Supporting Information

Planar Hexacoordinate Gallium

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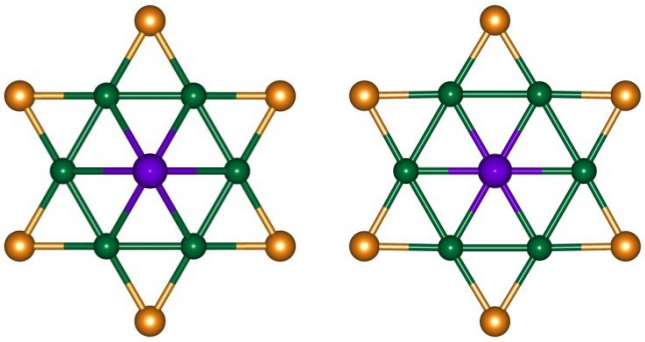
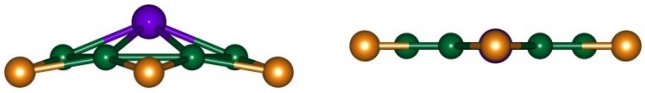
Top				
Side				
		C_{6v}, $^1A_1$	D_{6h}, $^1A_{1g}$	ΔE
$AlBe_6Au_6^+$	PBE0	-1145.204187 (11.9)	-1145.196027 (90.2*i*)	5.1
	B3LYP	-1145.812671 (10.9)	-1145.806572 (81.4*i*)	3.8
	TPSS	-1145.406239 (10.7)	-1145.399284 (85.3*i*)	4.4
$GaBe_6Au_6^+$	PBE0	–	-2827.508146 (8.0)	
	B3LYP	–	-2828.289040 (14.3)	
	TPSS	–	-2827.822827 (13.7)	
$InBe_6Au_6^+$	PBE0	-1093.027070 (14.3)	-1093.022396 (22.0*i*)	2.9
	B3LYP	-1093.571649 (13.4)	-1093.568520 (17.1*i*)	2.0
	TPSS	-1093.020139 (13.3)	-1093.016094 (20.0*i*)	2.5
$TlBe_6Au_6^+$	PBE0	–	-1075.397122 (15.0)	
	B3LYP	–	-1075.939462 (16.1)	
	TPSS	–	-1075.420601 (14.3)	

Figure S1. The absolute energy in (a.u.) and relative energy in kcal/mol (ΔE) of the quasi-phE and perfectly phE of $EBe_6Au_6^+$ (X=Al, Ga, In, Tl) computed by different DFT methods with def2-TZVP basis sets. All energies are corrected for zero-point energies (ZPE) at the corresponding DFT level. The minimum frequencies in cm^{-1} are given in bracket. For E = Ga and Tl, the corresponding C_{6v} isomer cannot be located as it automatically converges to D_{6h} isomer.

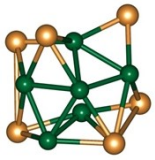
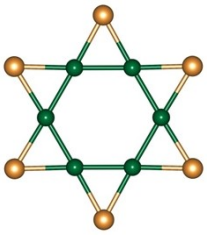
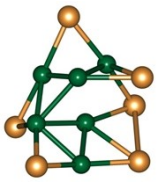
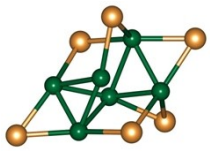
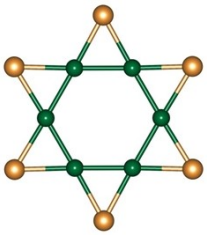
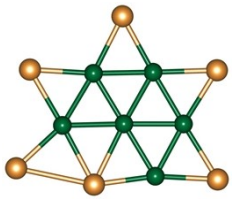
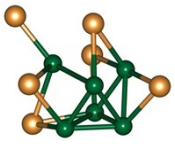
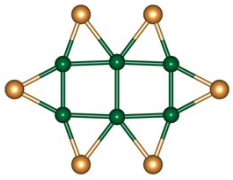
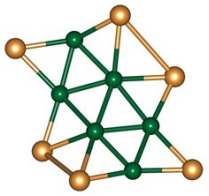
	Lower-energy minimum	Saddle point	→Local minimum
			
Be_6Au_6	C_1, ^1A 0.0 (19.1)	D_{6h}, $^1A_{1g}$ 165.8 (Nimag=3)	C_1, ^1A 98.3 (16.5)
			
$Be_6Au_6^-$	C_1, ^1A 0.0 (5.1)	D_{6h}, $^1A_{1g}$ 88.2 (Nimag=5)	C_1, ^1A 20.1 (10.7)
			
$Be_6Au_6^+$	C_1, ^1A 0.0 (19.1)	C_{2v}, $^1A_1$ 39.1 (Nimag=4)	C_1, ^1A 13.5 (7.1)

Figure S2. Structures and relative energies in kcal/mol of the neutral and charged Be_6Au_6 systems computed at the PBE0/def2-TZVP level. All energies are corrected for zero-point energies (ZPE). The frequencies given in the parenthesis (cm^{-1}) and Nimag refers to the numbers of imaginary frequencies.

