# Selective Semihydrogenation of Polarized Alkynes by a Gold Hydride Nanocluster

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phosphine ligand. The chelating effects of the bidentate ligand result in a more symmetric  $Au_{11}$  core with two labile Cl<sup>-</sup> ligands that can exchange with  $BH_4^-$ , leading to a novel undecagold hydride cluster. The new hydride cluster is discovered to readily undergo hydroauration reaction with alkynes containing electronwithdrawing groups, forming key gold-alkenyl semihydrogenation intermediates, which can be efficiently and selectively converted to Z-alkenes under acidic conditions. All key reaction intermediates are isolated and characterized, providing atomic-level insights into



the active sites and mechanisms of semihydrogenation reactions catalyzed by gold-based nanomaterials. The hydridic hydrogen in the undecagold cluster is found to be the key to prevent over hydrogenation of alkenes to alkanes. The current study provides fundamental insights into hydrogenation chemistry enabled by gold-based nanomaterials and may lead to the development of efficient catalysts for selective semihydrogenation or functionalization of alkynes.

# INTRODUCTION

The carbon–carbon double bond in olefins plays a critical role in many chemical transformations and is important in materials science, pharmaceutical and food industries, and agrochemistry.<sup>1</sup> The semihydrogenation of alkynes is a common route to create the carbon-carbon double bond.<sup>2</sup> Many transition metal-based catalysts have been developed for the semihydrogenation reaction.<sup>3-5</sup> In particular, gold-based nanomaterials are promising catalysts for the semihydrogenation of alkynes to alkenes due to their high selectivity under relatively mild conditions.<sup>6-9</sup> In addition to gaseous dihydrogen, bench-stable hydrogen sources have also been used in the semihydrogenation of alkynes as a safe and convenient method to prepare functional alkenes on the laboratory scale at ambient pressure.<sup>10</sup> One of the major challenges in catalysis is to identify and control the active sites of the catalysts.<sup>11-14</sup> Atomically precise gold nanoclusters with well-defined structures have emerged as a new class of model catalysts that allow the identification of the active sites and help the elucidation of catalytic mechanisms.<sup>15-22</sup> However, precise control of the catalytic active sites for specific reactions, which underlies enzyme catalysis, is challenging to achieve synthetically. Especially for hydrogenation reactions catalyzed by gold-based nanomaterials, the identification of the active sites is often not possible because of the difficulties in capturing gold hydride intermediates.<sup>6–9</sup> Gold hydrides that feature a hydridic hydrogen (H<sup>-</sup>) have been proposed as

reactive intermediates in hydrogenation reactions involving gold-based nanomaterials; however, prior clusters have featured metallic hydrogens  $(H^{\bullet})$ ,<sup>23–29</sup> while the identification of hydridic hydrogen has been limited to mononuclear gold complexes.<sup>30–32</sup>

We have been interested in the synthesis of gold nanoclusters with uncoordinated gold (*uc*Au) atoms as in situ catalytic active sites.<sup>33</sup> Our ultimate goal is to synthesize the Au<sub>20</sub> pyramidal cluster, which is known to be a highly stable gaseous cluster with all its atoms exposed on the cluster surface as potential *uc*Au sites.<sup>34</sup> Preliminary synthetic efforts led to the discovery of a Au<sub>22</sub>(dppo)<sub>6</sub> cluster (dppo = 1,8-bis(diphenyl-phosphino)octane), which contains eight well-defined *uc*Au atoms<sup>35</sup> and has been shown to exhibit catalytic activity for CO-to-CO<sub>2</sub> oxidation without ligand removal under ambient conditions.<sup>36</sup> Further studies led to the isolation of two gold hydride clusters,  $[Au_{22}H_4(dppo)_6]^{2+}$  and  $[Au_{22}H_3(dppe)_7]^{3+}$  (dppee = bis(2-diphenylphosphino)-ethylether), in which the H atoms are shown to bridge the

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*uc*Au sites between two Au<sub>11</sub> units.<sup>26,27</sup> Recently, a heteroleptic  $[Au_{22}H_3]^{3+}$  gold trihydride nanocluster has been synthesized and found to be an efficient and stable electrocatalyst for selective CO<sub>2</sub>-to-CO conversion.<sup>28</sup> The selective electrocatalytic reduction of CO<sub>2</sub> to CO using an NHC-stabilized hydrido gold nanocluster,  $[Au_{24}(NHC)_{14}Cl_2H_3]^{3+}$ , has also been reported very recently.<sup>29</sup>

