Investigating Active Site of Gold Nanoparticle \( \text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6 \) in Selective Oxidation

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Understanding the structure—activity—selectivity relationships of catalytic gold nanoparticles (AuNPs) is a challenging task. Gold nanoparticles in the size range of 1–3 nm exhibit extraordinary catalytic activity and selectivity in many industrially valuable reactions, for example, low-temperature oxidation of carbon monoxide, selective oxidation of olefin and alcohol, and water—gas shift reactions, etc.\(^{1–16}\) Although catalytic activity of bare gold clusters (with or without support) is now reasonably understood,\(^{17–20}\) characterization of the structure—activity—selectivity relationship for AuNPs in the size range of 1–3 nm remains elusive, largely due to the lack of precise atomic structure information of large-sized gold clusters. Previous studies have reported that catalytic activities of AuNPs can be greatly affected by a number of factors, for example, the size and shape of AuNPs, the ratio of low versus high coordination sites, solvent effects, and interaction and charge transfer between AuNPs and metal oxide support.

The gas-phase gold clusters had been widely used as model systems to investigate chemical activity as a function of cluster size and structure. In particular, it has been found that the binding of an \( \text{O}_2 \) molecule on small-sized gold clusters \( (N \leq 20) \) is sensitive to the cluster size and charge states. The even-number \( \text{Au}_{N}\text{Au}^- \) anion clusters can strongly interact with \( \text{O}_2 \) molecule (with an exception of \( \text{Au}_{16}^- \)), while the odd-number \( \text{Au}_{N}\text{Au}^- \) clusters hardly interact with the \( \text{O}_2 \).\(^{29,30}\) The neutral clusters \( \text{Au}_N \), the positive charged \( \text{Au}_{N}^+ \) clusters, and the \( \text{Au}_{N}\text{Au}^- \) with large \( N \) were found inert toward the \( \text{O}_2 \) adsorption, with the exception of \( \text{Au}_{10}^+ \) and \( \text{Au}_{10}\text{Au}^- .\(^{32,33}\) Such a size dependence has been explained on the basis of the electron affinity of \( \text{Au}^- \) clusters, that is, a low electron affinity requires higher free energy for the \( \text{Au}^- \)—\( \text{O}_2 \) binding.\(^{29,30}\)

Gold clusters on metal oxide supports (e.g., \( \text{TiO}_2 \) and \( \text{MgO} \)) show significantly enhanced activity and selectivity.\(^{16,18–22}\) Chen \textit{et al.} found that on a \( \text{TiO}_2 \) support Au bilayer nanostructures show a maximum reaction activity toward the \( \text{CO} \), about 10 times higher than that on monolayer Au nanostructures, and 45 times faster than the most active Au/\( \text{TiO}_2 \) catalysts prepared from conventional methods.\(^{8}\) Herzing \textit{et al.} identified that bilayer Au clusters with a diameter of 0.5 nm and containing \(~10\) atoms give rise to maximum activity toward the CO oxidation.\(^{14}\) Landman and Heiz \textit{et al.} showed that the charge transfer from the bottom F-center of \( \text{MgO} \) support to the \( \text{Au}_8 \) cluster plays a key role in promoting the chemical activity of \( \text{Au}_N \) clusters.\(^{19}\) Subsequent density functional theory (DFT) calculations confirmed the importance of the charge transfer between gold clusters and metal oxide to the enhancement of activity of Au clusters.\(^{34–38}\) Sinha \textit{et al.} reported that the silylated mesoporous titanosilicates

**ABSTRACT** We present an \textit{ab initio} investigation of structural, electronic, catalytic, and selective properties of the ligand-covered gold nanoparticle \( \text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6 \) and associated model clusters. The catalytic activity of the \( \text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6 \) nanoparticle in the presence of \( \text{O}_2 \) stems from a combined effect of triphenylphosphine ligands and surface structure of the “magic-number” quasi-icosahedral \( \text{Au}_{55} \) core, which entails numerous ligand-encompassed triangle \( \text{Au}_6 \) faces as the active sites. Under the Eley-Rideal mechanism, the “triangle-socket” active site not only can accommodate one pre-adsorbed \( \text{O}_2 \) (which is subsequently activated to the superoxo species) with one styrene molecule at a time but also can provide spatial confinement which favors the formation of an oxametallacycle intermediate that leads to unique selectivity in styrene oxidation.

