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Electronic Supporting Information

Cluster transformation of $[Cu_3(\mu_3\text{-}H)(\mu_3\text{-}BH_4)((PPh_2)_2NH)_3](BF_4)$ to $[Cu_3(\mu_3\text{-}H)(\mu_2,\mu_1\text{-}S_2CH)((PPh_2)_2NH)_3](BF_4)$ via reaction with CS_2. X-ray structural characterisation and reactivity of cationic clusters explored by multistage mass spectrometry and computational studies.

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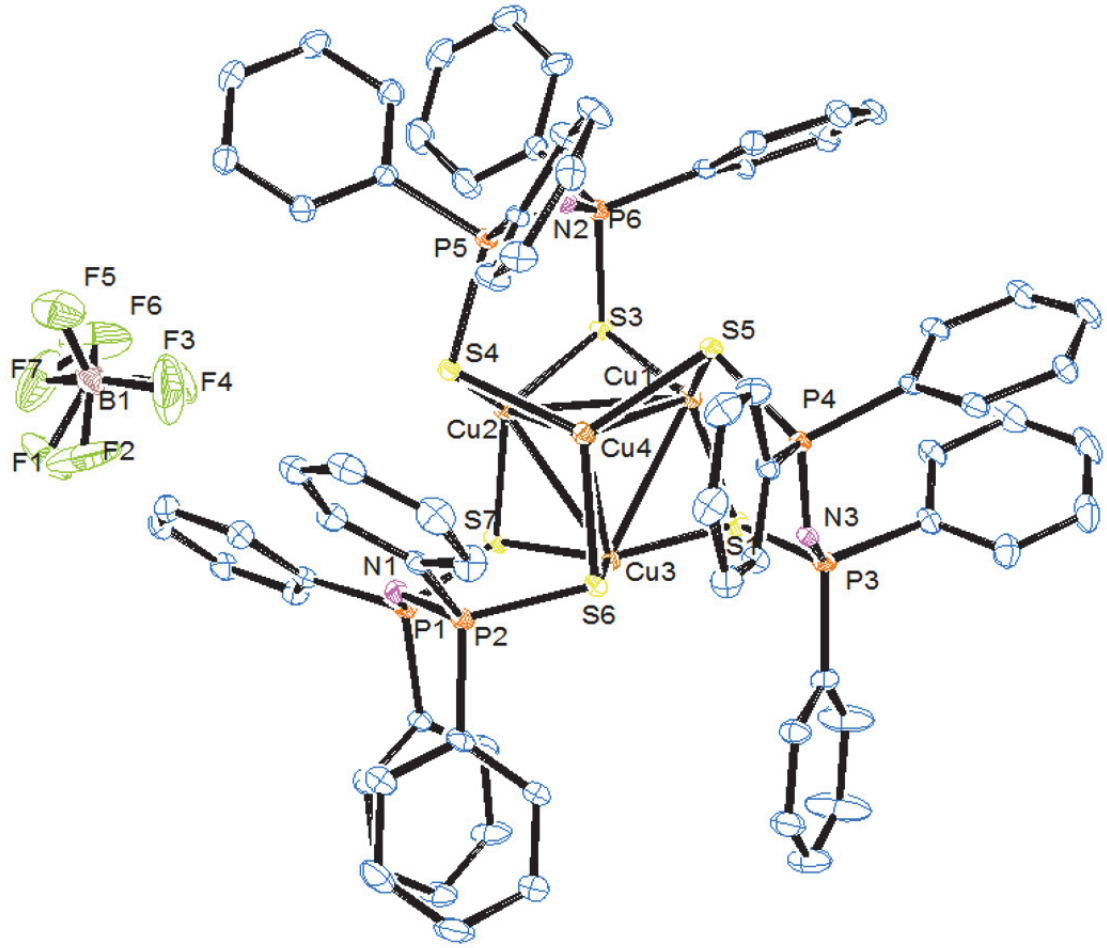


Figure S1: ORTEP-3 representation of the cluster $[Cu_4(L^{Ph}\text{-}H+2S)_3](BF_4)$ (**3.BF$_4$**). Displacement ellipsoids are set at the 30% probability level.

Table S1: Crystal data and structure refinement for cluster **3.BF$_4$**

Identification code	LiJ170519
Empirical formula	$C_{4.41}H_{4.09}B_{0.06}Cl_{0.45}Cu_{0.23}F_{0.23}N_{0.17}P_{0.35}S_{0.35}$
Formula weight	117.18
Temperature/K	130.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.6628(5)
b/Å	18.9702(14)
c/Å	30.924(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8601.7(11)
Z	69
ρ_{calc}g/cm^3	1.561
μ/mm^{-1}	6.186
F(000)	4092.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.376 to 154.066
Index ranges	$-17 \le h \le 6$, $-19 \le k \le 22$, $-38 \le l \le 24$

Reflections collected	26830
Independent reflections	11696 [R_{int} = 0.0290, R_{sigma} = 0.0390]
Data/restraints/parameters	11696/0/890
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0587, wR_2 = 0.1536
Final R indexes [all data]	R_1 = 0.0675, wR_2 = 0.1613
Largest diff. peak/hole / e $Å^{-3}$	1.32/-0.91

Table S2: Bond distances of X-ray crystallography for cluster **3.BF$_4$**.

Cu1	Cu2	2.8735(11)	C21	C22	1.3900
Cu1	Cu3	2.7763(12)	C21	C20	1.3900
Cu1	Cu4	2.7331(13)	C22	C23	1.3900
Cu1	S1	2.2506(15)	C23	C24	1.3900
Cu1	S5	2.2673(16)	C24	C19	1.3900
Cu1	S3	2.2633(14)	C19	C20	1.3900
Cu2	Cu3	2.8317(10)	C68	C69	1.3900
Cu2	Cu4	2.7840(11)	C68	C67	1.3900
Cu2	S4	2.2491(16)	C69	C70	1.3900
Cu2	S3	2.2665(17)	C70	C71	1.3900
Cu2	S7	2.2656(15)	C71	C72	1.3900
Cu3	Cu4	2.7958(11)	C72	C67	1.3900
Cu3	S1	2.2624(16)	C38	C39	1.3900
Cu3	S6	2.2597(16)	C38	C37	1.3900
Cu3	S7	2.2546(14)	C39	C40	1.3900
Cu4	S4	2.2679(13)	C40	C41	1.3900
Cu4	S5	2.2830(15)	C41	C42	1.3900
Cu4	S6	2.2663(14)	C42	C37	1.3900
S4	P5	2.0485(19)	C46	C47	1.3900
P5	N2	1.580(5)	C46	C45	1.3900
P5	C67	1.822(3)	C47	C48	1.3900
P5	C37	1.809(2)	C48	C43	1.3900
S1	P3	2.0475(18)	C43	C44	1.3900
P6	S3	2.0548(18)	C44	C45	1.3900
P6	N2	1.583(5)	C11	C10	1.3900
P6	C19	1.801(3)	C11	C12	1.3900
P6	C25	1.808(3)	C10	C9	1.3900
P2	S6	2.0507(19)	C9	C8	1.3900
P2	N1	1.599(4)	C8	C7	1.3900
P2	C55	1.796(3)	C7	C12	1.3900
P2	C49	1.815(3)	C29	C28	1.3900
S5	P4	2.0481(16)	C29	C30	1.3900
S7	P1	2.055(2)	C28	C27	1.3900
P1	C31	1.792(3)	C27	C26	1.3900
P1	N1	1.585(5)	C26	C25	1.3900
P1	C43	1.813(3)	C25	C30	1.3900
P4	N3	1.589(4)	C53	C54	1.3900
P4	C61	1.802(3)	C53	C52	1.3900

P4	C13	1.814(3)	C54	C49	1.3900
P3	N3	1.591(5)	C49	C50	1.3900
P3	C7	1.809(3)	C50	C51	1.3900
P3	C1	1.804(3)	C51	C52	1.3900
C36	C35	1.3900	C6	C5	1.3900
C36	C31	1.3900	C6	C1	1.3900
C35	C34	1.3900	C5	C4	1.3900
C34	C33	1.3900	C4	C3	1.3900
C33	C32	1.3900	C3	C2	1.3900
C32	C31	1.3900	C2	C1	1.3900
C56	C57	1.3900	Cl6	C76	1.760(8)
C56	C55	1.3900	F5	B1	1.363(10)
C57	C58	1.3900	F2	B1	1.30(3)
C58	C59	1.3900	F4	B1	1.362(13)
C59	C60	1.3900	B1	F7	1.377(19)
C60	C55	1.3900	B1	F6	1.395(15)
C62	C61	1.3900	B1	F3	1.318(19)
C62	C63	1.3900	B1	F1	1.314(19)
C61	C66	1.3900	Cl9	C77	1.734(16)
C66	C65	1.3900	Cl4	C73	1.741(10)
C65	C64	1.3900	Cl10	C77	1.66(3)
C64	C63	1.3900	Cl5	C73	1.760(10)
C14	C15	1.3900	C77	Cl8	1.788(14)
C14	C13	1.3900	Cl7	C76	1.733(9)
C15	C16	1.3900	Cl5A	C74	1.87(3)
C16	C17	1.3900	C74	Cl1	1.39(4)
C17	C18	1.3900	Cl1	C75	1.83(4)
C18	C13	1.3900	Cl3	C75	1.71(3)

Crystal Data for $C_{4.405797}H_{4.094203}B_{0.057971}Cl_{0.451594}Cu_{0.231884}F_{0.231884}N_{0.173913}P_{0.347826}S_{0.347826}$ (M =117.18 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 14.6628(5) Å, b = 18.9702(14) Å, c = 30.924(3) Å, β = 90°, V = 8601.7(11) Å^3, Z = 69, T = 130.00(10) K, μ(CuKα) = 6.186 mm^{-1}, $Dcalc$ = 1.561 g/cm^3, 26830 reflections measured (7.376° ≤ 2Θ ≤ 154.066°), 11696 unique (R_{int} = 0.0290, R_{sigma} = 0.0390) which were used in all calculations. The final R_1 was 0.0587 (I > 2σ(I)) and wR_2 was 0.1613 (all data).

