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# Diphosphine-Protected Au<sub>22</sub> Nanoclusters on Oxide Supports Are Active for Gas-Phase Catalysis without Ligand Removal

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**(5)** Supporting Information

**ABSTRACT:** Investigation of atomically precise Au nanoclusters provides a route to understand the roles of coordination, size, and ligand effects on Au catalysis. Herein, we explored the catalytic behavior of a newly synthesized  $Au_{22}(L^8)_6$  nanocluster (L = 1,8-bis(diphenylphosphino) octane) with in situ uncoordinated Au sites supported on TiO<sub>2</sub>, CeO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. Stability of the supported Au<sub>22</sub> nanoclusters was probed structurally by in situ extended X-ray absorption fine structure (EXAFS) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and their ability to adsorb and oxidize CO was investigated by IR absorption spectroscopy and a temperature-programmed flow reaction. Low-temperature CO oxidation activity was observed for the supported pristine  $Au_{22}(L^8)_6$  nanoclusters without ligand removal. Density functional theory (DFT) calculations confirmed that the eight uncoordinated Au sites in the intact  $Au_{22}(L^8)_6$  nanoclusters can chemisorb both



CO and  $O_2$ . Use of isotopically labeled  $O_2$  demonstrated that the reaction pathway occurs mainly through a redox mechanism, consistent with the observed support-dependent activity trend of  $CeO_2 > TiO_2 > Al_2O_3$ . We conclude that the uncoordinated Au sites in the intact  $Au_{22}(L^8)_6$  nanoclusters are capable of adsorbing CO, activating  $O_2$ , and catalyzing CO oxidation reaction. This work is the first clear demonstration of a ligand-protected intact Au nanocluster that is active for gas-phase catalysis without the need of ligand removal.

**KEYWORDS:** Gold nanoclusters, ligands, uncoordinated sites, CO oxidation, oxide support

• old nanoclusters have attracted intensive research interest J because they can be considered an ideal model system for understanding the intriguing catalytic properties of gold nanoparticles with molecular- and atomic-level details.<sup>1-3</sup> This is attributed to the unique electronic and geometric structure, atomic precision, and uniform molecular size of the ligand-protected gold nanoclusters.<sup>1,4-7</sup> They are often designated as  $Au_n R_m$ , where *n* and *m* denote the numbers of gold atoms and R ligands (mostly thiolate, SR), respectively. Gold nanoclusters have shown great promise in various reaction systems including oxidation, hydrogenation, carboncarbon coupling, electrocatalysis, and photocatalysis. These reactions were mostly carried out in the liquid phase under mild conditions and, thus, can take advantage of the uniqueness of the intact gold nanoclusters. Gas-phase catalysis was much-lessexplored with Au nanoclusters, which need to be dispersed on a support. The role of the ligands on the catalytic performance of Au nanoclusters in gas-phase reactions is widely debated. Although most studies<sup>8-14</sup> showed a negative role of the ligands because of their blockage of the active Au sites,

some<sup>15–17</sup> suggested the presence of ligands does not prevent the Au nanoclusters from catalyzing reactions. A recent study<sup>18</sup> even showed a promotional effect of ligands on the gas-phase catalysis of Au nanoclusters, although the underlying mechanism was not elaborated.

As most studies indicated, removal of the ligands on the Au nanoclusters provides "exposed" or so-called coordinatively unsaturated (*cus*) Au sites and, thus, improved catalytic performance in gas-phase reactions. However, stripping off the ligands can inevitably result in significant changes to the electronic or geometric structure of the Au nanoclusters and introduce complex metal—support interactions,<sup>8,13,14</sup> which makes the model catalysts of Au nanoclusters less-straightforward for fundamental understanding. It is, thus, highly desirable to synthesize ligand-protected Au nanoclusters with the presence of *cus* Au sites, i.e., some of the surface Au atoms

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**Figure 1.** (A,B) HAADF-STEM images of as-synthesized  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> in different magnifications. CO oxidation light-off curves for different temperature treated  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> samples (C) and the as-synthesized  $Au_{22}(L^8)_6$  supported on TiO<sub>2</sub>, CeO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> (D). The light-off curve from as-synthesized  $Au_{25}(SR)_{18}$ -CeO<sub>2</sub> is also included in the two figures for comparison.

