Electronic Supplementary Material (ESI) for Chemical Communications.

Exploiting Electronic Strategies to Stabilize a Planar Tetracoordinate Carbon in Cyclic Aromatic Hydrocarbons

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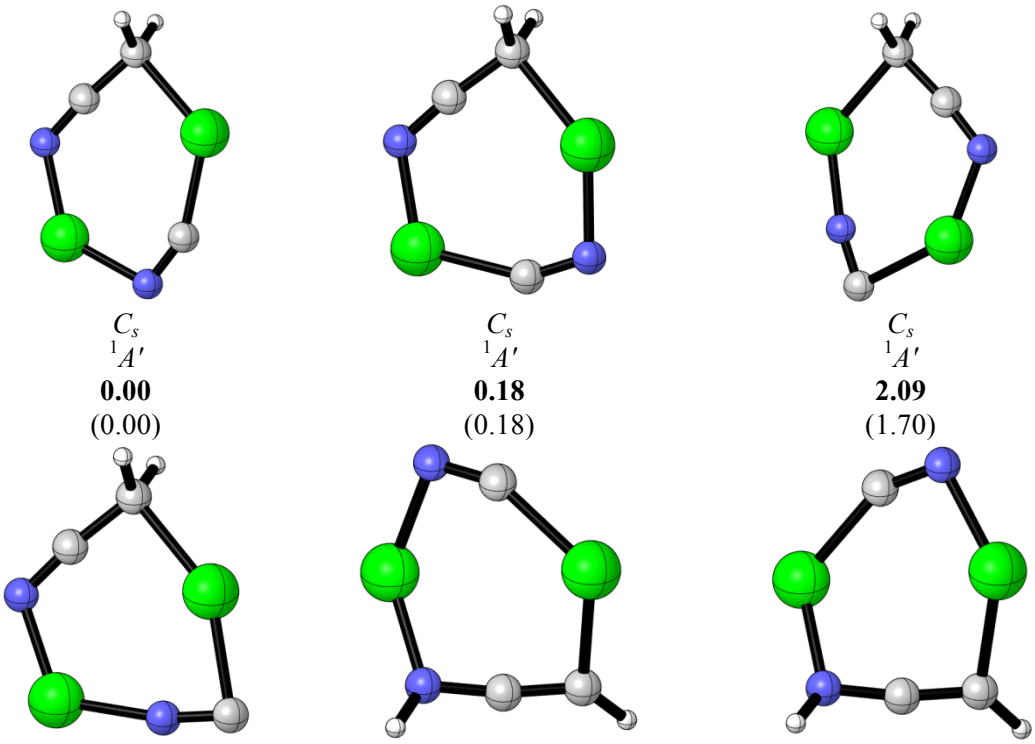
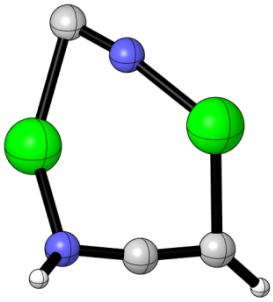
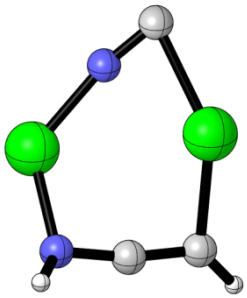
Fig. S1 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Li_2C_3N_2H_2$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.

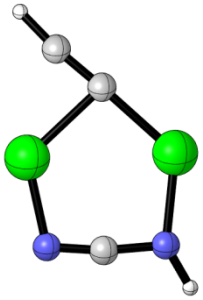




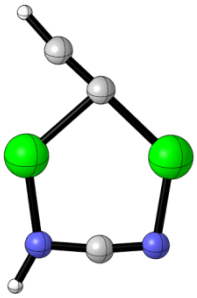
C_s
$^1A'$
26.99
(24.20)



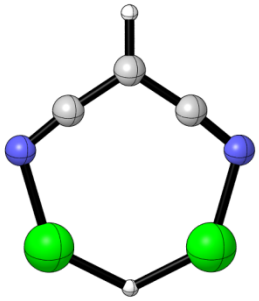
C_s
$^1A'$
27.23
(24.39)



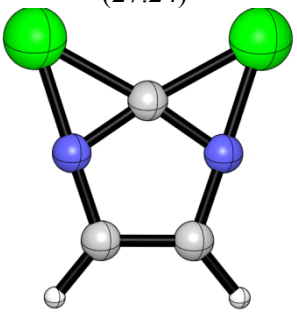
C_s
$^1A'$
30.09
(27.24)



C_s
$^1A'$
30.18
(27.43)



C_{2v}
$^1A_1$
32.00
(22.73)



C_{2v}
$^1A_1$
32.74
(24.18)

Fig. S2 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the C_7H_2 cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.

