Multiple Local σ-Aromaticity of the Nonagermanide Clusters

Nikolay V. Tkachenko and Alexander I. Boldyrev*
Department of Chemistry and Biochemistry
Utah State University
Logan, Utah 84322-0300

e-mail: a.i.boldyrev@usu.edu

KEYWORDS: multiple σ-aromaticity, Zintl anions, chemical bonding, germanium, reactivity

Supporting Information

Contents

1. Complete chemical bonding pattern of selected species.

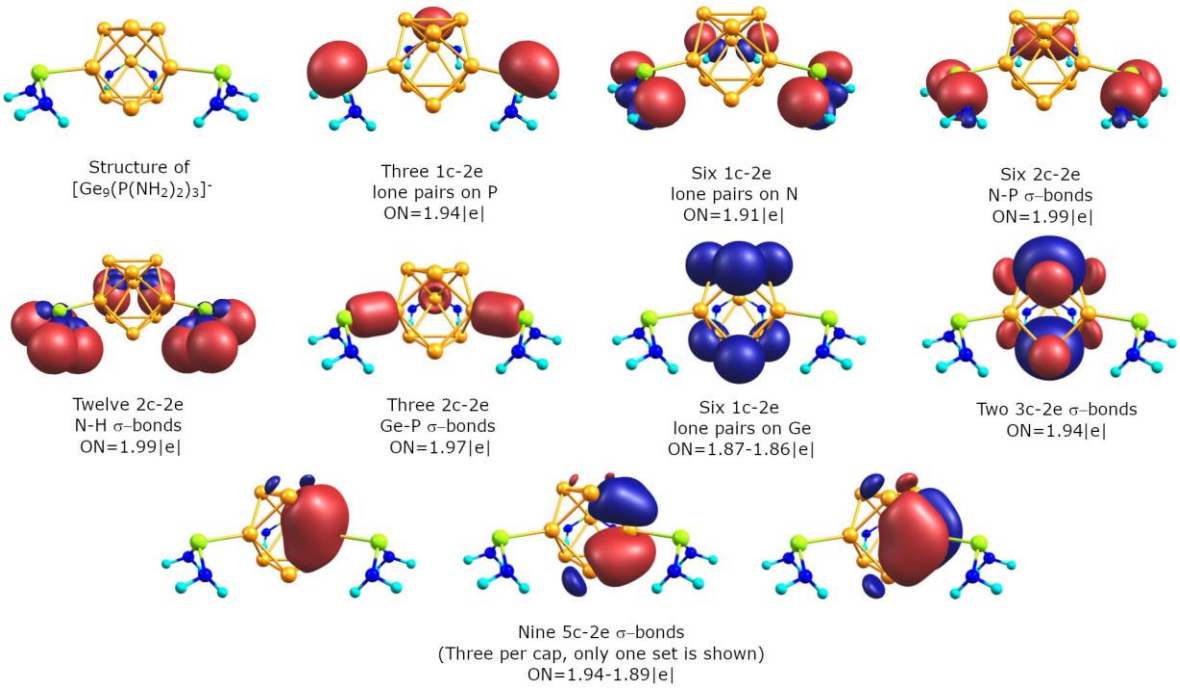

Figure S1. Chemical bonding picture of $[Ge_9\{P(NH_2)_2\}_3]^-$ cluster.

