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ARTICLE

The rise and fall of copper hydride clusters. A snapshot of hexanuclear-to-dodecanuclear expansion

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Phosphine-supported copper hydrides are prone to aggregation to form various clusters. This study focuses on the synthesis, structural characterization, and reactivity of a novel dodecanuclear copper hydride, $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ ($^{iPr}PN^{H}P$ = $HN(CH_2CH_2P^{i}Pr_2)_2$). This specific copper hydride species represents a transient cluster on the degradation pathway from $(^{iPr}PN^{H}P)_3Cu_6H_6$ to Cu(0), $^{iPr}PN^{H}P$, and H_2 as well as a frequently encountered by-product during the reduction of carbonyl compounds with $(^{iPr}PN^{H}P)_3Cu_6H_6$. These data complement the previous study of cluster expansion from $(^{iPr}PN^{H}P)_2Cu_4H_4$ to $(^{iPr}PN^{H}P)_3Cu_6H_6$ and deepen the understanding of how copper clusters grow and decay in solution. The effects of phosphorus substituents on the stability of the copper hydride clusters are also explored.

Introduction

Copper hydride species are key intermediates in a wide variety of copper-catalyzed reactions that employ H_2, silanes, or boranes.[1,2] For simplicity, the empirical formula LCuH has been frequently used to describe the hydride species, although it is well understood that the actual composition is far more complicated, likely involving the monomeric LCuH and its derived oligomers/clusters. The aggregation process can sometimes be minimized or even suppressed by introducing bulky substituents[3-6] or Lewis acidic groups[7] at appropriate sites of the supporting ligands. However, the vast majority of LCuH molecules do aggregate, at different rates, and the nuclearity may also change in response to a chemical transformation. Thus, for a better understanding of the catalytic reactions, identifying the structures of these oligomers/clusters and establishing their baseline reactivity are critically needed.

Well-defined copper hydrides, especially nanoclusters, have gained other attention in recent years, largely due to their fascinating molecular structures and potential applications in energy storage and conversion.[8-12] Low-nuclearity (Cu_3) copper hydrides have also been developed to model surface-adsorbed hydrogen atoms for CO_2 capture and reduction.[13] Some of the large copper hydride clusters, often referred to as atomically-precise nanoclusters,[9,12] have been directly used to catalyze hydrogen evolution, reduction of C=C, C≡C, or C=O bonds,[14,15] 1,3-dipolar cycloaddition, and aniline carbonylation reactions.

We have been interested in studying phosphine-stabilized copper hydrides as hydrogenation catalysts.[16,17] This specific class of compounds has a rich history dating back to the early 1970s, when the triphenylphosphine-ligated copper hydride was crystallographically characterized as $(Ph_3P)_6Cu_6H_6$, a hexamer of LCuH.[18,19] Studies of other phosphine systems have indicated that monodentate ligands usually lead to the formation of $L_6Cu_6H_6$.[20-23] In contrast, multidentate phosphines give rise to copper hydrides with more diverse structures,[24] featuring a neutral CuH core that can range from Cu_2H_2 to Cu_8H_8 (e.g., $L_2Cu_2H_2$,[25,26] $L_3Cu_3H_3$,[23] $L_2Cu_4H_4$,[27] $L_3Cu_6H_6$,[27] and $L_4Cu_8H_8$[21]). In some cases, the synthetic efforts have resulted in the isolation of cationic copper hydrides or hydride-deficient clusters such as $[L_2Cu_2H]^+$,[28,29] $[L_2Cu_3H]^{2+}$,[30] $[L_3Cu_3H]^{2+}$,[31,32] $[L_2Cu_4H_2]^{2+}$,[30] $[L_2Cu_4H_3]^+$,[28] $[L_5Cu_8H_6]^{2+}$,[33] $[L_3Cu_9H_7]^{2+}$,[34] and $[L_4Cu_{16}H_{14}]^{2+}$.[34] There are also reports showing that copper hydride clusters of varying size can co-exist in the same reaction mixture[28,34-36] or form separately under different conditions.[29,37,38] Compared to NHC (NHC = *N*-heterocyclic carbene) systems, which typically involve (NHC)CuH and $(NHC)_2Cu_2H_2$,[3,5,6,39] phosphine-stabilized copper hydrides have more complex structures, and it is often less clear how the small copper hydride species aggregate to yield the larger clusters.

