Supplementary Information

Hydride-Encapsulated Bimetallic Clusters Supported by 1, 1-Dithiolates

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Experimental Section

1.1 General remarks

All chemicals were purchased from commercial sources and used as received. Solvents were purified following standard protocols. All reactions were performed in oven-dried Schlenk glassware using standard inert atmosphere techniques. All reactions were carried out under N_2 atmosphere by using standard Schlenk techniques. $[Cu(CH_3CN)_4](PF_6)$,[1] $[Ag(CH_3CN)_4](PF_6)$,[1] and $(NH_4)[S_2P(O^iPr)_2]$[2] were prepared by a slightly modified procedure reported earlier in literature. ^1H, ^{109}Ag and ^{31}P, ^2H and VT-NMR spectra were recorded on a Bruker AV-800 TXI Cryo-probe, Bruker AV-600 BBO probe, and Bruker AVIIIHD-500 BBFO probe, respectively, operating at 800.24 MHz for ^1H, 242.86 MHz for ^{31}P, and 27.918 MHz for ^{109}Ag. The chemical shift (δ) and coupling constant (J) are reported in ppm and Hz, respectively. ESI-mass spectrum recorded on a Fison Quattro Bio-Q (Fisons Instruments, VG Biotech, U. K.). Melting points were measured by using a Fargo MP-2D melting point apparatus.

1.2 Synthesis

1.2.1 $[Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6]$, x = 1-6

$NH_4[S_2P(O^iPr)_2]$ (0.1345 g, 0.581 mmol) was dissolved in tetrahydrofuran (20 mL) and kept stirring for 20 minutes at -20 ℃. $[Ag(CH_3CN)_4]PF_6$ (0.1217 g, 0.292 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.1451 g, 0.389 mmol) were added and kept stirring for 2 minutes, and then $NaBH_4$ (0.0037 g, 0.098 mmol) was added and kept stirring for one hour. The black suspension was dried under vacuum, and the crude product was dissolved in CH_2Cl_2 (20 mL) and washed by DI-H_2O (30 mL x 3 times). The organic layer was evaporated to dryness and then flushed through the column (packed with

Al_2O_3 powder). 100% CH_2Cl_2 as eluting solvent was used to flush the column. The first colorless eluent was collected and dried to yield white powder. Yield: 0.1521 g. $^{31}P\{^1H\}$ NMR (242.86 MHz, *d*-chloroform, δ, ppm): 103.18 (s), 103.68 (s), 104.05 (s), 104.53 (s), 105.22 (s), 106.35 (s), 107.62 (s). ^1H NMR (800.24 MHz, *d*-chloroform, δ, ppm): 6.132 (septet of septets, $^1J_{1H\text{-}107Ag} = 44.6$ Hz, $^1J_{1H\text{-}109Ag} = 51.3$ Hz, $HCuAg_6$, 3.6%), 6.116 (sextet of sextets, $^1J_{1H\text{-}107Ag} = 52.3$ Hz, $^1J_{1H\text{-}109Ag} = 60.1$ Hz, HCu_2Ag_5, 11.4%), 6.078 (pentet of pentets, $^1J_{1H\text{-}107Ag} = 57.4$ Hz, $^1J_{1H\text{-}109Ag} = 66.0$ Hz, HCu_3Ag_4, 25.1%), 6.049 (quintet of quintets, $^1J_{1H\text{-}107Ag} = 62.9$ Hz, $^1J_{1H\text{-}109Ag} = 72.3$ Hz, HCu_4Ag_3, 40.9%), 5.441 (triplet of triplets, $^1J_{1H\text{-}107Ag} = 65.0$ Hz, $^1J_{1H\text{-}109Ag} = 74.7$ Hz, HCu_5Ag_2, 16.9%), 4.996 (doublet of doublets, $^1J_{1H\text{-}107Ag} = 86.7$ Hz, $^1J_{1H\text{-}109Ag} = 99.7$ Hz, HCu_6Ag, 2.1%), 4.792 (m, 12H, CH), 1.346 (d, 72H, CH_3, $^1J_{HH} = 6.4$ Hz). ^{109}Ag NMR (27.918 MHz, *d*-chloroform, δ, ppm): 1140.2 (d, $^1J_{1H\text{-}109Ag} = 66.6$ Hz, HCu_3Ag_4), 1137.4 (d, $^1J_{1H\text{-}109Ag} = 60.0$ Hz, HCu_2Ag_5), 1120.9 (d, $^1J_{1H\text{-}109Ag} = 72.7$ Hz, HCu_4Ag_3) 1080.5 (d, $^1J_{1H\text{-}109Ag} = 74.5$ Hz, HCu_5Ag_2). m.p.: 188℃. ESI-MS (m/z): $[CuAg_6(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ exp. 2134.2812 (calcd. 2134.3396), $[Cu_2Ag_5(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ exp. 2088.3080 (calcd. 2088.4214), $[Cu_3Ag_4(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ exp. 2044.3331 (calcd. 2044.4444), $[Cu_4Ag_3(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ exp. 2000.3582 (calcd. 2000.4689), $[Cu_5Ag_2(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ exp. 1956.3833 (calcd. 1956.4808), $[Cu_6Ag(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ exp. 1912.4087 (calcd. 1912.45165).

