

Gold Clusters

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The Synthesis, Bonding, and Transformation of a Ligand-Protected Gold Nanohydride Cluster

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Abstract: Gold does not react with H_2 to form bulk hydrides. Here we report the synthesis and characterization of a gold nanohydride protected by diphosphine ligands, [Au22H4- $(dppo)_6 l^{2+}$ [dppo=1,8-bis(diphenylphosphino)octane]. The Au_{22} core consists of two Au_{11} units bonded by eight Au atoms not coordinated by the diphosphine ligands. The four H atoms are found to bridge the eight uncoordinated Au atoms at the interface. Each Au₁₁ unit can be viewed as a tetravalent superatom forming four delocalized Au-H-Au bonds, similar to the quadruple bond first discovered in the $[Re_2Cl_8]^{2-}$ inorganic cluster. The $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride is found to lose H atoms over an extended time via H evolution (H_2) , proton (H^+) and hydride (H^-) releases. This complete repertoire of H-related transformations suggests that the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride is a versatile model catalyst for understanding the mechanisms of chemical reactions involving hydrogen on the surface of gold nanoparticles.

Introduction

Gold is considered the noblest metal and does not react with H₂.^[1] While copper hydride is known since 1844, gold does not form a bulk hydride even under extreme conditions.^[2] However, gold nanoparticles have been found to display remarkable catalytic activities,^[3] in particular, for hydrogenation reactions.^[4-6] Transient Au-H species have been detected on the surfaces of small gold nanoparticles and are considered to be important intermediates in hydrogenation reactions catalyzed by gold nanoparticles.^[7,8] NaBH₄ was commonly used as a hydride source for gold catalysis. The interaction between hydride and exposed surfaces of colloidal gold nanoparticles was known to induce localized surface plasmon resonance and reduction of 4-nitrophenol.^[9,10] The H₂ molecule was also known to react with small gold clusters to form gold hydride molecules that have been spectroscopically characterized.^[11-13] While mononuclear and dinuclear gold hydride complexes have long been known,^[14] no polynuclear gold hydride nanoclusters have been reported until recently.^[15,16] In contrast, numerous polynuclear copper and silver hydride clusters have been synthesized and characterized.^[17-25] Syntheses of gold hydride clusters would be important to understand the interactions of nanogold with

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 Supporting information and the ORCID identification number(s) for
the author(s) of this article can be found under: https://doi.org/10.1002/anie.202011748. hydrogen at the atomic level. Gold hydride clusters would also provide the ultimate model systems to elucidate the mechanisms of the remarkable range of hydrogen-related reactions catalyzed by gold nanoparticles.

The dramatic advance of nanoscience has led to the syntheses and characterization of atom-precise gold nanoclusters over the past decade.^[26-34] These gold nanoclusters have been found to display a wide range of interesting optical and chemical properties and can be viewed as molecular models to probe the catalytic mechanisms on the surface of gold nanoparticles.^[35-39] However, most of the gold clusters are fully coordinated by ligands. Thus, it is challenging to directly probe the hydrogen behaviors on gold clusters experimentally, and our knowledge about hydrogens on gold surfaces is mainly derived from theoretical studies.^[40-42]

We have been interested in synthesizing atom-precise gold nanoclusters that contain uncoordinated gold (ucAu) sites on the cluster surface to be used as in situ catalytic active sites.^[43] Our focus has been on the Au_{20} pyramid, which contains all surface atoms and was first discovered in the gas phase to be highly stable.^[44] Partial coordination of the corner sites in the Au₂₀ pyramid would create multiple *uc*Au sites.^[43a,b] While experimenting with a diphosphine ligand [dppo=1,8-bis (diphenylphosphino) octane, Figure 1a], we isolated a 22atom Au₂₂(dppo)₆ cluster,^[45] which consists of two Au₁₁ units joint by eight ucAu sites (Figure 1c). Au₂₂(dppo)₆ is the first atom-precise gold nanocluster synthesized with well-defined ucAu sites and has been shown to exhibit in situ catalytic activity for CO oxidation without ligand removal.^[46] Further theoretical calculations by Jiang et al. suggested that the Au₂₂(dppo)₆ cluster displays "stronger-than-Pt hydrogen adsorption for the hydrogen evolution reaction".^[47] The calculations predicted that the Au₂₂(dppo)₆ nanocluster can adsorb six H atoms with adsorption free energies close to zero, ideal for hydrogen evolution reactions. The calculations further predicted that the adsorption of the second H atom would lead to a particularly stable $Au_{22}H_2(dppo)_6$ dihydride cluster, suggesting that it might be observed simply by bubbling H_2 through an $Au_{22}(dppo)_6$ solution.

