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

Supplementary information for :

Metal-ligand bond in group-11 complexes and nanoclusters

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Electronic Supporting Information:

Table S1. Calculated bond angles for M-S-C in M-SR (R= SCH_3 and SC_8H_9) using PBE and BEEF-vdW.

M-SR	PBE	BEEF-vdW
Cu-SCH_3	105.5	105.3
Ag-SCH_3	105.5	105.2
Au-SCH_3	104.0	104.8
Cu-SC_8H_9	105.5	104.4
Ag-SC_8H_9	104.51	104.6
Au-SC_8H_9	102.48	102.2

Table S2. Calculated bond lengths (Å) of M-L complexes and binding energy (eV) using PBE and BEEF-vdW.

M-L	PBE		BEEF-vdW	
	ΔE (eV)	Bond length(Å)	ΔE (eV)	Bond length (Å)
Cu-SCH_3	-1.22	2.09	−1.08	2.12
Ag-SCH_3	-0.62	2.31	−0.55	2.36
Au-SCH_3	-0.97	2.25	−0.776	2.29
Cu-SC_8H_9	-1.28	2.09	−1.09	2.12
Ag-SC_8H_9	-0.69	2.31	−0.55	2.37
Au-SC_8H_9	-1.02	2.25	−0.786	2.29
Cu-PPh_3	-1.07	2.22	−0.75	2.29
Ag-PPh_3	-0.59	2.51	−0.40	2.65
Au-PPh_3	-1.35	2.35	−0.97	2.41
Cu-NHC^{Me}	-1.54	1.92	−1.14	1.96
Ag-NHC^{Me}	-0.90	2.18	−0.58	2.26
Au-NHC^{Me}	-1.63	2.08	−1.18	2.13
Cu-NHC^{Et}	-1.54	1.91	−1.16	1.96
Ag-NHC^{Et}	-0.90	2.17	−0.59	2.27
Au-NHC^{Et}	-1.65	2.08	−1.201	2.15
Cu-NHC^{iPr}	-1.55	1.92	−1.18	1.98
Ag-NHC^{iPr}	-0.90	2.18	−0.63	2.28
Au-NHC^{iPr}	-1.64	2.08	−1.216	2.16
Cu-NHC^{Bn}	-1.60	1.92	-1.2	1.96
Ag-NHC^{Bn}	-0.96	2.17	−0.61	2.27
Au-NHC^{Bn}	-1.69	2.09	−1.23	2.39
Cu-CCMe	-0.67	1.79	-0.48	1.81
Ag-CCMe	0.06	1.98	0.20	2.03
Au-CCMe	-0.37	1.91	-0.11	1.94
Cu-CCPh	-0.71	1.79	-0.52	1.82
Ag-CCPh	0.02	1.99	0.16	2.03
Au-CCPh	-0.40	1.91	-0.12	1.94

Figure S1. Projected density of states for (a) Cu-PPh_3 (b) Ag-PPh_3 and (c) Au-PPh_3.

