

UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

Synthesis, Characterization, and Reactivity of the Group 11 Hydrido Clusters [Ag₆H₄(dppm)₄(OAc)₂] and [Cu₃H(dppm)₃(OAc)₂]

Permalink

<https://escholarship.org/uc/item/9bm0100j>

Journal

Inorganic Chemistry, 55(23)

ISSN

0020-1669

Authors

Cook, Andrew W
Nguyen, Thuy-Ai D
Buratto, William R
[et al.](#)

Publication Date

2016-12-05

DOI

10.1021/acs.inorgchem.6b02385

Peer reviewed

Synthesis, Characterization, and Reactivity of the Group 11 Hydrido Clusters, $[\text{Ag}_6\text{H}_4(\text{dppm})_4(\text{OAc})_2]$ and $[\text{Cu}_3\text{H}(\text{dppm})_3(\text{OAc})_2]$

Andrew W. Cook, Thuy-Ai D. Nguyen, William R. Buratto, Guang Wu, and Trevor W. Hayton*

[†]Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, United States
Supporting Information Placeholder

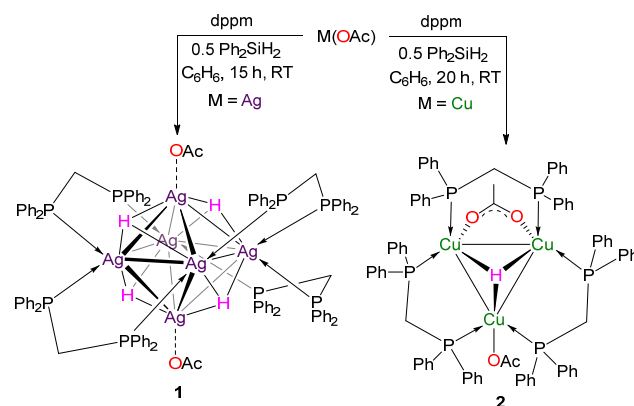
ABSTRACT: The group 11 hydride clusters $[\text{Ag}_6\text{H}_4(\text{dppm})_4(\text{OAc})_2]$ (**1**) and $[\text{Cu}_3\text{H}(\text{dppm})_3(\text{OAc})_2]$ (**2**) (dppm = 1,1-bis(diphenylphosphino)methane) were synthesized in moderate yields from the reaction of $\text{M}(\text{OAc})$ ($\text{M} = \text{Ag}, \text{Cu}$) with Ph_2SiH_2 , in the presence of dppm. Complex **1** is the first structurally characterized homometallic polyhydrido silver cluster to be isolated. Both **1** and **2** catalyze the hydrosilylation of (α,β -unsaturated) ketones. Notably, this represents the first example of hydrosilylation with an authentic silver hydride complex.

Copper hydrides have proven to be potent catalysts for the hydrogenation and hydrosilylation of α,β -unsaturated ketones, carbon-carbon multiple bonds, and CO_2 .¹⁻¹⁴ In contrast, only a handful of examples of silver-catalyzed hydrogenation and hydrosilylation are known.¹⁵⁻²⁰ For example, AgOTf has been shown to catalyze the hydrosilylation of aryl aldehydes in the presence of Me_2PhSiH and PEt_3 .¹⁶ Similarly, the semi-hydrogenation of alkynes by a heterobimetallic Ag/Ru catalyst has been reported.¹⁹ In both cases, catalysis is thought to proceed via a Ag-H intermediate, but this hypothesis has yet to be confirmed, though recently a silver hydride dimer, $[\{(\text{SIDipp})\text{Ag}\}_2(\mu\text{-H})]\text{X}$ ($\text{SIDipp} = 1,3$ -bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; $\text{X}^- = \text{OTf}^-$ or BF_4^-), was shown to stoichiometrically reduce CO_2 to formate.²¹ This limited understanding of Ag-H reactivity is due, in part, to the difficulty in generating stable silver hydride complexes; a consequence of this metal's relatively high $\text{M}(\text{I})/\text{M}(\text{O})$ half-cell potential (0.80 V).²² Because of this property, $\text{Ag}^{\text{I}}\text{-H}$ complexes more easily decompose to yield Ag^{0} and H_2 versus their Cu counterparts. Consequently, $\text{Ag}^{\text{I}}\text{-H}$ complexes have proven to be relatively rare.^{21, 23-38} Moreover, the examples isolated thus far are either homometallic monohydrides, e.g., $[\text{Ag}_7\text{H}\{\text{Se}_2\text{P}(\text{O}^i\text{Pr})_2\}_6]$,³¹ heterometallic polyhydrides, e.g., $[\text{Ag}(\mu\text{-H})_4\{\text{Re}_2(\mu\text{-H})(\text{CO})_8\}_2]^-$,³³ or polyhydrides observed via elec-

troscopy ionization mass spectrometry, (e.g., $[\text{Ag}_{10}\text{H}_8(\text{dppm})_6]^{2+}$)³⁴ or NMR spectroscopy (e.g., $[\text{Ag}_{18}\text{H}_{16}(\text{Ph}_3\text{P})_{10}]^{2+}$).³⁹ Herein, we report the synthesis and characterization of the first structurally characterized homometallic silver polyhydrido cluster, $[\text{Ag}_6\text{H}_4(\text{dppm})_4(\text{OAc})_2]$. In addition, we have examined its ability to catalyze the 1,4- and 1,2-hydrosilylations of (α,β -unsaturated) ketones.

Addition of 1 equiv of dppm and 0.5 equiv of diphenylsilane (Ph_2SiH_2) to a slurry of $\text{Ag}(\text{OAc})$ in benzene results in a rapid color change from white to dark red-brown. Work-up of the solution after stirring at room temperature for 15 h results in the isolation of the first silver polyhydrido cluster, $[\text{Ag}_6\text{H}_4(\text{dppm})_4(\text{OAc})_2]$ (**1**), as a colorless, crystalline solid in 47% yield (Scheme 1).