Table S3: Crystal data and structure refinement for cluster **2a.BF$_4$**

Identification code	LiJCu3CS2_orange_20170407
Empirical formula	$C_{76.94}H_{71.84}BCl_{3.9}Cu_3F_4N_4P_6S_2$
Formula weight	1718.30
Temperature/K	130.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	14.5606(5)
b/Å	15.3131(5)
c/Å	18.0023(8)
α/°	79.962(3)
β/°	84.904(3)
γ/°	84.146(3)
Volume/Å^3	3921.5(3)

Z	2
ρ_{calc}g/cm^3	1.455
μ/mm^{-1}	4.268
F(000)	1756.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.058 to 154.182
Index ranges	$-17 \leq h \leq 18$, $-19 \leq k \leq 16$, $-22 \leq l \leq 22$
Reflections collected	31081
Independent reflections	16180 [R_{int} = 0.0377, R_{sigma} = 0.0550]
Data/restraints/parameters	16180/0/821
Goodness-of-fit on F^2	1.089
Final R indexes [I>=2σ (I)]	R_1 = 0.0493, wR_2 = 0.1233
Final R indexes [all data]	R_1 = 0.0681, wR_2 = 0.1331

Table S4: Bond distances of X-ray crystallography for cluster **2a.BF$_4$**.

Cu1	Cu2	2.6530(7)	C60	C55	1.3900
Cu1	Cu3	2.7278(7)	C46	C45	1.3900
Cu1	P6	2.2588(10)	C46	C47	1.3900
Cu1	P1	2.2491(10)	C45	C44	1.3900
Cu1	S1	2.3568(12)	C44	C43	1.3900
Cu2	Cu3	2.5853(7)	C43	C48	1.3900
Cu2	P5	2.2542(9)	C48	C47	1.3900
Cu2	P4	2.2480(10)	N4	C73	1.132(6)
Cu2	S2	2.3985(12)	C69	C70	1.3900
Cu3	P3	2.2687(10)	C69	C68	1.3900
Cu3	P2	2.2638(10)	C70	C71	1.3900
Cu3	S2	2.4620(12)	C71	C72	1.3900
P6	N1	1.693(3)	C72	C67	1.3900
P6	C1	1.8322(18)	C67	C68	1.3900
P6	C37	1.829(2)	C9	C10	1.3900
P5	N1	1.676(3)	C9	C8	1.3900
P5	C55	1.841(2)	C10	C11	1.3900
P5	C61	1.824(2)	C11	C12	1.3900
P1	N2	1.696(3)	C12	C7	1.3900
P1	C67	1.832(2)	C7	C8	1.3900
P1	C7	1.829(2)	C24	C23	1.3900
P4	N3	1.688(3)	C24	C19	1.3900
P4	C43	1.824(2)	C23	C22	1.3900
P4	C49	1.837(2)	C22	C21	1.3900
P3	N3	1.683(3)	C21	C20	1.3900
P3	C31	1.832(2)	C20	C19	1.3900
P3	C25	1.832(2)	C40	C41	1.3900
P2	N2	1.685(3)	C40	C39	1.3900
P2	C13	1.829(2)	C41	C42	1.3900
P2	C19	1.835(2)	C42	C37	1.3900
S1	C75	1.637(5)	C37	C38	1.3900
S2	C75	1.706(4)	C38	C39	1.3900
Cl2	C76	1.762(7)	C64	C63	1.3900

Cl5	C77	1.76(3)	C64	C65	1.3900
Cl7	C77	1.741(15)	C63	C62	1.3900
F98	B1	1.349(6)	C62	C61	1.3900
C31	C36	1.3900	C61	C66	1.3900
C31	C32	1.3900	C66	C65	1.3900
C36	C35	1.3900	C73	C74	1.449(7)
C35	C34	1.3900	F97	B1	1.283(11)
C34	C33	1.3900	C52	C51	1.3900
C33	C32	1.3900	C52	C53	1.3900
F99	B1	1.492(18)	C51	C50	1.3900
C2	C3	1.3900	C50	C49	1.3900
C2	C1	1.3900	C49	C54	1.3900
C3	C4	1.3900	C54	C53	1.3900
C4	C5	1.3900	F95	B1	1.489(9)
C5	C6	1.3900	C27	C28	1.3900
C6	C1	1.3900	C27	C26	1.3900
C15	C16	1.3900	C28	C29	1.3900
C15	C14	1.3900	C29	C30	1.3900
C16	C17	1.3900	C30	C25	1.3900
C17	C18	1.3900	C25	C26	1.3900
C18	C13	1.3900	C76	Cl1	1.663(18)
C13	C14	1.3900	C76	Cl3	1.751(6)
C56	C57	1.3900	B1	F97A	1.626(15)
C56	C55	1.3900	B1	F95A	1.405(10)
C57	C58	1.3900	B1	F99A	1.243(9)
C58	C59	1.3900	C77	Cl6	1.739(8)
C59	C60	1.3900	C77	Cl4	1.726(8)

Crystal Data for $C_{76.94}H_{71.845}BCl_{3.905}Cu_3F_4N_4P_6S_2$ (M =1718.30 g/mol): triclinic, space group P-1 (no. 2), a = 14.5606(5) Å, b = 15.3131(5) Å, c = 18.0023(8) Å, α = 79.962(3)°, β = 84.904(3)°, γ = 84.146(3)°, V = 3921.5(3) Å^3, Z = 2, T = 130.01(10) K, μ(CuKα) = 4.268 mm^{-1}, *Dcalc* = 1.455 g/cm^3, 31081 reflections measured (7.058° ≤ 2Θ ≤ 154.182°), 16180 unique (R_{int} = 0.0377, R_{sigma} = 0.0550) which were used in all calculations. The final R_1 was 0.0493 (I > 2σ(I)) and wR_2 was 0.1331 (all data).

Table S5: Comparison of bond distances (in Å) of cluster **2a.BF$_4$** with reported values in related trinuclear copper clusters from previously reported X-ray crystallographic studies. **2a.BF$_4$** (this work), **1a.BF$_4$**[2] ([Cu_3(μ$_3$-H)(μ$_3$-BH_4)((Ph_2P)$_2$NH)$_3$](BF_4)), **Che**[22] ([Cu_3(μ$_3$-H)(dcpm)$_3$](BF_4)$_2$), **Norton**[23] ([Cu_3(μ-H)$_3$(dppbz)]) and **Hayton**[21] ([Cu_3(μ$_3$-H)(OAc)$_2$(dppm)$_3$]).

	2a.BF$_4$	**1a.BF$_4$**	**Che**[22]	**Norton**[23]	**Hayton**[21]
Cu-Cu	2.6530(7)	2.6164(5)	2.866(1)	2.564(2)	2.816(1)
	2.7278(7)	2.6706(5)	2.906(1)	2.555(1)	2.8077(9)
	2.5853(7)	2.6785(5)	2.865(1)	2.619(1)	3.114
Cu-H	1.73(4)	1.72(4)	1.62(4)	1.70(3)	1.58(4)
	1.80(5)	1.79(3)	1.63(4)	1.59(3)	1.79(4)
	1.74(4)	1.77(4)	1.74(5)	1.62(3)	1.72(3)
Cu-P	2.2588(10)	2.2624(7)	2.279(2)	2.277(1)	2.279(1)
	2.2491(10)	2.2709(6)	2.290(2)	2.277(1)	2.274(1)
	2.2542(9)	2.2815(9)	2.279(2)	2.292(1)	2.267(1)
	2.2480(10)	2.2681(7)	2.277(2)	2.293(1)	2.284(1)

	2.2687(10)	2.2731(7)	2.288(2)	2.298(1)	2.284(1)
	2.2638(10)	2.2525(9)	2.287(2)	2.292(2)	2.283(1)

Table S6: Comparison of key metal-sulfur bond distance (in Å), S-C-S bond angle (in °) and ^{1}H NMR resonance signal of the ^-S_2CH unit (in ppm) of cluster **2a.BF$_4$** with reported values in related dithioformate containing metallic clusters. **2a.BF$_4$** (this work), **Adams**[24a] ([Os_3(μ-H)(μ$_2$-S_2CH)(CO)$_{10}$]), **Böttcher**[24b] ([Ru_2(CO)$_4$(μ$_2$-S_2CH)(μ-P^{t}Bu$_2$)(μ-dppm)]), **Bianchini1**[5c] ((PPh$_3$)$_2$Cu(K_2-$S_2CSCH_2SCS_2$)Cu(PPh$_3$)$_2$) and **Bianchini2**[5c] (Cu(K^2-S_2CH)(triphos)).

