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Isolation and Structural Elucidation of 15-nuclear Copper Dihydride Clusters: An Intermediate in the Formation of a 2-electron Copper Superatom

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Highly reactive copper-dihydride clusters, $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$ {R =

ⁿBu (**1_H**), ⁿPr (**2_H**), ⁱBu (**3_H**)}, were isolated during the reaction of

$[\text{Cu}_{28}\text{H}_{15}\{\text{S}_2\text{CN}^n\text{Bu}_2\}_{12}](\text{PF}_6)$ with ten equivalents of phenylacetylene. They are found

to be intermediates in the formation of the earlier reported 2-electron superatom

$[\text{Cu}_{13}(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_4]^+$. Better yields were obtained by reacting dithiocarbamate

sodium salts, $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$, BH_4^- and phenylacetylene. The presence of two

hydrides in **1_H** was confirmed by the synthesis and characterization of its deuteride

analogue $[\text{Cu}_{15}(\text{D})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}_2\text{Ph})_6]^+$, **1_D**, and a single crystal neutron structure of

2_H. Structural characterization of **1_H** revealed a new bicapped icosahedral copper(I)

cage encapsulating a linear copper dihydride (CuH_2)⁻ unit. Reaction of **3_H** with Au(I) salts yielded a highly luminescent $[\text{AuCu}_{12}(\text{S}_2\text{CN}^i\text{Bu}_2)_6(\text{C}_2\text{Ph})_4]^+$ cluster.

The chemistry of transition-metal hydride clusters has recently received significant interest.^[1,2] Such compounds play a key role as intermediates in several homogeneous and heterogeneous catalyses^[3] with significant contributions in hydrogen storage.^[4] Importantly, copper hydride chemistry has evolved towards the design of nanosized ligand-protected polyhydrido copper clusters that have emerged as a new class of materials in the field of nanoscience, owing to their various potential applications.^[2f-h] Our group has made significant contributions in this endeavor by isolated a series of air-stable copper(I) monohydride clusters stabilized by 1,1-dichalcogenolates.^[5] Subsequently four nanoscale copper polyhydrides, $[\text{Cu}_{20}\text{H}_{11}\{\text{E}_2\text{P}(\text{O}^i\text{Pr})_2\}_9]$ (E = S, Se),^[6] $[\text{Cu}_{28}(\text{H})_{15}(\text{S}_2\text{CNR}_2)_{12}]\text{PF}_6$,^[7] $[\text{Cu}_{30}\text{H}_{18}\{\text{S}_2\text{P}(\text{O}^n\text{Pr})_2\}_{12}]$ ^[8] and $[\text{Cu}_{32}(\text{H})_{20}\{\text{S}_2\text{P}(\text{O}^i\text{Pr})_2\}_{12}]$ ^[9] were structurally characterized by both X-ray and neutron diffraction from which a new synthetic concept has been established, based on the fact that hydride additions assist the growth of nanoscale copper clusters. Indeed, these hydrides have been found to be intermediates in the fabrication of rhombus-shaped copper nanoparticles via a reduction route as well as electrocatalysts in the CO₂ reduction.^[9b]

In recent years, alkynyls have emerged as promising ligands for stabilizing metal nanoclusters.^[10-14] Alkynyl-protected Au-Ag alloy nanoclusters (NCs) have been isolated.^[11-14] Synthesis of copper NCs by reacting $[\text{Cu}_{28}(\text{H})_{15}(\text{dte})_{12}]^+$ (dte = di-*n*-butyldithiocarbamate, $\text{S}_2\text{CN}^n\text{Bu}_2$) with terminal alkynes was established, where the hydrides present in the Cu(I) cluster react with the acidic protons of the terminal alkynes, liberating H₂ under elevated temperature, which subsequently reduces the

leftover of alkynes to alkenes and some of Cu(I) to Cu(0).^[15] The participation of alkynyls in the reaction medium leads eventually to the formation of the brand-new NC [Cu₁₃(dtc)₆(alkynyl)₄]⁺, a 2-electron superatom. To explore this chemistry further, it is imperative to understand the mechanism involved in the formation of these superatomic clusters. A similar reaction in the presence of Pd(PPh₃)₂Cl₂ yielded [PdH₂@Cu₁₄{S₂CNⁿBu₂}₆{C≡CPh}₆].^[16] This serendipitous result gave us a hint of a potentially isolable intermediate [CuH₂@Cu₁₄{S₂CNⁿBu₂}₆{C≡CPh}₆]⁺ during the formation of [Cu₁₃(dtc)₆(alkynyl)₄]⁺. Here, we have successfully isolated and structurally characterized both hydride and deuteride analogs of such clusters, which not only depict a linear [CuH₂]⁻ complex embedded in a [Cu₁₄]¹⁴⁺ cage, but also readily convert to [Cu₁₃]¹¹⁺ at elevated temperatures.

In a typical experiment, to a THF suspension of [Cu₂₈H₁₅(S₂CNⁿBu₂)₁₂]⁺, a ten-fold excess of phenylacetylene was added and the reaction mixture was stirred at 30 °C for 12 hours. The color of the suspension changed from orange to red. Workup of this mixture leads to the isolation of [Cu₁₅(H)₂{S₂CNⁿBu₂}₆{C≡CPh}₆]⁺ (**1_H**) as an orange-yellow solid in 20% yield, along with [Cu₈H(S₂CNⁿBu₂)₆]⁺ and styrene as byproducts. The yield of **1_H** formation could be increased (70%) by an alternating strategy, from the mixture of Cu(I), dithiocarbamate, NaBH₄, phenylacetylene and NEt₃ in the 5:2:1:8:8 ratio, respectively (Scheme 1). The corresponding deuteride derivative [Cu₁₅(D)₂(S₂CNⁿBu₂)₆(C₂Ph)₆](PF₆) (**1_D**) (73%) was synthesized to support the presence of the hydride ligands in **1_H** through ¹H NMR studies. By using different carbamates, we have isolated analogous hydride and deuteride derivatives of **1_H**; namely [Cu₁₅(H/D)₂(S₂CNⁿPr₂)₆(C₂Ph)₆](PF₆) (**2_H**-65%/ **2_D**-65%) and [Cu₁₅(H/D)₂(S₂CNⁱBu₂)₆(C₂Ph)₆](PF₆), (**3_H**-74%/ **3_D**-75%). Their full characterization

was established by ESI-MS spectrometry, NMR spectroscopy, single crystal X-ray diffraction analysis and neutron diffraction (in the case of **2_H**).

