Electronic Structure and Geometries of *o*-Carborane Derived Cyclic Structures $[\mu\text{-}1,2\text{-}(C_2B_{10}H_{10})M]_nAg_m$, M = {Au, Hg}, *n* = {3, 4}, *m* = {0, 1, 2}

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Supplemetary Material

Table S1. Electronic energies for optimized structures.

Table S2. NPA charges of carborane cages.

Table S3. Comparison of optimized geometrical parameters for $[\mu\text{-}(1,2\text{-}C_2B_{10}H_{10})_zAu_z]^{z-}$ complexes (*z* = 3 or 4) by two basis sets: (first entry) 6-31g* and LANL2DZ, and (second entry in italics) 6-311g* and TZVP [**Error! Bookmark not defined.**], for main and metal elements, respectively.

Table S4. Cartesian coordinates of the optimized geometries for the $[\mu\text{-}(1,2\text{-}C_2B_{10}H_{10})_zAu_z]^{z-}$ complexes (*z* = 3 or 4) with the triple-zeta basis set 6-311g* and TZVP [**Error! Bookmark not defined.**] for main and metal elements, respectively.

Table S1. Electronic energies for optimized structures.

Metals System	Symmetry	Stationary Point	Energy (Ha)
Au_3	D_{3h}	Minimum	-1399.216764
Hg_3	C_{3v}	Minimum	-1120.808854
Au_4	D_{4h}	Minimum	-1865.498929
Au_4	S_4	Minimum	-1865.504370
Hg_4	D_{4h}	Transition State	-1494.403425
Hg_4	S_4	Minimum	-1494.411553
Au_3Ag	D_{3h}	Transition State	-1545.045514
Au_3Ag	C_{3v}	Minimum	-1545.087780
Au_3Ag_2	D_{3h}	Transition State	-1690.840967
Au_3Ag_2	C_s	Minimum	-1690.841227
Hg_3Ag	C_{2v}	Minimum	-1266.298884
Hg_3Ag	C_{3v}	Minimum	-1266.316630
Hg_3Ag	D_{3h}	Transition State	-1266.252055
Hg_3Ag_2	C_s	Minimum	-1411.806487
Au_4Ag	S_4	Minimum	-2011.468196
Au_4Ag_2	S_4	Minimum	-2157.302704
Hg_4Ag	C_{2v}	Minimum	-1639.955129
Hg_4Ag_2	D_2	Minimum	-1785.437349

Table S2. NPA charges of carborane cages.

Metals System	*Symmetry*	*Cage*	*C*	*B*	*H*
Au_3	D_{3h}	*-1.354*	*-0.677*	*-0.17 to +0.15*	*+0.03 to +0.05*
Hg_3	C_{3v}	*-1.162*	*-0.768*	*-0.17 to +0.13*	*+0.05 to +0.09*
Au_4	D_{4h}	*-1.385*	*-0.684*	*-0.18 to +0.15*	*+0.03 to +0.05*
Au_4	S_4	*-1.366*	*-0.674*	*-0.19 to +0.15*	*+0.03 to +0.06*
Hg_4	D_{4h}	*-1.168*	*-0.765*	*-0.17 to +0.14*	*+0.05 to +0.09*
Hg_4	S_4	*-1.166*	*-0.768*	*-0.17 to +0.15*	*+0.05 to +0.09*
Au_3Ag	C_{3v}	*-1.220*	*-0.682*	*-0.18 to +0.14*	*+0.03 to +0.06*
Au_3Ag_2	C_s	*-1.096*	*-0.677*	*-0.17 to +0.15*	*+0.02 to +0.08*
Hg_3Ag	C_{2v}	*-1.098(2),-0.840*	*-0.769 to –0.714*	*-0.16 to +0.14*	*+0.05 to +0.11*
Hg_3Ag	C_{3v}	*-1.110*	*-0.773*	*-0.16 to +0.17*	*+0.08 to +0.11*
Hg_3Ag_2	C_s	*-1.121*	*-0.766*	*-0.27 to +0.14*	*-0.08 to +0.11*
Au_4Ag	S_4	*-1.221*	*-0.674*	*-0.17 to +0.15*	*+0.04 to +0.06*
Au_4Ag_2	S_4	*-1.137*	*-0.678*	*-0.17 to +0.15*	*+0.01 to +0.07*
Hg_4Ag	C_{2v}	*-1.128*	*-0.759*	*-0.26 to +0.15*	*+0.06 to +0.10*
Hg_4Ag_2	D_2	*-1.110*	*-0.758*	*-0.25 to +0.14*	*+0.04 to +0.11*

Table S3. Comparison of optimized geometrical parameters for [μ-(1,2-$C_2B_{10}H_{10}$)$_z$Au$_z$]$^{z-}$ complexes (z = 3 or 4) by two basis sets: (first entry) 6-31g* and LANL2DZ, and (second entry in italics) 6-311g* and TZVP [**Error! Bookmark not defined.**], for main and metal elements, respectively.

