Polyhydrido Copper Nanoclusters with a Hollow Icosahedral Core \([\text{Cu}_{30}\text{H}_{18}\text{E}_2\text{P}(\text{OR})_{212}]\) (E = S or Se; \(\text{R} = \text{n Pr, i Pr or i Bu}\))

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Polyhydrido Copper Nanoclusters with a Hollow Icosahedral Core: \([\text{Cu}_{30}\text{H}_{18}(\text{E}_2\text{P(O\text{R})}_2)_2]_2\) (E = S or Se; R = \(^\text{7}\text{Pr}, \text{\text{10}}\text{Pr}\) or \(^\text{13}\text{Bu})\)

Subrata Kumar Barik,\(^{a[a]}\) Shou-Chih Huo,\(^{a[a]}\) Chun-Yen Wu,\(^{a[a]}\) Tzu-Hao Chiu,\(^{a[a]}\) Jian-Hong Liao,\(^{a[a]}\) Xiaoping Wang,\(^{b[a]}\) Samia Kahlal,\(^{c[a]}\) Jean-Yves Saillard,\(^{* [c]}\) and C. W. Liu\(^{* [a]}\)

Dedicated to our colleague and friend Dr. Jean-Rene Hamon on the occasion of his 65th birthday

**Abstract:** Although atomically precise polyhydrido copper nanoclusters are of prime interest for a variety of applications, they have so far remained scarce. Herein, we describe the synthesis of a dithiophosphate-protected copper(I) hydride-rich nanocluster (NC), \([\text{Cu}_{30}\text{P}_3\text{S}_6\text{P(O\text{R})}_2\text{H}_2]_2\) (1\(_\text{H}\)), fully characterized by various spectroscopic methods and single crystal X-ray diffraction. The X-ray structure of 1\(_\text{H}\) reveals an unprecedented central \(\text{Cu}_{20}\) hollow icosahedron. Six faces of this icosahedron are capped by \(\text{Cu}_3\) triangles, the whole \(\text{Cu}_{20}\) core being wrapped by twelve dithiophosphate ligands and the whole cluster has ideal \(S_3\) symmetry. The locations of the 18 hydrides in 1\(_\text{H}\) were ascertained by a single crystal neutron diffraction study. They are composed of three types: capping \(\mu_2\)-H, interstitial \(\mu_2\)-H (seesaw) and \(\mu_2\)-H ligands (square pyramidal), in good agreement with the DFT simulations. The numbers of hydrides and ligand resonances in the \(^1\)H NMR spectrum of 1\(_\text{H}\) are in line with their coordination environment in the solid-state, retaining the \(S_3\) symmetry in solution. Furthermore, two new Se-protected polyhydrido copper nanoclusters, \([\text{Cu}_{30}\text{H}_{15}\text{Se}_3\text{P(O\text{R})}_2\text{H}_2]_2\) (2\(_\text{Se}\)) \((\text{R} = \text{Pr}_2; \text{R} = \text{Bu})\) were synthesized from their sulfur relative 1\(_\text{H}\) via ligand displacement reaction and their X-ray structures feature the exceptional case where both the NC shape and size are fully conserved during the course of ligand exchange. DFT and TD-DFT calculations allow understanding the bonding and optical properties of clusters 1\(_\text{H}-3\(_\text{Se}\). In addition, the reaction of 1\(_\text{H}\) with [Pd(PPh\(_3\))\(_2\)] in the presence of terminal alkynes led to the formation of new bimetallic Cu-Pd alloy clusters [PdCu\(_3\)H\(_3\)S\(_2\)P(O\text{Pr})\(_2\)]\(_2\) (C=CR\(_3\)) (4): \(\text{R} = \text{Ph} ; 5\); \(\text{R} = \text{CuH}_2\text{F}\).

**Introduction**

Since the discovery of the first binary copper hydride in 1844 by Wurtz (hexagonal Wurtzite-type structure),\(^{[1, 2]}\) several multinuclear copper hydrido and polyhydrido complexes and clusters, protected by various types of ligands (phosphines, pyridines and N-heterocyclic carbenes) were synthesized.\(^{[3-14]}\) They have been capturing substantial interest, not only from the viewpoints of their fascinating structural features,\(^{[15-17]}\) but also owing to their promising applications as hydrogen storage materials\(^{[18-23]}\) and as key intermediates in various catalytic transformations in organic synthesis.\(^{[24, 25]}\) An emblematic example is the well characterized phosphine-protected [CuH(PPh\(_3\))]\(_2\), widely known as Stryker’s reagent, which was shown to be a mild and selective reagent for conjugate reduction of \(\alpha\), \(\beta\)-unsaturated carbonyl compounds.\(^{[26]}\) Related chiral phosphine-copper hydride catalysts were employed for the asymmetric hydroboration of alkenes.\(^{[27]}\)