are free from coordination with the ligands. Stimulated by the discovery of the Au<sub>20</sub> pyramid in the gas phase,<sup>19</sup> some of us have endeavored to synthesize it in bulk form with uncoordinated surface sites for in situ catalysis.<sup>20,21</sup> Such an Au nanocluster was recently achieved<sup>22</sup> with diphosphine ligands, i.e., a Au<sub>22</sub> nanocluster coordinated by six bidentate diphosphine ligands: 1,8-bis(diphenylphosphino) octane (L<sup>8</sup> for short). The Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanocluster was found to consist of two Au<sub>11</sub> units linked together by four L<sup>8</sup> ligands, in which the eight gold atoms at the interface of the two Au<sub>11</sub> units are not coordinated by any ligands (see Figure S1 for the structural model). It is anticipated that these *cus* Au atoms may be utilized as in situ active sites for catalysis without the need of ligand removal.<sup>23</sup>

In the current study, we investigated gas-phase CO oxidation over supported  $Au_{22}(L^8)_6$  nanoclusters. The structure, morphology, and nature of surface sites of the supported  $Au_{22}(L^8)_6$  nanoclusters were characterized in detail via scanning transmission electron microscopy (STEM), extended X-ray absorption fine structure (EXAFS), and in situ infrared spectroscopy. We found that regardless of the supports used (TiO<sub>2</sub>, CeO<sub>2</sub>, or Al<sub>2</sub>O<sub>3</sub>), the intact  $Au_{22}(L^8)_6$  nanoclusters readily show low-temperature catalytic activity for CO oxidation, implying that the *cus* Au atoms are indeed active for catalysis. This was substantiated by the ability of the  $Au_{22}(L^8)_6$  nanoclusters to adsorb CO molecules, as demonstrated by IR spectroscopy and reinforced by density functional theory (DFT). The combined efforts show convincingly that the *cus* Au atoms on supported, intact  $Au_{22}(L^8)_6$  are active for low-temperature catalytic CO oxidation, thereby demonstrating that ligand removal is not necessary for some gold nanoclusters to be catalytically active and that creating in situ *cus* Au atoms should be a promising direction in nanocluster synthesis for catalytic applications.

Characterization of Free-Standing and Supported  $Au_{22}(L^8)_6$  Nanoclusters. The free-standing  $Au_{22}(L^8)_6$  nanoclusters were synthesized using the method reported previously<sup>22</sup> and characterized by both UV–vis–near-infrared (NIR) absorption (Figure S2A) and mass spectrometry (Figure S2B) analysis. The UV–vis–NIR spectrum exhibits a main absorption band at ~457 nm, similar to that reported for pure  $Au_{22}(L^8)_6$  nanoclusters in previous work.<sup>22</sup> The main m/zpeaks at 3616 and 2410 in the mass spectrum corresponds to  $[Au_{22}(L^8)_6 + 4H]$  species in +2 and +3 charge states, respectively. The isotopic patterns (insert in Figure S2B) for the peak at 3616 agree well with the expected isotopic distribution.<sup>22</sup> Both the UV–vis–NIR and electrospray ionization mass spectrometry (ESI-MS) results demonstrate the successful synthesis of atomically precise  $Au_{22}(L^8)_6$ nanoclusters with monodispersity. High-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) images of the as-synthesized  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample are shown in panels A and B of Figure 1 with different magnifications. The Au nanoclusters are well dispersed on the TiO<sub>2</sub> surface with an average size of ~1.4 nm. Individual Au atoms are discernible in the nanoclusters in the higher magnification image (Figure 1B). These images clearly show that the  $Au_{22}(L^8)_6$  nanoclusters are highly dispersed on TiO<sub>2</sub> surface without obvious agglomeration.

Observation of CO Oxidation over Supported  $Au_{22}(L^8)_6$ .  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> samples that were O<sub>2</sub>-pretreated at different temperatures were tested for CO oxidation in the temperature range 295-450 K, and the CO oxidation light-off curves are shown in Figure 1C. The as-synthesized Au<sub>22</sub>Ti-295 sample shows mild CO oxidation activity starting at room temperature and increased activity at elevated temperatures. This is drastically different from our previously studied assynthesized Au<sub>25</sub> nanoclusters (shown in the figure for comparison), where surface Au atoms are fully coordinated with thiolate ligands and showed no CO oxidation activity.<sup>8</sup> The clear contrast indicates that the cus Au atoms in the  $Au_{22}(L^8)_6$  nanoclusters are readily active for CO oxidation at low temperature. With the O2-treatment temperature of the Au<sub>22</sub>Ti-295 sample, CO oxidation activity increases accordingly, a similar trend being observed for the Au<sub>25</sub> nanoclusters. This is attributable to the gradual removal of the surface ligands and simultaneous liberation of more *cus* Au sites for catalysis,<sup>8</sup> as supported by the following EXAFS and IR studies.