During our attempt to observe $Au_{22}H_2(dppo)_6$, we found that $[Au_{22}H_x(dppo)_6]^{n+}$ species were present in some assynthesized samples even without H_2 bubbling. In fact, $[Au_{22}H(dppo)_6]^{3+}$ was observed in the original mass spectrum along with $[Au_{22}M(dppo)_6]^{3+}$ (M = Na, K),^[45] and the protonated species was thought then to come from the electrospray process. Further experimentation led us to isolate a $[Au_{22}H_4-(dppo)_6]^{2+}$ tetrahydride species, which was actually the initial product of the synthesis and the $Au_{22}(dppo)_6$ final crystal used for X-ray diffraction was formed through the loss of hydrogen during the slow crystallization process (Figure 1b). This

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Figure 1. The discovery of the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride. a) The structure of the diphosphine ligand, dppo. b) The synthetic route of $[Au_{22}H_4(dppo)_6]^{2+}$ and its transformation to $Au_{22}(dppo)_6$. c) The X-ray structure of $Au_{22}(dppo)_6$ from Ref. [45]. d) The fully optimized structure of $[Au_{22}H_4(dppo)_6]^{2+}$ using DFT calculations. Au yellow, H blue, P orange, C black. The H atoms on the ligands are omitted for clarity. e) ESI-MS spectra of $[Au_{22}H_4(dppo)_6]^{2+}$ and $[Au_{22}D_4(dppo)_6]^{2+}$; the insets show the experimental and simulated isotopic distributions. The minor peaks labeled with * (from right to left) are: $[Au_{22}H(dppo)_6]^{3+}$, $[Au_{22}D_2(dppo)_6]^{4+}$, $[Au(dppo)_6]^{3+}$, $[Au_{22}D_2(dppo)_6]^{4+}$, $[Au(dppo)_6]^{3+}$.

 $[Au_{22}H_4(dppo)_6]^{2+}$ nanocluster is the largest gold nanohydride cluster reported heretofore. Its hydrogen loss behavior led us to observe a series of intermediate clusters ($[Au_{22}H_x$ - $(dppo)_6]^{n+}$, x = 0-3, n = 0, 2–4) and a complete repertoire of H-related transformations from hydrogen evolution (H_2) to proton (H^+) and hydride (H^-) releases. This finding provides direct experimental evidence towards hydrogen behaviors on gold surfaces, revealing versatile hydrogen transformation pathways. These findings provide valuable knowledge to elucidate the catalytic mechanisms for H-related transformations on gold nanoparticles.

Results and Discussion

The Synthesis of the Gold Nanohydride

The detailed synthetic procedure was similar to that in the original report of $Au_{22}(dppo)_6$ and is given in the Supporting Information. Briefly, the dppo ligand was used to make the precursor, Au₂(dppo)Cl₂, which was reacted with NaBH₄ to yield the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster. Under slow crystallization for several weeks, the $[Au_{22}H_4(dppo)_6]^{2+}$ species gradually transformed into crystals of the Au₂₂(dppo)₆ cluster (Figure 1 b), suitable for single-crystal X-ray crystallography (Figure 1 c).^[45] We found that fast crystallization led to precipitation of $[Au_{22}H_4(dppo)_6]^{2+}$. High purity $[Au_{22}H_4 (dppo)_6]^{2+}$ samples can be obtained by fast solvent diffusion of toluene into the CH₂Cl₂ solution of the crude product, as confirmed by electrospray ionization mass spectrometry (ESI-MS) (Figure 1e, top). To ensure that the four H atoms in $[Au_{22}H_4(dppo)_6]^{2+}$ are not produced during the ESI process, we carried out the same reaction with NaBD₄ dissolved in EtOD. The obtained $[Au_{22}D_4(dppo)_6]^{2+}$ sample also showed high purity with a dominant peak increased by 4 Da relative to $[Au_{22}H_4(dppo)_6]^{2+}$ (Figure 1e, bottom). It should be noted that the four H atoms come from both the reducing reagent NaBH₄ and the solvent EtOH (Supporting Information, Figure S1), showing that the EtOH solvent also plays a role in the formation of the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster.