In recent years, this copper hydride chemistry has evolved towards the design of nanosized ligand-protected polyhydrido copper clusters which have emerged as a new class of materials in the field of nanoscience, owing to their various potential applications,\(^{[15-25, 28-37]}\) Unlike the incredible success found in the chemistry of Ag and Au atomically precise nanoclusters (NCs), that of copper is still in its infancy, which is partly due to the much lower reduction potential of Cu than those of Ag and Au. In this context, only a handful of ligand-supported Cu(0)/Cu(I) mixed-valent polyhydrides have been so far reported,\(^{[38-41]}\) and Cu(I) hydrides are merely more numerous.\(^{[42, 43]}\) Our recent findings such as [Cu\(_2\)H\(_{11}\)(E\(_{2}\)P(O\text{Pr})\(_2\))]\(_2\) (E = S,\(^{[46]}\) Se\(^{[47]}\)) and [Cu\(_2\)H\(_{13}\)(S\(_2\)C\(_{12}\)\text{O}\_\text{3})(\text{PrP})\(_2\)]\(_2\)\(^{[48]}\) have not only uncovered fascinating structural architectures (elongated triangular orthobicopula, rhombicuboctahedral and pseudo-rombohedral core, respectively) but also shown potential applications in solar \(H_2\) evolution. In fact, the latter has been utilized in the electrocatalytic \(CO_2\) reduction via a lattice hydride mechanism and also led to the formation of rhombus-shaped copper nanoparticles under reduction with excessive amount of NaBH\(_4\).\(^{[53-49, 50]}\) These findings raise the question whether there could exist chalcogen-protected polyhydrido Cu(I) clusters with a hollow icosahedral core framework. Indeed, such a situation has been encountered before in case of Ag and Au clusters.\(^{[51, 52]}\)

The recent discovery of [Cu\(_{30}\)(RCOO)\(_{10}\)(C\(_\text{6}\)C\(_\text{6}\)Bu\(_3\))\(_\text{3}\)Cu\(_\text{3}\)]\(_\text{2}\) - nanocluster by Zheng and co-workers offered the existence of inner Cu\(_\text{12}\) cluster icoahedral within the four-concentric shell Cu\(_\text{12}\)@Cu\(_\text{12}\)Cl\(_\text{2}\)@Cu\(_\text{12}\)@Cu\(_\text{12}\), thus indicated the possibility of empty Cu\(_\text{12}\) icosahedral core within a polyhydrido copper NC.\(^{[53]}\)

In this article, we report the synthesis and full characterization of a series of 30-metal and 18-hydride dichalcogenolate-protected copper clusters, namely [Cu\(_{30}\)H\(_{11}\)(E\(_{2}\)P(O\text{R})\(_2\))]\(_2\) (1\(_\text{H}\) : E = S; R = \(^\text{7}\)Pr; 2\(_\text{H}\) : E = Se; R = \(^\text{7}\)Pr; 3\(_\text{H}\) : E = Se; R = \(^\text{13}\)Bu). They all feature a hollow Cu\(_\text{12}\) icosahedral core, a structure that has not been characterized before amongst Cu(I) NCs.

Single crystals suitable for a neutron diffraction analysis could be grown so that the precise location of all the hydrides in 1\(_\text{H}\) was successfully uncovered. Remarkably, six four-coordinated hydrides out of total 18 exhibited nearly seesaw geometry, where the central hydride bonds to four Cu atoms with a local \(C_7\) symmetry, hitherto unknown in metal hydride chemistry. The reaction of 1\(_\text{H}\) with Pd(PPh\(_3\))\(_2\)Cl\(_2\) in the presence of different alkynes as auxiliary ligands leads to the formation of the new materials.\(^{[18-23]}\)
Results and Discussion

In a typical one pot synthetic method, the treatment of \((\text{NH}_3)_2\text{S}_2\text{P(O^\text{OPr})_2}\) with \([\text{Cu(CH}_3\text{CN})_2]\text{PF}_6\) in THF resulted in an immediate color change from colorless to yellow. Addition of \text{NaBH}_4 to the solution at -20 °C resulted in a gradual color change to orange-red. Continuous stirring at low temperature for 4 hours followed by work-up led to the isolation of \([\text{Cu}_2\text{H}_2\text{Se}_2\text{P(O^\text{OPr})_2}]_{12}\), \(1\text{H}\) in 38 % yield (Scheme 1, Figure S1, see supporting information). Cluster \(1\text{H}\) has been fully characterized by a broad spectrum of standard chemical characterization protocols including ESI mass spectrometry, multinuclear NMR spectroscopy, UV-Vis, X-ray crystallography, and neutron diffraction study.