The positive-ion ESI spectrum of **1_H** displays three characteristic peaks corresponding to [**1_H**]⁺ at *m/z* 2786.72 (calc. 2787.72), its fragment ions [**1_H**-Cu(C₂Ph)]⁺ at 2620.74 (calc. 2621.74) and [**1_H**-{CuC₂Ph}₂]⁺ at 2456.77 (calc. 2456.77) (Figure 1). The latter two species correspond to a successive loss of one and two [Cu(C₂Ph)] fragments from **1_H** in the gas phase. The ESI-MS analysis of the deuteride analogue [Cu₁₅(D)₂{S₂CN^{*n*}Bu₂}₆(C₂Ph)₆](PF₆) (**1_D**) confirmed the presence of two deuterides by showing a band at *m/z* 2788.72 (calc. 2789.72) (Figure S1). Their theoretically determined isotopic patterns show good resemblance with the experimental ones, as shown in Figure S1 (inset). The deviation between the [**1_H**]⁺ and [**1_D**]⁺ peaks indicates the existence of 2 hydrides in [**1_H**]⁺. The positive-ion ESI-MS spectra of **2_H** (Figure S2) and **3_H** (Figure S3) also show identical bands for [**2_H**]⁺ and [**3_H**]⁺, at *m/z* 2618.5 (calc. 2618.5), and 2786.7 (calc. 2787.7), respectively, along with fragment ions by losing {Cu(C₂Ph)} and {Cu(C₂Ph)}₂ moieties. The ESI-MS results of **2_D** and **3_D** are in good agreement with the calculated patterns (Figure S4, S5).

The ¹H NMR spectrum of **1_H** (Figure S6a) shows the presence of two hydrides, six dithiocarbamates and six phenyl ligands. The two hydrides are associated with a resonance peak at 5.07 ppm in CD₂Cl₂, which is echoed by the presence of deuteride signal at 4.98 ppm for compound **1_D** in CH₂Cl₂ (Figure S6b). Similarly, the hydride and deuteride resonance for **2_H**/**2_D** and **3_H**/**3_D** appear at 4.93/4.86 and 4.99/5.13 ppm respectively, in CDCl₃/CHCl₃ (Figure S7-S10).

Single crystals of **1_H**, **2_H** and **3_H** were grown by vapour diffusion of hexanes into a concentrated acetone solution at 5 °C. The X-ray structures of **1_H**-**3_H** and the neutron structure of **2_H** are similar. They exhibit a linear CuH₂ unit (Figure 2, S11a)

encapsulated within a Cu₁₄ bicapped icosahedron (Table S1 and S2). The two capping coppers (Cu_{cap}) and the CuH₂ (Cu_{cent}H₂) unit are aligned along a C₃ axis so that the Cu₁₅H₂ core adopts *D*_{3d} ideal symmetry (Figure S12). Metrical data are given in Table S3. The hydride positions are fully ascertained by the neutron diffraction structure of **2_H**, which exhibits a short Cu_{cent}-H average distance (1.78(2) Å). Each hydride is located within a trigonal-bipyramidal cavity formed by three icosahedral Cu atoms (Cu_{ico}), one Cu_{cap}, and Cu_{cent}. However, the Cu_{ico}...H and Cu_{cap}...H distances (~ 2 Å) are much longer than their Cu_{cent}-H counterparts (Table S3). The [(CuH₂)@Cu₁₄] core is stabilized by six dithiocarbamates and six phenylacetylenes (Figure S11d). The dithiocarbamates are equally distributed on the cluster top and bottom, along the C₃ axis. They bridge four metal centers (one Cu_{cap} and three Cu_{ico}) in a (μ₂, μ₂) binding mode. The phenylacetylenes are arranged along the waist of the copper icosahedron, alternatively binding at the top and bottom Cu_{ico} triangles in μ₃ fashion. As a result, the ideal *D*_{3d} symmetry of the Cu₁₅H₂ core is reduced to *S*₆.

The UV-Vis spectrum of the [Cu₁₅(H)₂{S₂CNR₂}₆(C₂Ph)₆]⁺ NCs show broad multiband absorption peaks at 509, 540, and 570 nm and an intense absorption band at 310 nm. The stability of **2_H** in chloroform at ambient temperature was studied by UV-Vis spectra. The absorption spectrum changed steadily over time and within 24 hours a new band appeared at 360 nm, corresponding to [Cu₁₃{S₂CN^{*n*}Pr₂}₆(C₂Ph)₄]⁺ (Figure S13).^[15] Reaction of **3_H** with Au(PPh₃)Cl in dichloromethane for one hour at room temperature yielded a highly luminescent [AuCu₁₂(S₂CN^{*i*}Bu₂)₆(C₂Ph)₄]⁺ cluster (Figure S14). This result implies that the Au@Cu₁₂ alloy is generated through formation of [Cu₁₃{S₂CN^{*i*}Bu₂}₆(C₂Ph)₄]⁺.^[17]

