Supporting Information

for

Tuning of Aromaticity and Reactivity in Gold-Substituted Cyclopropenyl Cations

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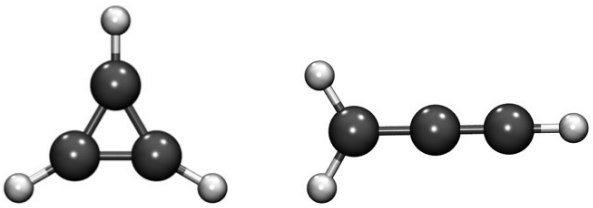
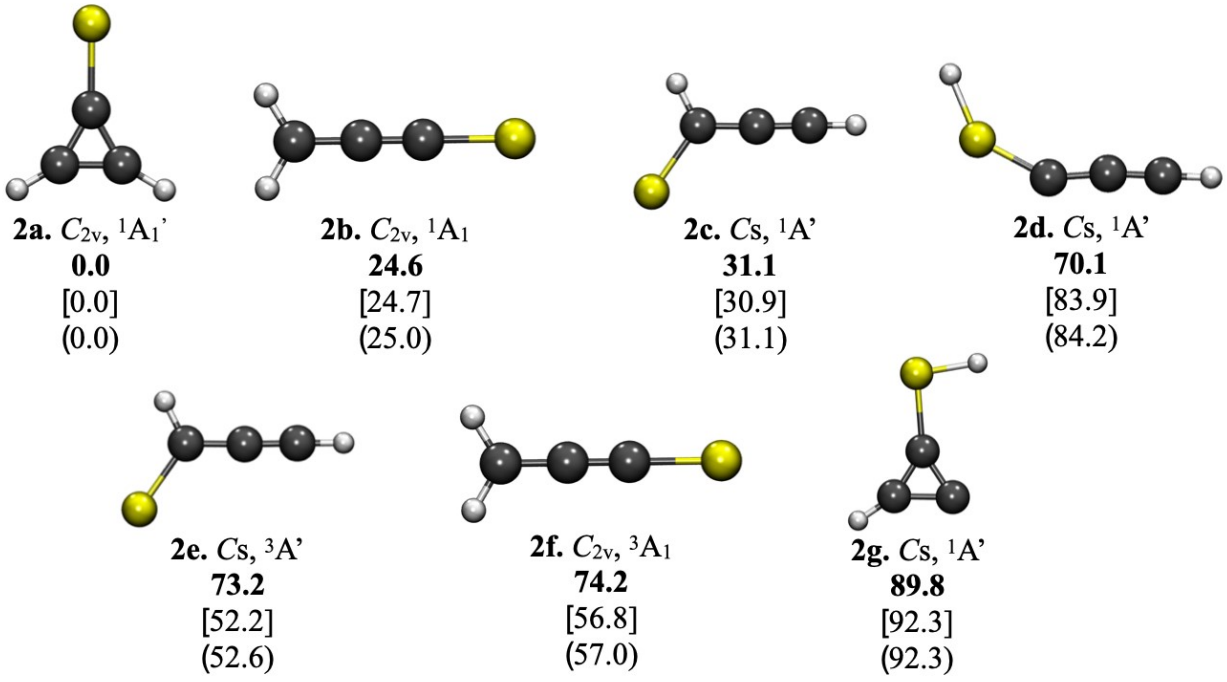


1a. D_{3h}, $^1A_1$'
0.0
[0.0]
(0.0)

1b. C_{2v}, $^1A_1$
32.3
[33.5]
(33.6)

Figure S1. Global minimum and low-energy isomers of $C_3H_3^+$, including point group symmetries and spectroscopic states. Relative energies are reported in kcal mol^{-1} at the MP2/def2-TZVP level (in bold), at the PBE0/def2-TZVP level [in brackets], and at the PBE0-D3/def2-TZVP level (in parentheses).



2a. C_{2v}, $^1A_1$'
0.0
[0.0]
(0.0)

2b. C_{2v}, $^1A_1$
24.6
[24.7]
(25.0)

2c. Cs, ^{1}A'
31.1
[30.9]
(31.1)

2d. Cs, ^{1}A'
70.1
[83.9]
(84.2)

2e. Cs, ^{3}A'
73.2
[52.2]
(52.6)

2f. C_{2v}, $^3A_1$
74.2
[56.8]
(57.0)

2g. Cs, ^{1}A'
89.8
[92.3]
(92.3)

Figure S2. Global minimum and low-energy isomers of $C_3H_2Au^+$, including point group symmetries and spectroscopic states. Relative energies are reported in kcal mol^{-1} at the MP2/def2-TZVP level (in bold), at the PBE0/def2-TZVP level [in brackets], and at the PBE0-D3/def2-TZVP level (in parentheses).