\[
\begin{align*}
30 \text{[Cu(CH}_3\text{CN})_2]\text{PF}_6 + 12 \text{NH}_4\text{S}_2\text{P(O^\text{OPr})_2} & \rightarrow \text{NaBH}_4 \\
\text{CH}_3\text{CN, THF} & \rightarrow 20 ^\circ\text{C, 4h} \\
\text{[Cu}_2\text{H}_2\text{Se}_2\text{P(O^\text{OPr})_2}]_{12} & (38.02 \%) \\
12 \text{NH}_4\text{S}_2\text{P(O^\text{OPr})_2} & \rightarrow \text{THF, -20^\circ\text{C, 2 min}} \\
-12 \text{NH}_4\text{S}_2\text{P(O^\text{OPr})_2} & \rightarrow \text{THF, 35 ^\circ\text{C, 48h}} \\
\text{[Cu}_2\text{H}_2\text{Se}_2\text{P(O^\text{OPr})_2}]_{12} & 1. \text{Pd(PPh}_3\text{)_2Cl}_2 \\
& 2. 15 \text{HC=CR}^1 \\
& \text{THF, 35 ^\circ\text{C, 48h}} \\
& \text{[Cu}_2\text{H}_2\text{Se}_2\text{P(O^\text{OPr})_2}]_{12} \\
2\text{R} & = \text{Ph (71.16 %)} \\
3\text{R} & = \text{Bu (64.20 %)} \\
\text{[PdCu}_4\text{H}_4\text{Se}_2\text{P(O^\text{OPr})_2}]_{3} \text{[C(C=CR}^1\text{)]_6} & 4. \text{R}^1 = \text{Ph (30.01 %)} \\
& 5. \text{R}^1 = \text{CuH}_4\text{F (32.68 %)}
\end{align*}
\]

Scheme 1. Synthesis of the dichalogenophosphate protected \text{Cu}_x \text{NCs (1x-3x)} and the reactivity of \(1\text{H}\) with \text{Pd}^{2+}.

The composition of \(1\text{H}\) was initially obtained by the analysis of its positive ion ESI-mass spectrum. The spectrum of \(1\text{H}\) evidently shows a most intense peak at \(m/z\) 4547.3 (calcd. 4547.4), corresponding to \([1\text{H}+\text{Cu}]^+\) and a slightly lower intense peak at \(m/z\) 4483.4 (calcd. 4483.6), corresponding to molecular weight of neutral \(1\text{H}\) (Figure 1). Their simulated isotopic patterns match well with the experimental observation (Figure 1).

The \(^{31}\text{P}\)\(^{1}\text{H}\) NMR spectrum of \(1\text{H}\) displays two signals at 112.69 and 108.88 ppm indicating two types of dipropyl dithiophosphate (dtp) ligands in solution at room temperature (Figure S2). \(^1\text{H}\) NMR spectrum of \(1\text{H}\) shows three different signals at 4.22-4.05, 1.70, and 0.97 ppm in 1:1:1.5 intensity ratios corresponding to the \(-\text{OCH}_2\), \(\text{CH}_3\), and \(\text{CH}_2\) protons, respectively attributed to propyl groups in dtp ligands (Figure 2a, S3). In addition to these propyl peaks, it also shows three broad hydride resonances at 3.52, 0.78, and 0.60 ppm, respectively in equal intensity (Figure 2a). In order to confirm the presence of hydrides in \(1\text{H}\), its deuteride analogue \([\text{Cu}_2\text{D}_2\text{Se}_2\text{P(O^\text{OPr})_2}]_{12}\) (1\text{D}) was synthesized. The \(^1\text{H}\) NMR spectrum of \(1\text{D}\) in \text{CHCl}_3 shows three broad signals at 3.62, 0.83, and 0.63 ppm with equal intensity (Figure 2b and Figure S4), clearly signifying the existence of three types of hydrides in \(1\text{D}\). Furthermore, the \(^1\text{H}\) variable temperature (VT) NMR of \(1\text{H}\) in \text{CDCl}_3 shows the conservation of three hydride signals, indicating the static nature of the molecule in solution (Figure S5). Cluster \(1\text{H}\) is air and moisture stable in solid state at ambient temperature, (Figure S6) while in solution state it is moderately stable at room temperature, losing its identity upon keeping the solution, especially in polar solvents (\text{CH}_2\text{Cl}_2 and \text{CHCl}_3), for several days (Figure S7).

Figure 1. Positive ion ESI-MS of \(1\text{H}\). Insets show experimental (blue) and simulated (green) spectra corresponding to \([1\text{H}]+ \) and \([1\text{H}+\text{Cu}]^+\).

![Figure 1](image1)

Figure 2. a) \(^1\text{H}\) NMR spectrum of cluster \(1\text{H}\) in \text{CDCl}_3. b) \(^1\text{H}\) NMR spectrum of \(1\text{D}\) in \text{CDCl}_3.