The $HN(CH_2CH_2PR_2)_2$ (denoted as $^{R}PN^{H}P$) ligand system that we studied recently provided us with a unique opportunity to observe the growth of copper hydride clusters from $(^{R}PN^{H}P)_2Cu_4H_4$ to $(^{R}PN^{H}P)_3Cu_6H_6$.[27] The rate of cluster expansion was found to be greatly influenced by the substituents on phosphorus. Of the three ligands investigated (Scheme 1), $^{iPr}PN^{H}P$ stabilizes Cu_4H_4 only transiently but long enough to render it spectroscopically observable. $^{Cy}PN^{H}P$ significantly slows down the Cu_4H_4-to-Cu_6H_6 conversion, allowing $(^{Cy}PN^{H}P)_2Cu_4H_4$ to be isolated and fully characterized. The bulkiest ligand $^{tBu}PN^{H}P$ appears to prevent the cluster growth beyond $(^{tBu}PN^{H}P)_2Cu_4H_4$. In this work, we report the further expansion of the hexanuclear clusters to dodecanuclear clusters, either spontaneously or in conjunction with the reactions having various substrates. The dodecanuclear

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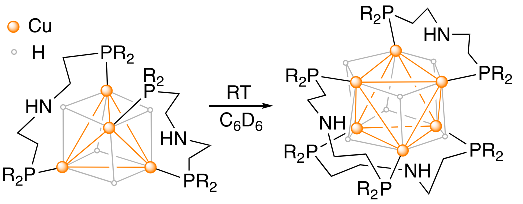
clusters can continue to evolve, eventually leading to the collapse of the ligand scaffold. These findings, combined with our previous studies,[17,27] present a more complete picture of the growth and decay of copper hydride clusters supported by a ^{R}PN^{H}P ligand.



R = ^{i}Pr, 100% conversion in ~1 h
R = Cy, ~20% conversion in 12 h
R = ^{t}Bu, no converion in 24 h

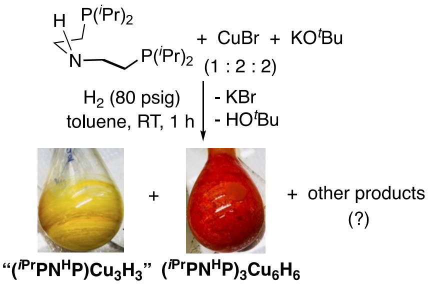
Scheme 1 Expansion of $(^{R}PN^{H}P)_2Cu_4H_4$ to $(^{R}PN^{H}P)_3Cu_6H_6$.

Results and discussion

Synthesis and characterization of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$

Our previous study of $(^{R}PN^{H}P)_3Cu_6H_6$ (R = ^{i}Pr, Cy) demonstrated that these hexanuclear copper hydrides are thermally sensitive compounds.[27] The isopropyl derivative in particular started to decompose within a few hours after it was dissolved in C_6D_6. As a result, the $^{13}C\{^{1}H\}$ NMR spectrum of $(^{iPr}PN^{H}P)_3Cu_6H_6$ had to be recorded at 10 °C to avoid degradation during data acquisition. At the time, very limited spectroscopic evidence was available to help identify the structures of the decomposition products. In addition to the signal attributed to the free ligand ($\delta_P = -1.1$ ppm), two broad phosphorus resonances were observed at 6.5 and 5.7 ppm, which incidentally also appeared in some of the reactions involving $(^{iPr}PN^{H}P)_3Cu_6H_6$.