Scheme 1. Synthesis of Complexes **1** and **2**



Complex **1** crystallizes in the triclinic space group $\text{P}\bar{1}$ as the benzene solvate $\mathbf{1} \cdot 2.5\text{C}_6\text{H}_6$ (Figure 1). In the solid state, the Ag atoms of the $[\text{Ag}_6]^{6+}$ core are arranged in an octahedron. The four dppm ligands coordinate to an equatorial belt formed by four Ag atoms. Each dppm ligand is deflected out of the $[\text{Ag}_4]^{4+}$ plane, with two arranged above the plane and two below the plane in an alternating fashion. While the four hydride ligands were not located in the difference Fourier map, the arrangement of the dppm ligands likely requires that the hydride ligands occupy the four trigonal faces that are opposite a dppm moiety with a μ_3 -binding mode. Lastly, the two acetate counterions are bound to

Ag atoms at axial positions of the $[\text{Ag}_6]^{6+}$ core, via κ^1 and κ^2 binding modes.

The average Ag–Ag bond length within the $[\text{Ag}_4]^{4+}$ belt is 3.08 Å, which is longer than the average $\text{Ag}_{\text{cap}}\text{--Ag}_{\text{belt}}$ bond length of 2.88 Å. The $\text{Ag}_{\text{cap}}\text{--Ag}_{\text{belt}}$ interaction is within the covalent radius for Ag,⁴⁰ and the $\text{Ag}_{\text{belt}}\text{--Ag}_{\text{belt}}$ interaction lies well within twice the van der Waals radius for Ag,⁴¹ suggestive of considerable argentophilic interactions within the $[\text{Ag}_6]^{6+}$ core. These values are also similar to those reported for other $\text{Ag}^{\text{I}}\text{--H}$ clusters^{21, 28–32, 35, 37, 38} and Ag_6 octahedra.^{42–48} Finally, the average Ag–P distance (2.51 Å) is typical of Ag–P bonds.^{32, 35, 38, 49–54}

In agreement with the high symmetry of complex **1** in the solid state, its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum features a single ^{31}P resonance at 8.06 ppm in C_6D_6 . This resonance features a complicated J-coupling pattern, due to one- and two-bond coupling to the ^{107}Ag and ^{109}Ag nuclei in the $[\text{Ag}_6]^{6+}$ core. The ^1H NMR spectrum of complex **1** in C_6D_6 shows a single acetate resonance at 2.92 ppm, while the diastereotopic methylene protons of the dppm ligand appear at 3.02 ppm and 5.44 ppm. Most notably, a complicated multiplet, centered at 5.82 ppm and integrating for 4H, is assignable to the four equivalent hydride moieties. The ^2H NMR spectrum of the isotopically labeled analogue, **1-d₄**, features a resonance at 5.76 ppm in $1,2\text{-C}_6\text{H}_4\text{Cl}_2\text{:C}_6\text{D}_6$ (99:1, v/v), confirming our assignment of this feature as a hydride resonance. The ^{109}Ag NMR spectrum of **1** in $1,2\text{-C}_6\text{D}_4\text{Cl}_2$, recorded using an INEPT pulse sequence,⁵⁵ features a single resonance at 1095 ppm. This chemical shift is in good agreement with the ^{109}Ag signals observed for the $\text{Ag}^{\text{I}}\text{--H}$ dichalcogenatophosphate clusters reported by Liu and co-workers.^{28–31} However, only one resonance was observed in the spectrum, despite the presence of two unique Ag environments in this complex, which may be a consequence of poor signal-to-noise due to its low solubility. Finally, the electrospray ionization (ESI) mass spectrum of **1** features a signal at 2246.942 m/z corresponding to $[\text{M-OAc}]^+$ (calculated m/z 2246.954). For comparison, the ESI mass spectrum of **1-d₄** gave rise to a signal at 2250.978 m/z (calculated m/z 2250.979), a shift of 4 m/z versus **1**, as anticipated for a tetra-hydrido complex. Interestingly, the ESI mass spectrum of **1** contains another major feature at 1537.098 m/z , which is assignable to the $[\text{Ag}_3(\text{dppm})_3\text{H}(\text{OAc})]^+$ fragmentation product, consistent with O’Hair’s observation that the $\text{Ag}_3(\mu_3\text{-H})$ core is especially stable.^{32, 34–36, 38} Its facile formation may also indicate a plausible mechanism for cluster assembly, as dimerization of $[\text{Ag}_3(\text{dppm})_3\text{H}(\text{OAc})]^+$, concomitant with dppm dissociation, would generate the Ag_6 core.

We also briefly explored the chemical properties of **1**. Complex **1** is modestly soluble in C_6H_6 and THF, insoluble in MeCN, Et_2O , and non-polar solvents, and rea-

sonably soluble in 1,2-dichlorobenzene. Complex **1** exhibits only modest thermal stability. On standing overnight in C_6D_6 , it partially decomposes to H_2 and silver metal, amongst other products (Figure S23). An ESI mass spectrum of this sample suggests that a mixture of larger silver nanoclusters is generated (Figure S41); however, their identities remain unknown. Complex **1** also reacts slowly with excess H_2O (10 equiv) in C_6D_6 , forming Ag° , as well as other products.

To better understand the formation of **1** we recorded ^1H and ^{31}P NMR spectra of the crude reaction mixture. These spectra reveal the presence of free dppm, complex **1**, and an unidentified silver hydride cluster, as indicated by broad hydride ligand resonances at 2.40 and 3.60 ppm (Figure S21) in the ^1H NMR spectrum. Accordingly, we speculate that the modest yield of **1** is due to the competing formation of these by-products, as well as its gradual decomposition over the course of the 15 h reaction time. The formation of these other Ag clusters also likely accounts for the dark brown color of the reaction mixture. Interestingly, if the reaction is performed using a Ag to dppm ratio that corresponds to the molecular formula (6:4), the yield of **1** drops precipitously. We suggest that the Ag to dppm ratio shown in Scheme 1 (i.e., 1:1) results in higher concentrations of dppm, which helps to stabilize transient “ $\text{Ag}^{\text{I}}\text{--H}$ ” monomers, and reduces the probability of decomposition.