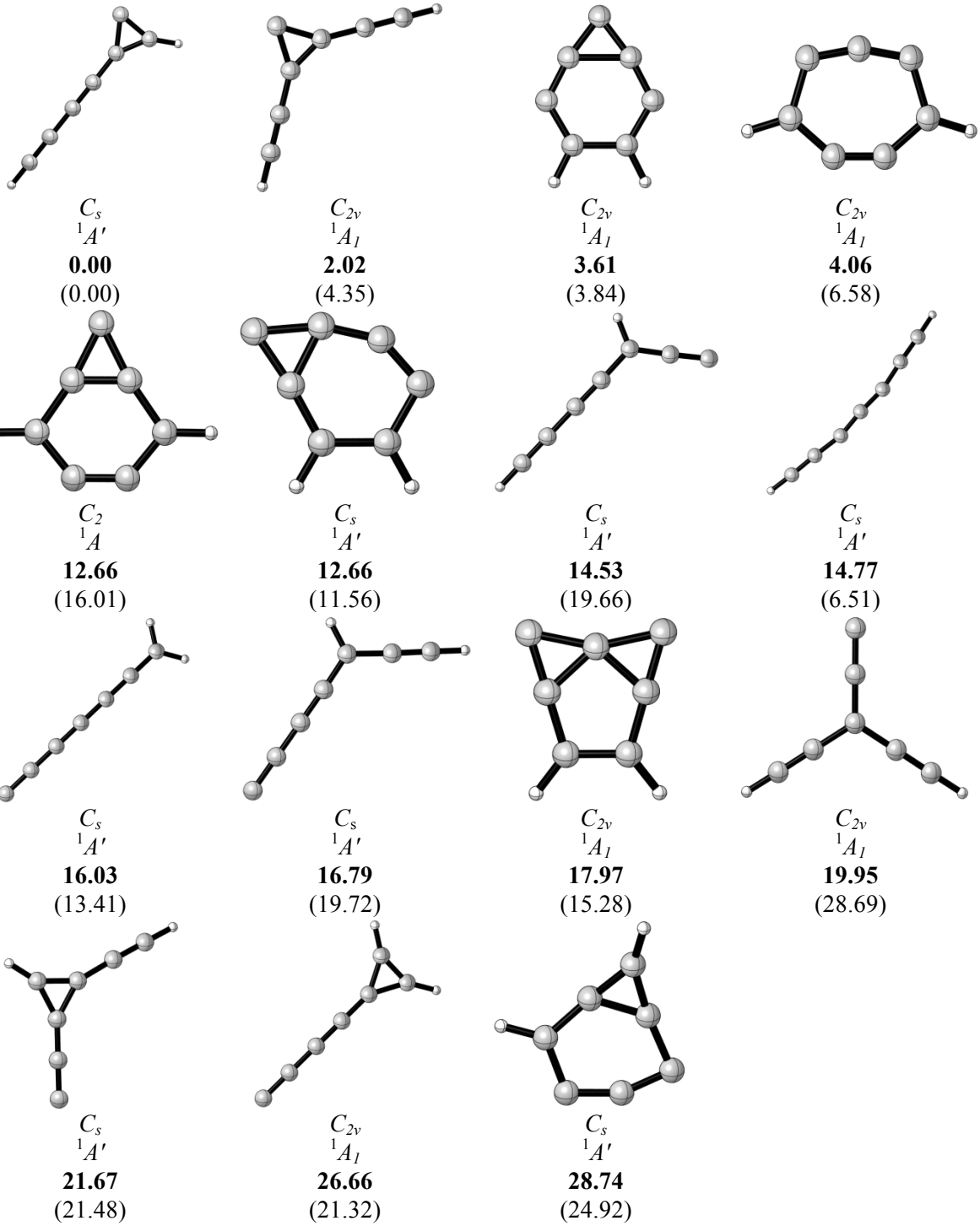
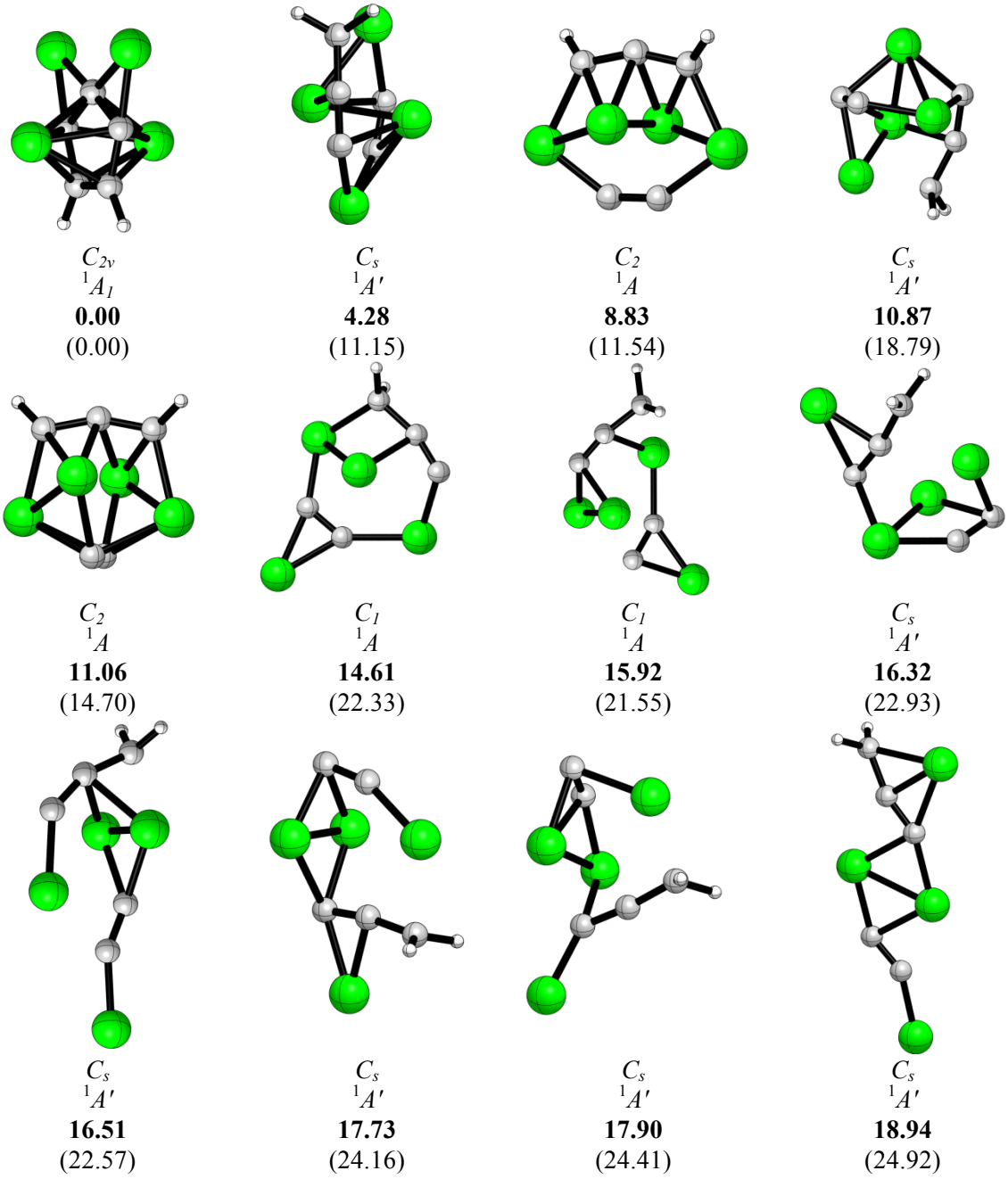
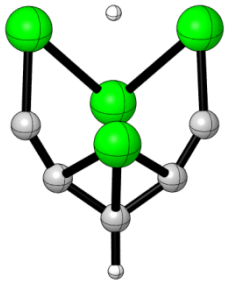
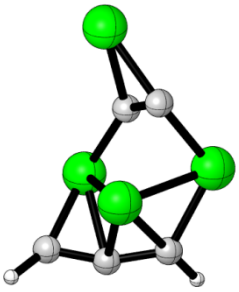


Fig. S3 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Li_4C_5H_2$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.

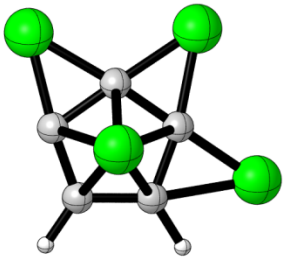




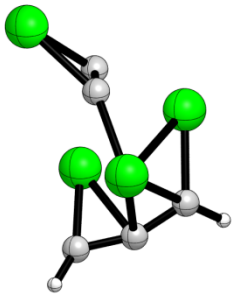
C_s
$^1A'$
19.20
(17.56)



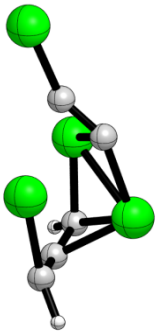
C_s
$^1A'$
19.93
(23.35)



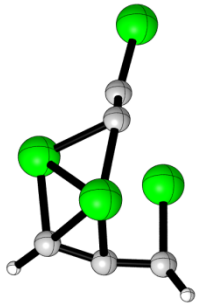
C_1
^1A
20.06
(18.76)



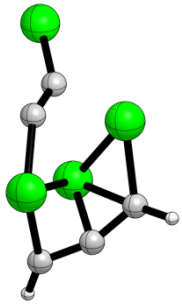
C_s
$^1A'$
20.44
(24.03)



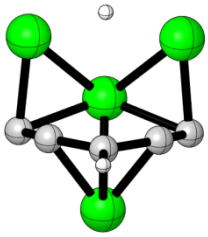
C_s
$^1A'$
22.97
(26.48)



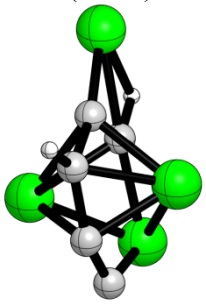
C_s
$^1A'$
23.05
(26.43)



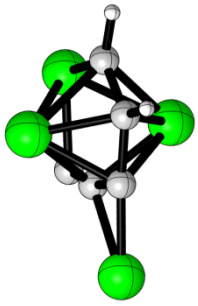
C_s
$^1A'$
23.08
(26.28)



