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A stable well-defined copper hydride cluster consolidated with hemilabile phosphines[†]

Shang-Fu Yuan, D Heng-Wang Luyang, D Zhen Lei, D Xian-Kai Wan, Jiao-Jiao Li and Quan-Ming Wang *

Copper hydrides are very useful in hydrogenation reactions. We report a stable Stryker-type copper hydride reagent protected by hemilabile phosphines: $[Cu_8H_6(dppy)_6](OTf)_2$ (Cu_8-H , dppy = diphenylphosphino-2-pyridine). The metal core of this cluster has a bicapped octahedral configuration, and the copper-bound hydrides each triply bridges over a triangular face of the octahedron. This cluster is attractive due to its facile preparation and excellent stability under ambient conditions. The comparable activity and selectivity both in the stoichiometric and catalytic reactions make Cu_8-H a promising alternative to Stryker's reagent.

Copper hydrides have been attracting wide interest owing to their applications as hydrogenation reagents and catalysts.^{1–5} A well-known example is Stryker's reagent, the hexameric cluster $Cu_6H_6(PPh_3)_6$.^{6–9} This isolable and well-defined copper hydride cluster is a good source of hydride both in stoichiometric reactions and in copper-catalyzed reductions.^{8–12} This complex was named "Reagent of the Year" in 1991 and is commercially available, because of the mild reaction conditions and excellent efficiencies in hydrogenation.

Although the reactivity of Stryker's reagent has been extensively explored, it has several drawbacks. This reagent is moisture- and air-sensitive,¹³ and can be prepared only under inert atmosphere; in addition, repeated crystallization is necessary for its purification.^{14,15} Therefore, a simpler and more convenient synthetic method is still required for the synthesis of copper hydride complexes, and it is highly demanded that the copper hydrides are stable under ambient conditions.

Inspired by our previous work for enhancing the rigidity of hexaauriomethane clusters,^{16–18} a facile approach is the use of P, N hemilabile phosphines to improve the stability by presenting bridging coordination in a copper complex. Herein, we report the

E-mail: qmwang@tsinghua.edu.cn; Web: http://www.wangqmlab.org.cn

synthesis, structural determination and reactivity of a novel phosphine-stabilized copper hydride, $[Cu_8H_6(dppy)_6](OTf)_2$ (Cu_8 -H) (dppy = diphenylphosphino-2-pyridine). Remarkably, Cu_8 -H can be easily prepared under ambient conditions, and is stable in the air. Cu_8 -H shows excellent activity and selectivity in selective hydrogenation reactions, which is comparable to the performance of Stryker's reagent.

The preparation and work up procedures do not need an inert atmosphere, and solvents are used as received. Typically, cluster Cu₈-H was prepared via the reaction of Cu(CH₃CN)₄OTf with NaBH₄ (freshly dissolved in ethanol) in the presence of dppy in CH₂Cl₂. The mixture was stirred at room temperature for 1 h, and then the red solution was evaporated to obtain red microcrystals and a yellow supernatant. ³¹P NMR in CD₂Cl₂ proved that the red microcrystals were of high purity with a characteristic singlet at 0.47 ppm (Fig. S1, ESI[†]). The resulting red solid was dissolved in CH2Cl2, and after filtration, the filtrate was subjected to the diffusion of ether to afford red block crystals of Cu₈-H after 5 days ($\sim 80\%$ yield on Cu basis, Fig. S2, ESI[†]). Its deuteride analogue [Cu₈D₆(dppy)₆](OTf)₂ (Cu₈-D) can be obtained by using NaBD₄ instead of NaBH₄ in the preparation. The preparation protocol works for various copper precursors such as Cu(CH₃CN)₄ClO₄, Cu(CH₃CN)₄PF₆ and Cu(CH₃CN)₄BF₄, *i.e.* the type of counteranion does not affect the synthesis. It is noteworthy that a slight excess amount of NaBH₄ (1.2 equiv.) was required in order to ensure complete reaction. It was found that large scale reactions, e.g. 5 times of precursors, can be easily performed under the same conditions. It is noted that a similar octacopper hydride cluster has been prepared from a Cu(II) precursor with 8% yield by Xu et al.¹⁹ The present work provides a facile synthetic method and the obtained yield is as high as 80%.