	2a.BF$_4$	**Adams**[24a]	**Böttcher**[24b]	**Bianchini1**[5c]	**Bianchini2**[5c]
M-S	2.3568(12)	2.445(7)	2.4692(1)	2.411(5)	n/a
	2.3985(12)	2.454(7)	2.4303(1)	2.479(5)	
	2.4620(12)			2.448(5)	
				2.449(5)	
S-C-S	128.7(3)	132.0(16)	129.4(3)	122.2(9)	n/a
				124.4(9)	
				113.3(9)	
				120.9(10)	
				113.7(9)	
				125.3(10)	
				113.6(10)	
^-S_2CH	9.87	n/a	10.67	n/a	11.26

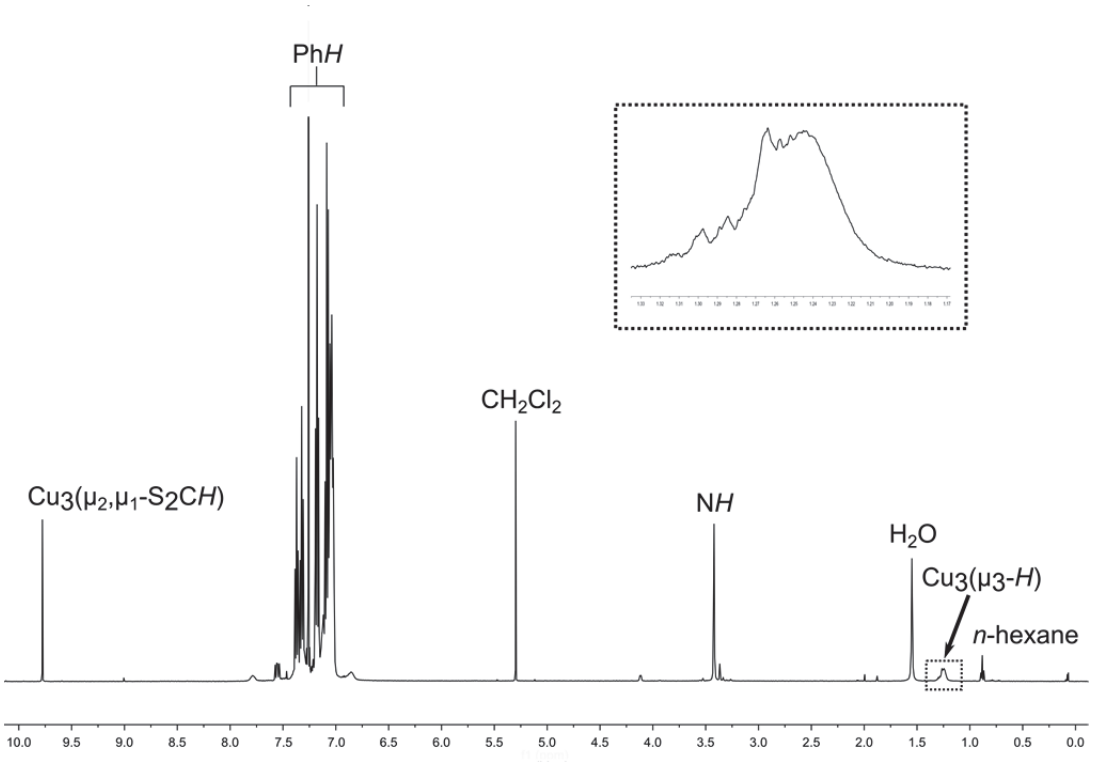


Figure S2: ^{1}H NMR spectra of cluster **2a.BF$_4$**. Deuterochloroform ($CDCl_3$) was used as the solvent for the measurement in a 500 MHz NMR spectrometer.

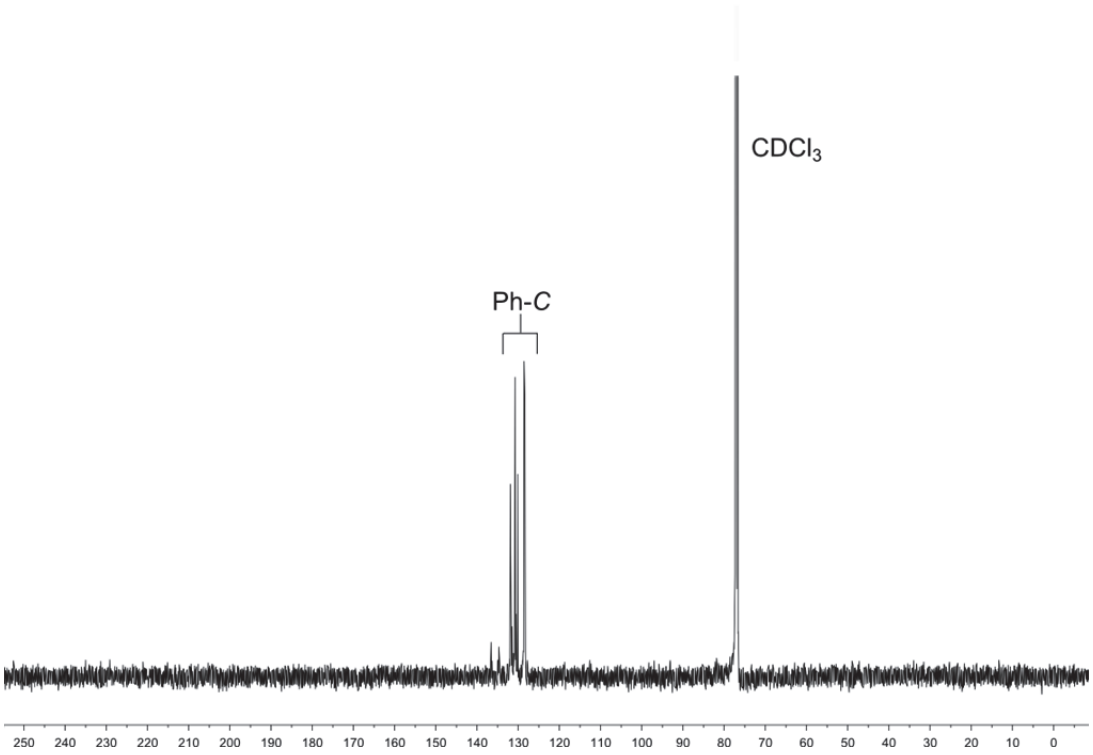


Figure S3: $^{13}C\{^{1}H\}$ NMR spectra of cluster **2a.BF$_4$**. Deuterochloroform ($CDCl_3$) was used as the solvent for the measurement in a 500 MHz NMR spectrometer.

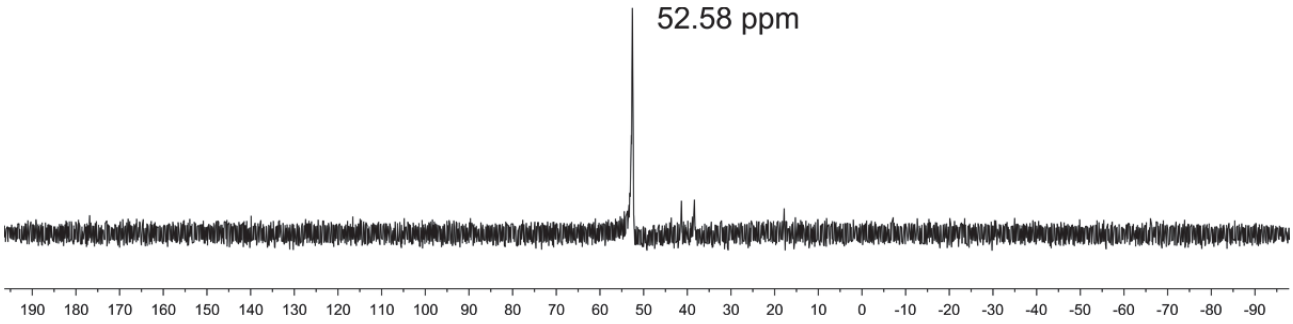


Figure S4: $^{31}P\{^{1}H\}$ NMR spectra of cluster **2a.BF$_4$**. Deuterochloroform ($CDCl_3$) was used as the solvent for the measurement in a 500 MHz NMR spectrometer.