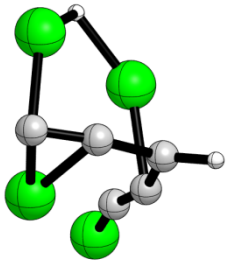
C_s
$^1A'$
25.53
(25.84)



C_s
$^1A'$
25.60
(25.86)

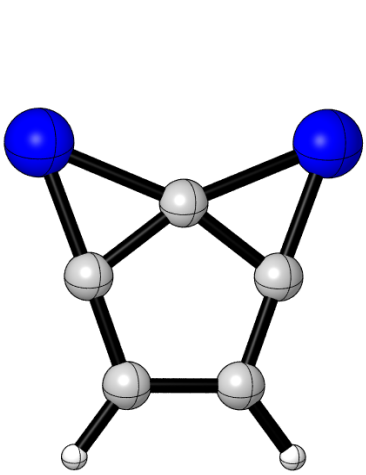


C_s
$^1A'$
27.70
(28.14)

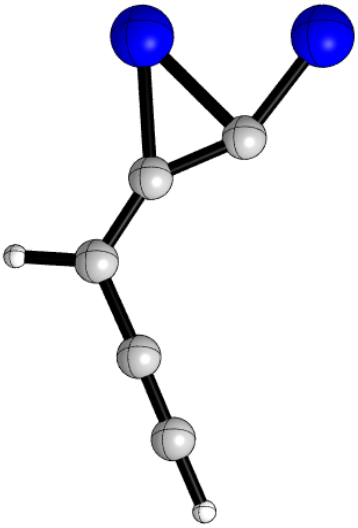


C_1
^1A
30.12
(29.88)

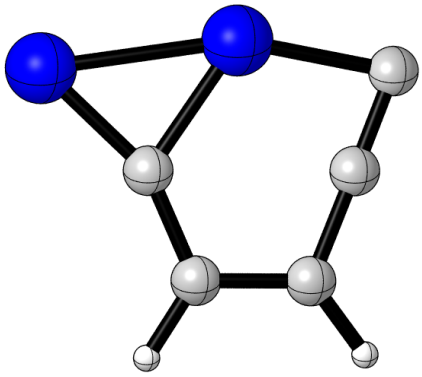
Fig. S4 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Si_2C_5H_2$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



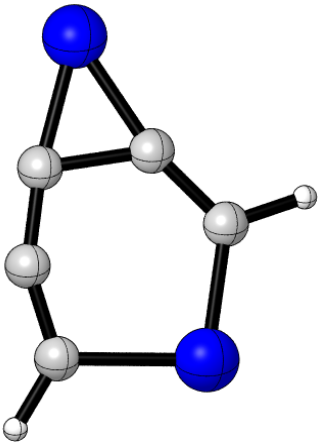
5, (C_{2v})
$^1A_1$
0.00
(0.00)



C_s
$^1A'$
24.62
(27.11)

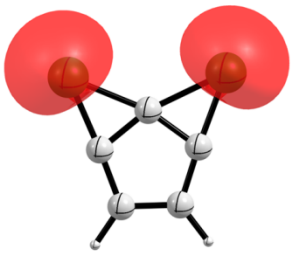


C_s
$^1A'$
26.82
(28.10)

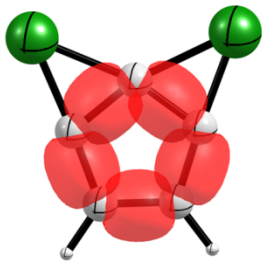


C_s
$^1A'$
28.08
(26.92)

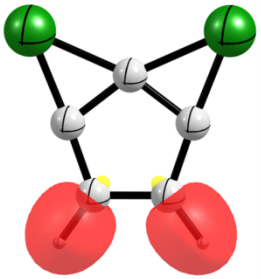
Fig. S5 σ- and π-bonding pattern revealed by the AdNDP analysis for the $Si_2C_5H_2$, $Ge_2C_5H_2$, $Sn_2C_5H_2$ and $Pb_2C_5H_2$ systems.



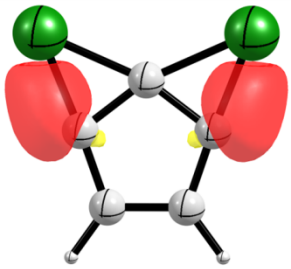
2 x 1c-2e E-LP
E = Si, ON = 1.96 |e|
E = Ge, ON = 1.97 |e|
E = Sn, ON = 1.98 |e|
E = Pb, ON = 1.98 |e|



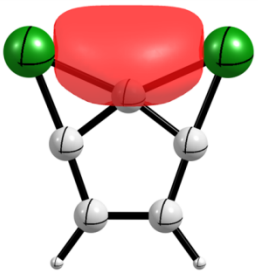
5 x 2c-2e C-C σ bonds
E = Si, ON = 1.99 – 1.91 |e|
E = Ge, ON = 1.99 – 1.93 |e|
E = Sn, ON = 1.98 – 1.95 |e|
E = Pb, ON = 1.98 – 1.95 |e|



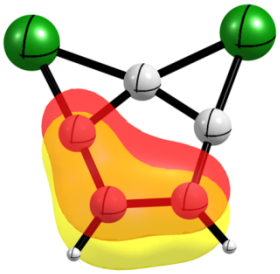
2 x 2c-2e C-H σ bonds
E = Si, ON = 1.98 |e|
E = Ge, ON = 1.98 |e|
E = Sn, ON = 1.98 |e|
E = Pb, ON = 1.98 |e|



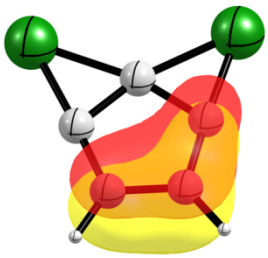
2 x 2c-2e C-E σ bonds
E = Si, ON = 1.96 |e|
E = Ge, ON = 1.97 |e|
E = Sn, ON = 1.96 |e|
E = Pb, ON = 1.96 |e|



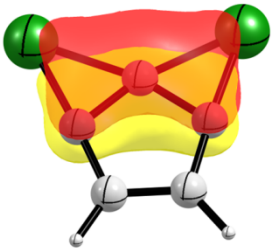
3c-2e E-C-E σ bond
E = Si, ON = 1.95 |e|
E = Ge, ON = 1.96 |e|
E = Sn, ON = 1.96 |e|
E = Pb, ON = 1.96 |e|



3c-2e π bond
E = Si, ON = 1.94 |e|
E = Ge, ON = 1.93 |e|
E = Sn, ON = 1.92 |e|
E = Pb, ON = 1.92 |e|

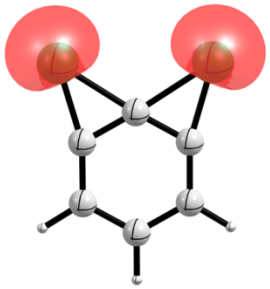


3c-2e π bond
E= Si, ON = 1.94 |e|
E= Ge, ON = 1.93 |e|
E= Sn, ON = 1.92 |e|
E= Pb, ON = 1.92 |e|

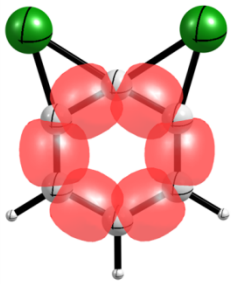


7c-2e π bond
E = Si, ON = 2.00 |e|
E = Ge, ON = 2.00 |e|
E = Sn, ON = 2.00 |e|
E = Pb, ON = 2.00 |e|

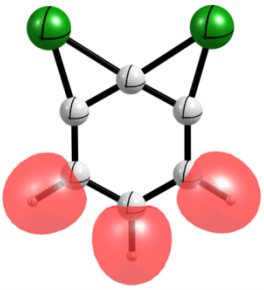
Fig. S6 σ- and π-bonding pattern revealed by the AdNDP analysis for the $Si_2C_6H_3^+$, $Ge_2C_6H_3^+$, $Sn_2C_6H_3^+$ and $Pb_2C_6H_3^+$ systems.