It is notable that the turnover frequency (TOF) of the *cus* Au atoms in the as-synthesized Au<sub>22</sub>Ti-295 sample is calculated to be ~0.02 s<sup>-1</sup> for CO oxidation at 303 K, comparable to the value for a typical Au–TiO<sub>2</sub> nanocatalyst (0.023 s<sup>-1</sup>).<sup>24</sup> The number of *cus* Au sites used for the TOF calculation was obtained in the following way: the maximum possible number of surface Au sites was approximated as being 91% of the total gold atoms because 20 out of 22 Au atoms in the Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanocluster are exposed on the outer surface. From this maximum possible number of sites, the number of accessible sites for the as-synthesized Au<sub>22</sub>Ti-295 sample was then calculated based on the CO band area observed during the IR measurements described below.

To verify whether the observation made on  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> is general, we also loaded  $Au_{22}(L^8)_6$  onto  $CeO_2$  and  $Al_2O_3$ supports and compared the as-synthesized samples for CO oxidation. The CO oxidation light-off curves for the three samples are compared in Figure 1D along with the assynthesized  $Au_{25}(SR)_{18}$ -CeO<sub>2</sub><sup>8</sup> sample. As a note, the CO oxidation activity is similar for these samples pretreated at room temperature with either 5% O2-He or pure He. The Au22Ce-295 sample shows much higher low-temperature CO oxidation activity than Au<sub>22</sub>Ti-295. Although the Au<sub>22</sub>Al-295 sample is much-less-active for CO oxidation than Au22Ti-295 and Au<sub>22</sub>Ce-295, it indeed shows some activity when the reaction temperature rises, especially in comparison to the assynthesized Au<sub>25</sub>(SR)<sub>18</sub>-CeO<sub>2</sub> sample, which is essentially not active at all in the tested temperature range. The result clearly supports that the cus Au atoms in the as-synthesized  $Au_{22}(L^8)_6$  nanoclusters are readily active for low-temperature CO oxidation. Furthermore, the activity is greatly impacted by the oxide supports because the reducible oxides (CeO<sub>2</sub> and  $TiO_2$ ) supports lead to higher activity than the nonreducible

 $Al_2O_3$ . This is similar to the general observation made on supported Au nanoparticles, where the nature of the oxide support has been shown to be the dominant factor affecting the catalysis by Au nanoparticles.<sup>25–27</sup> The underlying reason for the support effect is further discussed below (the Reaction Mechanisms section). For the rest of the sections, we will be focusing on the  $Au_{22}(L^8)_6/TiO_2$  system to better understand its catalytic behaviors in low-temperature CO oxidation.

State of the L<sup>8</sup> Ligands in the Supported  $Au_{22}(L^8)_6$ Clusters. One pressing question about the as-synthesized  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> is whether the Au nanoclusters are intact, i.e., whether the diphosphine ligands are partially removed upon dispersion on a TiO<sub>2</sub> surface. In situ extended X-ray absorption fine structure (EXAFS) was utilized to monitor the Au-P bond in the different temperature-treated samples, and the spectra are shown in Figure 2. Spectra from an unsupported  $Au_{22}(L^8)_6$ 



**Figure 2.** EXAFS spectra of various Au samples and  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample pretreated at different temperatures in O<sub>2</sub>. Spectra from Au foil and Mintek Au-TiO<sub>2</sub> catalyst are also shown as references.

nanocluster sample, the Mintek Au-TiO<sub>2</sub> standard, and gold foil are also shown for comparison. The Au-P single scattering peak has an apparent, nonphase-shift corrected position at 1.91 Å for the unsupported Au<sub>22</sub> nanoclusters. Fitting the spectrum for the unsupported Au<sub>22</sub> nanoclusters using the ARTEMIS program produces an actual Au-P distance of 2.28 Å. The Au-P coordination number (CN) was determined to be 0.5, which is in excellent agreement with actual value of 0.55. Although there appears to be a small shift in the Au-P peak to a longer distance when the  $Au_{22}(L^8)_6$  is supported on TiO<sub>2</sub>, possibly due to the interaction of the nanoclusters with the TiO<sub>2</sub> support, the fit to the data indicated that the Au-P distance is unchanged. The CN is also unchanged. This suggests that the Au nanoclusters dispersed on the TiO<sub>2</sub> surface are similarly coordinated with the diphosphine ligands as in the unsupported case. The structure of the Au<sub>22</sub> core in the as-synthesized  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> also largely resembles that of the unsupported nanoclusters as evident from the similar features of the Au-Au peaks in 2-3 Å range. The fit for the Au-Au peaks in the unsupported nanoclusters indicates an average Au-Au distance of 2.71 Å. The average distance for the nanoclusters supported on TiO<sub>2</sub> is 2.74 Å. The average Au–Au distance in these Au<sub>22</sub> nanoclusters is smaller than the Au-Au distance in either the nanoparticles supported on TiO<sub>2</sub> in the Mintek standard or in the Au foil, which were determined by EXAFS to be 2.84 and 2.87 Å, respectively. Note that the peak near 2.2 Å for the Au



