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Permalink
https://escholarship.org/uc/item/6xt1t98c

Journal
Chemistry - A European Journal, 21(14)

ISSN
0947-6539

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Publication Date
2015-03-27

DOI
10.1002/chem.201500422

Peer reviewed
Synthesis and Characterization of a Cu_{14} 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 [Cu_{14}H_{24}(phen)_4(PPh_3)_2][X]_2 \( (X = \text{Cl}, \text{OTf}) \) are obtained in good yields by reaction of \([\text{Ph}_3\text{P}]\text{CuH}_2\) with 1,10-phenanthroline, in the presence of a halide or pseudohalide source. Complex 1 reacts with \(\text{CO}_2\) in \(\text{CH}_2\text{Cl}_2\), in the presence of excess \(\text{Ph}_3\text{P}\), to form the formate complex, \([\text{Ph}_3\text{P}]\text{Cu}(\text{HCOO})\) (4), along with \([\text{phen}](\text{Ph}_3\text{P})\text{CuCl}\) (3).

For several decades, copper hydrides have attracted widespread interest for their ability to catalyze the reduction of \(\alpha\beta\)-unsaturated carbonyls, electron deficient alkenes, alkynes, and even \(\text{CO}_2\). More recently, the structural chemistry of copper hydrides has seen increased attention, partly in an effort to better understand their reactivity. For example, several large Cu(i) hydride clusters have been structurally characterized in recent years, including \([\text{Me}_2\text{tach}]_2\text{Cu}(\mu_2-\text{H})\text{Cl}_4\) \( \text{P}^2\text{Cl}_2 \), \([\text{Cu}_2\text{H}_2(\text{S}(\text{Ph})\text{PPh}_3)_2]\) \( \text{P}^2\text{Cl}_2 \), \([\text{Cu}_2\text{H}_2(\text{S}(\text{Ph})\text{PPh}_3)_2]\) \( \text{P}^2\text{Cl}_2 \), and \([\text{Cu}_2\text{H}_2(\text{S}(\text{Ph})\text{PPh}_3)_2]\) \( \text{P}^2\text{Cl}_2 \). A common feature of these materials is the presence of anionic supporting ligands. In contrast, copper hydride clusters that feature neutral \(\pi\)-ligands appear to be less common. 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 Cu_{14} hydride cluster, which features neutral donor ligands, and describe its reactivity with \(\text{CO}_2\).

Addition of 26 equiv of 1,10-phenanthroline (phen) to \([\text{Ph}_3\text{P}]\text{CuH}_2\) in \(\text{CH}_2\text{Cl}_2\) 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 13 h results in the isolation of the novel copper hydride cluster, \([\text{Cu}_{14}\text{H}_{24}(\text{phen})_4(\text{PPh}_3)_2][\text{Cl}]_2\) (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 \([\text{Ph}_3\text{P}]\text{CuH}_2\). 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, \([\text{Cp}^*\text{AlCuH}_2]\) \( \text{P}^2\text{Cl}_2 \), is also formed by displacement of \(\text{Ph}_3\text{P}\) in \([\text{Ph}_3\text{P}]\text{CuH}_2\); however, addition of excess \([\text{Cp}^*\text{AlCuH}_2]\) is not required to achieve a high yield, possibly because it has a stronger affinity to Cu(I) than does phen. Complex 1 crystallizes in the orthorhombic space group \(\text{P}2_1\text{P}_2_1\text{P}_2_1\), as a dichloromethane and benzene solvate, 1.3\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_6\text{H}_6 (\text{Figure} 1a). In the solid state, \([\text{Cu}_{14}\text{H}_{24}(\text{phen})_4(\text{PPh}_3)_2][\text{Cl}]_2\) features a tetrahedral \([\text{Cu}]^+\) 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 \(\text{Ph}_3\text{P}\) 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 \(\text{Ph}_3\text{P}\) ligand. The average Cu–Cu distance (av. 2.655 Å), Cu–Cu bond lengths (Table 1) are comparable to the Cu–Cu distances in \([\text{Ph}_3\text{P}]\text{CuH}_2\) (av. 2.630 Å) \( \text{P}^2\text{Cl}_2 \) and \([\text{Me}_2\text{tach}]_2\text{Cu}(\mu_2-\text{H})\text{Cl}_4\) \( \text{P}^2\text{Cl}_2 \) (av. 2.580 Å). Interestingly, the metrical parameters of the tetrahedral \([\text{Cu}]^+\) core in 1 (av. Cu–Cu = 2.893 Å) are nearly identical to those of the \([\text{Cu}_4(\mu_2-\text{H})\text{Cl}_4]\) \( \text{P}^2\text{Cl}_2 \) core in \([\text{Cu}_4(\text{S}(\text{Ph})\text{PPh}_3)_2]\) \( \text{P}^2\text{Cl}_2 \) (2.894(2)–2.989(2) Å). However, there is no evidence to support the presence of a \(\mu_2\)-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.

