9877137 (-1257.0713592)
	ZPE (kcal/mol)	2.75409	3.06697	N/A
	NImag	0	0	N/A
	Q(Al_4)	0.36304	N/A	N/A
	Q(Si)	-1.36304	N/A	N/A

Table S6. Calculated molecular properties of the $SiAl_4^{2-}$ and $SiAl_4^-$ clusters, isomer **II** (Figure S2).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$SiAl_4^{2-}$	E_{total} (a.u.)	-1259.26992	-1256.84984	-1256.9116329 (-1257.0012985)
	ZPE (kcal/mol)	2.75621	3.05223	N/A
	NImag	0	0	N/A
	Q(Al_4)	-1.02084	N/A	N/A
	Q(Si)	-0.97915	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$SiAl_4^-$	E_{total} (a.u.)	-1259.3405351	-1256.8997028	
	ZPE (kcal/mol)	2.78064	3.48727	N/A
	NImag	0	1	N/A
	Q(Al_4)	-0.11180	N/A	N/A
	Q(Si)	-0.88820	N/A	N/A

Table S7. Calculated molecular properties of the $SiAl_4^{2-}$ and $SiAl_4^-$ clusters, isomer **III** (Figure S2).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$SiAl_4^{2-}$	E_{total} (a.u.)	-1259.2646617	-1256.4890828	-1256.9043186 (-1256.9939401)
	ZPE (kcal/mol)	2.72964	2.93747	N/A
	NImag	0	1	N/A
	$Q(Al_4)$	-0.86498	N/A	N/A
	Q(Si)	-1.13502	N/A	N/A

Table S8. Calculated molecular properties of the $SiAl_4^{2-}$ and $SiAl_4^-$ clusters, isomer **IV** (Figure S2).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$SiAl_4^{2-}$	E_{total} (a.u.)	-1259.2530477	-1256.4737607	-1256.8852269 (-1256.9725459)
	ZPE (kcal/mol)	2.47231	5.29960	N/A
	NImag	0	1	N/A
	$Q(Al_4)$	-0.59989	N/A	N/A
	Q(Si)	-1.40011	N/A	N/A

Table S9. Calculated molecular properties of the $GeAl_4^{2-}$ and $GeAl_4^-$ clusters (isomer **I**, Fig. S3).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$GeAl_4^{2-}$	E_{total} (a.u.)	-3031.80627888	-3042.91309529	-3042.91349436 (-3042.92014803)
	ZPE (kcal/mol)	2.378635615	2.50093712	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	-0.73594	N/A	N/A
	Q(Ge)	-1.26408	N/A	N/A
		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$GeAl_4^-$	E_{total} (a.u.)	-3046.8783699	-3043.3387854	-3043.4056607 (3043.4740441)
	ZPE (kcal/mol)	2.40717	2.76504	N/A
	NImag	0	0	N/A
	$Q(Al_4)$	0.29532	N/A	N/A
	Q(Ge)	-1.29532	N/A	N/A

Table S10. Calculated molecular properties of the $GeAl_4^{2-}$ and $GeAl_4^{-}$ clusters (isomer **II**, Fig. S3).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$GeAl_4^{2-}$	E_{total} (a.u.)	-3046.79785	-3043.27220	-3043.3311466 ()
	ZPE (kcal/mol)	2.47553	2.68256	N/A
	NImag	0	0	N/A
	Q(Al_4)	-1.05376	N/A	N/A
	Q(Ge)	-0.94623	N/A	N/A
$GeAl_4^{-}$		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
	E_{total} (a.u.)	-3046.8596981	-3043.3203907	
	ZPE (kcal/mol)	2.45530	3.06652	N/A
	NImag	0	1	N/A
	Q(Al_4)	-0.15679	N/A	N/A
	Q(Ge)	-0.84321	N/A	N/A

Table S11. Calculated molecular properties of the $GeAl_4^{2-}$ and $GeAl_4^{-}$ clusters, isomer **III** (Figure S3).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$GeAl_4^{2-}$	E_{total} (a.u.)	-3046.79136974	-3042.90125717	-3042.9049196 ()
	ZPE (kcal/mol)	2.2728398	3.41302476	N/A
	NImag	0	0	N/A
	Q(Al_4)	-0.92390	N/A	N/A
	Q(Ge)	-1.07610	N/A	N/A
$GeAl_4^{-}$		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
	E_{total} (a.u.)	-3046.8683482	-3043.336688	
	ZPE (kcal/mol)	2.44740	2.84207	N/A
	NImag	0	0	N/A
	Q(Al_4)	0.30464	N/A	N/A
	Q(Ge)	-1.30464	N/A	N/A

Table S12. Calculated molecular properties of the $GeAl_4^{2-}$ and $GeAl_4^-$ clusters, isomer **IV** (Figure S3).