The preliminary result prompted us to re-examine the formation and degradation of $(^{iPr}PN^{H}P)_3Cu_6H_6$ under different reaction conditions (i.e., varying Cu(I) source, H_2 pressure, and reaction time). When a 1:2:2 mixture of ^{iPr}PN^{H}P, CuBr, and KO^{t}Bu in toluene was stirred under 80 psig of H_2 pressure for 1 h, it produced a significant amount of the decomposition products along with $(^{iPr}PN^{H}P)_3Cu_6H_6$. Identifying all copper-containing species present in the reaction mixture proved to be a highly challenging task. Nevertheless, it was feasible to isolate the major product as a yellow solid (Scheme 2), thanks to its poor solubility in pentane. The main contaminant, $(^{iPr}PN^{H}P)_3Cu_6H_6$, is readily soluble in pentane with a distinctive red-orange color. The ^{1}H NMR spectrum of the yellow compound supported a formulation of "$(^{iPr}PN^{H}P)Cu_3H_3$" or a molecule having three CuH moieties per ^{iPr}PN^{H}P ligand. The $^{31}P\{^{1}H\}$ NMR spectrum displayed two phosphorus resonances (integrate to a 1:1 ratio) that matched those described earlier.



Scheme 2 Isolation of two copper hydride clusters from the reaction of ^{iPr}PN^{H}P with CuBr and KO^{t}Bu under H_2.

The molecular structure of the yellow compound was studied by X-ray crystallography, which revealed an unprecedented $Cu_{12}H_{12}$ core protected by four ^{iPr}PN^{H}P ligands (Figure 1). Previously reported Cu_{12} clusters primarily rely on oxygen- or chalcogen-based ligands as building blocks to construct the dodecanuclear cores.[40-43] Prior to this study, $[Cu_{12}H_2\{S_2P(O^{i}Pr_2)_2\}_6(C{\equiv}CPh)_3]^+$ and $[Cu_{12}H_3(\text{Tf-dpf})_6(OAc)_2]^+$ (Tf-dpf = *N*,*N*'-di(5-trifluoromethyl-2-pyridyl)formamidinate) were the only known examples of hydride-containing Cu_{12} clusters. The former involves a CuH_2 fragment situated in a pentacapped trigonal prismatic cage formed by eleven copper atoms.[44] The latter showcases three face-sharing Cu_6 octahedra bearing three interstitial hydrides (μ_6-H).[45] Here, the dodecanuclear core can be viewed as two octahedral Cu_6 units (Cu1 through Cu6; Cu7 through Cu12) linked orthogonally via one of the Cu-Cu edges (Cu5-Cu6 and Cu11-Cu12). The twelve hydrides were all located directly from the difference map and found to cap twelve exterior Cu_3 faces. The copper and hydrogen atoms are arranged in such way that the $Cu_{12}H_{12}$ core possesses a C_2 axis passing through the centers of Cu2-Cu3 and Cu8-Cu9 edges. Each ^{iPr}PN^{H}P ligand bridges two contiguous copper centers, only leaving the four central copper atoms unbound. Of the 32 Cu-Cu edges, 4 are substantially longer (2.8086(3)-2.9389(3) Å), all spanning the two Cu_6 units (Cu1-Cu11, Cu4-Cu12, Cu5-Cu10, and Cu6-Cu7). There are also 14 markedly shorter Cu-Cu contacts (2.4823(3)-2.5742(3) Å): 10 within the Cu_6 units and 4 across the Cu_6 units (Cu5-Cu11, Cu6-Cu11, Cu5-Cu12, and Cu6-Cu12). The remaining 14 Cu-Cu contacts fall in the 2.6073(3)-2.8015(3) Å range: 12 are from the Cu_3 faces without a capping hydride (Cu1-Cu3-Cu5, Cu2-Cu4-Cu6, Cu7-Cu9-Cu11, and Cu8-Cu10-C12) and 2 are used to link the two Cu_6 units (Cu5-Cu6 and Cu11-Cu12).