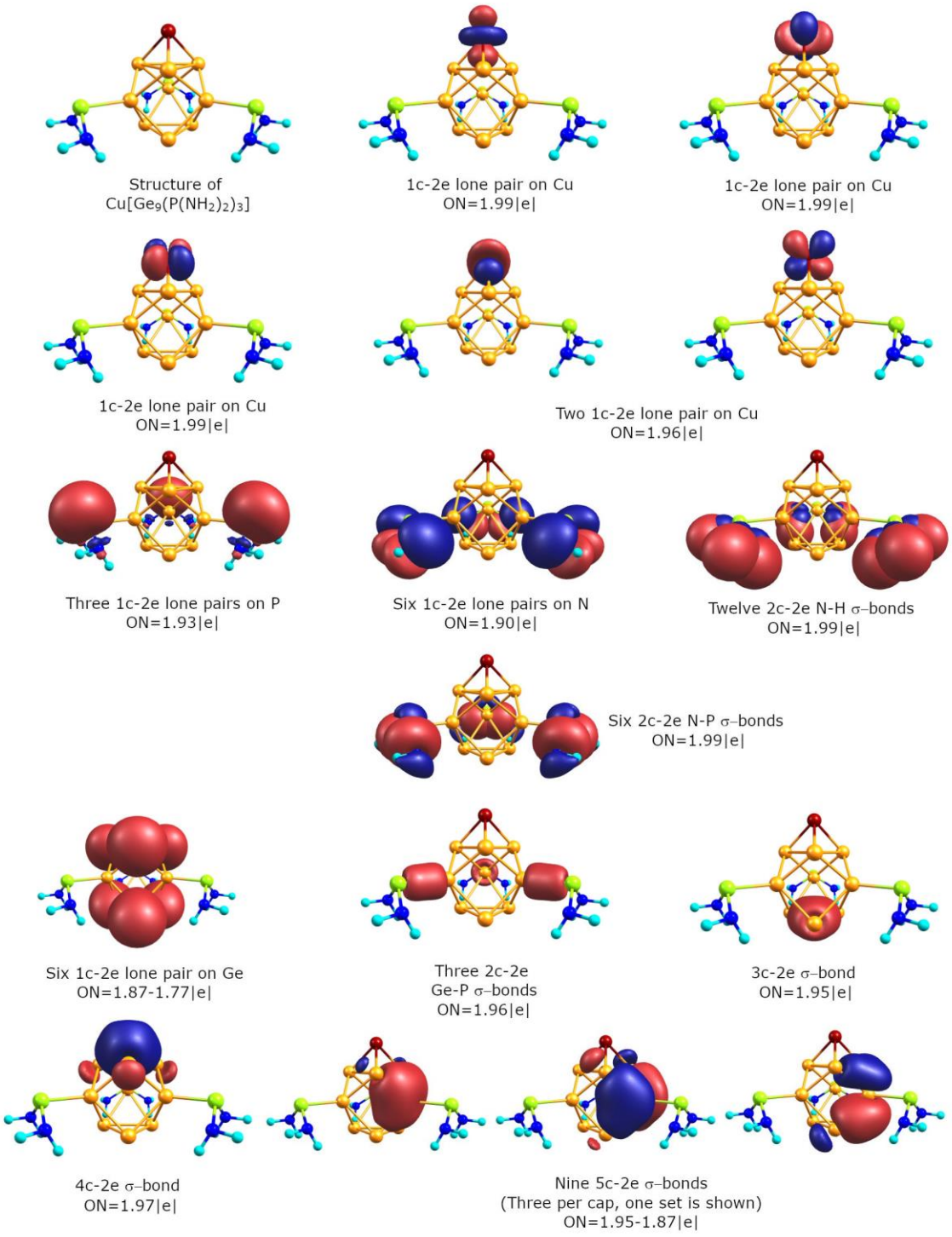

Figure S2. Chemical bonding picture of $Cu[Ge_9\{P(NH_2)_2\}_3]$ cluster.

