Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Regium Bonds between M_n Clusters (M=Cu,Ag,Au and n=2-6) and Nucleophiles NH_3 and HCN

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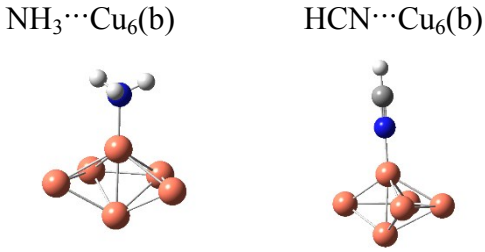


Fig S1. Optimized geometries of complexes of NH_3 and HCN with the secondary MEP maximum of Cu_6.

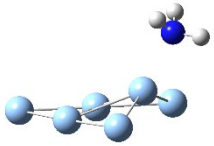


Fig S2. Optimized geometry of complex of NH_3 with Ag_6.

TABLE S1. Comparison of geometric data and MEP maxima between two levels of theory: MP2 and DFT for open-shell isolated clusters.

	MP2/aug-cc-pVDZ-PP			PBE0-D3(BJ)/def2-TVZPP		
	Cu_3	Ag_3	Au_3	Cu_3	Ag_3	Au_3
R1	2.269	2.592	2.651	2.339	2.640	2.605
R2	2.478	2.873	2.502	2.626	3.033	2.878
$V_{s,max}$ (a)	44.1	38.3	32.2	40.9	34.6	34.2
$V_{s,max}$ (b)	13.4	9.9	-3.8	15.4	13.0	9.7
	Cu_5	Ag_5	Au_5	Cu_5	Ag_5	Au_5
R1	2.328	2.646	2.593	2.417	2.720	2.669
R2	2.400	2.723	2.626	2.463	2.770	2.689
R3	2.321	2.636	2.548	2.399	2.695	2.619
R4	2.333	2.683	2.674	2.429	2.765	2.756
$V_{s,max}$ (a)	26.6	21.4	21.8	22.1	19.2	19.3
$V_{s,max}$ (b)	13.3	13.0	10.0	15.4	13.5	9.8

Table S2. MP2 calculated energy (kcal/mol) needed to distorted the indicated planar cluster to its nonplanar secondary minimum geometry.