The crystallization of \(1\text{H}\) was performed by vapor diffusion of hexanes into a concentrated \text{CH}_2\text{Cl}_2 solution at room temperature. Rectangular-shaped red crystals (\(P-1\) space group) were obtained within a week. The X-ray diffraction study of compound \(1\text{H}\) revealed a neutrally charged polyhydrido copper NC comprised of 30 copper atoms, 12 dtp ligands, and 18 hydrides (Figure 3a). Shell by shell molecular structure of \(1\text{H}\) can be seen in Figure 3. \(1\text{H}\) features a central core of 12 copper atoms arranged in a non-centered icosahedron, which displays elongation along the \(\text{Cu5-Cu6-Cu15}\) axis (Figure 3b). This \(\text{Cu2}_2\) core is connected, via \text{Cu-Cu} interactions to six \(\text{Cu}_3\) triangular motifs which cap the icosahedron in an octahedral arrangement (Figure 3d). Hence cluster \(1\text{H}\) possesses ideal \(S_6\) symmetry with the \(\text{Cu5}\) axis passing through the \(\text{Cu5-Cu6-Cu15}\) triangle (Figure 3b and d). Alternatively, the \(\text{Cu}_{12}\) metal framework in \(1\text{H}\) can be described as an empty \(\text{Cu}_{12}\) icosahedron embedded in an incomplete rhombicuboctahedral \(\text{Cu}_{30}\) framework (Figure 3e). Within the \(\text{Cu}_{12}\) icosahedron, the average \(\text{Cu}_{12}-\text{Cu}_{12}\) distance of 2.658 (7) Å (range: 2.504(6)-2.899(7) Å) is shorter than that observed in the severely distorted \(\text{Cu}_{13}\) centered icosahedral core in \([\text{Cu}_{2}\text{H}_{2}\text{Se}_{2}\text{P(O^\text{OPr})_2}]_{12}\text{Cl}[\text{PPh}_3]^3\) (avg. 2.777 Å, range: 2.470(3)-3.256(3) Å). It is actually closer to that observed for bulk copper.
metal (2.55 Å). In 1H, the Cu$_{120}$-Cu$_{230}$ distances between the atoms of the Cu$_{12}$ icosahedron and the outer capping Cu atoms (range: 2.534(7)-2.896(6)) are slightly longer than the corresponding distances observed in [Cu$_2$(H$_2$S$_2$)(PPh$_3$)$_2$]Cl (range: 2.389(3)-2.604(3) Å).[38] It is of note that the non-centered Cu$_{12}$ icosahedral core in 1H is similar to the M$_{12}$ cores observed in Ag and Au clusters, for example [Ag$_{14}$(p-MBA)$_{10}$]$^{2-}$[37] and [Au$_{12}$(PPh$_3$)$_3$(dpa)$_3$]$_2$ (MBA = p-mercaptobenzoic acid, dpa = 2,2'-dipyridylamine),[38] showing for the first time that structurally alike NCs with inner empty M$_{12}$ icosahedral core are isolable for all three coinage metals.

The entire Cu$_{120}$ metallic core in 1H is wrapped by twelve dtp ligands. Half of them (three atop and three at the bottom) have axial orientation along the (vertical) C$_3$ axis, whereas the six other ligands coordinate in an equatorial fashion perpendicular to the C$_3$ axis (Figure 3a). These bidentate dtp ligands are coordinated to both capping and icosahedral copper atoms in various binding modes: the axial dtp ligands bind in a trimetallic tricentricity fashion, while the equatorial dtp ligands prefer pentametallic pentacoordinatity pattern (Figure S8). The Cu-µ$_2$-S and Cu-µ$_2$-S distances are in the range of 2.329(1)-2.380(1) Å and 2.395(1)-2.795(1) Å, respectively. As far as we know, the existence of a pentametallic pentacoordinatity binding pattern for the equatorial dtp ligands in 1H is unique and hitherto unknown in the literature (Chart S1).[64,65]

The presence of 18 hydrides was initially inferred by $^1$H and $^2$H NMR spectra of 1H and 10, respectively followed by the X-ray structure determination of 1H. However, their position remained uncertain until the results from single-crystal neutron diffraction analysis of 1H, the corresponding neutron structure of 1H, were available (see supporting information for details). Within the [Cu$_2$(H$_2$S$_2$)$_2$H$_{18}$] framework in 1H (Figure 3) and k or 1H (Figure 3g-i) out of the 20 triangular faces of the Cu$_{12}$ icosahedron, six are capped by [Cu$_{12}$] triangles, twelve are capped by interstitial hydrides ($\mu_4$-H and $\mu_6$-H in equal ratio) and two along the C$_3$ axis (top and bottom) remain uncapped. Each of the six outer [Cu$_{12}$] triangles is capped by a $\mu_6$ hydride. The observed Cu-µ$_4$-H distances in 1H range from 1.61(4) to 1.89(3) Å. Specific bond lengths of 1H are noted in Table 1. Interestingly, the twelve $\mu_4$ and $\mu_6$ hydrides surround the Cu$_{12}$ icosahedron in such a way that they also form an icosahedral array (Figure 3g). Each $\mu_4$-H is coordinated to three icosahedral copper atoms (one icosahedron face) and one of Cu$_{120}$ atom and occupies symmetrical positions around the C$_3$ axis. To our dismay, they favor a distorted seesaw geometry (average $<\mu_4$-H-Cu$_{120}$ = 159.7°) and can be fairly compared with the well-known molecule SF$_6$ with conventional seesaw geometry ($<F$-S-$F$ = 173.1°). The Cu-µ$_6$-H distances in 1H range from 1.68(2) - 1.97(2) Å (avg, d$_{Cu-\mu_6-H}$ = 1.81(2) Å). To the best of our knowledge, hydrides with nearly seesaw coordination mode characterized by neutron diffraction is unprecedented whereas...
tetrahedral or near square-planar and trigonal pyramidal coordination modes of a four-coordinate hydride have been encountered before.\cite{10.1002/chem.202001449,10.1002/chem.202001449}

Each µ₂-H (d_{Cu-H} = 1.83 (2) Å) resides in a square pyramidal cavity formed by oneicosahedron face and two Cu₃C₆ trianglular capping units belonging to the same Cu₃ units.