1.2.2 $[Cu_xAg_{7-x}(D)\{S_2P(O^iPr)_2\}_6]$, x = 1-6

The synthetic procedure was similar to $[Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6]$, x = 1-6. $NaBD_4$ (0.0041 g, 0.098 mmol) was used instead of $NaBH_4$. Yield: 0.1579 g. $^{31}P\{^1H\}$ NMR (161.98 MHz, *d*-chloroform, δ, ppm): 103.14 (s), 103.65 (s), 104.01 (s), 104.49 (s), 105.19 (s), 106.32 (s), 107.59 (s). ^1H NMR (400.13 MHz, *d*-chloroform, δ, ppm): 1.351 (d, 72H, CH_3, $^1J_{HH} = 6.4$ Hz), 4.795 (m, 12H, CH). ^2H NMR (76.773 MHz, chloroform, δ, ppm): 6.229 (pentet, $^1J_{2H\text{-}107Ag} = 8.6$ Hz, $^1J_{2H\text{-}109Ag} = 9.9$ Hz, Cu_3Ag_4D), 6.184 (quintet, $^1J_{2H\text{-}107Ag} = 9.7$ Hz, $^1J_{2H\text{-}109Ag} = 11.2$ Hz, Cu_4Ag_3D), 5.572 (triplet, $^1J_{2H\text{-}107Ag} = 9.8$ Hz, $^1J_{2H\text{-}109Ag} = 11.3$ Hz, Cu_5Ag_2D).

1.3 X-ray crystallography

Single crystals suitable for X-ray diffraction analysis of **1**–**2** were obtained by diffusing hexane into concentrated acetone solution at 4 degree. The single crystal was mounted on the tip of glass fiber coated in paratone oil, then frozen at 100K and 150K, respectively. Data were collected on a Bruker APEX II CCD diffractometer using graphite mono-chromated Mo (K_α) radiation ($\lambda = 0.71073$ Å). Absorption corrections for area detector were performed with SADABS[3] and the integration of raw data frame was performed with SAINT[4]. The structure was solved by direct methods and refined by least-squares against F^2 using the SHELXL-2018/3 package,[5] incorporated in SHELXTL/PC V6.14.[6] The hydride in **1** was located from the Fourier density map and refined anisotropically to convergence. Anisotropic displacement parameters (ADPs or U_{ij}) of a hydride were manually added in the initial refinement. CCDC 1986441 (**1**) and 2001049 (**2**) contains the supplementary crystallo-graphic data for compounds **1**–**2** in this article. These data can be obtained free of charge from The Cam-bridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

1.4 Computational details

Geometry optimizations were performed by DFT calculations with the Gaussian 16 package,[7] using the BP86 functional,[8] together with Grimme's empirical DFT-D3 corrections[9] and the all-electron Def2-TZVP set from EMSL Basis Set Exchange Library.[10] All the optimized geometries were characterized as true minima on their potential energy surface by harmonic vibrational analysis. All the relative energies discussed in the manuscript are free Gibbs energies at 298 KThe ^{1}H NMR chemical shift were computed, according to the GIAO method,[11] as implemented in Gaussian 16.