The Positions of the Four H Atoms

Because the slow crystallization required to grow single crystals only resulted in $Au_{22}(dppo)_6$ due to hydrogen loss, one challenge was to locate the positions of the four H atoms in the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster. We characterized its structure using a combination of theoretical and experimental approach. We first performed a structural optimization using density functional theory (DFT) calculations and tested several H positions on the Au₂₂ skeleton. We found that the only stable structure is for the four H atoms to bridge the eight ucAu sites of the Au₂₂ cluster (Figure 1d; Supporting Information, Table S2). This structure agrees with that reported by Jiang et al. upon adsorption of four H atoms onto the $Au_{22}(\mbox{dppo})_6\ \mbox{cluster}.^{[47]}$ The $Au_{22}\ \mbox{core}$ in $[Au_{22}H_4\mbox{-}$ $(dppo)_6]^{2+}$ is similar to that in Au₂₂(dppo)₆ except that the four Au-Au bonds bridged by the H atoms are lengthened (Supporting Information, Figure S2). Interestingly, the Au₂H motif in the nanohydride is similar to the triangular Au₂H cluster^[48] and that suggested for the recently reported [Au₂₀- $(PPh_3)_{12}H_3]^{3+}$ cluster.^[16]

Since the positions of the H atoms are expected to influence the electronic structure of the gold core, we did TD-DFT calculations to simulate the electronic absorption spectra of $[Au_{22}H_4(dppo)_6]^{2+}$ (Figure 2a; Supporting Information, Table S1). The excellent agreement between the experimental UV/Vis spectrum and the simulated spectrum provides further confirmation for the structure of $[Au_{22}H_4(dppo)_6]^{2+}$.^[49] In addition, the infrared spectra of $[Au_{22}H_4(dppo)_6]^{2+}$ was also simulated (Figure 2b). The perfect match





Figure 2. UV/Vis and FTIR spectra of the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride. a) The experimental and simulated UV/Vis absorption spectra. The inset shows the experimental data in eV and the estimated energy gap. b) The experimental and simulated FTIR spectra. c) Illustration of one pair of Au hydride stretching vibrations.

between the experimental Fourier-Transform Infrared (FTIR) spectrum and the simulated spectrum again confirmed the structure of $[Au_{22}H_4(dppo)_6]^{2+}$. The FTIR results indicated that the vibrational structure of $[Au_{22}H_4(dppo)_6]^{2+}$ contains a gold hydride asymmetric stretching mode around 1260 cm⁻¹ (Figure 2 c), which is located between two aromatic ring distortion vibrations on the six dppo ligands. The asymmetric stretching mode consists of two peaks, because the four H atoms in $[Au_{22}H_4(dppo)_6]^{2+}$ are centrosymmetric and form two pairs. When $[Au_{22}H_4(dppo)_6]^{2+}$ lost all its hydrogens and transformed into the $Au_{22}(dppo)_6$ cluster, the bands assigned as the Au-H asymmetric stretching modes were almost completely suppressed (Supporting Information, Figure S3).

We further characterized [Au₂₂H₄(dppo)₆]²⁺ using ¹H-NMR at room temperature and observed four peaks at large chemical shifts around 15.6 ppm (Figure 3 a,b). These NMR peaks come from the four H atoms coordinated to Au, as confirmed by the fact that the ratio of their integrated area to that of the 120 aromatic H atoms on the six dppo ligands is 3.91:120. This observation is also corroborated by the ²H-NMR spectrum of $[Au_{22}D_4(dppo)_6]^{2+}$ (Supporting Information, Figure S4). Due to the conformations of the dppo ligands at room temperature, the four H atoms may experience different chemical environments in solution, giving rise to the four NMR peaks. Temperature-dependent ¹H-NMR showed a single peak at 55 °C (Figure 3 a), suggesting that at elevated temperatures the dppo ligands exhibit fast dynamics on the NMR time scale and resulting in similar chemical environments for the four H atoms.