Over the past few years the nanocluster community has produced hundreds of atomically precise nanoparticles with well resolved structures. The mainstream of NCs is produced via wet chemical borohydride reductions and subsequently the desired species can be purified from the mixtures of products in most cases. On the other hand, a promising alternative method to yield molecularly pure new NCs is the ligand exchange method. In general, ligand exchange reactions lead to the modification of both the size and structure of the NC, but in exceptional cases it can retain both of them.\cite{10.1002/chem.202001449} This is what happens when replacing the dtp ligands of 1H by their Se counterparts. The reaction of 1H with NH₃[Se₂P(OR)]₂ (R = Pr and Bu) afforded [Cu₃Se₂P(OR)]₂[2H]: R = Pr 3H, R = Bu) in 71 and 64 % yields (Scheme 1). These two compounds were characterized by using multinuclear (31P)¹H and 1H NMR spectroscopy and single crystal XRD.

The ¹H NMR spectra of 2H and 3H show three sets of broad singlets (2H: 3.07, 0.51, 0.18 ppm and 3H: 3.09, 0.54, 0.22 ppm) in equal intensities (Figure S9, S10). The observed upfield chemical shifts of hydrides in 2H and 3H are due to the higher polarizability of Cu-Se (2H and 3H) bonds, thus leading to more shielded hydrides in comparison to those in 1H. Further, the ³¹P NMR spectra of the deuteride analogues of 2H and 3H, \[\text{Cu}_3\text{Se}_2\text{P(OR)}\]₂[R = Pr; 3H; R = Bu] respectively in their solution phase (Figure S19, S20).

Table 1. Interatomic distances in Å (average and range) for 1H-3H (X-ray, 1H-2H (neutron). Their respective DFT-computed values for models 1H and 2H are given in parenthesis. The ¹H NMR chemical shifts (in ppm) of hydrides for 1H-3H are listed, together with their DFT-computed counterparts for 1H and 2H in parenthesis.

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<td>2.504(6)</td>
<td>2.900(7)</td>
<td>2.471(4)</td>
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<td>Cu₃-Cu₁₁</td>
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<td>2.657</td>
<td>2.634(5)</td>
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<td>2.537(7)-2.986(6)</td>
<td>2.494(1)-2.785(9)</td>
<td>2.449(4)-2.770(3)</td>
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<td>3.52 (4.09)</td>
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<td>3.14 (3.70), 0.57 (1.42),</td>
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</table>

[a, b] The Cu-µ₂-H and Cu-µ₄-H distances were considered after removing two out of six Cu₃ triangular capping units associated with positional disorder (occupancy of each copper atoms are 0.667) in 2H and 3H, respectively.

The positive-ion ESI-MS spectra of 2H and 3H show prominent bands for the molecular ions [2H]²⁺ and [3H+Cu]⁺ at m/z 2804.39 (calcd. 2805.4), and m/z 6013.6 (calcd. 6013.2), respectively. Their corresponding simulated isotopic patterns are in line with the observed experimental ones (Figure S13, S14). Finally, the substitution of dtp ligands with diselenenophosphates (dsep) was confirmed by ³¹P(¹H) NMR spectroscopy. The ³¹P(¹H) NMR spectra reveal the presence of two types of resonances for 2H (91.01 and 87.01 ppm) and for 3H (96.06 and 92.21 ppm) which are significantly shifted upfield in comparison with those observed in 1H (Figure S15, S16). Investigation of both ¹H(¹H) NMR spectra, ESI-MS (Figure S17, S18) and ³¹P(¹H), of 2H (2H) and 3H (3b) in comparison with 1H (1b) have predominantly suggested a sum of eighteen hydrides/deuterides and twelve diselenenophosphate ligands, which are closely related through the Cu₃ axis in solution. Based on the above spectroscopic data for 2H and 3H which are produced via ligand replacement on 1H, one can clearly deduce that geometry retention occurs in solution state. In 2H, out of two resonances in ³¹P(¹H) spectrum, the resonance at δ = 91.01 is flanked with one set of satellites and that at δ = 87.01 is flanked with two sets of satellites (Figure S15) which suggests two different types of dsep. Note that, the additional less intense peaks observed in both the ³¹P(¹H) spectra of 2H and 3H are allied with the decomposition of the samples at ambient temperature in solution state. Several attempts to improve the spectra quality were unsuccessful, even though single crystals were used for ³¹P(¹H) NMR spectroscopy. Compounds 2H and 3H gradually decompose to disopropylhydrogenphosphate, and disobutylhydrogenphosphate respectively in their solution phase (Figure S19, S20). Given the solid state structure of 1H and the geometry retention
of 2h in solution state, we suggest the observed chemical shift at lower frequency (δ = 86.3) in 31P(1H) NMR spectrum of 2h can be ascribed to the six axial dsep ligand with the trimetallic tricconectivity bonding fashion.