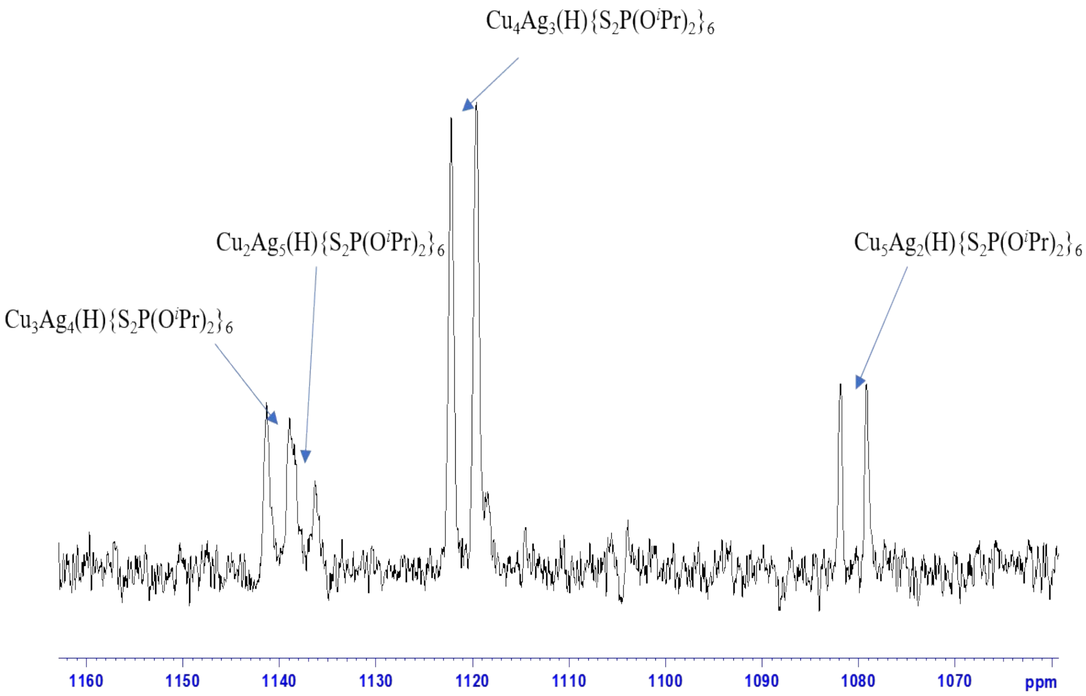


Figure S1. ^{109}Ag (27.918 MHz, $CDCl_3$) NMR spectrum (DEPT without proton decoupling) of $Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6$.

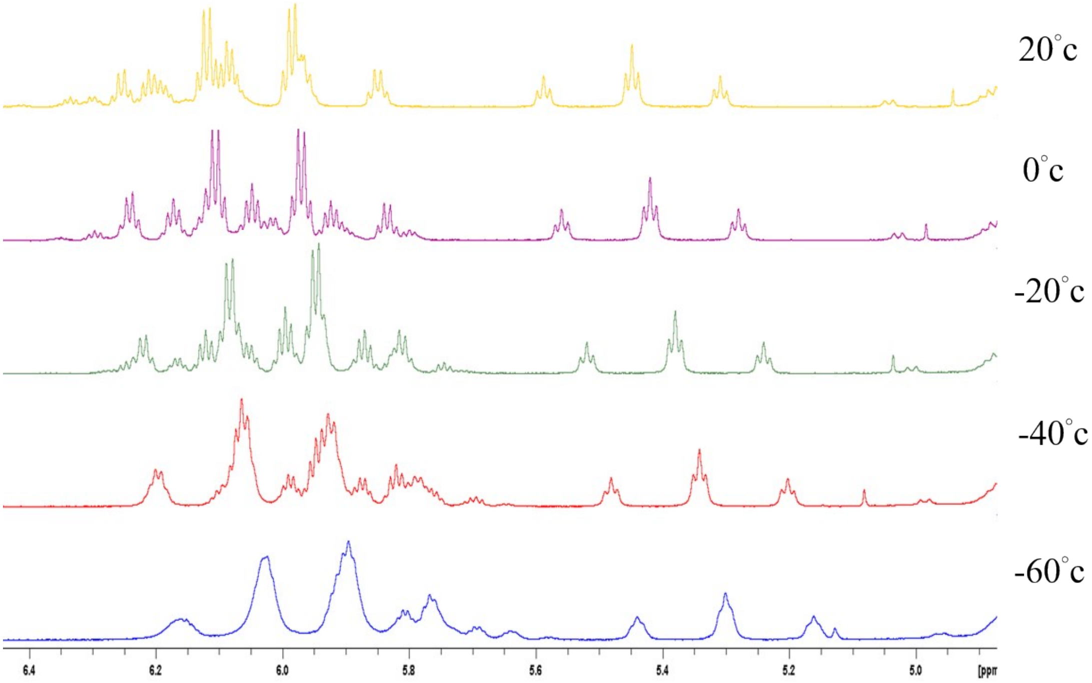


Figure S2. Variable-temperature ^1H NMR (500.13MHz, $CDCl_3$) spectra of $Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6$.