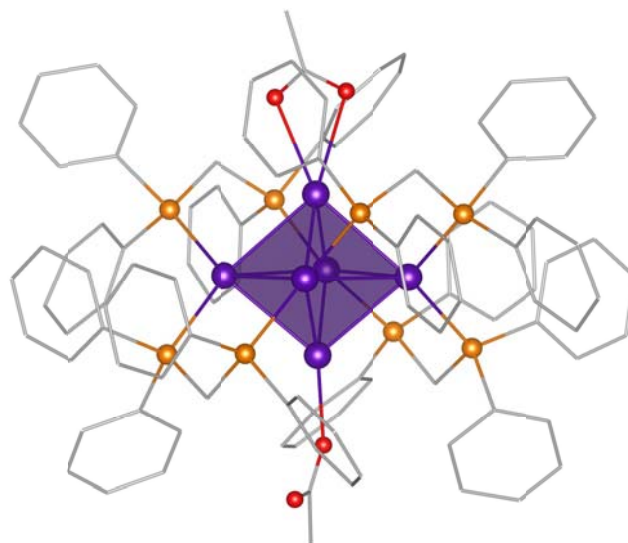


Figure 1. Ball and stick diagram of **1**. All hydrogen atoms and solvent molecules have been omitted for clarity. Color legend: Ag = purple; P = yellow-orange; O = red; C = grey wireframe.

For further comparison, we endeavored to synthesize the Cu congener of **1**. Previous attempts to make a dppm Cu–H cluster ended with decomposition because of the high basicity of the $[\text{Cu}(\text{O}^t\text{Bu})_4]$ starting material.⁵⁶ However, the combined use of $\text{Cu}(\text{OAc})$ and Ph_2SiH_2 to generate the $\text{Cu}^{\text{I}}\text{--H}$ moiety obviates the use

of an alkoxide precursor. Thus, addition of 1 equiv of dppm and 0.5 equiv of Ph_2SiH_2 to a slurry of $\text{Cu}(\text{OAc})$ in benzene results in the gradual color change from pale green to yellow. Work-up of the solution after 20 h affords the copper hydride cluster $[\text{Cu}_3\text{H}(\text{dppm})_3(\text{OAc})_2]$ (**2**), as colorless crystals in 83% yield (Scheme 1). Complex **2** is closely related to the known $\text{Cu}^{\text{I}}\text{-H}$ clusters, $[\text{Cu}_3\text{H}(\text{dcpm})_3]^{2+}$ (dcpm = 1,1-bis(dicyclohexylphosphino)methane) and $[\text{Cu}_3(\text{BH}_4)\text{H}(\text{dppa})_3]^+$ (dppa = bis(diphenylphosphino)amine).^{57, 58}

Complex **2** crystallizes as the benzene solvate, $2 \cdot 2\text{C}_6\text{H}_6$ (Figure 2), in the monoclinic space group $\text{P}2_1/\text{n}$. In the solid state, complex **2** contains a triangular $[\text{Cu}_3]^{3+}$ core with an average Cu–Cu distance of 2.91 Å. This distance is comparable to the average Cu–Cu distance of 2.882(1) Å reported for $[\text{Cu}_3\text{H}(\text{dcpm})_3]^{2+}$.⁵⁷ The average Cu–P distance in **2** (2.28 Å) is consistent with Cu–P bonds in other phosphine-supported $\text{Cu}^{\text{I}}\text{-H}$ clusters.^{13, 56, 57, 59–64} The hydride ligand was located in the difference Fourier map, and was found to display a μ_3 binding mode. Lastly, the two acetate counterions both bind to the Cu_3 core, via κ^1 and κ^2 binding modes.

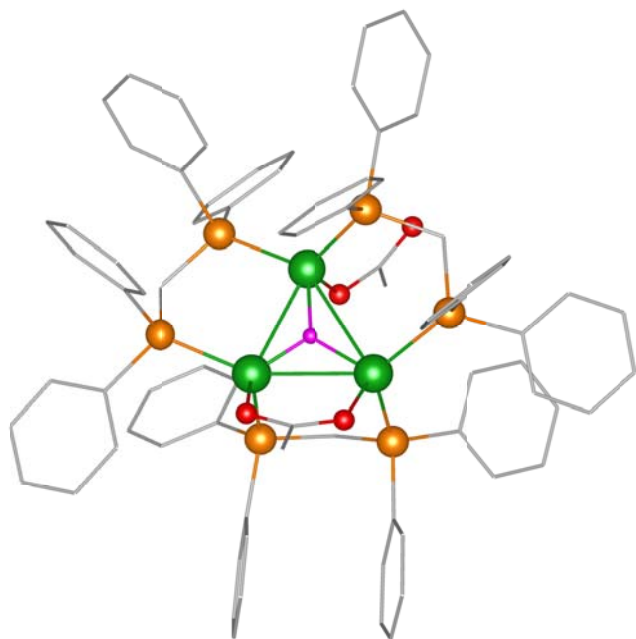


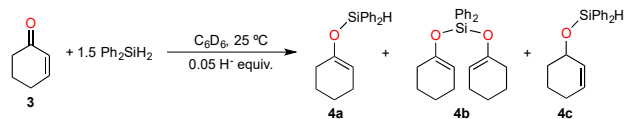
Figure 2. Ball and stick diagram of **2**. All hydrogen atoms (except the hydride ligand) and solvent molecules have been omitted for clarity. Color legend: Cu = green; H = magenta; P = yellow-orange; O = red; C = grey wireframe.

While complex **2** appears to have C_3 symmetry in the solid state, there is only one resonance observed in its $^3\text{P}\{\text{H}\}$ NMR spectrum, at -6.66 ppm, in $\text{MeCN-}d_3$. Likewise, complex **2** exhibits a sharp singlet at 1.91 ppm in its ^1H NMR spectrum, assignable to the methyl group of a single acetate environment. Overall, these data are consistent with fast exchange of the acetate

moieties at room temperature, which results in a higher effective symmetry in solution than observed in the solid-state. A septet centered at 2.10 ppm in the ^1H NMR spectrum ($^2J_{\text{PH}} = 14.4$ Hz) is assignable to the lone hydride moiety. This signal collapses to a singlet upon ^3P decoupling. To further confirm the presence of a single hydride ligand, we synthesized the isotopically labeled complex, **2-d**. Gratifyingly, complex **2-d** features a singlet at 1.74 ppm in the ^2H NMR spectrum in $\text{C}_6\text{H}_6:\text{C}_6\text{D}_6$ (9:1, v:v), assignable to the deuteride ligand. Finally, complex **2** produced a signal at 1379.120 m/z in the ESI mass spectrum, corresponding to the $[\text{Cu}_3\text{H}(\text{dppm})_3\text{Cl}]^+$ ion (calculated m/z 1379.125). For comparison, complex **2-d** features a signal at 1380.123 m/z in its ESI mass spectrum, corresponding to the $[\text{Cu}_3\text{D}(\text{dppm})_3\text{Cl}]^+$ ion (calculated m/z 1380.131), a shift of 1 m/z . A parent peak for **2** was not found in the mass spectrum, likely due to facile exchange of acetate for Cl^- during the ESI-MS ionization process.

