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Synthesis and Characterization of a Cu₁₄ Hydride Cluster Supported by Neutral Donor Ligands**

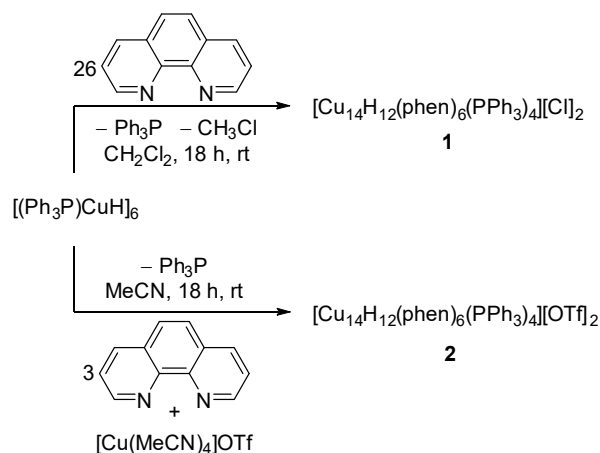
Thuy-Ai D. Nguyen, Bryan R. Goldsmith, Homaira T. Zaman, Guang Wu, Baron Peters, and Trevor W. Hayton*

Abstract: The copper hydride clusters [Cu₁₄H₁₂(phen)₆(PPh₃)₄][X]₂ (X = Cl, **1**; OTf, **2**) are obtained in good yields by reaction of [(Ph₃P)CuH]₆ with 1,10-phenanthroline, in the presence of a halide or pseudohalide source. Complex **1** reacts with CO₂ in CH₂Cl₂, in the presence of excess Ph₃P, to form the formate complex, [(Ph₃P)₂Cu(κ²-O₂CH)] (**4**), along with [(phen)(Ph₃P)CuCl] (**3**).

For several decades, copper hydrides have attracted widespread interest for their ability to catalyze the reduction of α,β-unsaturated carbonyls, electron deficient alkenes, alkynes, and even CO₂.^[1] More recently, the structural chemistry of copper hydrides has seen increased attention, partly in an effort to better understand their reactivity.^[2] For example, several large Cu(I) hydride clusters have been structurally characterized in recent years, including [(Me₃-tach)₃Cu₆(μ₆-H)Cl₄]²⁺, [Cu₇H(S₂P(OⁱPr)₂)₆], [Cu₁₈H₇(1,2-S(C₆H₄)PPH₂)₁₀(I)], [Cu₂₀H₁₁(S₂P(OⁱPr)₂)₉], and [Cu₂₆H₁₅(S₂CNⁱPr₂)₁₂]⁺.^[3] A common feature of these materials is the presence of anionic supporting ligands. In contrast, copper hydride clusters that feature neutral co-ligands appear to be less common.^[4] This distinction is significant because each anionic ligand reduces the total number of possible hydrides that can be present in a Cu(I) cluster, which has consequences for both reactivity and structure. Herein, we describe the synthesis of a novel Cu₁₄ hydride cluster, which features neutral donor ligands, and describe its reactivity with CO₂.

Addition of 26 equiv of 1,10-phenanthroline (phen) to [(Ph₃P)CuH]₆ in CH₂Cl₂ results in immediate formation of a dark red solution. On standing, this solution undergoes a color change to dark green and then to dark blue. Work-up of this solution after 18 h results in the isolation of the novel copper hydride cluster, [Cu₁₄H₁₂(phen)₆(PPh₃)₄][Cl]₂ (**1**), as a dark blue crystalline material in 80% yield (Scheme 1). While only 2.6 equiv of phen is required to form **1**, according to the stoichiometry of the reaction, reasonable yields were only achieved when a large excess of phen was added to the [(Ph₃P)CuH]₆. If excess phen was not added, then substantial