**KEYWORDS:** ligand-covered gold nanoparticles · catalytic properties and selectivity · active sites · quasi-icosahedral \( \text{Au}_{55} \) core · density-functional theory
support can greatly enhance the catalytic activity of gold catalysts for propylene epoxidation as well, even better than the TiO₂ support.⁴⁹

Organic ligand-protected AuNPs are generally synthesized in solutions. In recent years, determination of the atomic structures of ligand-protected gold clusters have attracted considerable interest. Many previous studies have shown that ligand (such as mixed —P(Ph)₃ and —Cl, or the thiolate group —SR) protected gold clusters typically have a highly symmetric Au core.⁴⁰–⁵³ The core size ranges from 0.5 to 1.3 nm. In general, ligand-protected Au clusters are considered ineffective for catalysis because the Au cores are mostly shielded by the ligands.⁵¹–⁵³ Recently, however, Tsunoyama et al. showed that the gold clusters stabilized by poly(N-vinyl-2-pyrrolidone) (PVP) and with a core size of 1.3 ± 0.3 nm can exhibit high catalytic activity for various aero-/hydroxylation reactions, such as oxidation of alcohol, homocoupling of arylboronic acids, generation of hydroxylation of benzaldehyde than to styrene epoxide and acetophenone.⁵² A mechanism for the high catalytic activity was attributed to the anionic Au core due to the electron donation effect of PVP molecules, which is akin to the electron-transfer mechanism between a gold cluster and a metal oxide support.¹⁸,⁵² Another recent experimental study also demonstrated that the thiolate-protected Au₅₅ core-based structures (Au₅₅[S(R)₃]₁₈) can selectively catalyze the hydrogenation of α,β-unsaturated ketones and aldehydes under mild conditions.⁵³ The active sites for the C=O activation were likely at the eight open facets of the Au₁₃ icosahedral core. Also recently, Turner et al. reported that the ligand-covered 55-atom gold cluster Au₅₅(PPh₃)₁₂Cl₆ can exhibit relatively high activity and selectivity towards styrene oxidation,¹⁰ as evident by the direct oxidation of styrene with O₂ to form benzaldehyde, styrene epoxide, and acetophenone.¹⁰ Especially, the Au₅₅(PPh₃)₁₂Cl₆ cluster gives a conversion rate of 12.6% and selectivity of 13.1% toward styrene epoxide. Moreover, the Au₅₅(PPh₃)₁₂Cl₆ cluster provides higher selectivity toward benzaldehyde than to styrene epoxide and acetophenone.

In this article, we present a systematic ab initio study of low-lying structures of Au₅₅(PPh₃)₁₂Cl₆. Particular attention has been placed on seeking the active site on the Au₅₅ core and a mechanism underlying the high selectivity of Au₅₅(PPh₃)₁₂Cl₆ in styrene oxidation. We found that the catalytic activity and selectivity of Au₅₅(PPh₃)₁₂Cl₆ can be attributed to a combination of several factors, including the quasi-icosahedral Au₅₅ core structure and the ligand arrangement as well as the triphenylphosphine-surrounded triangle Au₆ face as the active site.