Core	M···M	M···X	M-C	C-C	C-M-C	C-Cage-C
Au_3 (C_{3h})	3.779	2.182	2.104	1.725	178.5	58.5
Au_3 (C_{3h})	*3.784*	*2.185*	*2.100*	*1.739*	*178.2*	*58.2*
Au_4 (S_4)	4.051, 5.728	2.864	2.108	1.727	173.8	66.9
Au_4 (S_4)	*4.094, 5.790*	*2.895*	*2.105*	*1.746*	*173.0*	*67.8*
Au_4 (D_{4h})	4.351, 6.153	3.077	2.112	1.731	166.7	76.9
Au_4 (D_{4h})	*4.366, 6.175*	*3.087*	*2.107*	*1.745*	*166.9*	*76.9*

Table S4. Cartesian coordinates (Å) of the optimized geometries for the $[\mu\text{-}(1,2\text{-}C_2B_{10}H_{10})_zAu_z]^{z-}$ complexes (z = 3 or 4) with the triple-zeta basis set 6-311g* and TZVP [**Error! Bookmark not defined.**] for main and metal elements, respectively.

$[\mu\text{-}(1,2\text{-}C_2B_{10}H_{10})_3Au_3]^{3-}$ - D_{3h} symmetry

Atom	X	Y	Z
Au	0.000000	2.177738	0.000000
Au	-1.895668	-1.093382	0.000000
Au	1.895668	-1.093382	0.000000
C	-2.099574	2.212105	0.000000
C	-2.972169	0.709971	0.000000
B	-2.926612	1.687627	1.405464
B	-2.993421	3.382757	0.879900
B	-2.993421	3.382757	-0.879900
B	-2.926612	1.687627	-1.405464
B	-4.432781	0.905069	0.880423
B	-4.475085	2.586268	1.441130
B	-4.519589	3.638175	0.000000
B	-4.475085	2.586268	-1.441130
B	-4.432781	0.905069	-0.880423
B	-5.412179	2.103235	0.000000
C	2.099574	2.212105	0.000000
C	2.972169	0.709971	0.000000
B	2.926612	1.687627	-1.405464
B	2.993421	3.382757	-0.879900
B	2.993421	3.382757	0.879900
B	2.926612	1.687627	1.405464
B	4.432781	0.905069	-0.880423
B	4.475085	2.586268	-1.441130
B	4.519589	3.638175	0.000000
B	4.475085	2.586268	1.441130
B	4.432781	0.905069	0.880423
B	5.412179	2.103235	0.000000
C	-0.870809	-2.926217	0.000000
C	0.870809	-2.926217	0.000000
B	0.000000	-3.378026	1.403753
B	-1.432489	-4.288713	0.880071
B	-1.432489	-4.288713	-0.880071
B	0.000000	-3.378026	-1.403753
B	1.432489	-4.288713	0.880071
B	0.000000	-5.169055	1.440266
B	-0.888245	-5.736586	0.000000
B	0.000000	-5.169055	-1.440266
B	1.432489	-4.288713	-0.880071
B	0.888245	-5.736586	0.000000
H	-1.536546	-6.743237	0.000000
H	-2.441631	-4.187354	-1.500307
H	-2.441631	-4.187354	1.500307
H	0.000000	-5.761108	-2.479003
H	0.000000	-2.683833	-2.362495
H	2.441631	-4.187354	-1.500307
H	1.536546	-6.743237	0.000000
H	0.000000	-5.761108	2.479003
H	0.000000	-2.683833	2.362495
H	2.441631	-4.187354	1.500307
H	2.326434	1.337722	2.363826
H	4.851317	-0.019524	1.499584
H	4.851317	-0.019524	-1.499584
H	2.326434	1.337722	-2.363826

H	2.398473	4.205214	-1.498622

Table S4 (cont)

H	2.398473	4.205214	1.498622
H	5.064383	4.704563	0.000000
H	4.986750	2.884621	-2.479719
H	4.986750	2.884621	2.479719
H	6.608341	2.048950	0.000000
H	-2.326434	1.337722	-2.363826
H	-2.398473	4.205214	-1.498622
H	-4.986750	2.884621	-2.479719
H	-5.064383	4.704563	0.000000
H	-2.398473	4.205214	1.498622
H	-6.608341	2.048950	0.000000
H	-4.986750	2.884621	2.479719
H	-2.326434	1.337722	2.363826
H	-4.851317	-0.019524	1.499584
H	-4.851317	-0.019524	-1.499584