DFT calculations were performed on a simplified model of **1-3** (see SI), namely [Cu₁₅(H)₂(S₂CNH₂)₆(C₂Ph)₆]⁺ (**1'**). Its optimized geometry is of C_i symmetry, slightly

distorted away from S_6 . Its metric data are in good agreement with the X-ray structures of **1-3** (Table S3). It has a large HOMO-LUMO gap (3.90 eV), as expected for a stable Cu(I) species. Consistently, the copper natural atomic orbital (NAO) charges are substantially positive (0.29, 0.77 (av.) and 0.66 for Cu_{cent}, Cu_{ico} and Cu_{cap}, respectively). On the other hand, the hydride NAO charges are negative (-0.62). The small values of the Cu-Cu Wiberg indices (< 0.07, see Table S3) agree with the view of weakly interacting Cu(I) centers. The Cu_{cap}-H and Cu_{ico}-H Wiberg indices (av. 0.055) are much smaller than their Cu_{cent}-H counterpart (0.164), in line with the corresponding interatomic distances. These data are consistent with the view of a linear 14-electron [CuH₂]⁻ complex encapsulated within a [Cu₁₄]¹⁴⁺ cage.^[18] Similar calculations on the free [CuH₂]⁻ anion led to Cu-H distances, Cu-H Wiberg indices and Cu NAO charge of 1.571 Å, 0.486, and 0.21, respectively. These values support the view of a strong ionic interaction between [CuH₂]⁻ and its cage. TD-DFT calculations on **1'** (Figure S15) were unable to reproduce the low energy band. The intense band was found originating from three major transitions computed at 385, 364 and 306 nm and corresponding to dtc→Cu₁₅ charge transfer.

The degradation of **2_H** was investigated by variable temperature ¹H NMR (25 to 50 °C) in CDCl₃ (Figure S16). The results show good agreement with our UV-vis studies, where **2_H** was converted to [Cu₁₃{S₂CNⁿPr₂}₆(C₂Ph)₄]⁺ by the liberation of H₂ (peak at 4.8 ppm). This indicates that [Cu₁₅(H)₂{S₂CNⁿPr₂}₆(C₂Ph)₆]⁺ is unstable in chlorinated solvents at high temperature. This is supported by ESI-MS recorded by using dichloromethane as solvent (Figure S17). We suggest (Scheme 2) that **2_H** (m/z = 2618.8) disintegrates to [Cu₁₄(H)₂{S₂CNⁿPr₂}₆(C₂Ph)₅]⁺ (m/z = 2452.5) by the loss of [Cu(C₂Ph)]. The disintegration continues to peel away another [Cu(C₂Ph)], leading to [Cu₁₃H₂{S₂CNⁿPr₂}₆(C₂Ph)₄]⁺ and finally releasing H₂ to form the 2-electron

superatom $[\text{Cu}_{13}\{\text{S}_2\text{CN}^n\text{Pr}_2\}_6(\text{C}_2\text{Ph})_4]^+$ ($m/z = 2288.5$). The last stage of decomposition is possible via an internal redox reaction;

$(\text{Cu}^+ + 2\text{H}^- \longrightarrow \text{Cu}^0 + \text{H}_2)$, which is accompanied with icosahedron to cuboctahedron structural rearrangement of the centered Cu_{13} unit (Figure S18). This is supported by DFT calculations that found stable structures of $[\text{Cu}_{14}(\text{H})_2(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_5]^+$ and $[\text{Cu}_{13}(\text{H})_2(\text{S}_2\text{CNR}_2)_5(\text{C}_2\text{Ph})_4]^+$ compositions as potential intermediates (see SI). We thus propose that $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_6]^+$ is an intermediate product which releases external energy to form the stable $[\text{Cu}_{13}\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_4]^+$ NC. Here the reducing agents yielding Cu^0 from Cu^{I} are the hydrides.

In summary, we isolated the highly reactive clusters

$[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$, $\text{R} = n\text{Bu}$ (**1_H**), $n\text{Pr}$ (**2_H**) and $i\text{Bu}$ (**3_H**), which helps understanding the intermediates involved in the formation of a 2-electron copper superatom. The reaction was monitored and the intermediates were fully characterized. Furthermore, in CDCl_3 the $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$ undergoes degradation to release two $[\text{Cu}(\text{C}_2\text{Ph})]$ to form $[\text{Cu}_{13}\text{H}_2\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_4]^+$, which finally releases H_2 via a redox reaction to form superatom clusters.

Supporting Information

Supporting Information is available from the Wiley Online Library.

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Scheme 1. Synthesis of clusters **1-3** from a) polyhydrido copper clusters, and b) mixing of substrates and borohydrides.

Scheme 2: Degradation of $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_6]^+$ into a two electron superatom $[\text{Cu}_{13}\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_4]^+$.

Figure 1. Positive mode ESI-MS of $[\mathbf{1_H}]^+$ (a) and fragment ion peaks $[\text{Cu}_{14}(\text{H})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}_2\text{Ph})_5]^+$ (b), $[\text{Cu}_{13}(\text{H})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}_2\text{Ph})_4]^+$ (c), $[\text{Cu}_8\text{H}(\text{S}_2\text{CN}^n\text{Bu}_2)_6]^+$ (d). Insets shows isotopic patterns for $[\mathbf{1_H}]^+$, experimental on top and simulated on bottom.

Figure 2. a) Structure of $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CN}^n\text{Pr}_2\}_6(\text{C}_2\text{Ph})_6]^+$ ($\mathbf{2_H}$) from neutron diffraction data. b). Side view of the bicapped icosahedral Cu_{14} shell encapsulating a copper dihydride unit. Color: green, copper; yellow, sulphur; blue, nitrogen; grey, carbon; pink, hydrogen.

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A 15 nuclear copper dihydride cluster $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$ (**1**) containing a linear $[\text{CuH}_2]^-$ complex embeded in a $[\text{Cu}_{14}]^{14+}$ cage was isolated and structurally characterized. This cluster readily converts to a two electron superatom cluster $[\text{Cu}_{13}]^{11+}$ at elevated temperatures. Highly luminescent $[\text{AuCu}_{12}(\text{S}_2\text{CNR}_2)_6(\text{C}_2\text{Ph})_4]^+$ cluster was isolated by recting **1** with Au(I) salts.