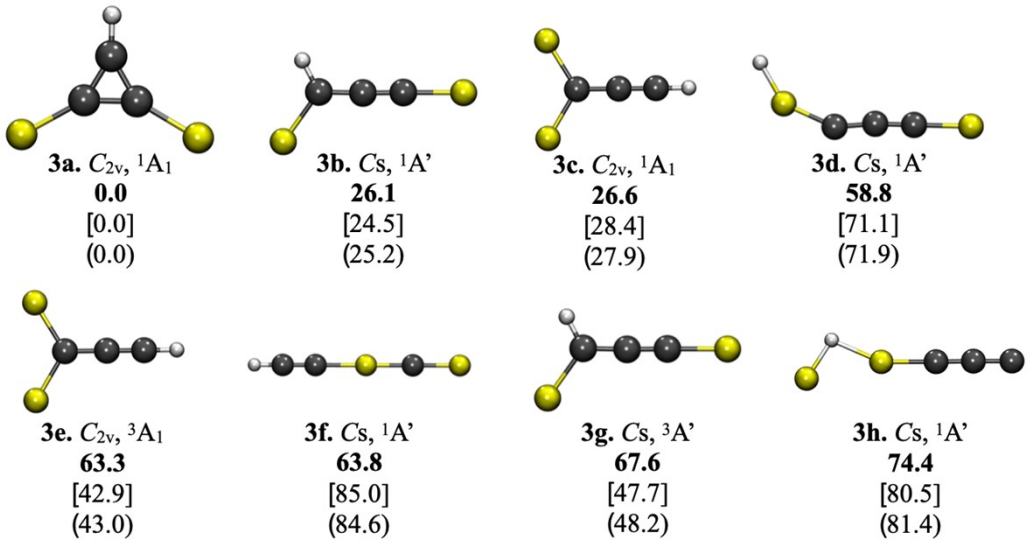


Figure S3. Global minimum and low-energy isomers of $C_3HAu_2^+$, including point group symmetries and spectroscopic states. Relative energies are reported in kcal mol^{-1} at the MP2/def2-TZVP level (in bold), at the PBE0/def2-TZVP level [in brackets], and at the PBE0-D3/def2-TZVP level (in parentheses).

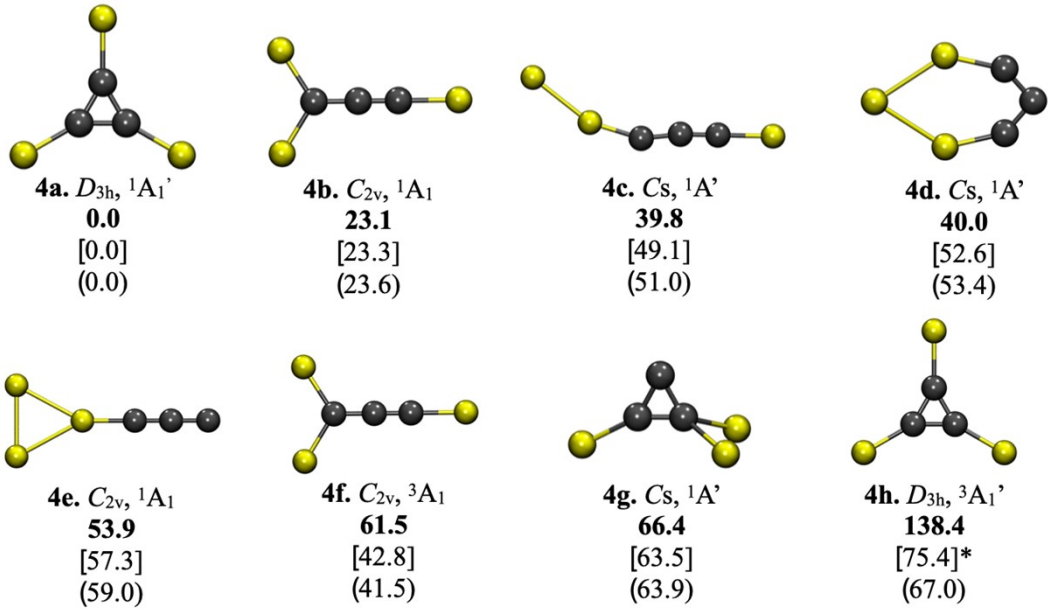


Figure S4. Global minimum and low-energy isomers of $C_3Au_3^+$, including point group symmetries and spectroscopic states. Relative energies are reported in kcal mol^{-1} at the MP2/def2-TZVP level (in bold), at the PBE0/def2-TZVP level [in brackets], and at the PBE0-D3/def2-TZVP level (in parentheses).

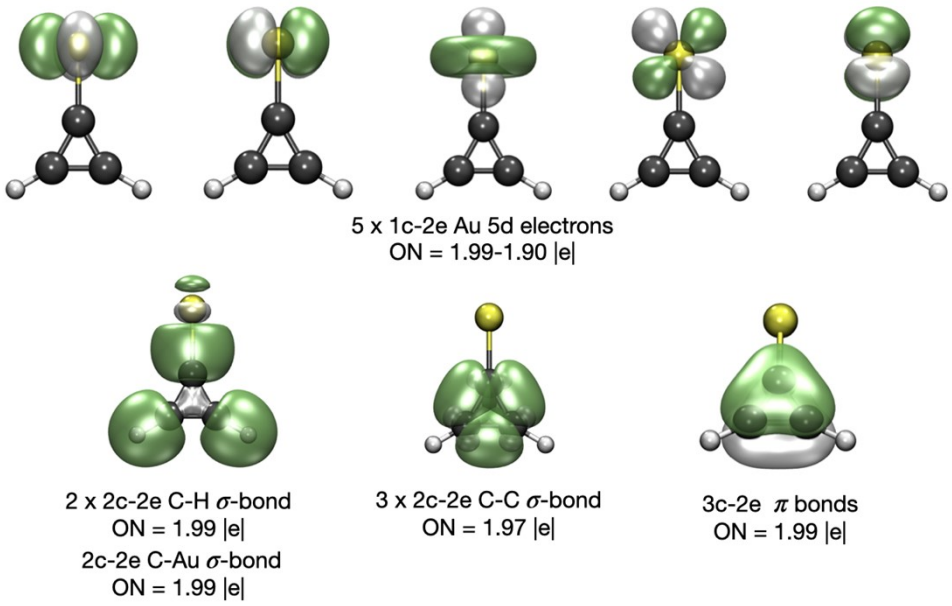


Figure S5. AdNDP plots of the $C_3H_2Au^+$ system at the PBE0-D3/def2-TZVP level, using pseudopotentials for the Au atom.