$[\mu\text{-}(1,2\text{-}C_2B_{10}H_{10})_4Au_4]^{4-}$ - D_{4h} symmetry

Atom	X	Y	Z
Au	0.000000	3.087483	0.000000
Au	-3.087483	0.000000	0.000000
C	-2.093378	3.327596	0.000000
C	-3.327596	2.093378	0.000000
B	-3.030409	3.030409	1.400779
B	-2.670440	4.691504	0.880283
B	-2.670440	4.691504	-0.880283
B	-3.030409	3.030409	-1.400779
B	-4.691504	2.670440	0.880283
B	-4.301675	4.301675	1.440476
B	-4.077656	5.331838	0.000000
B	-4.301675	4.301675	-1.440476
B	-4.691504	2.670440	-0.880283
B	-5.331838	4.077656	0.000000
C	2.093378	3.327596	0.000000
C	3.327596	2.093378	0.000000
B	3.030409	3.030409	-1.400779
B	2.670440	4.691504	-0.880283
B	2.670440	4.691504	0.880283
B	3.030409	3.030409	1.400779
B	4.691504	2.670440	-0.880283
B	4.301675	4.301675	-1.440476
B	4.077656	5.331838	0.000000
B	4.301675	4.301675	1.440476
B	4.691504	2.670440	0.880283
B	5.331838	4.077656	0.000000
C	-3.327596	-2.093378	0.000000
C	-2.093378	-3.327596	0.000000
B	-3.030409	-3.030409	1.400779
B	-4.691504	-2.670440	0.880283
B	-4.691504	-2.670440	-0.880283
B	-3.030409	-3.030409	-1.400779
B	-2.670440	-4.691504	0.880283
B	-4.301675	-4.301675	1.440476
B	-5.331838	-4.077656	0.000000
B	-4.301675	-4.301675	-1.440476
B	-2.670440	-4.691504	-0.880283
B	-4.077656	-5.331838	0.000000

H	-6.504117	-4.326978	0.000000

Table S4 (cont)

H	-5.336115	-1.889215	-1.501471
H	-5.336115	-1.889215	1.501471
H	-4.719119	-4.719119	-2.481269
H	-2.541981	-2.541981	-2.362430
H	-1.889215	-5.336115	-1.501471
H	-4.326978	-6.504117	0.000000
H	-4.719119	-4.719119	2.481269
H	-2.541981	-2.541981	2.362430
H	-1.889215	-5.336115	1.501471
H	2.541981	2.541981	2.362430
H	5.336115	1.889215	1.501471
H	5.336115	1.889215	-1.501471
H	2.541981	2.541981	-2.362430
H	1.889215	5.336115	-1.501471
H	1.889215	5.336115	1.501471
H	4.326978	6.504117	0.000000
H	4.719119	4.719119	-2.481269
H	4.719119	4.719119	2.481269
H	6.504117	4.326978	0.000000
H	-2.541981	2.541981	-2.362430
H	-1.889215	5.336115	-1.501471
H	-4.719119	4.719119	-2.481269
H	-4.326978	6.504117	0.000000
H	-1.889215	5.336115	1.501471
H	-6.504117	4.326978	0.000000
H	-4.719119	4.719119	2.481269
H	-2.541981	2.541981	2.362430
H	-5.336115	1.889215	1.501471
H	-5.336115	1.889215	-1.501471
Au	0.000000	-3.087483	0.000000
Au	3.087483	0.000000	0.000000
B	2.670440	-4.691504	-0.880283
B	2.670440	-4.691504	0.880283
B	3.030409	-3.030409	1.400779
B	4.301675	-4.301675	-1.440476
B	4.691504	-2.670440	-0.880283
B	4.077656	-5.331838	0.000000
H	1.889215	-5.336115	-1.501471
B	4.691504	-2.670440	0.880283
B	4.301675	-4.301675	1.440476
H	1.889215	-5.336115	1.501471
H	2.541981	-2.541981	2.362430
B	5.331838	-4.077656	0.000000
H	4.719119	-4.719119	-2.481269
H	5.336115	-1.889215	-1.501471
H	4.326978	-6.504117	0.000000
H	5.336115	-1.889215	1.501471
H	4.719119	-4.719119	2.481269
H	6.504117	-4.326978	0.000000
C	3.327596	-2.093378	0.000000
B	3.030409	-3.030409	-1.400779
H	2.541981	-2.541981	-2.362430
C	2.093378	-3.327596	0.000000