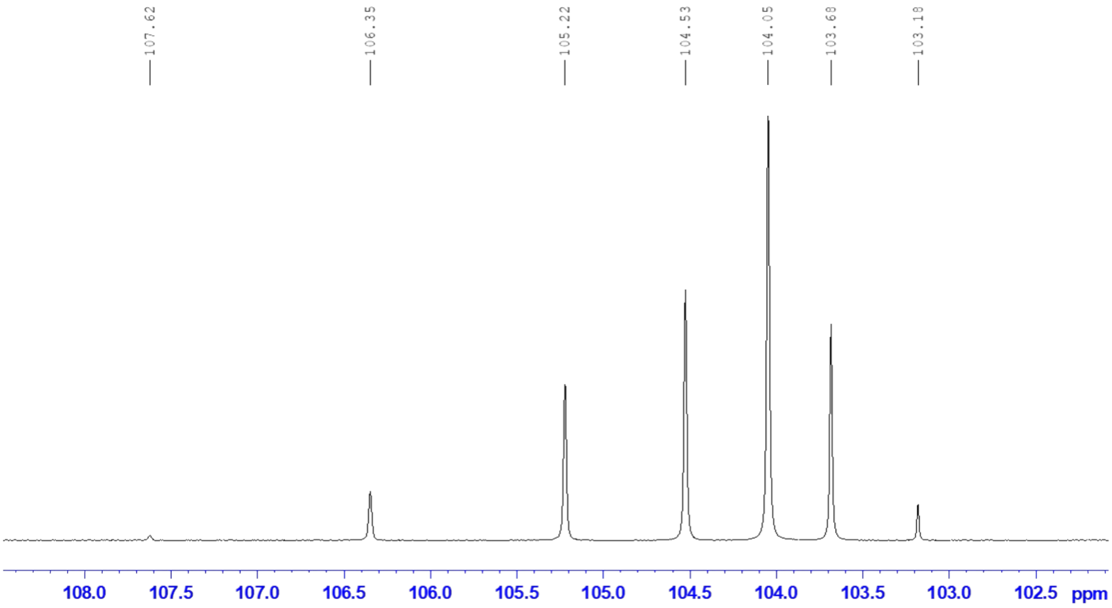


Figure S3. ^{31}P NMR (242.86 MHz, $CDCl_3$, r.t.) spectrum of $Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6$.

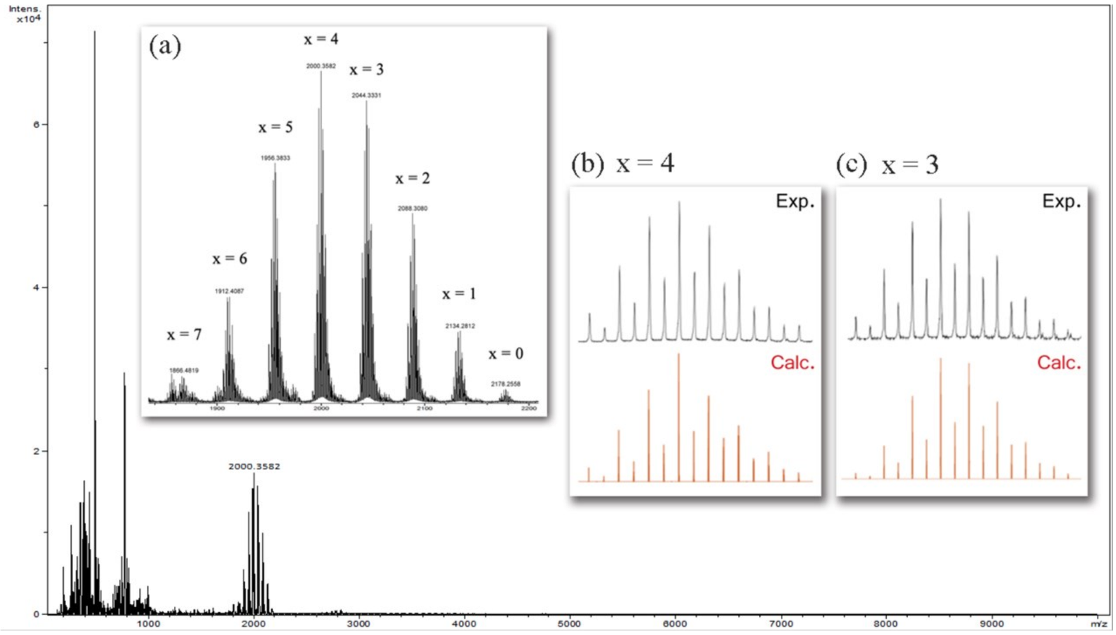


Figure S4. ESI mass spectrum of $Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6$. (a) The distribution of $[Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ (x = 0 - 7). (b) Experimental and simulated isotopic patterns of $[Cu_4Ag_3(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$ and (c) $[Cu_3Ag_4(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$, respectively.