![Scheme 1. Syntheses of complexes 1 and 2.](https://example.com/scheme1.png)

**This work was supported by the Center for Sustainable Use of Renewable Feedstocks (CenSURF), a National Science Foundation (NSF) Center for Chemical Innovation (CCI).

Supporting information for this article is given via a link at the end of the document.
Consistent with the high symmetry observed in the solid-state, complex 1 features a single resonance in its $^{31}$P($^1$H) NMR spectrum at -5.35 ppm in CD$_2$Cl$_2$. Likewise, complex 1 features resonances at 6.67, 7.88, and 8.10, and 8.85 ppm in its $^1$H NMR spectrum, which are assignable to the six magnetically equivalent phen ligands. Also present in the $^1$H 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 [M]$^{3+}$ ion (calcd. m/z 1515.94). Conductivity measurements also support the proposed formulation. In MeCN, 1 exhibits a $\lambda_{DD}$ of 220.5 ohm$^{-1}$cm$^{-2}$mol$^{-1}$ at 25 °C, which is in excellent agreement with expected molar conductivity for a 2:1 electrolyte in MeCN (220–300 ohm$^{-1}$cm$^{-2}$mol$^{-1}$).[3] Finally, we synthesized the deuteride analogue, 1-d$_{12}$, by reaction of phen with ($[$Ph$_2$P]$)$CuD$_2$ (see SI). As anticipated, complex 1-d$_{12}$ features a singlet at 3.58 ppm in its $^2$H NMR spectrum, which is assignable to the 12 deuteride ligands. In addition, complex 1-d$_{12}$ features a signal at m/z 1522.04 in its ESI mass spectrum, which corresponds to the [N]$^{3+}$ parent ion (calcd. m/z 1521.98), a shift of 6 m/z versus the signal observed for 1-h$_{12}$.