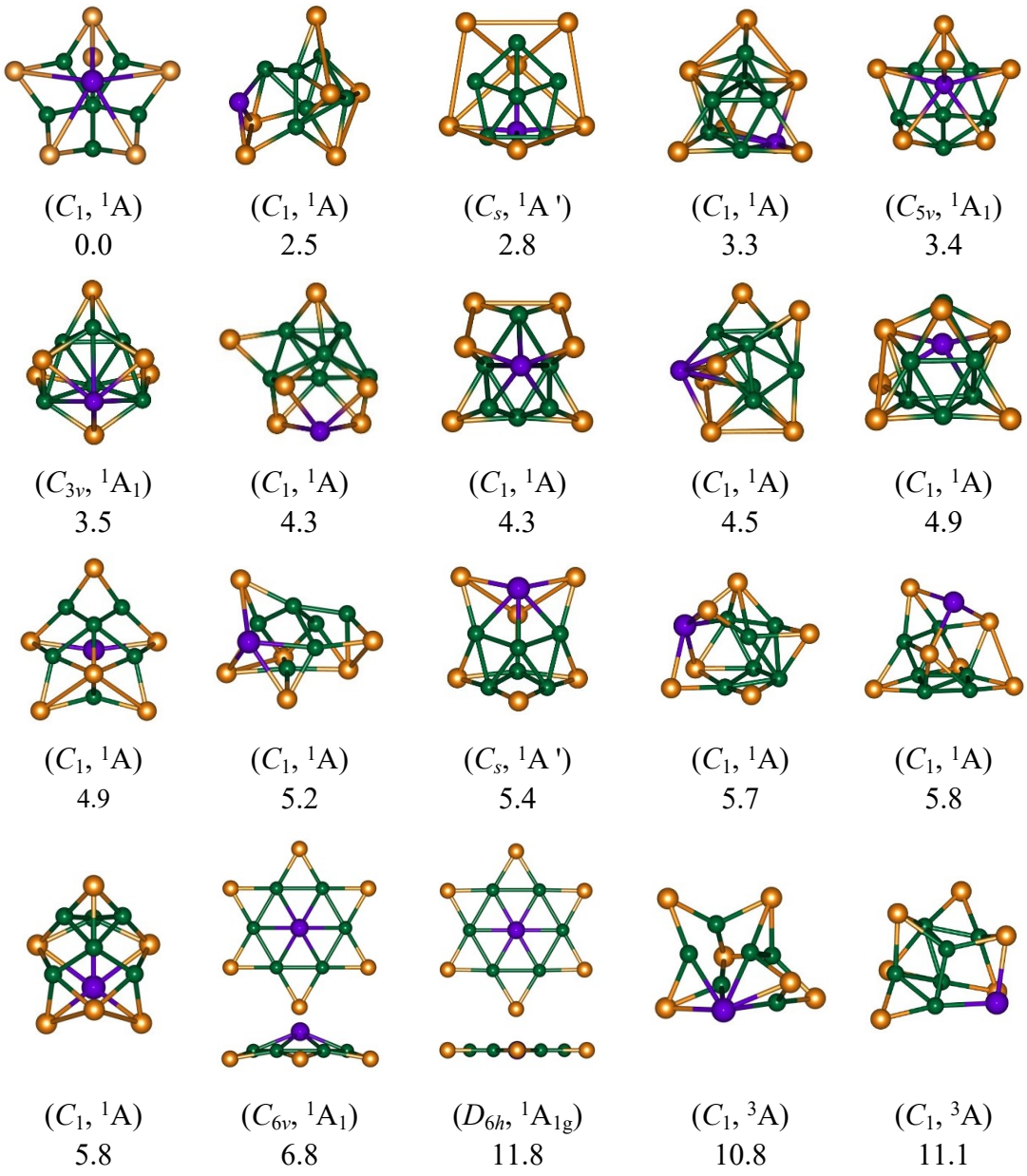


Figure S3. Calculated structures of $AlBe_6Au_6^+$ at the PBE0/def2-TZVP level. The relative energies of the structures were given in kcal/mol, point group and spectroscopic states were given in parenthesis. "*" refer to the structure with an imaginary frequency.