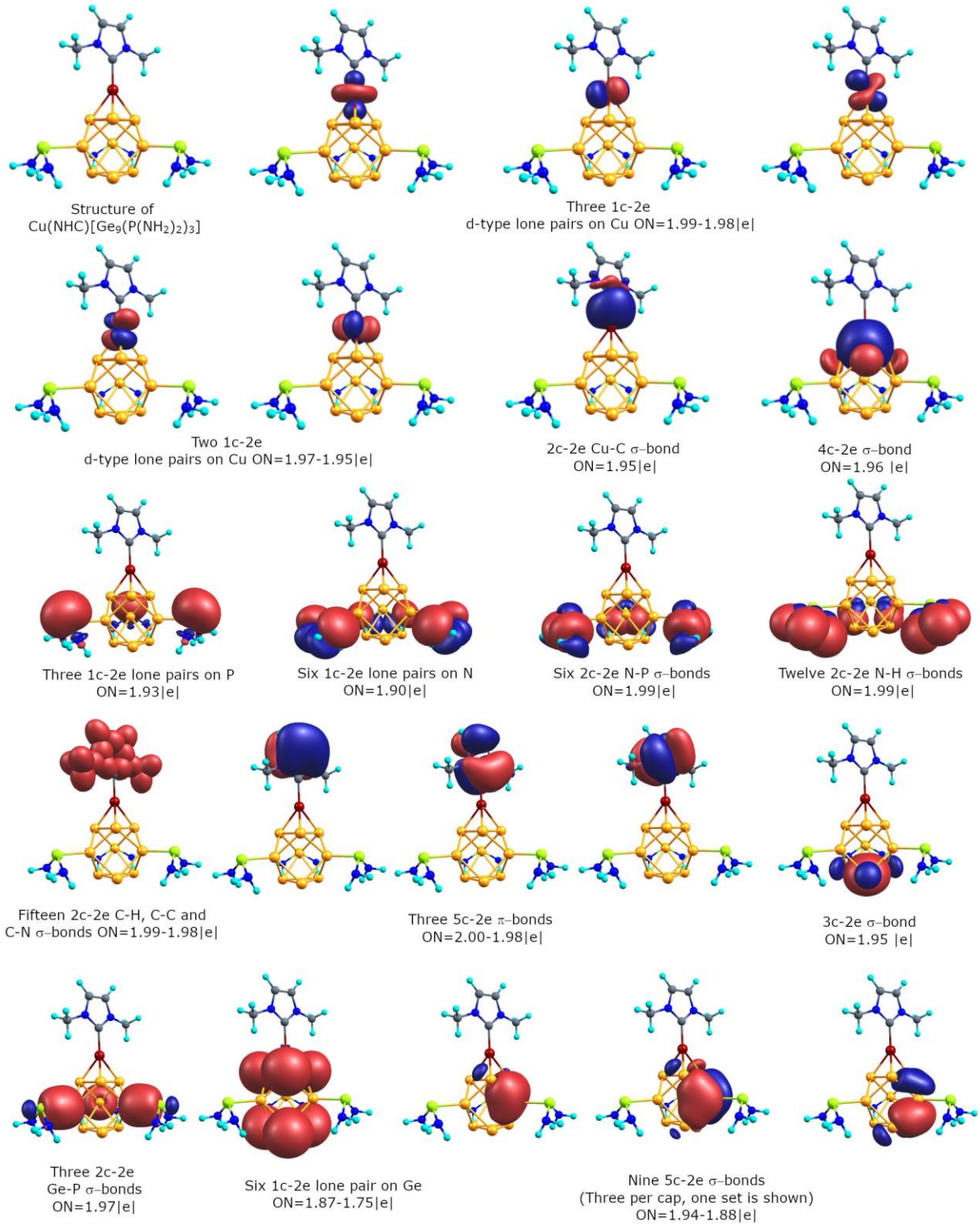

Figure S3. Chemical bonding picture of Cu(NHC)[Ge_9{$P(NH_2)_2$}$_3$] cluster.

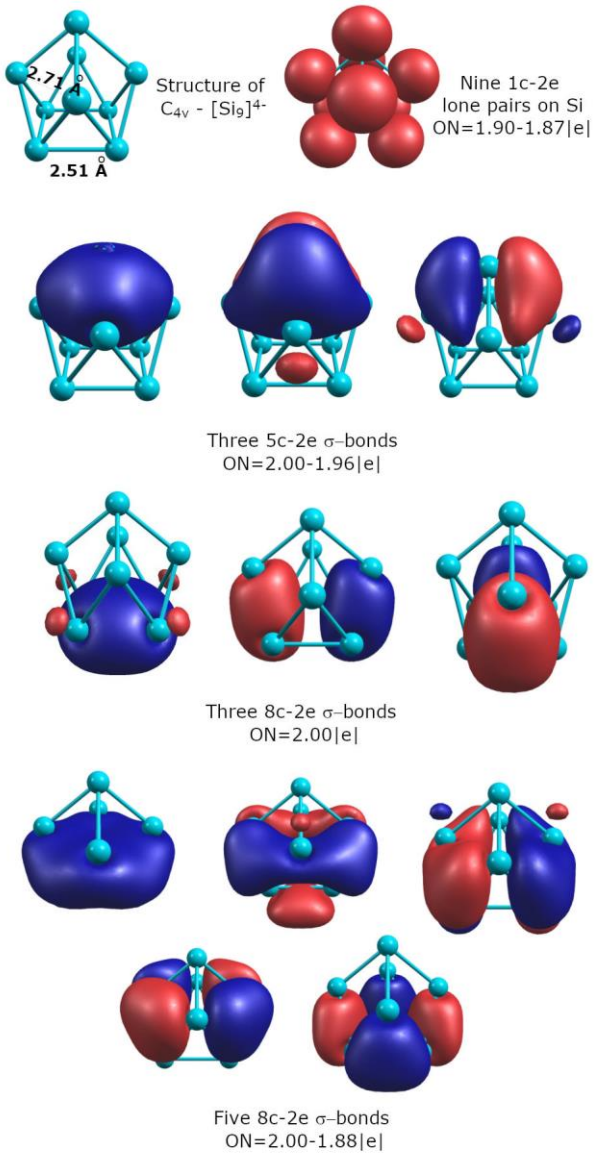

Figure S4. Chemical bonding picture of C_{4v} $[Si_9]^{4-}$ cluster.

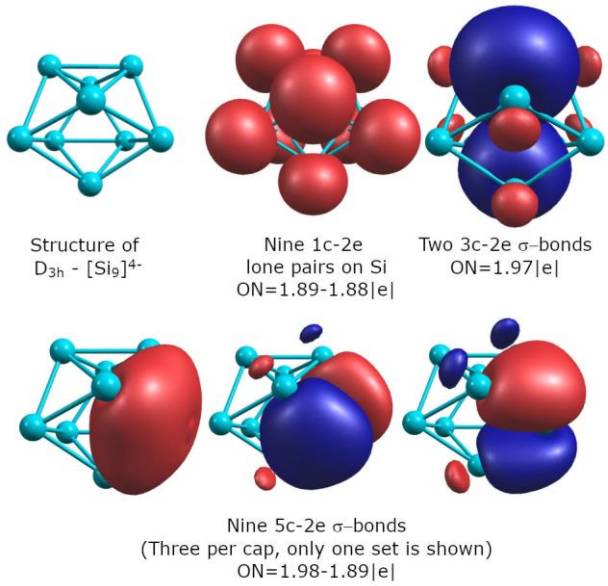

Figure S5. Chemical bonding picture of D_{3h} $[Si_9]^{4-}$ cluster.