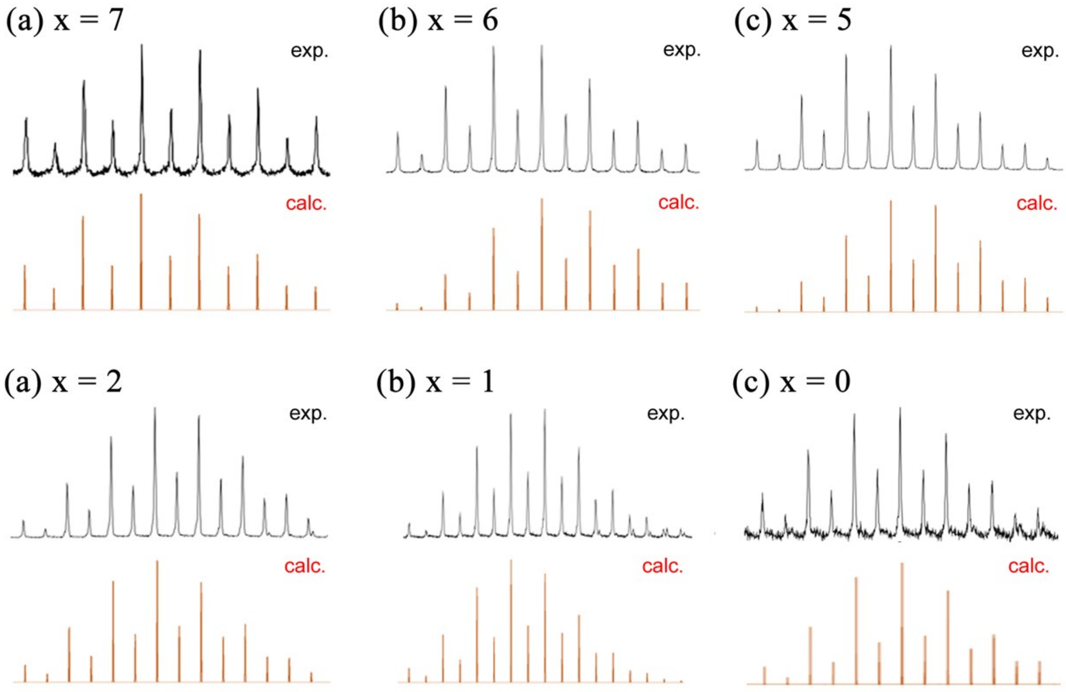


Figure S5. The experimental (black) and simulated (red) isotopic patterns of $[Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6 + Ag^+ + 2(H_2O)]^+$, exp. (calc.) m/z: (a) x = 7, 1866.4819 (1866.5419); (b) x = 6, 1912.4087 (1912.5165); (c) x = 5, 1956.3833 (1956.4808); (d) x = 2, 2088.3080 (2088.4214); (e) x = 1, 2134.2812 (2334.3396); (f) x = 0, 2178.2558 (2178.3172). x = 4 and 3 are in the inset spectra of Figure S3.

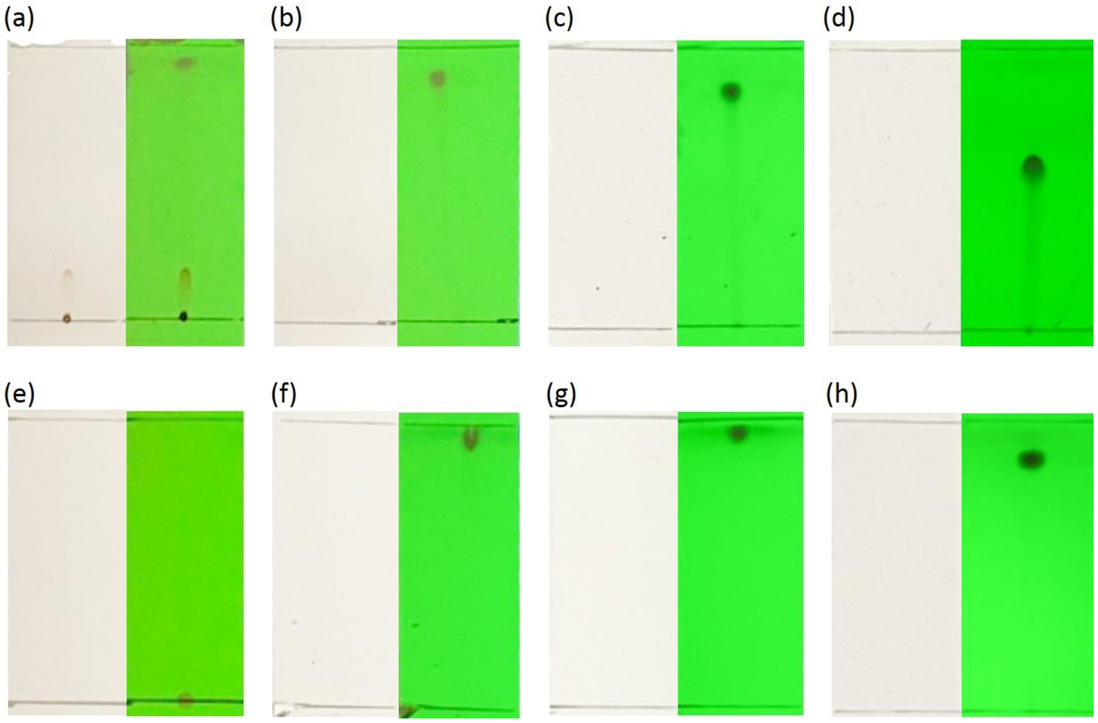


Figure S6. Photographs of Cu_xAg_{7-x} loading on the TLC plates under visible light (left) and UV irradiation (right). (a) Crude product before purification (running in 100% DCM). (b) $[Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6]$ (x = 1-6) was isolated by column chromatography, running in DCM (100%); (c) DCM:hexane (80:20, v/v); (d) DCM:hexane (60:40, v/v); (e) DCM:hexane (20:80, v/v); (f) ethyl acetate (100%); (g) EA:hexane (80:20, v/v); (h) EA:hexane (40:60, v/v), respectively. The mixture of $[Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6]$ (x = 1-6) cannot be further separated due to the highly similar polarities.