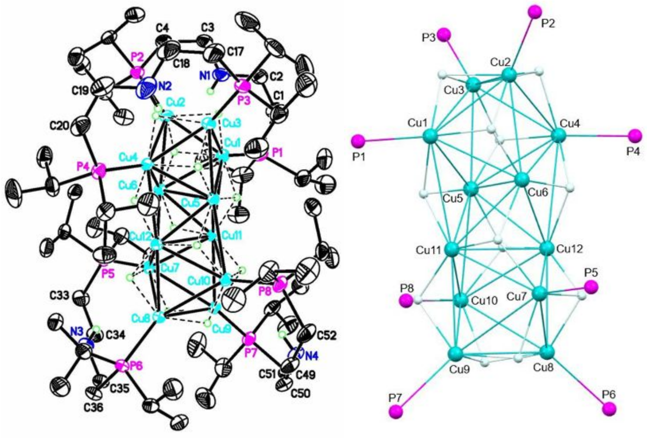


Figure 1 ORTEP of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ (left) and the $P_8Cu_{12}H_{12}$ core (right) at the 50% probability level (all hydrogen atoms except those bound to copper and nitrogen are omitted for clarity; phosphorus atoms are numbered in sequence so that P1/P2, P3/P4, P5/P6, and P7/P8 belong to the same ^{iPr}PN^{H}P ligand).

The solid-state structure studied by X-ray diffraction is likely maintained in solution. The observation of two phosphorus resonances for the yellow compound is consistent with the fact that $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ has four outer phosphorus atoms (P2, P3, P6, and P7) and four inner phosphorus atoms (P1, P4, P5, and P8). Furthermore, the $^{13}C\{^1H\}$ NMR spectrum featured two sets of NCH_2 and PCH_2 resonances, which was expected for the binding mode of $^{iPr}PN^{H}P$ as illustrated above. The crystal structure also suggests that $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ has three sets of hydride ligands decorating different parts of the Cu_{12} core (Figure 2): near the short edges (red), near the center (blue), and in between along the long edges (purple). The ^1H NMR spectrum of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ (in C_6D_6) showed a broad resonance at 0.87 ppm ($w_{1/2}$ = 22 Hz), an even broader resonance at 2.37 ppm ($w_{1/2}$ = 58 Hz), and the third resonance that was unfortunately obscured by the NCH_2 resonances (2.72-3.28 ppm). Hydride ligands in phosphine-stabilized copper clusters are known to have fluxional behavior.[33,46] The broadening thus can be caused not only by the quadrupolar ^{63}Cu and ^{65}Cu nuclei but also by rapid exchange of the hydride ligands. Interestingly, of the many $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ samples analyzed, one displayed a further broadened CuH resonance ($w_{1/2}$ > 150 Hz) that was shifted to 2.70 ppm, although the resonance at 0.87 ppm was largely unaffected. It is possible that the adventitious water present in that particular NMR sample accelerated the exchange of two different sets of hydride ligands, resulting in coalescence of the two Cu*H* resonances. The deuterium-labelled sample $(^{iPr}PN^{H}P)_4Cu_{12}D_{12}$ (prepared from $^{iPr}PN^{H}P$, CuBr, KO^{t}Bu, and D_2) gave two broad resonances at 2.73 and 0.92 ppm (in C_6H_6), which integrated to a 2:1 ratio. Considering that the red and purple hydrides are in similar chemical environments as the hydrides in $(^{iPr}PN^{H}P)_3Cu_6H_6$ (δ_{CuH} = 2.07 ppm), we attentively assign the downfield resonances (2.3-3.1 ppm) to these hydrides and the resonance at 0.87 ppm to the blue hydrides.

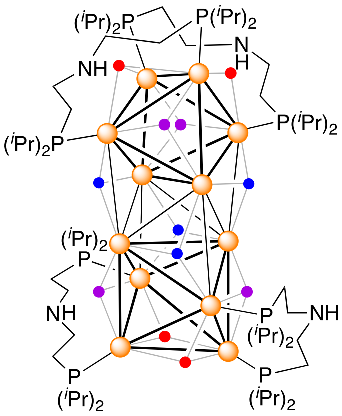
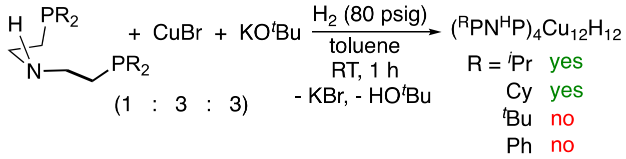


Figure 2 Illustration of the three unique sets of hydride ligands (color-coded) in $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$.