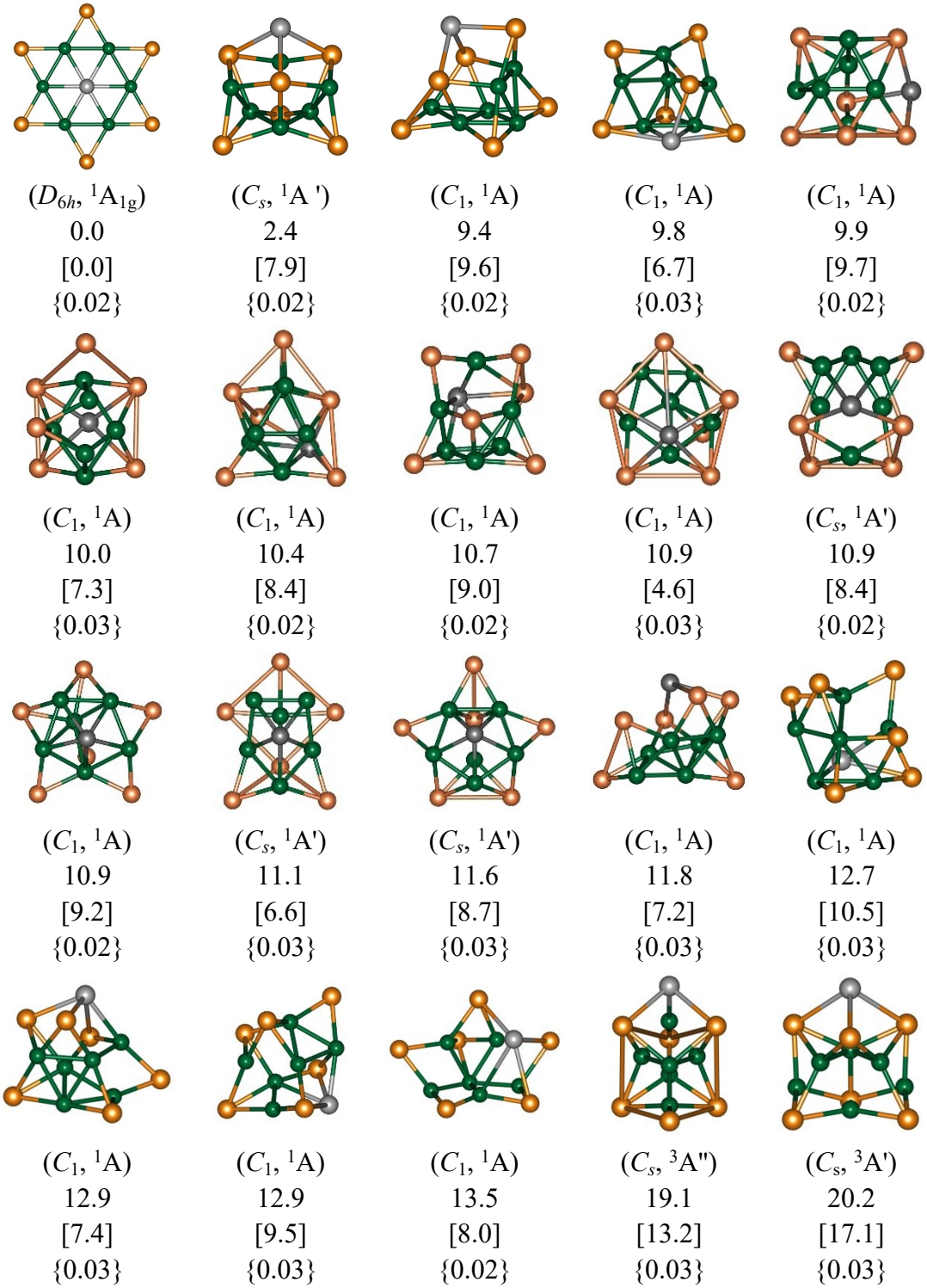


Figure S4. Structures and relative energies in kcal/mol of the low-lying isomers of $GaBe_6Au_6^+$ computed at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP and PBE0/def2-TZVP (in square brackets) levels. All energies are corrected for zero-point energies (ZPE) at the PBE0/def2-TZVP level. The point group symmetries and spectroscopic states are given, and T1 Diagnostic is given in braces.