As anticipated, the solid state structures of 2h and 3h (Figure 4, S21) unveil arrangements of 30 copper atoms, 18 hydrides and 12 diselenophosphate ligands with the same parent cluster 1h. The Cuico-Se distances in 2h (avg. 2.571 Å) and in 3h (avg. 2.554 Å) are slightly longer than the Cuico-Se (2c: avg. 2.543 Å) and (3h: avg. 2.539 Å) distances. Further, the observed Se⋯Se bite distances in 2h (avg. 3.613 Å) and 3h (avg. 3.632 Å) can be compared with those encountered in [Cu20(H)11(Se2P(OR))2] (R = Pr and Bu) (avg. 3.657 and 3.656 Å, respectively). The average Cuico-Cuico distance in 2h (2.657(4) Å) is similar to that observed in its parent cluster 1h (Cuico-Cuico: 2.658(7) Å) while in case of 3h (2.684(2) Å) it is somewhat larger (Table 1). The Cuico-Cu1p and Cu1p-Cu1p bond distances range from 2.448(4)-2.770(4) Å and 2.595(4)-2.613(7) in 2h and (2.479(2)-2.801(2) Å and 2.596(2)-2.626(4) Å) in 3h, respectively which are comparable to those encountered in 1h (Table 1). The average Cu-μ-3-H, Cu-μ-μ-H and Cu-μ-5-H distances in 2h (1.68, 1.71 and 1.82 Å) and in 3h (1.72, 1.70 and 1.83 Å), are similar to that encountered in 1h (1.72, 1.70 and 1.83 Å) (Table 1). Clearly, both 2h and 3h retain the structural framework of 1h with extreme precision. To the best of our knowledge, the Se-donor stabilized clusters 2h and 3h synthesized via a ligand exchange method are the first structural evidences where the cluster shape and size are nearly unaffected upon complete ligand translation.[47] This is in stark contrast to the only existing Se-stabilized Cu10 cluster.[47]

Density functional theory (DFT) calculations[60] were carried out on the simplified models [Cu10H6][E3PH2]12 (E = S: 1h; E = Se: 2h). Their optimized molecular structures were found to be of S8 symmetry (see SI). They are consistent with the X-ray structures of 1h, 2h and 3h, as exemplified by the relevant computed metrical data provided in Table 1. With respect to the hydride positions, the consistency with the neutron structure is particularly satisfying. No other hydride equilibrium position could be found. The computed 1H NMR chemical shifts are in a qualitative agreement with the experimental ones (see Table 1) and there is a linear correlation between the two sets of values for both S and Se species, with a slope close to 1 (Figure S22). Such linear correlation is a general feature in this type of large polyhydrido copper clusters,[47-49] making DFT a useful tool for hydride localization when neutron data are not available. The copper natural atomic orbital (NAO) charges and the Cu⋯Cu Wiberg indices (Table 2) are typical of Cu(I) clusters.[47-50] The six less positively charged Cu(I) centers are those with the highest connectivity. The hydride NAO charges and the Cu-H Wiberg indices are also typical of Cu(I) polyhydrides. As expected, the chalcogen charges indicate somewhat larger covalency in the case of Se, as compared to S. Both 1h and 2h exhibit substantial HOMO-LUMO gaps (1.75 and 1.71 eV at the BP86 level, respectively). The MO diagram of 1h is given in Figure 5. The highest occupied levels are of large metal character and can be described as stemming from the 3d(Cu) block, with some ligand admixture. Among them, the five highest have substantial (~ 20%) hydride participation. The three lowest unoccupied orbitals have also substantial metal character.

Figure 4. (a, b) Top and side view of solid state structure of 2h. (c, d) Top and side view of solid state structure of 3h. The dotted circles in (a) and (c) emphasize the different alkyl chains attached to 2h and 3h.

Figure 5. The Kohn-Sham MO diagram of 1h with % localization given as: Cu10 (of which Cu10:dpH2/H12). The UV-vis spectrum of 1h shows a major broad absorption band at 416 nm (Figure 6a), which is slightly blue-shifted with respect to its counterpart 2h (λmax = 432 nm). The time dependent density functional theory (TD-DFT)[60] simulated
Table 2. Relevant computed NAO charges and Wiberg indices (range and average).

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<tr>
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<tr>
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<tr>
<td>μ-H</td>
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<td>6 x 0.61</td>
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<tr>
<td>μ-H</td>
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<td>μ-H</td>
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<td>-0.65</td>
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<tr>
<td>E = S or Se (range)</td>
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<td>-0.58</td>
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The absorption spectra of 2_{1H} and 3_{1H} recorded in CH_{2}Cl_{2} at 25 °C changed with time and decomposed within two days (Figure S23 and S24) while the absorption spectra of their parent cluster 1_{1H} retains its identity for 3 days in CH_{2}Cl_{2} at 25 °C (Figure S7) indicating higher stability of the latter in solution state.