RESULTS AND DISCUSSIONS

Au₅₅ Core Structure in Au₅₅(PPh₃)₁₂Cl₆. The structure of Au₅₅ core in the Au₅₅(PPh₃)₁₂Cl₆ nanoparticle has been under debate since the first synthesis of the nanoparticle in 1981.⁴₀ The cluster was hard to crystallize and therefore a single-crystal X-ray analysis was not possible. A cuboctahedral structure of Au₅₅ core was first proposed by Schmid et al. based on Mössbauer, extended x-ray absorption fine structure (EXAFS), x-ray absorption near edge structure (XANES), and wide-angle x-ray scattering (WAXS) measurements as well as geometric consideration.⁵⁴,⁵⁵ However, an icosahedral Au₅₅ core structure was later suggested on the basis of the Debye-function analysis of X-ray diffraction (XRD) data.⁵⁶,⁵⁷ To determine the most likely structure of the Au₅₅ core, we performed geometric optimization of 49 different structures of Au₅₅(PR)₁₂Cl₆ (labeled as Iso-1 to Iso-49), but the original phenyl groups were replaced by —H (e.g., R = —H) to reduce computational cost. Three groups of Au₅₅ core structures were considered: (a) three high-symmetry Au₅₅-core structures composed of icosahedral (I₅₅), cuboctahedral (O₅₅), and decahedral (D₅₅) structures; (b) five low-symmetry disordered Au₅₅ structures, derived from a global-minimum search using the basin-hopping method;⁵₈,⁵₉ composed of the top five lowest-lying isomers among 200 low-energy Au₅₅ isomers; the lowest-lying Au₅₅ isomer is 0.47, 1.40, and 1.97 eV lower in energy than the I₅₅, D₅₅, and O₅₅ Au₅₅ cluster, respectively, based on the PBE/DNP level of theory (see Computational Methods). Our result is consistent with a recent joint experimental and theoretical study in that the lowest-energy isomer of anion Au₅₅— exhibits a disordered structure,⁶₀ (c) two Au₅₅ structures which are composed of a Au₁₇ nucleus and a Au₁₈ shell, where each Au atom in the Au₁₈ shell is directly bonded with one of 18 ligands (e.g., [Au₁₇(R)₁₈]₀[Au₅₅(PH₃)₁₂Cl₆]).

Figure 1 illustrates relative energies of totally 48 isomers of Au₅₅(PPh₃)₁₂Cl₆. The O₅₅-Au₅₅ core-based structure (Iso-49) was not included since the O₅₅-Au₅₅ core was converted to a quasi-I₅₅-Au₅₅ core after geometric optimization. In general, the I₅₅-Au₅₅ core-based (Iso-1 to Iso-22) and D₅₅-Au₅₅ core-based (Iso-23 to Iso-34) isomers possess relatively lower energies. The lowest-energy isomer (Iso-1) has a quasi-I₅₅-Au₅₅ core, and it is 0.41 eV lower in energy than the lowest-energy D₅₅-Au₅₅.
The initial Au₅₅ core geometries and ligand arrangements among the 48 Au₅₅(PH₃)₁₂Cl₆ isomers indicate clusters, for instance, the quasi-Ih-Au₅₅ and quasi-D₅h-Au₅₅ cores. Similar behavior has been observed in small-sized ligand-protected gold nanoparticles. In fact, the replacement of the phenyl group by PH₃ and PPh₃ groups can stabilize both the quasi-Ih-Au₅₅ and quasi-D₅h-Au₅₅ cores. Similar behavior has been observed in small-sized ligand-protected gold clusters, for instance, the quasi-Ih-Au₁₃ core in [Au₁₃(PMe₂Ph)₁₀Cl₆]³⁺ cluster and the hexagonal anti-prismatic D₅h-Au₁₉ core in [Au₁₉(PPh₃)₄Cl₆]²⁺ cluster.

Note that the simplified model structures of Au₅₅(PH₃)₁₂Cl₆ shown above provide only approximate structures for the Au₅₅(PH₃)₁₂Cl₆ nanoparticles. In fact, the replacement of the phenyl group by —PH₃ in the simplified model Au₅₅(PH₃)₁₂Cl₆ can lead to a strong hydrogen-bonding interaction between the —PH₃ and —Cl groups and can also underestimate non-bonding repulsion among the —PPh₃ ligands in Au₅₅(PPh₃)₁₂Cl₆.