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

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>PBE</th>
<th>PW91</th>
</tr>
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<tbody>
<tr>
<td>Cu$<em>{1}$ = Cu$</em>{12}$</td>
<td>2.893$^a$</td>
<td>2.809</td>
<td>2.826</td>
</tr>
<tr>
<td>Cu$<em>{1}$ = Cu$</em>{11}$</td>
<td>2.655</td>
<td>2.681</td>
<td>2.684</td>
</tr>
<tr>
<td>Cu$<em>{1}$ = Cu$</em>{10}$</td>
<td>2.514</td>
<td>2.557</td>
<td>2.559</td>
</tr>
<tr>
<td>Cu$<em>{5}$ = Cu$</em>{1}$</td>
<td>2.663</td>
<td>2.710</td>
<td>2.711</td>
</tr>
<tr>
<td>Cu$_{5}$ = P</td>
<td>2.298</td>
<td>2.335</td>
<td>2.333</td>
</tr>
<tr>
<td>Cu$_{6}$ = N</td>
<td>2.100</td>
<td>2.101</td>
<td>2.101</td>
</tr>
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[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.$^{[5]}$ 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.$^{[2d]}$ The PBE$^{[15]}$ and PW91$^{[18]}$ 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 $\mu_3$ coordination mode, similar to the $\mu_3$-H environment found in [Cu$_2$H$_3$(S$_2$P(O)$_3$)$_6$].$^{[3a]}$ 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 (Cu$_{1}$–Cu$_{6}$, Cu$_{7}$–Cu$_{12}$, and Cu$_{13}$–Cu$_{18}$), 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 $^1$H NMR spectroscopy. Addition of 26 equiv of phen to [(Ph$_2$P)$_2$CuH]$_6$ in CD$_2$Cl$_2$ 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 $^1$H NMR spectrum at 3.47 ppm, assignable to the 12 $\mu_3$-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 $^1$H NMR spectrum. Significant amounts of starting material are also present in this sample. After 1 h, the $^1$H 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 concomitantly 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 $^1$H NMR spectrum, and the only hydride resonance observed in the dark blue solution is that assignable to 1. An in situ $^2$H 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$_2$HCl, the by-product of a CD$_2$Cl$_2$ / 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.
To further confirm the importance of the chloride counterion in the formation of the Cu₄ cluster, we performed the reaction of phen with [(Ph₃P)CuH]₆, in the presence of a [OTf]⁻ source. Thus, addition of MeCN to a vial charged with 1 equiv of [(Ph₃P)CuH]₆, 3 equiv of phen, and 1 equiv of [Cu(MeCN)]_n[OTf]⁻ results in the formation of [Cu₄H₉(phen)₃(PPh₃)][OTf]⁻ (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 [Cu(MeCN)]_n[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 ³¹P NMR spectral parameters as 1. It also features a singlet at -79.33 ppm in its ¹⁹F(¹H) 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 [M]⁺⁺ species (calcd m/z 1515.94).

Finally, 2 features a λₘₜ of 261.5 nm (cm²mol⁻¹). Also consistent with its formulation as a 2⁺ electrolyte.[⁶]

Complex 1 is soluble in CH₂Cl₂ and MeCN, and insoluble in THF, Et₂O, and non-polar solvents. It is stable in MeCN for at least 72 h. However, it slowly reacts with CH₂Cl₂ to generate a new species, [(phen)(Ph₃P)CuCl] (3), along with H₂, 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 CH₂Cl₂ solvent. Remarkably, though, in the presence of excess phen, 1 is indefinitely stable in CH₂Cl₂, 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 CO₂. Several research groups have previously described the reactivity of discrete copper hydrides with CO₂. Of most relevance to our study, Sneeden and co-workers reported that reaction of [(Ph₃P)CuH]₆ with CO₂ in the presence of 6 equiv PPh₃, resulted in the formation of the formate complex, [(Ph₃P)₃Cu(O₂CC)] (4). Similarly, complex 1 was reacted with CO₂ in CD₂Cl₂ in the presence of excess PPh₃.[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 CO₂ and CH₂Cl₂.
In summary, we have isolated and structurally characterized a novel Cu₆₄ 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


[15] We should note that complex 1 will react with CO₂ in the absence of extra PPh₃. However, the addition of extra PPh₃ found to increase the yield of complex 4.
The copper hydride clusters $[\text{Cu}_{14}H_{12}(\text{phen})_6\text{PPh}_3]_2[X]_2$ ($X = \text{Cl, OTf}$) were obtained in good yields by reaction of $[(\text{Ph}_3\text{P})\text{CuH}]_6$ with 1,10-phenanthroline, in the presence of a halide or pseudohalide source. This work demonstrates that $[(\text{Ph}_3\text{P})\text{CuH}]_6$ is a viable precursor for the generation of high nuclearity copper clusters.