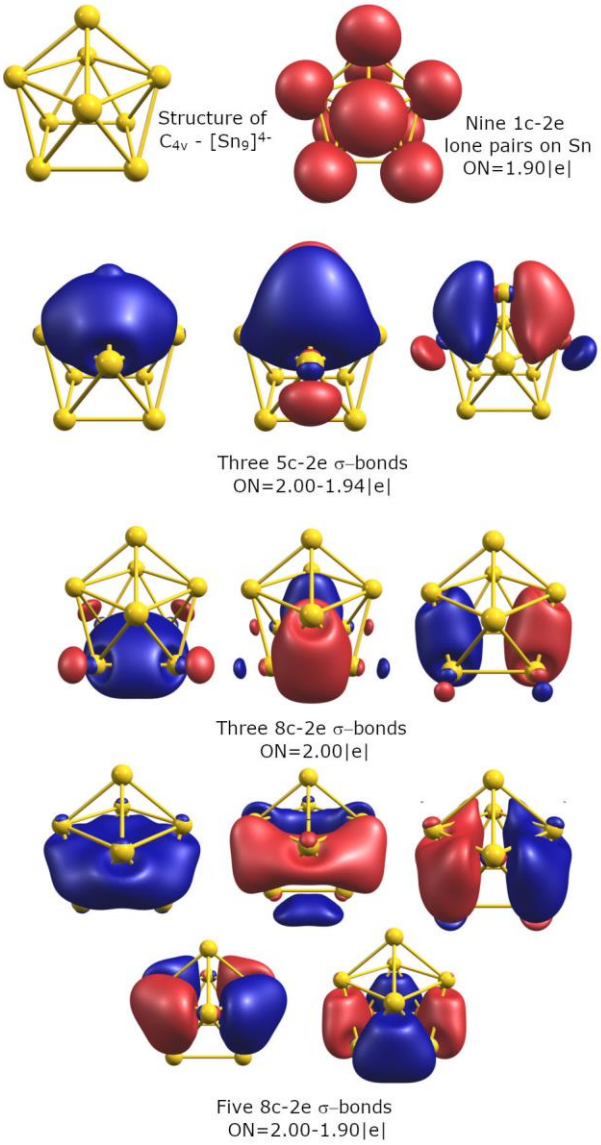

Figure S6. Chemical bonding picture of C_{4v} $[Sn_9]^{4-}$ cluster.

2. Optimized geometries of investigated molecules.

Table S1. Coordinates of optimized geometries, total energies and ZPE corrections of investigated molecules.

C_{4v} - $[Ge_9]^{4-}$	PBE0/LANL2DZ (0 imaginary Frequencies, E_{elec}= -33.6748928, ZPE correction= 0.006780)			
	32	0.000000000	2.145834000	0.814083000
	32	2.145834000	0.000000000	0.814083000

	32 1.377314000 1.377314000 -1.443071000 32 -2.145834000 0.000000000 0.814083000 32 -1.377314000 -1.377314000 -1.443071000 32 0.000000000 -2.145834000 0.814083000 32 -1.377314000 1.377314000 -1.443071000 32 0.000000000 0.000000000 2.515949000 32 1.377314000 -1.377314000 -1.443071000
D_{3h} - $[Ge_9]^{4-}$	PBE0/LANL2DZ (0 imaginary Frequencies, E_{elec}= -33.6748643, ZPE correction= 0.006748)
	32 -0.808114000 1.399561000 1.671373000 32 -0.808114000 -1.399716000 1.671129000 32 1.616349000 0.000069000 1.671003000 32 -0.808114000 1.399561000 -1.671373000 32 1.616349000 0.000069000 -1.671003000 32 -0.808114000 -1.399716000 -1.671129000 32 1.239488000 2.147435000 0.000000000 32 -2.479494000 0.000067000 0.000000000 32 1.239764000 -2.147329000 0.000000000
C_{4v} - $[Ge_9]^{4-}$	PBE0/aug-cc-pvdz (1 imaginary Frequency (-42.3924 cm^{-1}), E_{elec}= -18690.3069900, ZPE correction= 0.007066)
	32 2.031521000 0.000000000 0.789827000 32 0.000000000 -2.031521000 0.789827000 32 1.322067000 -1.322517000 -1.404647000 32 0.000000000 2.031521000 0.789827000 32 -1.322067000 1.322517000 -1.404647000 32 -2.031521000 0.000000000 0.789827000 32 1.322517000 1.322067000 -1.404647000