We performed additional geometric optimization of three triphenylphosphine-covered Au₅₅(PPh₃)₁₂Cl₆ isomers which possess a quasi-Ih- and quasi-D₅h-Au₅₅ core, respectively. The three more realistic structures are labeled as 2a, 2b, and 2c, respectively. The initial Au₅₅ core geometries and ligand arrangements of 2a, 2b, and 2c were identical to those of Iso-15, Iso-23, and Iso-35, except the —PH₃ groups were replaced by —PPh₃ groups. In 2a and 2b, the 12 —PPh₃ groups occupy 12 vertices of a Au₅₅ core to minimize steric interactions. We also considered an O₅-Au₅₅ core-based isomer of Au₅₅(PPh₃)₁₂Cl₆ (namely, 2d), built with six —Cl ligands attached to the center Au atom on the six quadrangle faces, which is a homologue to the structure originally proposed by Schm β et al.²⁴,⁵⁵ Figure 2a displays optimized structures and relative energies of 2a – d. The structures 2a and 2b containing a quasi-Ih- and quasi-D₅h-Au₅₅ core, respectively, are nearly isoenergetic (with an energy difference less than 0.02 eV), while 2c and 2d are 0.28 and 2.23 eV higher in energy than 2a, respectively. This energy ordering is consistent with that obtained from the simplified model Au₅₅(PH₃)₁₂Cl₆ (Figure 1).

Our prediction of the quasi-Ih-Au₅₅ core for Au₅₅(PPh₃)₁₂Cl₆ nanoparticle is consistent with earlier XRD studies.⁵⁶,⁵⁷ We note that the quasi-Ih-Au₅₅ core structure was also concluded in a recent theoretical study of Au₅₅(PH₃)₁₂Cl₆.⁶¹ In Figure 2b, we display simulated XRD patterns for 2a – d based on the Debye–function analysis (see Computational Methods). The first major peak (at ∼4.2 nm⁻¹) of simulated XRD patterns of 2a – c is in good agreement with that of the experimental one,⁶⁶ but that of 2d is not because of the presence of two peaks in the 6 – 9 nm⁻¹ region. The simulated XRD spectrum of 2a exhibits another weaker peak at 5.7 nm⁻¹ while a weak peak at ∼4.9 nm⁻¹ was also observed in the experiment (Figure 6 in ref 55). Despite the difference in the location of the weak peak, it seems that the structure of quasi-Ih-Au₅₅ core-based isomer 2a is closer to the isomer detected in the XRD experiment (ref 55) than that of isomer 2b and 2c, in light of this weak signature peak.

Structure – Activity Relationship of Au₅₅(PPh₃)₁₂Cl₆. In the quasi-Ih-Au₅₅ core-based Au₅₅(PPh₃)₁₂Cl₆ (2a), the 12 —PPh₃ ligands occupy 12 vertices of the quasi-Ih-Au₅₅ core-based isomer.
core. Hence, only edge sites and triangle Au$_6$ faces can be potential active sites for O$_2$ adsorption and activation. To compute the O$_2$ dissociation pathway, we used a simplified model 2a$'$ which is derived from 2a by keeping only three —PPh$_3$ groups for encompassing a triangle Au$_6$ face while all other —PPh$_3$ groups are replaced by —PH$_3$ groups (Figure 3). Both doublet and quartet spin states were examined when computing the O$_2$ dissociation pathway.

It is worth noting that, on the basis of the lowest-lying Au$_{55}$ cluster obtained from the basin-hopping search, it appears the bare Au$_{55}$ is chemically quite inert toward O$_2$ activation. An O$_2$ dissociation route is computed and shown in Supporting Information Figure S1. We found that a fairly high energy barrier (1.95 eV) is required for the O$_2$ dissociation when the O$_2$ is adsorbed at a triangle-like surface site. Such a high energy barrier indicates that the bare disordered Au$_{55}$ cluster, based on our model, is unlikely to catalyze O$_2$ dissociation.

