Supporting Information

Mechanistic Elucidation of the Structure and Reactivity of Bare and Hydride-Protected Ag_{17}^+ Clusters

Ananya Baksi,[†,§] Madhuri Jash,[†,§] Soumabha Bag, [†,§] Sathish Kumar Mudedla,[‡§] Mohammad Bodiuzzaman,[†] Debasmita Ghosh,[†] Ganesan Paramasivam,[†] Venkatesan Subramanian,[‡] and Thalappil Pradeep*[,†]

[†]DST Unit of Nanoscience and Thematic Unit of Excellence, Indian Institute of Technology Madras, India

[‡]Chemical Laboratory, CSIR-Central Leather Research Institute, Adyar, Chennai 600020, India

*Email: pradeep@iitm.ac.in

[§] Contributed equally

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Supporting Information 1:

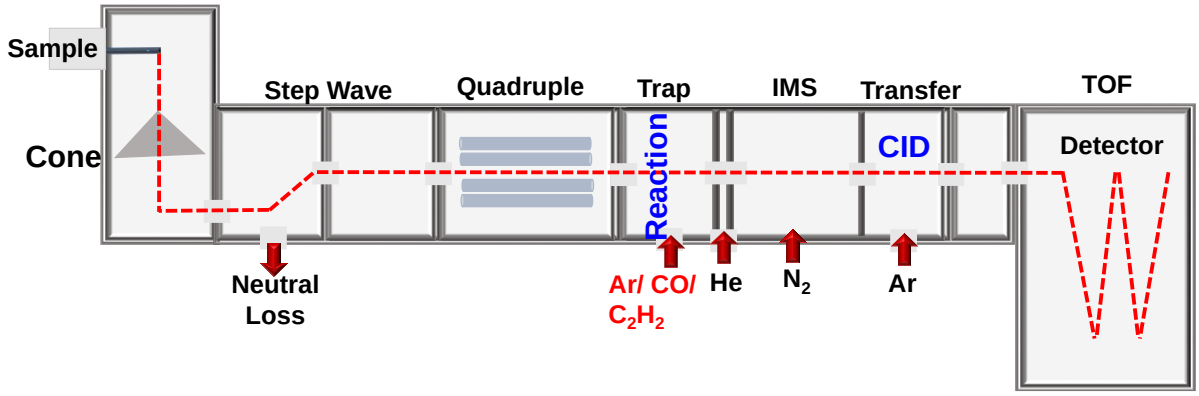

Figure S1. Schematic representation of the instrument. All the reactions were carried out in the trap region where Ar is used as collision gas. The Ar gas line was modified and reactive gases like CO and C_2H_2 were incorporated.

Supporting Information 2:

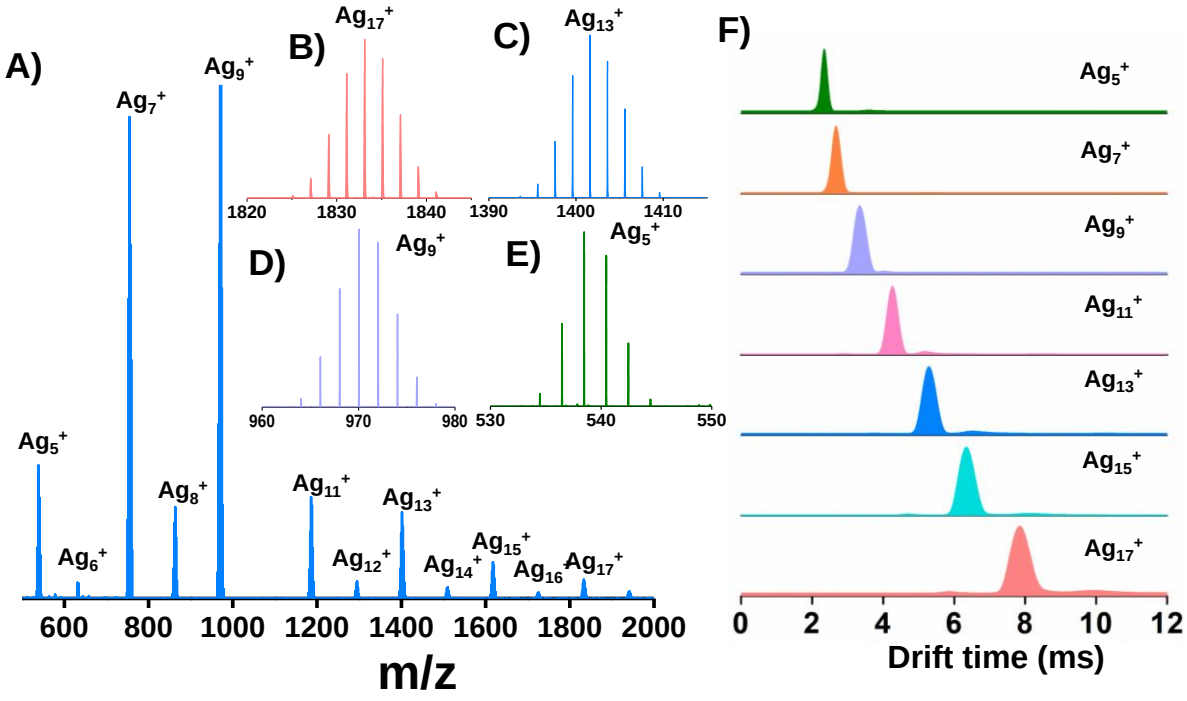

Figure S2. A) CID of Ag_{17}^+ shows different bare clusters. Odd numbered clusters are more stable than the even ones. Complete absence of Ag_{10}^+ confirms lesser stability of the clusters in the experimental condition. On the contrary higher intensity of Ag_7^+ and Ag_9^+ cluster confirms very high stability of these clusters in the experimental condition. Expanded m/z region for Ag_{17}^+, Ag_{13}^+, Ag_9^+ and Ag_5^+ are shown in B) to E). Extracted ion mobilogram of

each of the odd numbered clusters are shown in F). Despite of the possibility of having multiple structural isomers of such gas phase clusters, only one isomer appeared at maximum abundance.

Table S1. CCS of bare Ag cluster cations with varying nuclearity.

Cluster	Arrival Time (ms)	$^{TWIMS}CCS_{N2}$ (Å^2)
Ag_{17}^+	7.86	174
Ag_{15}^+	6.37	157
Ag_{13}^+	5.29	143
Ag_{11}^+	4.26	128
Ag_9^+	3.36	114
Ag_7^+	2.64	101
Ag_5^+	2.32	95

Supporting Information 3:

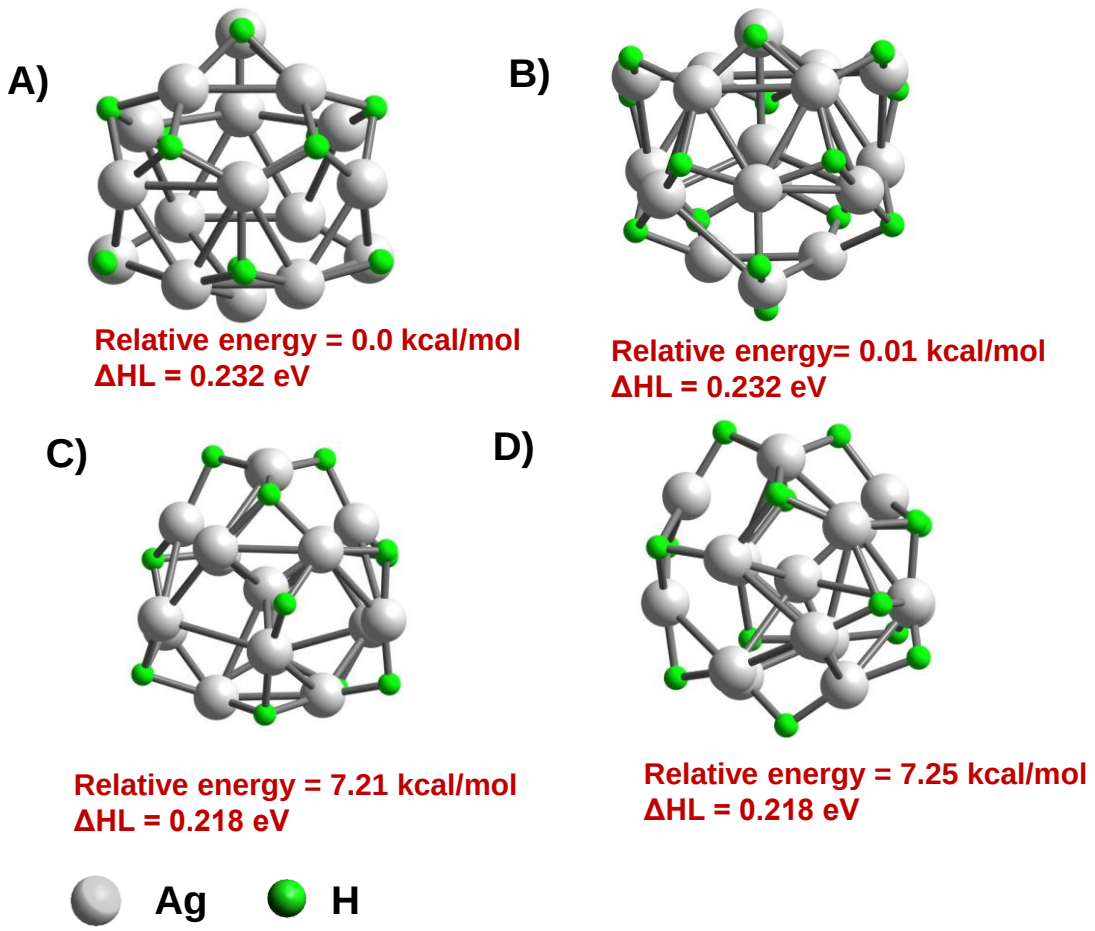

Figure S3. Four different isomeric structures of $Ag_{17}H_{14}$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 4:

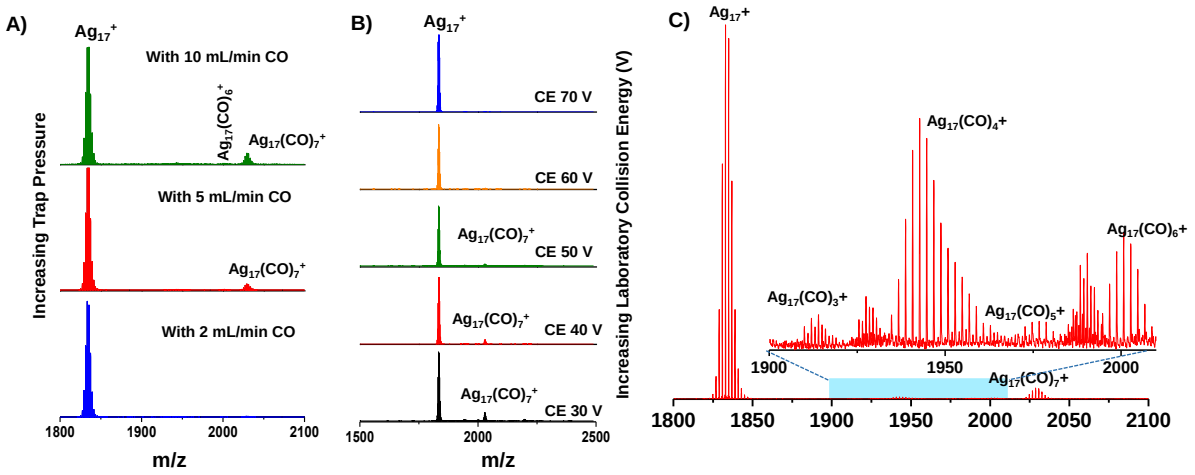

Figure S4. A) Reaction of Ag_{17}^+ with different flow of CO showing $Ag_{17}(CO)_7^+$ formation. B) CID of $Ag_{17}(CO)_7^+$ with increasing collision energy lead to bare Ag_{17}^+ cluster. C) CID of $Ag_{17}(CO)_7^+$ in IMS mode showing stepwise fragmentation. Mass range of m/z 1900-2010 is expanded in the inset and the peaks are labelled.

Table S2. Atomic coordinates and the Mulliken charges of all the atoms of Ag_{17}^{+}.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	-0.422181	1.119245	-2.065327	-0.433489
Ag	0.904745	-0.363006	0.289899	3.807301
Ag	1.481851	1.162071	2.671400	-0.162205
Ag	2.217860	-1.732583	2.545697	-0.175852
Ag	-1.064040	1.919193	0.938372	-0.433275
Ag	0.070397	-3.284642	0.889789	-0.225769
Ag	3.796133	0.309430	0.729353	-0.190571
Ag	2.836309	-2.500819	-0.332910	-0.175120
Ag	-3.045344	2.361957	-1.281071	0.110276
Ag	-1.218084	-0.730765	2.276860	-0.384785
Ag	-3.580418	0.262739	0.804231	0.005461
Ag	1.926890	2.484994	-0.249938	-0.321240
Ag	-0.458616	4.004579	-1.163998	0.177069
Ag	2.501173	-0.112171	-2.100598	-0.161443
Ag	-2.670202	-2.532826	0.101708	-0.057895
Ag	-2.953935	-0.519175	-2.135160	0.005956
Ag	-0.322537	-1.848222	-1.918304	-0.384422

Table S3. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}H_{14}^{+}$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	-2.479023	1.249976	-1.155632	0.002647
Ag	0.001521	-0.017348	-0.019685	2.289170
Ag	-1.358441	-2.011040	1.876284	-0.029752
Ag	1.367113	-2.031403	1.860834	-0.033481
Ag	-0.009942	-2.697551	-0.712330	-0.064818
Ag	3.027114	0.173746	1.536286	-0.107033
Ag	0.025561	0.294630	2.947703	-0.181389
Ag	1.414600	2.356064	1.385474	-0.040407
Ag	-1.465850	-1.116059	-2.547743	-0.064548
Ag	3.088052	-1.894396	-0.411921	-0.047127
Ag	1.438257	-1.121575	-2.560186	-0.065203
Ag	-3.027125	0.187463	1.554364	-0.112696
Ag	-3.096791	-1.888877	-0.385404	-0.048021
Ag	-1.386158	2.349688	1.401058	-0.034828
Ag	2.471274	1.240128	-1.177955	0.000428
Ag	-0.011379	1.391885	-2.709750	-0.021194
Ag	0.001081	3.486149	-0.846334	-0.089703
H	-0.016786	-2.346686	-2.799532	-0.009143
H	3.156187	1.833362	0.405569	-0.035586
H	3.312273	-1.731771	1.466822	-0.023872
H	-0.007941	3.298960	-2.598925	-0.007038
H	1.852161	0.755666	-2.859995	-0.034733
H	3.014384	-2.105384	-2.166916	-0.002376
H	1.780342	0.977247	2.855188	-0.051908
H	-3.306520	-1.719491	1.495331	-0.024255
H	0.013985	-1.825987	3.241125	-0.007378
H	-3.038416	-2.100553	-2.140916	-0.002192
H	-3.147381	1.847584	0.434769	-0.035114
H	0.009287	3.675321	1.005386	-0.031324
H	-1.878198	0.762037	-2.843923	-0.034475
H	-1.736908	0.960212	2.858079	-0.052651