Cu₈-**H** is soluble in dichloromethane, dimethyl sulfoxide, acetone or acetonitrile, but insoluble in benzene, toluene, methanol or ethanol. The UV-vis absorption spectrum of **Cu**₈-**H** shows two absorption bands at 321 and 449 nm (shoulder) in CH₂Cl₂ (Fig. S3, ESI†), which are blue shifted in comparison to Cu₆H₆(PPh₃)₆ ($\lambda_{max} = 524$ nm).²⁰ The presence of hydrides in

Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China.

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Fig. 1 Mass spectra of **Cu**_B-**H** in CH₂Cl₂. Inset: The experimental (black trace) and simulated (red trace) isotopic patterns of $[Cu_8H_6(dppy)_5]^{2+}$ (Peak A). Peaks B–D are assigned to $[Cu_8H_6(dppy)_6]^{2+}$, $[Cu_4H(dppy)_3Cl_2]^+$ and $[Cu_4H(dppy)_4Cl_2]^+$, respectively.

 Cu_8 -H was confirmed by the H₂-liberation as measured using gas chromatography. No H₂ evolution was observed in the presence of C₂H₅OH at room temperature. Upon acidification with HCl, the hydrides in Cu₈-H can react with the H⁺ to produce H₂ gas, and Cu₈-H can release 3 equiv. of H₂ per molecule (Fig. S4, ESI[†]). The ability of hydrogen liberation suggests its potential as a good catalyst in hydrogenation reactions.

To verify the number of hydrides, an ESI-MS study of Cu₈-H was carried out. As shown in Fig. 1, a small peak (Peak B) was observed at m/z = 1047.01, corresponding to the dicationic ion $[Cu_8H_6(dppy)_6]^{2+}$ (calcd 1047.00). The prominent peak (Peak A) at 915.45 is ascribed to $[Cu_8H_6(dppy)_5]^{2+}$ (calcd 915.46), which is a fragment ion with the leaving of one dppy ligand. Both of the observed isotopic patterns are in perfect agreement with the simulated ones (Fig. S5, ESI[†]). Two singly charged fragment peaks (Peaks C and D) at 1115.91 and 1379.03 are assigned to $[Cu_4H(dppy)_3Cl_2]^+$ and $[Cu_4H(dppy)_4Cl_2]^+$, respectively. In contrast, a clear peak corresponding to $[Cu_8D_6(dppy)_6]^{2+}$ at 1050.02 (calcd 1050.02) was detected with the deuterated cluster Cu₈-D (Fig. S6, ESI[†]). The shift of 3.0 m/z between $[Cu_8H_6(dppy)_6]^{2+}$ and $[Cu_8D_6(dppy)_6]^{2+}$ confirms the presence of six hydrides in the cluster, which also indicates that the cluster remains intact in solution.

Single crystal structural analysis‡ revealed that Cu_8 -H comprises a dicationic cluster $[Cu_8H_6(dppy)_6]^{2+}$ and two $[OTf]^-$ counteranions. The structure of the cationic part is centrosymmetric and the Cu_8 skeleton is a bicapped octahedron as shown in Fig. 2a. Six copper atoms form a distorted octahedron, and the remaining two copper atoms each capps one of the two opposite Cu_3 triangles. Each vertex of the octahedral Cu_6 core is ligated by the P donor of dppy, and the other two capping Cu atoms are each bound with three pyridyl N donors. Therefore, Cu_8 -H can be formally viewed as a bi-coppercapped Stryker's reagent with the N donors of dppy providing additional binding sites.