Figure 3. ¹H NMR spectra of the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride. a) Variable-temperature ¹H NMR spectra of the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster in CD₂Cl₂. The integrated areas from the hydride region to that of the 120 aromatic H atoms on the six dppo ligands are all around 3.9:120. b) The enlarged room temperature ¹H NMR signal due to the hydrides on the Au₂₂ cluster. c) The enlarged ¹H-NMR signal from the H₂ molecule detected due to H-loss from the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster. Note its increased intensity with temperature. The peak labeled with * is due to the solvent (CH₂Cl₂).

Chemical Bonding

We analyzed the canonical Kohn-Sham molecular orbitals (MOs) of $[Au_{22}H_4(dppo)_6]^{2+}$ (Supporting Information, Figure S5), which is found to contain 24 valence electrons with the hydride-based orbitals lying at similar energies as the metal-based orbitals. The fact that hydrogen participates in the electronic structure of the gold clusters have been suggested for $[Au_9H(PPh_3)_8]^{2+}$, $[Au_{25}H(SR)_{18}]$, and $[Au_{25}H_2$ -(SR)₁₈]⁺.^[15,50] A recent study indicated that halides may play similar roles as the hydride.^[51] We also found that [Au₂₂H₄- $(dppo)_{6}^{2+}$ has a highly stable electronic structure with a large HOMO-LUMO gap (2.44 eV), consistent with the experimentally estimated energy gap (inset in Figure 2a). The large HOMO-LUMO gap explains the high stability of [Au₂₂H₄- $(dppo)_6]^{2+}$ relative to the $[Au_{22}H_4(dppo)_6]$ neutral state, which was not observed. This result is consistent with the prediction by Jiang et al.^[47] about the higher stability of Au₂₂H₂(dppo)₆, which is isoelectronic with $[Au_{22}H_4(dppo)_6]^{2+}$. Each Au_{11} unit in $[Au_{22}H_4(dppo)_6]^{2+}$ possesses eight valence electrons, and the remaining eight valence electrons form four bonds between the two Au₁₁ units along with the four H atoms. This bonding can be seen more clearly from the adaptive natural density partitioning (AdNDP) analysis (Supporting Information, Figure S6).^[52] Remarkably, the four Au-H-Au bonds in $[Au_{22}H_4(dppo)_6]^{2+}$ are reminiscent of the first metal-



Figure 4. Comparison of the quadruple bond in the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster and the $[Re_2Cl_8]^{2-}$ inorganic cluster complex. The ligands are dimmed in both clusters for better views.

metal quadruple bond discovered in the $[Re_2Cl_8]^{2-}$ inorganic cluster complex,^[53] as shown in Figure 4. Both clusters contain the same quadruple bond pattern, one σ bond, two π bonds, and one δ bond. Thus, each Au₁₁ unit in $[Au_{22}H_4(dppo)_6]^{2+}$ can be viewed as a tetravalent superatom that originally carry 12 valence electrons before the quadruple bond formation. Compared with $Au_{22}(dppo)_6$, which contains 22 valence electrons^[45] and a triple superatom-bond between the two Au₁₁ units,^[54] the four H atoms in $[Au_{22}H_4(dppo)_6]^{2+}$ actually strengthen the bonding between the two Au₁₁ units, consistent with the increased stability observed for the tetrahydride cluster.