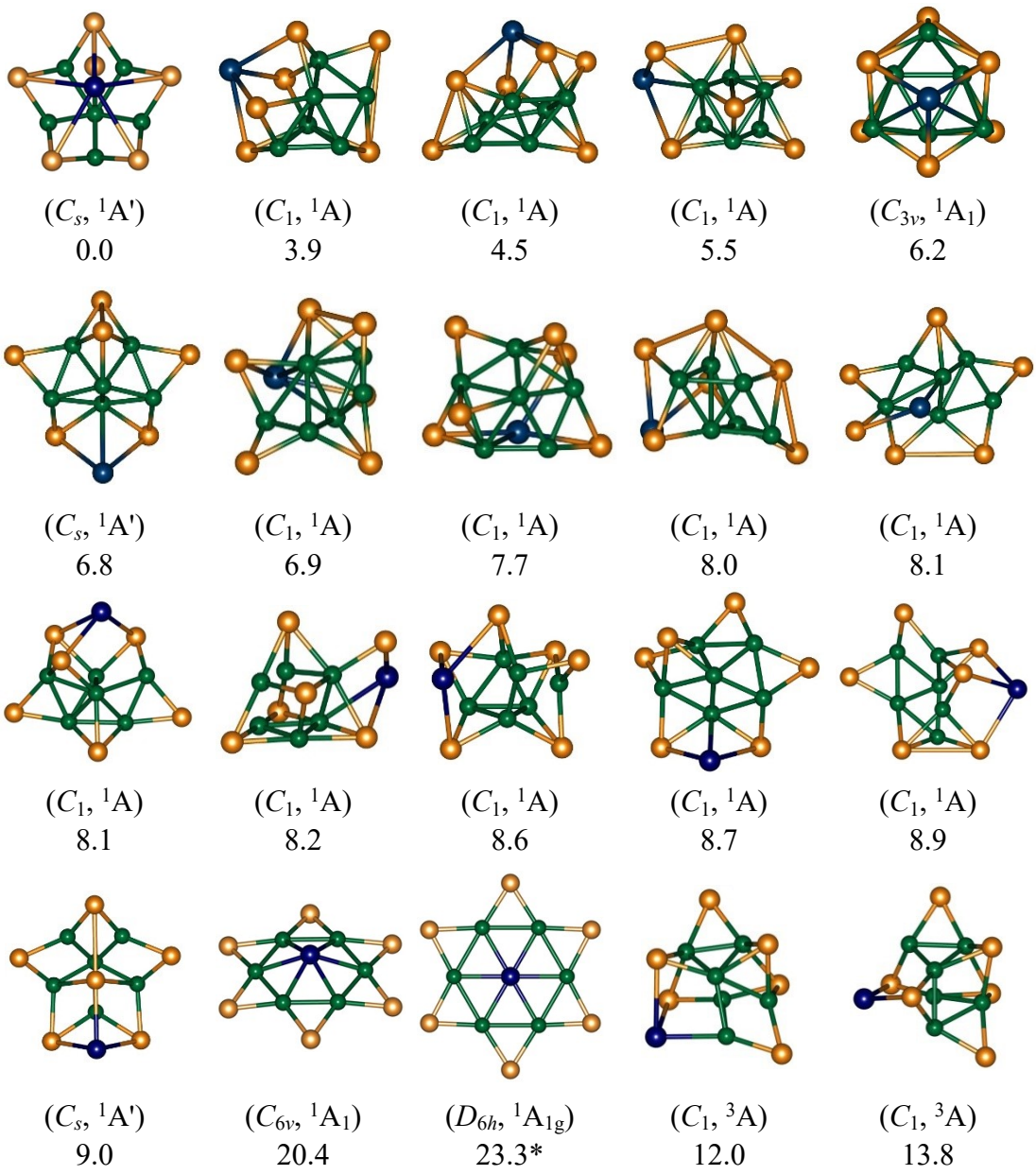


Figure S5. Calculated structures of $InBe_6Au_6^+$ at the PBE0/def2-TZVP level. The relative energies of the structures were given in kcal/mol, point group and spectroscopic states were given in parenthesis. "*" refer to the structure with an imaginary frequency.