	M_5	M_6
Cu	1.31	1.05
Ag	4.76	8.08
Au	14.07	25.66

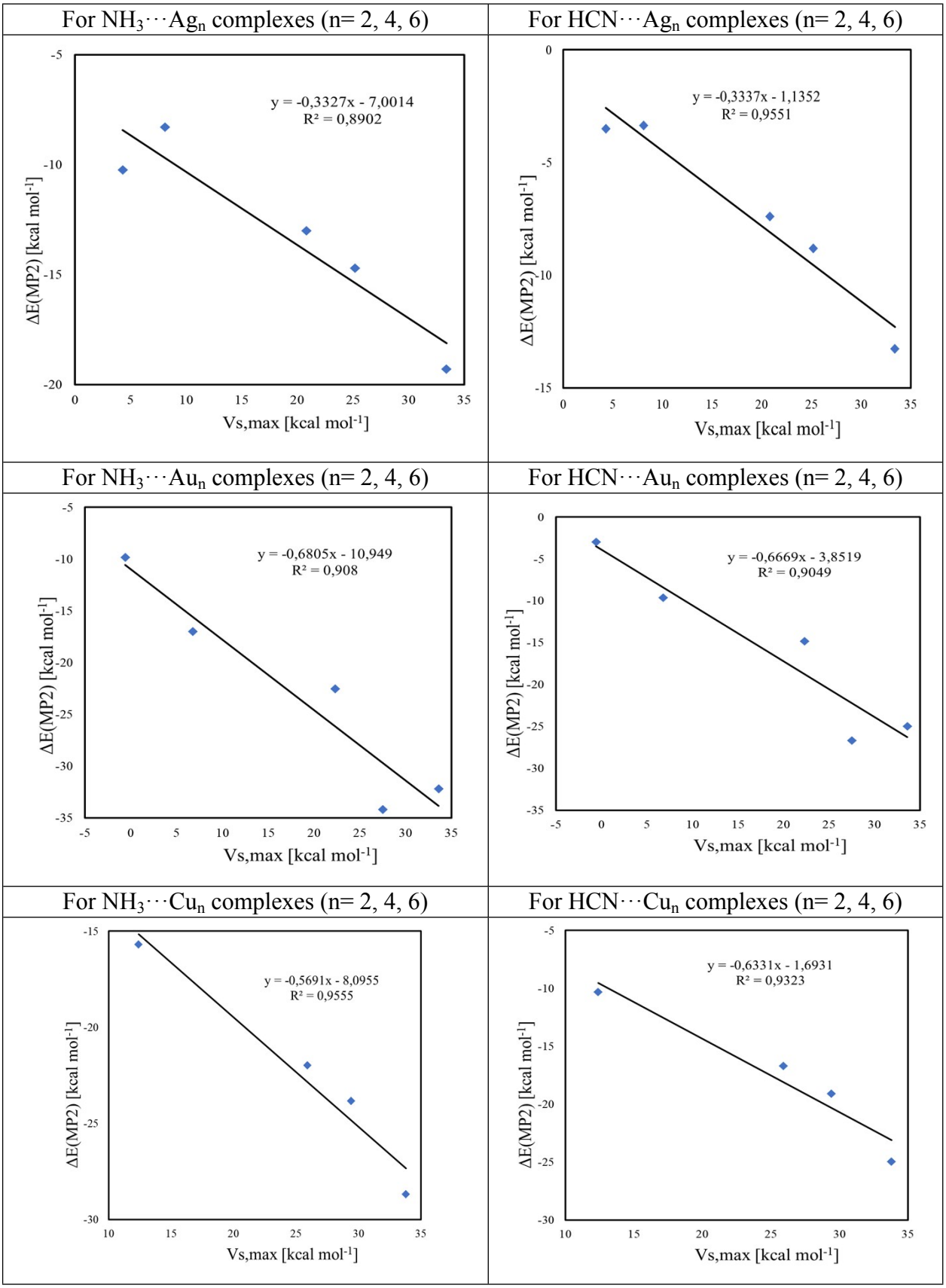


Fig. S3. Correlations between E_{int} and $V_{s,max}$ for closed-shell Mn (n= 2, 4, 6) complexes.

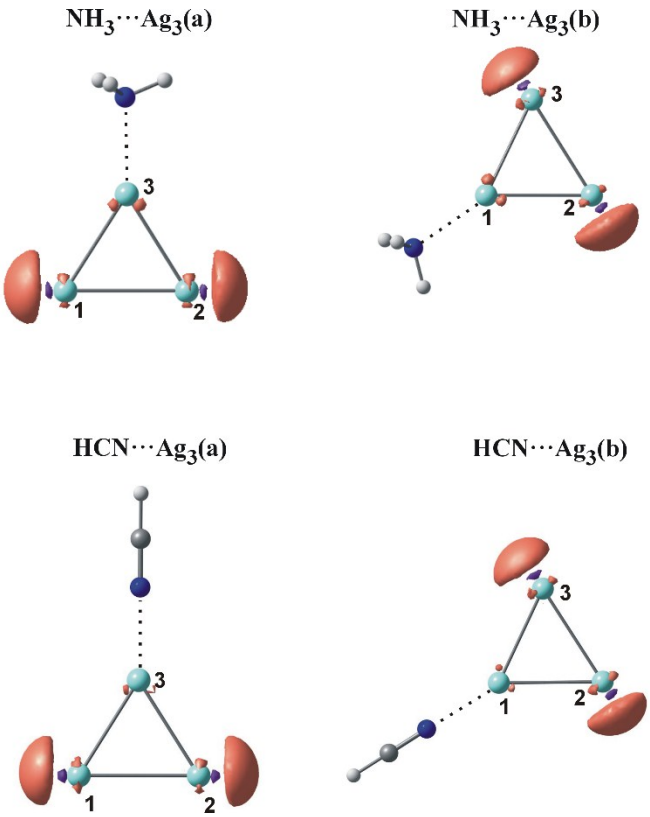


Fig. S4. DFT spin density isosurfaces (±0.006 a.u.) calculated in doublet states of Ag_3 complexes. Orange color corresponds to positive values of spin density and purple color means negative values of it. Calculations performed at the PBE0-D3(BJ)/def2-TVZPP level of theory.