Figure 3. (A) IR spectra of CO adsorption at room temperature on  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> pretreated in O<sub>2</sub> at different temperatures. (B) IR spectra from CO desorption at room temperature in flowing O<sub>2</sub> on as-synthesized  $Au_{22}(L^8)_6$ -TiO<sub>2</sub>.

foil and the Mintek Au–TiO<sub>2</sub> in Figure 2 is the result of the Fourier transform of the Au–Au single scattering and not an indication of an additional nearest neighbor. The average Au–Au coordination number was determined to be 3, which is smaller than the actual average CN of 6 for an intact Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanocluster. The smaller value based on the EXAFS is probably due to the actual variety of Au–Au distances, which have been approximated by a single distance in the fit. Therefore, it can be concluded that the Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanoclusters remain intact on the TiO<sub>2</sub> support and that the observed low-temperature CO oxidation activity on the as-synthesized Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub>–TiO<sub>2</sub> sample can be ascribed to the *cus* Au atoms available in the intact nanoclusters.

Upon higher-temperature O<sub>2</sub> treatment (423 and 523 K), the Au–P peak starts to decrease in the  $Au_{22}(L^8)_6$ –TiO<sub>2</sub> sample, and the Au-P CN in the fit decreases by ca. 30% between 295 and 523 K samples. This implies the breaking of the Au-P bonds and removal of the diphosphine ligands. After 523 K treatment, there is no appreciable change in the Au-Au coordination in the 2-3 Å region. It appears that the structure and size of the Au<sub>22</sub> nanoclusters is well-maintained after the thermal treatment. This is further visualized from the brightfield HAADF-STEM images (Figure S3) of the  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample heated at different temperatures in static O<sub>2</sub> atmosphere, at 300 Torr in a Protochips in situ gas cell. A series of images of the same area recorded at lower magnification are also shown in Figure S4. Any change in the Au nanoclusters can be easily tracked by imaging the same sample area from the in situ STEM. Heating to 373 and 473 K does not result in any change to the Au nanoclusters. A slight change is seen when the sample is heated to 523 K as two Au nanoclusters in the lowerleft corner appear to coalesce. Further changes to these Au nanoclusters are evident when the heating temperature is raised to 623 K and higher, where some of the nanoclusters coalesced, while others may have become mobile and migrated out of the imaged area. Briefly, we conclude that the Au<sub>22</sub> nanoclusters are fairly stable on the TiO<sub>2</sub> surface at temperatures below 623 K.

The growth of Au nanoclusters at temperature above 573 K is likely associated with the removal of the diphosphine ligands. This is supported by the thermal gravity analysis (TGA) results of unsupported  $Au_{22}(L^8)_6$  nanoclusters (Figure S5A), where the major mass loss occurs at 587 K. The weight loss of ~40% is consistent with the complete removal of the  $L^8$  diphosphine ligands. IR spectra collected on the  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample

after O<sub>2</sub> treatment at different temperatures are shown in Figure S5B. C–H stretching modes are observed at 3067 (aromatic C–H), 2963, 2927, and 2858 cm<sup>-1</sup> (aliphatic C–H) due to the L<sup>8</sup> ligands. These features are fairly weak on the assynthesized sample, possibly due to the presence of water on the TiO<sub>2</sub> surface, similar to the observation on an assynthesized Au<sub>25</sub>(SR)<sub>18</sub>–CeO<sub>2</sub> sample.<sup>8</sup> These C–H stretching modes are fairly stable in intensity in the temperature range from 423–523 K but show a certain degree of decline after 573 K treatment and disappear after 673 K treatment. This trend is in good agreement with the TGA result, suggesting a treatment temperature above 573 K is needed to fully remove the L<sup>8</sup> ligands from the Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub>/TiO<sub>2</sub> sample.