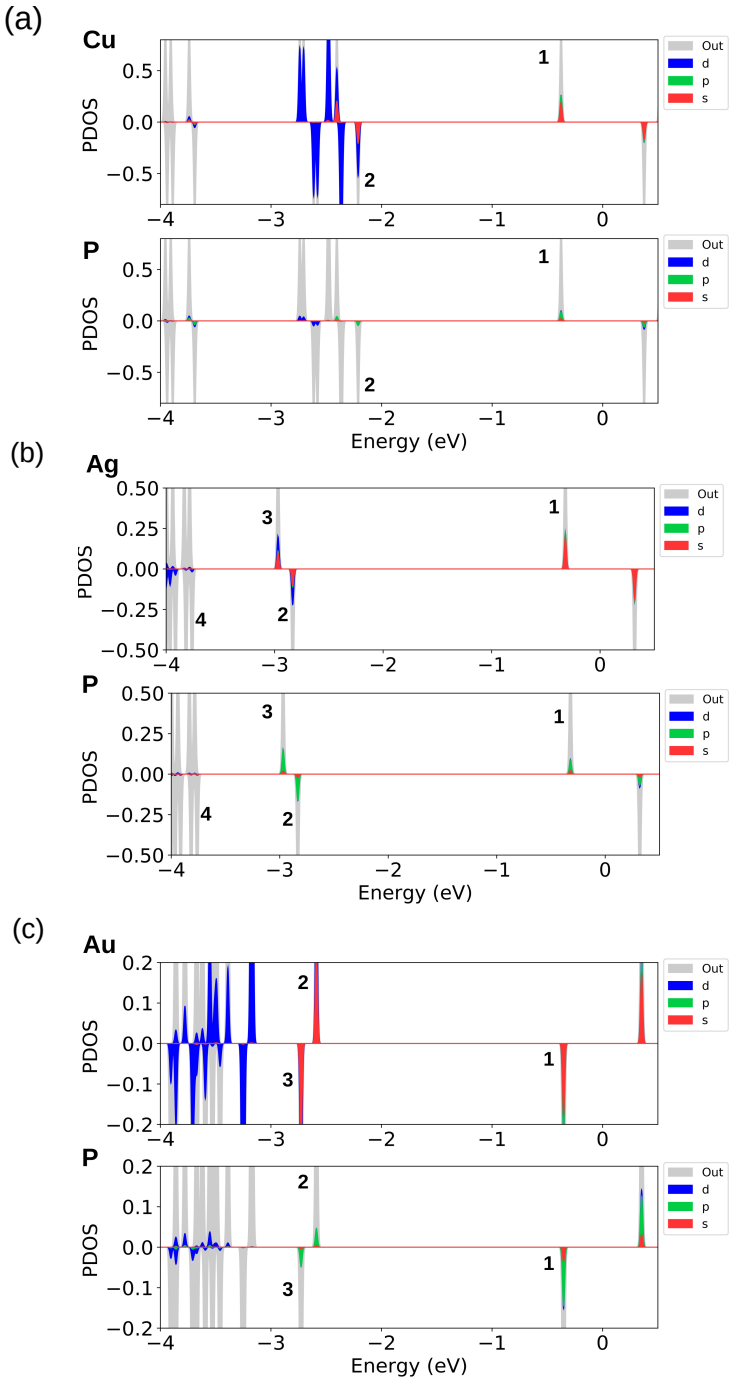


Figure S2. Projected density of states for (a) Cu-NHC^{Me} (b) Ag-NHC^{Me} and (c) Au- NHC^{Me}.