We also explored the chemical properties of **2**. Complex **2** is soluble in MeCN, partially soluble in C_6H_6 and THF, and insoluble in Et_2O and non-polar solvents. It is stable in MeCN for at least 3d, showing no signs of decomposition over this time. In contrast to complex **1**, complex **2** does not appear to react with excess H_2O , even over the course of 24 h.

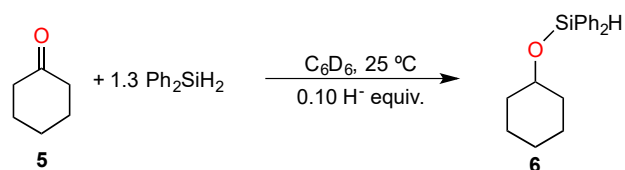
Group 11 hydrides are known to catalyze both 1,4- and 1,2-hydrosilylations of (α,β -unsaturated) ketones, in the presence of a silane.^{6, 7, 16, 65, 66} Given this precedent, we screened the ability of complex **1** to catalyze the 1,4-hydrosilylation of 2-cyclohexen-1-one (**3**). Thus, addition of Ph_2SiH_2 (1.5 equiv) to **3**, in the presence of **1** (0.05 H^- equivalents), in C_6D_6 results in 76% conversion to the corresponding silyl enol **4a** after 24 h (Table 1). Also formed in small amounts is the 1,2-hydrosilylation product, **4c**.⁶⁷ To our knowledge, this transformation represents the first example of hydrosilylation with an authentic silver hydride complex.⁶⁸ Complex **2** is also an effective pre-catalyst for the 1,4-hydrosilylation of **3**, achieving 96% total conversion after 24 h using a similar catalyst loading. However, this pre-catalyst features somewhat lower selectivity for the 1,4-hydrosilylation reaction. Surprisingly, in the absence of silane, neither **1** nor **2** can perform the stoichiometric reduction of **3**. A similar observation has been reported for other copper hydrides,^{68, 69} and can be rationalized by assuming that formation of the copper enolate intermediate is reversible, but its equilibrium concentration is very low. As a result, the presence of silane is required to trap the enolate and drive the reaction to completion.^{68, 70} For comparison, we also monitored the ability of $[\text{CuH}(\text{PPh}_3)]_6$ to catalyze 1,4-hydrosilylation of **3** under similar conditions. Of the three complexes tested, this reagent proved the most effective, reaching >99% conversion in only 15 min.

Table 1. 1,4-hydrosilylation of 2-cyclohexen-1-one catalyzed by **1**, **2**, and [CuH(PPh₃)₆]

catalyst ^a	reaction time (h)	conversion (%) ^b	4a:4b:4c
1	24	79	76:0:3
2	24	96	57:29:10
[CuH(PPh ₃) ₆]	<0.25	>99	79:21:0

^aFor experimental details see Supplementary Information. ^bTotal conversion to **4** determined by ¹H NMR integration with long pulse delay (d₁ = 60 s) against an internal standard of hexamethyldisiloxane.

We also screened the ability of **1**, **2**, and [CuH(PPh₃)₆] to catalyze the 1,2-hydrosilylation of cyclohexanone (**5**). Thus, addition of Ph₂SiH₂ (1.3 equiv) to **5**, in the presence of **1** (0.10 H⁺ equivalents), in C₆D₆ resulted in 42% conversion to the silyl ether **6** after 24h (Table 2). Complex **2** is an even better pre-catalyst for the 1,2-hydrosilylation of **5**, achieving >99% conversion after just 2 h, using a similar catalyst loading. Surprisingly, [CuH(PPh₃)₆] was the least effective pre-catalyst for this reaction, achieving only 26% conversion after 24 h. It is not readily apparent why complex **2** is a more effective pre-catalyst relative to **1** or [CuH(PPh₃)₆]; however, the changes in efficacy, relative to the results observed for the 1,4-hydrosilylation (Table 1), could indicate a change in the reaction mechanism.⁷¹

Table 2. 1,2-hydrosilylation of cyclohexanone catalyzed by **1**, **2**, and [CuH(PPh₃)₆]

catalyst ^a	reaction time (h)	conversion (%) ^b
1	24	42
2	2	>99
[CuH(PPh ₃) ₆]	24	26

^aFor experimental details see Supplementary Information. ^bTotal conversion to **6** determined by ¹H NMR integration with long pulse delay (d₁ = 60 s) against an internal standard of hexamethyldisiloxane.

In summary, we have isolated and characterized the diphosphine ligated clusters, [Ag₆H₄(dppm)₄(OAc)₂] (**1**) and [Cu₃H(dppm)₃(OAc)₂] (**2**). Complex **1** is the first

homometallic silver polyhydrido cluster to be structurally characterized. Interestingly, both **1** and **2** are the products of incomplete reduction; each cluster features the incorporation of two acetate moieties. While the cause of this is not certain, we posit that the [Cu₃H]²⁺ and [Ag₆H₄]²⁺ cores are unusually stable, and a more powerful hydride source would be required to drive the reduction to completion. Finally, both **1** and **2** are effective pre-catalysts for the hydrosilylation of (α,β-unsaturated) ketones. Most notably, these results represent the first example of catalysis with an authentic, isolable silver hydride, expanding the scope of catalytic reactivity known for the group 11 hydrides.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

X-ray data for compound **1**-2·5C₆H₆ (CIF)

X-ray data for compound **2**-2C₆H₆ (CIF)

Experimental details, spectral data, and additional figures and tables (PDF)

AUTHOR INFORMATION

Corresponding Author

*hayton@chem.ucsb.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Center for Sustainable Use of Renewable Feedstocks (CenSURF), a National Science Foundation (NSF) Center for Chemical Innovation (CCI). We thank Chris Ravelo for preliminary experiments in this area. We also thank Dr. Jerry Hu of the Materials Research Laboratory (MRL) at UCSB for assistance with the Ag NMR spectroscopy. NMR spectral acquisition was supported by the NIH Shared Instrument Grant 1S10OD012077-01A1. Mass spectrometry was performed at the MRL Shared Experimental Facilities supported by the MRSEC Program of the NSF under Award No. DMR 1121053; a member of the NSF-funded Materials Research Facilities Network.

