Inorganic Chemistry

Synthesis, Characterization, and Reactivity of the Group 11 Hydrido Clusters $[Ag_6H_4(dppm)_4(OAc)_2]$ and $[Cu_3H(dppm)_3(OAc)_2]$

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Supporting Information

ABSTRACT: The group 11 hydride clusters $[Ag_6H_4(dppm)_4(OAc)_2]$ (1) and $[Cu_3H-(dppm)_3(OAc)_2]$ (2) (dppm = 1,1-bis(diphenylphosphino)methane) were synthesized in moderate yields from the reaction of M(OAc) (M = Ag, Cu) with Ph₂SiH₂, 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.



opper hydrides have proven to be potent catalysts for the \checkmark hydrogenation and hydrosilylation of α,β -unsaturated ketones, carbon-carbon multiple bonds, and CO₂.¹⁻¹⁴ 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 Me₂PhSiH and PEt₃.¹⁶ Similarly, the semihydrogenation 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, $[{(SIDipp)Ag}_2(\mu-H)]X$ (SIDipp = 1,3-bis(2,6diiso-propylphenyl)imidazolin-2-ylidene; $X^- = OTf^-$ or BF_4^-), was shown to stoichiometrically reduce CO₂ to formate.²¹ This limited understanding of Ag-H reactivity is due, in part, to the difficulty in generating stable silver hydride complexes, which is a consequence of this metal's relatively high M(I)/M(0) halfcell potential (0.80 V).²² Because of this property, Ag^I-H complexes more easily decompose to yield Ag⁰ and H₂ versus their Cu counterparts. Consequently, Ag^I–H complexes have proven to be relatively rare.^{21,23–38} Moreover, the examples isolated thus far are either homometallic monohydrides, for example, $[Ag_7H{Se_2P(O^iPr)_2}_6]$,³¹ heterometallic polyhydrides, for example, $[Ag(\mu-H)_4 \{Re_2(\mu-H)(CO)_8\}_2]^{-,33}$ or polyhydrides observed via electrospray ionization (ESI) mass spectrometry (e.g., $[Ag_{10}H_8(dppm)_6]^{2+})^{34}$ (dppm = 1,1-bis-(diphenylphosphino)methane) or NMR spectroscopy (e.g., $[Ag_{18}H_{16}(Ph_3P)_{10}]^{2+})$.³⁹ Herein, we report the synthesis and characterization of the first structurally characterized homometallic silver polyhydrido cluster, $[Ag_6H_4(dppm)_4(OAc)_2]$. In addition, we examined its ability to catalyze the 1,4- and 1,2hydrosilylations of (α_{β} -unsaturated) ketones.

Addition of 1 equiv of dppm and 0.5 equiv of diphenylsilane (Ph_2SiH_2) to a slurry of Ag(OAc) in benzene results in a rapid color change from white to dark red-brown. Workup of the solution after stirring at room temperature for 15 h results in the isolation of the silver polyhydrido cluster,

 $[Ag_6H_4(dppm)_4(OAc)_2]$ (1), as a colorless, crystalline solid in 47% yield (Scheme 1).





Complex 1 crystallizes in the triclinic space group $P\overline{1}$ as the benzene solvate $1\cdot 2.5C_6H_6$ (Figure 1). In the solid state, the Ag atoms of the $[Ag_6]^{6+}$ 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 $[Ag_4]^{4+}$ 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 $[Ag_6]^{6+}$ core, via κ^1 and κ^2 binding modes.

The average Ag–Ag bond length within the $[Ag_4]^{4+}$ belt is 3.08 Å, which is longer than the average Ag_{cap} – Ag_{belt} bond

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

length of 2.88 Å. The Ag_{cap}–Ag_{belt} interaction is within the covalent radius for Ag,⁴⁰ and the Ag_{belt}–Ag_{belt} interaction lies well within twice the van der Waals radius for Ag,⁴¹ suggestive of considerable argentophilic interactions within the $[Ag_6]^{6+}$ core. These values are also similar to those reported for other Ag^I–H clusters^{21,28–32,35,37,38} and Ag₆ 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 ³¹P{¹H} NMR spectrum features a single ³¹P 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 $[Ag_6]^{6+}$ core. The ¹H NMR spectrum of complex 1 in C₆D₆ shows a single acetate resonance at 2.92 ppm, while the diastereotopic methylene protons of the dppm ligand appear at 3.02 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, $1-d_4$, features a resonance at 5.76 ppm in 1,2- $C_6H_4Cl_2/C_6D_6$ (99:1, v/v), confirming our assignment of this feature as a hydride resonance. The ¹⁰⁹Ag NMR spectrum of 1 in 1,2-C₆D₄Cl₂, recorded using an INEPT pulse sequence,⁵⁵ features a single resonance at 1095 ppm. This chemical shift is in good agreement with the ¹⁰⁹Ag signals observed for the Ag^I-H dichalcogenatophosphate clusters reported by Liu and coworkers.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 ESI mass spectrum of 1 features a signal at 2246.942 m/zcorresponding to $[M-OAc]^+$ (calculated m/z 2246.954). For comparison, the ESI mass spectrum of $1-d_4$ gave rise to a signal at 2250.978 m/z (calculated m/z 2250.979), a shift of 4 m/zversus 1, as anticipated for a tetrahydrido complex. Interestingly, the ESI mass spectrum of 1 contains another major feature at 1537.098 m/z, which is assignable to the $[Ag_3(dppm)_3H(OAc)]^+$ fragmentation product, consistent with O'Hair's observation that the Ag₃(μ_3 -H) core is especially stable.^{32,34–36,38} Its facile formation may also indicate a

plausible mechanism for cluster assembly, as dimerization of $[Ag_3(dppm)_3H(OAc)]^+$, 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 tetrahydrofuran (THF), insoluble in MeCN, Et_2O , and nonpolar solvents, and reasonably 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, among 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^0 , as well as other products.