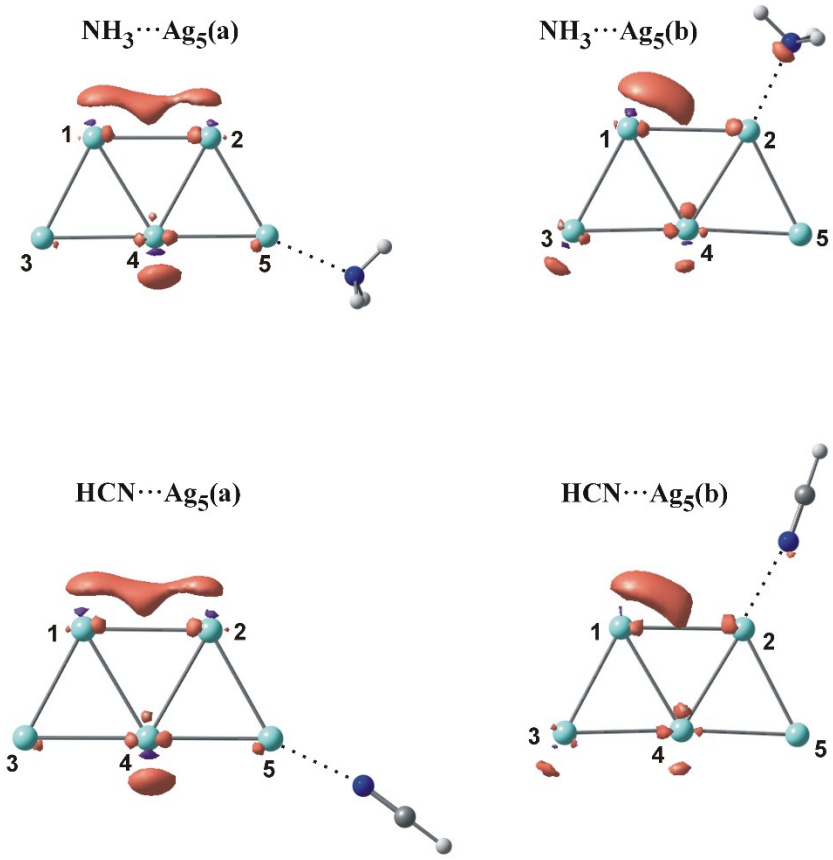


Fig. S5. DFT spin density isosurfaces (±0.006 a.u.) calculated in doublet states of Ag_5 complexes. Orange color corresponds to positive values of spin density and purple color refers to negative. Calculations performed at the PBE0-D3(BJ)/def2-TVZPP level of theory.

TABLE S3. EDA/PBE0-D3(BJ)/ZORA/TZ2P decomposition of the interaction energy of closed-shell Au_n and Cu_n complexes into Pauli repulsion (E_{Pauli}), electrostatic (E_{elstat}), orbital interaction (E_{oi}) and dispersion (E_{disp}) terms. All energies in kcal mol^{-1}. The relative values in percent express the contribution of each to the sum of all attractive energy terms.