	32 0.000000000 0.000000000 2.459284000 32 -1.322517000 -1.322067000 -1.404647000
D_{3h} - $[Ge_9]^{4-}$	PBE0/ aug-cc-pvdz (0 imaginary Frequencies, E_{elec}= -18690.3096466, ZPE correction= 0.007200)
	32 0.791113000 1.370249000 1.502480000 32 -1.582227000 0.000000000 1.502480000 32 0.791113000 -1.370249000 1.502480000 32 0.791113000 1.370249000 -1.502480000 32 0.791113000 -1.370249000 -1.502480000 32 -1.582227000 0.000000000 -1.502480000 32 2.456815000 0.000124000 0.000000000 32 -1.228515000 2.127602000 0.000000000 32 -1.228300000 -2.127726000 0.000000000
C_{4v} - $[Ge_9]^{4-}$	PBE0/aug-cc-pvtz (1 imaginary Frequency (-123.5556 cm^{-1}), E_{elec}= -18690.9296291, ZPE correction= 0.006898)
	32 1.419027000 1.419014000 0.793758000 32 1.419014000 -1.419027000 0.793758000 32 1.857957000 0.000000000 -1.413427000 32 -1.419014000 1.419027000 0.793758000 32 -1.857957000 0.000000000 -1.413427000 32 -1.419027000 -1.419014000 0.793758000 32 0.000000000 1.857957000 -1.413427000 32 0.000000000 0.000000000 2.478676000 32 0.000000000 -1.857957000 -1.413427000
D_{3h} - $[Ge_9]^{4-}$	PBE0/ aug-cc-pvtz (0 imaginary Frequencies, E_{elec}= -18690.9465320, ZPE correction= 0.007440)
	32 -1.608451000 0.000005000 1.410505000

	32 0.804247000 -1.393009000 1.410273000 32 0.804247000 1.392987000 1.410320000 32 -1.608451000 0.000005000 -1.410505000 32 0.804247000 1.392987000 -1.410320000 32 0.804247000 -1.393009000 -1.410273000 32 -1.250522000 2.165909000 0.000000000 32 -1.250512000 -2.165864000 0.000000000 32 2.500947000 -0.000012000 0.000000000
C_{4v} - $[Ge_9]^{4-}$	B3LYP/LANL2DZ (0 imaginary Frequencies, E_{elec}= -33.5632179412, ZPE correction= 0.006303)
	32 1.536155000 1.536160000 0.820880000 32 1.536160000 -1.536155000 0.820880000 32 1.970253000 0.000000000 -1.454127000 32 -1.536160000 1.536155000 0.820880000 32 -1.970253000 0.000000000 -1.454127000 32 -1.536155000 -1.536160000 0.820880000 32 0.000000000 1.970253000 -1.454127000 32 0.000000000 0.000000000 2.532987000 32 0.000000000 -1.970253000 -1.454127000
D_{3h} - $[Ge_9]^{4-}$	B3LYP/LANL2DZ (0 imaginary Frequencies, E_{elec} = -33.5631968217, ZPE correction= 0.006273)
	32 -0.815929000 1.413230000 1.693468000 32 -0.815929000 -1.413230000 1.693468000 32 1.631858000 0.000000000 1.693468000 32 -0.815929000 1.413230000 -1.693468000 32 1.631858000 0.000000000 -1.693468000 32 -0.815929000 -1.413230000 -1.693468000

	32 1.251034000 2.166937000 0.000000000 32 -2.502139000 -0.000041000 0.000000000 32 1.251105000 -2.166895000 0.000000000
C_{4v} - $[Ge_9]^{4-}$	B3LYP/aug-cc-pvdz (1 imaginary Frequency (-18.8437 cm^{-1}), E_{elec}= -18693.0103353, ZPE correction= 0.006405)
	32 1.472724000 1.472709000 0.801639000 32 1.472709000 -1.472724000 0.801639000 32 1.909141000 0.000000000 -1.422199000 32 -1.472709000 1.472724000 0.801639000 32 -1.909141000 0.000000000 -1.422199000 32 -1.472724000 -1.472709000 0.801639000 32 0.000000000 1.909141000 -1.422199000 32 0.000000000 0.000000000 2.482237000 32 0.000000000 -1.909141000 -1.422199000
D_{3h} - $[Ge_9]^{4-}$	B3LYP/aug-cc-pvdz (0 imaginary Frequencies, E_{elec} = -18693.0109539, ZPE correction= 0.006433)
	32 1.601809000 -0.000051000 1.576911000 32 -0.800922000 1.387309000 1.576725000 32 -0.800922000 -1.387194000 1.576915000 32 1.601809000 -0.000051000 -1.576911000 32 -0.800922000 -1.387194000 -1.576915000 32 -0.800922000 1.387309000 -1.576725000 32 1.233353000 -2.136376000 0.000000000 32 1.233544000 2.136261000 0.000000000 32 -2.466828000 -0.000013000 0.000000000
C_{4v} - $[Ge_9]^{4-}$	B3LYP/aug-cc-pvtz (1 imaginary Frequency (-129.9552 cm^{-1}), E_{elec}= -18693.6362612, ZPE correction= 0.006211)