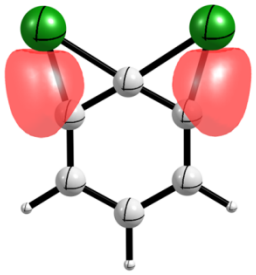
2 x 1c-2e Ge-LP
E = Si, ON = 1.97 |e|
E = Ge, ON = 1.98 |e|
E = Sn, ON = 1.98 |e|
E = Pb, ON = 1.99 |e|



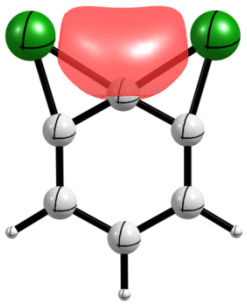
6 x 2c-2e C-C σ bonds
E = Si, ON = 1.99 – 1.95 |e|
E = Ge, ON = 1.99 – 1.96 |e|
E = Sn, ON = 1.98 – 1.97 |e|
E = Pb, ON = 1.98 – 1.97 |e|



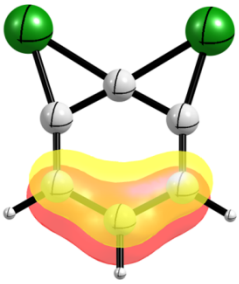
3 x 2c-2e C-H σ bonds
E = Si, ON = 1.97 |e|
E = Ge, ON = 1.97 |e|
E = Sn, ON = 1.98 |e|
E = Pb, ON = 1.97 |e|



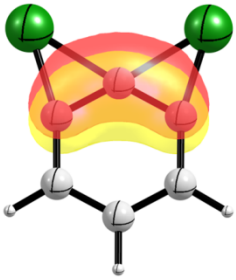
2 x 2c-2e C-E σ bonds
E = Si, ON = 1.96 |e|
E = Ge, ON = 1.96 |e|
E = Sn, ON = 1.95 |e|
E = Pb, ON = 1.95 |e|



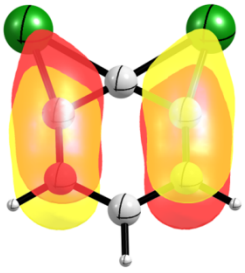
3c-2e E-C-E σ bond
E = Si, ON = 1.95 |e|
E = Ge, ON = 1.95 |e|
E = Sn, ON = 1.95 |e|
E = Pb, ON = 1.95 |e|



3c-2e π bond
E = Si, ON = 1.90 |e|
E = Ge, ON = 1.90 |e|
E = Sn, ON = 1.91 |e|
E = Pb, ON = 1.91 |e|

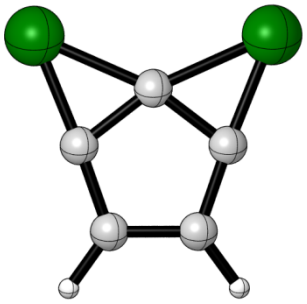


8c-2e π bond
E = Si, ON = 2.00 |e|
E = Ge, ON = 2.00 |e|
E = Sn, ON = 2.00 |e|
E = Pb, ON = 2.00 |e|

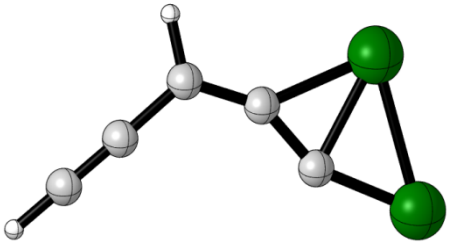


8c-2e π bond
E = Si, ON = 2.00 |e|
E = Ge, ON = 2.00 |e|
E = Sn, ON = 2.00 |e|
E = Pb, ON = 2.00 |e|

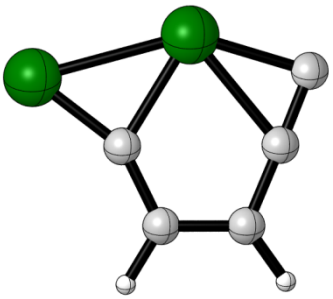
Fig. S7 Optimized within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Ge_2C_5H_2$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



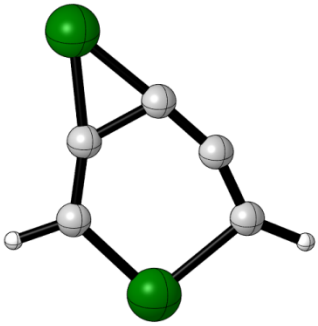
6, (C_{2v})
$^1A_1$
0.00
(0.00)



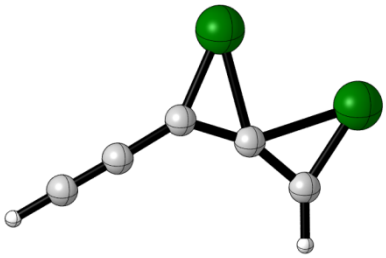
C_s
$^1A'$
17.43
(19.69)



C_s
$^1A'$
22.25
(26.05)

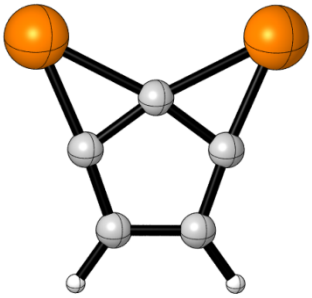


C_s
$^1A'$
24.74
(23.98)

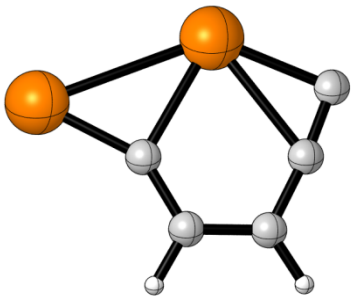


C_s
$^1A'$
31.72
(29.96)

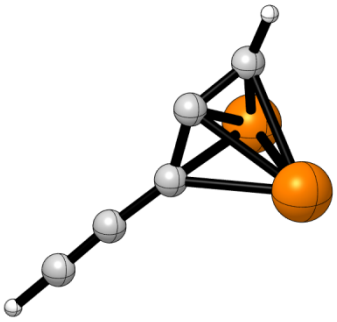
Fig. S8 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Sn_2C_5H_2$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



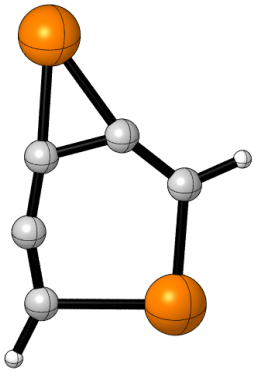
7, (C_{2v})
$^1A_1$
0.00
(0.00)



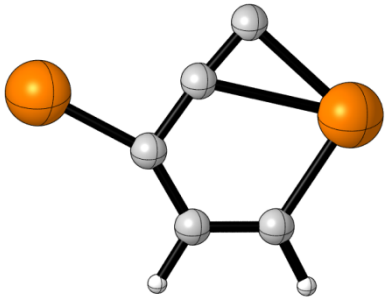
C_s
$^1A'$
16.07
(19.17)