Here, we report the discovery of a new undecagold hydride cluster, which has a hydridic hydrogen and can engage in selective semihydrogenation reactions with alkynes containing electron-withdrawing groups. We have synthesized and crystalized a new  $[Au_{11}Cl_2(dppee)_4]^+$  nanocluster using the bidentate dppee ligand. The structure of this cluster is different from the many well-known dichloride undecagold clusters reported previously.<sup>37-42</sup> The Au<sub>11</sub> core in the new cluster is more symmetric with a local  $C_2$  symmetry and the two Cl<sup>-</sup> ligands are found to be more labile, allowing it to be readily converted to a gold hydride  $[Au_{11}HCl(dppee)_4]^+$  cluster. This new gold hydride cluster is discovered to undergo hydroauration reactions with polarized alkynes under ambient conditions, giving rise to the all-important gold-alkenyl intermediates. Under acidic conditions, the gold-alkenyl intermediates selectively release Z-alkene products with high efficiency, completing the semihydrogenation reaction cycle. The hydridic hydrogen in the  $[Au_{11}HCl(dppee)_4]^+$  cluster is found to be the key in preventing over hydrogenation of alkenes to alkanes. The identification, isolation, and characterization of all the reaction intermediates provide fundamental insights into the semihydrogenation of alkynes and critical knowledge for the design and control of the catalytic active sites for semihydrogenation reactions by gold-based nanocatalysts.

# RESULTS AND DISCUSSION

Discovery of a New Undecagold Cluster with Labile **Cl<sup>-</sup> Ligands.** The new  $[Au_{11}Cl_2(dppee)_4]^+$  cluster was first observed as a by-product during our synthesis of the  $[Au_{22}H_3(dppee)_7]^{3+}$  trihydride cluster.<sup>27</sup> Detailed synthetic procedures can be found in the Supporting Information (Figures S1-S6). X-ray crystallography showed that the Au<sub>11</sub> metal core of  $[Au_{11}Cl_2(dppee)_4]^+$  is more symmetric with a local C<sub>2</sub> symmetry (Figure 1a, Figure S7, and Tables S1-S3) and different from previously reported dichloride undecagold clusters.<sup>37–42</sup> Compared to the well-known triphenylphosphine (PPh<sub>3</sub>)-supported cluster,  $[Au_{11}Cl_2(PPh_3)_8]^+$  (Figure S8),<sup>39</sup> the aromatic protons and phosphorus atoms in the new dppeesupported cluster showed different chemical shifts in the <sup>1</sup>H and <sup>31</sup>P NMR spectra (Figures S9-S14), even though both clusters have an eight-electron closed-shell electronic structure and give similar UV-Vis absorption spectra (Figure S15). Due to the chelating effect of the dppee ligands, the Au<sub>11</sub> metal core in  $[Au_{11}Cl_2(dppee)_4]^+$  is arranged in an eclipsed pattern with local  $C_2$  symmetry (Figure 1b). This is different from the Au<sub>11</sub> metal core in  $[Au_{11}Cl_2(PPh_3)_8]^+$ ,<sup>39</sup> where one square face was rotated by around ~45°, giving rise to a low-symmetry staggered structure. The ligand effects on the Au<sub>11</sub> core in  $[Au_{11}Cl_2(dppee)_4]^+$  and  $[Au_{11}Cl_2(PPh_3)_8]^+$  can be further seen by their different Au–Au bond lengths (Figure S16 and Table S4) and Au-P bond lengths. Most notably, the Au-P bonds are shorter, and the Au-Cl bonds are longer in the new  $[Au_{11}Cl_2(dppee)_4]^+$  cluster than their counterparts in  $[Au_{11}Cl_2(PPh_3)_8]^+$ . Collision-induced dissociation (CID) experiments indicate that the dppee ligands bind more strongly



**Figure 1.** Discovery of a new undecagold cluster with labile Cl<sup>-</sup> ligands. (a) Single-crystal X-ray structure for the new  $[Au_{11}Cl_2(dppee)_4]^+$  cluster. Colors: Au = yellow; H = white; P = orange; O = red; C = black; Cl = green. (b) The new undecagold structure (eclipsed) can be obtained by rotating one square face around 45° of the known  $[Au_{11}Cl_2(PPh_3)_8]^+$  cluster,<sup>39</sup> which has a staggered structure. (c) Comparison of the ESI-MS spectra of  $[Au_{11}Cl_2(dppee)_4]^+$  with that of  $[Au_{11}Cl_2(PPh_3)_8]^+$ ,<sup>43</sup> showing the labile nature of the Cl<sup>-</sup> ligands in the new undecagold cluster.

than the PPh<sub>3</sub> ligand:  $[Au_{11}Cl_2(dppee)_4]^+$  only loses a single Au(dppee)Cl unit without any ligand loss under any collision energies (Figure S17), while  $[Au_{11}Cl_2(PPh_3)_8]^+$  was shown to readily lose a single PPh<sub>3</sub> ligand previously.<sup>42,43</sup> The stronger binding between the dppee ligand and the gold core results in a more stable  $[Au_{11}Cl_2(dppee)_4]^+$  cluster. In the solid state, it can be stored indefinitely under ambient conditions, while CH<sub>2</sub>Cl<sub>2</sub> solutions show no signs of decomposition after 2 months (Figures S18 and S19).