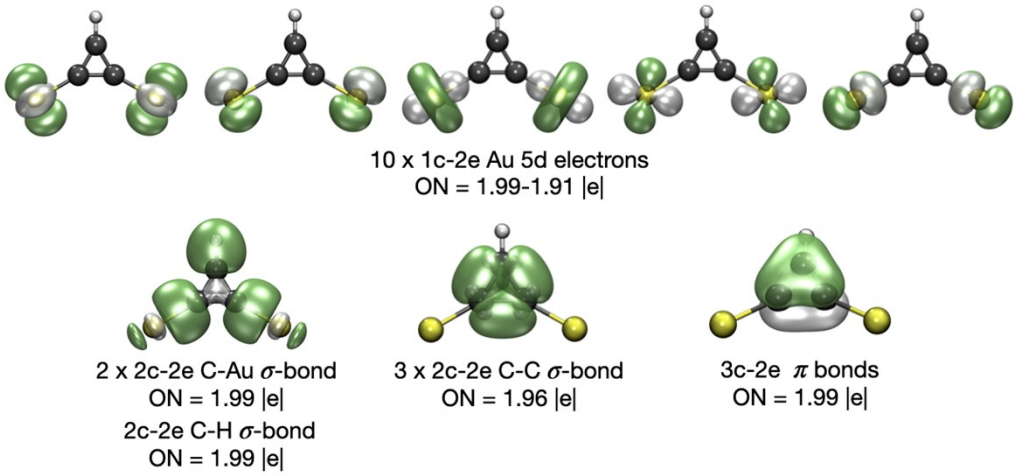


Figure S6. AdNDP plots of the $C_3HAu_2^+$ system at the PBE0-D3/def2-TZVP level, using pseudopotentials for the Au atom.

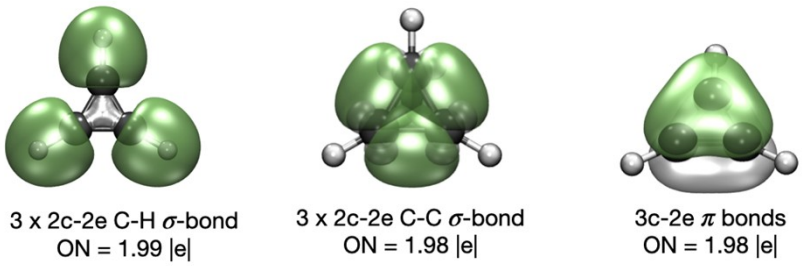


Figure S7. AdNDP plots of the $C_3H_3^+$ system at the PBE0-D3/def2-TZVP level.

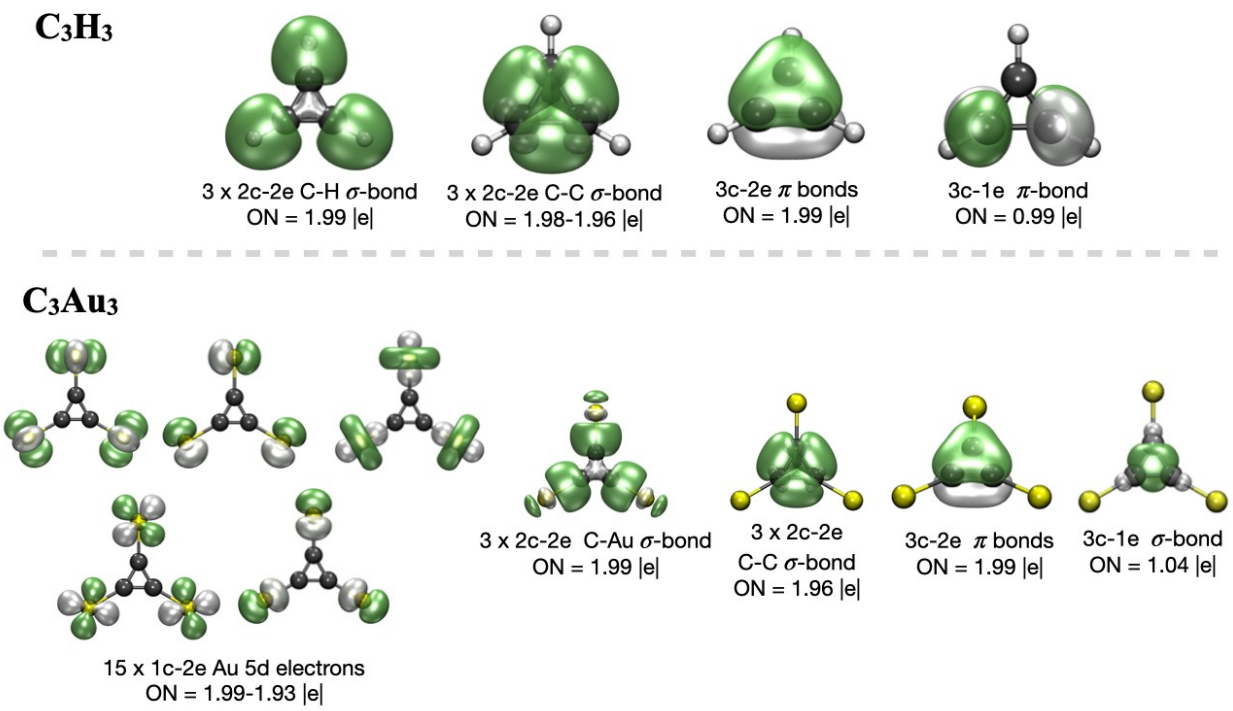


Figure S8. AdNDP plots of the C_3H_3 and C_3Au_3 systems at the PBE0-D3/def2-TZVP level, using pseudopotentials for the Au atom.