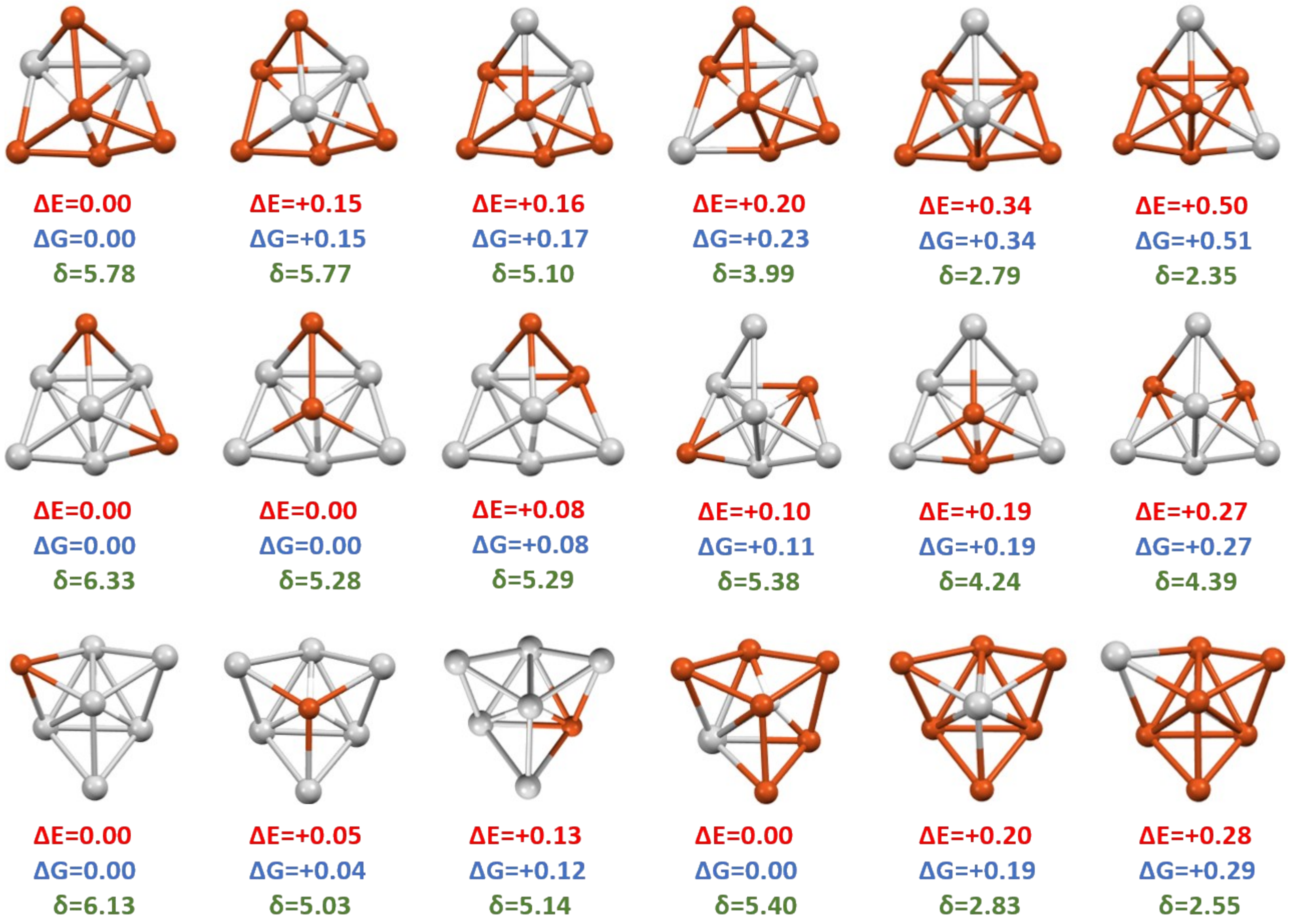
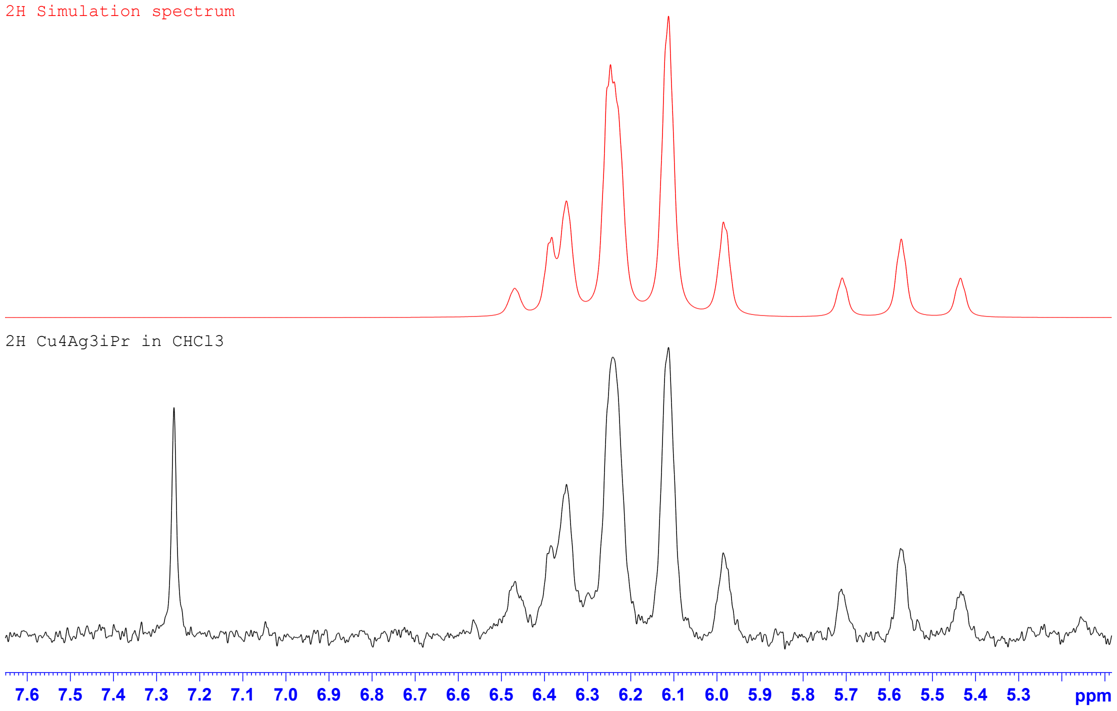