Although the dppee ligands bind tightly to the Au<sub>11</sub> metal core, the two Cl<sup>-</sup> ligands in  $[Au_{11}Cl_2(dppee)_4]^+$  are more loosely bonded (Figure 1b). The ESI-MS spectrum of  $[Au_{11}Cl_2(dppee)_4]^+$  showed three distinct peaks, corresponding to the parent  $[Au_{11}Cl_2(dppee)_4]^+$ , as well as  $[Au_{11}Cl_2(dppee)_4]^{2+}$  and  $[Au_{11}(dppee)_4]^{3+}$  due to Cl<sup>-</sup> loss (Figure 1c and Figures S19 and S20). In contrast, only one single parent  $[Au_{11}Cl_2(PPh_3)_8]^+$  peak was observed in its ESI-MS spectrum



**Figure 2.** The synthesis and characterization of a novel  $[Au_{11}HCl(dppe)_4]^+$  hydride cluster. (a) Synthetic route from  $[Au_{11}Cl_2(dppe)_4]^+$  to  $[Au_{11}(BH_4)Cl(dppe)_4]^+$  and  $[Au_{11}HCl(dppe)_4]^+$ . (b, c) ESI-MS spectra of  $[Au_{11}(BH_4)Cl(dppe)_4]^+$  and  $[Au_{11}HCl(dppe)_4]^+$ . The insets show the experimental and simulated isotopic distributions. The peaks labeled with \* and ^ in (b) are  $[Au_{11}(dppe)_4]^{3+}$  and  $[Au_{11}(BH_4)_2(dppe)_4]^+$ , respectively. (d) Experimental isotopic distributions for  $[Au_{11}HCl(dppe)_4]^+$  synthesized from NaBH<sub>4</sub> and  $[Au_{11}DCl(dppe)_4]^+$  synthesized from NaBD<sub>4</sub>, showing that the hydridic hydrogen in  $[Au_{11}HCl(dppe)_4]^+$  only comes from NaBH<sub>4</sub>. (e) Enlarged room temperature <sup>1</sup>H-NMR signal due to the hydridic hydrogen in  $[Au_{11}HCl(dppe)_4]^+$ . (f) In situ <sup>11</sup>B-NMR spectrum for the reaction sample. (g, h) In situ <sup>1</sup>H- and <sup>31</sup>P-NMR spectra for the reaction sample. Note that  $[Au_{11}HCl(dppe)_4]^+$  and  $[Au_{11}(BH_4)Cl(dppe)_4]^+$  appear concomitantly in the same reaction sample after synthesis and (c) is an enlarged spectrum of (b).

(Figure 1c).<sup>43</sup> The labile nature of the two Cl<sup>-</sup> ligands in  $[Au_{11}Cl_2(dppee)_4]^+$  are also reflected in the longer Au–Cl bonds compared to those in  $[Au_{11}Cl_2(PPh_3)_8]^+$  (Figure S16 and Table S4). Theoretical calculations further confirmed that the weaker binding of the Cl<sup>-</sup> ligands in  $[Au_{11}Cl_2(dppee)_4]^+$  is due to the eclipsed structure of the Au<sub>11</sub> core. To demonstrate that the eclipsed structure in  $[Au_{11}Cl_2(dppee)_4]^+$  is due to the chelating effects of the dppee ligands, we did a calculation by replacing the dppee ligands with eight PPh<sub>3</sub> ligands. We found that the resulting cluster with the eclipsed structure is higher in energy with longer Au–Cl bonds (Figure S21).

Isolation and Characterization of an Undecagold Cluster Containing a H<sup>-</sup> Ligand. The labile nature of the Au-Cl bonds in  $[Au_{11}Cl_2(dppee)_4]^+$  suggests that the Cl<sup>-</sup> ligands may be exchanged with other negatively charged ligands. Upon adding an ethanol solution of NaBH<sub>4</sub> into a  $CH_2Cl_2$  solution of  $[Au_{11}Cl_2(dppee)_4]Cl$  at room temperature, we observed that the  $Cl^-$  ligands readily exchanged with the  $BH_4^-$  ion, leading to the formation of  $[Au_{11}(BH_4)Cl-(dppee)_4]^+$  and  $[Au_{11}(BH_4)_2(dppee)_4]^+$  (Figure 2a,b and Figures S22–S25). At the same time, some  $[Au_{11}(BH_4)Cl-(dppee)_4]^+$  clusters spontaneously lose  $BH_3$  to form a new hydride cluster,  $[Au_{11}HCl(dppee)_4]^+$  (Figure 2a,c and Figure S26). When we did the same experiment using NaBD<sub>4</sub>, we obtained  $[Au_{11}DCl(dppee)_4]^+$ , showing that the hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  comes solely from  $BH_4^-$  (Figure 2d and Figure S27).