Copper-dihydride

Kiran Kumarvarma Chakrahari, Jingping Liao, Rhone P. Brocha Silalahi, Tzu-Hao Chiu, Jian-Hong Liao, Xiaoping Wang,* Samia Kahlal, Jean-Yves Saillard,* and C. W. Liu*

Isolation and Structural Elucidation of 15-nuclear Copper Dihydride Clusters: An Intermediate in the Formation of a 2-electron Copper Superatom

Supporting Information

Isolation and Structural Elucidation of 15-nuclear Copper Dihydride Clusters: An Intermediate in the Formation of a 2-electron Copper Superatom

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EXPERIMENTAL SECTION

Materials and Methods: All chemicals were purchased from commercial sources and used as received. All the reactions were conducted under an Ar/N₂ atmosphere using standard Schlenk techniques. [Cu₂₈H₁₅{S₂CNR₂}₁₂](PF₆), [Cu(CH₃CN)₄](PF₆), K(S₂CNR) ligands (NR= NⁿPr₂, NⁿBu₂ and NⁱBu₂), Triethylamine and phenylacetylene were prepared as described in the literature.^[1-3] Solvents were purified following standard protocols. Melting points were measured by using a Fargo MP-2D melting point apparatus. The elemental analyses were done using a Perkin-Elmer 2400 NCSH analyzer. NMR spectra were recorded on Bruker Advance DPX300 FT-NMR spectrometer that operates at 300 MHz while recording ¹H, 121.5 MHz for ³¹P, 75.5 MHz for ¹³C, and 46.1 MHz for ²H. Residual solvent protons were used as a reference (δ, ppm, CDCl₃, 7.26). ³¹P NMR spectra were referenced to external 85% H₃PO₄ at δ 0.00; Bruker Advance DPX400 FT-NMR spectrometer recording ¹H, 161.96 MHz for ³¹P, 100.6 MHz for ¹³C, and 61.4 MHz for ²H. Residual solvent protons were used as a reference (ppm, CDCl₃, δ = 7.26). ³¹P NMR spectra were referenced to external 85% H₃PO₄ at δ 0.00. ESI-mass spectra were recorded on a Bruker maXis ESI-QTOF (quadrupole time-of-flight) tandem mass spectrometer. UV-Visible absorption spectra were measured on a Perkin Elmer Lambda 750 spectrophotometer using quartz cells with path length of 1 cm.

Synthesis of [Cu₁₅(H)₂(S₂CNⁿBu₂)₆(C₂Ph)₆]⁺ from [Cu₂₈(H)₁₅(S₂CNⁿBu₂)₁₂]⁺

In a Flame-dried Schlenk tube, [Cu₂₈(H)₁₅(S₂CNⁿBu₂)₁₂](PF₆), (0.1 g, 0.022 mmol) was suspended in THF (5 mL) along with phenylacetylene (24 μL, 0.22 mmol) resulting mixture was stirred at 30 °C for 12 h. The solvent was evaporated under vacuum and the residue was washed with diethyl ether (3×15 mL) to remove styrene, followed by methanol (3×5 mL) to remove [Cu₈(H)(S₂CNⁿBu₂)₆]⁺ and other ligand impurities. The residue was extracted in dichloromethane and filtered through

aluminum oxide. Finally solvent was evaporated to dryness under vacuum to get a pure orange red powdered $[\text{Cu}_{15}\text{H}_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)$ (**1_H**) (0.035 g, 54%, based on Cu). Similarly, deuterium analogue (**1_D**) was synthesized by reacting $[\text{Cu}_{28}(\text{D})_{15}(\text{S}_2\text{CN}^n\text{Bu}_2)_{12}](\text{PF}_6)$, (0.1 g, 0.022 mmol), phenylacetylene (24 μL , 0.22 mmol) resulted in the formation of $[\text{Cu}_{15}(\text{D})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)$ (**1_D**), (0.03 g, 46%, based on Cu) along with mono deuterated-styrene and $[\text{Cu}_8(\text{D})(\text{S}_2\text{CN}^n\text{Bu}_2)_6]^+$ as byproducts.

Synthesis of $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)$ from Cu(I).

In a Flame-dried Schlenk tube, $\text{K}(\text{S}_2\text{CN}^n\text{Bu}_2)$ (0.0486 g, 0.2 mmol) and phenylacetylene (80 μL , 0.8 mmol) was suspended in THF (30 mL) addition $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ (0.1863 g, 0.5 mmol) and Triethylamine (80 μL , 0.8 mmol) reaction 5 minutes, additional NaBH_4 (0.0037 g, 0.1 mmol) the resulting mixture was stirred at room temperature for 3hr. The solvent was evaporated under vacuum and residue was dissolved in DCM and washed with water (3 $\times$ 15 mL). After separation of organic layer, the organic layer was passed through Al_2O_3 , Finally the Al_2O_3 red solid was dissolved with Acetone, and solvent was evaporated under vacuum to get a orange red powdered for $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)$ (**1_H**), (0.068 g, 70%, based on Cu), Mp: 242 $^\circ\text{C}$ (dec.). The deuterium analog (**1_D**) was synthesized by reacting NaBD_4 (0.0042 g, 0.1 mmol), formation of $[\text{Cu}_{15}(\text{D})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)$ (**1_D**) (0.070 g, 73%, based on Cu), Mp: 242 $^\circ\text{C}$ (dec.).

(**1_H**): ESI-MS: m/z (Cal. 2786.7) 2787.7 (M^+) for $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$ (**1_H**) ^1H NMR (300 MHz, CDCl_3 , ppm): 7.12~7.45 (m, 30H, $-\text{C}_2\text{Ph}$), 5.07 (bs, 2H, $\mu_5\text{-H}$), 3.89~4.01 (m, 24H, CH_2), 1.52~1.76 (m, 24H, CH_2), 1.11~1.32 (m, 24H, CH_2), 0.68~0.86 (d, 36H, CH_3); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm): 202.30, 132.11, 128.44, 127.46, 125.18, 49.35, 29.14, 20.04, 13.73; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CDCl_3 , ppm): -143.11 ($^1J_{\text{PF}} = 714$ Hz). (**1_H**) Elem. Anal: (Cal. C% 41.77; H% 4.81; N% 2.87; S% 13.12). Found: C% 40.91; H% 4.73; N% 2.96; S% 12.95.