Search of other $Cu_{12}H_{12}$ clusters

Given the 1:3 ligand-to-copper ratio in $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$, the synthetic protocol was slightly modified to reflect the stoichiometry (Scheme 3). The reaction did produce more $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$, although $(^{iPr}PN^{H}P)_3Cu_6H_6$ still formed as a by-product. The isolated yield for $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ was only marginally improved due to the need of a recrystallization step to purify the cluster. The same procedure was then applied to $^{Cy}PN^{H}P$, $^{tBu}PN^{H}P$, and $^{Ph}PN^{H}P$ with the objective to obtain the analogous $Cu_{12}H_{12}$ clusters. In the latter case, the reaction failed to produce any copper hydrides that were stable enough to be isolated or spectroscopically observed. Replacing $^{iPr}PN^{H}P$ with $^{tBu}PN^{H}P$ yielded primarily $(^{tBu}PN^{H}P)_2Cu_4H_4$ along with some unidentified species. A sample prepared under D_2 in place of H_2 showed a deuterium resonance at 4.98 ppm consistent with $(^{tBu}PN^{H}P)_2Cu_4D_4$. A minor resonance (<5%) was also observed at 1.20 ppm, which could be for a new copper deuteride cluster other than $(^{tBu}PN^{H}P)_4Cu_{12}D_{12}$. This result is in alignment with our previous observation that, in C_6D_6, purified $(^{tBu}PN^{H}P)_2Cu_4H_4$ showed no sign of decomposition or cluster expansion (monitored at 23 °C for 24 h). The reaction of $^{Cy}PN^{H}P$ was most promising, signaled by the same color change as the reaction of $^{iPr}PN^{H}P$. The NMR spectra of the reaction mixture contained $^{Cy}PN^{H}P$, $(^{Cy}PN^{H}P)_2Cu_4H_4$, $(^{Cy}PN^{H}P)_3Cu_6H_6$, and possibly $(^{Cy}PN^{H}P)_4Cu_{12}H_{12}$. Efforts to isolate the dodecanuclear cluster were thwarted by the difficulty of removing the tetranuclear and hexanuclear clusters, whose full degradation took more than a month to complete. However, the two ^{31}P resonances (0.8 and –2.4 ppm) and the two ^2H resonances (2.79 and 1.30 ppm) detected for the deuterium-labelled sample supported the presence of $(^{Cy}PN^{H}P)_4Cu_{12}D_{12}$.



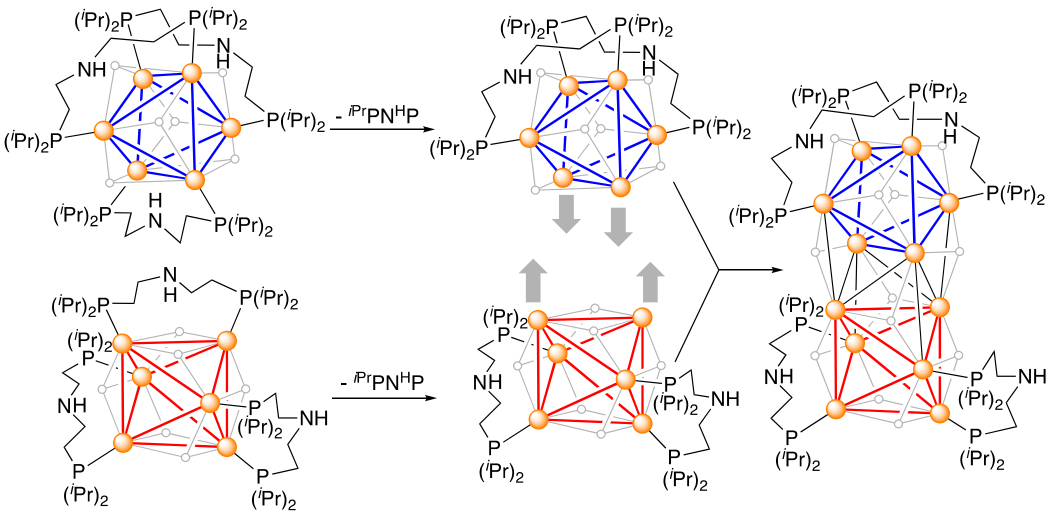
Scheme 3 Synthesis of $(^{R}PN^{H}P)_4Cu_{12}H_{12}$ based on the stoichiometry.