Nature of the Au Sites on the Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> Cluster Surface. IR spectroscopy combined with CO adsorption was employed to probe the nature of the cus Au sites available in the as-synthesized and the different-temperature-treated  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> samples. As shown in Figure 3A, CO adsorption on the as-synthesized sample results in an IR band at 2107 cm<sup>-1</sup>, ascribed to CO adsorbed on metallic Au sites.<sup>28–30</sup> This observation clearly demonstrates that the *cus* Au sites in the intact nanoclusters can indeed adsorb CO molecules. Furthermore, the adsorbed CO species can be readily oxidized by O<sub>2</sub> at room temperature, as is evident from Figure 3B. The IR band at 2107 cm<sup>-1</sup> decreases in intensity and shifts slightly to higher wavenumbers when the sample was exposed to O<sub>2</sub> purging at room temperature. This band vanishes after O2 purging for 8 min, indicating complete oxidation of the adsorbed CO species. A similar observation was also made on the as-synthesized  $Au_{22}(L^8)_6$ -CeO<sub>2</sub> sample, as shown in Figure S6. Therefore, the cus Au sites in the intact  $Au_{22}(L^8)_6$  nanoclusters can not only adsorb CO molecules but also activate and oxidize them in the presence of O<sub>2</sub> at room temperature, supporting the observed activity of the assynthesized sample in CO oxidation, as shown in Figure 1. It is interesting to note that the nature of the cus Au sites (metallic) in  $Au_{22}(L^8)_6$  nanoclusters is quite different from that of the cus sites (cationic) on slightly dethiolated Au<sub>25</sub> clusters (CO band at 2150 cm<sup>-1</sup>).<sup>8</sup> This is directly related to the electron-donating diphosphine ligands on the Au<sub>22</sub> nanoclusters compared to the electron-withdrawing thiolate ligands on the Au<sub>25</sub>. A recent DFT study<sup>23</sup> shows that the eight *cus* Au atoms are barely affected by the charge transfer from the phosphine ligands to the Au nanoclusters and thus close to neutral charge,



Figure 4. QMS profiles of  $CO_2$  isotopomers evolved during  $CO + {}^{18}O_2$  over as-synthesized  $Au_{22}(L^8)_6$ -Ti $O_2$  (A) and  $Au_{22}(L^8)_6$ -Al<sub>2</sub>O<sub>3</sub> (B).

which is in line with our observed IR band position at 2107 cm<sup>-1</sup>. It is also noteworthy that these neutral Au atoms are not oxidized by exposure to  $O_2$  during room-temperature CO oxidation (Figure 3B).

With increasing treatment temperatures of the  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample, the IR band from adsorbed CO increases in intensity and simultaneously shifts from 2107 cm<sup>-1</sup> on the assynthesized sample to 2148 cm<sup>-1</sup> on the sample pretreated at 673 K (Figure 3A). The increase in CO band area is a result of the liberation of more cus Au sites upon ligands removal. The change in the band area is plotted in Figure S7A as a function of treatment temperature. If we use the CO band area to estimate the percentage of exposed Au sites (Figure S7B), we find that the sample exposes the most abundant cus Au sites after treatments at 573 K and above (~91% by assuming 20 of 22 atoms in the Au<sub>22</sub> nanocluster are exposed completely after the ligand removal; see the structure model in Figure S1). The exposure of *cus* Au sites in the as-synthesized  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample ( $\sim 6\%$ ) is much smaller than the theoretical value of 40% (8 out of 20 surface Au atoms as inferred from the structure of a  $Au_{22}(L^8)_6$  nanocluster in Figure S1), likely due to the partial blockage of the cus Au sites by the bulky ligands.

The blue shift of the CO band from 2107 to 2148 cm<sup>-1</sup> implies the generation of positively charged Au sites (Au<sup> $\delta$ +</sup>, 0 <  $\delta$  < 1).<sup>31</sup> This can be attributed to (1) oxidation of the Au sites upon high-temperature O<sub>2</sub> treatment<sup>32</sup> and (2) a strong interaction between the Au nanoclusters and the TiO<sub>2</sub> support after the ligand removal, resulting in charge transfer from the Au sites to the oxide support. Again, the shifting trend of the CO band is in the opposite direction to that observed on different temperature-treated thiolated Au<sub>25</sub> nanoclusters (CO band from 2150 to 2117 cm<sup>-1</sup> for low- to high-temperaturetreated samples)<sup>8</sup> due to the different electronic nature of the phosphine and thiolate ligands.