We found that both  $[Au_{11}(BH_4)Cl(dppee)_4]^+$  and  $[Au_{11}HCl(dppee)_4]^+$  in  $CH_2Cl_2$  solutions were relatively stable with a shelf-life of ~4 h (Figure S28), which allowed us to



**Figure 3.** Isolation and characterization of the semihydrogenation intermediates. (a) The synthetic route from the  $[Au_{11}HCl(dppe)_4]^+$  to  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$  clusters. (b) ESI-MS spectra of the  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$  cluster. The insets show the experimental and simulated isotopic distributions. The peaks labeled with \* and ^ are  $[Au_{11}(dppe)_4]^{3+}$  and  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$  and  $D-[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$  and  $D-[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$  and  $D-[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$  synthesized from  $[Au_{11}DCl(dppe)_4]^+$ . (d) Enlarged <sup>1</sup>H-NMR signal from the H atom in the alkenyl ligand. The quartet signal showed an adjacent coupling with the neighboring  $-CH_3$  group. (e) Experimental and simulated UV–Vis absorption spectra of  $[Au_{11}Cl_2(dppe)_4]^+$  and  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$ . (f) Experimental and simulated FTIR spectra of  $[Au_{11}Cl_2(dppe)_4]^+$  and  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$ . The shaded areas indicate the changes of spectra due to the replacement of the Cl<sup>-</sup> ligand in  $[Au_{11}Cl_2(dppe)_4]^+$  with the alkenyl ligand in  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]^+$ . (g, h) <sup>1</sup>H- and <sup>31</sup>P-NMR spectra of pure  $[Au_{11}Cl_2(dppe)_4]Cl$  and  $[Au_{11}(C=C^{CH3})Cl(dppe)_4]Cl$  samples.

characterize them using <sup>11</sup>B-, <sup>1</sup>H-, and <sup>31</sup>P-NMR experiments. The <sup>11</sup>B-NMR spectrum showed three peaks at -40.5, -32.8, and 18.1 ppm, which corresponded to the excess reducing agent (NaBH<sub>4</sub>), the salt-exchange product ([Au<sub>11</sub>(BH<sub>4</sub>)Cl-(dppee)<sub>4</sub>]<sup>+</sup>), and triethoxyborane (B(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>), respectively (Figure 2f). Three sets of new peaks were evident in the <sup>1</sup>H and <sup>31</sup>P NMR, which were assigned to the formation of monoand diborohydride products [Au<sub>11</sub>(BH<sub>4</sub>)Cl(dppee)<sub>4</sub>]<sup>+</sup> and [Au<sub>11</sub>(BH<sub>4</sub>)<sub>2</sub>(dppee)<sub>4</sub>]<sup>+</sup>, along with the gold hydride cluster,  $[Au_{11}HCl(dppee)_4]^+$  (Figure 2g,h and Figures S29 and S30). A weak signal for the Au–H hydride was observed at 13.3 ppm in the <sup>1</sup>H NMR (Figure 2e), which was more upfield (shielded) than the chemical shifts for the previously reported gold hydrides<sup>24,26–29</sup> and in agreement with the hydridic nature of H<sup>-</sup> in  $[Au_{11}HCl(dppee)_4]^+$ . The labile Cl<sup>-</sup> ligands are critical to the formation of the hydridic hydrogen in the  $[Au_{11}HCl(dppee)_4]^+$  cluster. As a comparison, we added an EtOH solution of NaBH<sub>4</sub> into a CH<sub>2</sub>Cl<sub>2</sub> solution of  $[Au_{11}Cl_2(PPh_3)_8]$ 

able 1. Selective Semihydrogenation of Polarized	ed Alkynes by Stepwise H	ydride and Proton Transfers
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Entry	Reactant	Obtained <sup>a</sup> cluster	Released <sup>b</sup> product	Conversion <sup>c</sup> (%)	Z-Selectivity <sup>c</sup> (%)
1	сн,оосс=ссн,	CH <sub>2</sub> OOC Au <sub>11</sub> H	CH300C CH3	> 99	91
2	CH₃OOCC <b>≕</b> CPh	CH <sub>3</sub> OOC Au <sub>11</sub> Ph	CH <sub>3</sub> OOC Ph	> 99	90
3	сн,оосс <del>=</del> ссоосн,	CH <sub>2</sub> OOC H	CH <sup>2</sup> OOC	> 99	99
4	с, <b>н</b> ₅оосс <b>≕</b> ссоос,н₅	C <sub>2</sub> H <sub>6</sub> OOC Au <sub>11</sub> H COOC <sub>5</sub> H <sub>5</sub>	C2H500C COOC2H5	> 99	97
5	cH₂CH₂C≡ccH₂CH₂	None	None	_	-
6	PhC == CPh	None	None	_	-