REFERENCES

- (1) Osborn, M. E.; Pegues, J. F.; Paquette, L. A.; Reduction of α,β-unsaturated nitriles with a copper hydride complex. *J. Org. Chem.* **1980**, *45*, 167-168.
- (2) Goeden, G. V.; Caulton, K. G.; Soluble copper hydrides: solution behavior and reactions related to carbon monoxide hydrogenation. *J. Am. Chem. Soc.* **1981**, *103*, 7354-7355.
- (3) Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M.; Selective hydride-mediated conjugate reduction of α,β-unsaturated carbonyl compounds using [(Ph₃P)CuH]₆. *J. Am. Chem. Soc.* **1988**, *110*, 291-293.
- (4) Daeuble, J. F.; McGettigan, C.; Stryker, J. M.; Selective reduction of alkynes to cis-alkenes by hydrometallation using [(Ph₃P)CuH]₆. *Tetrahedron Lett.* **1990**, *31*, 2397-2400.

- (5) Lautens, M.; Ren, Y.; Transition Metal Catalyzed Stereospecific Intramolecular [3 + 2] Cycloadditions of Methylenecyclopropanes with Alkynes. *J. Am. Chem. Soc.* **1996**, *118*, 9597-9605.
- (6) Lipshutz, B. H.; Keith, J.; Papa, P.; Vivian, R.; A convenient, efficient method for conjugate reductions using catalytic quantities of Cu(I). *Tetrahedron Lett.* **1998**, *39*, 4627-4630.
- (7) Lipshutz, B. H.; Chrisman, W.; Noson, K.; Hydrosilylation of aldehydes and ketones catalyzed by $[\text{Ph}_3\text{P}(\text{CuH})]_6$. *J. Organomet. Chem.* **2001**, *624*, 367-371.
- (8) Ren, Y.; Xu, X.; Sun, K.; Xu, J.; A new and effective method for providing optically active monosubstituted malononitriles: selective reduction of α,β -unsaturated dinitriles catalyzed by copper hydride complexes. *Tetrahedron: Asymmetry* **2005**, *16*, 4010-4014.
- (9) Yun, J.; Kim, D.; Yun, H.; A new alternative to Stryker's reagent in hydrosilylation: synthesis, structure, and reactivity of a well-defined carbene-copper(II) acetate complex. *Chem. Commun.* **2005**, 5181-5183.
- (10) Baker, B. A.; Bošković, Ž. V.; Lipshutz, B. H.; (BDP)CuH: A "Hot" Stryker's Reagent for Use in Achiral Conjugate Reductions. *Org. Lett.* **2008**, *10*, 289-292.
- (11) Zhang, L.; Cheng, J.; Hou, Z.; Highly efficient catalytic hydrosilylation of carbon dioxide by an N-heterocyclic carbene copper catalyst. *Chem. Commun.* **2013**, *49*, 4782-4784.
- (12) Zhang, L.; Hou, Z.; N-Heterocyclic carbene (NHC)-copper-catalysed transformations of carbon dioxide. *Chem. Sci.* **2013**, *4*, 3395-3403.
- (13) Nguyen, T.-A. D.; Goldsmith, B. R.; Zaman, H. T.; Wu, G.; Peters, B.; Hayton, T. W.; Synthesis and Characterization of a Cu_4 Hydride Cluster Supported by Neutral Donor Ligands. *Chem. - Eur. J.* **2015**, *21*, 5341-5344.
- (14) Zall, C. M.; Linehan, J. C.; Appel, A. M.; Triphosphine-Ligated Copper Hydrides for CO_2 Hydrogenation: Structure, Reactivity, and Thermodynamic Studies. *J. Am. Chem. Soc.* **2016**, *138*, 9968-9977.
- (15) Halpern, J.; Czapski, G.; Jortner, J.; Stein, G.; Mechanism of the Oxidation and Reduction of Metal Ions by Hydrogen Atoms. *Nature* **1960**, *186*, 629-630.
- (16) Wile, B. M.; Stradiotto, M.; Silver-catalyzed hydrosilylation of aldehydes. *Chem. Commun.* **2006**, 4104-4106.
- (17) Jia, Z.; Liu, M.; Li, X.; Chan, A. S. C.; Li, C.-J.; Highly Efficient Reduction of Aldehydes with Silanes in Water Catalyzed by Silver. *Synlett* **2013**, *24*, 2049-2056.
- (18) Jia, Z.; Zhou, F.; Liu, M.; Li, X.; Chan, A. S. C.; Li, C.-J.; Silver-Catalyzed Hydrogenation of Aldehydes in Water. *Angew. Chem., Int. Ed.* **2013**, *52*, 11871-11874.
- (19) Karunananda, M. K.; Mankad, N. P.; E-Selective Semi-Hydrogenation of Alkynes by Heterobimetallic Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 14598-14601.
- (20) Zavras, A.; Khairallah, G. N.; Krstić, M.; Girod, M.; Daly, S.; Antoine, R.; Maitre, P.; Mulder, R. J.; Alexander, S.-A.; Bonačić-Koutecký, V.; Dugourd, P.; O'Hair, R. A. J.; Ligand-induced substrate steering and reshaping of $[\text{Ag}_2(\text{H})]^+$ scaffold for selective CO_2 extrusion from formic acid. *Nat. Comm.* **2016**, *7*, 11746.
- (21) Tate, B. K.; Wyss, C. M.; Bacsá, J.; Kluge, K.; Gelbaum, L.; Sadighi, J. P.; A dinuclear silver hydride and an umpolung reaction of CO_2 . *Chem. Sci.* **2013**, *4*, 3068-3074.
- (22) Bratsch, S. G.; Standard Electrode Potentials and Temperature Coefficients in Water at 298.15 K. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1-21.