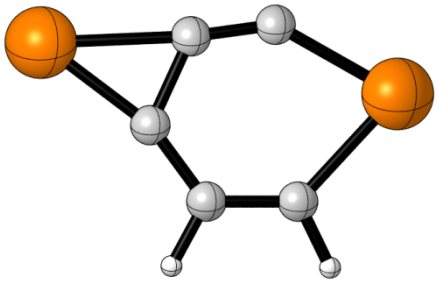
C_1
^1A
20.30
(18.93)



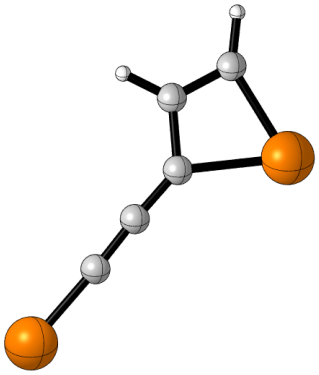
C_s
$^1A'$
23.24
(21.39)



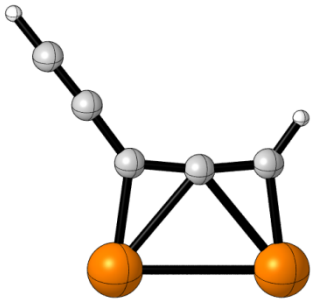
C_s
$^1A'$
26.09
(27.89)



C_s
$^1A'$
27.46
(28.58)

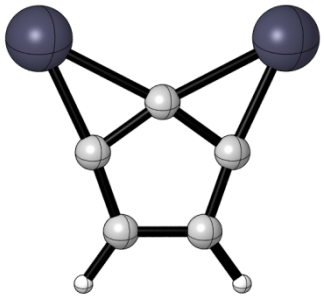


C_s
$^1A'$
30.07
(28.55)

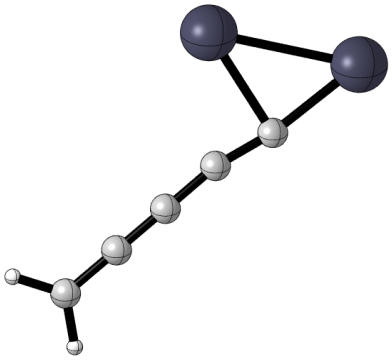


C_s
$^1A'$
30.26
(25.63)

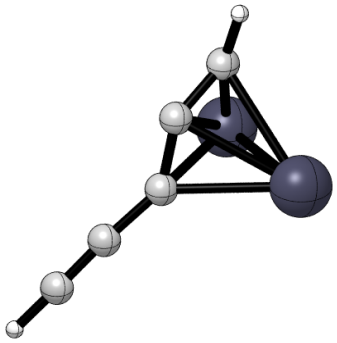
Fig. S9 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Pb_2C_5H_2$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



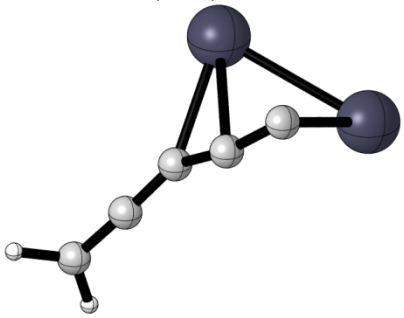
8, (C_{2v})
$^1A_1$
0.00
(0.00)



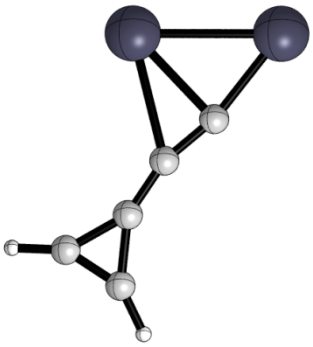
C_s
$^1A'$
10.70
(2.75)



C_1
^1A
10.75
(8.70)

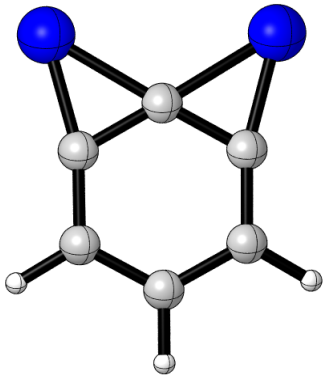


C_1
^1A
20.59
(16.18)

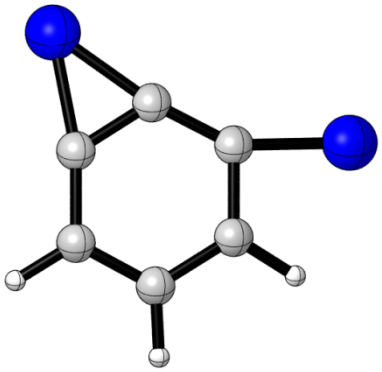


C_s
$^1A'$
36.69
(28.12)

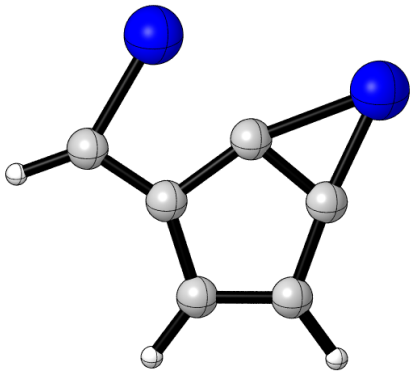
Fig. S10 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Si_2C_6H_3^+$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



C_{2v}
$^1A_1$
0.00
(0.00)

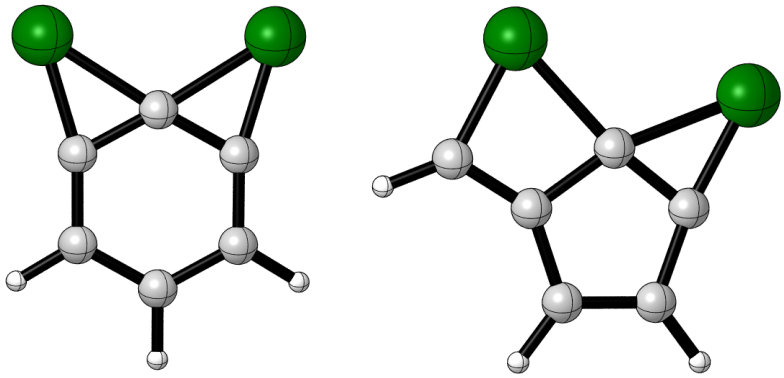


C_s
$^1A'$
21.73
(22.18)



C_s
$^1A'$
23.16
(24.27)

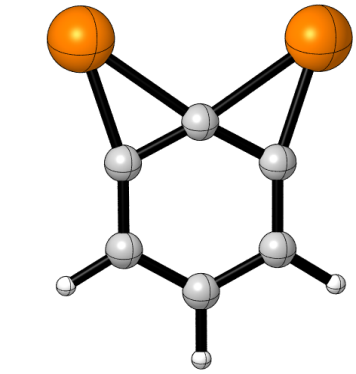
Fig. S11 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Ge_2C_6H_3^+$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



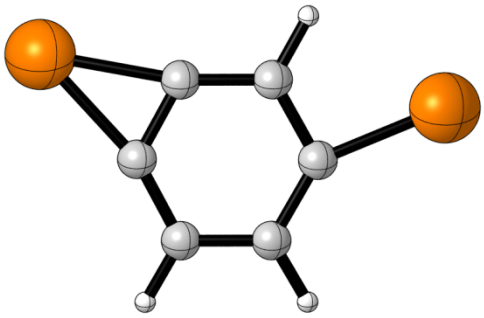
C_{2v}
$^1A_1$
0.00
(0.00)