In addition to the main IR band from CO adsorbed on the  $Au^{\delta+}$  ( $0 < \delta < 1$ ) sites, two new bands appear at 2184 and 2160 cm<sup>-1</sup> after 423 K treatment of the  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample (Figure 3A) due to CO adsorbed on Ti<sup>4+</sup> sites created from the thermal dehydration<sup>32,33</sup> and cationic Au sites (most likely  $Au^+$ ),<sup>31,32</sup> respectively. The CO-Ti<sup>4+</sup> band increases in intensity with pretreatment temperatures due to the enhanced dehydration of TiO<sub>2</sub> surface at elevated temperatures. At elevated treatment temperatures, the band at 2160 cm<sup>-1</sup> is overshadowed by the main CO adsorption band at 2148 cm<sup>-1</sup> and is not readily discernible. However, its presence can be confirmed in the experiment shown in Figure S8. After CO

adsorption on the 573 K-treated sample, desorption was carried out at room temperature, first in inert He to remove the gasphase CO and the CO-Ti<sup>4+</sup> species (unstable at room temperature) and then in flowing  $O_2$ -He. The series spectra during O<sub>2</sub> purging in Figure S8 show that the CO band at 2136 cm<sup>-1</sup> gradually shifts to higher wavenumbers, with an accompanying decrease in intensity as a function of reaction time. Production of  $CO_2$  is observed at the beginning of the reaction and decreases as most of the CO adsorbed on the Au<sup> $\delta$ +</sup>  $(0 < \delta < 1)$  sites has reacted with oxygen. The IR band at 2162  $cm^{-1}$  due to CO-Au<sup>+</sup> persists in the presence of O<sub>2</sub> at room temperature, consistent with the high stability and lower reactivity of CO adsorbed on Au<sup>+</sup> sites.<sup>34</sup> The contrast clearly suggests that the partially positively charged Au sites (Au<sup> $\delta$ +</sup> (0 <  $\delta < 1$ ) are the major active sites for CO oxidation on  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> catalyst at low temperatures, while the fully charged Au<sup>+</sup> sites may contribute to CO oxidation only at elevated temperatures. This observation agrees well with those made on other supported Au nanocatalysts, where the less positively charged the Au species are, the more active they are for low-temperature CO oxidation.<sup>8,28,29,34-36</sup>

The observations made in the TGA and IR spectra in Figure S5 (ligand removal at 573 K and above) seem to contradict those made in the EXAFS spectra in Figure 2 (Au-P breakage between 423 and 523 K) and IR of CO probing in Figure 3A (continuous increase of Au sites availability up to 673 K). This can be reconciled by the situation in which the diphosphine ligands are gradually stripped off the Au sites at temperature above 423 K yet the ligand molecules still remain on the catalyst surface, possibly on the oxide support due to the high boiling point. This is supported by the TGA profile from a physical mixture of  $TiO_2$  and the L<sup>8</sup> ligand (Figure S9), where the maximum weight loss occurs at 595 K. Thus, it is likely the P ligands start to vaporize at temperature above 573 K, giving the TGA weight loss and the loss of C-H modes in the IR spectra (Figure S5) above 573 K in the  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample.

**Reaction Mechanisms.** To reveal the reaction mechanisms of the low-temperature CO oxidation over the  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> catalyst, we chose the as-synthesized sample because it already had the *cus* Au sites and the ligands were still attached. It is evident from the above IR work that CO is adsorbed on the *cus* Au sites and can be oxidized by co-feeding O<sub>2</sub>. To investigate how O<sub>2</sub> is activated for CO oxidation, we carried out an isotopic labeling experiment by co-feeding CO and <sup>18</sup>O<sub>2</sub> over the 295 K-treated  $Au_{22}(L^8)_6$ -TiO<sub>2</sub> sample. The evolved CO<sub>2</sub>



**Figure 5.** Front (upper panel) and side (lower panel) views of the  $Au_{22}(L^8)_6$  nanocluster (A), CO adsorption (B), and O<sub>2</sub> coadsorption (C). Ligands are omitted for clarity in panels b and c. *cus* Au, blue; other Au, yellow; C, gray; H, white; P, pink; O, red.

isotopomers were followed by online QMS as a function of reaction time, and the profiles are shown in Figure 4A. CO<sub>2</sub> production is dominated by  $C^{16}O^{16}O$  in the temperature range 300–450 K, while a small contribution from  $C^{16}O^{18}O$  is observed at temperatures above 360 K and  $C^{18}O^{18}O$  production is negligible. The observation of only  $C^{16}O^{16}O$  at the initial stage of CO oxidation light-off and its dominance over the tested temperature range indicate that CO is reacting with  $Ti^{16}O_2$  lattice oxygen to form  $CO_2$ , i.e., going through a Mars–van Krevelen (MvK) mechanism.