(**1_D**): ESI-MS: m/z (Cal. 2789.7) 2788.7 (M^+) for $[\text{Cu}_{15}(\text{D})_2(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$ (**1_D**): ^1H NMR (300 MHz, CDCl_3 , ppm): 7.12~7.45 (m, 30H, $-\text{C}_2\text{Ph}$), 3.89~4.01 (m, 24H, CH_2), 1.52~1.76 (m, 24H, CH_2), 1.11~1.32 (m, 24H, CH_2), 0.68~0.86 (d, 36H, CH_3) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (121.49 MHz, CDCl_3 , ppm): -143.11 ($^1J_{\text{PF}} = 714$ Hz); ^2H NMR (46.1 MHz, CDCl_3 , ppm): 4.98 (bs, 2D, $\mu_5\text{-D}$).

Synthesis of $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CN}^n\text{Pr}_2)_6(\text{C}\equiv\text{CPh})_6](\text{PF}_6)$ from Cu(I).

In a Flame-dried Schlenk tube, $\text{K}(\text{S}_2\text{CN}^n\text{Pr}_2)$ (0.0432 g, 0.2 mmol) and phenylacetylene (80 μL , 0.8 mmol) was suspended in THF (30 mL) addition $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$ (0.1863 g, 0.5 mmol) and Triethylamine (80 μL , 0.8 mmol)

reaction 5 minute, additional NaBH₄ (0.0037 g, 0.1 mmol) the resulting mixture was stirred at room temperature for 3 hr. The solvent was evaporated under vacuum and residue was dissolved in DCM and washed with water (3×15 mL). After separation of organic layer, the organic layer was passed through Al₂O₃. Finally the Al₂O₃ red solid was dissolved with acetone, and solvent was evaporated under vacuum to get a orange red powdered for [Cu₁₅(H)₂(S₂CNⁿPr₂)₆(C≡CPh)₆](PF₆) (**2_H**), (0.057 g, 65%, based on Cu), Mp: 185 °C (dec.). The deuterium analog (**2_D**) was synthesized by reacting NaBD₄ (0.0042 g, 0.1 mmol), formation of [Cu₁₅(D)₂(S₂CNⁿPr₂)₆(C≡CPh)₆](PF₆) (**2_D**) (0.059 g, 65%, based on Cu), Mp: 185 °C (dec.).

(**2_H**): ESI-MS: *m/z* (Cal. 2616.5) 2618.5 (M⁺) for [Cu₁₅(H)₂(S₂CNⁿPr₂)₆(C₂Ph)₆](PF₆) (**2_H**) ¹H NMR (300 MHz, CDCl₃, ppm): 7.14~7.49 (m, 30H, -C₂Ph), 4.92 (bs, 2H, μ₅-H), 3.67~4.03 (t, 24H, CH₂), 1.65~1.85 (m, 24H, CH₂), 0.82~0.98 (d, 36H, CH₃) ppm; ¹³C NMR (75.5 MHz, CDCl₃, ppm): 203.12, 132.10, 131.83, 128.13, 128.07, 123.57, 59.48, 20.44, 11.126; ³¹P{¹H} NMR (121.49 MHz, CDCl₃, ppm): -143.11 (¹J_{PF} = 714 Hz). Elem. Anal: (Cal. C% 39.10; H% 4.23; N% 3.04; S% 13.91). Found: C% 39.22; H% 4.23; N% 3.08.

(**2_D**): ESI-MS: *m/z* (Cal. 2620.5) 2620.7 (M⁺) for [Cu₁₅(D)₂(S₂CNⁿPr₂)₆(C₂Ph)₆](PF₆) (**2_D**) ¹H NMR (300 MHz, CDCl₃, ppm): 7.14~7.49 (m, 30H, -C₂Ph), 3.67~4.03 (t, 24H, CH₂), 1.65~1.85 (m, 24H, CH₂), 0.82~0.98 (d, 36H, CH₃); ²H NMR (46.1 MHz, CDCl₃, ppm): 5.04 (bs, 2D, μ₅-D); ³¹P{¹H} NMR (121.49 MHz, CDCl₃, ppm): -143.11 (¹J_{PF} = 714 Hz).

Synthesis of [Cu₁₅(H)₂(S₂CNⁱBu₂)₆(C≡CPh)₆](PF₆) from Cu(I).

In a Flame-dried Schlenk tube, K(S₂CNⁱBu₂) (0.0486 g, 0.2 mmol) and phenylacetylene (80 μL, 0.8 mmol) was suspended in THF (30 mL) addition [Cu(CH₃CN)₄](PF₆) (0.1863 g, 0.5 mmol) and Triethylamine (80 μL, 0.8 mmol) reaction 5 minutes, additional NaBH₄ (0.0037 g, 0.1 mmol) the resulting mixture was stirred at room temperature for 3 hours. The solvent was evaporated under vacuum and residue was dissolved in DCM and washed with water (3×15 mL). After separation of organic layer, the organic layer was passed through Al₂O₃, finally the Al₂O₃ red solid was dissolved with acetone, and solvent was evaporated under vacuum to get a orange red powdered for [Cu₁₅(H)₂(S₂CNⁱBu₂)₆(C≡CPh)₆](PF₆) (**3_H**), (0.071 g, 74%, based on Cu), Mp: 235 °C (dec.). The deuterium analog (**3_D**) was synthesized by reacting NaBD₄ (0.0042 g, 0.1 mmol), formation of [Cu₁₅(D)₂(S₂CNⁱBu₂)₆(C≡CPh)₆](PF₆) (**3_D**) (0.074 g, 75%, based on Cu), Mp: 235 °C (dec.).

(**3_H**): ESI-MS: *m/z* (Cal. 2786.7) 2787.7 (M⁺) for [Cu₁₅(H)₂(S₂CNⁱBu₂)₆(C₂Ph)₆](PF₆) (**3_H**). ¹H NMR (300 MHz, CDCl₃, ppm): 7.12~7.45 (m, 30H, -C₂Ph), 4.99 (bs, 2H, μ₅-H), 3.67~3.95 (t, 24H, CH₂), 2.31~2.49 (m, 12H, CH), 0.68~0.97 (d, 36H, CH₃); ¹³C

NMR (75.5 MHz, CDCl₃, ppm): 203.33, 132.12, 128.33, 127.98, 123.01, 65.74, 27.46, 20.04; ³¹P{¹H} NMR (121.49 MHz, CDCl₃, ppm): -143.11 (¹J_{PF} = 714 Hz). Elem. Anal: (Cal. C% 41.77; H% 4.81; N% 2.87; S% 13.12). Found: C% 40.99; H% 5.02; N% 2.97; S% 13.17.