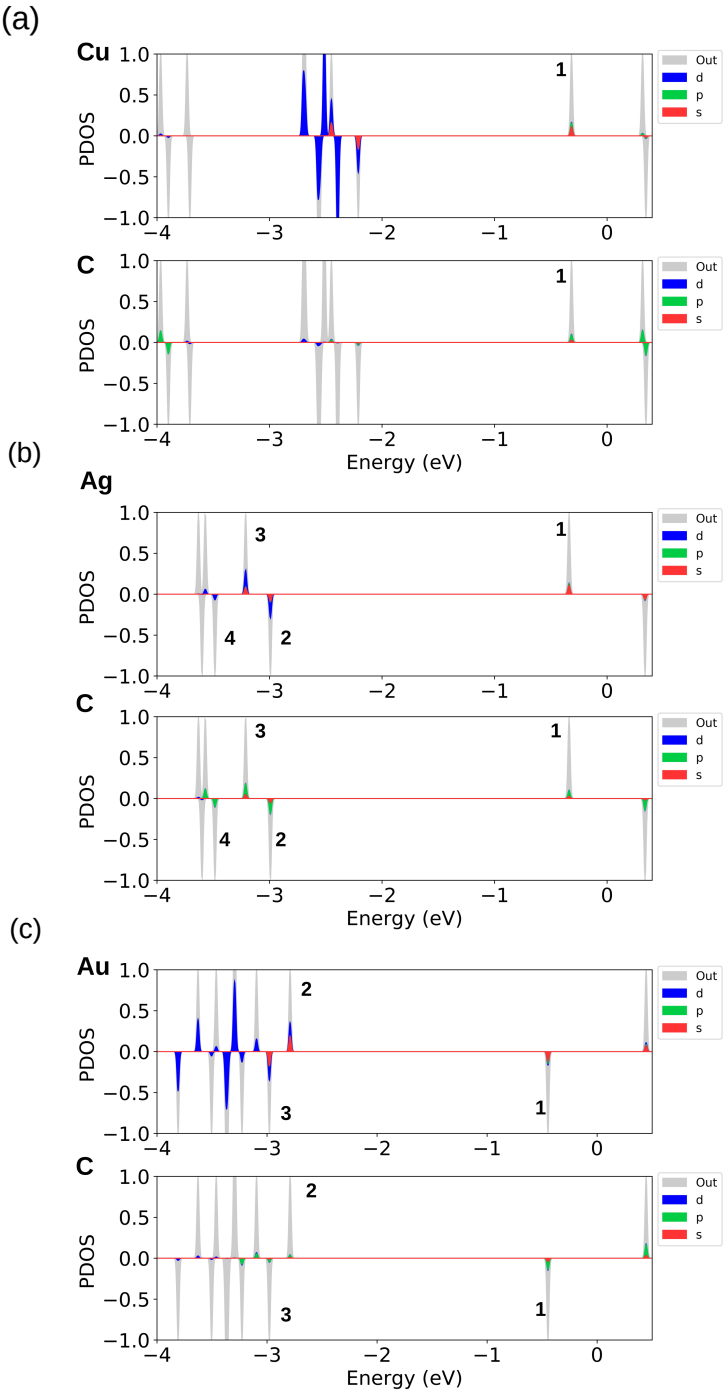


Figure S3.
(a) Cu-CCMe (b) Ag-CCMe, and (c) Au-CCMe