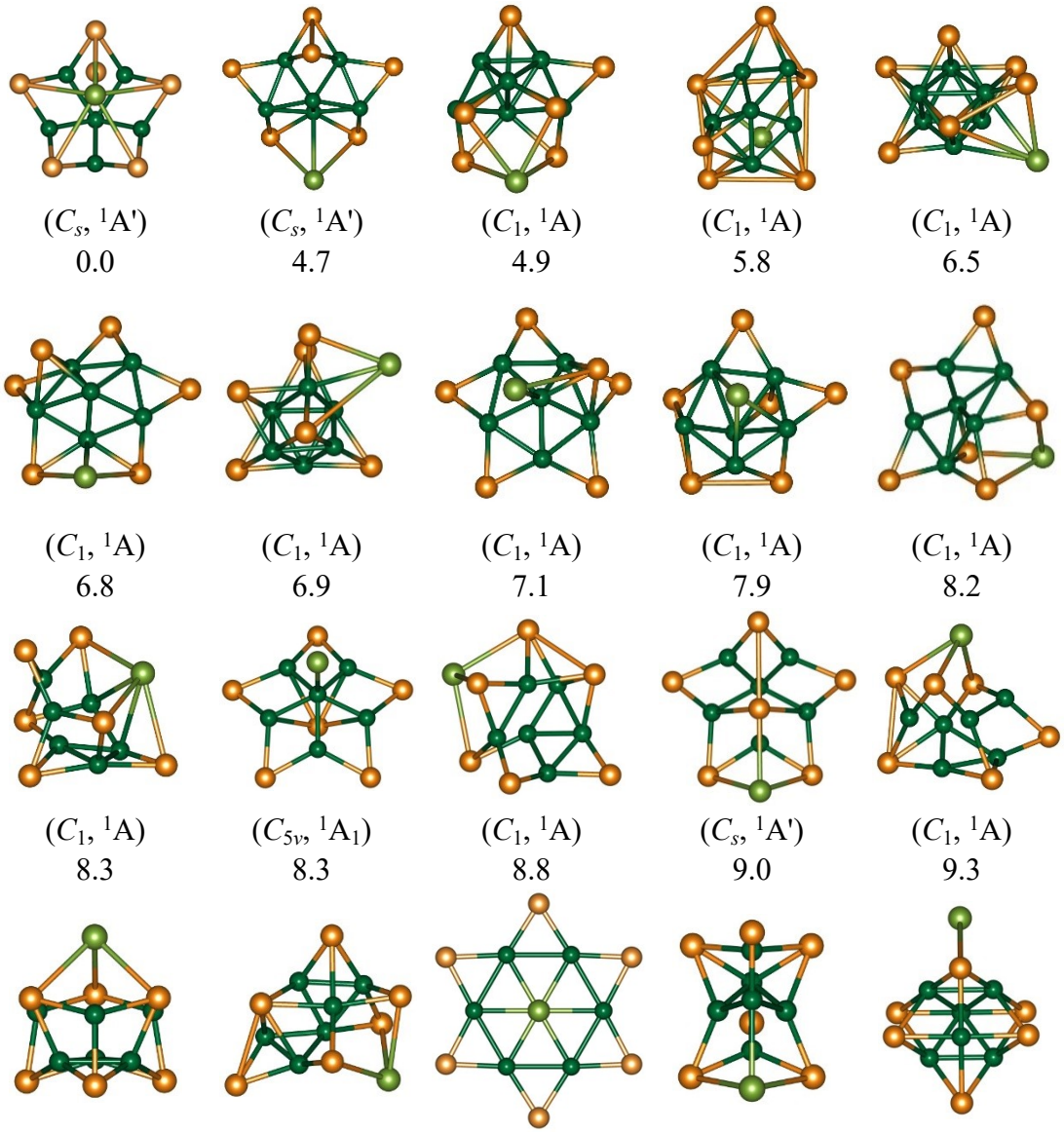
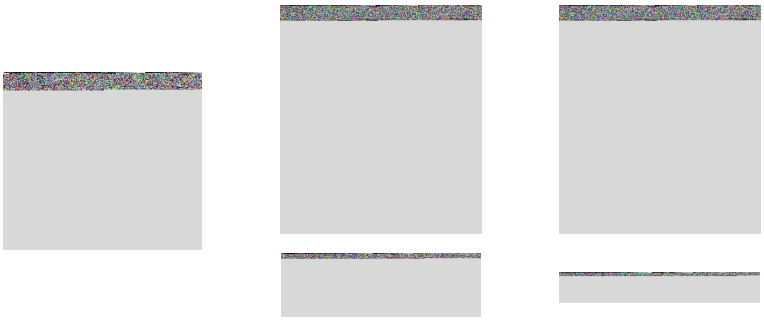


Figure S6. Calculated structures of $TlBe_6Au_6^+$ at the PBE0/def2-TZVP level. The relative energies of the structures were given in kcal/mol, point group and spectroscopic states were given in parenthesis.



	C_s, ^{1}A'	C_{6v}, ^{1}A$_1$	D_{6h}, ^{1}A$_{1g}$
$AlBe_6Au_6^+$	0.0$^{\#}$	6.7	11.8*
$GaBe_6Au_6^+$	4.6$^{\#}$	–	0.0
$InBe_6Au_6^+$	0.0	20.4	23.3*
$TlBe_6Au_6^+$	0.0	–	27.0

Figure S7. Structures and relative energies in kcal/mol of $EBe_6Au_6^+$ (E = Al, Ga, In, Tl) computed at the PBE0/def2-TZVP level. All energies are corrected for zero-point energies (ZPE). "#" refers to the structure with C_1 point group symmetry, "*" refers to the structure with an imaginary frequency, and "–" means that the structure change into the perfectly planar configuration.