System	E_{int}	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
$NH_3\cdots Au_2$(a)	-28.27	99.22	-90.82	71	-35.32	28	-1.35	1
$NH_3\cdots Au_4$(a)	-30.58	103.75	-93.63	70	-38.77	29	-1.93	1
$NH_3\cdots Au_4$(b)	-15.65	112.20	-90.38	71	-35.80	28	-1.66	1
$NH_3\cdots Au_6$(a)	-20.76	87.05	-75.76	70	-30.50	28	-1.55	1
$NH_3\cdots Au_6$(b)	-11.80	72.83	-57.08	67	-25.05	30	-2.50	3
$NH_3\cdots Cu_2$(a)	-24.31	70.50	-69.22	73	-24.50	26	-1.10	1
$NH_3\cdots Cu_4$(a)	-29.34	68.55	-70.27	72	-25.86	26	-1.75	2
$NH_3\cdots Cu_4$(b)	-16.05	71.40	-63.24	72	-22.94	26	-1.26	1
$NH_3\cdots Cu_6$(a)	-21.67	69.87	-65.93	72	-24.27	27	-1.35	1
$NH_3\cdots Cu_6$(b)	-22.43	67.62	-63.49	71	-24.30	27	-2.26	3

TABLE S4. Interaction energy (E_{int}) corrected for BSSE, cluster deformation energy (E_{def}), and intermolecular geometrical parameters (energies in kcal/mol, distances in Å, angles in degrees) in open-shell regium bonded M_n (M = Cu, Ag, Au and n= 3, 5) complexes with NH_3 and HCN. Data obtained at the PBE0-D3(BJ)/def2-TVZPP level of theory.

System	E_{int}	R(N···M)	System	E_{int}	R(N···M)	θ(M···N-C)
$NH_3\cdots Cu_3$(a)	-28.13	2.000	HCN···Cu_3(a)	-24.01	1.880	180.0
$NH_3\cdots Cu_3$(b)	-28.12	2.000	HCN···Cu_3(b)	-24.01	1.880	180.0
$NH_3\cdots Ag_3$(a)	-19.85	2.261	HCN···Ag_3(a)	-13.57	2.189	178.4
$NH_3\cdots Ag_3$(b)	-19.85	2.263	HCN···Ag_3(b)	-13.57	2.191	179.8
$NH_3\cdots Au_3$(a)	-32.02	2.142	HCN···Au_3(a)	-25.19	2.017	179.9
$NH_3\cdots Au_3$(b)	-31.85	2.142	HCN···Au_3(b)	-25.19	2.017	179.9
$NH_3\cdots Cu_5$(a)	-20.29	2.040	HCN···Cu_5(a)	-14.84	1.931	176.7
$NH_3\cdots Cu_5$(b)	-19.81	2.040	HCN···Cu_5(b)	-14.78	1.921	176.7
$NH_3\cdots Cu_5$(c)	-19.16	2.057	HCN···Cu_5(c)	-13.89	1.929	177.9
$NH_3\cdots Ag_5$(a)	-13.71	2.317	HCN···Ag_5(a)	-7.33	2.297	170.2
$NH_3\cdots Ag_5$(b)	-13.57	2.309	HCN···Ag_5(b)	-7.09	2.282	171.7
$NH_3\cdots Ag_5$(c)	-11.84	2.330	HCN···Ag_5(c)	-5.82	2.338	171.4
$NH_3\cdots Au_5$(a)	-21.64	2.208	HCN···Au_5(a)	-13.92	2.099	176.7
$NH_3\cdots Au_5$(b)	-21.83	2.191	HCN···Au_5(b)	-13.68	2.080	175.8
$NH_3\cdots Au_5$(c)	-17.67	2.217	HCN···Au_5(c)	-8.56	2.152	180.0

Table S5. DFT atomic spin densities [Δρ, in e] on atoms in M_3 complexes. Data obtained at the PBE0-D3(BJ)/def2-TVZPP level of theory.