	32	0.000000000	2.051750000	0.805061000
	32	2.051750000	0.000000000	0.805061000
	32	1.337526000	1.337526000	-1.430326000
	32	-2.051750000	0.000000000	0.805061000
	32	-1.337526000	-1.337526000	-1.430326000
	32	0.000000000	-2.051750000	0.805061000
	32	-1.337526000	1.337526000	-1.430326000
	32	0.000000000	0.000000000	2.501061000
	32	1.337526000	-1.337526000	-1.430326000
D_{3h} - $[Ge_9]^{4-}$	B3LYP/aug-cc-pvtz (0 imaginary Frequencies, E_{elec} = -18693.6512336, ZPE correction= 0.006719)			
	32	-0.822647000	1.424872000	1.434270000
	32	-0.822647000	1.424872000	-1.434270000
	32	-2.525391000	0.000000000	0.000000000
	32	1.645296000	0.000000000	1.434394000
	32	1.262693000	-2.186984000	0.000000000
	32	1.645296000	0.000000000	-1.434394000
	32	-0.822647000	-1.424872000	1.434271000
	32	1.262693000	2.186984000	0.000000000
	32	-0.822647000	-1.424872000	-1.434271000
$[Ge_9(P(NH_2)_2)_3]^-$	PBE0/ aug-cc-pvdz (2 degenerate imaginary Frequencies (rotation of -$P(NH_2)_2$ groups, -11.8015 cm^{-1}), E_{elec}= -20049.9555733, ZPE correction= 0.169815)			
	32	1.359718000	0.785033000	1.924924000
	32	-1.359718000	0.785033000	1.924924000
	32	0.000000000	-1.570067000	1.924924000
	32	1.342156000	0.774894000	-1.584128000

	32	0.000000000	-1.549788000	-1.584128000
	32	-1.342156000	0.774894000	-1.584128000
	32	1.779103000	-1.027166000	0.187338000
	32	0.000000000	2.054332000	0.187338000
	32	-1.779103000	-1.027166000	0.187338000
	15	0.000000000	4.396758000	0.087242000
	7	1.437965000	4.563066000	-0.895191000
	1	1.543398000	3.946082000	-1.696258000
	1	1.656366000	5.522403000	-1.141854000
	7	-1.437965000	4.563066000	-0.895191000
	1	-1.656366000	5.522403000	-1.141854000
	1	-1.543398000	3.946082000	-1.696258000
	15	3.807705000	-2.198379000	0.087242000
	7	3.232748000	-3.526847000	-0.895191000
	1	2.645708000	-3.309663000	-1.696258000
	1	3.954358000	-4.195656000	-1.141854000
	7	4.670713000	-1.036219000	-0.895191000
	1	5.610724000	-1.326747000	-1.141854000
	1	4.189106000	-0.636419000	-1.696258000
	15	-3.807705000	-2.198379000	0.087242000
	7	-3.232748000	-3.526847000	-0.895191000
	1	-3.954358000	-4.195656000	-1.141854000
	1	-2.645708000	-3.309663000	-1.696258000
	7	-4.670713000	-1.036219000	-0.895191000
	1	-4.189106000	-0.636419000	-1.696258000
	1	-5.610724000	-1.326747000	-1.141854000

$[Ge_9(P(NH_2)_2)_3]^-$	PBE0/LANL2DZ (0 imaginary Frequencies, E_{elec}= -389.038813956, ZPE correction= 0.171352)
	32 1.437706000 0.830060000 1.968781000
	32 -1.437706000 0.830060000 1.968781000
	32 0.000000000 -1.660119000 1.968781000
	32 1.417056000 0.818138000 -1.637792000
	32 0.000000000 -1.636275000 -1.637792000
	32 -1.417056000 0.818138000 -1.637792000
	32 1.830812000 -1.057020000 0.179480000
	32 0.000000000 2.114040000 0.179480000
	32 -1.830812000 -1.057020000 0.179480000
	15 0.000000000 4.525417000 0.102796000
	7 1.417310000 4.738741000 -0.927912000
	1 1.718004000 4.068239000 -1.623332000
	1 1.987586000 5.564738000 -0.819768000
	7 -1.417310000 4.738741000 -0.927912000
	1 -1.987586000 5.564738000 -0.819768000
	1 -1.718004000 4.068239000 -1.623332000
	15 3.919126000 -2.262708000 0.102796000
	7 3.395215000 -3.596797000 -0.927912000
	1 2.664196000 -3.521955000 -1.623332000
	1 3.825411000 -4.503669000 -0.819768000
	7 4.812525000 -1.141944000 -0.927912000
	1 5.812998000 -1.061069000 -0.819768000
	1 4.382201000 -0.546284000 -1.623332000
	15 -3.919126000 -2.262708000 0.102796000