Table S4 (cont)

$[\mu\text{-}(1,2\text{-}C_2B_{10}H_{10})_4Au_4]^{4-}$ - S_4 symmetry

Atom	X	Y	Z
Au	-2.438923	1.559658	0.000855
Au	-1.559725	-2.438768	-0.000942
C	-3.510540	0.122916	-1.102893
C	-3.135529	-1.582478	-1.102586
B	-4.517109	-0.992379	-0.280445
B	-5.212180	0.319662	-1.256154
B	-4.148203	0.554278	-2.638551
B	-2.820575	-0.618767	-2.483046
B	-4.597871	-2.474525	-1.256561
B	-5.917891	-1.300450	-1.359986
B	-5.675402	-0.338470	-2.843861
B	-4.177465	-0.917099	-3.623503
B	-3.533187	-2.240676	-2.638750
B	-5.293530	-2.071409	-2.843731
C	-1.582531	3.135517	1.102565
C	0.122902	3.510421	1.102988
B	-0.992259	4.517002	0.280379
B	-2.474478	4.597961	1.256384
B	-2.240865	3.533284	2.638605
B	-0.619032	2.820484	2.483083
B	0.319792	5.211983	1.256206
B	-1.300262	5.917854	1.359887
B	-2.071418	5.293627	2.843555
B	-0.917311	4.177445	3.623477
B	0.554152	4.148005	2.638715
B	-0.338450	5.675300	2.843867
C	-0.122933	-3.510408	1.103016
C	1.582501	-3.135476	1.102627
B	0.618916	-2.820228	2.483032
B	-0.554256	-4.147745	2.638819
B	-0.319808	-5.211955	1.256504
B	0.992288	-4.517113	0.280636
B	2.240759	-3.532981	2.638767
B	0.917153	-4.176994	3.623669
B	0.338353	-5.674988	2.844283
B	1.300252	-5.917780	1.360393
B	2.474456	-4.597887	1.256734
B	2.071316	-5.293290	2.844000
H	-0.127045	-6.587922	3.466724
H	-1.238473	-5.729745	0.707080
H	-1.638782	-3.914802	3.065390
H	1.538439	-7.000594	0.908416
H	1.003439	-4.568604	-0.902511
H	3.525507	-4.682741	0.707629
H	2.877196	-5.926406	3.466237
H	0.879398	-4.005145	4.806525
H	0.375102	-1.710106	2.807600
H	3.127929	-2.867123	3.065247
H	-0.375253	1.710413	2.807851
H	1.638653	3.915121	3.065381
H	1.238492	5.729667	0.706744
H	-1.003344	4.568297	-0.902775
H	-3.525498	4.682737	0.707207
H	-3.128067	2.867504	3.065144

H	-2.877325	5.926859	3.465641

Table S4 (cont)

H	-1.538407	7.000596	0.907716
H	-0.879624	4.005796	4.806365
H	0.126931	6.588337	3.466171
H	-1.710554	-0.374825	-2.807855
H	-3.915450	1.638845	-3.065101
H	-4.005775	-0.879259	-4.806361
H	-6.588468	0.126887	-3.466132
H	-5.730021	1.238249	-0.706642
H	-5.926656	-2.877326	-3.465901
H	-7.000620	-1.538738	-0.907850
H	-4.568514	-1.003574	0.902715
H	-4.682609	-3.525618	-0.707494
H	-2.867332	-3.127766	-3.065387
Au	2.438926	-1.559768	0.000671
Au	1.559752	2.438668	-0.000774
B	4.148216	-0.554144	-2.638686
B	5.212225	-0.319690	-1.256282
B	4.517172	0.992237	-0.280407
B	4.177466	0.917353	-3.623465
B	3.533204	2.240811	-2.638553
B	5.675415	0.338631	-2.843926
H	3.915452	-1.638658	-3.065359
B	4.597910	2.474497	-1.256348
B	5.917933	1.300435	-1.359939
H	5.730076	-1.238341	-0.706885
H	4.568598	1.003300	0.902754
B	5.293547	2.071573	-2.843577
H	4.005755	0.879653	-4.806323
H	2.867342	3.127952	-3.065070
H	6.588469	-0.126649	-3.466271
H	4.682659	3.525524	-0.707156
H	7.000669	1.538672	-0.907794
H	5.926662	2.877566	-3.465658
C	3.135566	1.582438	-1.102470
B	2.820598	0.618886	-2.483019
H	1.710570	0.374981	-2.807830
C	3.510601	-0.122954	-1.102950