(**3D**): ESI-MS: *m/z* (Cal. 2789.7) 2788.7 (M⁺) for [Cu₁₅(D)₂(S₂CN^{*i*}Bu₂)₆(C₂Ph)₆](PF₆) (**3D**) ¹H NMR (300 MHz, CDCl₃, ppm): 7.12~7.45 (m, 30H, -C₂Ph), 3.67~3.95 (t, 24H, CH₂), 2.31~2.49 (m, 12H, CH), 0.68~0.97 (d, 36H, CH₃); ²H NMR (46.1 MHz, CDCl₃, ppm): 5.13 (bs, 2D, μ₅-D).

Synthesis of [AuCu₁₂(S₂CN^{*i*}Bu₂)₆(C≡CPh)₄]⁺ from **3H**:

Clusters **3H** (0.02 g, 0.007 mmol) and Au(PPh₃)Cl (0.003 g, 0.007 mmol) were dissolved in 2 mL of 2-methyltetrahydrofuran solvent and the reaction mixture was stirred at 20 °C for one hour. The solvent was evaporated and the residue was subjected to alumina yielded [AuCu₁₂(S₂CN^{*i*}Bu₂)₆(C≡CPh)₄]⁺ (0.01 g, 52%). ESI-MS:*m/z* (Cal. 2588.79) 2588.84 for [AuCu₁₂(S₂CN^{*i*}Bu₂)₆(C₂Ph)₄]⁺; ¹H NMR (300 MHz, CDCl₃, ppm): 7.12~7.44 (m, 20H, -C₂Ph), 3.66~3.94 (t, 24H, CH₂), 2.30~2.48 (m, 12H, CH), 0.68~0.97 (d, 36H, CH₃).

X-ray Crystallography

Single crystals suitable for X-ray diffraction analysis of **1H**, **2H** and **3H** were obtained by slowly diffusing hexane into a concentrated acetone solution at -5 °C temperature. The single crystals were mounted on the tip of glass fiber coated in paratone oil, then frozen at 150 K. Data were collected on a Bruker APEX II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was performed with SAINT,^[4] Absorption corrections for the area detector were performed by using the SADABS program.^[5] The structure was solved by direct methods and refined by least-squares against *F*² using the SHELXL-2018/3 package,^[6] Incorporated in SHELXTL/PC V6.14.^[7]

Single Crystal Neutron Diffraction Experiment

The location of hydrides in **2H** was confirmed by single crystal neutron diffraction experiment using the TOPAZ single-crystal neutron time-of-flight (TOF) Laue diffractometer at ORNL's Spallation Neutron Source.^[8] A reddish plate-shaped crystal (0.75 × 0.60 × 0.35 mm) was attached to a MiTeGen loop using a perfluorinated grease (Krytox GPL 205) and cooled to 100 K for data collection. A total of 23 crystal orientations optimized with CrystalPlan software^[9] were used to ensure better than 95% coverage of a hemisphere of reciprocal space. Each orientation was measured for approximately 6.5 hrs with 30 C of proton charge at the beam power of 1.4 MW. Peak integration and data reduction were performed in accordance

with previously reported procedures.^[10] A spherical absorption correction was applied with $\mu = 0.1213 + 0.08834 \lambda \text{ mm}^{-1}$. The reduced data were saved in SHELX HKLF2 format in which the neutron wavelength for each reflection was recorded separately. Non-hydrogen atom positions in the X-ray structure of **2_H** were used for initial refinement of the neutron structure. Hydrogen atoms on carbon atoms are placed using the riding model available in SHELXL2014^[11] with the default C-H distances for neutrons; only their displacement parameters are refined. Hydrogen is a negative scatter for neutrons. The peak for missing hydrogen atom appears as negative densities or holes in the difference Fourier map of the neutron data. The hydride peak (the deepest hole of -5.64) was located at 1.78 Å from Cu1 atom in the asymmetric unit of **2_H**. The final refinement with the hydride atom included converged to low residues and featureless difference Fourier maps (deepest hole of -0.65). Selected neutron crystallographic data are listed in Table S2.

ESI MS measurements

Mass spectra of all samples were recorded on a Bruker maXis ESI-QTOF quadrupole time-of-flight tandem mass spectrometer. Mass spectrometry was calibrated with a tuning mix. The operating parameters of the electrospray ionization interface (ESI) in positive mode were: capillary voltage, 4000 V; end plate offset, 500 V; dry gas temperature, 200 °C (N₂); dry gas flow, 4 L/min; and nebulizer pressure, 0.2 bar. Nitrogen was used as the nebulizing gas. The mass range scanned from 50 m/z to 10000 m/z.

Computational details

For the sake of substantial CPU time saving, the substituents R = ⁿBu, ⁿPr, ⁱBu in **1_H**, **2_H** and **3_H**, respectively, were replaced by H. Such a simplification has been proven not to significantly affect the structure, bonding and most of properties of the investigated compounds (see for example ref. 14 of the manuscript). The geometry optimizations were performed by DFT calculations with the Gaussian 16 package,^[12] using the PBE0 functional,^[13] and the all-electron Def2-TZVP set from EMSL Basis Set Exchange Library.^[14] All the optimized geometries were characterized as true minima on their potential energy surface by harmonic vibrational analysis. The Wiberg bond indices were computed with the NBO 6.0 program.^[15] The UV-visible transitions were calculated by means of TD-DFT calculations.^[16] Only singlet-singlet, *i.e.* spin-allowed, transitions were computed. The UV-visible spectra were simulated from the computed from the TD-DFT transitions and their oscillator strengths by using the SWizard program,^[17] each transition being associated with a Gaussian function of half-height width equal to 3000 cm⁻¹. The compositions of the molecular orbitals were calculated using the AOMix program.^[18]

Table S1. Crystallographic data for [Cu₁₅(H)₂{S₂CNR₂}₆(C₂Ph)₆](PF₆), R = ⁿBu, 1_H; ⁿPr, 2_H (data collected at 150 K and 100 K, respectively); ⁱBu, 3_H.