<sup>*a*</sup>Conditions: CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 1 h,  $[Au_{11}HCl(dppee)_4]^+$ . Detailed synthetic procedures are given in the Supporting Information. <sup>*b*</sup>The products were released by adding 1 equiv of diluted HCl (aq.) into the CH<sub>2</sub>Cl<sub>2</sub> solution of alkenyl-modified gold clusters at room temperature. <sup>*c*</sup>The conversion and selectivity for Z-alkenes were determined by <sup>1</sup>H-NMR. Conversion = [alkene]/[alkyne] + [alkene]. Z-selectivity = [Z]/[E] + [Z].

Cl by following the same procedure. We found that most of the  $[Au_{11}Cl_2(PPh_3)_8]^+$  sample decomposed to the  $[Au_{10}Cl-(PPh_3)_8]^+$  cluster (Figure S31) with only a very small amount of  $[Au_{11}H(PPh_3)_8]^{2+}$  being detected. It is also possible for  $[Au_{11}(BH_4)_2(dppee)_4]^+$  to lose two BH<sub>3</sub> molecules to form the dihydride cluster, but only a negligible amount of  $[Au_{11}H_2(dppee)_4]^+$  was detected as indicated by both the ESI-MS and NMR spectra (Figure 2b,c,g,h).

The hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  can be viewed as H<sup>-</sup>, which does not participate in the electronic structure of the Au<sub>11</sub> core and is very different from the metallic-like hydrogens in gold hydride clusters reported previously.<sup>23-28</sup> Prior studies have indicated that adding or removing the metallic hydrogen in Au clusters, such as  $[Au_9H(PPh_3)_8]^{2+}$ ,  $[Au_{22}H_4(dppo)_6]^{2+}$ , and  $[Au_{22}H_3(dppee)_7]^{3+}$ , results in significant changes of the UV–Vis absorption spectra<sup>24,26,27</sup> because the metallic hydrogens participate in the cluster bonding by contributing their 1s electrons to the gold metal cores. In the current case, the addition of NaBH<sub>4</sub> to the  $[Au_{11}Cl_2(dppee)_4]^+$  solution did not induce significant changes in the corresponding UV-Vis spectra (Figures S32 and S33) because the Cl<sup>-</sup> ligand was simply exchanged with a  $BH_4^-$  or  $H^-$  ligand, while the  $Au_{11}$ metal core still maintains an eight-electron closed-shell electronic structure from  $[Au_{11}Cl_2(dppee)_4]^+$  to  $[Au_{11}(BH_4) Cl(dppee)_4]^+$ ,  $[Au_{11}(BH_4)_2(dppee)_4]^+$ , or  $[Au_{11}HCl (dppee)_4]^+$  as per bonding analyses using the adaptive natural density partitioning (AdNDP) method (Figures S35-S38).<sup>44</sup> The AdNDP analyses showed that the Au<sub>11</sub> core has similar chemical bonding independent of the ligands. Each of the Au<sub>11</sub> clusters contains a delocalized s-type bond and three p-type bonds, corresponding to the eight-electron superatom bonding configuration. Since optical excitations above 350 nm for these clusters are mainly metal $\rightarrow$  metal transitions (Tables S5–S8),

the independence of the UV–Vis absorption spectra on the ligands are borne out from the simulated spectra (Figure S39). CID experiments suggested that  $[Au_{11}HCl(dppee)_4]^+$  exhibited similar dissociation behaviors as the dichloride parent with the loss of  $[Au(dppee)]^+$  as the major dissociation channel (Figure S40).