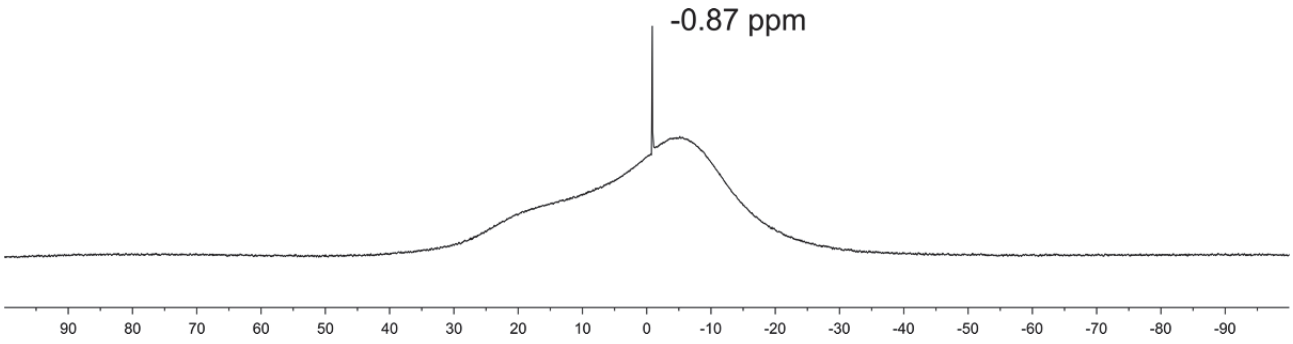


Figure S5: $^{11}B\{^{1}H\}$ NMR spectra of cluster **2a.BF$_4$**. Deuterochloroform ($CDCl_3$) was used as the solvent for the measurement in a 500 MHz NMR spectrometer.

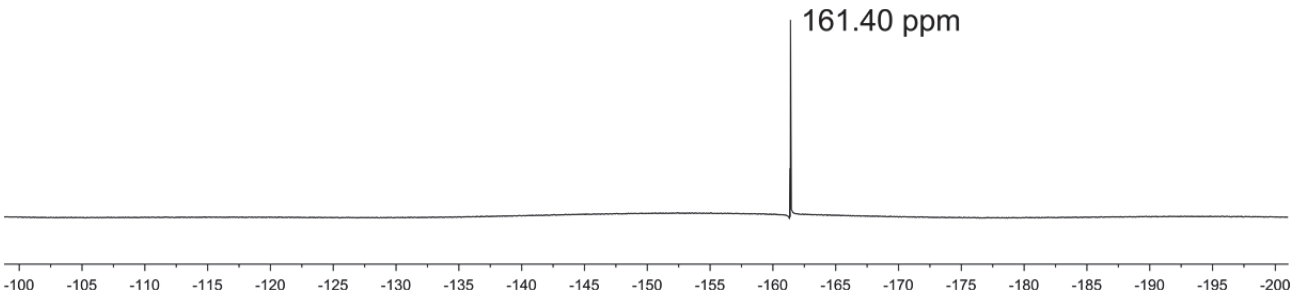


Figure S6: $^{19}F\{^{1}H\}$ NMR spectra of cluster **2a.BF$_4$**. Deuterochloroform ($CDCl_3$) was used as the solvent for the measurement in a 500 MHz NMR spectrometer.

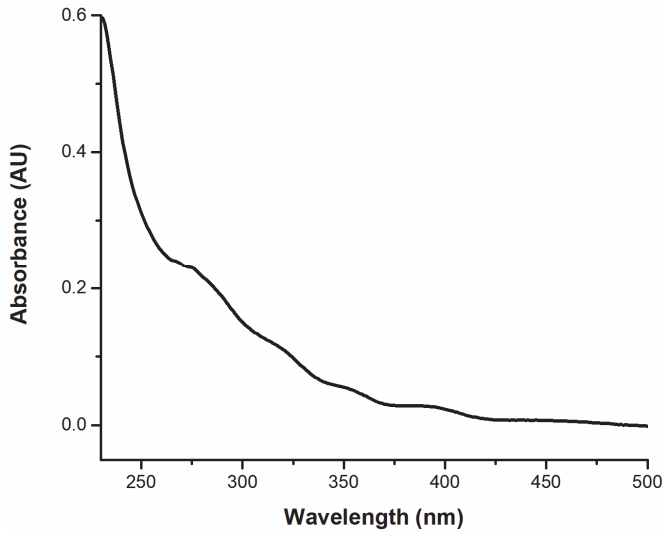


Figure S7: UV/Vis absorption spectra of cluster **2a.BF$_4$** dissolved in dichloromethane (CH_2Cl_2) at a concentration of 20 μM.

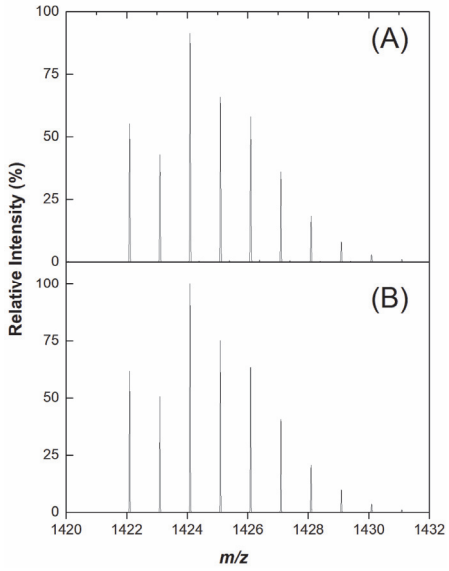


Figure S8: ESI-MS of **2a.BF$_4$** in the positive ion mode, HRMS a) measured, b) stimulated.

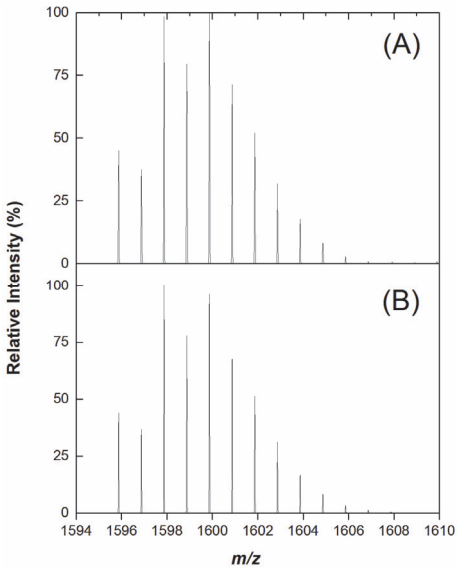


Figure S9: ESI-MS of **3.BF$_4$** in the positive ion mode, HRMS a) measured, b) stimulated.

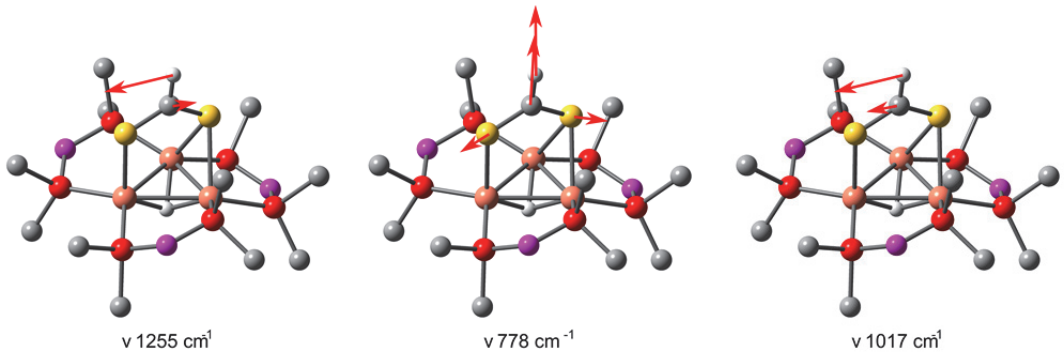


Figure S10: DFT calculated vibrational vectors of C-S and C-H stretches in the model system for cluster **2a.BF$_4$**, **2b**, whereby the phenyl rings of the dppa ligand have been replaced with methyl groups. Vectors are shown as red arrows. Vibrational frequencies are unscaled. Level of theory: M06/6-31+G(d)/SDD. Hydrogen atoms of the ligand have been removed for clarity.