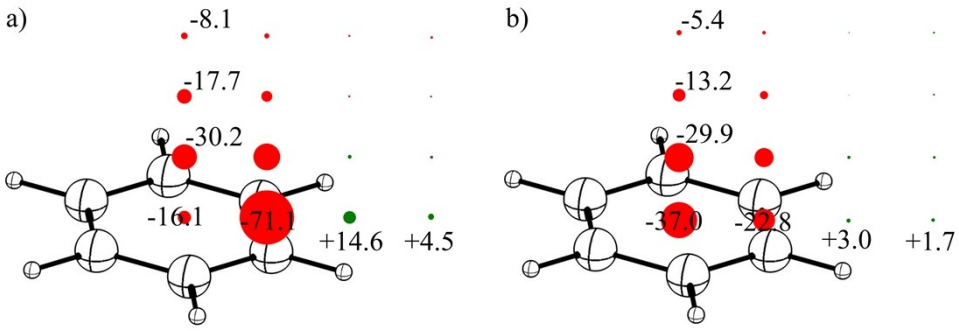


Figure S8. a) $NICS_{zz}$ and b) $NICS_{zz}(\pi)$ of the benzene obtained at the PBE0/def2-TZVP level. Diatropic and paratropic tensors are shown in red and green, respectively. NICS values are in ppm.

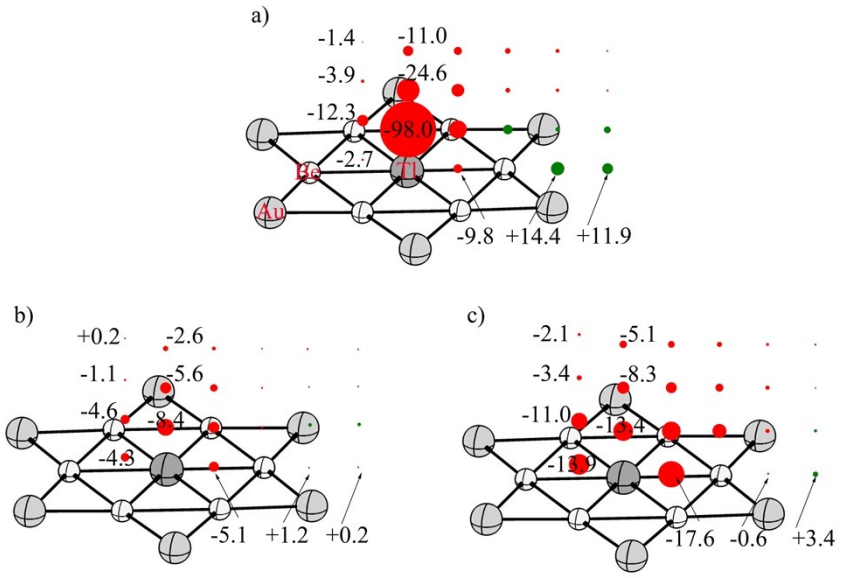


Figure S9. a) $NICS_{zz}$, b) $NICS_{zz}(\pi)$, and c) $NICS_{zz}(\sigma$-delocalization) of the D_{6h} $TlBe_6Au_6^+$ obtained at the PBE0/def2-TZVP level (the values in left column refer to the center of Be-Tl-Be triangle). Diatropic and paratropic tensors are shown in red and green, respectively. NICS values are in ppm.

Table S1. The atomic charges (Q, in |e|) analysis of $GaBe_6Au_6^+$ computed at the PBE0/def2-TZVP level.

		Q_{Ga}	Q_{Be}	Q_{Au}
	NPA[a]	-3.28	+0.94	-0.23
	Hirshfeld[b]	-0.06	-0.01	+0.18
	SCPA[c]	-0.10	+0.13	+0.06
	Becke[d]	-1.07	+0.69	-0.34
	MK[e]/RESP[f]	+0.64	-0.31	+0.37
	ESP[g]	+0.73	-0.31	+0.36
	Mulliken[h]	+1.18	-0.30	+0.27

[a]Natural population analysis (NPA) charge
[b]Hirshfeld atomic charge
[c]Modified Mulliken atom population defined by Ros & Schuit (SCPA)
[d]Becke atomic charge with atomic dipole moment correction
[e]Merz-Kollmann (MK) ESP fitting atomic charge
[f]Restrained ElectroStatic Potential (RESP) atomic charge
[g]ElectroStatic Potential (ESP) atomic charge
[h]Mulliken atomic charge

Table S2. The EDA results of $GaBe_6Au_6^+$ cluster considering Ga and Be_6Au_6 in different charge and electronic states as interacting fragments at the PBE0/TZ2P-ZORA//PBE0/def2-ZVP level.