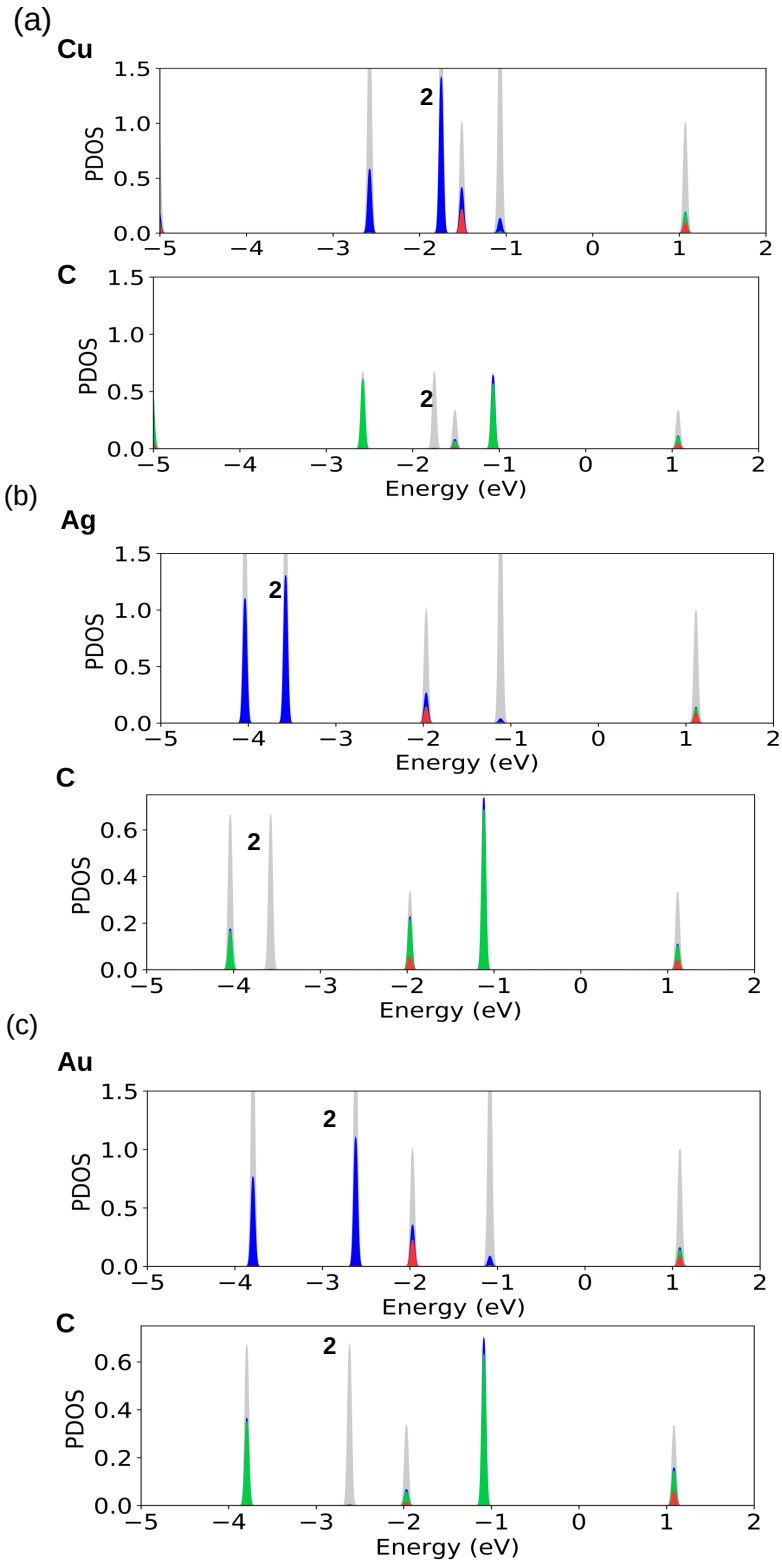
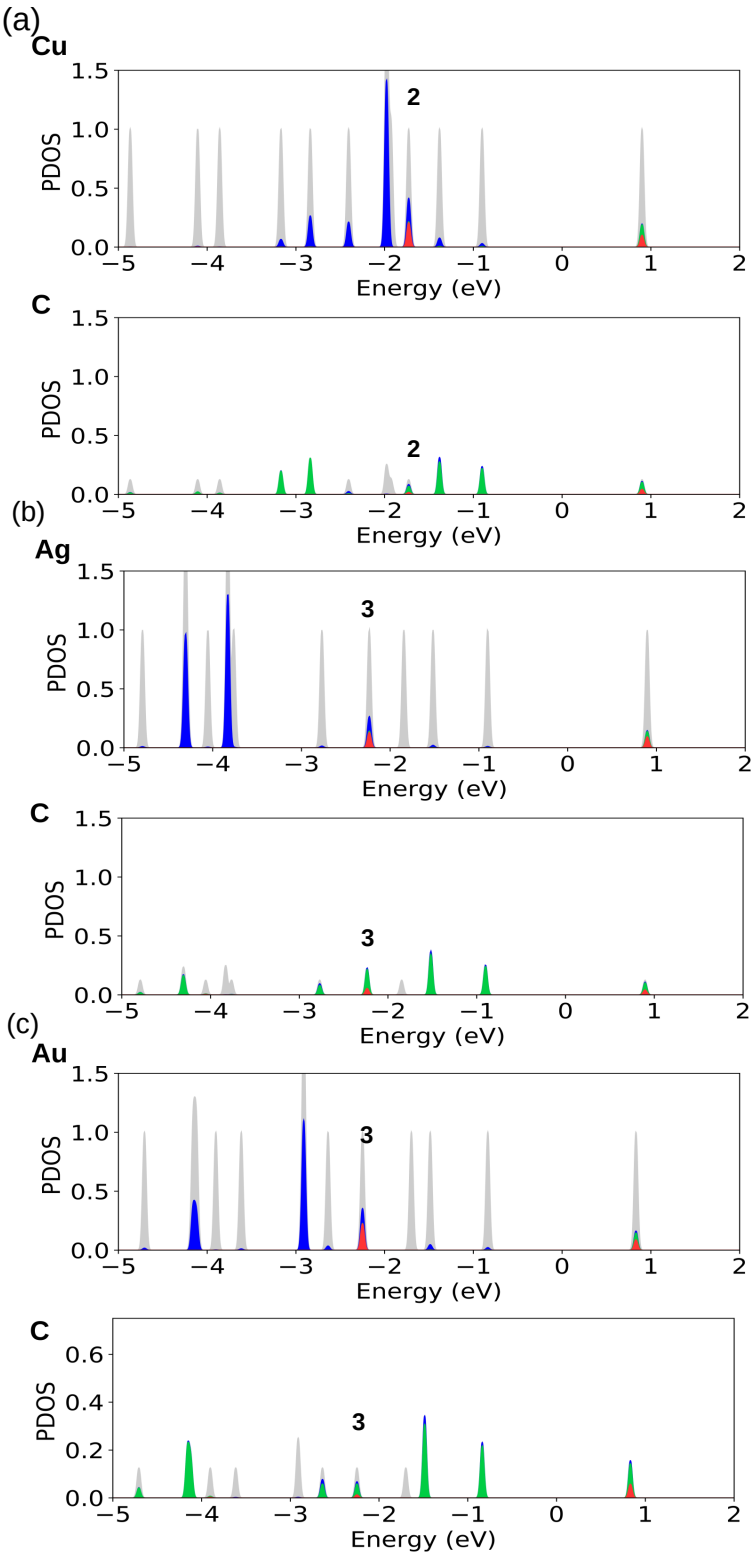