- (23) Brown, S. S. D.; Salter, I. D.; Sik, V.; Colquhoun, I. J.; McFarlane, W.; Bates, P. A.; Hursthouse, M. B.; Murray, M.; The heteronuclear cluster chemistry of the group 1B metals. Part 9. Stereochemical non-rigidity of the metal skeletons of cluster compounds in solution. ^{109}Ag -{H} INEPT nuclear magnetic resonance studies on $[\text{Ag}_2\text{Ru}_4(\mu_3\text{-H})_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)\text{PPh}_2\}(\text{CO})_{12}]$ ($n = 1, 2, \text{ or } 4$) and X-ray crystal structure of $[\text{Ag}_2\text{Ru}_4(\mu_3\text{-H})_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\text{CO})_{12}]$. *J. Chem. Soc., Dalton Trans.* **1988**, 2177-2185.
- (24) Albinati, A.; Chaloupka, S.; Demartin, F.; Koetzle, T. F.; Ruegger, H.; Venanzi, L. M.; Wolfer, M. K.; Complexes with platinum-hydrogen-silver bonds. *J. Am. Chem. Soc.* **1993**, *115*, 169-175.
- (25) Brunner, H.; Mijolovic, D.; Wrackmeyer, B.; Nuber, B.; NMR analysis of trinuclear silver(I) complexes with μ_2 -H bridged group VI metallocene hydrides as ligands and X-ray structure analysis of $\{[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Mo}(\mu_2\text{-H})_2]\text{Ag}\}\text{PF}_6$. *J. Organomet. Chem.* **1999**, *579*, 298-303.
- (26) Gorol, M.; Mosch-Zanetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Unprecedented stabilisation of the Ag_2^{2+} -ion by two hydrido-iridium(III) complexes. *Chem. Commun.* **2003**, 46-47.
- (27) Bruce, M. I.; Low, P. J.; Nicholson, B. K.; Skelton, B. W.; Zaitseva, N. N.; Zhao, X.-I.; Preparation and molecular structures of the decanuclear diynyl-ruthenium-silver and -copper complexes $[\text{M}_6\{\mu_3\text{-CCCC}[\text{Ru}(\text{dppe})\text{Cp}^*]\}_4(\mu\text{-dppm})_2](\text{BF}_4)_2$ ($\text{M} = \text{Ag}, \text{Cu}$). *J. Organomet. Chem.* **2010**, *695*, 1569-1575.
- (28) Liu, C. W.; Chang, H.-W.; Sarkar, B.; Saillard, J.-Y.; Kahlal, S.; Wu, Y.-Y.; Stable Silver(I) Hydride Complexes Supported by Diselenophosphate Ligands. *Inorg. Chem.* **2010**, *49*, 468-475.
- (29) Liao, P.-K.; Liu, K.-G.; Fang, C.-S.; Liu, C. W.; Fackler, J. P.; Wu, Y.-Y.; A Copper(I) Homocubane Collapses to a Tetracapped Tetrahedron Upon Hydride Insertion. *Inorg. Chem.* **2011**, *50*, 8410-8417.
- (30) Liu, C. W.; Liao, P.-K.; Fang, C.-S.; Saillard, J.-Y.; Kahlal, S.; Wang, J.-C.; An eleven-vertex deltahedron with hexacapped trigonal bipyramidal geometry. *Chem. Commun.* **2011**, *47*, 5831-5833.
- (31) Liu, C. W.; Lin, Y.-R.; Fang, C.-S.; Latouche, C.; Kahlal, S.; Saillard, J.-Y.; $[\text{Ag}_7(\text{H})\{\text{E}_2\text{P}(\text{OR})_2\}_6]$ ($\text{E} = \text{Se}, \text{S}$): Precursors for the Fabrication of Silver Nanoparticles. *Inorg. Chem.* **2013**, *52*, 2070-2077.
- (32) Zavras, A.; Khairallah, G. N.; Connell, T. U.; White, J. M.; Edwards, A. J.; Donnelly, P. S.; O'Hair, R. A. J.; Synthesis, Structure and Gas-Phase Reactivity of a Silver Hydride Complex $[\text{Ag}_3\{(\text{PPh}_2)_2\text{CH}_2\}_3(\mu_3\text{-H})(\mu_3\text{-Cl})]\text{BF}_4$. *Angew. Chem., Int. Ed.* **2013**, *52*, 8391-8394.
- (33) Donghi, D.; Maggioni, D.; D'Alfonso, G.; Beringhelli, T.; Rhenium-silver bicyclic "spiro" hydrido-carbonyl clusters: NMR investigation of their formation and reversible fragmentation. *J. Organomet. Chem.* **2014**, *751*, 462-470.
- (34) Girod, M.; Krstić, M.; Antoine, R.; MacAleese, L.; Lemoine, J.; Zavras, A.; Khairallah, G. N.; Bonačić-Koutecký, V.; Dugourd, P.; O'Hair, R. A. J.; Formation and Characterisation of the Silver Hydride Nanocluster Cation $[\text{Ag}_3\text{H}_2((\text{Ph}_2\text{P})_2\text{CH}_2)]^+$ and Its Release of Hydrogen. *Chem. - Eur. J.* **2014**, *20*, 16626-16633.
- (35) Zavras, A.; Khairallah, G. N.; Connell, T. U.; White, J. M.; Edwards, A. J.; Mulder, R. J.; Donnelly, P. S.; O'Hair, R. A. J.; Synthesis, Structural Characterization, and Gas-Phase Unimolecular Reactivity of the Silver Hydride Nanocluster $[\text{Ag}_5((\text{PPh}_2)_2\text{CH}_2)_3(\mu_3\text{-H})](\text{BF}_4)_2$. *Inorg. Chem.* **2014**, *53*, 7429-7437.
- (36) Daly, S.; Krstic, M.; Giuliani, A.; Antoine, R.; Nahon, L.; Zavras, A.; Khairallah, G. N.; Bonačić-Koutecký, V.; Dugourd, P.; O'Hair, R. A. J.; Gas-phase VUV photoionisation and photofragmentation of the silver deuteride nanocluster $[\text{Ag}_{10}\text{D}_8\text{L}_6]^{2+}$ ($\text{L} = \text{bis}(\text{diphenylphosphino})\text{methane}$). A joint experimental and theoretical study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 25772-25777.