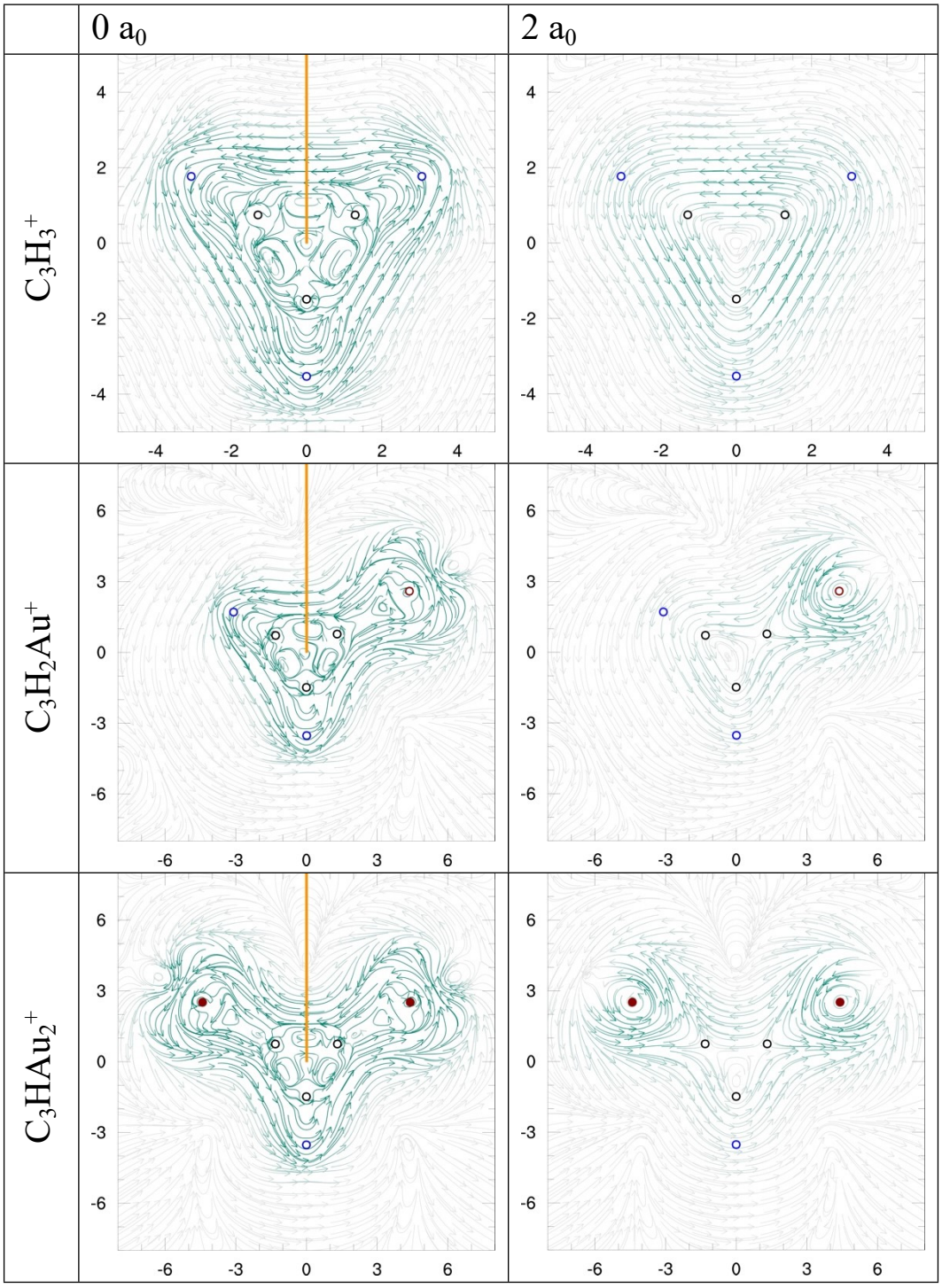


Figure S9a. Magnetically induced current density (MICD) maps computed at the molecular plane (0 a_0) and 2 Bohr (2 a_0) above the molecular plane for: $C_3H_3^+$, $C_3H_2Au^+$, and $C_3HAu_2^+$. Counterclockwise direction indicates diatropic response. Black, blue, and red circles represent C, H, and Au atoms, respectively. The orange line indicates the current integration plane. *(Part 1 of 2)*