Figure S4.
(a) Cu-CCPh (b) Ag-CCPh, (c) Au-CCPh



The numbers 2 and 3 in the Figures S3 and 4 refer to HOMO-2 and HOMO-3.

Table S3. Bader charges for M-L complexes optimized with PBE.

M-L	M Total Q (e) N=1	S Total Q (e) N=1	C,H Total Q (e) N= 4
Cu-SCH_3	0.27	-0.27	-0.001
Ag-SCH_3	0.26	-0.22	-0.04
Au-SCH_3	0.03	-0.0006	-0.034
	M Total Q (e) N=1	S Total Q (e) N=1	C,H Total Q (e) N= 17
Cu-SC_8H_9	0.27	-0.30	0.03
Ag-SC_8H_9	0.26	-0.27	0.01
Au-SC8H_9	0.03	-0.08	0.05
	M Total Q (e) N=1	P Total Q (e) N=1	C,H Total Q (e) N= 33
Cu-PPh_3	-0.16	1.55	-1.39
Ag-PPh_3	-0.19	1.54	-1.35
Au-PPh_3	-0.37	1.67	-1.31
	M Total Q (e) N=1	C Total Q (e) N=1	C,H, N Total Q (e) N= 20
Cu-NHC^{Me}	-0.11	0.67	-0.57
Ag-NHC^{Me}	-0.14	0.73	-0.59
Au-NHC^{Me}	-0.27	0.82	-0.54
	M Total Q (e) N=1	C Total Q (e) N=1	C,H, N Total Q (e) N= 26
Cu-NHC^{Et}	-0.12	0.71	-0.59
Ag-NHC^{Et}	-0.16	0.69	-0.53
Au-NHC^{Et}	-0.27	0.77	-0.50
	M Total Q (e) N=1	C Total Q (e) N=1	C,H, N Total Q (e) N= 32
Cu-NHC^{iPr}	-0.12	0.69	-0.57