The Properties of the Gold Nanohydride

The purified $[Au_{22}H_4(dppo)_6]^{2+}$ samples always contained minor species with fewer H atoms (Figure 1e). The amounts of such species increased when we left the sample in a CH₂Cl₂ solution for six days (Supporting Information, Figure S7), suggesting spontaneous and slow H loss from [Au22H4-(dppo)₆]²⁺ under ambient and dark conditions. Its main UV/ Vis absorption peak at 456 nm also showed a slow decrease as a function of time (Supporting Information, Figure S8a). These observations are consistent with the results of the slow crystallization and corroborated by the study by Jiang et al., who predicted that the differential adsorption energies of the first four H atoms on the $Au_{22}(dppo)_6$ clusters range from -0.1 to -0.7 eV and the adsorption free energy range from 0.1 to -0.4 eV.^[47] The thermal stability of the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster is intermediate between the only two known small gold hydride clusters, $[Au_9H(PPh_3)_8]^{2+}$ which is metastable with a half-life of only several hours,^[15] and $[Au_{20}(PPh_3)_{12}H_3]^{3+}$ which is stable for up to three months.^[16] Our collisioninduced dissociation experiment also revealed that the four H atoms in $[Au_{22}H_4(dppo)_6]^{2+}$ can be dissociated, while the Au_{22} cluster core remained intact (Supporting Information, Figure S9). Solid samples of $[Au_{22}H_4(dppo)_6]^{2+}$ are stable for more than two weeks under ambient and dark conditions,

whereas $[Au_{22}H_4(dppo)_6]^{2+}$ samples stored in the dark at -40 °C under N₂ atmosphere are stable for at least six months.

We found that H loss from $[Au_{22}H_4(dppo)_6]^{2+}$ can be accelerated by heating or in an alcohol solution. Because of its absorption in the visible part of the spectrum (Figure 2a), we found that H loss can also be accelerated when we put the $[Au_{22}H_4(dppo)_6]^{2+}$ sample under ambient light. Such light sensitive behavior of gold hydride clusters was also observed previously.^[55] Different H-loss products are formed as a function of time and the mechanisms can be described approximately to proceed through two stages. In fresh samples, $[Au_{22}H_4(dppo)_6]^{2+}$ was detected as the dominating species (Figure 1e; Supporting Information, Figure S10a) and exhibited a major absorption band at around 456 nm (Figure 2a). In the first stage of H loss, prominent signals of [Au₂₂H₂- $(dppo)_6]^{4+}$ and $[Au_{22}H_4(dppo)_6]^{4+}$ (detected with a putative Cl⁻ adduct) were observed (Figure 5a; Supporting Information, Figure S10b,c). The UV/Vis absorption spectrum at this stage showed an obvious decrease of the 456 nm peak and the appearance of a new peak at longer wavelengths (Figure 5b). In the second stage of H loss, [Au₂₂H(dppo)₆]³⁺ was detected as the major species (Figure 5c; Supporting Information, Figure S10d). At the same time, the original [Au₂₂H₄- $(dppo)_6]^{2+}$ absorption peak at 456 nm was almost fully suppressed, and the major absorption peak was red-shifted to around 485 nm (Figure 5d; Supporting Information, Figure S8b). The absorption spectrum of $[Au_{22}H_4(dppo)_6]^{2+}$ in the visible spectral range involves metal→metal transitions in the Au₂₂ core (Supporting Information, Table S1), consistent with the spectral change induced by H loss from [Au₂₂H₄- $(dppo)_6]^{2+}$. Remarkably, the UV/Vis spectrum in Figure 5d agrees well with the absorption spectrum calculated previously for the Au₂₂(dppo)₆ cluster,^[56] confirming it as the major product upon H loss. At ambient and dark conditions, without heating or using alcohol solution, the first stage can be detected in about a week and lasts for several weeks before the second stage is reached.

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Figure 5. The H loss mechanisms from the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride. a),b) The ESI-MS spectra and the corresponding UV-vis absorption spectra in the stage 1 of hydrogen loss. The $[Au_{22}H_4CI]^{3+}$ consists of a putative adduct between $[Au_{22}H_4]^{4+}$ and CI^- . c),d) The ESI-MS spectra and the corresponding UV-vis absorption spectra in the stage 2 of hydrogen loss.