Selective Semihydrogenation of Polarized Alkynes. We further investigated the chemical properties of the hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  and found that it can underdo hydroauration reactions with alkynes containing electron-withdrawing groups but is inert to other types of unsaturated C-C bonds, such as alkenes or unpolarized alkynes. Upon adding methyl but-2-ynoate (CH<sub>3</sub>OOCC≡  $CCH_3$ ) to a  $CH_2Cl_2$  solution of  $[Au_{11}HCl(dppee)_4]Cl$  at room temperature, we observed the hydroauration reaction after 1 h of stirring, yielding the alkenyl-coordinated intermediate  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]^+$  (Figure 3a,b and Figures S41 and S42). Isotopic labeling showed that a deuterated  $[Au_{11}(C = C^{CH3})Cl(dppee)_4]^{\overline{+}}$  intermediate was produced using [Au<sub>11</sub>DCl(dppee)<sub>4</sub>]Cl as the starting material, indicating that the C=C double bond was formed by transferring the hydridic hydrogen from  $[Au_{11}HCl(dppee)_{4}]^{+}$  to the C  $\equiv$  C triple bond in methyl but-2-ynoate (Figure 3c and S43). There are two possibilities for the hydroauration reaction. One possibility is to transfer the hydrogen to the  $\alpha$ -position of the  $-CH_3$  group, and the other one is to transfer the hydrogen to the  $\alpha$ -position of the -COOCH<sub>3</sub> group (Figure S44). Since  $-COOCH_3$  is an electron-withdrawing group, it polarizes the C  $\equiv$  C triple bond and induce a negatively charged  $\alpha$ -carbon, which can substitute the hydride ligand. Thus, it is more favorable for the hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  to be transferred to the more positively charged  $\alpha$ -position of the  $-CH_3$  group. This expectation was borne out by the <sup>1</sup>H-NMR of  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]^+$ , where a quartet signal was



**Figure 4.** Computed free energy profile and reaction path for the semihydrogenation reactions. (a) Semihydrogenation reaction pathway demonstrated by the new  $[Au_{11}Cl_2(dppee)_4]^+$  cluster . One labile  $Cl^-$  ligand in the new undecagold cluster first exchanges with  $BH_4^-$  to form a  $[Au_{11}(BH_4)]^+$  complex. With the help of one EtOH molecule,  $[Au_{11}(BH_4)]^+$  loses one  $BH_3$  molecule and forms  $[Au_{11}H]^+$  containing one hydridic hydrogen via the transition state (TS1).  $[Au_{11}H]^+$  further undergoes hydride migration to enable the bonding of the incoming alkyne onto the gold surface. The hydride then transfers to the alkenyl ligand to form  $[Au_{11}(C=C^{CH3})]^+$  via TS2. HCl finally reacts with  $[Au_{11}(C=C^{CH3})]^+$  to recover  $[Au_{11}Cl]^+$  and release the Z-alkene product. A, B, and C are transient reaction intermediates. (b) Simplified reaction cycle. All intermediate clusters were experimentally identified, isolated, and characterized.

observed for the hydrogen connected to the C=C double bond, indicating its adjacent coupling with the  $-CH_3$  group instead of the  $-COOCH_3$  group (Figure 3d).

We also observed that  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]^+$  displays similar UV-Vis absorption features as  $[Au_{11}Cl_2(dppee)_4]^+$ , except that the main absorption peaks are slightly redshifted as reproduced by theoretical calculations (Figure 3e). We found that the redshift is due to the mixing of the alkenyl ligand orbitals with those of the metal core (Figure S45 and Table S9): the HOMO and HOMO-1 of  $[Au_{11}(C =$  $C^{CH3}$ )Cl(dppee)<sub>4</sub>]<sup>+</sup> consist of contributions from the C=C<sup>CH3</sup> alkenyl ligand, but much less Cl<sup>-</sup> ligand orbitals are involved in the frontier orbitals of  $[Au_{11}Cl_2(dppee)_4]^+$  (Figure S46). We also measured the Fourier-transform infrared (FTIR) spectra for  $[Au_{11}Cl_2(dppee)_4]^+$  and  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]^+$ (Figure 3f). The excellent agreement between the experimental and simulated FTIR spectra further confirmed the structures of both clusters. Compared with the FTIR spectrum of  $[Au_{11}Cl_2(dppee)_4]^+$ , several new absorption features were observed in  $[Au_{11}C=C^{CH3})Cl(dppee)_4]^+$ , due to the vibrational modes of the  $-C=C^{CH3}$  alkenyl ligand, according to our theoretical calculations (Tables S10 and S11). There is only one chemical environment for the aromatic protons and phosphorus atoms in  $[Au_{11}Cl_2(dppee)_4]^+$ , whereas the alkenyl ligand in [Au<sub>11</sub>(C=C<sup>CH3</sup>)Cl(dppee)<sub>4</sub>]<sup>+</sup> creates two types of chemical environments for both <sup>1</sup>H- and <sup>31</sup>P-NMR signals

(Figure 3g). In order to confirm the different chemical properties between the hydridic and metallic hydrogens in gold, we performed the same experiments for the  $[Au_9H-(PPh_3)_8]^{2+}$  cluster with a metallic hydrogen (Figures S47–S49).<sup>24</sup> No reactions were observed between  $[Au_9H(PPh_3)_8]^{2+}$  and methyl but-2-ynoate (CH<sub>3</sub>OOCC=CCH<sub>3</sub>), indicating that the metallic hydrogen in the gold hydride cluster does not react with the C=C triple bond.