C_s
$^1A'$
21.31
(22.87)

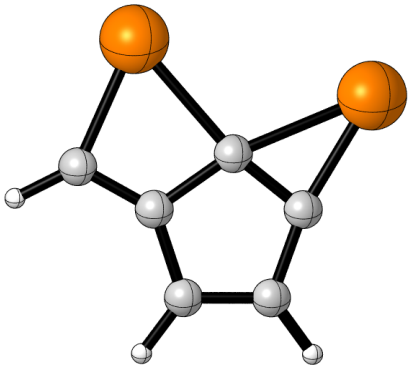
Fig. S12 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Sn_2C_6H_3^+$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



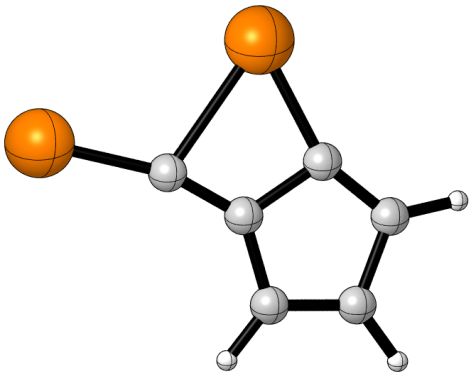
C_{2v}
$^1A_1$
0.00
(0.00)



C_s
$^1A'$
19.40
(18.72)

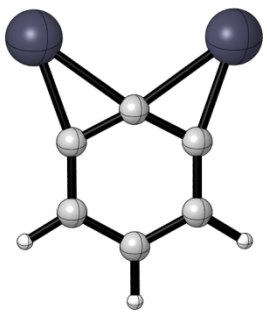


C_s
$^1A'$
20.64
(22.08)

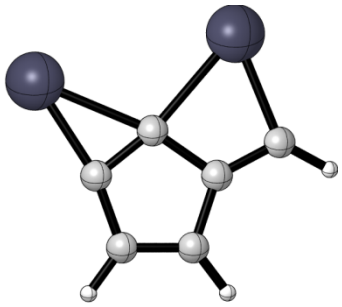


C_s
$^1A'$
27.06
(28.41)

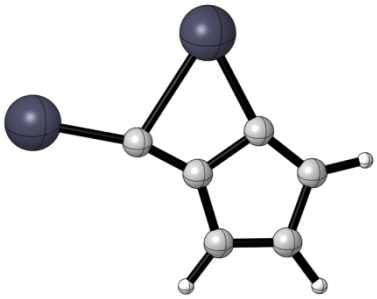
Fig. S13 Optimized structures within the range of 0–30 kcal.mol^{-1} with respect to the global minimum structure of the $Pb_2C_6H_3^+$ cluster at the PBE0/def2-TZVP level. Relative energies are listed in kcal.mol^{-1} at the single-point CCSD(T)/def2-TZVP//PBE0/def2-TZVP (in **bold**) and PBE0/def2-TZVP (in parentheses) levels, with zero-point energy (ZPE) corrections.



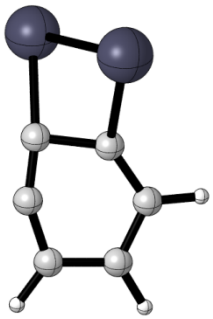
C_{2v}
$^1A_1$
0.00
(0.00)



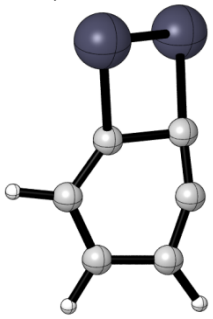
C_s
$^1A'$
21.30
(22.87)



C_s
$^1A'$
26.95
(27.59)

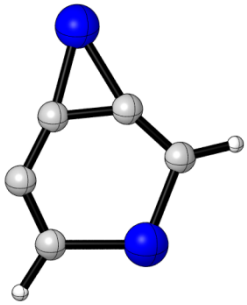


C_1
^1A
33.04
(29.77)

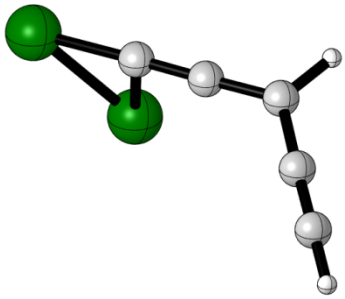


C_1
^1A
33.04
(29.77)

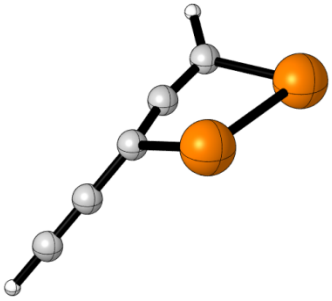
Fig. S14 Optimized structures for the lowest-energy triplets of $Si_2C_5H_2$, $Ge_2C_5H_2$, $Sn_2C_5H_2$. $Pb_2C_5H_2$, $Si_2C_6H_3^+$, $Ge_2C_6H_3^+$, $Sn_2C_6H_3^+$ and $Pb_2C_6H_3^+$. Relative energies with respect to their corresponding global minimum are listed in kcal.mol^{-1}, calculated at the PBE0/def2-TZVP level of theory, with zero-point energy (ZPE) corrections.



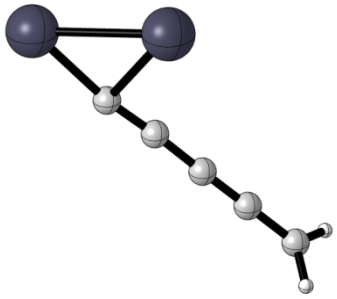
$Si_2C_5H_2$
C_s
49.87



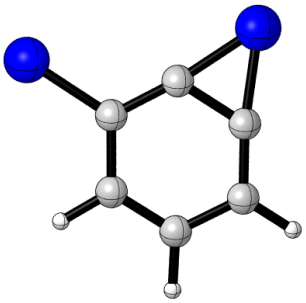
$Ge_2C_5H_2$
C_1
43.52



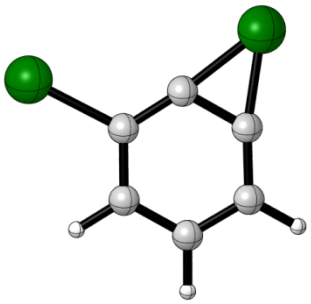
$Sn_2C_5H_2$.
C_1
29.28



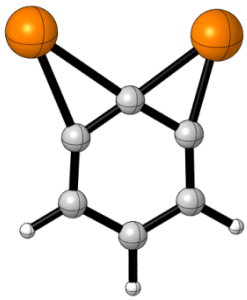
$Pb_2C_5H_2$
C_s
10.44



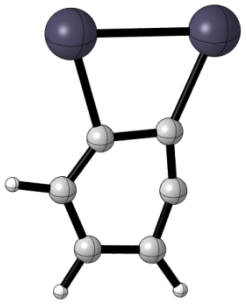
$Si_2C_6H_3^+$
C_s
48.19



$Ge_2C_6H_3^+$
C_s
46.73



$Sn_2C_6H_3^+$
C_s
41.71



$Pb_2C_6H_3^+$
C_s
35.06

Fig. S15 Isolines of B^{ind}_z in $Si_2C_5H_2$, $Ge_2C_5H_2$, $Sn_2C_5H_2$, $Pb_2C_5H_2$ and $C_5H_5^-$systems