Energy	Ga (D, $4s^2 4p_z^1$) + $Be_6Au_6^+$ (D)	Ga (D, $4s^1 4p_z^2$) + $Be_6Au_6^+$ (D)	Ga (Q, $4s^0 4p_z^1 4p_x^1 4p_y^1$) + $Be_6Au_6^+$ (Q)	Ga^- (S, $4s^2 4p_z^2$) + $Be_6Au_6^{2+}$ (S)	Ga^- (Q, $4s^1 4p_z^1 4p_x^1 4p_y^1$) + $Be_6Au_6^{2+}$ (Q)
ΔE_{int}	-261.6	-352.6	-442.4	-467.1	-491.3
ΔE_{Pauli}	137.1	137.7	356.7	139.0	534.1
ΔE_{elstat}	-137.5	-201.5	-477.0	-321.8	-657.6
ΔE_{orb}	-261.1	-288.8	-322.0	-284.2	-367.8
Energy	Ga^- (T, $4s^0 4p_z^2 4p_x^1 4p_y^1$) + $Be_6Au_6^{2+}$ (T)	Ga^{2-} (Q, $4s^2 4p_z^1 4p_x^1 4p_y^1$) + $Be_6Au_6^{3+}$ (Q)	Ga^{2-} (Q, $4s^2 4p_z^1 4p_x^1 4p_y^1$) + $Be_6Au_6^{3+}$ (Q)	Ga^{3-} (T, $4s^2 4p_z^2 4p_x^1 4p_y^1$) + $Be_6Au_6^{4+}$ (T)	
ΔE_{int}	-635.0	-834.5	-877.2	-1367.7	
ΔE_{Pauli}	444.8	789.0	687.6	875.8	
ΔE_{elstat}	-705.0	-995.8	-1019.0	-1470.7	
ΔE_{orb}	-374.9	-627.7	-545.8	-772.8	

Table S3. The EDA-NOCV results of D6h symmetric $EBe_6Au_6^+$ (E = Ga, In, Tl) cluster considering E (D, $ns^2np_\perp^1$) and $Be_6Au_6^+$ (D) as interacting fragments at the PBE0/TZ2P-ZORA//PBE0/def2-ZVP level.

Energy	Interaction	Al (D, $3s^23p_\perp^1$) + $Be_6Au_6^+$ (D)	Ga (D, $4s^24p_\perp^1$) + $Be_6Au_6^+$ (D)	In (D, $5s^25p_\perp^1$) + $Be_6Au_6^+$ (D)	Tl (D, $6s^26p_\perp^1$) + $Be_6Au_6^+$ (D)
ΔE_{int}	–	-253.5	-261.6	-229.6	-220.1
ΔE_{Pauli}	–	114.2	137.1	178.1	214.5
ΔE_{elstat}[a]	–	-115.7 (31.5%)	-137.5 (34.5%)	-169.4 (41.6%)	-200.1 (46.0%)
ΔE_{orb}[a]	–	-251.9 (68.5%)	-261.1 (65.5%)	-238.3 (58.4%)	-234.5 (54.0%)
$\Delta E_{orb(1)}$[b]	$E(p_\perp)$–$[Be_6Au_6^+]$ electron-sharing π-bond	-47.8 (19.0%)	-50.7 (19.4%)	-49.3 (20.7%)	-51.1 (21.8%)
$\Delta E_{orb(2)}$[b]	$E(s)\rightarrow[Be_6Au_6^+]$ σ-backdonation	-84.5 (33.5%)	-78.5 (30.1%)	-74.6 (31.3%)	-63.8 (27.2%)
$\Delta E_{orb(3)}$[b]	$E(p_{||})\leftarrow[Be_6Au_6^+]$ σ-donation	-55.5 (22.0%)	-61.0 (23.4%)	-50.8 (21.3%)	-50.2 (21.4%)
$\Delta E_{orb(4)}$[b]	$E(p_{||})\leftarrow[Be_6Au_6^+]$ σ-donation	-55.3 (22.0%)	-60.8 (23.3%)	-50.6 (21.2%)	-50.1 (21.4%)
$\Delta E_{orb(rest)}$[b]	–	-8.8 (3.5%)	-10.1 (3.9%)	-13.0 (5.5%)	-19.3 (8.2%)
ΔE_{Steric}		-1.5	-0.4	8.7	14.4

[a]The percentage contribution with respect to total attraction is given in parentheses; [b]The percentage contribution in parentheses is given with respect to total orbital interaction.

Table S4. The EDA results for $EBe_6Au_6^+$ (E = In, Tl) cluster taking E (D, $ns^2np_\perp^1$) as one fragment and $Be_6Au_6^+$ (D) as another fragment at the PBE0/TZ2P-ZORA//PBE0/def2-TZVP level.

Energy	$InBe_6Au_6^+$		$TlBe_6Au_6^+$	
	D_{6h}	C_{6v}	D_{6h}	C_{6v}
ΔE_{int}	-229.6	-234.1	-220.1	-219.3
ΔE_{Pauli}	178.1	186.0	214.5	219.2
ΔE_{elstat}	-169.4	-171.2	-200.1	-195.5
ΔE_{orb}	-238.3	-248.9	-234.5	-243.0
ΔE_{Steric}	8.7	14.8	14.4	23.7

The lowest vibrational frequencies (ν_{min}), the corresponding energies and the cartesian coordinates of the low-lying energy isomers with $GaBe_6Au_6^+$ obtained at the PBE0/def2-TZVP level.