quantities of starting material were recovered from the reaction mixture. For comparison, the related copper hydride cluster, [(Cp*AlCu)₆H₄] is also formed by displacement of Ph₃P in [(Ph₃P)CuH]₆; however, addition of excess [(Cp*Al)₄] is not required to achieve a high yield, possibly because it has a stronger affinity to Cu(I) than does phen.^[5] Complex **1** crystallizes in the orthorhombic space group P2₁2₁1, as a dichloromethane and benzene solvate, 1·3CH₂Cl₂·C₆H₆ (Figure 1a). In the solid state, [Cu₁₄H₁₂(phen)₆(PPh₃)₄][Cl]₂ features a tetrahedral [Cu₄]⁴⁺ core (Figure 1d), which is connected, via Cu-Cu bonds, to a diamondoid arrangement of ten Cu(I) centers (Figure 1c). These 10 copper centers are coordinated by four PPh₃ ligands, which are arranged at the corners of a tetrahedron, and six phen ligands, which are arranged in the corners of an octahedron. As a result of this arrangement, complex **1** features four hexagonal faces, wherein each face is situated opposite to a Ph₃P ligand. The average Cu_{tet}-Cu_p (av. 2.655 Å), Cu_{tet}-Cu_N (av. 2.514 Å), and Cu_p-Cu_N (2.663 Å) bond lengths (Table 1) are comparable to the Cu-Cu distances in [(Ph₃P)CuH]₆ (av. 2.630 Å),^[6] [(Me₃-tach)₃Cu₆(μ₆-H)Cl₄]²⁺ (av. 2.580 Å),^[3a] and the outer Cu-Cu distances in [Cu₂₀H₁₁(S₂P(OⁱPr)₂)₉] (2.5284(9)-2.7542(7) Å).^[3c] The Cu_p-P bond length (av. 2.298 Å) is typical of Cu(I)-P bonds.^[6-7] Similarly, the Cu_N-N bond length (av. 2.100 Å) is comparable to Cu-N bonds in [(Me₃-tach)₃Cu₆(μ₆-H)Cl₄]²⁺ (2.11 Å) and [(Me₃-tach)₂Cu₃Cl₂]₂²⁺ (2.03 Å).^[3a] Interestingly, the metrical parameters of the tetrahedral [Cu₄]⁴⁺ core in **1** (av. Cu_{tet}-Cu_{tet} = 2.893 Å) are nearly identical to those of the [Cu₄(μ₄-H)]³⁺ core in [Cu₈H{S₂CNⁱPr₂}]⁺ (2.894(2)-2.989(2) Å).^[3b] However, there is no evidence to support the presence of a μ₄-H ligand in complex **1**. Lastly, the two Cl⁻ counterions in **1** were observed to be disordered, and were modelled over 8 positions with partial occupancies.



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 the document.

Scheme 1. Syntheses of complexes **1** and **2**.

Consistent with the high symmetry observed in the solid-state, complex **1** features a single resonance in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -5.35 ppm in CD_2Cl_2 . Likewise, complex **1** features resonances at 6.67, 7.88, and 8.10, and 8.85 ppm in its ^1H NMR spectrum, which are assignable to the six magnetically equivalent phen ligands. Also present in the ^1H NMR spectrum is a broad resonance (FWHM = 31 Hz) at 3.45 ppm, which integrates for 12H, and is assignable to the hydride ligand environments. Complex **1** features a signal at m/z 1515.93 in its ESI mass spectrum, which corresponds to the parent $[\text{M}]^{2+}$ ion (calcd m/z 1515.94). Conductivity measurements also support the proposed formulation. In MeCN, **1** exhibits a Λ_{M} of $220.5 \text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ at 25 °C, which is in excellent agreement with expected molar conductivity for a 2:1 electrolyte in MeCN ($220\text{--}300 \text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$).^[8] Finally, we synthesized the deuteride analogue, **1-d₁₂**, by reaction of phen with $[(\text{Ph}_3\text{P})\text{CuD}]_6$ (see SI). As anticipated, complex **1-d₁₂** features a singlet at 3.58 ppm in its ^2H NMR spectrum, which is assignable to the 12 deuteride ligands. In addition, complex **1-d₁₂** features a signal at m/z 1522.04 in its ESI mass spectrum, which corresponds to the $[\text{M}]^{2+}$ parent ion (calcd. m/z 1521.98), a shift of 6 m/z versus the signal observed for **1-h₁₂**.

Table 1. Comparison of bond lengths (Å) between **1** and its calculated molecular structure using the PBE and PW91 functionals.

	Expt.	PBE	PW91
$\text{Cu}_{\text{tet}} - \text{Cu}_{\text{tet}}$	2.893 ^[9]	2.809	2.826
$\text{Cu}_{\text{tet}} - \text{Cu}_{\text{P}}$	2.655	2.681	2.684
$\text{Cu}_{\text{tet}} - \text{Cu}_{\text{N}}$	2.514	2.557	2.559
$\text{Cu}_{\text{P}} - \text{Cu}_{\text{N}}$	2.663	2.710	2.711
$\text{Cu}_{\text{P}} - \text{P}$	2.298	2.335	2.333
$\text{Cu}_{\text{N}} - \text{N}$	2.100	2.101	2.101

[a] All lengths are average bond lengths.