Alkenyl complexes are common intermediates for all semihydrogenation reactions of alkynes by transition metal catalysts.<sup>2–5</sup> The alkenyl intermediates of Au(I) and Au(III) complexes are also well known<sup>45,46</sup> but have not been observed for nanogold catalysts. The  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]^+$  species represents the first gold cluster alkenyl intermediate ever observed. Addition of 1 equiv dilute HCl (aq.) into a  $CH_2Cl_2$  solution of  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]Cl$  at room temperature leads to rapid and quantitative protonation to liberate the alkene (91% *Z*; Table 1, entry 1, and Figure S50) and starting  $[Au_{11}Cl_2(dppee)_4]^+$  cluster and completes the semihydrogenation cycle.

The range of the hydroauration reactions by  $[Au_{11}HCl(dppee)_4]^+$  was examined for different polarized alkynes,  $CH_3OOCC \equiv CR$  (R = Ph,  $COOCH_3$ ,  $COOC_2H_5$ ), where the resulting alkenyl intermediates and alkene products were characterized (Figures S51–S56). Isotopic labeling experiments confirmed that the hydride was transferred from the

undecagold cluster to the C≡C triple bonds (Figures S57-S59). <sup>1</sup>H-NMR further verified that the hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  was always transferred to the  $\alpha$ -positions of the R groups (Figures S60-S62). Similar to  $[Au_{11}(C=$  $C^{CH3}$ )Cl(dppee)<sub>4</sub>]<sup>+</sup>, the experimental and calculated UV–Vis spectra of  $[Au_{11}(C=C^R)Cl(dppee)_4]^+$  (Figures S63–S65) were redshifted compared to the spectrum of  $[Au_{11}Cl_2(dppee)_4]^+$  (Table S12) due to the contributions from the  $-C = C^{R}$  alkenyl ligands to the corresponding HOMO orbitals (Figures S66-S68 and Tables S13-S15). The presence of the alkenyl fragment in  $[Au_{11}(C=C^R)Cl$ - $(dppee)_4$ <sup>+</sup> was confirmed by the distinct C=C stretch in the IR around 1600 cm<sup>-1</sup> (Figure S72), and the experimental FTIR spectra and the simulated spectra were in excellent agreement with one another (Figures S69–S71 and Tables S16–S18). Similar to  $[Au_{11}(CC^{CH3})Cl(dppee)_4]^+$ , the <sup>1</sup>H-NMR (Figures S73–S75) and <sup>31</sup>P-NMR (Figures S76–S78) for  $[Au_{11}(C=C^R)Cl(dppee)_4]^+$  exhibit two chemical environments, while the exact chemical shifts vary slightly depending on the -R groups of the alkenyl ligands (Figures \$79-\$80). Regardless of the -R group, the type of alkenyl ligands does not influence the overall structure of the Au<sub>11</sub> metal core. In accordance with our theoretical calculations and AdNDP analyses (Figures S81-S85), this is because all the alkenyl intermediates keep the same eight-electron closed-shell structures. Addition of 1 equiv of dilute HCl (aq.) into the  $CH_2Cl_2$  solutions of these gold alkenyl species,  $[Au_{11}(C=$  $C^{R}$ )Cl(dppee)<sub>4</sub>]<sup>+</sup>, again leads to rapid and quantitative protonation to form the Z-alkenes with >90% Z-selectivity (Table 1, entries 2-4, and Figures S86-S88).

We further confirmed that the hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  is key for the hydroauration reaction of the alkynes and for preventing overhydrogenation of the alkene intermediates to alkanes. When we added the alkene products from entries 1-4 as starting reactants into the solution of  $[Au_{11}HCl(dppee)_4]^+$  at room temperature, no reactions were observed, indicating that the hydridic hydrogen cannot be transferred to the C=C double bonds. We also found that the hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  can only undergo hydroauration reactions with polarized alkynes, i.e., one of the R groups connected to the C $\equiv$ C triple bond has to be an electron-withdrawing group. When we performed the same reactions for alkynes without electron-withdrawing groups, no reactions were observed under ambient conditions (Table 1, entries 5 and 6). The isolation and characterization of all the semihydrogenation intermediates,  $[Au_{11}(C=C^R)Cl(dppee)_4]^+$ (R = CH<sub>3</sub>, Ph, COOCH<sub>3</sub>, COOC<sub>2</sub>H<sub>5</sub>), are unprecedented for gold-based nanocatalysts. No gold nanoclusters coordinated by alkenyl ligands are known heretofore, albeit such species have been hypothesized as semihydrogenation intermediates catalyzed by gold-based nanomaterials.<sup>6</sup> Using hydridic hydrogen in the new undecagold nanocluster to obtain alkenylcoordinated gold nanoclusters provides new possibilities to explore their important roles in the catalytic semihydrogenation or functionalization of alkynes.