Ag-NHC^{iPr}	-0.16	0.75	-0.59
Au-NHC^{iPr}	-0.29	0.84	-0.55
	M Total Q (e) N=1	C Total Q (e) N=1	C,H, N Total Q (e) N= 40
Cu-NHC^{Bn}	-0.08	0.70	-0.62
Ag-NHC^{Bn}	-0.14	0.74	-0.60
Au-NHC^{Bn}	-0.27	0.84	-0.57
	M Total Q (e) N=1	C Total Q (e) N=1	C,H Total Q (e) N= 5
Cu-CCMe	0.38	-0.11	-0.27
Ag-CCMe	0.37	-0.35	-0.016
Au-CCMe	0.16	0.09	-0.25
	M Total Q (e) N=1	C Total Q (e) N=1	C,H Total Q (e) N= 12
Cu-CCPh	0.40	0.09	-0.49
Ag-CCPh	0.39	-0.42	0.03
Au-CCPh	0.18	0.09	-0.27

Table S4. Calculated bond lengths (Å) of M-L_1 and M-L_2 in the L_1-M-L_2 complexes and using PBE.

L_1-M-L_2	Bond length (Å)	
	M-L_1	M-L_2
NHC^{Bn}-Cu-CCPh	1.89	1.84
NHC^{Bn}-Ag-CCPh	2.07	2.00
NHC^{Bn}-Au-CCPh	2.04	1.98
PPh_3-Cu-CCPh	2.18	1.84
PPh_3-Ag-CCPh	2.36	2.02
PPh_3-Au-CCPh	2.31	1.99

Table S5. Bader charges of L_1-M-L_2 complexes. Labelling: L_x: NHC/PPh_3 groups without the terminal atom A_1 (C or P) binding the metal atom M, A_1: terminal atom of NHC/PPh_3 binding the metal atom, M: metal atom (Cu,Ag,Au) in the center, A_2: terminal atom C of the alkynyl group binding the metal atom M, L_y: alkynyl group without the terminal atom A_2. Charges are given in |e| units.

L_1-M-L_2 Structure	L_x	L_x - **A_1** - M	M	M – **A_2** – L_y	L_y
NHC^{Bn}-Cu-CCPh	-0.51	+0.71	+0.37	-0.13	-0.43
NHC^{Bn}-Ag-CCPh	-0.46	+0.72	+0.27	-0.45	-0.08
NHC^{Bn}-Au-CCPh	-0.47	+0.78	+0.13	+0.05	-0.48
PPh_3-Cu-CCPh	-1.15	+1.42	+0.26	-0.27	-0.26
PPh_3-Ag-CCPh	-0.93	+1.18	+0.30	-0.46	-0.09
PPh_3-Au-CCPh	-1.13	+1.58	+0.01	-0.60	+0.14

Table S6. Calculated average bond lengths (Å) for M(center)-M(peripheral) and M-Br in $[TM_{13}L_6Br_6]^-$ clusters using PBE and BEEF-vdW.

$[M_{13}L_6Br_6]^-$	PBE		BEEF-vdW	
	M(c)-M(p)	M-Br	M(c)-M(p)	M-Br
$[Cu_{13}(PPh_3)_6Br_6]^-$	1.88	2.31	2.54	2.35
$[Ag_{13}(PPh_3)_6Br_6]^-$	2.81	2.53	2.88	2.58
$[Au_{13}(PPh_3)_6Br_6]^-$	2.86	2.51	2.90	2.55
$[Cu_{13}(NHC^{Me})_6Br_6]^-$	1.87	2.33	2.53	2.36
$[Ag_{13}(NHC^{Me})_6Br_6]^-$	2.80	2.56	2.86	2.60
$[Au_{13}(NHC^{Me})_6Br_6]^-$	2.82	2.51	2.87	2.56
$[Cu_{13}(NHC^{Et})_6Br_6]^-$	2.49	2.33	-	-
$[Ag_{13}(NHC^{Et})_6Br_6]^-$	2.80	2.54	-	-
$[Au_{13}(NHC^{Et})_6Br_6]^-$	2.83	2.51	-	-
$[Cu_{13}(NHC^{iPr})_6Br_6]^-$	2.51	2.33	-	-
$[Ag_{13}(NHC^{iPr})_6Br_6]^-$	2.81	2.55	-	-
$[Au_{13}(NHC^{iPr})_6Br_6]^-$	2.82	2.52	-	-
$[Cu_{13}(NHC^{Bn})_6Br_6]^-$	2.50	2.32	-	-
$[Ag_{13}(NHC^{Bn})_6Br_6]^-$	2.80	2.54	-	-
$[Au_{13}(NHC^{Bn})_6Br_6]^-$	2.84	2.51	-	-