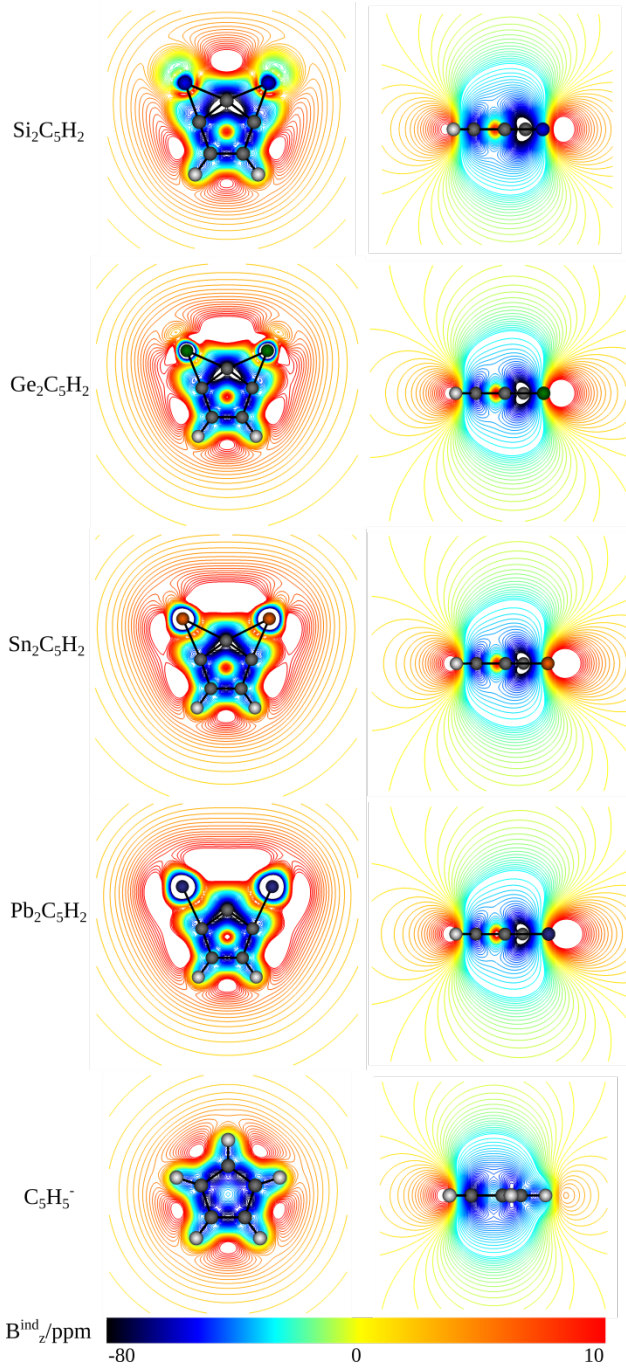


Fig. S16 Isolines of B^{ind}_z in $Si_2C_6H_3^+$, $Ge_2C_6H_3^+$, $Sn_2C_6H_3^+$, $Pb_2C_6H_3^+$ and C_6H_6 systems

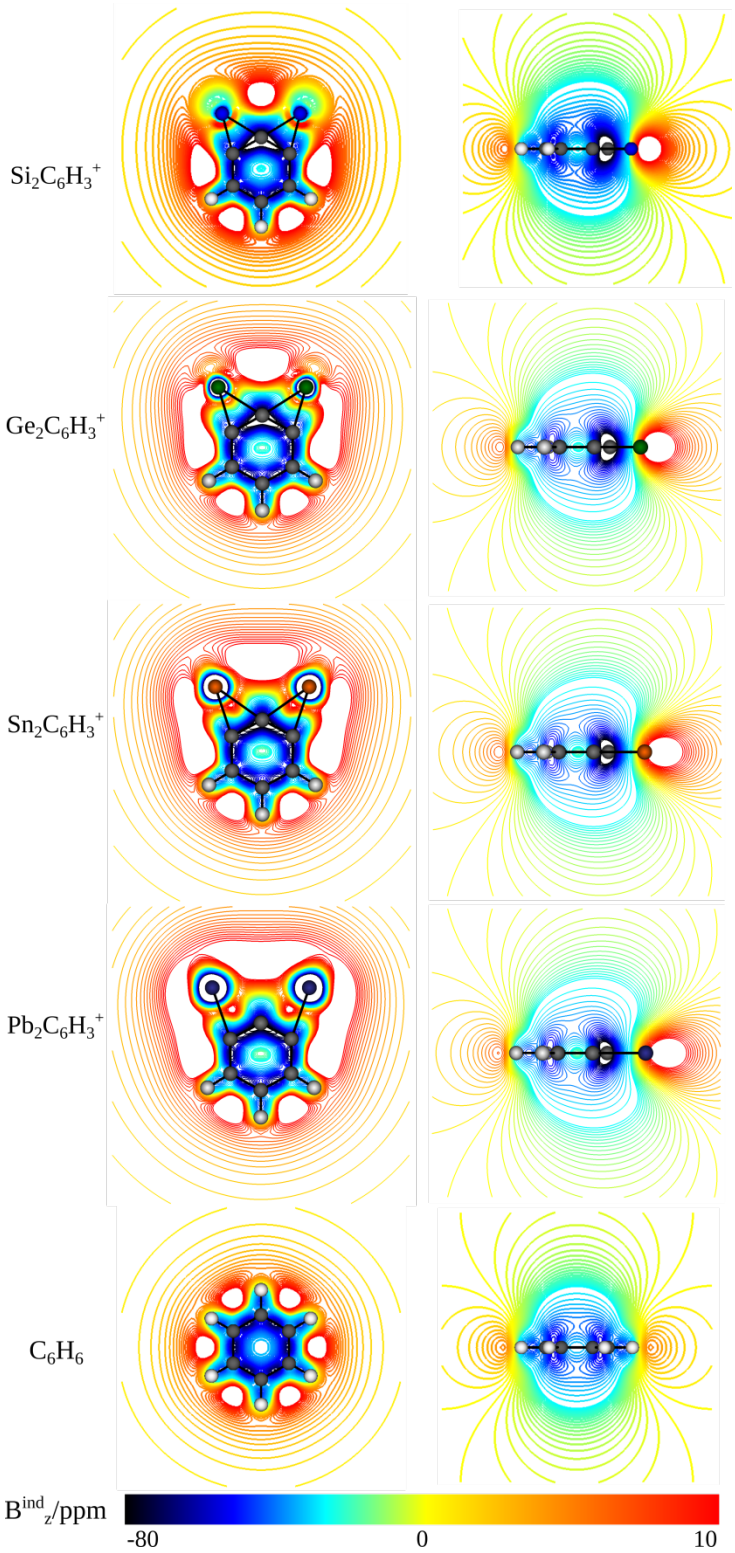


Table S1. HOMO-LUMO energy gaps, singlet-triplet energy differences, smallest vibrational frequencies, T_1-diagnostics for the studied systems.