We explored the structure of complex **1** using density functional theory as implemented with the VASP 5.3.5 software, in part, to find reasonable positions for the 12 hydride ligands.^[9] The Kohn–Sham wave functions were expanded by plane waves with a kinetic energy cutoff of 400 eV. The interactions between valence electrons and ions were described using the PAW method.^[10] The PBE^[11] and PW91^[12] exchange-correlation functionals were both utilized to check consistency between

different density functional approximations. The structure of complex **1** was relaxed and found to be minima on the potential energy surface (Table S2). The 12 hydride ligands were found to coordinate to the hexagonal copper faces, in four groups of three (Figure 1b). Each hydride ligand features a μ_3 coordination mode, similar to the $\mu_3\text{-H}$ environment found in $[\text{Cu}_{20}\text{H}_{11}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_9]$.^[39] This is fully consistent with the NMR spectroscopic data indicating that the 12 hydride ligands are magnetically equivalent. In addition, the average calculated Cu–Cu bond lengths of **1** ($\text{Cu}_{\text{P}}\text{--}\text{Cu}_{\text{N}}$, $\text{Cu}_{\text{tet}}\text{--}\text{Cu}_{\text{N}}$, and $\text{Cu}_{\text{tet}}\text{--}\text{Cu}_{\text{P}}$), using either the PBE or PW91 functionals (Table 1), are in good agreement with experimental values.

To better understand the vibrant color changes that occur during the synthesis of **1**, and confirm the source of its chloride counterions, we followed its formation by ^1H NMR spectroscopy. Addition of 26 equiv of phen to $[(\text{Ph}_3\text{P})\text{CuH}]_6$ in CD_2Cl_2 results in formation of a dark red solution. After 5 min, complex **1** is observed in the reaction mixture in small amounts, as evidenced by the diagnostic resonance in the ^1H NMR spectrum at 3.47 ppm, assignable to the 12 $\mu_3\text{-H}$ ligands. However, several other hydride-containing complexes are also present in this reaction mixture, as evidenced by broad resonances at 2.13 and 2.75 ppm in the ^1H NMR spectrum. Significant amounts of starting material are also present in this sample. After 1 h, the ^1H NMR spectrum of the reaction mixture reveals a decrease in the amount of starting material. In addition, the hydride signal at 2.13 ppm decreases in intensity, while those at 3.47 ppm and 2.75 ppm increase. This change occurs concomitant with a color change to green and formation of a dark precipitate. After 17 h, the signals at 2.13 and 2.75 ppm are no longer present in the ^1H NMR spectrum, and the only hydride resonance observed in the dark blue solution is that assignable to **1**. An *in situ* ^2H NMR spectrum of the reaction mixture was also recorded. This spectrum features a broad singlet at 3.27 ppm, which we have assigned to CD_2HCl , the by-product of a $\text{CD}_2\text{Cl}_2 / \text{CuH}$ metathesis reaction,^[13] confirming that the Cl^- counterions in **1** are derived from dichloromethane. This result also rationalizes the long reaction times required to form **1** in high yield, as the hydride metathesis step is likely slow and rate-determining.