Figure S5. Projected density of states for (a) $[M_{13}(PPh_3)_6Br_6]^-$ and (b) $[M_{13}(NHC^{Me})_6Br_6]^-$ (M= Cu, Ag, Au).

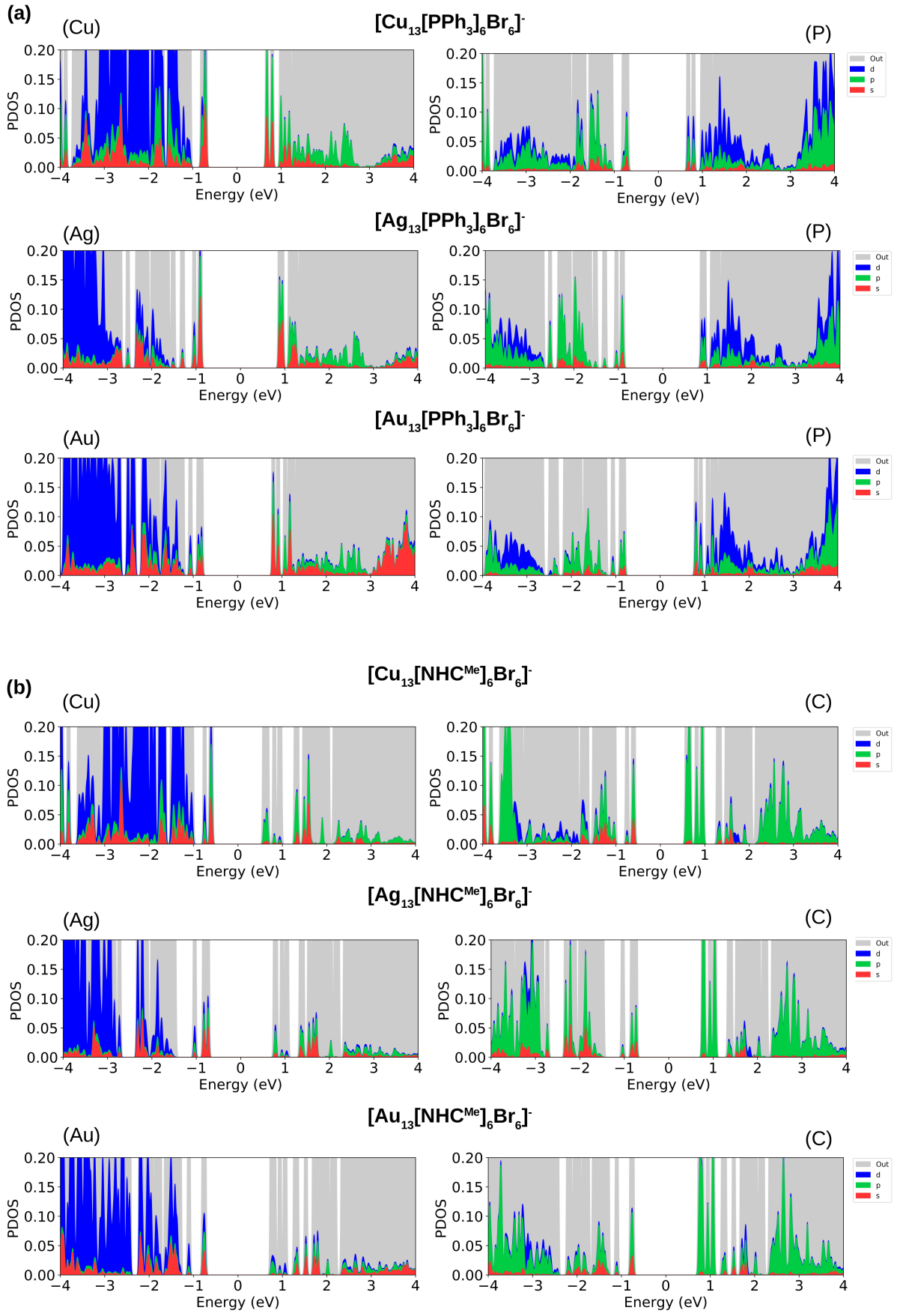


Table S7. Bader charges for $[M_{13}L_6Br_6]^-$ clusters optimized with PBE (M_L is refering to the coinage metals bonded to ligand groups and M_{Br} is the coinage metals bonded to Br atoms).

	M_L Total Q (e) N=6	M_{center} Total Q (e) N=1	M_{Br} Total Q (e) N=6	P Total Q (e) N=6	C,H Total Q (e) N= 198	Br Total Q (e) N=6
$[Cu_{13}(PPh_3)_6Br_6]^-$	0.77	-0.13	0.96	8.39	-7.61	-3.38
$[Ag_{13}(PPh_3)_6Br_6]^-$	0.53	-0.10	0.84	8.82	-7.64	-3.46
$[Au_{13}(PPh_3)_6Br_6]^-$	-0.28	-0.15	0.23	9.52	-7.46	-2.87
	M_L Total Q (e) N=6	M_{center} Total Q (e) N=1	M_{Br} Total Q (e) N=6	C Total Q (e) N=6	C,H, N Total Q (e) N= 120	Br Total Q (e) N=6
$[Cu_{13}(NHC^{Me})_6Br_6]^-$	1.18	-0.18	0.94	4.24	-3.55	-3.62
$[Ag_{13}(NHC^{Me})_6Br_6]^-$	0.82	-0.12	0.82	4.64	-3.46	-3.71
$[Auu_{13}(NHC^{Me})_6Br_6]^-$	0.37	-0.20	0.24	4.84	-3.18	-3.06