As shown in Figure 3, when O$_2$ is adsorbed on the triangle Au$_6$ face, the activation of O$_2$ takes two steps: the formation of a superoxo-like species (3a to 3c) and the dissociation of superoxo species into two O atoms (3c to 3d). Initially, an O$_2$ molecule is adsorbed on an edge site (3a) with an adsorption energy of -0.21 eV, where the whole system is at quartet spin ground state. The O—O bond length is 1.264 Å (about 0.06 Å longer than the gas phase O—O bond length). The net spin population on two O atoms is 0.71 and 0.80, respectively (cf. Supporting Information Table S1), indicating that O$_2$ is scarcely activated. The barrier for O$_2$ activation from 3a to 3c is 0.19 eV and the process is slightly exothermic (-0.07 eV). Note that for 3c the doublet spin state gives rise to a lower energy than the quartet spin state. At the intermediate state 3c, the O—O bond is elongated to ~1.36 Å, and the spin population on the two O atoms decreases to 0.13 (cf. Table S1). Charge analysis shows that both O atoms are negatively charged (cf. Figure 3. The O$_2$ dissociation pathway on the triangle Au$_6$ active site encompassed by —PPh$_3$ ligands, which is calculated on the basis of a model system 2a$'$. The energy is in units of eV. The superscripts qt and db represent the quartet and doublet spin states, respectively. For states 3a-3c, both top and side views are shown. The bond lengths shown in parentheses correspond to the quartet spin state of 3a-3c.)
than the barrier to O₂ dissociation on the Au(111) surface.

Figure 4. Summarization of O₂ adsorption and activation on four types of surface site on the Au₅₅(PPh₃)₁₂Cl₆ nanoparticle with different Au₅₅ core structures: 4a,b,d–g are based on quasi-Iₕ-Au₅₅ and quasi-D₅₅-Au₅₅ core isomers; 4h–l are based on isomers with decahedral Au₅₅ core; 4m,n present adsorption sites on isomers with the disordered Au₅₅ core. Detailed geometries of various adsorption modes (4a–o) and the spin/charge distributions of O and Au atoms are given in Figure 5 and Supporting Information Table S1, respectively.

Table S1), confirming the formation of a superoxo-like species. Next, the barrier from the intermediate state to O₂ dissociation state is 1.22 eV, about 0.6 eV lower than the barrier to O₂ dissociation on the Au(111) surface (~1.80 eV) but comparable to that on the step of Au(211).[^64] Note also that the experiment[^10] was carried out at ~100 °C, which can further promote O₂ dissociation.

Although the O₂ dissociation is endothermic, a relatively high association barrier (~0.77 eV from 3e to 3d) may hinder the reverse reaction. At the dissociation state 3e, the two O atoms are separated by 3.15 Å with each O adsorbed on a threefold fcc hollow site.

A number of sites for O₂ adsorption on the homologue Au₅₅(PPh₃)₁₂Cl₆ with different Au₅₅ core structures (from the isomer database shown in Figure 1) were examined. Figures 4 and 5 list 15 representative O₂ adsorption sites, including edge sites (4a–c) and triangle faces (4d–i,m) as well as quadrangle faces (4j–l) on the D₅₅⁵-Au₅₅ core and a few irregular sites (4n,o) on the disordered Au₅₅ core. Here, 4g has the same ligand arrangement as 3c. Adsorption energies, charge, and spin densities on O atoms for 4a–o are given in Supporting Information Table S1. By comparing the O–O bond length in 4g and 3c, it can be seen that the replacement of phenyl group by —H incurs little change on the O–O bond length in the superoxo species, validating the use of simplified model Au₅₅(PPh₃)₁₂Cl₆ for testing O₂ activation. As shown in Figures 4 and 5, the O–O bond length is significantly elongated when O₂ is located near the triangle Au₆ face (4d–i,m), regardless of the Au₅₅ core structure, arrangement of ligands, and spatial orientation of O₂.