To better understand the formation of 1 we recorded ¹H and ³¹P 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 byproducts, 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 "AgI-H" monomers and reduces the probability of decomposition.

For further comparison, we endeavored to synthesize the Cu congener of **1**. Previous attempts to make a Cu–H dppm cluster ended with decomposition because of the high basicity of the $[Cu(O^tBu)]_4$ starting material.⁵⁶ However, the combined use of Cu(OAc) and Ph₂SiH₂ to generate the Cu^I–H moiety obviates the use of an alkoxide precursor. Thus, addition of 1 equiv of dppm and 0.5 equiv of Ph₂SiH₂ to a slurry of Cu(OAc) in benzene results in the gradual color change from pale green to yellow. Workup of the solution after 20 h affords the copper hydride cluster $[Cu_3H(dppm)_3(OAc)_2]$ (2), as colorless crystals in 83% yield (Scheme 1). Complex 2 is closely related to the known Cu^I–H clusters, $[Cu_3H(dcpm)_3]^{2+}$ (dcpm = 1,1-bis(dicyclohexylphosphino)methane) and $[Cu_3(BH_4)H-(dppa)_3]^+$ (dppa = bis(diphenylphosphino)amine).^{57,58}

Complex 2 crystallizes as the benzene solvate $2 \cdot 2C_6H_6$ (Figure 2) in the monoclinic space group $P2_1/n$. In the solid state, complex 2 contains a triangular $[Cu_3]^{3+}$ 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 $[Cu_3H(dcpm)_3]^{2+,57}$ The average Cu–P distance in 2 (2.28 Å) is consistent with Cu–P bonds in other phosphine-supported Cu¹–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 Cu₃ core, via κ^1 and κ^2 binding modes.

While complex 2 appears to have C_s symmetry in the solid state, there is only one resonance observed in its ³¹P{¹H} NMR spectrum, at -6.66 ppm, in 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



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

effective symmetry in solution than observed in the solid-state. A septet centered at 2.10 ppm in the ¹H NMR spectrum (${}^{2}J_{PH}$ = 14.4 Hz) is assignable to the lone hydride moiety. This signal collapses to a singlet upon ³¹P decoupling. To further confirm the presence of a single hydride ligand, we synthesized the isotopically labeled complex, $2 - d_1$. Gratifyingly, complex $2 - d_1$ features a singlet at 1.74 ppm in the ²H NMR spectrum in C_6H_6/C_6D_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 $[Cu_3H(dppm)_3Cl]^+$ ion (calculated m/z 1379.125). For comparison, complex 2- d_1 features a signal at 1380.123 m/z in its ESI mass spectrum, corresponding to the $[Cu_3D(dppm)_3Cl]^+$ ion (calculated m/z1380.131), 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 mass spectrometry 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 nonpolar solvents. It is stable in MeCN for at least 3 d, 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 1,2hydrosilylations of $(\alpha,\beta$ -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 2cyclohexen-1-one (3). Thus, addition of Ph₂SiH₂ (1.5 equiv) to 3, in the presence of 1 (0.05 H⁻ equiv), in C₆D₆ 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 precatalyst for the 1,4-hydrosilylation of 3, achieving 96% total conversion after 24 h using a similar catalyst loading. However, this precatalyst features somewhat lower selectivity for the 1,4-





^{*a*}For experimental details see Supporting Information. ^{*b*}Total conversion to 4 determined by ¹H NMR integration with long pulse delay ($d_1 = 60$ s) against an internal standard of hexamethyldisiloxane.

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 $[CuH(PPh_3)]_6$ to catalyze 1,4-hydrosilylation of 3 under similar conditions. Of the three complexes tested, this reagent proved the most effective, reaching >99% total conversion in only 15 min.

We also screened the ability of 1, 2, and $[CuH(PPh_3)]_6$ 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⁻ equiv), in C₆D₆ resulted in 42% conversion to the silyl ether 6 after 24 h (Table 2). Complex 2 is an even better precatalyst

Table 2. 1,2-Hydrosilyation of Cyclohexanone Catalyzed by 1, 2, and $[CuH(PPh_3)]_6$



^{*a*}For experimental details see Supporting Information. ^{*b*}Total conversion to **6** determined by ¹H NMR integration with long pulse delay ($d_1 = 60$ s) against an internal standard of hexamethyldisiloxane.

for the 1,2-hydrosilylation of 5, achieving >99% conversion after just 2 h, using a similar catalyst loading. Surprisingly, $[CuH(PPh_3)]_6$ was the least effective precatalyst for this reaction, achieving only 26% conversion after 24 h. It is not readily apparent why complex 2 is a more effective precatalyst relative to 1 or $[CuH(PPh_3)]_6$; 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

In summary, we have isolated and characterized the diphosphine ligated clusters $[Ag_6H_4(dppm)_4(OAc)_2]$ (1) and $[Cu_3H(dppm)_3(OAc)_2]$ (2). Complex 1 is the first homometallic silver polyhydrido cluster to be structurally charac-

terized. 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 $[Cu_3H]^{2+}$ and $[Ag_6H_4]^{2+}$ 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 precatalysts for the hydrosilylation of $(\alpha,\beta$ -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

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site at http://pubs.acs.org/doi/abs/10.1021/acs.inorgchem.6b02385.

X-ray data for compounds $1.2.5C_6H_6$ and $2.2C_6H_6$ (CIF) Experimental details, spectral data, and additional figures and tables (PDF)

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The authors declare no competing financial interest.

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