This MvK mechanism implies that the intact  $Au_{22}(L^8)_6$ nanoclusters have to be in close proximity to the TiO<sub>2</sub> surface so that the adsorbed CO on the nanoclusters can readily react with the lattice oxygen of the oxide support. The observation of the redox mechanism is supposedly a result of ligand relaxation. That is, the conformations and tilting angles of the R groups on the phosphorus atoms of the ligands on the Au<sub>22</sub> surface can adapt to the TiO<sub>2</sub> support to bring the cus gold atoms close to the TiO<sub>2</sub> surface to enable the MvK mechanism. This argument is partly supported by the STEM observation (Figure 1A) that many of the Au<sub>22</sub> nanoclusters are found to locate at the valleys and boundaries between TiO<sub>2</sub> particles, where the ligand-TiO<sub>2</sub> interaction is strong, and hence, the ligand relaxation is expected to be the greatest, allowing the cus Au atoms to be close to the TiO2 surface. For the Au22 nanoclusters on the terraces of TiO<sub>2</sub>, the curvature and the presence of steps and corners on TiO<sub>2</sub> particles may also offer close proximity of lattice oxygen atoms to the cus Au atoms in the Au<sub>22</sub> nanoclusters. The postulation here is only qualitative in nature, and the detailed mechanism warrants further investigation on how in general ligand-protected metal nanoclusters interact with an oxide surface.

The growth of  $C^{16}O^{18}O$  at higher temperature is thus due to the reaction of CO with lattice <sup>18</sup>O replenished by the gasphase <sup>18</sup>O<sub>2</sub>. Once oxygen vacancies on TiO<sub>2</sub> are created via CO reduction, gas-phase <sup>18</sup>O<sub>2</sub> can adsorb on the vacancy sites to form various species such as superoxide and peroxide.<sup>37</sup> It was shown that these adsorbed O<sub>2</sub> species can readily dissociate and refill the oxygen vacancies at elevated temperatures so that the CO oxidation cycle is complete.

The demonstrated MvK mechanism for low-temperature CO oxidation can well explain the large activity difference in CO oxidation over  $Au_{22}(L^8)_6$  brought about by varying the oxide support (Figure 1D). The higher reducibility of  $CeO_2$  than  $TiO_2$  (see Figure S10 for the CO–TPR profiles) is in line with the better activity of Au<sub>22</sub>Ce-295 than Au<sub>22</sub>Ti-295. MvK mechanism for CO oxidation was also observed on other gold nanoclusters supported on oxides.<sup>8,38</sup> Because Al<sub>2</sub>O<sub>3</sub> is nonreducible, the MvK mechanism involving lattice oxygen is not possible for CO oxidation over Au<sub>22</sub>Al-295. The weak activity for CO oxidation on Au<sub>22</sub>Al-295 can be attributed to a possible role of the Langmuir-Hinshelwood (L-H) mechanism on the cus Au sites in the  $Au_{22}(L^8)_6$  nanoclusters, where both CO and O2 are activated and reacted. This kind of L-H route was also observed to play a minor role in CO oxidation over a dethiolated Au<sub>25</sub>(SR)<sub>18</sub>-CeO<sub>2</sub> catalyst.<sup>8</sup> The L-H mechanism is further confirmed with an isotope labeling experiment. As shown in Figure 4B, CO oxidation with  ${}^{18}O_2$ over the 295 K-treated  $Au_{22}(L^8)_6 - Al_2O_3$  sample produces dominantly C<sup>16</sup>O<sup>18</sup>O and C<sup>16</sup>O<sup>16</sup>O, implying the ability of the cus Au sites in intact  $Au_{22}(L^8)_6$  nanoclusters to activate and dissociate  $O_2$  molecules. The production of  $C^{16}O^{16}O$  is likely due to the presence of reactive surface hydroxyl groups that can react with adsorbed CO on  $Au_{22}(L^8)_6$  nanoclusters to produced CO<sub>2</sub>, which has been previously observed for CO oxidation on Al<sub>2</sub>O<sub>3</sub>-supported Au nanoparticles.<sup>39</sup>