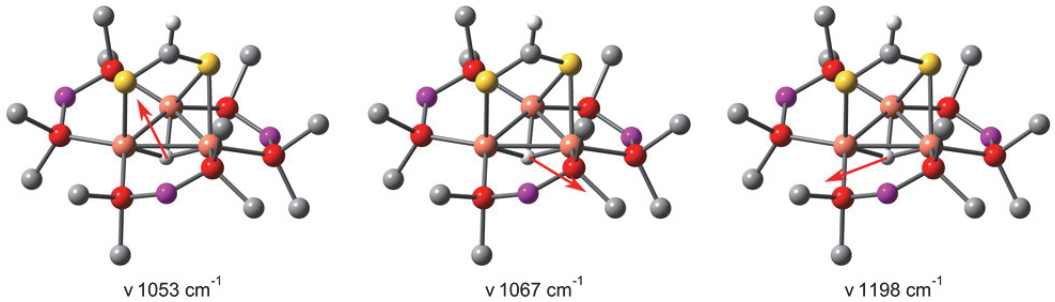
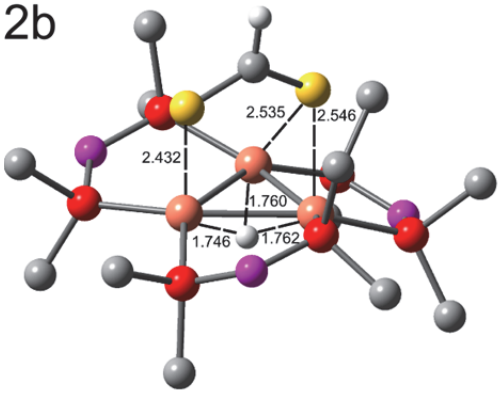
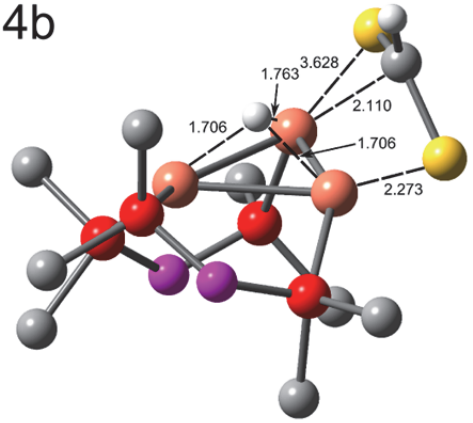


Figure S11: DFT Calculated vibrational vectors of Cu-H bonds in the model system for cluster **2a.BF$_4$**, **2b**, whereby the phenyl rings of the dppa ligand have been replaced with methyl groups. Vectors are shown as red arrows. Vibrational frequencies are unscaled. Level of theory: M06/6-31+G(d)/SDD. Hydrogen atoms of the ligand have been removed for clarity.

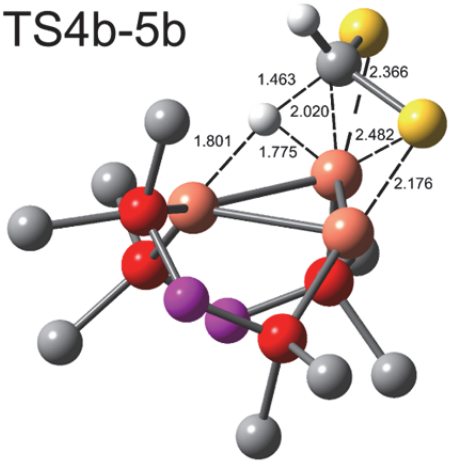
2b



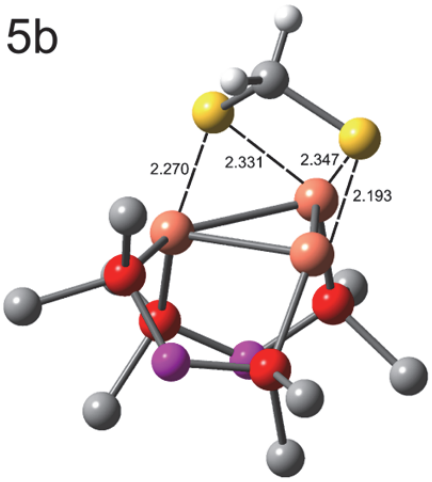
4b



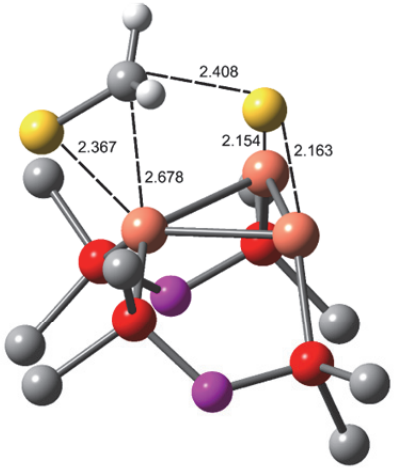
TS4b-5b



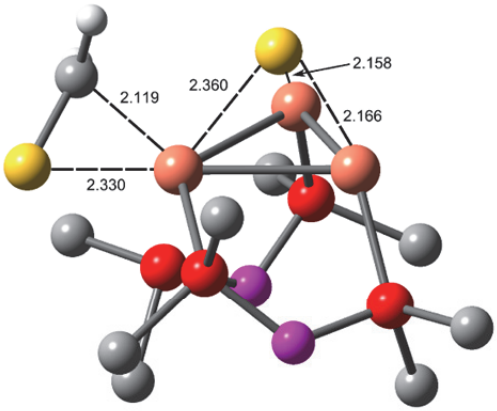
5b



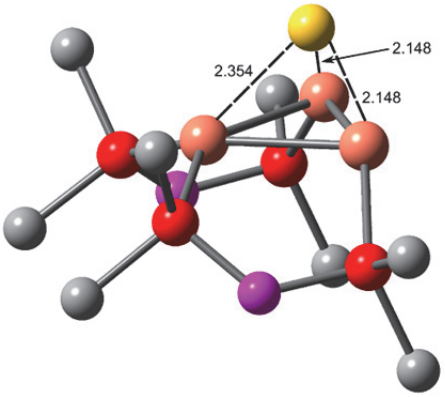
TS5b-6b



6b



7b



8b

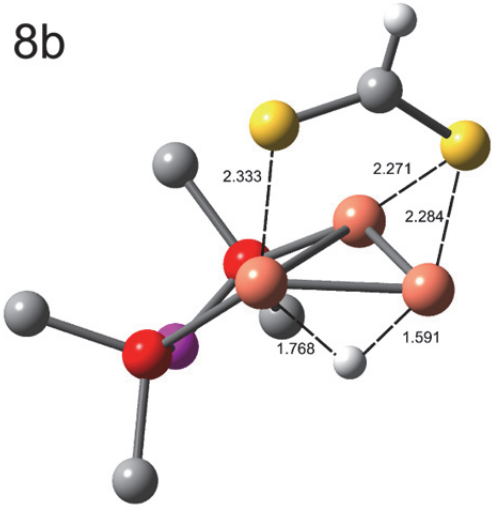
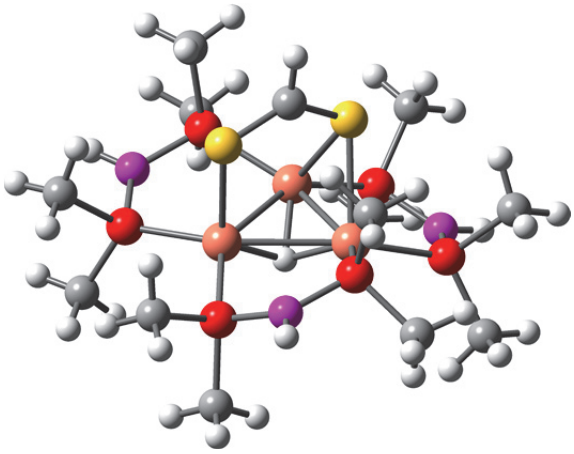


Figure S12: DFT calculated structures illustrating key interactions and bond distances within each fragment. Hydrogens on the dmpa (L^{Me}) ligand have been removed for clarity.

Cartesian coordinates of DFT calculated structures associated with Figure 8

E(B1) = energy of optimized structure for basis set 1 (M06/6-31+G(d))
E(ZPE) = zero-point energy of optimized structure for basis set 1 (M06/6-31+G(d))
E(B2) = single point energy at basis set 2 (M06/def2-TZVP)

$[Cu_3(\mu_3\text{-}H)(\mu_2,\mu_1\text{-}S_2CH)(L^{Me})_3]^+$ (2b)

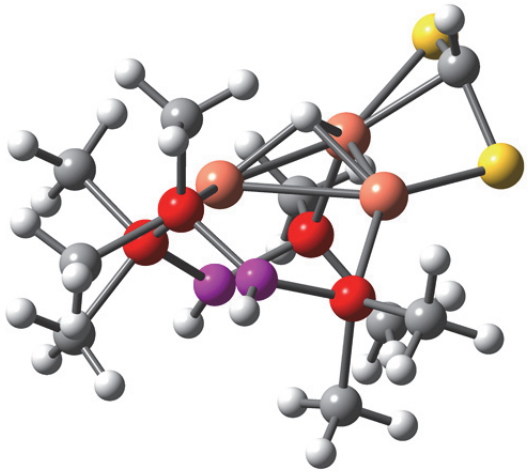


Cu3S2C13P6N3H41
E(B1) = -4119.834563 Hartrees
E(ZPE) = 0.536712 Hartrees
E(B2) = -8449.680825 Hartrees