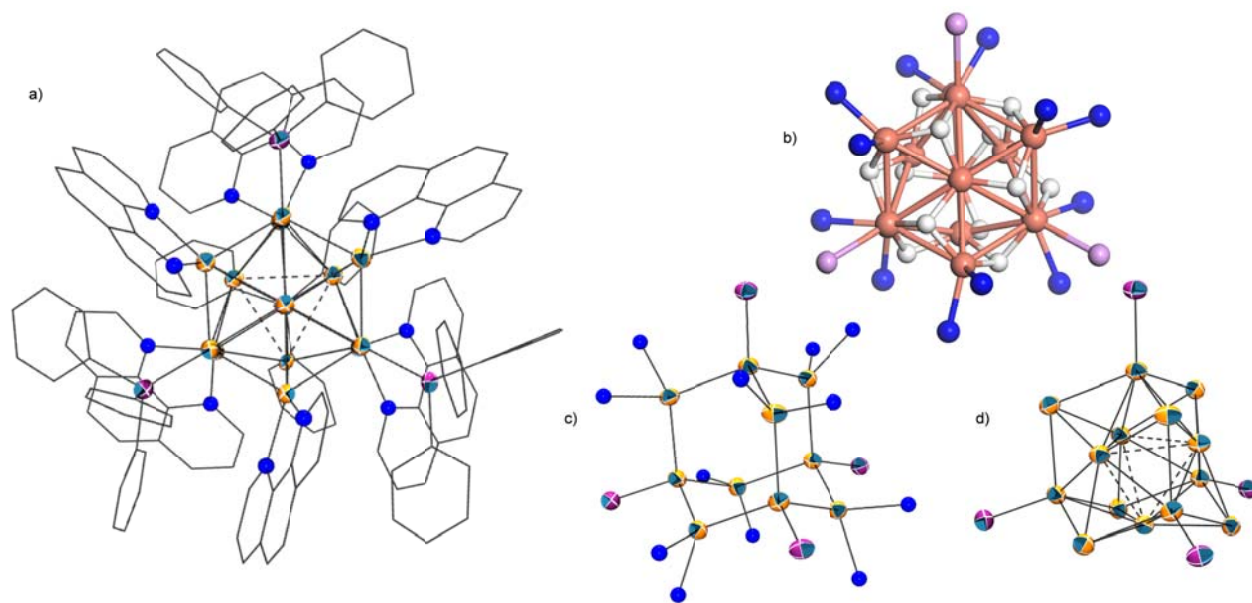
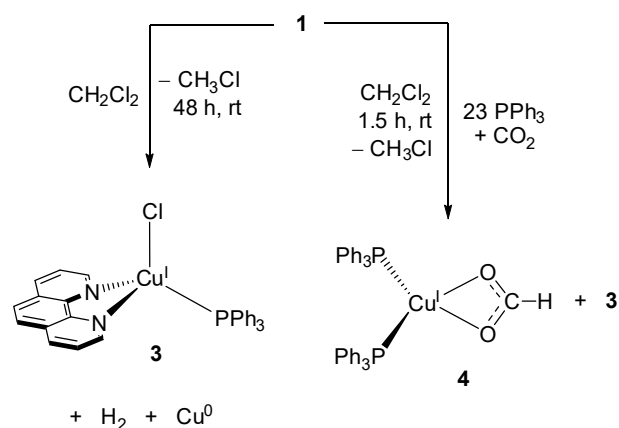


Figure 1. a) ORTEP diagram of **1** with 50% probability ellipsoids for copper and phosphorus atoms. All hydrogen atoms, two disordered chloride counterions and solvent molecules have been omitted for clarity. b) Optimized structure of $[\text{Cu}_{14}\text{H}_{12}(\text{phen})_6(\text{PPh}_3)_6][\text{Cl}]_2$, as determined using the PW91 functional, showing a hexagonal copper face with its three $\mu_3\text{-H}$ environments. c) Diamondoid arrangement of the outer copper shell in **1**, with the $[\text{Cu}_4]^{4+}$ core removed. d) ORTEP diagram of **1** with carbon, nitrogen, chloride, and hydrogen atoms removed. $\text{Cu}_{1\text{tet}}\text{-Cu}_{1\text{tet}}$ bonds depicted using dashed lines. Color legend: copper, yellow-orange; hydrogen, white; phosphorus, fuchsia; nitrogen, blue.

To further confirm the importance of the chloride counterion in the formation of the Cu_{14} cluster, we performed the reaction of phen with $[(\text{Ph}_3\text{P})\text{CuH}]_6$, in the presence of a $[\text{OTf}]^-$ source. Thus, addition of MeCN to a vial charged with 1 equiv of $[(\text{Ph}_3\text{P})\text{CuH}]_6$, 3 equiv of phen, and 1 equiv of $[\text{Cu}(\text{MeCN})_4][\text{OTf}]$ results in the formation of $[\text{Cu}_{14}\text{H}_{12}(\text{phen})_6(\text{PPh}_3)]_2$ (**2**), which can be isolated as a blue crystalline solid in 41% yield (Scheme 1). Importantly, complex **2** forms immediately upon mixing of the reagents, as revealed by the rapid color change to blue. Interestingly, if $[\text{Cu}(\text{MeCN})_4][\text{OTf}]$ is not added to the reaction mixture, then a brown intractable suspension is formed instead, demonstrating the required presence of a counterion for the formation of **2**. Complex **2** features similar ^1H and ^{31}P NMR spectral parameters as **1**. It also features a singlet at -79.33 ppm in its $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum, which is assignable to the OTf anion, consistent with our proposed formulation. Complex **2** features a signal at m/z 1515.96 in its ESI mass spectrum, which corresponds to the parent $[\text{M}]^{2+}$ species (calcd m/z 1515.94). Finally, **2** features a Λ_M of $261.5 \text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, also consistent with its formulation as a 2:1 electrolyte.^[8]