- (37) Tate, B. K.; Nguyen, J. T.; Bacsá, J.; Sadighi, J. P.; Heterolysis of Dihydrogen by Silver Alkoxides and Fluorides. *Chem. – Eur. J.* **2015**, *21*, 10160–10169.
- (38) Zavras, A.; Ariafard, A.; Khairallah, G. N.; White, J. M.; Mulder, R. J.; Canty, A. J.; O'Hair, R. A. J.; Synthesis, structure and gas-phase reactivity of the mixed silver hydride borohydride nanocluster $[Ag_3(\mu_3-H)(\mu_3-BH_4)LPh_3]BF_4$ (LPH = bis(diphenylphosphino)methane). *Nanoscale* **2015**, *7*, 18129–18137.
- (39) Bootharaju, M. S.; Dey, R.; Gevers, L. E.; Hedhili, M. N.; Basset, J.-M.; Bakr, O. M.; A New Class of Atomically Precise, Hydride-Rich Silver Nanoclusters Co-Protected by Phosphines. *J. Am. Chem. Soc.* **2016**, *138*, 13770–13773.
- (40) Cordero, B.; Gomez, V.; Platero-Prats, A. E.; Reves, M.; Echeverria, J.; Cremades, E.; Barragan, F.; Alvarez, S.; Covalent radii revisited. *Dalton Trans.* **2008**, 2832–2838.
- (41) Bondi, A.; van der Waals Volumes and Radii. *J. Phys. Chem.* **1964**, *68*, 441–451.
- (42) Wei, Q.-H.; Zhang, L.-Y.; Shi, L.-X.; Chen, Z.-N.; Octahedral hexanuclear silver(I) and copper(I) ferrocenylacetylde complexes. *Inorg. Chem. Commun.* **2004**, *7*, 286–288.
- (43) Yue, C.; Yan, C.; Feng, R.; Wu, M.; Chen, L.; Jiang, F.; Hong, M.; A Polynuclear d^{10} – d^{10} Metal Complex with Unusual Near-Infrared Luminescence and High Thermal Stability. *Inorg. Chem.* **2009**, *48*, 2873–2879.
- (44) Sun, D.; Luo, G.-G.; Zhang, N.; Huang, R.-B.; Zheng, L.-S.; Simultaneous self-assembly of a cage-like silver(I) complex encapsulating an Ag_6 neutral cluster core and carbon dioxide fixation. *Chem. Commun.* **2011**, *47*, 1461–1463.
- (45) Kikukawa, Y.; Kuroda, Y.; Suzuki, K.; Hibino, M.; Yamaguchi, K.; Mizuno, N.; A discrete octahedrally shaped $[Ag_6]^{4+}$ cluster encapsulated within silicotungstate ligands. *Chem. Commun.* **2013**, *49*, 376–378.
- (46) Yang, H.; Lei, J.; Wu, B.; Wang, Y.; Zhou, M.; Xia, A.; Zheng, L.; Zheng, N.; Crystal structure of a luminescent thiolated Ag nanocluster with an octahedral Ag_6^{4+} core. *Chem. Commun.* **2013**, *49*, 300–302.
- (47) Lane, A. C.; Vollmer, M. V.; Laber, C. H.; Melgarejo, D. Y.; Chiarella, G. M.; Fackler, J. P.; Yang, X.; Baker, G. A.; Walensky, J. R.; Multinuclear Copper(I) and Silver(I) Amidinate Complexes: Synthesis, Luminescence, and CS_2 Insertion Reactivity. *Inorg. Chem.* **2014**, *53*, 11357–11366.
- (48) Rajput, G.; Yadav, M. K.; Drew, M. G. B.; Singh, N.; Impact of Ligand Framework on the Crystal Structures and Luminescent Properties of Cu(I) and Ag(I) Clusters and a Coordination Polymer Derived from Thiolate/Iodide/dppm Ligands. *Inorg. Chem.* **2015**, *54*, 2572–2579.
- (49) Ho, D. M.; Bau, R.; Preparation and structural characterization of $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^{2-}$: conformational flexibility in the M_2P_4 core structure of bis(diphenylphosphino)methane complexes. *Inorg. Chem.* **1983**, *22*, 4073–4079.
- (50) Neo, S. P.; Zhou, Z.-Y.; Mak, T. C. W.; Hor, T. S. A.; Solid-State Tetramer vs. Solution-State Dimer. Reinvestigation of $[Ag_2(OAc)_2(dppm)]_2$ and Its dppm Addition Product $[Ag_2(OAc)(dppm)]_2$ (dppm = $Ph_2PCH_2PPh_2$). *Inorg. Chem.* **1995**, *34*, 520–523.
- (51) Deivaraj, T. C.; Vittal, J. J.; Synthesis, structures and ^{31}P NMR studies of bis(diphenylphosphino)methane adducts of copper and silver thiocarboxylates. *J. Chem. Soc., Dalton Trans.* **2001**, 322–328.
- (52) Djordjevic, B.; Schuster, O.; Schmidbaur, H.; A Cyclic Hexamer of Silver Trifluoroacetate Supported by Four Triphenylphosphine Sulfide Template Molecules. *Inorg. Chem.* **2005**, *44*, 673–676.
- (53) Partyka, D. V.; Deligonul, N.; Phosphine- and Carbene-Ligated Silver Acetate: Easily-Accessed Synthons for Reactions with Silylated Nucleophiles. *Inorg. Chem.* **2009**, *48*, 9463–9475.
- (54) Kaeser, A.; Delavaux-Nicot, B.; Duhayon, C.; Coppel, Y.; Nierengarten, J.-F.; Heteroleptic Silver(I) Complexes Prepared from Phenanthroline and Bis-phosphine Ligands. *Inorg. Chem.* **2013**, *52*, 14343–14354.
- (55) Brevard, C.; Van Stein, G. C.; Van Koten, G.; Silver-109 and rhodium-103 NMR spectroscopy with proton polarization transfer. *J. Am. Chem. Soc.* **1981**, *103*, 6746–6748.