Hydrogen Transformation Mechanisms

An interesting question is the fate and mechanisms of the hydrogen lost from [Au₂₂H₄(dppo)₆]²⁺. The observations of $[Au_{22}H_4(dppo)_6]^{4+}$ and $[Au_{22}H_2(dppo)_6]^{4+}$ (Figure 5a) or $[Au_{22}H_4(dpp0)_6]^{3+}$ (Figure 5c) suggest H₂ release or redox reactions involving H^+/H^- transfers. X-ray photoelectron spectroscopy (XPS) further showed that the Au $4f_{7/2}$ binding energy was slightly smaller after the hydrogen loss (ca. 0.2 eV), suggesting the formation of neutral Au₂₂(dppo)₆ cluster through a disproportionation reaction (Supporting Information, Figure S11). The H₂ loss channel was readily confirmed by the detection of H₂ ($\delta = 4.59$ ppm) in the room temperature NMR spectrum (Figure 3c). The H₂ signal was observed more prominently at elevated temperatures (Figure 3a). The fact that the alcohol solution can accelerate H loss suggests the participation of H⁺, because alcohols are good proton acceptors. Combining all the experimental observations, we inferred the mechanisms for the transformation of $[Au_{22}H_4(dppo)_6]^{2+}$ to the $Au_{22}(dppo)_6$ crystals on the bases of the different hydride clusters observed, as shown schematically in Figure 6. In the first step, two $[Au_{22}H_4 (dppo)_6]^{2+}$ clusters undergo a disproportionation reaction, forming two H₂ molecules, one Au₂₂(dppo)₆ cluster and one $[Au_{22}H_4(dppo)_6]^{4+}$ product. The $[Au_{22}H_4(dppo)_6]^{4+}$ intermediate loses one H₂ molecule via hydrogen evolution to give $[Au_{22}H_2(dppo)_6]^{4+}$ without change of charge state. Finally, the $[Au_{22}H_2(dppo)_6]^{4+}$ intermediate can lose one H⁺ to form the $[Au_{22}H(dppo)_6]^{3+}$ intermediate. These major H loss pathways have all been confirmed using the deuterated cluster, $[Au_{22}D_4(dppo)_6]^{2+}$ (Supporting Information, Figure S9). Apart from the major H loss channels described above,



Figure 6. The spontaneous H loss mechanisms from $[Au_{22}H_{4}-(dppo)_{6}]^{2+}$ to different $[Au_{22}H_{x}(dppo)_{6}]^{n+}$ clusters (x = 0-3, n = 0, 2–4). The transformations indicated by the three straight arrows are major H loss channels, while the ones indicated by the four perpendicular arrows are minor H loss channels.

ESI-MS observations and isotopic substitution experiments provide evidence that the four hydride species ($[Au_{22}H_4(dppo)_6]^{2+}$, $[Au_{22}H_4(dppo)_6]^{4+}$, $[Au_{22}H_2(dppo)_6]^{4+}$, $[Au_{22}H_4(dppo)_6]^{3+}$) can all spontaneously lose H through hydrogen evolution and/or proton release as minor H loss channels, forming $[Au_{22}H_2(dppo)_6]^{2+}$, $[Au_{22}H_3(dppo)_6]^{3+}$, $[Au_{22}-(dppo)_6]^{4+}$ and $[Au_{22}(dppo)_6]^{2+}$ hydride clusters (Figure 6; Supporting Information, Figure S12).

We have also found that $[Au_{22}H_4(dppo)_6]^{2+}$ can spontaneously undergo hydride release, which was discovered when we added an ethanol solution of NaBD4 into a CH2Cl2 solution of $[Au_{22}H_4(dppo)_6]^{2+}$. Rapid hydride transfers between $[Au_{22}H_4(dppo)_6]^{2+}$ and $NaBD_4$ were observed, resulting in $[Au_{22}H_{4-x}D_x(dppo)_6]^{2+}$ species (x = 1-4; Figure 7a). Adding NaBH₄ into a CH₂Cl₂ solution of $[Au_{22}D_4(dppo)_6]^{2+}$ led to similar isotopic scrambling (Supporting Information, Figure S13). As a control experiment, we found that ethanol does not react with $[Au_{22}H_4(dppo)_6]^{2+}$ (Figure 7b; Supporting Information, Figure S14), despite the fact that it plays a role during the cluster synthesis (Supporting Information, Figure S1) or accelerates the H loss as a proton acceptor. Furthermore, two-dimensional ¹H-NMR NOESY spectrum displayed significant cross signals between the hydride peaks (Figure 7c), suggesting that the four H atoms in [Au₂₂H₄- $(dppo)_{6}^{2^{+}}$ are close to each other and may exchange positions, that is, internal H transfer on the NMR time scale. The hydridic nature of the four H atoms was further verified by the Bader charge analysis of the $[Au_{22}H_4]^{2+}$ core (Figure 7d). The results showed that the four H atoms carry negative charges, in agreement with the previous result by Jiang et al.^[47] about the hydridic nature of hydrogens adsorbed on $Au_{22}(dppo)_6$.