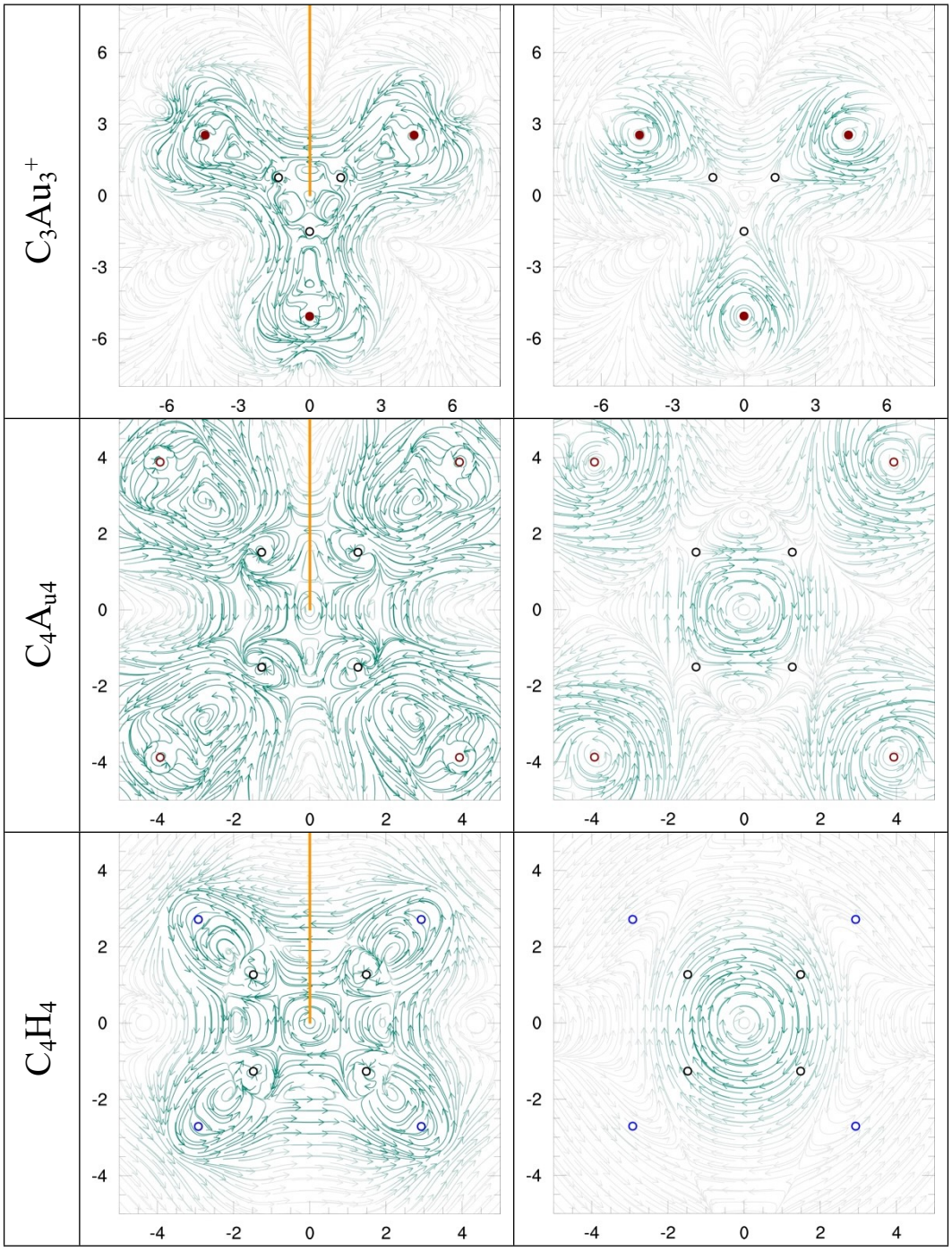


Figure S9b. Continued: MICD maps for $C_3Au_3^+$, C_4Au_4, and C_4H_4, at 0 a_0 and 2 a_0. Color scheme and integration plane as in Figure S9a. *(Part 2 of 2)*

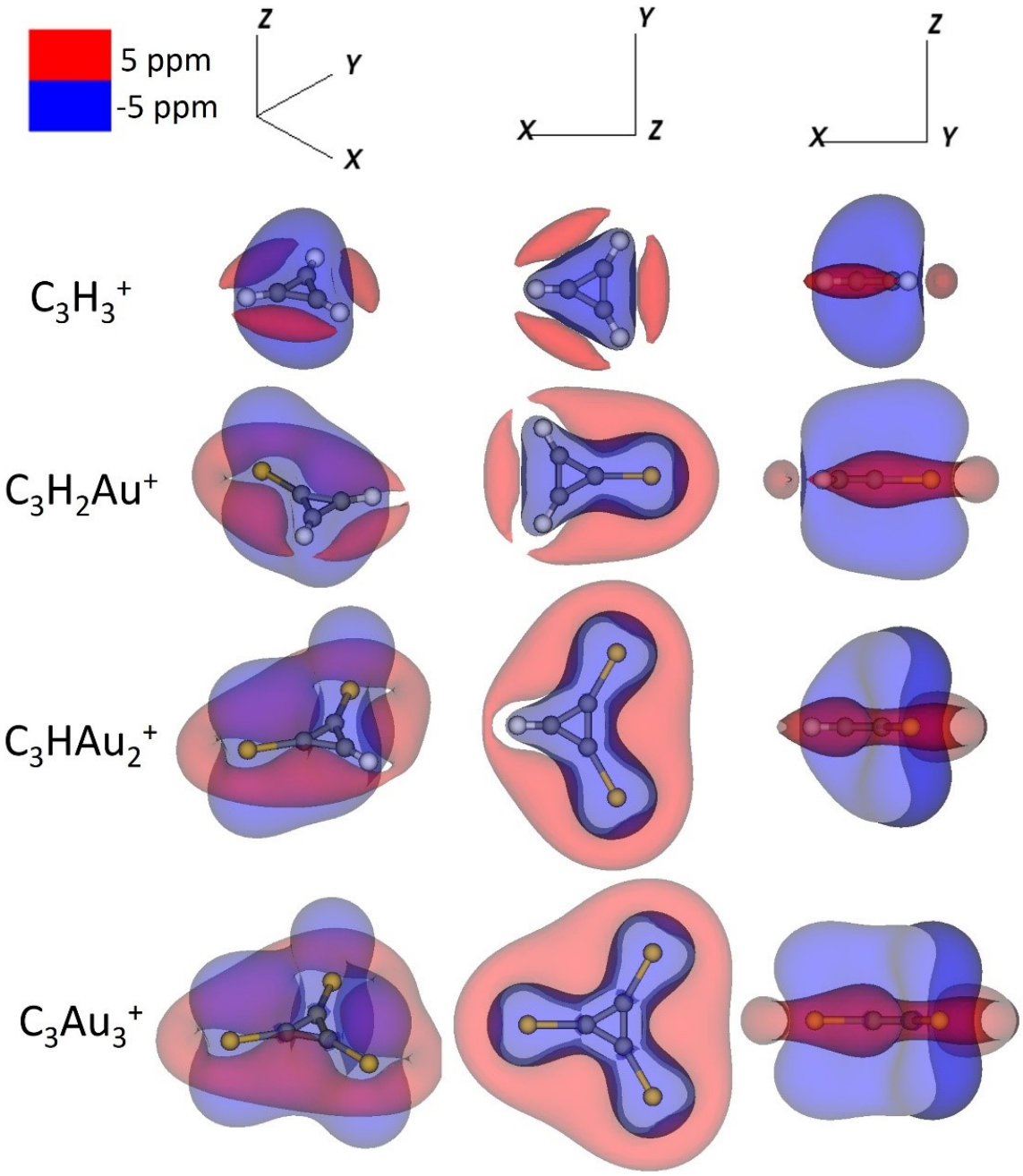


Figure S10. Isosurfaces of the z-component of the induced magnetic field component (B_z^{ind}) for $C_3H_3^+$, $C_3H_2Au^+$, $C_3HAu_2^+$, and $C_3Au_3^+$.