- (56) Lemmen, T. H.; Folting, K.; Huffman, J. C.; Caulton, K. G.; Copper polyhydrides. *J. Am. Chem. Soc.* **1985**, *107*, 7774–7775.
- (57) Mao, Z.; Huang, J.-S.; Che, C.-M.; Zhu, N.; Leung, S. K.-Y.; Zhou, Z.-Y.; Unexpected Reactivities of Cu_2 (diphosphine) $_2$ Complexes in Alcohol: Isolation, X-ray Crystal Structure, and Photoluminescent Properties of a Remarkably Stable $[Cu_2(diphosphine)_2(\mu_3-H)]^{2+}$ Hydride Complex. *J. Am. Chem. Soc.* **2005**, *127*, 4562–4563.
- (58) Li, J.; White, J. M.; Mulder, R. J.; Reid, G. E.; Donnelly, P. S.; O'Hair, R. A. J.; Synthesis, Structural Characterization, and Gas-Phase Unimolecular Reactivity of Bis(diphenylphosphino)amino Copper Hydride Nanoclusters $[Cu_3(X)(\mu_3-H)((PPh_2)_2NH)_3](BF_4)$, Where $X = \mu_2-Cl$ and μ_3-BH_4 . *Inorg. Chem.* **2016**, *55*, 9858–9868.
- (59) Bezman, S. A.; Churchill, M. R.; Osborn, J. A.; Wormald, J.; Preparation and crystallographic characterization of a hexameric triphenylphosphinecopper hydride cluster. *J. Am. Chem. Soc.* **1971**, *93*, 2063–2065.
- (60) Goeden, G. V.; Huffman, J. C.; Caulton, K. G.; A copper- $(\mu_2$ -hydrogen) bond can be stronger than an intramolecular phosphorus \rightarrow copper bond. Synthesis and structure of di- μ -hydridobis[$\eta^{2-1,1}$ -tris(diphenylphosphinomethyl)ethane]dicopper. *Inorg. Chem.* **1986**, *25*, 2484–2485.
- (61) Albert, C. F.; Healy, P. C.; Kildea, J. D.; Raston, C. L.; Skelton, B. W.; White, A. H.; Lewis-base adducts of Group 11 metal(I) compounds. 49. Structural characterization of hexameric and pentameric (triphenylphosphine)copper(I) hydrides. *Inorg. Chem.* **1989**, *28*, 1300–1306.
- (62) Eberhart, M. S.; Norton, J. R.; Zuzek, A.; Sattler, W.; Rucolo, S.; Electron Transfer from Hexameric Copper Hydrides. *J. Am. Chem. Soc.* **2013**, *135*, 17262–17265.
- (63) Nguyen, T.-A. D.; Jones, Z. R.; Goldsmith, B. R.; Buratto, W. R.; Wu, G.; Scott, S. L.; Hayton, T. W.; A Cu_{25} Nanocluster with Partial Cu(0) Character. *J. Am. Chem. Soc.* **2015**, *137*, 13319–13324.
- (64) Nakamae, K.; Kure, B.; Nakajima, T.; Ura, Y.; Tanase, T.; Facile Insertion of Carbon Dioxide into $Cu_2(\mu-H)$ Dinuclear Units Supported by Tetrakisphosphine Ligands. *Chem. – Asian J.* **2014**, *9*, 3106–3110.
- (65) Chen, J.-X.; Daeuble, J. F.; Brestensky, D. M.; Stryker, J. M.; Highly Chemoselective Catalytic Hydrogenation of Unsaturated Ketones and Aldehydes to Unsaturated Alcohols Using Phosphine-Stabilized Copper(I) Hydride Complexes. *Tetrahedron* **2000**, *56*, 2153–2166.
- (66) Lipshutz, B. H.; Caires, C. C.; Kuipers, P.; Chrisman, W.; Tweaking Copper Hydride (CuH) for Synthetic Gain. A Practical, One-Pot Conversion of Dialkyl Ketones to Reduced Trialkylsilyl Ether Derivatives. *Org. Lett.* **2003**, *5*, 3085–3088.
- (67) Ojima, I.; Donovan, R. J.; Clos, N.; Rhodium and cobalt carbonyl clusters $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $Co_3Rh(CO)_{12}$ as effective catalysts for hydrosilylation of isoprene, cyclohexanone, and cyclohexenone. *Organometallics* **1991**, *10*, 2606–2610.
- (68) Jordan, A. J.; Lalic, G.; Sadighi, J. P.; Coinage Metal Hydrides: Synthesis, Characterization, and Reactivity. *Chem. Rev.* **2016**, *116*, 8318–8372.

(69) Lipshutz, B. H.; Noson, K.; Chrisman, W.; Lower, A.; Asymmetric Hydrosilylation of Aryl Ketones Catalyzed by Copper Hydride Complexed by Nonracemic Biphenyl Bisphosphine Ligands. *J. Am. Chem. Soc.* **2003**, *125*, 8779-8789.
(70) Issenhuth, J.-T.; Notter, F.-P.; Dagonne, S.; Dedieu, A.; Bellemin-Laponnaz, S.; Mechanistic Studies on the Copper-

Catalyzed Hydrosilylation of Ketones. *Eur. J. Inorg. Chem.* **2010**, *2010*, 529-541.

(71) Shirobokov, O. G.; Kuzmina, L. G.; Nikonov, G. I.; Nonhydride Mechanism of Metal-Catalyzed Hydrosilylation. *J. Am. Chem. Soc.* **2011**, *133*, 6487-6489.

The first structurally characterized silver polyhydride complex, $[\text{Ag}_6\text{H}_4(\text{dppm})_4(\text{OAc})_2]$ (dppm = 1,1-bis(diphenylphosphino)methane), catalyzes the 1,4- and 1,2-hydrosilylations of (α,β -unsaturated) ketones.