In the octahedral Cu₆ core, six short Cu···Cu contacts, 2.4304(11)–2.5106(12) Å (avg. 2.4757 Å), and six long ones, 2.6657(11)–2.8153(12) Å (avg. 2.7247 Å), were found (Fig. S7, ESI†). Similar Cu···Cu distances have been observed in the case



Fig. 2 (a) Molecular structure of the cationic part of Cu_8 -H. Hydrogen atoms are omitted for clarity. Atom colors: light blue = Cu, red = Hydride, purple = P, blue = N, gray = C. (b) The Cu₈H₆ core structure. Symmetry code: # 1 - x, 2 - y, -z.

of $Cu_6H_6[P(p-tolyl)_3]_6$.⁹ Alternatively, the Cu_6 unit may be viewed as a trigonal-antiprismatic array, in which the six longer $Cu \cdots Cu$ distances form two parallel triangles on opposite faces, and the apices of these triangles are interconnected by six shorter ones (Fig. S7b, ESI[†]).²¹ In addition, the two capping Cu atoms are away from the Cu_6 core, with $Cu \cdots Cu$ distances from 2.7669(11) Å to 2.9924(12) Å (avg. 2.8618 Å). The average distance is longer than twice the van der Waals radius of copper (2.8 Å), indicating that dppy plays an important role in holding the Cu atoms together.

Fortunately, copper-bound hydrides could be located and isotropically refined (Fig. 2b). Similar to the result from neutron diffraction analysis of $Cu_6H_6[P(p-tolyl)_3]_6$,⁹ all hydrides cap the six small triangular faces of the octahedron. It was found that the Cu–H bond lengths (1.641–2.025 Å) are comparable to those in $Cu_6H_6[P(p-tolyl)_3]_6$. Different from the semiface-bridging mode in $Cu_6H_6[P(p-tolyl)_3]_6$, the capping mode of the six hydrides in **Cu**₈-H is more symmetrical. Detailed Cu–H bond lengths are shown in Fig. S7b (ESI†). Although the positions of hydrides look a bit different from those in Xu *et al.*'s report,¹⁹ they are actually the same. They are seemingly different due to the four μ_3 -H⁻ being disordered over the six triangular faces of the octahedron.

For comparison, schematic structures of $Cu_6H_6(PPh_3)_6$ and $[Cu_8H_6(dppy)_6]^{2+}$ are shown in Scheme 1. The arrangement of Cu, P, and hydride atoms is quite the same. Thanks to the bridging of dppy, two extra copper atoms are attached to two



 $\label{eq:scheme1} \begin{array}{ll} \mbox{Scheme1} & \mbox{Scheme1$



opposite Cu_3 triangles to form two tetrahedra in Cu_8 -H. Thus, the two μ_3 -H⁻ in Stryker's reagent turn into μ_4 -H⁻ in Cu_8 -H.

The ¹H NMR peak of Cu₈-H shows a singlet resonance at 2.46 ppm in CD₂Cl₂ which is not observed in Cu₈-D (Fig. 3). The integration ratio of H in dppy ligands to hydrides is calculated to be 14.4:1 (14:1 in theory, Fig. S8, ESI⁺), which evidences that the number of hydrides is 6. The ²H NMR peak of Cu₈-D in CH₂Cl₂ exhibits a broad resonance at 2.54 ppm (Fig. S9, ESI[†]), also confirming the presence of hydrides in the cluster. The chemical shift for the hydrides in Cu₈-H has a similar value to that of different hexameric clusters: the hydride signal of $Cu_6H_6(PPh_3)_6$ appears near 3.50 ppm¹³ and a singlet (2.81 ppm) is detected when $P(NMe_2)_3$ is used as the ligand.²¹ The presence of two types of hydrides in Cu₈-H is confirmed by the ¹H NMR resonance peaks at 2.81 and 2.19 ppm (2:1) in CD_2Cl_2 at -80 °C (Fig. S10, ESI[†]). In addition, the ³¹P NMR peak of Cu₈-H in CD₂Cl₂ shows one broad singlet at 0.47 ppm (full width at half-height \sim 90 Hz) due to the fluxional behavior of the cluster, which makes it impossible to determine the J_{P-H} (Fig. S11, ESI[†]).

Stryker's reagent is air-sensitive. Interestingly, Cu_8 -H was found to be stable under ambient conditions. In the solid state, Cu_8 -H is not sensitive to air and moisture at least for a couple of weeks, and can stay intact in CH_2Cl_2 at room temperature for more than 6 hours as evidenced by the ³¹P NMR spectra (Fig. S12, ESI[†]). It is much more stable in an anaerobic solvent or at low temperature (5 °C). The good stability of Cu_8 -H makes it a promising copper hydride complex for various applications.