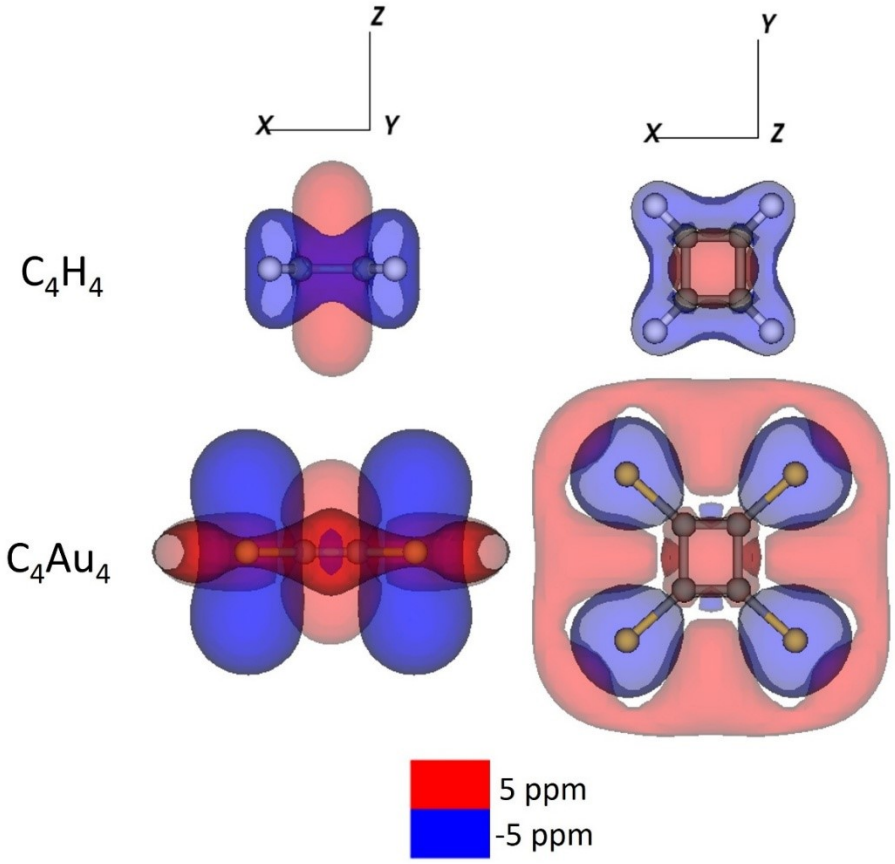


Figure S11. Isosurfaces of the z-component of the induced magnetic field component (B^{ind}_{z}) for C_4H_4 and C_4Au_4.

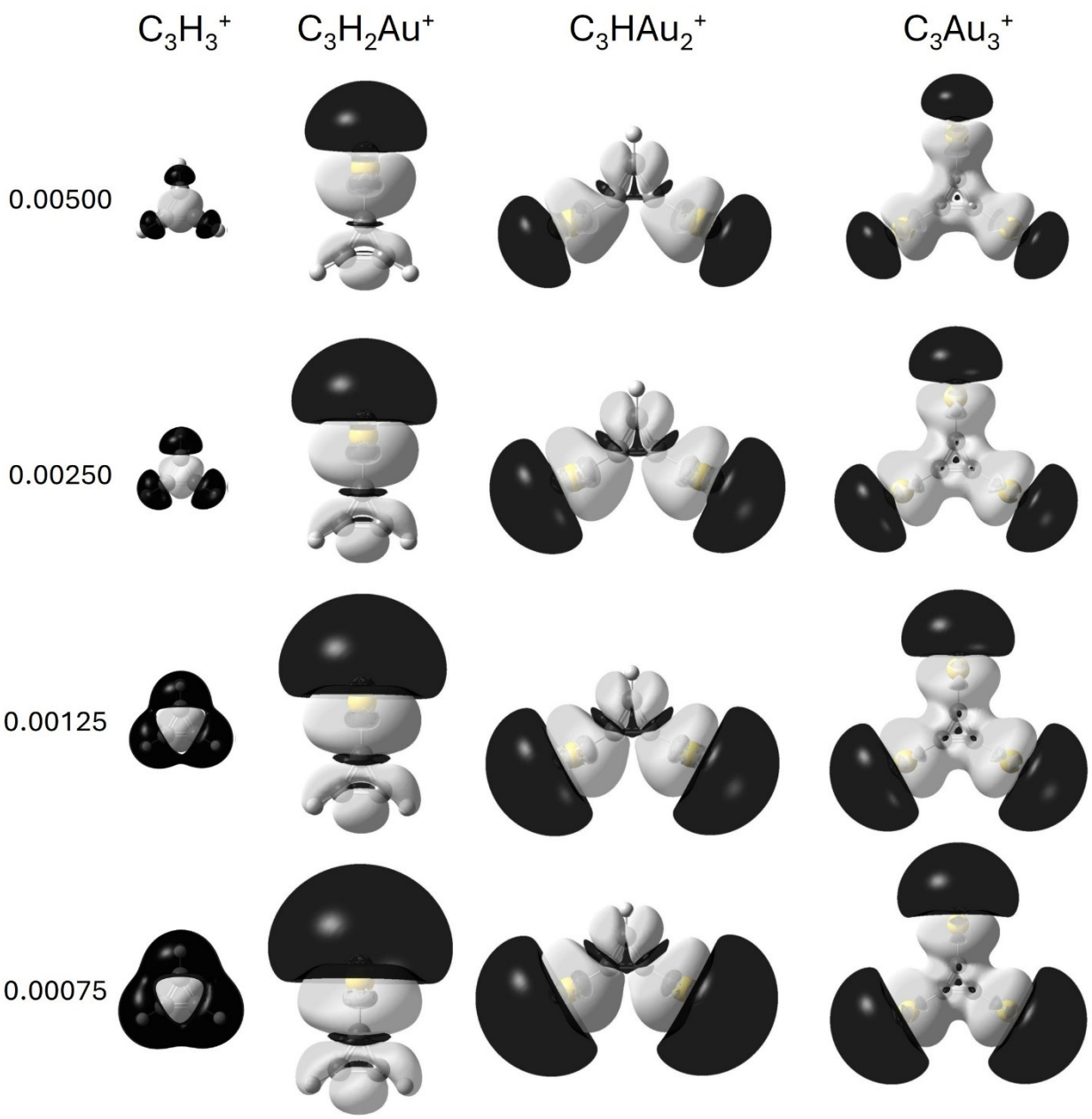


Figure S12. Local hyper-softness isosurfaces $s^{(2)}(\mathbf{r})$ at various values (from 0.00500 to 0.00075 $|e|^3 \cdot hartree^{-2} \cdot bohr^{-3}$). At this range, the $C_3H_3^+$ cation exhibits predominantly electrophilic behavior, whereas the gold-containing species show a dual local reactivity: electrophilic behavior localized at the vertices opposite each Au atom, and nucleophilic regions surrounding both carbon and gold atoms.