Upon O₂ adsorption, electron transfer takes place from Au to O due to stronger electronic affinity of the O atom. On the triangle Au₆ face (4d–i,m), the electron transfer (σₐu) is much more than that on other type sites. The three inner Au atoms (Au(1), Au(2), and Au(3); see Figure 5) of the triangle Au₆ face are mainly involved in the charge transfer (cf. Supporting Information Table S1). All Au–Au bonds on the triangle active sites are significantly stretched upon O₂ adsorption (cf. 4d–i in Figure 5). Spin-density analysis shows that the net spin on the two O atoms is fairly small in 4d–i,m (<0.30 for each O atom), consistent with strong activation of O₂. On the quadrangle face of 4j–l, O₂ is moderately activated, as evident from modest elongation of O–O bond length (~1.31 Å) and spin density on O atoms (cf. Figure 5 and Supporting Information Table S1). On an edge site (4a–c) or an irregular face (4n,o), O₂ is only weakly activated. The charge on each O atom is less than 0.01 e and the spin density is close to that of gas-phase O₂ in 4a–c,o. In addition, we examined numerous adsorption sites on 11 isomers containing the disordered-Au₅₅ core (Iso-35 to Iso-46 in Figure 1). No evidence of strong O₂ activation was found. We therefore conclude that the —PPh₃ encompassed triangle Au₆ face is the primary active site on Au₅₅(PPh₃)₁₂Cl₆. The quasi-Iₕ-Au₅₅ core possesses 20 triangle Au₆ faces, offering the largest number of active sites for O₂ activation; the D₅₅⁵-Au₅₅ core possesses 10 triangle Au₆ faces, while the disordered-Au₅₅ core has an irregular surface with fewer active sites.

The underlying mechanism for the activity of the —PPh₃-encompassed triangle Au₆ face is due to several factors. First, at the 12 vertices of the quasi-Iₕ-Au₅₅ core, the —PPh₃ ligand strongly binds with the undercoordinated vertex Au site. A back donation of electrons from P to the vertex Au renders all unpassivated edge...
Au atoms negatively charged. The negatively charged Au atoms at the edge of Au$_{55}$(PPh$_3$)$_{12}$Cl$_6$ lead to strong O$_2$ activation. A similar mechanism was found for the supported Au$_8$ cluster on the MgO surface, where Au$_8$ is negatively charged due to the F-center on the MgO surface. In Figure 6a–c, we plot the partial density of state (PDOS) of an edge Au atom in the triangle Au$_6$ face for both bare $I_5$-Au$_{55}$ and ligand-covered quasi-$I_5$-Au$_{55}$ (2a') clusters, and the DOS of the O$_2$ molecule. The Fermi energy of the Au atom is shifted to a higher en-

Figure 5. Local geometries of O$_2$ adsorbed on various sites with different Au$_{55}$ core structures: 4a,b,d–g are based on isomers with quasi-$I_5$-Au$_{55}$ and quasi-$D_5$-Au$_{55}$ cores; 4h–l are based on isomers with decahedral Au$_{55}$ core; 4m,n represent adsorption sites on isomers with the disordered Au$_{55}$ core.
ergy due to the presence of ligands (Figure 6c), resulting
in more overlap between the highest occupied mo-
lecular orbital (HOMO) of the Au atom and the lowest
unoccupied molecular orbital (LUMO) (down-spin 2
\(2^\downarrow\)) of \(\text{O}_2\). Moreover, the spatial orientation of the HOMO of
\(2\text{a} = \text{PPh}_3\) (Supporting Information Figure S2) matches nicely
with the 2\(^\downarrow\) (LUMO) of \(\text{O}_2\) at the triphenylphosphine-
compassed triangle Au\(_6\) face, facilitating orbital inter-
action and electron transfer. Figures 6 panels d and e
display the PDOS of \(\text{O}_2\) adsorbed on the bare \(\text{I}_{\text{h}}\)-Au\(_{55}\)
cluster and the ligand-covered Au\(_{55}\) (\(2\text{a}\)), respectively.
A strong resonance between the 2\(^\uparrow\) orbital of \(\text{O}_2\) and
the 5d and 6s bands of the edge Au atom occurs on \(2\text{a}^\ast\).
The spin-down 2\(^\uparrow\) orbital is partially occupied due to
the charge transfer from Au to O. In contrast, less orbital
resonance is seen for \(\text{O}_2\) adsorbed on the bare \(\text{I}_{\text{h}}\)-Au\(_{55}\)
cluster (Figure 6d) as the spin-down 2\(^\uparrow\) orbital of \(\text{O}_2\) re-
mains unoccupied. These observations indicate that
the ligands in Au\(_{55}\)(PPh\(_3\))\(_{12}\)Cl\(_6\) not only stabilize the Au\(_{55}\)
core, but also significantly affect the electronic struc-
ture of the inner Au core. We note that such a promo-
tion effect of \(\text{O}_2\) activation by linking the electron-
donation ligands on gold clusters was also proposed
independently in recent experimental\(^{52}\) and theoreti-
cal\(^{65}\) studies.