Figure 7. The hydride exchange experiments. a) The isotopic distribution of $[Au_{22}H_4(dppo)_6]^{2+}$ after hydride exchange with NaBD₄. b) The isotopic distribution of $[Au_{22}H_4(dppo)_6]^{2+}$ before and after the addition of EtOD. c) The two-dimensional ¹H NMR NOESY spectrum of the $[Au_{22}H_4(dppo)_6]^{2+}$ cluster in the hydride region. d) The Bader charge analysis for the metal core of $[Au_{22}H_4(dppo)_6]^{2+}$. The dppo ligands are all omitted in the formula labels in the figure.

Figure 8 summarizes the three spontaneous H loss pathways on a gold surface revealed by the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride. In the proton release pathway, the hydrogen is released as a proton and simultaneously transferring an electron to the gold metal core (Figure 8a), that is, an electron-coupled proton release process. This pathway is akin to an inverse process of the Volmer step in the hydrogen evolution reaction $(H^+ + e^- \rightarrow H)$. In the hydrogen evolution



Figure 8. Illustration of the three spontaneous hydrogen loss pathways on a nanogold surface revealed by the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride. a) Proton (H⁺) release, that is, electron-coupled proton release. b) Hydrogen evolution. c) Hydride (H⁻) release.

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pathway, two hydrogens combine intramolecularly, releasing a H₂ molecule while leaving the charge state of the gold core unchanged (Figure 8b). This pathway is similar to the Tafel step in the hydrogen evolution reaction $(H+H\rightarrow H_2)$, providing the first direct experimental evidence of this process on the surface of a gold nanocluster. In the hydride release pathway, the hydrogen comes off as a hydride by withdrawing an electron from the gold core (Figure 8c). The diverse range of spontaneous H loss mechanisms revealed by the [Au₂₂H₄- $(dppo)_6]^{2+}$ nanohydride is unprecedented, suggesting that it should be a versatile catalyst for different chemical reactions involving hydrogen, such as hydrogenation or hydrogen evolution reactions. More importantly, the $[Au_{22}H_4(dppo)_6]^{2+}$ nanohydride provides fundamental information about the behaviors of hydrogen on nanogold surfaces, broadening our understanding about the mechanisms of different hydrogenrelated reactions catalyzed by gold nanoparticles.

Conclusion

We have isolated and characterized the hitherto largest gold nanohydride cluster $[Au_{22}H_4(dppo)_6]^{2+}$ and elucidated its bonding and chemical properties. The Au₂₂ core in the nanohydride consists of two Au₁₁ units bonded via eight uncoordinated gold atoms, where the four H atoms are found to be located in the bridging positions. The Au₁₁ unit behaves as a tetravalent eight-electron superatom forming four delocalized Au-H-Au bonds at the interface, similar to the metal-metal quadruple bond in the classical $[Re_2Cl_8]^{2-}$ inorganic cluster complex. The nanohydride is stable at low temperatures, but over extended time it is found to slowly lose hydrogens. A complete range of hydrogen transformations via proton release (H^+) , H_2 evolution, and hydride release (H^-) were observed. The present work suggests that a wide range of H loss channels can spontaneously occur on nanogold surfaces. This fundamental knowledge will be valuable to understand the catalytic mechanisms of hydrogen-related transformations on gold nanoparticles. The current study also suggests new routes to discover novel gold nanohydrides.

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Conflict of interest

The authors declare no conflict of interest.

Stichwörter: catalytic mechanisms · chemical bonding · gold clusters · gold hydride · hydrogen transformation



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