Implications of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ in CuH-based reactions

It is worth noting that $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ was not observed when $(^{iPr}PN^{H}P)$CuBr was treated with KO^{t}Bu under H_2. The reaction produced mainly $(^{iPr}PN^{H}P)_3Cu_6H_6$ along with $^{iPr}PN^{H}P$ and, in some cases, also $(^{iPr}PN^{H}P)_2Cu_4H_4$ when the reaction time was kept brief (≤ 30 min). This result implies that $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ does not emerge directly from aggregation of the in-situ generated $(^{iPr}PN^{H}P)$CuH. Under the ligand-deficient conditions (Scheme 2 and 3), unsupported CuH likely grows into clusters of various size with and without $(^{iPr}PN^{H}P)$CuH, eventually leading to the formation of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$.

When purified, $(^{iPr}PN^{H}P)_3Cu_6H_6$ (dissolved in C_6D_6) would undergo thermal decomposition to $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ and other products. However, the rate was significantly slower than the rate of generating $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ under the conditions outlined in Scheme 2 and 3. This decomposition or cluster expansion process was monitored by NMR spectroscopy for days with multiple samples. Depending on the purity of $(^{iPr}PN^{H}P)_3Cu_6H_6$ and the moisture level in the sample, the formation of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ began in 2-6 h. The reaction was accompanied by a color change of the solution from red orange to dull orange and precipitation of a black solid inside the NMR tube. Presumably, the initial ligand dissociation from $(^{iPr}PN^{H}P)_3Cu_6H_6$ gives $(^{iPr}PN^{H}P)_2Cu_6H_6$, which in turn aggregates with the second $(^{iPr}PN^{H}P)_2Cu_6H_6$ fragment to produce $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ (Scheme 4). In doing so, two hydride ligands (i.e., the blue hydrides) of each $(^{iPr}PN^{H}P)_2Cu_6H_6$ fragment need to bridge a new copper atom.

The hexanuclear-to-dodecanuclear cluster expansion is not a reversible process. Stirring a pure sample of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ with the free $^{iPr}PN^{H}P$ ligand in C_6D_6 did not yield $(^{iPr}PN^{H}P)_3Cu_6H_6$. The



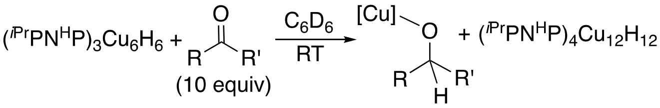
Scheme 4 Proposed mechanism for hexanuclear-to-dodecanuclear cluster expansion.

dodecanuclear species may not be the endpoint of cluster growth. Under ambient conditions, the solution of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ in C_6D_6 gradually degraded to $^{iPr}PN^{H}P$ and a black precipitate over a period of a month. The involvement of larger copper clusters ($Cu_{>12}$) under this condition cannot be ruled out, although the fate of unsupported CuH is known to be Cu(0) and H_2.[47] Taken together, the decomposition studies highlight the importance of having $^{iPr}PN^{H}P$ to stabilize the copper hydride clusters, regardless of the size of the clusters. In fact, in the presence of $^{iPr}PN^{H}P$, both $(^{iPr}PN^{H}P)_3Cu_6H_6$ and $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ displayed improved thermal stability.

Another interesting structural feature of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ is that the NH groups show close contact with the nearby hydrides (Figure 1). The NH…HCu short contacts have been previously observed with other copper hydrides supported by a $^{R}PN^{H}P$ ligand[27] and rationalized by invoking dihydrogen bonding interactions.[48,49] It is possible that these weak interactions may play some role in stabilizing the copper hydride clusters. Mixing $(^{iPr}PN^{H}P)_3Cu_6H_6$ or $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ with 10 equiv of D_2O resulted in an immediate disappearance of the NH resonance. In the case of $(^{iPr}PN^{H}P)_3Cu_6H_6$, a faster degradation to $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ and $^{iPr}PN^{H}P$ was also observed. Protic molecules such as water might disrupt the dihydrogen bonds between the NH and CuH moieties and accelerate the decomposition process.