	$NH_3\cdots M_3$(a)			$NH_3\cdots M_3$(b)		
Atom	**Cu_3**	**Ag_3**	**Au_3**	**Cu_3**	**Ag_3**	**Au_3**
1	0.50	0.51	0.00	0.00	0.00	0.57
2	0.50	0.49	0.50	0.50	0.52	0.43
3	0.00	0.00	0.50	0.50	0.48	0.00
	HCN···M_3(a)			HCN···M_3(b)		
Atom	**Cu_3**	**Ag_3**	**Au_3**	**Cu_3**	**Ag_3**	**Au_3**
1	0.47	0.48	-0.02	0.00	-0.01	0.50
2	0.47	0.50	0.50	0.47	0.49	0.49
3	0.00	-0.01	0.50	0.47	0.49	-0.02

Table S6. DFT atomic spin densities [Δρ, in e] on atoms in M_5 complexes. Data obtained at the PBE0-D3(BJ)/def2-TVZPP level of theory.

	$NH_3\cdots M_5$(a)			$NH_3\cdots M_5$(b)			$NH_3\cdots M_5$(c)		
Atom	**Cu_5**	**Ag_5**	**Cu_5**	**Cu_5**	**Ag_5**	**Cu_5**	**Cu_5**	**Ag_5**	**Au_5**
1	0.34	0.33	0.31	0.29	0.31	0.36	0.17	0.17	0.10
2	0.19	0.20	0.23	0.16	0.16	0.12	0.17	0.17	0.10
3	0.09	0.10	0.07	0.35	0.33	0.36	0.30	0.30	0.34
4	0.25	0.24	0.28	0.09	0.09	0.08	0.05	0.04	0.08
5	0.11	0.11	0.09	0.09	0.09	0.04	0.30	0.31	0.34
	$HCN\cdots M_5$(a)			$HCN\cdots M_5$(b)			$HCN\cdots M_5$(c)		
Atom	**Cu_5**	**Ag_5**	**Cu_5**	**Cu_5**	**Ag_5**	**Cu_5**	**Cu_5**	**Ag_5**	**Au_5**
1	0.33	0.33	0.30	0.26	0.29	0.33	0.18	0.19	0.12
2	0.20	0.21	0.24	0.15	0.17	0.12	0.18	0.19	0.12
3	0.09	0.10	0.07	0.37	0.32	0.38	0.28	0.27	0.34
4	0.26	0.23	0.28	0.08	0.09	0.08	0.04	0.06	0.06
5	0.10	0.11	0.09	0.09	0.10	0.05	0.29	0.27	0.34

TABLE S7. EDA/PBE0-D3(BJ)/ZORA/TZ2P decomposition of the interaction energy of open-shell Au_n and Cu_n complexes into Pauli repulsion (E_{Pauli}), electrostatic (E_{elstat}), orbital interaction (E_{oi}) and dispersion (E_{disp}) terms. All energies in kcal mol^{-1}. The relative values in percent express the contribution of each to the sum of all attractive energy terms.

System	E_{int}	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
$NH_3\cdots Au_3$(a)	-31.62	101.68	-93.75	70	-37.99	28	-1.56	1
$NH_3\cdots Au_3$(b)	-31.48	107.38	-95.26	69	-42.03	30	-1.57	1
$NH_3\cdots Au_5$(a)	-20.96	98.39	-80.80	68	-36.99	31	-1.56	1
$NH_3\cdots Au_5$(b)	-21.46	114.85	-86.65	64	-47.69	35	-1.97	1
$NH_3\cdots Cu_3$(a)	-30.29	68.78	-71.53	72	-26.18	26	-1.36	1
$NH_3\cdots Cu_3$(b)	-30.29	68.79	-71.54	72	-26.18	26	-1.36	1
$NH_3\cdots Cu_5$(a)	-21.75	79.29	-69.18	68	-30.51	30	-1.34	1
$NH_3\cdots Cu_5$(b)	-21.74	85.86	-70.38	65	-35.50	33	-1.71	2

TABLE S8. NBO values of E(2) for LP(N)→σ*(Ag-Ag) orbital interaction (kcal/mol) and charge transfer from Lewis base to M_n clusters (CT, me) in open-shell Ag_n complexes obtained at PBE0-D3(BJ)/def2-TVZPP level.