Table S1. Electrophilicity index (ω), electroaccepting power (ω^+), electrodonating power (ω^-), net electrophilicity ($\Delta\omega^{\pm}$), and global softness (S). All values are reported in hartree, except for S, which is given in $|e|^2\text{hartree}^{-1}$. The chemical potential and molecular hardness used to compute these descriptors were obtained using the finite difference approximation.

Structure	ω	ω^+	ω^-	$\Delta\omega^{\pm}$	S
$C_3H_3^+$	0.1942	0.1872	0.6623	0.8495	1.7210
$C_3H_2Au^+$	0.1720	0.1809	0.5593	0.7402	2.4031
$C_3HAu_2^+$	0.1624	0.1736	0.5229	0.6965	2.6615
$C_3Au_3^+$	0.1922	0.2135	0.6052	0.8187	2.5045

Cartesian Coordinates

Cartesian Coordinates of the global minimum and the lowest energy local minimum in the $C_3H_3^+$, $C_3H_2Au^+$, $C_3HAu_2^+$, $C_3Au_3^+$, C_3H_3 and C_3Au_3 calculated at the MP2/def2-TZVP level.

1a-Singlet				1b-Singlet			
6	0.000000000	0.787990718	0.000000000	6	0.078048737	0.000000000	0.000000000
6	0.682420000	-0.393995282	0.000000000	6	-1.275625263	0.000000000	0.000000000
6	-0.682420000	-0.393995282	0.000000000	6	1.304967737	0.000000000	0.000000000
1	1.618549000	-0.934470282	0.000000000	1	-1.829722263	0.938117000	0.000000000
1	0.000000000	1.868938718	0.000000000	1	-1.829722263	-0.938117000	0.000000000
1	-1.618549000	-0.934470282	0.000000000	1	2.380755737	0.000000000	0.000000000

2a-Singlet				2b-Singlet			
6	2.648144087	0.677339000	0.000000000	6	2.569208299	0.000000000	0.000000000
6	2.648144087	-0.677339000	0.000000000	6	1.324848299	0.000000000	0.000000000
79	-0.443338913	0.000000000	0.000000000	6	3.913643299	0.000000000	0.000000000
6	1.444245087	0.000000000	0.000000000	79	-0.521433701	0.000000000	0.000000000
1	3.193270087	1.609943000	0.000000000	1	4.471298299	0.934671000	0.000000000
1	3.193270087	-1.609943000	0.000000000	1	4.471298299	-0.934671000	0.000000000
2c-Singlet				2d-Singlet			
6	-2.404790584	-0.144229227	0.000000000	6	1.275754578	0.450098267	0.000000000
6	-3.493337432	0.415941693	0.000000000	79	-0.479654709	-0.009305360	0.000000000
79	0.462029713	0.037276201	0.000000000	6	2.550001994	0.043440532	0.000000000
6	-1.208686208	-0.801371631	0.000000000	6	3.762120153	-0.197790242	0.000000000
1	-1.235571443	-1.894389807	0.000000000	1	-1.421641056	-1.287762124	0.000000000
1	-4.442601583	0.915794418	0.000000000	1	4.816465045	-0.415051922	0.000000000
2e-Triplet				2f-Triplet			
6	2.192364000	0.258145000	0.000000000	6	-1.322670593	0.000000000	0.000000000
79	-0.206944000	-0.178439000	0.000000000	79	0.524740407	0.000000000	0.000000000
6	1.229822000	1.136099000	0.000000000	6	-2.604190593	0.000000000	0.000000000
6	3.110011000	-0.599320000	0.000000000	6	-3.933301593	0.000000000	0.000000000
1	3.887590000	-1.335475000	0.000000000	1	-4.482091593	0.938298000	0.000000000
1	1.091305000	2.206828000	0.000000000	1	-4.482091593	-0.938298000	0.000000000
2g-Singlet							
6	-1.514823434	-0.069774153	0.000000000				
6	-2.613882852	0.676283570	0.000000000				
79	0.428219922	0.010224197	0.000000000				
6	-2.685405275	-0.781101743	0.000000000				
1	0.635778290	-1.511345082	0.000000000				
1	-3.191421003	1.591997571	0.000000000				