	1 _H	2 _H	2 _H	3 _H
CCDC number	1981041	1981042	1981043	1981045
formula	C ₁₀₂ H ₁₄₀ Cu ₁₅ F ₆ N ₆ PS ₁₂	C ₉₀ H ₁₁₆ Cu ₁₅ F ₆ N ₆ PS ₁₂	C ₉₀ H ₁₁₆ Cu ₁₅ F ₆ N ₆ PS ₁₂	C ₁₀₂ H ₁₄₀ Cu ₁₅ F ₆ N ₆ PS ₁₂
fw	2932.98	2764.67	2764.67	2932.98
Crystal symmrtry	Triclinic	Trigonal	Trigonal	Triclinic
space group	<i>P</i> (-) <i>1</i>	<i>R</i> (-) <i>3</i>	<i>R</i> (-) <i>3</i>	<i>P</i> (-) <i>1</i>
a, Å	13.8757(6)	16.5595(4)	16.5411(6)	13.6613(3)
b, Å	14.0092(5)	16.5595(4)	16.5411(6)	13.9755(3)
c, Å	15.3927(6)	31.6951(8)	31.4310(12)	17.5675(4)
α, deg	71.3606(7)	90	90	68.7807(5)
β, deg	85.5309(7)	90	90	86.6061(6)
γ, deg	81.6909(8)	120	120	71.4007(6)
V, Å ³	2803.84(19)	7526.9(4)	7447.6(6)	2957.34(11)
Z	1	3	3	1
T, K	150(2)	150(2)	100(2)	150(2)
ρ _{calcd} , g/cm ³	1.737	1.830	1.849	1.647
μ, mm ⁻¹	3.074	3.429	3.465	2.914
θ _{max} , deg.	28.29	25.99	27.49	26.40
Reflections collected	27259	18675	11539	18166
Independent reflections	13510 (<i>R</i> _{int} = 0.0125)	3283 (<i>R</i> _{int} = 0.0271)	3817 (<i>R</i> _{int} = 0.0304)	11656 (<i>R</i> _{int} = 0.0153)
restraints / parameters	356 / 669	7 / 224	0 / 201	4 / 661
Final R indices [<i>I</i> > 2σ(<i>I</i>) ^{a,b}]	<i>R</i> 1 = 0.0273, <i>wR</i> 2 = 0.0743	<i>R</i> 1 = 0.0193, <i>wR</i> 2 = 0.0522	<i>R</i> 1 = 0.0456, <i>wR</i> 2 = 0.1339	<i>R</i> 1 = 0.0268, <i>wR</i> 2 = 0.0657
R indices (all data)	<i>R</i> 1 = 0.0312, <i>wR</i> 2 = 0.0773	<i>R</i> 1 = 0.0230, <i>wR</i> 2 = 0.0539	<i>R</i> 1 = 0.0544, <i>wR</i> 2 = 0.1425	<i>R</i> 1 = 0.0351, <i>wR</i> 2 = 0.0695
GOF	1.041	1.061	1.083	1.037
Δρ _{max} , e Å ⁻³	1.353	0.511	2.378	0.805
Δρ _{min} , e Å ⁻³	-0.622	-0.285	-0.462	-0.659

Table S2. Selected neutron crystallographic data of **2_N**.

CCDC number	1980144
Chemical formula	C ₉₀ H ₁₁₆ Cu ₁₅ F ₆ N ₆ PS ₁₂
M_r	2764.67
Crystal system, space group	Trigonal, $R\bar{3}$
Temperature (K)	100(2)
a (Å)	16.5308(15)
b (Å)	16.5308(15)
c (Å)	31.519(5)
V (Å ³)	7459.2 (18)
Z	3
Radiation type	Neutrons, $\lambda = 0.4 - 3.5$ Å
μ (mm ⁻¹)	0.12130 + 0.08834 λ
Crystal size (mm ³)	0.75 × 0.60 × 0.35
Data collection	
Diffractometer	TOPAZ
$T_{\min}$, $T_{\max}$	0.812, 0.929
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7837, 1351, 1141
R_{int}	0.120
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.108, 1.13
No. of reflections	1351
No. of parameters	316
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (fm Å ⁻³)	1.27, -0.63
Computer programs: SNS PyDas, Mantidplot, SHELXL2018/3 (Sheldrick, 2015).	

Table S3. Selected X-ray and/or neutron bond lengths (Å) for **1_H**, **2_H**, **3_H** and [Pd(H)₂Cu₁₄{S₂CNⁿBu₂}₆(C₂Ph)₆] (**1_{HPd}**).^[19] DFT-optimized distances of **1'** are also given, together with their corresponding Wiberg indices in brackets.