Cu	1.52364	0.16382	-0.28047
Cu	-0.67261	-1.35914	-0.05122
Cu	-0.94942	1.15251	-0.02565
P	2.91730	-1.59362	-0.75776
P	0.62253	-3.17326	0.38427
P	2.39608	2.20977	-0.84894
P	-2.83913	-1.83637	-0.65689
P	-3.16666	1.17006	-0.63360
P	-0.10804	3.19689	0.50221
S	1.81548	0.25120	2.13188
S	-1.20506	-0.18051	2.12861
N	2.17294	-3.08593	-0.34474
N	-3.73944	-0.41037	-0.97904
N	1.48550	3.44407	-0.07735
H	1.86778	4.39094	-0.05364
C	-4.28755	1.75329	0.69886
C	4.47778	-1.64127	0.20852
C	-0.03789	3.70144	2.26033
C	0.02430	-4.78571	-0.25193
C	-3.24046	-2.87989	-2.10918
C	0.31772	0.02750	2.84300
C	2.46885	2.74590	-2.60182
C	4.09714	2.60212	-0.28939

C	-1.00633	4.62165	-0.22737
C	3.55683	-1.89737	-2.44870
C	0.94471	-3.59556	2.13863
C	-3.82304	-2.66956	0.64991
C	-3.80103	2.12350	-2.06441
H	0.30945	0.01784	3.93961
H	-4.73662	-0.51779	-1.17751
H	2.76171	-3.92032	-0.30611
H	-0.05699	-0.01183	-1.00197
H	5.09500	-0.76720	-0.04051
H	4.24963	-1.60509	1.28140
H	5.06244	-2.54788	-0.00409
H	4.16189	-2.81332	-2.49875
H	2.72117	-1.97887	-3.15285
H	4.18444	-1.04743	-2.75210
H	0.73899	-5.59440	-0.04300
H	-0.92908	-5.03987	0.23123
H	-0.13405	-4.72223	-1.33485
H	1.45025	-2.75399	2.62989
H	-0.00950	-3.77182	2.65436
H	1.56944	-4.49544	2.22516
H	-3.39451	-3.65792	0.86632
H	-3.78568	-2.07364	1.57090
H	-4.87178	-2.80240	0.34850
H	-2.84768	-3.89344	-1.95360
H	-4.32667	-2.95092	-2.26226
H	-2.77902	-2.46110	-3.01028
H	-3.25086	1.84875	-2.97111
H	-4.87200	1.93484	-2.22465
H	-3.66523	3.19799	-1.88430
H	-4.07078	2.80553	0.93117
H	-5.34586	1.66840	0.41405
H	-4.10947	1.16307	1.60708
H	0.35051	4.72345	2.36869
H	-1.04836	3.65491	2.68988
H	0.60705	3.00921	2.81510
H	-1.10707	4.48202	-1.31098
H	-2.01015	4.69287	0.21354
H	-0.48479	5.57048	-0.03672
H	4.35965	3.65379	-0.47333
H	4.19482	2.38936	0.78250
H	4.81035	1.97078	-0.83706
H	3.12387	2.07176	-3.17056
H	1.46166	2.68757	-3.03360
H	2.84550	3.77334	-2.70069

$[Cu_3(\mu_3\text{-}H)(\mu_1,\kappa^2\text{-}S_2CH)(L^{Me})_2]^+$ (4b)

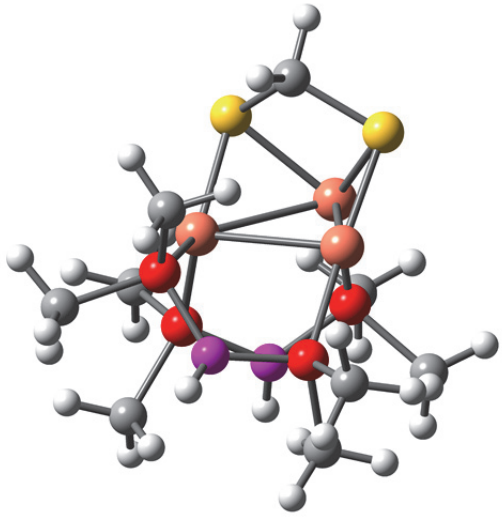


Cu3S2C9P4N2H28
E(B1) = -3222.413246 Hartrees
E(ZPE) = 0.366765 Hartrees
E(B2) = -7552.109705 Hartrees

Cu	0.71066	0.84074	-0.73466
Cu	-1.66390	-0.46066	-0.65117
Cu	0.42444	-1.64784	-0.01869
P	-0.28608	2.68920	0.13845
P	-2.51917	0.87150	0.93380
P	2.99760	0.66344	-0.90753
P	2.33279	-1.46824	1.11372
S	-3.51873	-1.58637	-1.58785
S	-1.43959	-2.92691	0.21753
N	-1.52430	2.24350	1.23819
N	3.45853	-0.44522	0.31861
H	4.44373	-0.50800	0.57927
C	-1.07383	3.83484	-1.05592
C	3.32440	-2.96178	1.45121
C	-2.70505	0.08513	2.56760
C	-2.07264	-2.41593	-1.33122
C	4.10681	2.07947	-0.56846
C	0.71251	3.83218	1.15872
C	-4.18109	1.56513	0.63040
C	3.70858	-0.01909	-2.44861
C	2.12613	-0.74262	2.78224
H	1.61831	0.22725	2.69101
H	1.49932	-1.40235	3.39680
H	3.09390	-0.59934	3.28154
H	4.78279	-0.21835	-2.33582
H	3.19286	-0.95403	-2.69943
H	3.56348	0.68653	-3.27677
H	0.09672	4.63236	1.59244
H	1.20630	3.28219	1.96864
H	1.48256	4.29634	0.52909
H	-0.31887	4.26956	-1.72384
H	-1.79432	3.28110	-1.67141
H	-1.59671	4.64839	-0.53452
H	-1.90619	2.98303	1.83171

H	-1.47900	-2.70181	-2.20647
H	4.24451	-2.71048	1.99718
H	2.73411	-3.65442	2.06335
H	3.58361	-3.46520	0.51366
H	-3.12354	0.77900	3.30907
H	-3.37170	-0.78110	2.46212
H	-1.72725	-0.27629	2.90841
H	3.97543	2.84550	-1.34314
H	3.86285	2.51982	0.40577
H	5.16216	1.77272	-0.56722
H	-4.18383	2.14274	-0.30188
H	-4.89360	0.73711	0.52240
H	-4.50779	2.20789	1.45935
H	-0.06292	-0.53318	-1.38501

$[Cu_3(\mu_2,\mu_2\text{-}S_2CH_2)(L^{Me})_2]^+$ (5b)

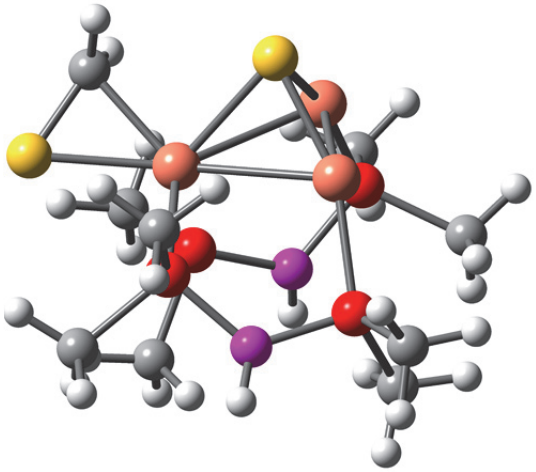


Cu3S2C9P4N2H28
E(B1) = -3222.466461 Hartrees
E(ZPE) = 0.372398 Hartrees
E(B2) = -7552.159374 Hartrees

Cu	0.23479	0.37398	-1.28120
Cu	-1.56323	-1.30993	-0.14722
Cu	0.87185	-1.37758	0.85706
P	-1.17066	2.08884	-0.63902
P	-2.69360	0.13083	1.08891
P	2.45282	0.78891	-0.99918
P	2.01738	0.22289	1.88242
S	-0.85375	-1.29575	-2.36726
S	-0.07727	-3.12464	-0.06764
N	-2.04341	1.70654	0.80278
N	2.73814	1.17916	0.66134
H	3.59532	1.68363	0.89659
C	-2.45051	2.47071	-1.89541
C	3.42583	-0.32656	2.90651
C	-2.63436	0.03241	2.91395
C	0.14197	-2.76070	-1.86631
C	3.05418	2.30846	-1.81958