To further elucidate the catalytic mechanisms of CO oxidation, we investigated CO adsorption on the  $Au_{22}(L^8)_6$  nanocluster with DFT. We found that CO only adsorbs on the eight *cus* Au atoms (Figure 5A). Due to the symmetry of the cluster, the eight Au atoms can be divided into four groups. Figure 5B shows the most stable CO adsorption site on one of the *cus* Au atoms with an adsorption energy of -0.98 eV, indicating strong adsorption of CO. After adsorption, the C–O bond length slightly increases to 1.167 Å from the gas-phase value of 1.143 Å. For the other three groups of *cus* Au sites, the adsorption energies are -0.92, -0.90, and -0.79 eV; in contrast, CO adsorption on the non-*cus* Au sites is much weaker ( $\sim$ -0.22 eV). This indicates that *cus* Au atoms have a strong ability to adsorb and activate CO molecules for CO oxidation. To test if the *cus* Au sites can activate O<sub>2</sub>, we studied

the coadsorption of CO and O<sub>2</sub> on the cluster. We found that the adsorption of O<sub>2</sub> is very favorable on the CO–adsorbed Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanocluster with an adsorption energy of -1.44 eV (Figure 5C). In addition, the O–O bond is significantly weakened after adsorption, as is evident from its lengthening to 1.352 Å in comparison with the gas-phase value of 1.236 Å. Hence, our DFT results show that the *cus* Au sites of the Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanocluster can coadsorb CO and O<sub>2</sub> with very favorable interaction for the subsequent oxidation of CO, supporting our experimental observation of the low-temperature CO oxidation activity of the supported Au<sub>22</sub>(L<sup>8</sup>)<sub>6</sub> nanoclusters.

In conclusion, we have deposited the atomically precise, monodispersed  $Au_{22}(L^8)_6$  nanoclusters ( $L^8 = 1,8$ -bis-(diphenylphosphino) octane) with in situ cus Au sites intactly onto reducible and nonreducible oxide supports ( $TiO_2$ ,  $CeO_2$ , and Al<sub>2</sub>O<sub>3</sub>). A variety of in situ approaches including EXAFS, atomically resolved HAADF-STEM, and IR spectroscopy consistently demonstrates that the supported  $Au_{22}(L^8)_6$  nanoclusters are stable to heating in vacuum or dilute O2 without aggregation up to 573 K. Unlike the previously studied thiolated Au<sub>25</sub> nanocluster catalyst<sup>8</sup> that showed no activity for CO adsorption and oxidation prior to ligand removal, the supported  $Au_{22}(L^8)_6$  nanoclusters in the present work readily exhibit CO adsorption and CO oxidation activity in the asdeposited state without ligand removal, thanks to the presence of the in situ uncoordinated Au sites. DFT models for the unsupported  $Au_{22}(L^8)_6$  nanocluster suggest that, unlike the case for the thiolated Au<sub>25</sub> nanocluster, the fully ligated Au<sub>22</sub> nanoclusters present coordinatively unsaturated, neutral Au atoms that are available for bonding to CO and catalyzing its oxidation. CO oxidation activity is enhanced on the more reducible CeO<sub>2</sub> support than TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and isotope labeling demonstrates that the primary low-temperature pathway is through a Mars--van Krevelen route utilizing the lattice oxygen of the oxide support. This work represents the first example of an Au nanocluster active for gas-phase reaction without the necessity of ligand removal due to the presence of in situ uncoordinated Au sites. Synthesizing such type of nanoclusters with cus Au atoms is a promising route for the utilization of Au nanoclusters for catalytic applications.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.6b03221.

Experimental details. Figures showing views, a UV–vis spectrum, an MS pattern, TGA, the  $Au_{22}(L^8)_6$  nanocluster; in situ HAADF-STEM images and IR background spectra of  $Au_{22}(L^8)_6$ –TiO<sub>2</sub>; IR spectra from CO desorption at room temperature in flowing O<sub>2</sub> on assynthesized  $Au_{22}(L^8)_6$ –CeO<sub>2</sub>; integrated IR band area from adsorbed and Au sites exposure calculated from IR band area of CO on the Au sites in  $Au_{22}(L^8)_6$ –TiO<sub>2</sub> pretreated in O<sub>2</sub> at different temperatures; IR spectra from CO desorption on the  $Au_{22}$ Ti-573 sample in different atmospheres at room temperature; TGA profiles of pure  $Au_{22}(L^8)_6$ , TiO<sub>2</sub>, and a mixture of TiO<sub>2</sub> (80%) and the L<sup>8</sup> ligand; and CO–TPR profiles of CeO<sub>2</sub> and TiO<sub>2</sub>.(PDF)

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#### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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# Notes

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