	M_{cent}-Cu_{ico}	Cu_{ico}-Cu_{ico}	Cu_{cap}-Cu_{ico}	M_{cent}-H	M_{cap}...H	M_{ico}...H	Cu_{ico}-S	Cu_{cap}-S	Cu_{ico}-C	C≡C
1_H	2.6538(3)- 2.7629(3) av. 2.7079(3)	2.5963(4)-3.3130(4) av. 2.8473(4)	2.5824(4)- 2.6511(4) av. 2.6160(4)	1.68(3)	2.13(3)	1.87(3)-1.94(3) av. 1.90(3)	2.3273(5)- 2.4655(6) av. 2.3771(6)	2.2389(6)- 2.2613(6) av. 2.2503(6)	1.980(2)-2.103(2) av. 2.033(2)	1.219(3)-1.226(3) av. 1.222(3)
2_H (150K)	2.6821(2)- 2.7174(2) av. 2.6997(2)	2.6253(3)-3.2081(7) av. 2.8384(4)	2.6058(4)	1.84(3)	1.99(3)	1.858(2)	2.3056(5)- 2.4663(5) av. 2.3834(5)	2.2593(5)	1.9901(19)- 2.0720(18) av. 2.0238(19)	1.223(3)
2_H (100K)	2.6742(5)- 2.7123(5) av. 2.6932(5)	2.6193(7)-3.201(1) av. 2.832(1)	2.6013(8)	1.79(13)	2.03(13)	1.858(14)	2.3201(12)- 2.4639(12) av. 2.3808(12)	2.2592(11)	1.980(4)-2.053(4) av. 2.006(4)	1.241(7)
2_N (100K, neutron)	2.670(4)-2.720(4) av. 2.695(4)	2.624(6)-3.205(7) av. 2.833(6)	2.612(7)	1.78(2)	2.06(2)	1.863(5)	2.310(13)- 2.485(13) av. 2.388(13)	2.271(11)	1.993(7)-2.069(7) av. 2.024(7)	1.227(7)
3_H	2.6138(3)- 2.7183(3) av. 2.6765(3)	2.5622(4)-3.1484(6) av. 2.8172(4)	2.6733(5)- 2.7223(4) av. 2.6998(5)	1.62(3)	2.39(2)	1.81(3)-1.90(3) av. 1.85(3)	2.3402(7)- 2.4056(7) av. 2.3680(7)	2.2390(7)- 2.2582(8) av. 2.2469(7)	1.989(3)-2.083(3) av. 2.030(3)	1.212(4)-1.215(4) av. 1.213(4)
1' (DFT)	2.687-2.726 av. 2.707 [0.069]	2.636-3.011 av. 2.747 [0.052]	2.636-2.666 av. 2.651 [0.069]	1.725 [0.164]	2.212 [0.040]	1.838-1.847 av. 1.843 [0.069]	2.366-2.493 av. 2.427 [0.158]	2.279-2.287 av. 2.282 [0.224]	2.000-2.092 av. 2.036 [0.1873]	1.231-1.235 av. 1.233 [2.602]
1_{HPd} (neutron)	2.694(7)-2.795(7) av. 2.735(7)	2.628(9)- 3.324(8) av. 2.877(9)	2.555(10)- 2.610(10) av. 2.585(10)	1.759(14)	2.020(16)	1.875(19)- 1.930(18) av. 1.910(18)	2.30(2)-2.50(2) av. 2.40(2)	2.27(2)-2.28(2) av. 2.28(2)	1.980(11)- 2.110(11) av. 2.039(11)	1.217(12)-1.244(12) av. 1.231(12)

Figure S1. Positive ES-MS spectrum of $[\mathbf{1D}]^+$, the inset shows experimental one in the top and simulated one in the bottom.

Figure S2. Positive ES-MS spectrum of $[2H]^+$, the inset shows experimental one in the top and simulated one in the bottom.

Figure S3. Positive ES-MS spectrum of $[\mathbf{3_H}]^+$, the inset shows experimental one in the top and simulated one in the bottom.

Figure S4. Positive ES-MS spectrum of $[2D]^+$, the inset shows experimental one in the top and simulated one in the bottom.

Figure S5. Positive ES-MS spectrum of $[3D]^+$, the inset shows experimental one in the top and simulated one in the bottom.

Figure S6. a) ^1H NMR spectrum of compound **1_H** in CDCl_3 ; b) ^2H NMR spectrum of compound **1_D** in CHCl_3 .

Figure S7. ¹H NMR spectrum of **2H** in CDCl₃.

Figure S8. ^2H NMR spectrum of **2_D** in CHCl_3 .

Figure S9. ^1H NMR spectrum of **3H** in CDCl_3 .

Figure S10. ^2H NMR spectrum of **3D** in CHCl_3 .

Figure S11. Shell by shell construction of cationic cluster $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_6]^+$: a). Linear copper dihydride unit; b). The bicapped icosahedral Cu_{14} shell; c). Cu_{15}H_2 shell; d.) six dithiocarbamate and six phenylacetylene ligands; e). Structure of $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_6]^+$ (Hydrogen atoms of the ligands are deleted for clarity). Color: red, copper; yellow, sulphur; blue, nitrogen; grey, carbon; white, hydrogen.

Figure S12. The D_{3d} symmetry of a bicapped Cu_{15}H_2 icosahedral along (a) C_3 and C_2 axis; (b) σ_d .

Figure S13. Time dependent UV-visible spectrum for $[\text{Cu}_{15}(\text{H})_2(\text{S}_2\text{CN}(\text{nPr})_2)_6(\text{C}_2\text{Ph})_6](\text{PF}_6)$ change to $[\text{Cu}_{13}(\text{S}_2\text{CN}(\text{nPr})_2)_6(\text{C}_2\text{Ph})_4](\text{PF}_6)$.

Figure S14. Positive ESI mass spectrum of $[\text{AuCu}_{12}(\text{S}_2\text{CN}^i\text{Bu}_2)_6(\text{C}_2\text{Ph})_4]^+$ isolated from the reaction of **3_H** with $\text{Au}(\text{PPh}_3)\text{Cl}$. Inset shows the luminescence behavior of the synthesized complex.

Figure S15. TD-DFT simulated spectrum of **1'**.

Figure S16. The VT-NMR of [Cu₁₅H₂{S₂CN^{*i*Pr}₆(C₂Ph)₆](PF₆) in CDCl₃.}

Figure S17. The ESI-MS spectrum showing the decomposition of $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph})_6]^+$ to $[\text{Cu}_{13}\{\text{S}_2\text{CNR}_2\}_6(\text{C}_2\text{Ph}_4)]^+$ cluster.

Figure S18. Decompositions of $[\text{Cu}_{15}(\text{H})_2\{\text{S}_2\text{CN}^{\text{Pr}}\text{Pr}_2\}_6(\text{C}_2\text{Ph})_6]^+$ in chlorinated solvent en route to $[\text{Cu}_{13}\text{H}_2\{\text{S}_2\text{CN}^{\text{Pr}}\text{Pr}_2\}_6(\text{C}_2\text{Ph})_4]^+$ followed by an internal redox reaction as well as Cu_{13} core rearrangement to reach a two-electron species.

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