Table S4. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}CO^{+}$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	-0.152740	-0.500183	-2.814555	-0.358639
Ag	0.016431	0.498993	-0.101547	4.248543
Ag	1.915894	-2.327944	1.772689	-0.090673
Ag	0.215125	-0.395975	2.929026	-0.135699
Ag	2.450072	0.449498	1.200759	-0.204132
Ag	-2.200389	0.519183	1.724306	-0.296592
Ag	-0.918054	-2.023904	1.105803	-0.065900
Ag	-3.622692	-1.708569	0.579099	-0.229536
Ag	2.325148	0.492051	-1.739962	-0.303678
Ag	0.114637	2.264144	2.089015	-0.283129
Ag	1.703455	2.832196	-0.140776	-0.312597
Ag	1.138859	-1.980251	-0.904499	-0.114686
Ag	3.807412	-1.485343	-0.242043	-0.244531
Ag	-1.685695	-2.474936	-1.495468	-0.059903
Ag	-1.640564	2.746040	-0.122042	-0.290208
Ag	0.054305	2.255208	-2.345054	-0.212777
Ag	-2.545217	0.242918	-1.088555	-0.197366
C	-0.805967	-0.441984	-4.883512	0.304239
O	-1.075726	-0.459408	-5.997726	-0.152738

Table S5. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}(CO)_2^{+}$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	0.697529	-2.769410	-0.283397	-0.343317
Ag	-0.011385	0.119446	0.348692	4.427883
Ag	-2.216992	1.108913	-2.444557	-0.038707
Ag	-0.784577	2.835312	-0.780180	-0.343296
Ag	-2.708319	0.841597	0.342705	-0.225303
Ag	1.867895	2.252202	0.126717	-0.310825
Ag	0.713868	1.084873	-2.228090	-0.183476
Ag	3.495723	0.993279	-1.842896	-0.242624
Ag	-1.886662	-2.002342	0.681838	-0.310813
Ag	-0.475947	2.403456	1.957476	-0.228255
Ag	-1.603030	-0.052212	2.744464	-0.295113
Ag	-0.913914	-1.323290	-1.932005	-0.183492
Ag	-3.661291	-1.138804	-1.372205	-0.242633
Ag	1.993781	-1.409743	-2.350629	-0.038700
Ag	1.747713	0.742342	2.544117	-0.295112
Ag	0.584193	-1.811420	2.333078	-0.228245
Ag	2.683156	-0.609122	0.288573	-0.225317
C	1.571351	-4.705508	0.181543	0.306693
O	1.989165	-5.757502	0.363132	-0.153022
C	-1.636326	4.830978	-0.638560	0.306694
O	-2.047446	5.901120	-0.635195	-0.153022

Table S6. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}(CO)_3^+$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	2.073421	-1.856447	-0.240905	-0.457123
Ag	0.014384	-0.008445	0.424871	4.338729
Ag	-2.373356	-0.009712	-2.687379	-0.053522
Ag	-2.112236	1.965991	-0.642065	-0.318334
Ag	-2.662695	-0.720065	0.149719	-0.224654
Ag	0.424905	2.789402	0.322033	-0.296522
Ag	0.030733	1.502430	-2.244675	-0.030647
Ag	2.367497	2.927843	-1.759476	-0.247100
Ag	-0.596065	-2.828610	0.409528	-0.318347
Ag	-1.593555	1.524077	2.065906	-0.340130
Ag	-1.525585	-1.232281	2.630336	-0.273557
Ag	-0.066094	-1.384489	-1.979222	-0.139929
Ag	-2.531253	-2.740890	-1.713860	-0.277391
Ag	2.435214	0.073405	-2.268820	-0.053295
Ag	1.254262	1.022915	2.691318	-0.223261
Ag	1.168526	-1.802865	2.438562	-0.288702
Ag	2.669650	1.039254	0.302314	-0.260382
C	3.869733	-3.029590	0.195866	0.312390
O	4.813426	-3.659870	0.357882	-0.155385
C	-4.025279	2.991385	-0.744380	0.306019
O	-5.019021	3.558909	-0.821681	-0.156288
C	-2.375485	2.670492	3.764035	0.308493
O	-2.932579	3.252207	4.578761	-0.151062

Table S7. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}(CO)_4^+$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	-2.876297	0.316087	0.631337	-0.387951
Ag	-0.003281	-0.356177	-0.149902	5.036299
Ag	2.027715	1.574328	2.201072	-0.034081
Ag	2.876913	0.639211	-0.297400	-0.385682
Ag	1.878347	-1.224010	1.728909	-0.413041
Ag	1.075403	0.451156	-2.604003	-0.341202
Ag	0.695727	2.392347	-0.454380	-0.223466
Ag	-0.627908	2.639475	-3.023203	-0.189002
Ag	-1.083199	-1.369807	2.225401	-0.341015
Ag	2.146289	-1.865249	-1.087965	-0.477254
Ag	0.260152	-3.250178	0.377936	-0.263599
Ag	-0.679169	1.507277	1.904206	-0.216795
Ag	0.634449	-0.025683	3.986586	-0.187281
Ag	-2.007882	2.663906	-0.618013	-0.028895
Ag	-0.289485	-2.169840	-2.462235	-0.266955
Ag	-2.168377	-2.090205	-0.441224	-0.482644
Ag	-1.887355	0.255159	-2.124530	-0.418073
C	-4.513388	1.482321	1.580087	0.327809
O	-5.366384	2.091307	2.044538	-0.152506
C	4.500915	2.154583	-0.205941	0.328340
O	5.341732	2.929692	-0.123491	-0.152735
C	3.663475	-2.920065	-2.146084	0.290269
O	4.508678	-3.488750	-2.674313	-0.155501
C	-3.689247	-3.574192	-0.297161	0.290383
O	-4.533563	-4.348922	-0.236562	-0.155422

Table S8. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}(CO)_5^+$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	2.576615	0.601299	1.332050	-0.370551
Ag	0.144972	0.383839	-0.289139	4.494785
Ag	-1.700948	-2.733521	2.160618	-0.168713
Ag	-1.724181	-1.660058	-0.503622	-0.409807
Ag	-1.875282	0.069068	1.767872	-0.092390
Ag	-1.205090	-0.085288	-2.862200	-0.376148
Ag	0.271550	-3.545136	0.190560	-0.045716
Ag	0.413823	-2.337349	-2.397542	-0.034533
Ag	0.338176	1.286612	2.935412	-0.178923
Ag	-2.594012	1.088815	-0.719655	-0.385007
Ag	-0.714128	2.778189	0.778755	-0.299342
Ag	0.705978	-1.362657	1.950637	0.026075
Ag	-0.862041	-0.915131	4.214668	-0.221115
Ag	2.197424	-1.488067	-0.446062	-0.464810
Ag	-0.547301	2.519964	-2.121373	-0.321695
Ag	1.879456	2.503425	-0.730216	-0.457041
Ag	1.655409	0.317938	-2.587137	-0.467918
C	4.342199	1.567571	2.221995	0.300159
O	5.295811	1.796673	2.816728	-0.153147
C	-3.185658	-3.054397	-1.335641	0.346521
O	-3.986831	-3.771742	-1.738096	-0.167946
C	-4.552838	2.031719	-0.913719	0.304403
O	-5.606456	2.446451	-1.094654	-0.158070
C	3.250730	4.243792	-0.932958	0.309784
O	3.858800	5.136014	-1.314481	-0.148041
C	4.018763	-2.583322	-0.737535	0.304222
O	4.988703	-3.179231	-0.888608	-0.165035