	7	-3.395215000	-3.596797000	-0.927912000
	1	-3.825411000	-4.503669000	-0.819768000
	1	-2.664196000	-3.521955000	-1.623332000
	7	-4.812525000	-1.141944000	-0.927912000
	1	-4.382201000	-0.546284000	-1.623332000
	1	-5.812998000	-1.061069000	-0.819768000
$Cu[Ge_9(P(NH_2)_2)_3]$	PBE0/aug-cc-pvdz (0 imaginary Frequencies, E_{elec}= -21690.2344825, ZPE correction= 0.171381)			
	32	-1.832411000	-1.524237000	0.000000000
	32	0.915843000	-1.525714000	-1.586340000
	32	0.915843000	-1.525714000	1.586340000
	32	-1.525858000	1.819144000	0.000000000
	32	0.762526000	1.820033000	1.320857000
	32	0.762526000	1.820033000	-1.320857000
	32	-1.047006000	0.002151000	1.814481000
	32	-1.047006000	0.002151000	-1.814481000
	32	2.094135000	0.001998000	0.000000000
	15	-2.217161000	0.053768000	-3.841491000
	7	-3.550553000	1.018891000	-3.287048000
	1	-3.368867000	1.909562000	-2.835208000
	1	-4.308501000	1.097390000	-3.955883000
	7	-1.066319000	1.012624000	-4.720766000
	1	-1.266239000	1.089902000	-5.711760000
	1	-0.762763000	1.903025000	-4.339280000
	15	-2.217161000	0.053768000	3.841491000
	7	-1.066319000	1.012624000	4.720766000

	1	-0.762763000	1.903025000	4.339280000
	1	-1.266239000	1.089902000	5.711760000
	7	-3.550553000	1.018891000	3.287048000
	1	-4.308501000	1.097390000	3.955883000
	1	-3.368867000	1.909562000	2.835208000
	15	4.434631000	0.053933000	0.000000000
	7	4.620662000	1.015870000	1.434219000
	1	5.578837000	1.094309000	1.756300000
	1	4.137761000	1.905953000	1.505161000
	7	4.620662000	1.015870000	-1.434219000
	1	4.137761000	1.905953000	-1.505161000
	1	5.578837000	1.094309000	-1.756300000
	29	-0.001142000	-3.157266000	0.000000000
$Cu(NHC)[Ge_9(P(NH_2)_2)_3]$	PBE0/aug-cc-pvdz (0 imaginary Frequencies, E_{elec}= -21994.7799089, ZPE correction= 0.300350)			
	32	0.857327000	0.820130000	-1.477631000
	32	0.856931000	0.864125000	1.450580000
	32	0.822825000	-1.694321000	0.023991000
	32	-2.566494000	0.761778000	-1.338993000
	32	-2.565595000	-1.517848000	0.023398000
	32	-2.563176000	0.801571000	1.317863000
	32	-0.772535000	-1.052814000	-1.793477000
	32	-0.755714000	2.078736000	-0.032481000
	32	-0.770432000	-1.000388000	1.823657000
	15	-0.745359000	4.417255000	-0.064860000
	7	-1.704877000	4.613442000	-1.503010000

	1	-2.587304000	4.116812000	-1.579312000
	1	-1.802711000	5.576594000	-1.804579000
	7	-1.701575000	4.653473000	1.369472000
	1	-1.799227000	5.624731000	1.643900000
	1	-2.583623000	4.158850000	1.461638000
	15	-0.796980000	-2.275113000	-3.787313000
	7	-1.742966000	-3.613260000	-3.202164000
	1	-2.617730000	-3.426687000	-2.721335000
	1	-1.850945000	-4.364848000	-3.874264000
	7	-1.775481000	-1.163465000	-4.700374000
	1	-1.885852000	-1.417750000	-5.675700000
	1	-2.653569000	-0.839069000	-4.306979000
	15	-0.793480000	-2.160187000	3.854532000
	7	-1.744081000	-3.513210000	3.312706000
	1	-1.852545000	-4.243480000	4.007836000
	1	-2.619462000	-3.339072000	2.828349000
	7	-1.767362000	-1.018473000	4.734813000
	1	-2.645620000	-0.704388000	4.333505000
	1	-1.876025000	-1.242124000	5.717807000
	29	2.733465000	-0.025586000	-0.000610000
	6	4.700274000	-0.023220000	-0.000173000
	7	5.549359000	-1.081642000	0.000878000
	6	6.865137000	-0.673636000	0.000318000
	6	6.847118000	0.685325000	-0.001361000
	7	5.520983000	1.057507000	-0.001290000
	1	7.695455000	-1.369301000	0.001306000

	1	7.658702000	1.402737000	-0.002295000
	6	5.123837000	-2.467599000	0.001885000
	1	5.504613000	-2.979523000	0.893895000
	1	4.029489000	-2.491057000	0.010527000
	1	5.490371000	-2.976943000	-0.897583000
	6	5.056142000	2.430674000	-0.003893000
	1	5.408830000	2.948986000	-0.903648000
	1	3.961980000	2.422019000	0.002106000
	1	5.418513000	2.955310000	0.888268000
$\{Cu[Ge_9\{P(NH_2)_2\}_3]_2\}^-$	PBE0/aug-cc-pvdz (0 imaginary Frequencies, E_{elec}= -41740.2521030, ZPE correction= 0.341278)			
	32	-1.971214000	-1.152141000	-1.224550000
	32	-1.969346000	1.630427000	-0.392466000
	32	-1.967227000	-0.482928000	1.602278000
	32	-5.418742000	-1.053371000	-1.113708000
	32	-5.408335000	-0.439755000	1.476214000
	32	-5.412880000	1.496423000	-0.350742000
	32	-3.614915000	-2.009963000	0.472926000
	32	-3.619490000	0.590070000	-1.978850000
	32	-3.609580000	1.417595000	1.500758000
	15	-3.719878000	1.264191000	-4.218769000
	7	-4.702972000	-0.061273000	-4.784673000
	1	-5.535730000	-0.311560000	-4.259463000
	1	-4.891173000	-0.037709000	-5.780679000
	7	-4.692634000	2.688657000	-3.958213000
	1	-4.878365000	3.219906000	-4.801575000