System	ΔE_{H-L} (eV)	ΔE_{S-T} (kcal/mol)	ν_{min} (cm^{-1})	T_1 Diagnostic
[redacted]				
$Si_2C_5H_2$	5.11	49.87	196.1	0.015
$Ge_2C_5H_2$	4.81	43.52	135.6	0.014
$Sn_2C_5H_2$	4.09	29.28	90.9	0.017
$Pb_2C_5H_2$	3.79	10.44	62.4	0.016
[redacted]				
$Si_2C_6H_3^+$	4.12	48.19	111.5	0.014
$Ge_2C_6H_3^+$	4.01	46.73	99.6	0.014
$Sn_2C_6H_3^+$	3.74	41.71	80.1	0.016
$Pb_2C_6H_3^+$	3.65	35.06	56.6	0.014

Table S2. NPA charges on carbon (q(C1), q(C2), q(C4), q(C6)), and E atoms (E=C, Si, Ge, Sn, Pb) (q(E)), sum of the charges of the C and H atoms (q(ΣC+ΣH)), and Wiberg bond indices of the C1-E (WBI_{C1-E}), C2-E (WBI_{C2-E}), C1-C2 (WBI_{C1-C2}), C2-C4 (WBI_{C2-C4}) and C4-C5 (WBI_{C4-C5}) bonds computed at the PBE0/def2-TZVP level of theory

System	q(C1)	q(C2)	q(C4)	q(C6)	q(ΣC+ΣH)	q(E)	WBI C1-E	WBI C2-E	WBI C1-C2	WBI C2-C4	WBI C4-C5[a]
[redacted]											
$Si_2C_5H_2$	-0.79	-0.58	-0.22		-1.93	0.96	0.57	0.99	1.21	1.29	1.57
$Ge_2C_5H_2$	-0.75	-0.58	-0.23		-1.93	0.96	0.54	0.99	1.25	1.29	1.56
$Sn_2C_5H_2$	-0.75	-0.60	-0.26		-2.04	1.02	0.51	0.93	1.28	1.31	1.52
$Pb_2C_5H_2$	-0.70	-0.59	-0.27		-1.97	0.99	0.50	0.94	1.30	1.31	1.51
[redacted]											
$Si_2C_6H_3^+$	-0.69	-0.57	-0.09	-0.16	-1.41	1.20	0.45	0.80	1.34	1.37	1.44
$Ge_2C_6H_3^+$	-0.64	-0.57	-0.11	-0.17	-1.41	1.20	0.43	0.78	1.37	1.37	1.44
$Sn_2C_6H_3^+$	-0.61	-0.56	-0.15	-0.18	-1.48	1.24	0.41	0.72	1.41	1.39	1.44
$Pb_2C_6H_3^+$	-0.55	-0.53	-0.17	-0.18	-1.42	1.21	0.41	0.72	1.43	1.39	1.44

[a] For the 6MR systems, this corresponds to the WBI_{C4-C6}.

Table S3 - Cartesian coordinates of the global minimum of $Si_2C_5H_2$, $Ge_2C_5H_2$, $Sn_2C_5H_2$ and $Pb_2C_5H_2$ calculated at the PBE0/def2-TZVP level of theory.

$Si_2C_5H_2$				**$Ge_2C_5H_2$**			
6	1.153436000	0.514514000	0.002633000	6	-0.000001000	0.092698000	0.000153000
6	0.688311000	1.848214000	0.000815000	6	1.154867000	0.979499000	0.000209000
14	1.755987000	-1.122837000	-0.001440000	6	-1.154863000	0.979500000	-0.000010000
1	1.325419000	2.723843000	0.002894000	32	-1.844323000	-0.726383000	-0.000022000
6	-0.000253000	-0.387651000	0.001999000	32	1.844322000	-0.726384000	-0.000017000
6	-1.155217000	0.513975000	-0.001263000	6	0.690610000	2.315911000	0.000005000
6	-0.690001000	1.847772000	-0.001635000	6	-0.690607000	2.315912000	-0.000102000
14	-1.754246000	-1.124879000	0.000490000	1	1.324663000	3.193717000	-0.000033000
1	-1.327446000	2.723236000	-0.004886000	1	-1.324659000	3.193719000	-0.000252000
$Sn_2C_5H_2$				**$Pb_2C_5H_2$**			
6	0.000524000	0.434134000	-0.002069000	6	0.000017000	0.679616000	0.001734000
6	1.164479000	1.295705000	0.002142000	6	-1.162654000	1.529658000	-0.002883000
6	-1.163641000	1.295117000	-0.004001000	6	1.162683000	1.529678000	0.004737000
50	1.980194000	-0.567407000	-0.000144000	82	-2.057142000	-0.392312000	0.000161000
6	0.693775000	2.630094000	0.001439000	6	-0.695282000	2.867106000	-0.002479000
6	-0.693940000	2.629826000	-0.000635000	6	0.695286000	2.867116000	0.001438000
1	-1.322296000	3.512109000	0.000095000	1	1.322837000	3.750259000	0.002358000
1	1.321835000	3.512605000	0.004263000	1	-1.322845000	3.750236000	-0.005293000
50	-1.980328000	-0.567272000	0.000432000	82	2.057138000	-0.392316000	-0.000311000

Table S4 - Cartesian coordinates of the global minimum of $Si_2C_6H_3^+$, $Ge_2C_6H_3^+$, $Sn_2C_6H_3^+$ and $Pb_2C_6H_3^+$ calculated at the PBE0/def2-TZVP level of theory.

$Si_2C_6H_3^+$				**$Ge_2C_6H_3^+$**			
6	0.455971000	-0.000003000	-0.000036000	6	0.000005000	0.132970000	-0.000268000
6	-0.245602000	-1.229961000	-0.000060000	6	1.228581000	0.815647000	-0.000251000
6	-0.245595000	1.229958000	0.000018000	6	-1.228570000	0.815649000	0.000051000
6	-1.636898000	-1.217314000	-0.000034000	32	-1.768887000	-0.998001000	0.000009000
6	-1.636891000	1.217320000	0.000078000	32	1.768881000	-0.998011000	0.000045000
14	1.483281000	1.686158000	-0.000037000	6	1.220319000	2.207305000	-0.000153000
14	1.483275000	-1.686161000	0.000024000	6	-1.220309000	2.207306000	0.000205000
6	-2.314658000	0.000005000	0.000040000	6	0.000006000	2.882120000	0.000051000
1	-2.195523000	-2.147088000	-0.000066000	1	2.147466000	2.770003000	-0.000191000
1	-2.195509000	2.147098000	0.000149000	1	-2.147456000	2.770002000	0.000468000
1	-3.398707000	0.000008000	0.000072000	1	0.000006000	3.966387000	0.000161000
$Sn_2C_6H_3^+$				**$Pb_2C_6H_3^+$**			
6	-0.001174000	0.545817000	-0.003363000	6	-0.000358000	0.871869000	0.001653000
6	-1.232609000	1.200518000	-0.000881000	6	-1.229715000	1.511391000	0.000058000
6	1.230537000	1.199719000	-0.001686000	6	1.229152000	1.511067000	0.002700000
50	-1.891717000	-0.790757000	0.000067000	82	1.955870000	-0.556556000	-0.000208000
50	1.892103000	-0.790243000	0.000330000	82	-1.955815000	-0.556633000	0.000029000
6	1.222468000	2.592111000	-0.000151000	6	-1.223718000	2.904493000	-0.001120000
6	-1.222748000	2.593054000	0.001560000	6	1.223712000	2.904120000	0.000599000
6	0.000158000	3.265277000	0.000458000	6	0.000098000	3.576004000	-0.000864000
1	-2.146539000	3.161504000	0.003712000	1	-2.146864000	3.473852000	-0.002272000
1	2.146922000	3.159596000	0.000733000	1	2.147098000	3.473078000	0.000508000
1	0.000545000	4.349949000	0.000059000	1	0.000243000	4.660936000	-0.001726000