		B3LYP/6-311+G*	MP2/6-311+G*	CCSD(T)/6-311+G* (CCSD(T)/6-311+G(2df)
$GeAl_4^{2-}$	E_{total} (a.u.)	-3046.79486170	-3042.8994692	-3043.3230275 (-3043.397134)
	ZPE (kcal/mol)	2.17870	2.63172	N/A
	NImag	0	1	N/A
	Q(Al_4)	-0.93141	N/A	N/A
	Q(Ge)	-1.06859	N/A	N/A

Table S13. Calculated molecular properties of the $SiGa_4^{2-}$ and $SiGa_4^-$ clusters, isomer **I** (Figure 3A, main text).

	$SiGa_4^{2-}$		$SiGa_4^-$	
	B3LYP/cep-121g+spd	MP2/ cep-121g+spd	B3LYP/ cep-121g+spd	MP2/ cep-121g+spd
E_{total} (a.u.)	-7989.01621	-7982.13520	-7989.08008	-7982.13520
ZPE (kcal/mol)	1.899	1.920	1.850	2.020
NImag	0	0	0	0
ΔE (kcal/mol)[a]	0.0	0.0	0.0	0.0

[a] ZPE-corrected values.

Table S14. Calculated molecular properties of the $SiGa_4^{2-}$ and $SiGa_4^-$ clusters, square pyramidal isomer **II** (Figure 3A, main text).

	$SiGa_4^{2-}$		$SiGa_4^-$	
	B3LYP/cep-121g+spd	MP2/ cep-121g+spd	B3LYP/ cep-121g+spd	MP2/ cep-121g+spd
E_{total} (a.u.)	-7989.00818	-7989.073167		
ZPE (kcal/mol)	1.967	1.980		
Nimag	0	0	2[b]	2[b]
ΔE (kcal/mol)[a]	4.97	1.99		
R(Si-Ga), Å	2.481	2.482		
R(Ga-Ga), Å	3.121	3.115		

[a] ZPE-corrected values.

[b] the pyramidal singly-charged ion is a saddle point. Following the normal mode of the imaginary frequency leads to structure **I** (Figure 3A, main text).

Table S15. Calculated molecular properties of the $SiIn_4^{2-}$ and $SiIn_4^-$ clusters, square pyramidal isomer **II** (Figure 3B, main text).

	$SiIn_4^{2-}$		$SiIn_4^-$	
	B3LYP/cep-121g+spd	MP2/ cep-121g+spd	B3LYP/ cep-121g+spd	MP2/ cep-121g+spd
E_{total} (a.u.)	-1046.42359	-142.67848	-1046.48456	-1042.72171
ZPE (kcal/mol)	1.544	1.794	1.390	1.720
NImag	0	0	0[b]	0
ΔE (kcal/mol)[a]	0.0	0.0	0.0	0.0
R(Si-In), Å	2.680	2.663	2.688	2.669
R(In-In), Å	3.525	3.353	3.260/4.317	3.429

[a] ZPE-corrected values.
[b] This minimum is a C_s species with one In-In bond being significantly elongated. The C_{4v} structure was a saddle point with a single doubly-degenerate imaginary frequency.

Table S16. Calculated molecular properties of the $SiIn_4^{2-}$ and $SiIn_4^-$ clusters, planar isomer **III** (Figure 3B, main text).

	$SiIn_4^{2-}$		$SiIn_4^-$	
	B3LYP/cep-121g+spd	MP2/ cep-121g+spd	B3LYP/ cep-121g+spd	MP2/ cep-121g+spd
E_{total} (a.u.)	-1046.41281	-1042.66395	-1046.47181	-1042.70807
ZPE (kcal/mol)	1.457	1.576	1.434	1.444
NImag	0	0	0	0
ΔE (kcal/mol)[a]	6.85	9.34	8.29	8.28

[a] ZPE-corrected values.