Figure S7. The metal cores of the DFT-optimized structures of the $Cu_xAg_{7-x}(S_2PH_2)_6$ ($x = 1, 2, 5, 6$) skeletal isomers corresponding to the non-structurally characterized $Cu_xAg_{7-x}(H)\{S_2P(O^iPr)_2\}_6$ clusters. Brown spheres: Cu; grey spheres: Ag. Relative energies are in eV and the ^{1}H NMR hydride chemical shifts in ppm.



Compound	Chemical shift (ppm)	^{2}H-^{107}Ag (Hz)	^{2}H-^{109}Ag (Hz)
Ag_2Cu_5D	5.5722	9.8	11.3
Ag_3Cu_4D	6.1841	9.7	11.2
Ag_4Cu_5D	6.2287	8.6	9.9

Figure S8. Simulated (red) and experimental (black) splitting patterns of a deuteride in $[Cu_xAg_{7-x}(D)\{S_2P(O^iPr)_2\}_6]$ in ^{2}H NMR (76.773 MHz, chloroform, δ, ppm) spectrum. The ompounds with corresponding chemical shift and coupling constant were listed below.

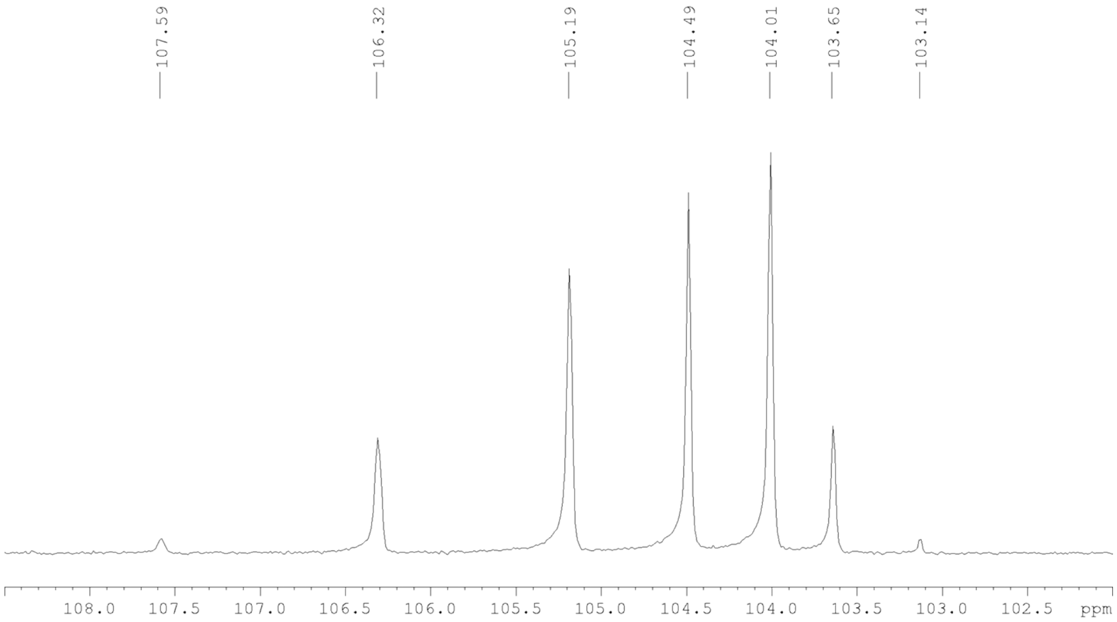


Figure S9. A $^{31}P\{^1H\}$ NMR (161.78 MHz, $CDCl_3$, r.t.) spectrum of $Cu_xAg_{7-x}(D)\{S_2P(O^iPr)_2\}_6$.