		Isomer-a	
		ν_{min} = 8.0365 cm^{-1}	
		HF = -2827.529234 a.u.	
Au	0.000000000000	-3.832243000000	0.000000000000
Au	3.318820000000	-1.916122000000	0.000000000000
Au	3.318820000000	1.916122000000	0.000000000000
Au	0.000000000000	3.832243000000	0.000000000000
Au	-3.318820000000	1.916122000000	0.000000000000
Au	-3.318820000000	-1.916122000000	0.000000000000
Be	-1.114577000000	-1.930504000000	0.000000000000
Be	1.114577000000	-1.930504000000	0.000000000000
Be	2.229155000000	0.000000000000	0.000000000000
Be	1.114577000000	1.930504000000	0.000000000000
Be	-1.114577000000	1.930504000000	0.000000000000
Be	-2.229155000000	0.000000000000	0.000000000000
Ga	0.000000000000	0.000000000000	0.000000000000
		Isomer-b	
		ν_{min} = 22.2548 cm^{-1}	
		HF = -2827.515782 a.u.	
Au	1.120577000000	-1.940897000000	1.254061000000
Au	-2.241155000000	0.000000000000	1.254061000000
Au	1.120577000000	1.940897000000	1.254061000000
Au	2.490089000000	0.000000000000	-1.559438000000
Au	-1.245044000000	-2.156480000000	-1.559438000000
Au	-1.245044000000	2.156480000000	-1.559438000000
Be	0.649113000000	-1.124297000000	-0.823031000000
Be	-1.298226000000	0.000000000000	-0.823031000000
Be	0.649113000000	1.124297000000	-0.823031000000
Be	2.129959000000	0.000000000000	0.667849000000
Be	-1.064980000000	-1.844599000000	0.667849000000
Be	-1.064980000000	1.844599000000	0.667849000000
Ga	0.000000000000	0.000000000000	2.678862000000
		Isomer-c	
		ν_{min} = 25.7784 cm^{-1}	
		HF = -2827.513433 a.u.	
Au	-1.107633000000	2.233098000000	-1.507020000000
Au	-1.636274000000	-0.921900000000	-1.043417000000
Au	1.791205000000	-1.349233000000	-1.855532000000
Au	-2.842952000000	0.113101000000	1.514388000000

Au	1.009685000000	-1.196823000000	1.884037000000
Au	2.638836000000	1.911002000000	0.935943000000
Be	-1.076828000000	0.876177000000	0.367687000000
Be	1.720514000000	0.006102000000	-0.082528000000
Be	0.726923000000	1.882263000000	-0.280934000000
Be	0.720374000000	1.000678000000	1.686633000000
Be	0.191519000000	0.302025000000	-1.578045000000
Be	-0.913441000000	-0.084130000000	2.511230000000
Ga	0.198300000000	-2.525252000000	-0.156121000000
		Isomer-d	
		ν_{min} = 17.8219 cm^{-1}	
		HF = -2827.518542 a.u.	
Au	2.729802000000	-0.631686000000	-1.567647000000
Au	1.592595000000	2.555402000000	1.389479000000
Au	0.766738000000	-1.506444000000	2.400824000000
Au	-1.986683000000	2.055402000000	-1.074604000000
Au	-3.005237000000	-0.783394000000	0.643976000000
Au	-0.249738000000	-1.955469000000	-1.099232000000
Be	-1.591458000000	0.889059000000	0.769219000000
Be	0.542262000000	0.563538000000	1.408113000000
Be	0.048257000000	1.981740000000	-0.186823000000
Be	1.357471000000	-1.063449000000	0.218673000000
Be	-0.850119000000	-1.189675000000	0.915498000000
Be	1.869770000000	0.954208000000	-0.245489000000
Ga	0.211116000000	0.402816000000	-2.137021000000
		Isomer-e	
		ν_{min} = 22.7693 cm^{-1}	
		HF = -2827.509002 a.u.	
Au	1.737733303483	1.457311185056	-1.765774825003
Au	2.412104385564	-2.150416702597	0.000000000000
Au	1.737733303483	1.457311185056	1.765774825003
Au	-3.639818992789	1.170244243609	0.000000000000
Au	-1.168665136247	-1.511918649720	-1.806786941428
Au	-1.168665136247	-1.511918649720	1.806786941428
Be	-0.118652194684	0.377197082754	-1.041936955776
Be	0.282769306971	-1.500679422341	0.000000000000
Be	1.767729844149	-0.020546627793	0.000000000000
Be	-1.925234289480	-0.264694613885	0.000000000000
Be	-1.527921424850	1.758590922053	0.000000000000
Be	-0.118652194684	0.377197082754	1.041936955776
Ga	0.470412954209	3.018038054952	0.000000000000