	1	-5.524698000	2.613900000	-3.380127000
	15	-3.711111000	-4.284855000	1.018202000
	7	-4.676581000	-4.107123000	2.460185000
	1	-5.508994000	-3.525959000	2.423315000
	1	-4.859349000	-4.979635000	2.943176000
	7	-4.700665000	-4.774197000	-0.332697000
	1	-4.888390000	-5.770040000	-0.365492000
	1	-5.534778000	-4.235883000	-0.548350000
	15	-3.700004000	3.022004000	3.203426000
	7	-4.673196000	2.088038000	4.309726000
	1	-4.855171000	2.553989000	5.191642000
	1	-5.507807000	1.627635000	3.958268000
	7	-4.681092000	4.177648000	2.340242000
	1	-5.516077000	3.851154000	1.862536000
	1	-4.864231000	5.030006000	2.857768000
	29	0.000031000	-0.002229000	-0.007930000
	32	1.969367000	-1.633628000	0.380613000
	32	1.967452000	1.149452000	1.215651000
	32	1.971364000	0.479684000	-1.611072000
	32	5.413882000	-1.494335000	0.357465000
	32	5.418376000	0.442300000	-1.468105000
	32	5.408008000	1.055446000	1.122155000
	32	3.619878000	-1.415739000	-1.503481000
	32	3.610096000	-0.594802000	1.976939000
	32	3.614528000	2.008449000	-0.478929000
	15	3.700787000	-1.262764000	4.219091000

	7	4.684947000	-2.680932000	3.967424000
	1	5.519929000	-2.601658000	3.394284000
	1	4.869323000	-3.209164000	4.812942000
	7	4.670835000	0.070573000	4.788331000
	1	4.851664000	0.051704000	5.785750000
	1	5.505090000	0.326321000	4.268023000
	15	3.720331000	-3.021939000	-3.203939000
	7	4.703990000	-2.091069000	-4.303470000
	1	5.536518000	-1.631559000	-3.946047000
	1	4.891984000	-2.558063000	-5.183514000
	7	4.692314000	-4.179004000	-2.332163000
	1	4.878226000	-5.031775000	-2.848146000
	1	5.524243000	-3.853320000	-1.848512000
	15	3.708909000	4.286202000	-1.012143000
	7	4.696047000	4.118413000	-2.440720000
	1	4.881951000	4.993715000	-2.917400000
	1	5.530667000	3.541133000	-2.393899000
	7	4.676384000	4.774241000	0.354846000
	1	5.509307000	4.238500000	0.581331000
	1	4.858722000	5.770737000	0.395311000

3. Coordinates of chosen points for NICS calculation.

Table S2. Coordinates of points for NICS calculation.

D_{3h} - $[Ge_9]^{4-}$	32	1.608480000	0.000000000	-1.410366000
	32	-0.804240000	-1.392985000	-1.410366000
	32	-0.804240000	1.392985000	-1.410366000

	32 1.608480000 0.000000000 1.410366000 32 -0.804240000 1.392985000 1.410366000 32 -0.804240000 -1.392985000 1.410366000 32 1.250482000 2.165898000 0.000000000 32 1.250482000 -2.165898000 0.000000000 32 -2.500963000 0.000000000 0.000000000 Point 1 -1.652600000 0.000000000 0.000000000 Point 2 -0.804240000 0.000000000 0.000000000 Point 3 0.000000000 0.000000000 0.000000000 Point 4 0.000000000 0.000000000 -1.410366000 Point 5 0.000000000 0.000000000 -2.410366000
C_{4v} - $[Ge_9]^{4-}$	32 1.419021000 1.419021000 -0.793758000 32 -1.419021000 1.419021000 -0.793758000 32 0.000000000 1.857957000 1.413427000 32 1.419021000 -1.419021000 -0.793758000 32 0.000000000 -1.857957000 1.413427000 32 -1.419021000 -1.419021000 -0.793758000 32 1.857957000 0.000000000 1.413427000 32 0.000000000 0.000000000 -2.478676000 32 -1.857957000 0.000000000 1.413427000 Point 1 0.000000000 0.000000000 -1.636218000 Point 2 0.000000000 0.000000000 -0.793758000 Point 3 0.000000000 0.000000000 0.309837000 Point 4 0.000002000 0.000000000 1.413427000 Point 5 0.000002000 0.000000000 2.413427000