Selectivity in Styrene Oxidation. Another intriguing prop-
erty of Au\(_{55}\)(PPh\(_3\))\(_{12}\)Cl\(_6\) is its catalytic selectivity in sty-
rene oxidation. Turner et al. reported that, for styrene
oxidation, Au\(_{55}\)(PPh\(_3\))\(_{12}\)Cl\(_6\) gives rise to a much higher
yield of benzaldehyde than styrene epoxide and ace-
tophenone.\(^{10}\) This selectivity can be attributed to the
special local geometry of the active site (PPh\(_3\) en-
compassed triangle Au\(_6\) face), named as a “triangle
socket” here in light of the spatial confinement by sur-
rounding ligands. In Scheme 1, four probable reaction
pathways under Eley-Rideal mechanism\(^{19,20,26,31,66–68}\)
are shown, as well as the corresponding energy dia-
grams, for the case when a styrene molecule, along with
pre-adsorbed two O atoms, is trapped in the “triangle
socket”. Figure 7 displays corresponding molecular
snapshots and diagrams of the intermediate and transi-
tion states associated with the four reaction pathways.

On a bare gold cluster or surface, a known step for sty-
rene oxidation is the initial formation of the oxametallacy-
cle (OMME) intermediate through an electrophilic attack
of \(==\text{C}\) double bond to a positively charged gold
moiety.\(^{69–71}\) With an oxygen atom adsorbed on \(\text{I}_{\text{h}}\)-
Au\(_{55}\)(PPh\(_3\))\(_3\)Cl\(_6\) (3e), the Au(2) site (cf. Figure 3) possesses
a significant amount of positive charge due to its interac-
tion with two O atoms. Thus, the reaction pathway for sty-
rene oxidation starts most likely from an initial attack of
the Au(2) site by the \(==\text{C}\) double bond. Scheme 1a pre-
sents four most probable reaction pathways for the sty-
rene oxidation. The corresponding energy diagram
(scheme 1b) shows that trapping a styrene molecule, along with
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of 1.36 eV. Starting from the OMME intermediate (6b), four pathways (through transition states 6c, 6c', 6c'', 6c''', respectively) are possible toward the formation of three different products as illustrated in Scheme 1a. As shown in Scheme 1a,b, the most favorable pathway (6b→6c→6d→6e→6f) entails a key step for the formation of a second OMME intermediate (6d) which involves two C=O bonds with both oxygens bonded to gold atoms underneath. The activation energy to the formation of the second OMME intermediate (6b→6d) is 0.22 eV lower than that in the epoxide process (6b→6d=), and 0.30 eV lower than the intramolecular hydrogen transfer reaction (6b→6d'=). Finally, the benzaldehyde (and formic aldehyde) can readily form through the path (6d→6f) with a low-energy barrier (0.64 eV), which involves the breaking of the C–C bond. This path is responsible for a very high yield of benzaldehyde. In contrast, the energy barrier (1.5 eV) through the path 6b→6d'' is much higher than that (0.86 eV) through 6b→6d, suggesting that the formation of the second OMME intermediate containing two C–O bonds is a critical step to the high yield of benzaldehyde.