Complex **1** is soluble in CH_2Cl_2 and MeCN, and insoluble in THF, Et_2O and non-polar solvents. It is stable in MeCN for at least 72 h. However, it slowly reacts with CH_2Cl_2 to generate a new species, $[(\text{phen})(\text{Ph}_3\text{P})\text{CuCl}]$ (**3**), along with H_2 , copper metal, and other unidentified decomposition products (Scheme 2, see SI for full characterization details). Presumably, **3** is formed via a hydride metathesis with the CH_2Cl_2 solvent. Remarkably, though, in the presence of excess phen, **1** is indefinitely stable in CH_2Cl_2 , suggesting that the loss of the phen ligand is the first step in its decomposition. Complex **1** is air sensitive, and rapidly decomposes upon exposure to air. However, it only slowly reacts with water. Finally, we explored the reactivity of complex **1** with CO_2 . Several research groups have previously described

the reactivity of discrete copper hydrides with CO_2 .^[1i,4c,Ad,14] Of most relevance to our study, Sneed and co-workers reported that reaction of $[(\text{Ph}_3\text{P})\text{CuH}]_6$ with CO_2 , in the presence of 6 equiv PPh_3 , resulted in the formation of the formate complex, $[(\text{Ph}_3\text{P})_2\text{Cu}(\kappa^2\text{-O}_2\text{CH})]$ (**4**).^[14a] Similarly, complex **1** was reacted with CO_2 in CD_2Cl_2 , in the presence of excess PPh_3 .^[15] Monitoring the reaction by NMR spectroscopy revealed the rapid consumption of **1** and the formation of **4** in 37% yield (Scheme 2, see SI for full characterization details), demonstrating that the hydride ligands in **1** are accessible to incoming substrates. Complex **3** is also formed in this reaction.



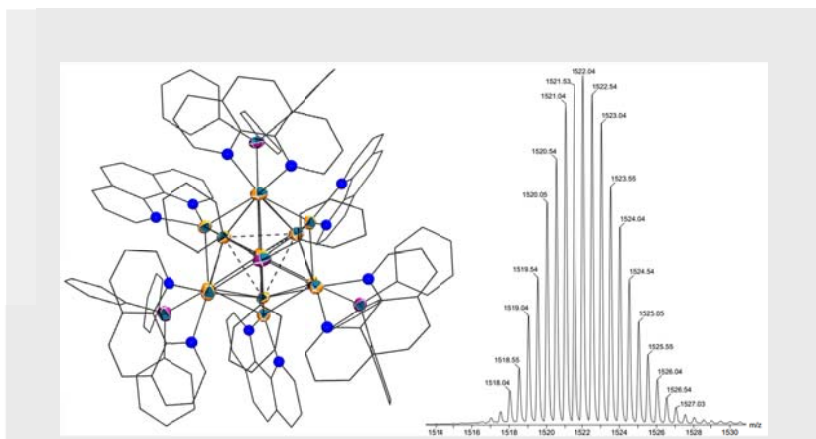
Scheme 2. Reactivity of complex **1** with CO_2 and CH_2Cl_2 .

In summary, we have isolated and structurally characterized a novel Cu₁₄ hydride cluster. This complex is the largest structurally characterized CuH cluster supported by neutral donor ligands. As a consequence, it has a larger H:Cu ratio than other reported high nuclearity clusters. Importantly, the capping hydride ligands in this cluster are accessible to incoming substrates, as demonstrated by its reaction with CO₂. Moreover, the synthesis of complex **1** demonstrates that [(Ph₃P)CuH]₆ is a viable precursor for the generation of copper hydride clusters with high nuclearity. We suggest that with the appropriate choice of co-ligand, even larger Cu nano-crystals could be accessible via this route. We will continue to explore the synthesis of new copper hydride complexes from [(Ph₃P)CuH]₆ and we will probe their reactivity with CO₂.

Keywords: copper • hydride • cluster • CO₂ insertion • density functional theory

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- [15] We should also note that complex **1** will react with CO₂ in the absence of added PPh₃. However, the addition of extra PPh₃ was found to increase the yield of complex **4**.

COMMUNICATION



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