The NMR data of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ reminded us that the reduction of carbonyl compounds with $(^{iPr}PN^{H}P)_3Cu_6H_6$ should be reexamined (Table 1). The $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ resonances sometimes appeared in the product spectra but were unaccounted for in our previous studies. A further inspection of these spectra suggested that, for the more reactive substrates (PhCHO and $4\text{-}CF_3C_6H_4CHO$), the amount of $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ generated during the reaction was negligible (<5%). In contrast, cyclohexanecarboxaldehyde, *N*-methyl-2-pyrrolecarboxaldehyde, benzophenone, and acetophenone underwent carbonyl reduction with $(^{iPr}PN^{H}P)_3Cu_6H_6$ more slowly, likely giving sufficient time for copper hydride intermediates to aggregate to form $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$. In particular, the reactions of *N*-methyl-2-pyrrolecarboxaldehyde and acetophenone resulted in 50% of the $^{iPr}PN^{H}P$ ligand ending up in $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$. During the catalytic hydrogenation process, the formation of the dodecanuclear copper hydride, clusters with higher nuclearity, and Cu(0) would represent the deactivation pathway for the catalyst. As a matter of fact, *N*-methyl-2-pyrrolecarboxaldehyde failed to react with $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}$ in C_6D_6, even when the reaction was monitored for 7 days.

Table 1 Fate of $^{iPr}PN^{H}P$ during the carbonyl reduction with $(^{iPr}PN^{H}P)_3Cu_6H_6$.



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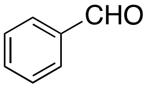
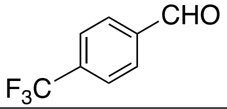
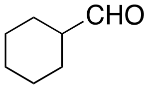
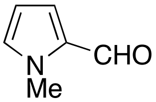
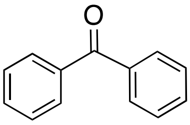
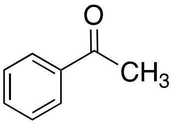
	>95%	<5%
	>95%	<5%
	72%	28%
	50%	50%
	67%	33%
	50%	50%

Conclusions

In summary, we have captured and characterized a new copper cluster with an unprecedented $Cu_{12}H_{12}$ core stabilized by four $^{iPr}PN^{H}P$ ligands. This dodecanuclear copper hydride forms from thermal decomposition of the “upstream” clusters (i.e., $(^{iPr}PN^{H}P)_2Cu_4H_4$ →

($^{iPr}PN^HP)_3Cu_6H_6$ → ($^{iPr}PN^HP)_4Cu_{12}H_{12}$), during the reactions of ($^{iPr}PN^HP)_3Cu_6H_6$ (e.g., reduction of carbonyl compounds and H/D exchange with D_2O), and, more favorably, under the conditions where an insufficient amount of the $^{iPr}PN^HP$ ligand is available. Through the studies of other $^RPN^HP$ ligands, we have also shown that phosphorus substituents play profound roles in governing the stability, size, and growth rate of the clusters. The data presented here, coupled with our previous studies of the smaller clusters, have shed more light on how copper hydrides can evolve in solution.

Author contributions

Dewmi A. Ekanayake: Writing – original draft, Investigation, Formal analysis, Data curation. **Jeanette A. Krause**: Writing – review & editing, Investigation, Formal analysis, Data curation. **Hairong Guan**: Writing – review & editing, Supervision, Project administration, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for ($^{iPr}PN^HP)_4Cu_{12}H_{12}{\bullet}C_7H_8$ have been deposited at the CCDC under 2401031.†

Conflicts of interest

The authors declare no conflict of interest.

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Data availability Statement

The data supporting this article have been included as part of the ESI.† Crystallographic data for $(^{iPr}PN^{H}P)_4Cu_{12}H_{12}{\bullet}C_7H_8$ have been deposited at the CCDC under 2401031.†

†Electronic supplementary information (ESI) available: NMR and IR spectra of the copper complexes and X-ray crystallographic information. CCDC 2401031. For ESI and crystallographic data in CIF or other electronic formate see DOI: 10.1039/x0xx00000x