	M_L Total Q (e) N=6	M_{center} Total Q (e) N=1	M_{Br} Total Q (e) N=6	C Total Q (e) N=6	C,H, N Total Q (e) N= 156	Br Total Q (e) N=6
$[Cu_{13}(NHC^{Et})_6Br_6]^-$	1.18	-0.18	0.92	4.35	-3.75	-3.53
$[Ag_{13}(NHC^{Et})_6Br_6]^-$	0.83	-0.13	0.81	4.62	-3.54	-3.60
$[Au_{13}(NHC^{Et})_6Br_6]^-$	0.34	-0.21	0.23	4.87	-3.26	-2.98
	M_L Total Q (e) N=6	M_{center} Total Q (e) N=1	M_{Br} Total Q (e) N=6	C Total Q (e) N=6	C,H, N Total Q (e) N= 192	Br Total Q (e) N=6
$[Cu_{13}(NHC^{iPr})_6Br_6]^-$	1.22	-0.16	0.86	4.04	-3.47	-3.49
$[Ag_{13}(NHC^{iPr})_6Br_6]^-$	0.83	-0.12	0.82	4.64	-3.58	-3.58
$[Au_{13}(NHC^{iPr})_6Br_6]^-$	0.34	-0.19	0.23	4.96	-3.36	-2.97
	M_L Total Q (e) N=6	M_{center} Total Q (e) N=1	M_{Br} Total Q (e) N=6	C Total Q (e) N=6	C,H, N Total Q (e) N= 240	Br Total Q (e) N=6
$[Cu_{13}(NHC^{Bn})_6Br_6]^-$	1.18	-0.18	0.92	4.14	-3.58	-3.49
$[Ag_{13}(NHC^{Bn})_6Br_6]^-$	0.83	-0.12	0.80	4.60	-3.56	-3.55
$[Au_{13}(NHC^{Bn})_6Br_6]^-$	0.34	-0.20	0.23	4.84	-3.27	-2.94