C	-0.56316	3.76269	-0.20832
C	-4.49069	0.32015	0.79108
C	3.76509	-0.41530	-1.43124
C	1.15245	1.40666	2.97041
H	0.26010	1.79142	2.45847
H	0.83713	0.90044	3.89250
H	1.81278	2.24301	3.23633
H	4.76397	-0.01935	-1.20140
H	3.60996	-1.34844	-0.87301
H	3.71351	-0.65029	-2.50260
H	-1.37533	4.41545	0.14230
H	0.20950	3.69857	0.56785
H	-0.12179	4.22406	-1.10116
H	-1.98017	2.90249	-2.78880
H	-2.94980	1.54136	-2.19955
H	-3.19806	3.17793	-1.50924
H	-2.58357	2.48014	1.20120
H	-0.22985	-3.63535	-2.41227
H	4.00043	0.53290	3.27890
H	3.06298	-0.90128	3.76729
H	4.08415	-0.97279	2.31350
H	-3.10586	0.90908	3.37980
H	-3.16166	-0.87010	3.24756
H	-1.59158	-0.03721	3.24560
H	3.01099	2.17534	-2.90747
H	2.41780	3.15834	-1.54669
H	4.09364	2.53105	-1.54046
H	-4.67840	0.50615	-0.27281
H	-5.01038	-0.60495	1.07105
H	-4.90621	1.14743	1.38362
H	1.20089	-2.62339	-2.11172

$[Cu_3(\mu_3\text{-}S)(\kappa_2\text{-}SCH_2)(L^{Me})_2]^+$ (6b)

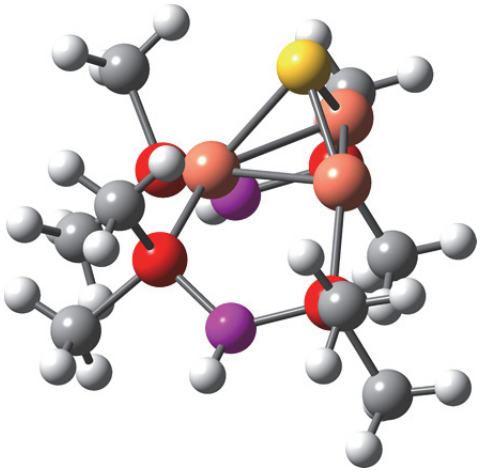


Cu3S2C9P4N2H28
E(B1) = -3222.441839 Hartrees
E(ZPE) = 0.371907 Hartrees
E(B2) = -7552.135693 Hartrees

Cu	0.45481	-0.31002	-1.36934

Cu	-1.50036	-1.46339	0.34981
Cu	1.03039	-1.33300	1.06829
P	-1.19102	1.50065	-0.71236
P	-2.77738	0.03809	1.33125
P	2.51509	0.67148	-0.81127
P	2.10532	0.26944	2.13152
S	0.53178	0.40772	-3.58426
S	0.16943	-2.50093	-0.53932
N	-2.05143	1.50137	0.80776
N	2.71940	1.19743	0.82858
H	3.49985	1.82855	1.02212
C	-2.52266	1.75511	-1.95598
C	3.57104	-0.09857	3.15412
C	-2.69780	0.13858	3.15136
C	-0.31178	-0.99718	-3.22105
C	3.08721	2.16779	-1.69323
C	-0.46449	3.18295	-0.65382
C	-4.56887	0.21399	1.01306
C	3.89198	-0.48933	-1.13788
C	1.17781	1.47483	3.14251
H	0.28184	1.79790	2.59366
H	0.86655	1.01186	4.08807
H	1.79855	2.35239	3.36873
H	4.86634	-0.04583	-0.89124
H	3.74868	-1.41057	-0.55797
H	3.87784	-0.76128	-2.20263
H	-1.22074	3.95209	-0.44128
H	0.32489	3.23338	0.10763
H	-0.02561	3.40171	-1.63654
H	-2.07513	1.92847	-2.94374
H	-3.14667	0.85352	-2.02141
H	-3.16008	2.61140	-1.69371
H	-2.54088	2.36742	1.05228
H	-1.39765	-0.98736	-3.07991
H	4.08905	0.82419	3.44937
H	3.27192	-0.63656	4.06185
H	4.26190	-0.73513	2.58833
H	-3.12149	1.08543	3.51312
H	-3.26242	-0.69176	3.59322
H	-1.65519	0.06044	3.48015
H	3.16069	1.94127	-2.76414
H	2.37975	2.99382	-1.55846
H	4.07974	2.48065	-1.33970
H	-4.76301	0.27111	-0.06401
H	-5.10397	-0.65684	1.41210
H	-4.96344	1.11794	1.49734
H	0.12735	-1.97964	-3.40331

$[Cu_3(\mu_3\text{-}S)(L^{Me})_2]^+$ (7b)

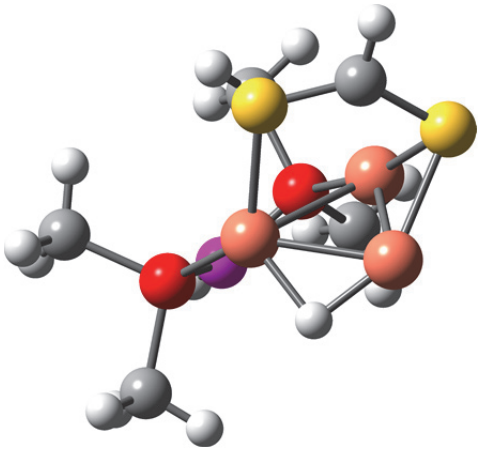


Cu3SC8P4N2H26
E(B1) = -2785.050371 Hartrees
E(ZPE) = 0.342803 Hartrees
E(B2) = -7114.700105 Hartrees

Cu	0.00000	0.80140	-0.55963
Cu	-1.45286	-1.37442	-0.68788
Cu	1.45286	-1.37443	-0.68787
P	-2.00826	1.69487	0.13668
P	-3.08072	-1.06983	0.76131
P	2.00827	1.69486	0.13667
P	3.08072	-1.06983	0.76132
S	0.00000	-0.89212	-2.19531
N	-2.99110	0.61652	1.06716
N	2.99110	0.61652	1.06716
H	3.79240	1.03962	1.54145
C	-3.06482	2.19160	-1.27645
C	4.79123	-1.33840	0.17427
C	-3.11667	-1.80831	2.42997
C	2.08555	3.18282	1.20086
C	-2.08554	3.18282	1.20088
C	-4.79124	-1.33839	0.17426
C	3.06483	2.19158	-1.27646
C	3.11666	-1.80831	2.42998
H	2.16028	-1.63644	2.93508
H	3.28606	-2.88948	2.35370
H	3.92368	-1.36726	3.03067
H	4.05965	2.51530	-0.94032
H	3.16840	1.34443	-1.96728
H	2.58962	3.01384	-1.82777
H	-3.12286	3.48525	1.40333
H	-1.57425	2.99442	2.15177
H	-1.58226	4.01422	0.69120
H	-2.58961	3.01385	-1.82775
H	-3.16839	1.34445	-1.96727
H	-4.05964	2.51532	-0.94031
H	-3.79240	1.03962	1.54145
H	5.52180	-0.95035	0.89754
H	4.97490	-2.41078	0.03341
H	4.93527	-0.83537	-0.78934
H	-3.92369	-1.36726	3.03066

H	-3.28607	-2.88948	2.35368
H	-2.16029	-1.63645	2.93507
H	1.58227	4.01423	0.69118
H	1.57426	2.99443	2.15175
H	3.12287	3.48525	1.40332
H	-4.93527	-0.83536	-0.78934
H	-4.97491	-2.41077	0.03340
H	-5.52180	-0.95034	0.89753

$[Cu_3(\mu_2\text{-}H)(\mu_2,\mu_1\text{-}S_2CH)(L^{Me})_1]^+$ (8b)

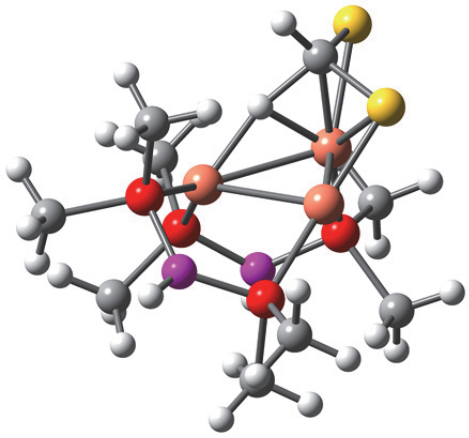


Cu3S2C5P2N1H15
E(B1) = -2325.015122 Hartrees
E(ZPE) = 0.197702 Hartrees
E(B2) = -6654.559511 Hartrees