3a-Singlet				3b-Singlet			
79	-2.332838000	-0.118540906	0.000000000	79	2.853572820	0.089927858	0.000000000
6	-0.696845000	0.817297094	0.000000000	6	-1.098670718	-0.420475260	0.000000000
6	0.000000000	1.998275094	0.000000000	6	0.103816244	-0.725597060	0.000000000
6	0.696845000	0.817297094	0.000000000	6	1.401653690	-1.102278512	0.000000000
79	2.332838000	-0.118540906	0.000000000	79	-2.886742415	0.058147407	0.000000000
1	0.000000000	3.078653094	0.000000000	1	1.638884257	-2.168686802	0.000000000
3c-Singlet				3d-Singlet			
79	-1.600192000	-0.202413764	0.000000000	79	3.066197992	0.025588934	0.000000000
6	0.000000000	2.141852236	0.000000000	6	1.233993375	-0.158760101	0.000000000
79	1.600192000	-0.202413764	0.000000000	6	-0.016304026	-0.278472815	0.000000000
6	0.000000000	0.766624236	0.000000000	6	-1.309920089	-0.544134226	0.000000000
6	0.000000000	3.363808236	0.000000000	79	-3.040257865	0.027488267	0.000000000
1	0.000000000	4.435338236	0.000000000	1	-3.971490065	1.311710977	0.000000000
3e-Triplet				3f-Singlet			
79	-1.397278000	-0.227560761	0.000000000	6	5.347211634	-0.474986240	0.000000000
6	0.000000000	2.385492239	0.000000000	6	4.046368562	-0.292514463	0.000000000
79	1.397278000	-0.227560761	0.000000000	6	2.782809055	-0.131112897	0.000000000
6	0.000000000	1.077599239	0.000000000	79	0.931703709	0.128624912	0.000000000
6	0.000000000	3.613988239	0.000000000	79	-1.670266978	-0.079545233	0.000000000
1	0.000000000	4.682099239	0.000000000	1	-0.639445299	1.107643270	0.000000000
3g-Triplet				3h-Singlet			
79	2.441368000	0.286765000	0.000000000	79	2.029191403	0.000000000	0.000000000
6	-1.026932000	-0.393378000	0.000000000	6	-4.674424597	0.000000000	0.000000000
6	0.150458000	-0.864791000	0.000000000	6	-3.432937597	0.000000000	0.000000000
6	1.374864000	-1.329032000	0.000000000	6	0.250970403	0.000000000	0.000000000
79	-2.767611000	0.248963000	0.000000000	79	-1.521145597	0.000000000	0.000000000
1	1.816367000	-2.315900000	0.000000000	1	-5.746337597	0.000000000	0.000000000

4a-Singlet				4b-Singlet			
79	2.321279000	-1.340191000	0.000000000	6	-0.845154691	0.000000000	0.000000000
79	-2.321279000	-1.340191000	0.000000000	79	3.604129309	0.000000000	0.000000000
6	0.691513000	-0.399245000	0.000000000	6	0.513785309	0.000000000	0.000000000
79	0.000000000	2.680382000	0.000000000	79	-1.845305691	1.588278000	0.000000000
6	0.000000000	0.798490000	0.000000000	79	-1.845305691	-1.588278000	0.000000000
6	-0.691513000	-0.399245000	0.000000000	6	1.750875309	0.000000000	0.000000000
4c-Singlet				4d-Singlet			
79	-1.403563125	0.606427216	0.000000000	6	2.371800696	0.996994000	0.000000000
6	0.385117146	0.773696100	0.000000000	6	2.371800696	-0.996994000	0.000000000
79	4.688160846	-0.203107230	0.000000000	6	3.238152696	0.000000000	0.000000000
79	-3.583407063	-0.481221231	0.000000000	79	0.552736696	1.409358000	0.000000000
6	1.641605134	0.368343849	0.000000000	79	0.552736696	-1.409358000	0.000000000
6	2.877896911	0.136621356	0.000000000	79	-1.591754304	0.000000000	0.000000000
4e-Singlet				4f-Triplet			
79	1.279388530	0.000000000	0.000000000	6	-0.653979625	0.000000000	0.000000000
6	4.406638530	0.000000000	0.000000000	79	3.751380375	0.000000000	0.000000000
6	3.128848530	0.000000000	0.000000000	6	0.646262375	0.000000000	0.000000000
79	-1.043393470	1.247697000	0.000000000	79	-1.933166625	1.420055000	0.000000000
79	-1.043393470	-1.247697000	0.000000000	79	-1.933166625	-1.420055000	0.000000000

6	5.717049530	0.000000000	0.000000000	6	1.894539375	0.000000000	0.000000000
4g-Singlet				4h-Triplet			
6	0.130826936	0.000000000	0.699370588	79	-1.316436000	-2.280134000	0.000000000
79	-2.905042741	0.000000000	-0.095258771	79	-1.316436000	2.280134000	0.000000000
79	1.500689247	-1.281071000	-0.056320628	6	-0.393387000	-0.681366000	0.000000000
6	-1.222119608	0.000000000	0.723679691	79	2.632872000	0.000000000	0.000000000
79	1.500689247	1.281071000	-0.056320628	6	0.786773000	0.000000000	0.000000000
6	-0.489950321	0.000000000	1.989394764	6	-0.393387000	0.681366000	0.000000000

Cartesian Coordinates of the local minimum in the C_3H_3, C_3Au_3, C_4H_4 and C_4Au_4 calculated at the PBE0-D3/def2-TZVP level.

C_3H_3-Doublet				C_3Au_3-Doublet			
6	0.000000000	0.749431071	0.000000000	79	-2.756356000	0.000000000	0.000000000
6	-0.747208000	-0.377399929	0.000000000	79	1.378178000	2.387074000	0.000000000
6	0.747208000	-0.377399929	0.000000000	6	-0.790012000	0.000000000	0.000000000
1	-1.691004000	-0.883431929	0.000000000	79	1.378178000	-2.387074000	0.000000000
1	0.000000000	1.830789071	0.000000000	6	0.395006000	-0.684170000	0.000000000
1	1.691004000	-0.883431929	0.000000000	6	0.395006000	0.684170000	0.000000000
C_4H_4- Singlet				C_4Au_4-Singlet			
6	0.000000000	0.670959000	0.784025000	6	0.000000000	0.798831000	0.668624000
6	0.000000000	0.670959000	-0.784025000	6	0.000000000	-0.798831000	0.668624000
6	0.000000000	-0.670959000	-0.784025000	6	0.000000000	-0.798831000	-0.668624000
6	0.000000000	-0.670959000	0.784025000	6	0.000000000	0.798831000	-0.668624000
1	0.000000000	1.434777000	1.548389000	79	0.000000000	2.052405000	-2.078718000
1	0.000000000	1.434777000	-1.548389000	79	0.000000000	2.052405000	2.078718000
1	0.000000000	-1.434777000	-1.548389000	79	0.000000000	-2.052405000	2.078718000
1	0.000000000	-1.434777000	1.548389000	79	0.000000000	-2.052405000	-2.078718000