Table S9. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}(CO)_6^+$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	-2.976161	-1.016472	-1.728311	-0.293969
Ag	0.035193	0.493358	0.829594	4.697460
Ag	2.342580	-2.261354	-1.213469	-0.261852
Ag	2.419791	-0.566938	1.358948	-0.478297
Ag	1.755838	0.492423	-1.378643	-0.178389
Ag	1.081410	1.405862	3.254348	-0.403868
Ag	0.597782	-2.816834	0.988047	-0.018511
Ag	-0.013720	-1.197958	3.152971	-0.361085
Ag	-0.871196	0.732489	-2.716627	-0.127955
Ag	2.140262	2.279881	0.801783	-0.462497
Ag	-0.014074	2.790833	-1.078540	-0.214532
Ag	-0.320857	-1.555304	-1.285048	0.244664
Ag	1.153981	-1.100599	-3.586197	-0.189954
Ag	-2.000001	-1.375325	0.984539	-0.494681
Ag	-0.577402	3.135926	1.644695	-0.380328
Ag	-2.330687	1.299265	-0.152565	-0.463265
Ag	-1.973108	0.872238	2.708072	-0.517160
C	-4.760212	-1.753630	-2.885572	0.299206
O	-5.370659	-2.434977	-3.574917	-0.141476
C	4.198512	-1.580913	2.060994	0.314680
O	5.166155	-2.067569	2.439349	-0.165486
C	3.616309	3.858018	0.597702	0.303189
O	4.440774	4.653630	0.555274	-0.159030
C	-4.031776	2.417355	-0.878447	0.321667
O	-4.937046	3.011344	-1.259339	-0.166780
C	-3.232286	-3.029425	1.633299	0.313358
O	-3.925460	-3.882383	1.966280	-0.167176
C	4.069433	-3.617798	-1.512833	0.301076
O	4.776269	-4.469164	-1.810094	-0.149008

Table S10. Atomic coordinates and Mulliken charges of all the atoms of $Ag_{17}(CO)_7^+$.

Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
Ag	-1.777119	-2.098640	-0.750455	-0.340047
Ag	-0.486815	0.469798	0.472462	4.031895
Ag	3.264833	-0.965593	1.142947	-0.220736
Ag	1.996354	1.726158	1.108778	-0.453451
Ag	2.001002	0.069326	-1.117654	0.174550
Ag	-0.428460	3.144670	1.352029	-0.393860
Ag	0.913589	-0.452412	2.743868	-0.323198
Ag	-1.694297	1.062457	2.882072	-0.405597
Ag	0.505095	-1.898356	-2.437015	-0.127586
Ag	0.476223	2.397418	-1.311271	-0.283872
Ag	0.940922	0.693563	-3.630534	-0.214385
Ag	0.815632	-2.100697	0.382095	-0.002107
Ag	3.075575	-2.466573	-1.277925	-0.186068
Ag	-1.556185	-1.610957	2.013415	-0.399965
Ag	-2.280087	2.555560	-0.735842	-0.273250
Ag	-1.369994	0.354782	-2.165050	-0.159403
Ag	-3.225933	0.136290	0.502871	-0.472134
C	-3.017956	-4.021252	-0.983809	0.315655
O	-3.178874	-5.124977	-0.710711	-0.150463
C	3.515651	2.879886	2.229671	0.308272
O	4.308777	3.663341	2.503008	-0.159696
C	1.165158	4.264886	-2.117403	0.303635
O	1.569171	5.255987	-2.534772	-0.168095
C	-2.803296	-0.993393	-3.157460	0.329908
O	-3.554418	-1.474873	-3.888344	-0.172061
C	-2.173786	-3.278195	3.244541	0.299562
O	-2.498248	-4.138389	3.931030	-0.160567
C	5.002751	-1.325545	2.475532	0.301337
O	5.788076	-1.726224	3.207733	-0.151265
C	-5.464250	-0.035281	0.519477	0.306300
O	-6.478401	-0.546861	0.682247	-0.153308

Supporting Information 5:

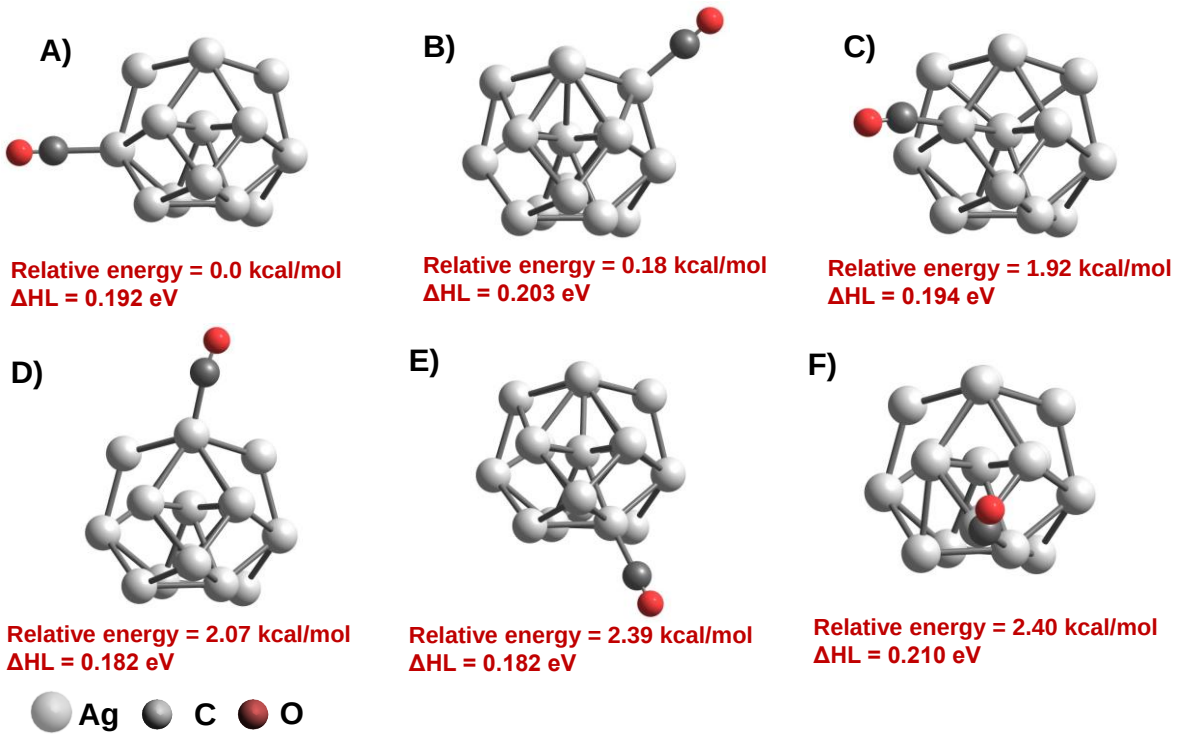

Figure S5. Six different isomeric structures of $Ag_{17}(CO)_1$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 6:

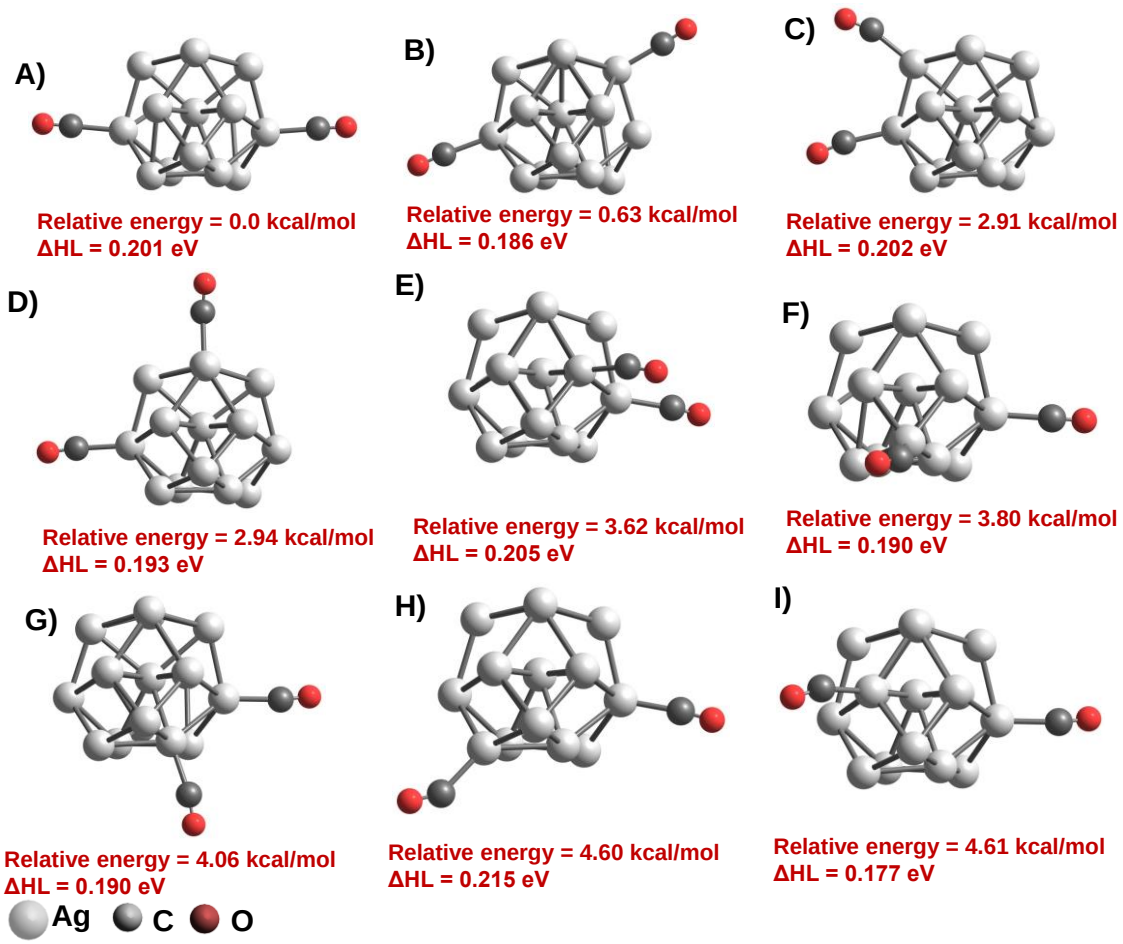

Figure S6. Nine different isomeric structures of $Ag_{17}(CO)_2$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 7:

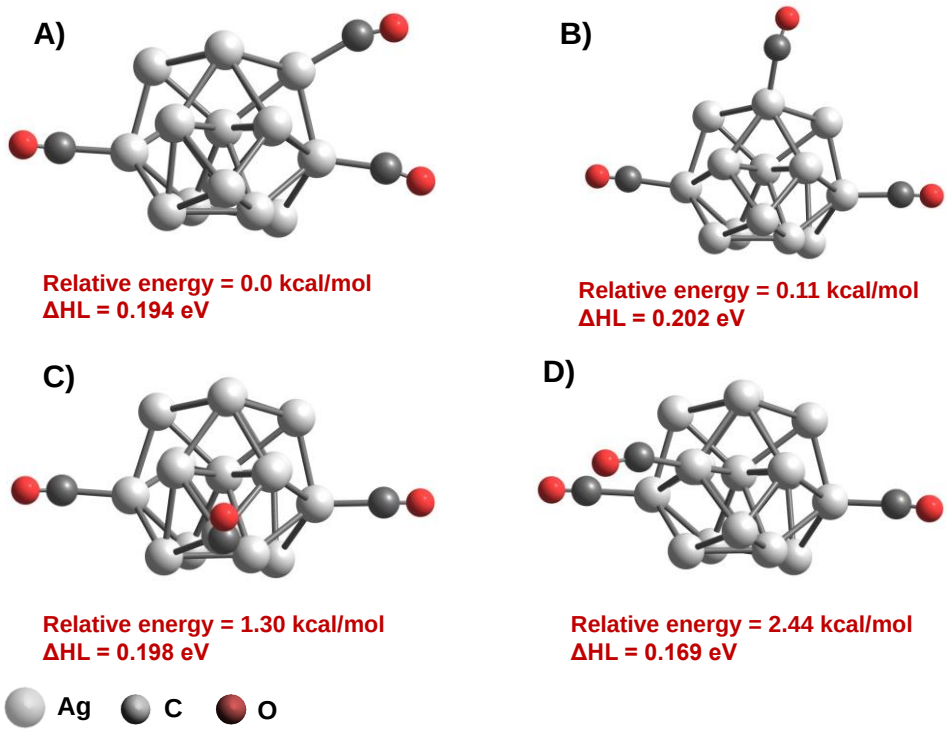

Figure S7. Four different isomeric structures of $Ag_{17}(CO)_3$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 8:

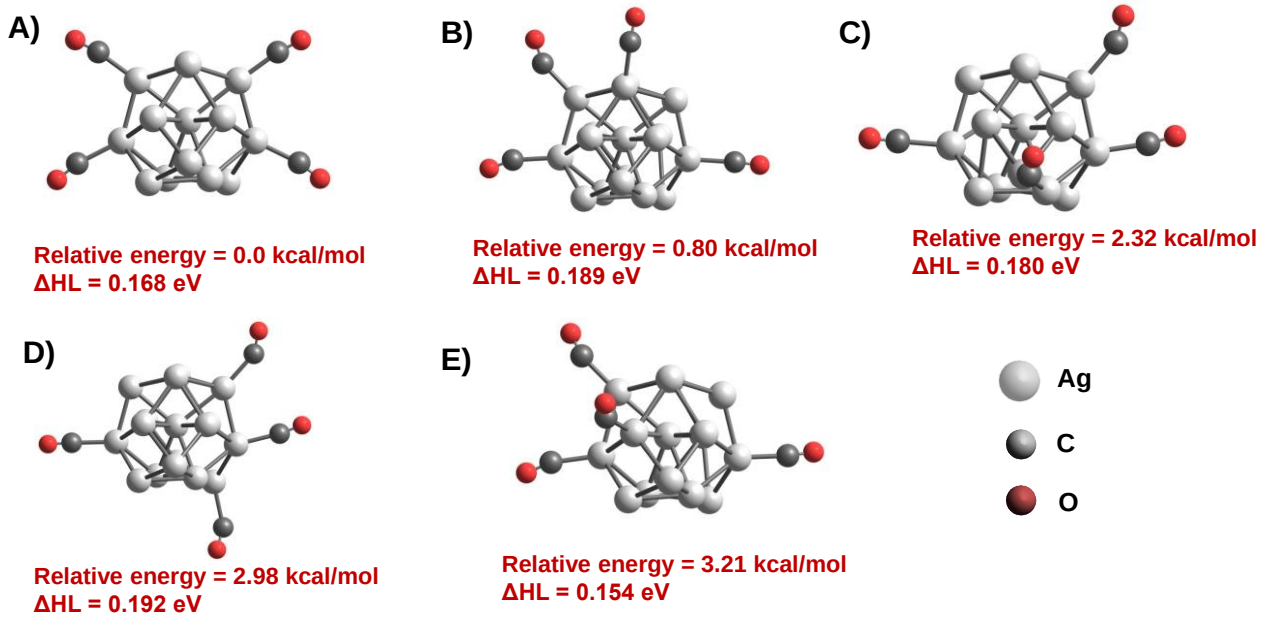

Figure S8. Five different isomeric structures of $Ag_{17}(CO)_4$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 9:

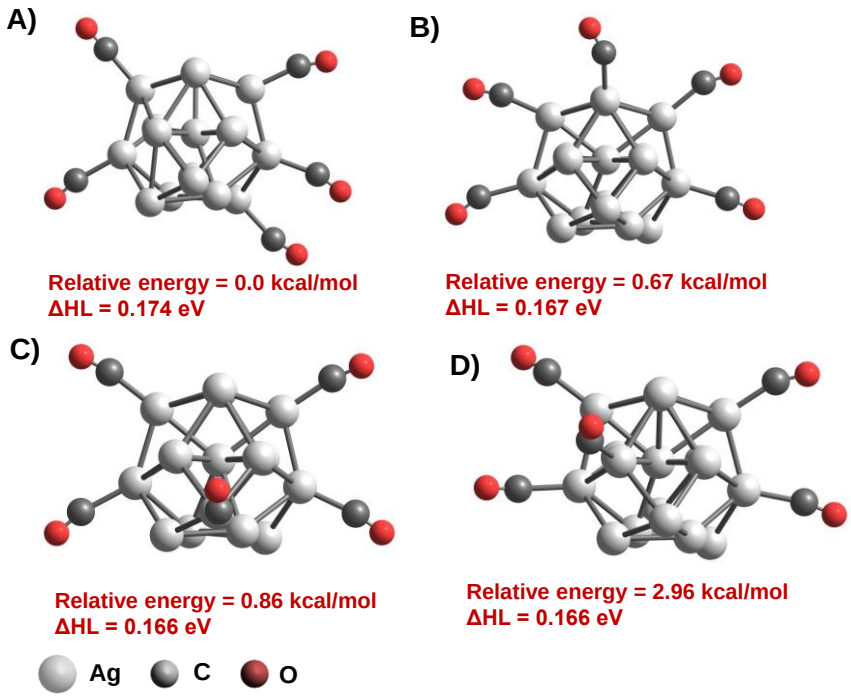

Figure S9. Four different isomeric structures of $Ag_{17}(CO)_5$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 10:

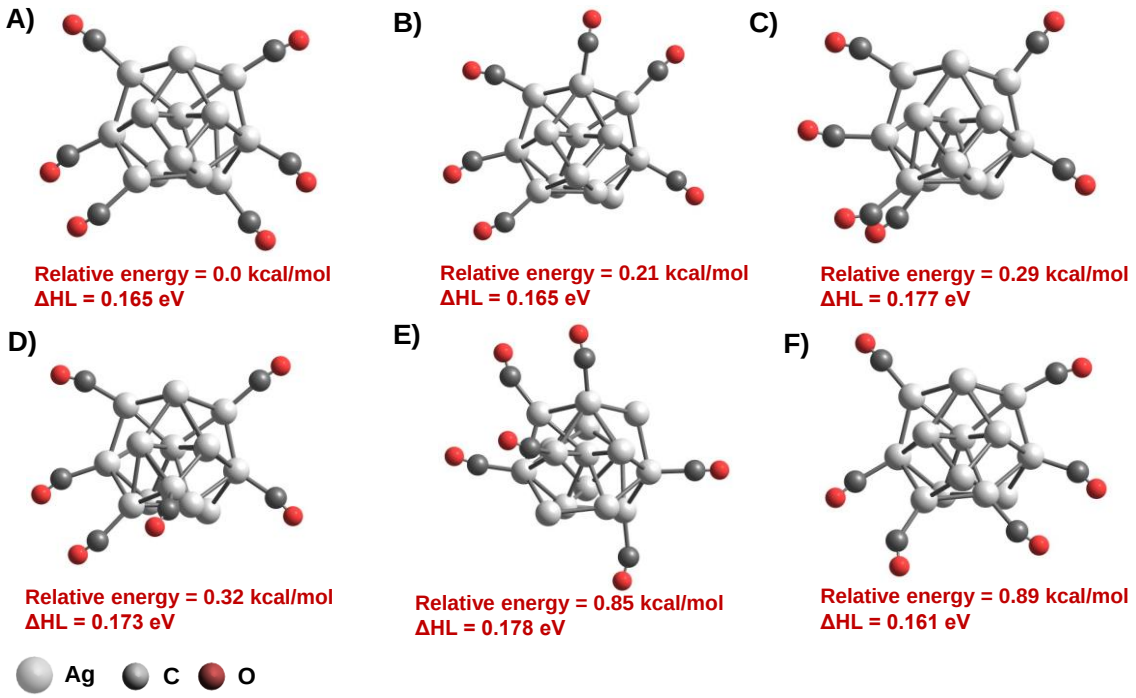

Figure S10. Six different isomeric structures of $Ag_{17}(CO)_6$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 11:

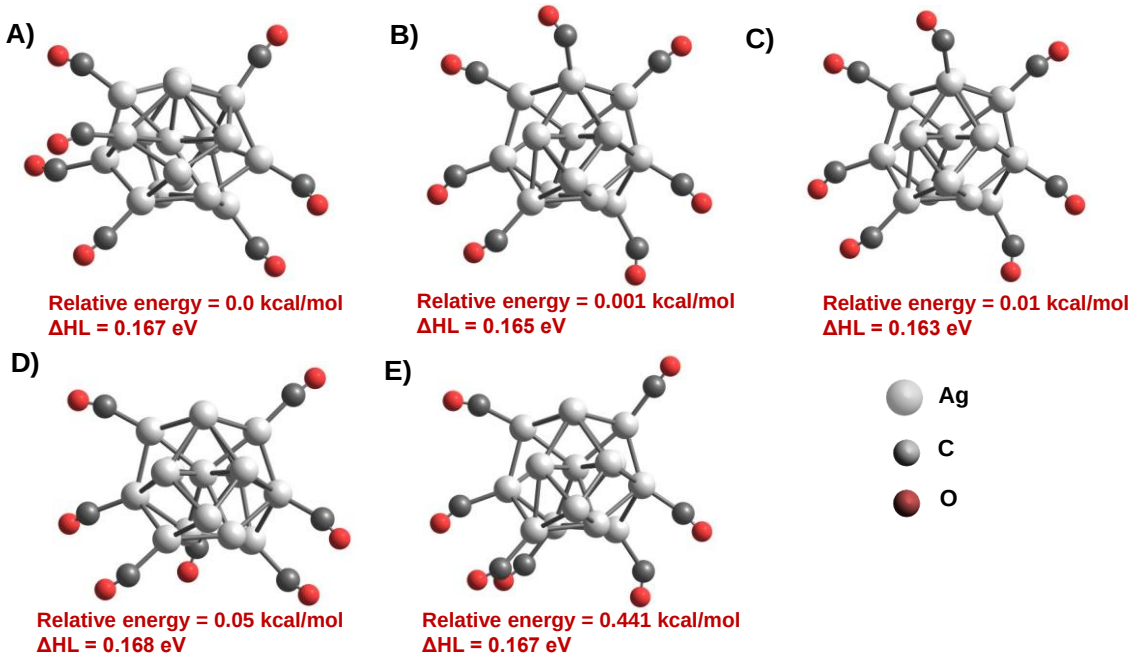

Figure S11. Six different isomeric structures of $Ag_{17}(CO)_7$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 12:

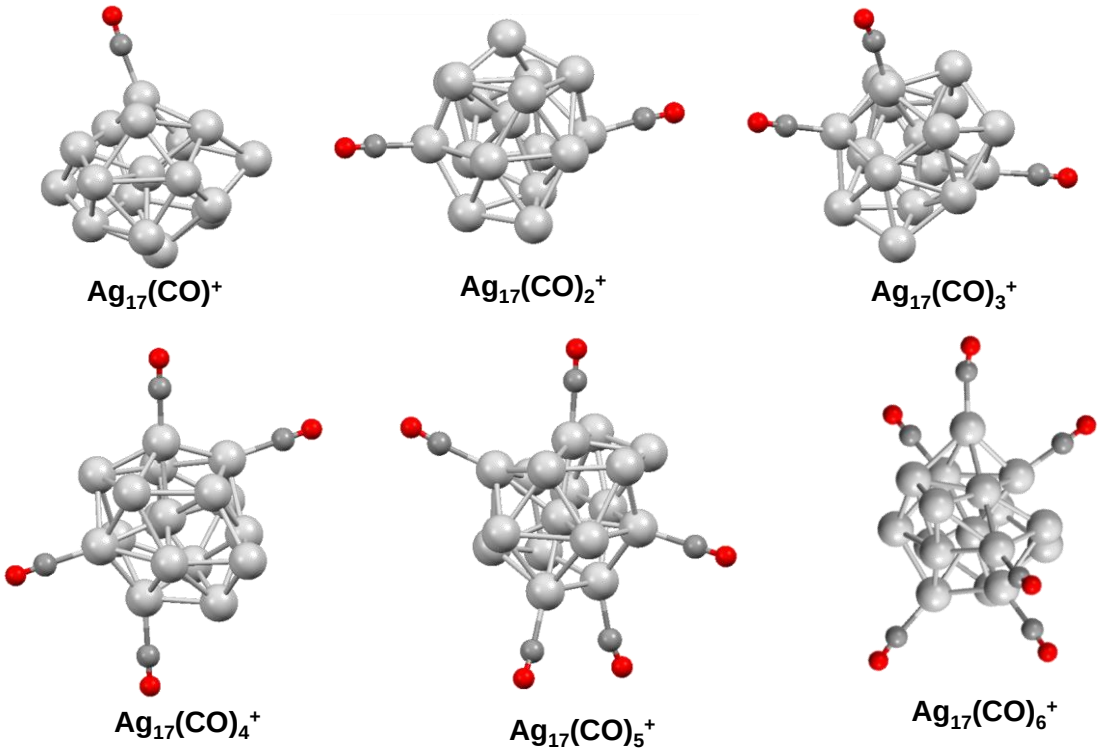

Figure S12. DFT optimized structures of $Ag_{17}(CO)_n^+$ (n = 1-6). For $Ag_{17}(CO)_7^+$, the DFT optimized structure is given in Figure 4.

Table S11. Calculated free energy change with sequential CO addition for Ag_{17} and Ag_{17}^{+}.

Cluster + CO	ΔG (kcal/mol)	Cluster + CO	ΔG (kcal/mol)
$Ag_{17}(CO)^{+}$	3.61	$Ag_{17}(CO)$	-1.39
$Ag_{17}(CO)_2^{+}$	-0.69	$Ag_{17}(CO)_2$	-4.89
$Ag_{17}(CO)_3^{+}$	-3.84	$Ag_{17}(CO)_3$	-5.54
$Ag_{17}(CO)_4^{+}$	-4.95	$Ag_{17}(CO)_4$	-7.28
$Ag_{17}(CO)_5^{+}$	-15.85	$Ag_{17}(CO)_5$	-6.64
$Ag_{17}(CO)_6^{+}$	-23.95	$Ag_{17}(CO)_6$	-6.18
$Ag_{17}(CO)_7^{+}$	-17.89	$Ag_{17}(CO)_7$	-6.65

Table S12. Calculated binding energy change with sequential CO addition for Ag_{17} and Ag_{17}^{+}.

Cluster + CO	Binding Energy (kcal/mol)	Cluster + CO	Binding Energy (kcal/mol)
$Ag_{17}(CO)^{+}$	-4.83	$Ag_{17}(CO)$	-14.18
$Ag_{17}(CO)_2^{+}$	-19.17	$Ag_{17}(CO)_2$	-12.23
$Ag_{17}(CO)_3^{+}$	-30.73	$Ag_{17}(CO)_3$	-9.18
$Ag_{17}(CO)_4^{+}$	-41.46	$Ag_{17}(CO)_4$	-10.21
$Ag_{17}(CO)_5^{+}$	-63.41	$Ag_{17}(CO)_5$	-8.75
$Ag_{17}(CO)_6^{+}$	-78.51	$Ag_{17}(CO)_6$	-7.88
$Ag_{17}(CO)_7^{+}$	-81.16	$Ag_{17}(CO)_7$	-7.82

Supporting Information 13:

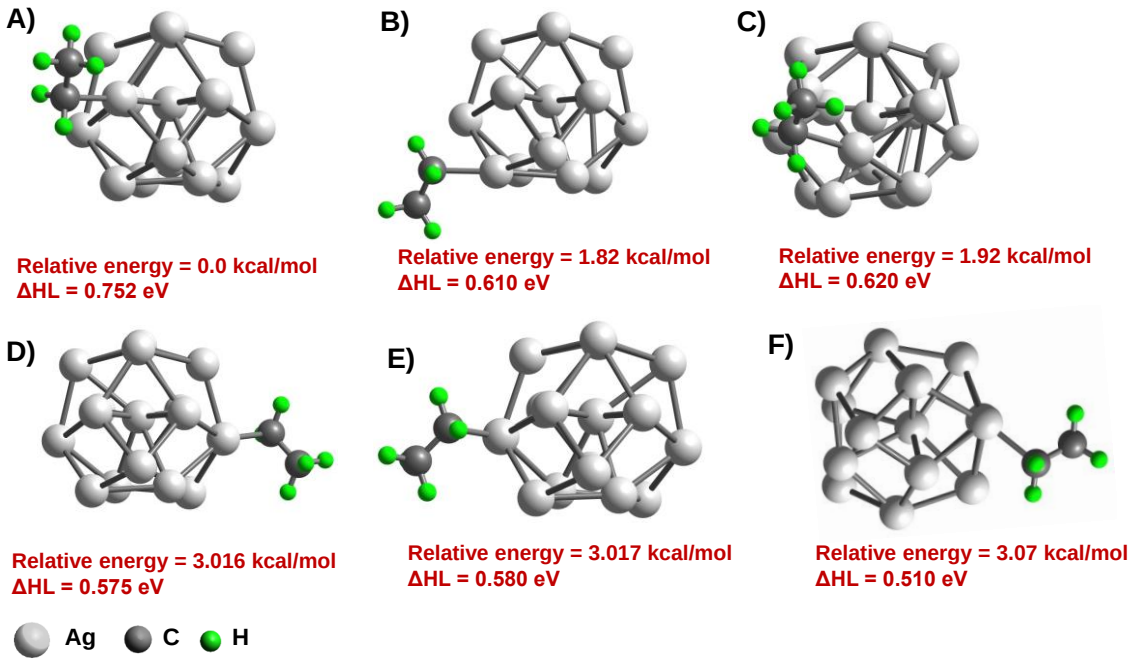

Figure S13. Six different isomeric structures of $Ag_{17}(C_2H_5)_1$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 14:

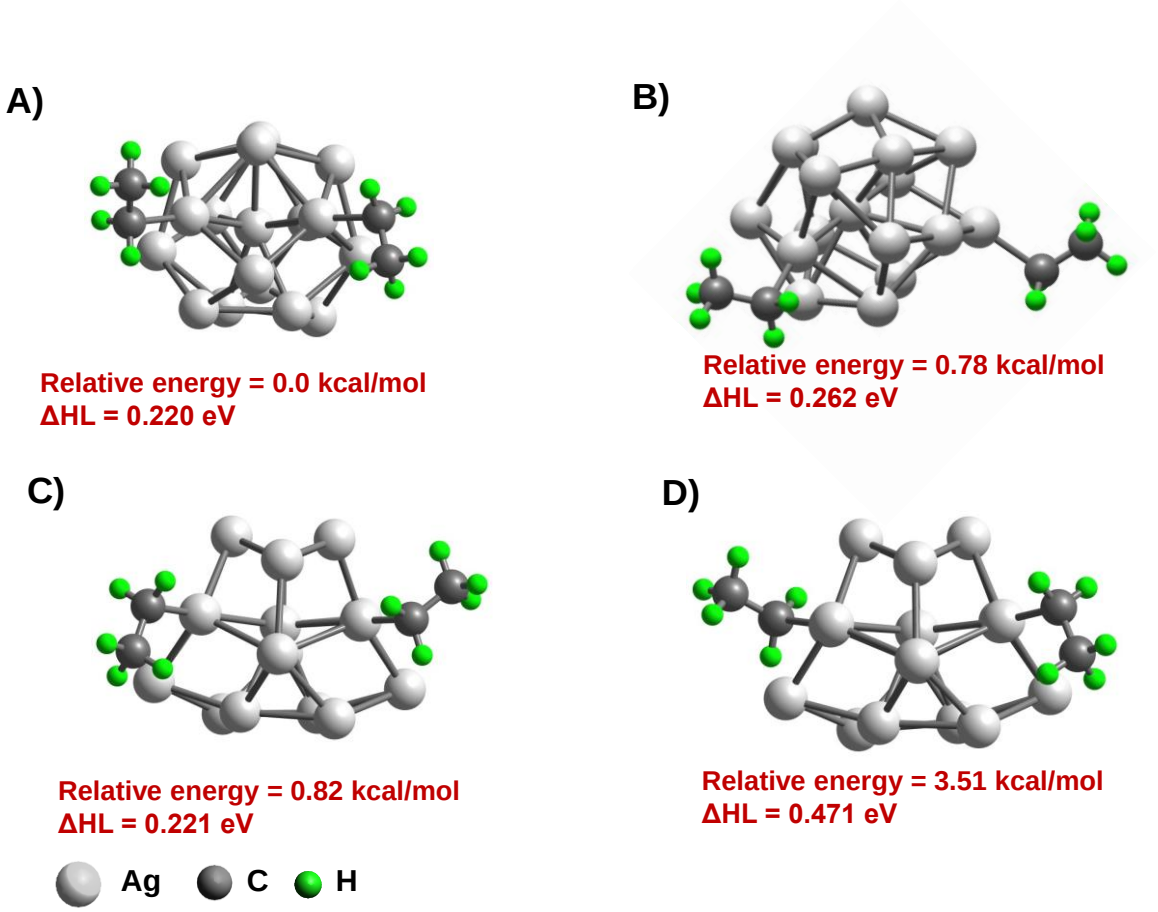

Figure S14. Four different isomeric structures of $Ag_{17}(C_2H_5)_2$. The most stable geometry is shown in A. Other structures are arranged in their decreasing stability order.

Supporting Information 15:

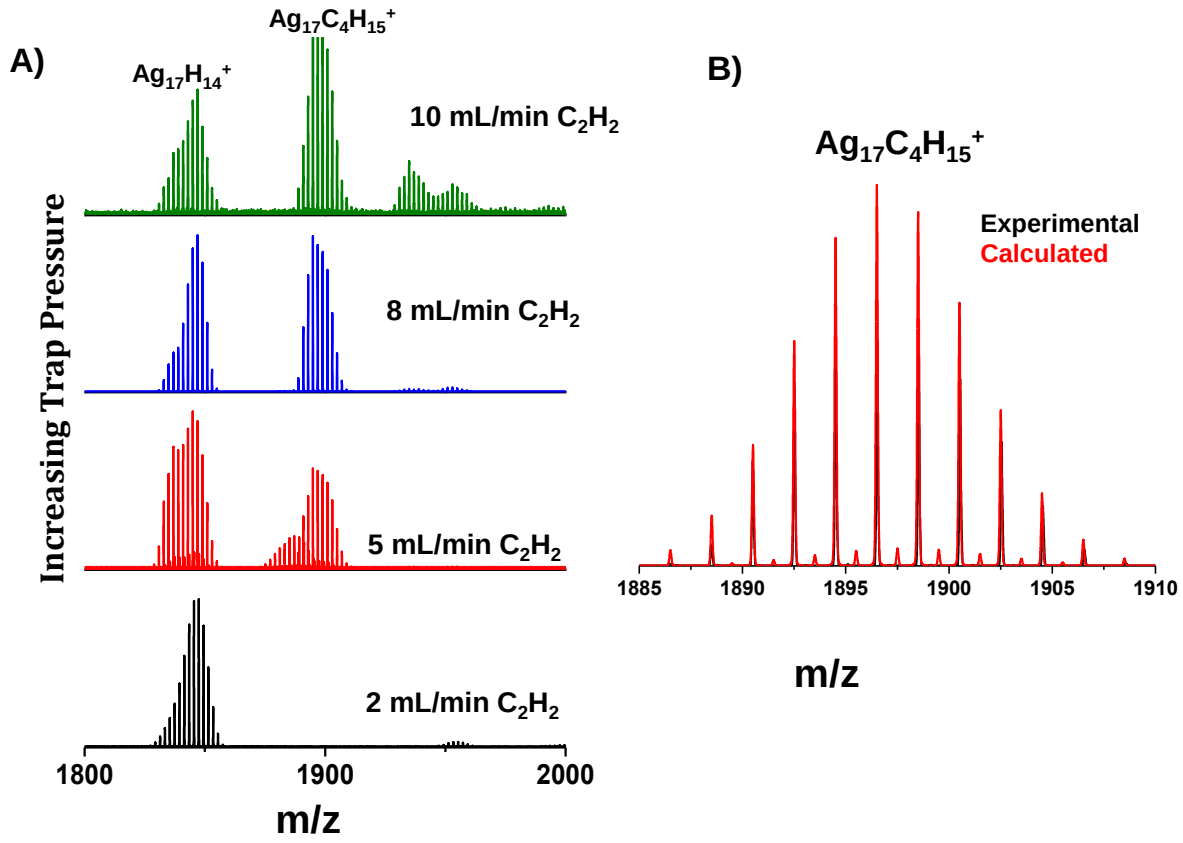

Figure S15. A) Reaction of $Ag_{17}H_{14}^+$ with different flow of C_2H_2 showing $Ag_{17}C_4H_{15}^+$ formation. B) Experimental isotope distribution of $Ag_{17}C_4H_{15}^+$ matches exactly with the calculated one.

Supporting Information 16:

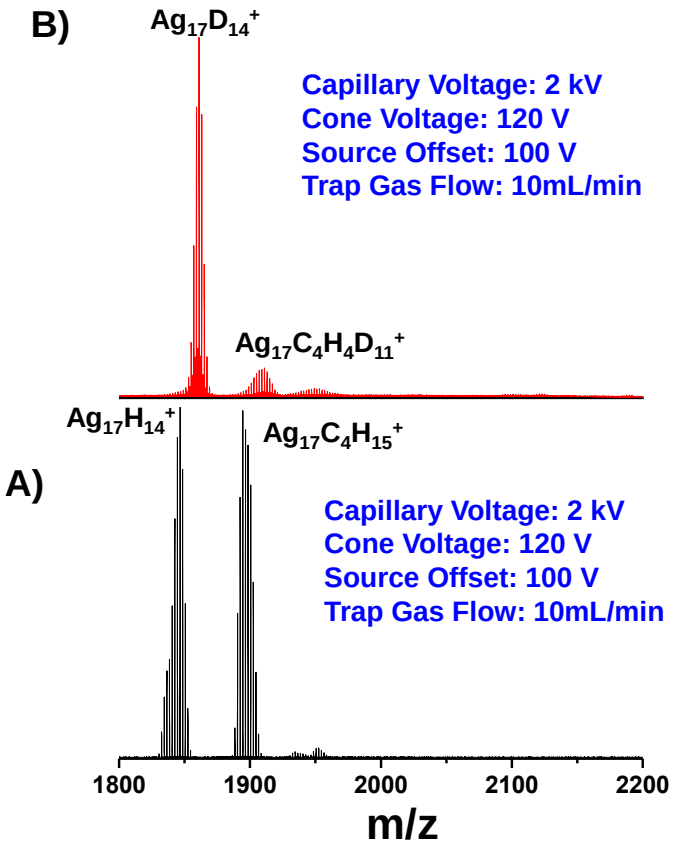

Figure S16. Comparison between reaction of C_2H_2 with A) $Ag_{17}H_{14}^+$ and B) $Ag_{17}D_{14}^+$ showing H exchange and formation of $Ag_{17}C_4H_{15}^+$ and $Ag_{17}C_4H_4D_{11}^+$. Three H sites are now replaced with two acetylene.