We examined the reaction of Cu₈-H with organic compounds containing unsaturated groups, such as phenylacetylene and cinnamaldehyde. As shown in Table 1 (entry 1), 90% conversion and 100% selectivity for styrene were obtained in CH₂Cl₂ (Fig. S13, ESI[†]). It should be noted that water is necessary to supply protons.¹⁰ Because a small amount of H₂ was produced as detected by ¹H NMR, it is suggested that more than 1/6 equivalent of Cu₈-H is required to completely consume the starting materials. In contrast, no 1,2-diphenylethyne was reduced under the same conditions, indicating that the internal alkyne is difficult to adsorb on the catalyst. Although a 91% yield was obtained at elevated temperature (80 °C), only trace conversion was observed in benzene at room temperature after 24 h with Stryker's reagent,¹⁰ which is very similar to our case with Cu₈-H in CH₂Cl₂. In addition, the conjugated reduction of α,β -unsaturated carbonyl compounds has also been realized. Cinnamaldehyde was reduced to 3-phenylpropanal at 70%

Table 1 Selectivity reaction/catalytic reduction of unsaturated organic compounds with $\mathbf{Cu}_{\mathbf{B}}\text{-}\mathbf{H}$



^{*a*} Reaction conditions: 28 mg Cu₈-H (8 × 10⁻³ mmol), PhC \equiv CH 5.5 µL (0.05 mmol), H₂O 2 µL, DCM 3 mL, stirred for 4 h. ^{*b*} Reduction conditions: 1 mg Cu₈-H (3 × 10⁻⁴ mmol), *trans*-Benzalacetone 14 µL (0.1 mmol), Ph₂SiH₂ 25 µL (0.2 mmol), EtOH 2 mL, stirred for 12 h at 30 °C. ^{*c*} The turnover number is based on Cu₈-H. The conversion and selectivity were determined by NMR analysis.

yield, and no 1,2-reduction of the carbonyl moiety was observed. The comparable activity and selectivity of Cu_8 -H to Stryker's reagent make it a useful hydrogenation reagent.^{8,10} Due to the different nature between Stryker's reagent and Cu_8 -H, such as charges and solubility, we believe that Cu_8 -H may play a complementary role in different solvents.

Moreover, Cu_8 -H was found to show excellent performance toward site-specific catalytic reduction of α , β -unsaturated organic compounds in the presence of Ph₂SiH₂. Two substrates, *trans*-Benzalacetone (entry 4) and β -Nitrosytrene (entry 5) were examined, and only C=C hydrogenation products were detected with the turnover number up to 326 and 215 based on Cu₈-H, respectively. These facts indicate that Cu₈-H provides active catalytic centers that can be regenerated with silyl hydrides, and the hydrogenation takes place through the 1, 4-reduction mechanism as previously described with Cu₆H₆ (PPh₃)₆.¹³ Therefore, Cu₈-H is a very useful alternative to Stryker's reagent. When 3-nitrostyrene was tested under the same conditions, neither C=C nor nitro group was found to be reduced. This means that Cu₈-H is completely inert toward unactivated alkenes.

In summary, a novel copper hydride reagent, $[Cu_8H_6 (dppy)_6](OTf)_2$, was prepared with the stabilization of dppy ligands. The precise structure was determined using X-ray single crystal diffraction. The facile preparation and the stability under ambient conditions make **Cu₈-H** a promising hydrogenation catalyst, which offers a very useful alternative to Stryker's reagent.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Crystal data for Cu₈-H, [C₁₀₄H₉₀N₆O₆F₆P₆S₂Cu₈·2.5CH₂Cl₂]₂, *a* = 14.0215(4) Å, *b* = 15.7562(4) Å, *c* = 25.1672(6) Å, *a* = 90.777(2)°, *β* = 91.477(2)°, γ = 105.027(2)°, *V* = 5367.0(2) Å³, space group *P*I, *Z* = 1, *T* = 173.00(10) K, 35502 reflections measured, 18123 unique (*R*_{int} = 0.0433), The final *R*1 was 0.0672 (*I* > 2 σ (*I*)) and w*R*2 was 0.1784 (all data). CCDC 2067584.

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