CONCLUSIONS

We show that Au55(PPh3)3Cl6 nanoparticles likely possess a quasi-i6-Au55 core. The ligands not only can ef-
Effectively stabilize the quasi-$l_{s}$ Au$_{55}$ core structure but also can significantly affect the electronic structure of the inner gold cluster. The catalytic activity of the Au$_{55}$(PPh$_3$)$_{12}$Cl$_6$ nanoparticle in the presence of O$_2$ stems from a combined effect of triphenylphosphine ligands and surface structure of the “magic-number” quasi-$l_{s}$ Au$_{55}$ core, which entails numerous ligand-encompassed triangle Au$_6$ faces as active sites. The electron back-donation from the $\text{OP(PPh}_3\text{)}_3$ groups makes the Au$_{55}$ core negatively charged. The negative charged and low-coordinated Au atoms in the active site facilitate O$_2$ activation. Furthermore, the spatial confinement by ligands gives rise to a new form of OMME intermediate containing two C–O bonds, leading to a high yield of benzaldehyde in the styrene oxidation. Identification of the ligand—encompassed gold active site will facilitate improved molecular design of a ligand-covered nanogold catalyst. Finally, we note that Turner et al. have also reported that the removal of ligands by heat treatment can significantly increase the activity and selectivity of Au nanoparticles around the size of 1.4 nm or smaller.$^{10}$ Recent DFT calculations showed that catalytic activity of a bare Au$_{55}$ nanocluster can be strongly dependent on the structure of the cluster.$^{28}$ Hence, a complete understanding of the unique catalytic activity and selectivity of bare Au nanoclusters around 1.4 nm (after heat treatment) must await experimental determination of atomic structure of these gold clusters. In future, we will investigate structure-activity-selectivity relationship of the ligand-covered cluster under the Langmuir-Hinshelwood mechanism.$^{19,20,26,31,66,67}$ This mechanism requires co-adsorption of both O$_2$ and styrene molecules at the active site. Research in this direction is under way.

Figure 7. Snapshots of key reaction intermediates and transition states in the styrene oxidation pathway shown in Scheme 1.
COMPUTATIONAL METHODS

Density functional theory (DFT) calculations were carried out using the DMol3 4.3 package. Geometric optimization of Au55(PPh3)12Cl6 and Au55(PH3)12Cl6 nanoparticles were performed by using the generalized gradient approximation in the form of the Perdew–Burke–Ernzerhof (PBE) functional, as used in many previous theoretical studies of gold cluster catalysis. The d-polarization-included basis set (DNP) with the effective core potential (ECP) including partial consideration of scalar relativity for the Au element was chosen. All-electron calculations were otherwise applied for H, C, Cl, and P elements.

The self-consistent-field calculation has convergence criteria of 10−3 Hartree. The tolerances of energy, maximum force, and maximum displacement for the geometry optimization were set to be 1.0 × 10−3 au, 0.003 au, and 0.005 au, respectively. Optimization convergence thresholds for the root-mean-square forces on the atoms were set to be 0.002 au in transition-state search. The combined linear synchronous transit (LST) and quadratic synchronous transit (QST) methods were adopted to locate the transition state.

Theoretical XRD patterns are calculated based on the Debye formula:
\[
I(s) = \sum \sum \frac{\cos \theta}{(1 + \cos \theta)^2} \exp \left( - \frac{B s^4}{2} \right) \sin(2\pi d_s) \]

where \(s\) is the diffraction vector length, satisfying \(s = 2 \sin \theta / \lambda\). The wavelength \(\lambda\) and \(\alpha\) parameter are 0.1051967 nm and 1.01, respectively (determined from the experimental set-up); \(B\) is 0.03 nm², a damping factor reflecting thermal vibration; \(d_s\) is the distance between atoms \(i\) and \(j\). The corresponding atomic numbers are used for the scattering factors \(f\).

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Supporting Information Available: Adsorption energies, Hirshfield charges, Mulliken spin density of O2 adsorption on various active sites, and an energy profile for the O2 dissociation on a reaction site of Au55. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