The thermal decomposition for the compound 2_{1H} was studied by thermogravimetric analysis (TGA) using the N_{2} gas atmosphere which shows main thermal decomposition at the temperature range 150-200°C with weight loss of ~36 %, attributed to the elimination of hydrides, isopropyl substituents and phosphorous atoms present in the cluster (Figure 6b). The residual weight after the major decomposition produces the stable Cu-selenide complex [Cu_{2}S_{2}2_{1H}], whereas the parent cluster, 1_{1H} shows the major decomposition at a slightly higher temperature range 180-250 °C in comparison to 2_{1H} with similar weight loss (Figure 6b).

Owing to their synergetic and enhanced catalytic, \[61-65\] optical, \[66-78\] and electrochemical development, alloy NCs have recently outpaced that of their homometal counterparts. Unlike Au and Ag, Cu has realized fewer accomplishments as a host metal for the generation of alloy NCs. Very recently, we reported the first and still unique structurally-precise Cu-M (M = group 10 element) bimetallic NC, namely [PdH_{2}Cu(μ-S)(P(μ-OPr)_{2})_{6}(C≡CPh)_{2}]\[75\]. It was synthesized by the reaction of a polyhydrido copper cluster ([Cu_{2}H_{4}(μ-S)(P(μ-OPr)_{2})_{6}]) or [Cu_{2}H_{2}(μ-S)(P(μ-OPr)_{2})_{6}]) with Pd(II) in the presence of alkenes. We were thus tempted to react 1_{1H} with Pd(II) in the presence of phenyl acetylene as an auxiliary ligand. The reaction leads to the isolation of the new cluster [PdH_{2}Cu(μ-S)(P(μ-OPr)_{2})_{6}(C≡CPh)_{2}] (4) (Scheme 1). We also synthesized the fluorinated derivative [PdH_{2}Cu(μ-S)(P(μ-OPr)_{2})_{6}(C≡CPh)_{2}] (5) by introducing the HCl=CCF=HF alkyn. Clusters 4 and 5 have been fully characterized by multinuclear NMR spectroscopy, ESI-mass spectrometry and single crystal X-ray diffraction.

The 31P\((^{1}\text{H})\) NMR spectrum of 4 and 5 exhibits single resonance at 106.7 and 106.2 ppm, respectively (Figure S25, S26). The \(^{1}\text{H}\) NMR spectra of both clusters 4 and 5 show the characteristic signals corresponding to dithiophosphates (Figures S27, S28). In addition, each spectrum shows a broad singlet hydride resonance at 0.46, and 0.33 ppm for 4 and 5, respectively. The positive-ion ESI mass spectra of 4 and 5 clearly display prominent bands attributed to their respective molecular ions [4] at m/z 2882.8 (calcd. 2883.3), and [5+H]\(^{+}\) at m/z 2991.3 (calcd. 2990.2). Their respective theoretical isotopic patterns are in good agreement with the experimental ones (Figure S29, S30).
The coordination of alkynes adopting a \( \mu_2\eta^1 \), \( \eta^1 \), \( \eta^2 \) pattern to Cu metals in clusters 4 and 5 was monitored initially by a \( ^{13} \)C NMR spectroscopy. The \( ^{13} \)C[\( ^{1} \)H] NMR spectra showed two signals corresponding to carbon atoms of alkyne for 4 (\( \delta = 127.5 \) and 90.5 ppm) and for 5 (\( \delta = 126.0 \) and 91.9 ppm) (Figure S31, S32) whereas free phenyl acetylene and 3-fluoro phenyl acetylene moieties show signals at \( \delta = 81.4 \) and 82.3, respectively. This indicates the true coordination of alkynes within 4 and 5. Out of two signals for each clusters the quaternary carbons in 4 and 5 can be assigned to the less intense peaks at \( \delta = 90.5 \) and 91.9 ppm in 4 and 5, respectively. Furthermore, the bonding of alkynes to the Cu metals in 4 and 5 were supported by FT-IR spectra. The results showed a weak and broad band at 1990 cm\(^{-1}\) corresponding to \( \nu_{\text{C≡C}} \) in 4 which is about 120 cm\(^{-1}\) lower than the observed value for free phenyl acetylene (2110 cm\(^{-1}\)) (Figure S33). The respective \( \nu_{\text{C≡C}} \) frequency in 5 was also occurred at similar position (Figure S34).