Cu	-0.28934	0.55978	0.32921
Cu	0.79474	-1.04980	-1.07498
Cu	-1.51496	-1.72831	-0.26371
P	-2.08044	1.91438	0.15246
P	-3.49874	-0.75016	-0.20220
S	0.41794	-0.71070	2.15351
S	0.35006	-2.98470	0.05382
N	-3.39872	0.94261	-0.38702
H	-4.28467	1.42521	-0.55562
C	-4.34327	-1.05006	1.38861
C	0.68925	-2.24822	1.59787
C	-2.00722	3.21627	-1.11944
C	-2.74761	2.80595	1.60214
C	-4.74113	-1.21777	-1.44555
H	-4.36778	-1.01081	-2.45391
H	-4.95740	-2.28960	-1.36237
H	-5.67605	-0.66396	-1.28306
H	-3.66769	3.34905	1.34635
H	-2.96006	2.09752	2.41195
H	-2.00765	3.52960	1.96699
H	1.14816	-2.94539	2.30822
H	-5.29510	-0.50389	1.43708
H	-4.54118	-2.12223	1.51587
H	-3.69782	-0.72066	2.21338
H	-1.27617	3.97761	-0.81991

H	-1.68485	2.78293	-2.07265
H	-2.98396	3.70214	-1.24911
H	0.65326	0.53182	-1.16604

[$Cu_3(\mu_2\text{-}H)(\mu_2,\kappa_2\text{-}S_2CH)(L^{Me})_2]^+$ (TS4b-5b)

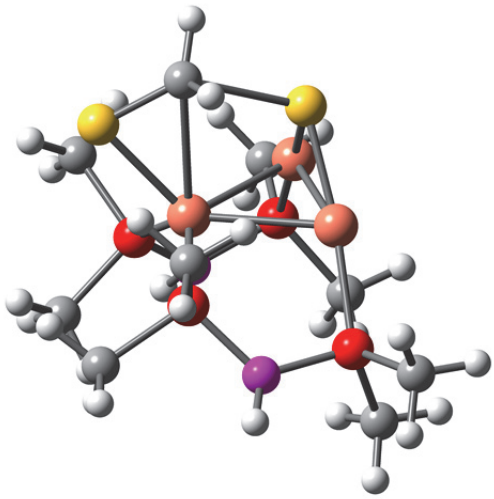


Cu3S2C9P4N2H28
E(B1) = -3222.379869 Hartrees
E(ZPE) = 0.365197 Hartrees
E(B2) = -7552.074888 Hartrees
Imaginary frequency: -576.75

Cu	0.30186	0.77023	-0.84838
Cu	-1.53306	-0.96491	-0.16567
Cu	0.99679	-1.54839	0.59622
P	-1.16894	2.42013	-0.31414
P	-2.47850	0.30814	1.31762
P	2.52942	0.76777	-1.27925
P	2.56513	-0.28980	1.51167
S	-2.67321	-2.10095	-1.89973
S	-0.24209	-3.07842	-0.33052
N	-2.02211	1.95179	1.10279
N	3.32498	0.55248	0.22836
H	4.30695	0.81505	0.31821
C	-2.43921	2.69042	-1.60410
C	3.95406	-1.15303	2.31773
C	-2.14977	-0.02012	3.07963
C	-0.93984	-2.08488	-1.73867
C	3.32090	2.29120	-1.90464
C	-0.66665	4.12417	0.11922
C	-4.29889	0.30489	1.21688
C	3.19438	-0.52054	-2.39080
C	2.11332	0.99235	2.73443
H	1.33187	1.63817	2.31216
H	1.72021	0.51851	3.64368
H	2.98383	1.60639	3.00099
H	4.29092	-0.48292	-2.43800
H	2.87901	-1.50902	-2.03151
H	2.78911	-0.37970	-3.40170

H	-1.53201	4.74526	0.38922
H	0.04095	4.10981	0.95627
H	-0.17377	4.58388	-0.74652
H	-1.98212	3.13347	-2.49866
H	-2.87594	1.72414	-1.89144
H	-3.23365	3.35862	-1.24392
H	-2.61370	2.66061	1.54173
H	-0.32010	-2.12582	-2.63964
H	4.74434	-0.44460	2.60264
H	3.59662	-1.65636	3.22409
H	4.36747	-1.91037	1.64271
H	-2.67533	0.69746	3.72377
H	-2.48538	-1.03503	3.32712
H	-1.07130	0.04530	3.26668
H	2.96868	2.49445	-2.92335
H	3.05486	3.14127	-1.26560
H	4.41469	2.18840	-1.93532
H	-4.60904	0.58786	0.20359
H	-4.66533	-0.71183	1.40737
H	-4.74765	0.99028	1.94911
H	-0.41835	-0.73454	-1.52708

$[Cu_3(\mu_2\text{-}S)(\kappa_2\text{-}SCH_2)(L^{Me})_2]^+$ (TS5b-6b)

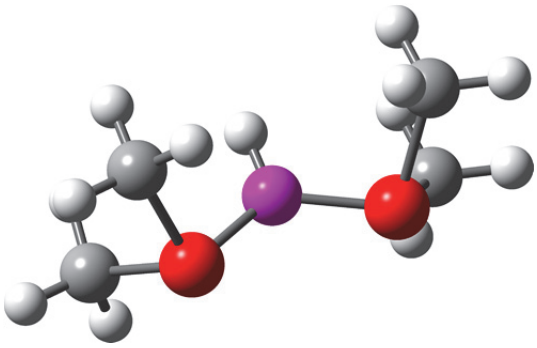


Cu3S2C9P4N2H28
E(B1) = -3222.429057 Hartrees
E(ZPE) = 0.371263 Hartrees
E(B2) = -7552.121792 Hartrees
Imaginary frequency: -170.93

Cu	0.26038	0.26279	-0.90734
Cu	-1.60045	-1.04065	0.47429
Cu	1.05622	-1.32837	1.00434
P	-1.51394	1.71061	-0.88197
P	-2.97766	0.45051	1.34519
P	2.44027	0.90614	-0.56470
P	2.45267	-0.10660	2.21181
S	0.32950	-0.20494	-3.22689
S	-0.18534	-2.41136	-0.39644

N	-2.48799	1.88099	0.54464
N	3.01970	1.02581	1.06410
H	3.90462	1.50511	1.24150
C	-2.72087	1.45320	-2.23395
C	3.96115	-0.86363	2.90653
C	-2.89994	0.86807	3.11866
C	0.51481	-1.78600	-2.61356
C	2.83576	2.56450	-1.22246
C	-1.00889	3.44608	-1.15826
C	-4.77478	0.30089	1.05391
C	3.68224	-0.13317	-1.42007
C	1.82331	0.90968	3.59081
H	0.98239	1.51458	3.23042
H	1.47695	0.26852	4.41107
H	2.60594	1.58077	3.96892
H	4.69348	0.27951	-1.30229
H	3.66056	-1.15100	-1.00736
H	3.43516	-0.18463	-2.48915
H	-1.87597	4.11090	-1.27724
H	-0.39689	3.79703	-0.31898
H	-0.40935	3.49215	-2.07731
H	-2.21760	1.55047	-3.20411
H	-3.12624	0.43425	-2.18019
H	-3.54074	2.18221	-2.16915
H	-3.10672	2.69452	0.59478
H	-0.16029	-2.56093	-2.97762
H	4.63796	-0.09673	3.30784
H	3.69455	-1.55103	3.71856
H	4.48284	-1.43349	2.12855
H	-3.50680	1.75691	3.33725
H	-3.27798	0.02830	3.71465
H	-1.86188	1.06440	3.40800
H	2.56956	2.58453	-2.28763
H	2.25587	3.33214	-0.69739
H	3.90627	2.79437	-1.12871
H	-4.97353	0.13211	-0.01070
H	-5.17282	-0.55303	1.61616
H	-5.30124	1.20867	1.37948
H	1.51006	-2.14776	-2.35050

dmpa (L)

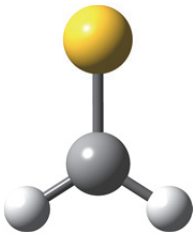


C4P2N1H13
E(B1) = -897.3386603 Hartrees

E(ZPE) = 0.166819 Hartrees
E(B2) = -897.4793544 Hartrees

P	-1.51423	0.04189	-0.56603
P	1.51423	0.04189	-0.56603
N	-0.00000	0.26967	0.23448
C	2.15873	-1.46374	0.31156
C	-2.15873	-1.46374	0.31156
C	2.52577	1.29326	0.35173
C	-2.52577	1.29326	0.35173
H	-2.21865	2.30455	0.06121
H	-3.58785	1.17068	0.10155
H	-2.41293	1.19017	1.44188
H	-0.00000	0.26137	1.25886
H	3.20575	-1.64766	0.03495
H	2.10125	-1.35554	1.40557
H	1.57143	-2.34220	0.01546
H	2.21865	2.30455	0.06121
H	2.41293	1.19017	1.44188
H	3.58785	1.17068	0.10155
H	-3.20575	-1.64766	0.03495
H	-1.57143	-2.34220	0.01546
H	-2.10125	-1.35554	1.40557

CH_2S



SCH2
E(B1) = -437.3707119 Hartrees
E(ZPE) = 0.024638 Hartrees
E(B2) = -437.4122528 Hartrees

S	0.00000	0.00000	0.58684
C	-0.00000	-0.00000	-1.02655
H	0.00000	0.92435	-1.61508
H	-0.00000	-0.92435	-1.61508