Table S1. Selected bond lengths (Å) and angles (deg.) of structure **1**-**3**. DFT-computed values of the corresponding models $Cu_3Ag_4(H)\{S_2PH_2\}_6$ (**1'**) and $Cu_4Ag_3(H)\{S_2PH_2\}_6$ (**2'**) are also given in brackets.

Cpd.	**$[Cu_3Ag_4(H)\{S_2P(O^iPr)_2\}_6]_{0.5}[Cu_4Ag_3(H)\{S_2P(O^iPr)_2\}_6]_{0.5}$ (1)** **DFT: $Cu_3Ag_4(H)\{S_2PH_2\}_6$ [1']**	**$Cu_4Ag_3(H)\{S_2P(O^iPr)_2\}_6$ (2)** **DFT: $Cu_4Ag_3(H)\{S_2PH_2\}_6$ [2']**	**$[Bu_4N]_6[Ag_7(H)\{S_2CC(CN)_2\}_6]$ (3)**
M_{top}-M_{tri}	3.0890(3)-3.2531(3), avg. 3.1667(3) [3.204]	3.0970(5)-3.2543(5), avg. 3.1697 [3.115]	3.942(1)-4.019(1), avg. 3.990(1)
M_{tri}-M_{tri}	2.9925(3)-3.0270(3), avg. 3.0088(3) [3.061]	2.9938(4)-3.0148(4), avg. 3.0035(4) [3.037]	2.9011(9)-3.0218(9), avg. 2.9605(9)
M_{cap}-M_{top}	2.7368(4)- 2.7499(4), avg. 2.7431(4) [2.776]	2.7152(6)-2.7312(6), avg. 2.7235(6) [2.645]	2.8808(10)-2.9095(10), avg. 2.8911(10)
M_{cap}-M_{tri}	2.9208(3)-3.0324(4), avg. 2.9642(3) [2.955]	2.8950(5)- 3.0118(6), avg. 2.9418(5) [2.872]	2.8379(9)-2.9722(10), avg. 2.900(10)
H-M_{tri}	1.85(3)-1.96(4), avg. 1.92(4) [1.937]	1.96(3) -2.02(3), avg. 2.00(3) [1.990]	1.91(5)-2.11(6), avg. 1.98(6)
H-M_{top}	1.83(4) [1.879]	1.65(2) [1.635]	2.62(7)
S….S bite	3.4142(8)-3.4913(8), avg. 3.450(1) [3.561]	3.416(1)-3.490(1), avg. 3.449(1) [3.541]	3.059(4)-3.067(3), avg. 3.063(3)
M_{top}-H-M_{tri}	109(2)-118(2), avg. 115(2) [114.2]	117.6(5)-124.3(5), avg. 120.0(5) [118.2]	112(3)-124(3), avg. 120(3)
M_{tri}-H-M_{tri}	100(2)-105(2), avg. 103(2) [104.4]	96.3(4)-97.7(4), avg. 97.1(4) [99.5]	92(3)-101(3), avg. 97(3)

Table. S2. Selected X-ray crystallographic data of **1** and **2**.

Compound	**1**	**2**
CCDC Number	1986441	2001049
Chemical formula	$C_{36}H_{85}Ag_{3.5}Cu_{3.5}O_{12}P_6S_{12}$	$C_{36}H_{85}Ag_3Cu_4O_{12}P_6S_{12}$
Formula weight	1880.56	1858.34
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	13.0789(3)	13.1365(3)
b, Å	23.2720(6)	23.3343(5)
c, Å	22.9115(6)	22.8775(5)
α, deg.	90	90
β, deg.	98.1810(5)	98.1499(5)
γ, deg.	90	90
V, $Å^3$	6902.7(3)	6941.8(3)
Z	4	4
Temperature, K	100(2)	150(2)
ρ_{calcd}, g/cm^3	1.810	1.778
μ, mm^{-1}	2.578	2.576
θ_{max}, deg.	28.983	27.109
Resolution, Å	Inf - 0.73	Inf - 0.78
Redundancy	4.15	3.17
Completeness, %	100.0	99.9
Reflection collected / unique	76857 / 18305 [R_{int} = 0.0282]	49150 / 15299 [R_{int} = 0.0197]
Restraints / parameters	273 / 736	4 / 686
$^aR1$, $^bwR2$ [$I > 2\sigma(I)$]	0.0255, 0.0640	0.0342, 0.0931
$^aR1$, $^bwR2$ (all data)	0.0325, 0.0679	0.0404, 0.0974
GOF	1.019	1.024
Largest diff. peak and hole, e/$Å^3$	1.674 and -0.994	2.377 and -1.399

^{a} $R1 = \Sigma \mid \square F_o \square - \square Fc \square \mid / \Sigma \square F_o \square$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Reference

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S6. SHELXTL, version 6.14. (Bruker AXS Inc., Madison, Wisconsin, USA, 2003).

S7. Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

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