The X-ray structures of 4 and 5 are consistent with all the spectroscopic assignments (Figure 7). They exhibit a Pd-centered bi-capped icosahedron (PdH\(_2\)@Cu\(_{12}\)) co-protected by 6 dtp and 6 alkyln ligands. In addition, two hydrides bonded to Pd are embodied in the icosahedron. The metallic frameworks of 4 and 5 have idealized \( D_{5d} \) symmetry, where the C\(_3\) passes through the two capping Cu atoms, the two hydrides and the central Pd atom. Their overall geometry is similar to our recently reported cluster [PdH\(_2\)Cu\(_{14}\)\( \{\text{SeOP(OR)}\}_2\\{\text{SeOCPh}\}_6\}]\(^{76}\) (Figure 7a-c). One of the noteworthy features in 4 and 5 is that the central Pd(0) atom is connected to the two hydrides and twelve Cu atoms, thus reaching a coordination number of 14, the highest so far documented.

Unsurprisingly, DFT calculations indicate that 4 and 5 have the same electronic structure as their isostructural relative [PdH\(_2\)Cu\(_{14}\)\( \{\text{P(OR)}\}_2\\{\text{SeOCPh}\}_6\}]\(^{76}\). They can be described as made of a linear 14-electron [PdH\(_2\)]\(^{2-}\) complex encapsulated in a bicapped icosahedron made of 14 Cu(I) centers, the resulting [(PdH\(_2\))@Cu\(_{14}\)]\(^{2-}\) core being further stabilized by 6 dtp and 6 alkyln anionic ligands.

Both clusters 4 and 5 are red in color with a marginal variance to the naked eye. The UV-Vis spectrum of 4 and 5 shows a broad absorption band around 495-540 nm with nearly the same intensity. The absorption spectrum of 4 recorded in CH\(_2\)Cl\(_2\) at 25 °C changed with time and completely decomposed within 10 days (Figure S35), while 5 sustains its identity for 5 days (Figure S36). However, the time-dependent UV-Vis spectra of 4 and 5 remain unchanged for months when the powders or crystalline forms of 4 and 5 dissolve in CH\(_2\)Cl\(_2\) to obtain the spectra each time; indicating their high stability in solid-state. Both clusters 4 and 5 are luminescent in their solid and solution state at cryogenic temperature. The emission spectrum of 4 features a maximum at 659 nm in 2-methyl tetrahydrofuran at 77K, whereas the emission maximum occurs at 644 nm for 5, which is a blue-shift compared to 4 (Figure 8, S37).

**Figure 8.** UV-Vis (solid lines) and emission (dashed lines) spectra of 4 and 5.

**Conclusion**

In summary, this work describes the synthesis and structural characterization of a polyhydrido Cu(I) cluster [Cu\(_{25}\)H\(_{27}\)\( \{\text{SeOP(OR)}\}_4\\{\text{SeOCPh}\}_6\}]\(^{1-}\), 1H which is the first example embodying a non-centered Cu\(_{12}\) icosahedron. This hollow icosahedron is capped by six [Cu\(_3\)] triangles, resulting in a Cu\(_{30}\) core of ideal \( \text{S}_5 \) symmetry. Six among the twelve surface dtp ligands show a unique binding mode of pentametallic pentacoordination, hitherto unknown in the literature. Furthermore, two new Se-protected Cu\(_{25}\) clusters [Cu\(_{25}\)H\(_{27}\)\( \{\text{SeP(OR)}\}_4\\{\text{SeOCPh}\}_6\}]\(^{2-}\), 2H (\( R = \text{Pr} \)) and 3H (\( R = \text{Bu} \)), have been isolated via a ligand exchange protocol from 1H. Their X-ray structures reveal strict conservation of cluster structure and size upon ligand exchange. This methodology is predominantly beneficial for the Se-donor stabilizing ligands, which readily decomposes in solution in the presence of reducing reagents. In addition, two new Pd-Cu alloys containing Pd(0) have been synthesized by using 1H as a synthon, which show photoluminescence in both solid and solution states at 77K. We anticipate that the isolation of this novel hollow icosahedral (Cu\(_{12}\)) based NCs in their pure forms will become new templates for the synthesis of various alloy clusters with enhanced synergistic properties for multiple potential applications.

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**Figure 7.** (a, d) Total structures of 4 and 5, respectively (hydrogen atoms are removed for clarity). (b) A PdCu\(_{14}\) metal core framework in 4. (c) A Pd-centred Cu\(_{12}\) icosahedron in 4. Color code: Cu (cyan), S (yellow), P (pink), O (red), F (green), and H (light Pink).

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Keywords: Copper • nanocluster • hollow icosaedron • hydride • neutron diffraction • ligand exchange • palladium


Atomically and structurally precise polyhydrido copper nanocluster \([\text{Cu}_{30}\text{H}_{18}\{\text{S}_2\text{P(O)Pr}_2\}_12]\) which embodied an unprecedented inner hollow \(\text{Cu}_{12}\) icosahedron core has been isolated and fully characterized by single-crystal neutron diffraction analysis; while existence of \(\text{Ag}_{12}\) and \(\text{Au}_{12}\) icosahedra have reported in the year 2013 and 2019, respectively.

*E-mail: chenwei@mail.ndhu.edu.tw. (ORCID iD- C. W. Liu: 0000-0003-0801-6499)