Complete Pathways of the Semihydrogenation Reaction Cycle. The current study provides a detailed atomic-level understanding for the catalytic active sites and mechanisms for the semihydrogenation of alkynes by gold nanocatalysts. The UV–Vis spectra of  $Au_{11}$  clusters at different steps in the semihydrogenation cycle feature the same fourpeak pattern, with only minor blue- or redshifts in peak position (~10–20 nm) depending on the identity of the surface ligand (e.g., Cl<sup>-</sup>, H<sup>-</sup>, and -MeO(O)CC=C(H)C-(O)OR<sup>–</sup>). This further supports the substitution reactions that only occur on the surface of the Au<sub>11</sub> cluster and reflects the high stability of the Au<sub>11</sub> clusters under the reaction conditions (Figure S89). To gain further insight into the reaction paths and transition states, we performed theoretical calculations for the energy profile from the initial  $[Au_{11}Cl_2(dppee)_4]^+$ nanocluster, [Au<sub>11</sub>Cl]<sup>+</sup>, to the final alkene product as illustrated in Figure 4. First, due to the labile nature of the  $Cl^{-}$  ligands in  $[Au_{11}Cl_2(dppee)_4]^+$ ,  $[Au_{11}Cl]^+$ , one  $Cl^{-}$  ligand was exchanged with a BH<sub>4</sub><sup>-</sup> ion. The conversion of the  $[Au_{11}(BH_4)Cl(dppee)_4]^+$  intermediate,  $[Au_{11}BH_4]^+$ , to the  $[Au_{11}HCl(dppee)_4]^+$  hydride cluster,  $[Au_{11}H]^+$ , goes through a transition state (TS1) with the assistance of one EtOH solvent molecule. We found that the removal of the BH3 molecule from the transient reaction intermediate B to form [Au<sub>11</sub>HCl- $(dppee)_4^+$ ,  $[Au_{11}H]^+$ , is endothermic (by 9.5 kcal/mol). The endothermicity explains why there was only a small amount of  $[Au_{11}(BH_4)Cl(dppee)_4]^+$  converted  $[Au_{11}HCl(dppee)_4]^+$ (10.2%), whereas very little  $[Au_{11}H_2(dppee)_4]^+$  was observed in our experiment under ambient conditions.

The hydridic hydrogen in  $[Au_{11}HCl(dppee)_4]^+$  is found to be highly reactive. When the incoming alkyne molecule is adsorbed onto the Au<sub>11</sub> surface, the hydridic hydrogen is transferred to the neighboring gold atom concomitant with phosphorus exchange and chloride dissociation (transient reaction intermediate C in Figure 4a). This process happens very fast with a very low energetic increase of about 2.0 kcal/ mol (Table S19). Subsequently, the hydridic hydrogen is transferred to the C $\equiv$ C triple bond via a transition state (TS2), forming the highly stable alkenyl-coordinated  $[Au_{11}(C=C^{CH3})Cl(dppee)_4]^+$ ,  $[Au_{11}(C=C^{CH3})]^+$ . Finally,  $[Au_{11}(C=C^{CH3})]^+$  reacts with HCl to release the alkene product with simultaneous regeneration of the starting  $[Au_{11}Cl_2(dppee)_4]^+$  nanocluster. The calculation further reveals a strong preference for hydride addition from one side of the C $\equiv$ C triple bond as illustrated in TS2 (Figure 4a), which leads to the high Z-selectivity observed experimentally. The entire transformation pathway can be simplified in a reaction cycle, as shown in Figure 4b, where all the intermediate clusters were isolated, identified, and characterized experimentally.

#### 

We discovered a new undecagold nanocluster,  $[Au_{11}Cl_2(dppee)_4]^+$ , which possesses a more symmetric  $Au_{11}$ core with stronger Au-dppee interactions. The two Cl<sup>-</sup> ligands were found to be labile and can be exchanged with BH<sub>4</sub>-, resulting in the formation of a  $[Au_{11}HCl(dppee)_4]^+$  hydride cluster with a H<sup>-</sup> ligand. The hydridic hydrogen in the undecagold hydride was highly activated and can undergo hydroauration reactions with alkynes containing electronwithdrawing groups, forming stable gold-alkenyl intermediates. Under acidic conditions, the gold-alkenyl intermediates readily release Z-alkene products with a high conversion rate and high Z-selectivity. The current study not only provides atomic-level insights into the active sites and the detailed mechanisms of a class of alkyne semihydrogenation reactions but may also lead to the development of novel nanogold catalysts for the efficient and selective semihydrogenation reactions of specific alkynes.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c05046.

Experimental methods; synthetic procedures; computational details; crystal structure (PDF)

#### Accession Codes

CCDC 2158148 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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