System	LP(N)→σ*Ag-Ag [kcal/mol]	CT[a] [me]
$NH_3\cdots Ag_3$(a)	14.11 (14.94)[b]	36
$NH_3\cdots Ag_3$(b)	14.14 (14.90)[b]	36
$NH_3\cdots Ag_5$(a)	22.07	36
$NH_3\cdots Ag_5$(b)	20.69	41
$NH_3\cdots Ag_5$(c)	10.14	39
$HCN\cdots Ag_3$(a)	12.26 (12.63)[b]	15
$HCN\cdots Ag_3$(b)	12.15 (12.58)[b]	15
$HCN\cdots Ag_5$(a)	16.56	14
$HCN\cdots Ag_5$(b)	16.05	17
$HCN\cdots Ag_5$(c)	6.89	10

[a] Charge transfer from Lewis base to the metal cluster.
[b]LP(N)→LP(Ag) .

Table S9. DFT atomic spin densities (Δρ,e) on atoms in isolated M_7 as well as its complexes. Data obtained at the PBE0-D3(BJ)/def2-TVZPP level of theory.

Atom	isolated	$NH_3\cdots Ag_7$ (a)	$NH_3\cdots Ag_7$ (b)
1	0.00	0.01	0.01
2	0.00	0.00	0.01
3	0.00	0.00	0.01
4	0.00	0.00	0.01
5	0.00	0.00	0.01
6	0.50	0.49	0.33
7	0.50	0.50	0.60

Table S10. Secondary minima for dimers of NH_3 with Ag_n clusters. Data obtained at the PBE0-D3(BJ)/def2-TVZPP level of theory. E_{int} corrected for BSSE (in kcal/mol). Distances are in Å.

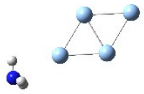
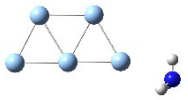
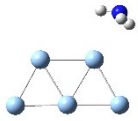
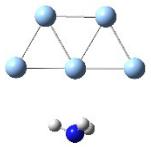
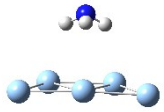
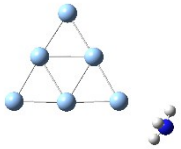
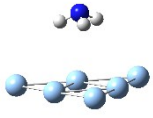
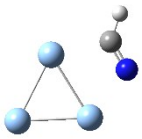
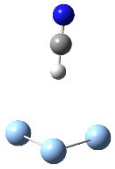
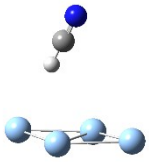
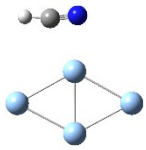
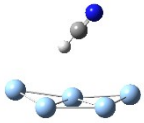
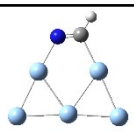
System	E_{int}	R(N···M)	structure
NH_3···Ag_2	-	-	-
NH_3···Ag_3	-	-	-
NH_3···Ag_4(c)	-2.65	3.031	
NH_3···Ag_5(d)	-4.66	2.785	
NH_3···Ag_5(e)	-4.67	2.792	
NH_3···Ag_5(f)	-3.59	3.027	
NH_3···Ag_5(g)	-3.92	3.204	
NH_3···Ag_6(c)	-4.70	2.788	
NH_3···Ag_6(d)	-3.49	3.065	
NH_3···Ag_6(e)	-4.16	3.665	

Table S11. Secondary minima for dimers of HCN with Ag_n clusters. Data obtained at the PBE0-D3(BJ)/def2-TVZPP level of theory. E_{int} corrected for BSSE (in kcal/mol). Distances are in Å.

System	E_{int}	structure
HCN···Ag_2(c)	-3.04	
HCN···Ag_3(c)	-27.55	
HCN···Ag_3(d)	-3.21	
HCN···Ag_4(c)	-3.99	
HCN···Ag_4(d)	-10.86	
HCN···Ag_5(d)	-4.61	
HCN···Ag_5(e)	-35.06	
HCN···Ag_6(c)	-5.09