



# Theoretical insights into the selectivity of 1,6-enyne cycloisomerization on gold clusters: Orbital interaction role



Yafei Luo<sup>a</sup>, Zhongzhu Chen<sup>a</sup>, Dianyong Tang<sup>a,b,\*</sup>, Ying Tang<sup>b</sup>, Jin Zhang<sup>a,b,\*</sup>, Jianping Hu<sup>c</sup>

<sup>a</sup>International Academy of Targeted Therapeutics and Innovation, Chongqing University of Arts and Sciences, Chongqing 402160, PR China

<sup>b</sup>Chongqing Key Laboratory of Environmental Materials and Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, PR China

<sup>c</sup>College of Chemistry, Leshan Normal University, No. 778, Binhe Road, Leshan, Sichuan 614000, PR China

## ARTICLE INFO

### Article history:

Received 24 October 2016

Received in revised form 30 March 2017

Accepted 13 May 2017

Available online 17 May 2017

### Keywords:

Gold nanoclusters

Density functional theory

Cycloisomerization

Orbital interaction

Regio-selectivity

## ABSTRACT

In the present article, the mechanism of 1,6-enyne cycloisomerization catalyzed by the planar Au<sub>8</sub> cluster was investigated in details by means of density functional theory. The effects of the size and shape of the gold nanoclusters (Au<sub>7-20</sub>) on their catalysis of 1,6-enyne cycloisomerization were also studied. The computational results indicate that the main reaction channels of the 1,6-enyne cycloisomerization on the Au<sub>8</sub> cluster are the 5-exo-anti-cycloisomerization, and the single cleavage pathway is slightly more feasible than the double cleavage pathway. The selectivity of 1,6-enyne cycloisomerization catalyzed by the gold clusters is controlled by the orbital interaction between the gold atoms and the carbene fragment in the migration of CH<sub>2</sub> group. In addition, the influence of coordinate environment of the gold atoms on adsorption energy, catalytic activity, and regio-selectivity were amply interpreted as well.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Gold nanoparticles have received much attention because of distinctive catalytic properties. Haruta et al. reported that highly dispersed gold nanoparticles on metal oxide supports exhibit exceptional catalytic activity towards CO oxidation [1]. Subsequently, numerous experimental studies have shown that gold nanoparticles supported on metal oxides are active for numerous reactions, including the CO oxidation [1,2], the selective oxidation of olefins and alcohols [3,4], synthesis of H<sub>2</sub>O<sub>2</sub> [5], the water-gas shift reaction [6], and the furan-yne reaction [7]. Gold nanoparticles supported on metal oxides, such as TiO<sub>2</sub> and CeO<sub>2</sub>, were recently found to catalyze organic transformations [8]. Examples include the cycloisomerization of 1,6-enynes [9–11], C–C and C–N coupling reactions, and the selective hydrogenation of unsaturated compounds [12,13]. Our limited understanding of the catalytic activity of gold nanoparticles, particularly the effect of their size and shape on activity, hampers the design and synthesis of cost-effective catalysts for large-scale application [14].

\* Corresponding authors at: International Academy of Targeted Therapeutics and Innovation, Chongqing University of Arts and Sciences, Chongqing 402160, PR China.

E-mail address: [tangdy2008@163.com](mailto:tangdy2008@163.com) (D. Tang).

The oxidation of CO and alkenes has attracted the most attention among all the gold cluster-catalyzed reactions [15–23]. Several studies have investigated the organic transformations, such as the selective oxidation of styrene and C–C coupling [24–30]. The mechanism of C–C coupling on gold nanoparticles was investigated by Boronat et al. [28,29]. The effects of the size and shape of the gold nanoclusters on this reaction may significantly differ from those on CO oxidation [13]. Herein, 1,6-enyne cyclization on the various-sized and shaped gold nanoclusters were investigated to clarify the effects of size and shape on their catalysis [31]. This investigate is different from the previously reported results, that is, the cycloisomerization of 1,6-enyne catalyzed by the bare Au<sub>38</sub> cluster was explored with the help of density functional theory (DFT) [30].

We expect that our investigation could provide some useful information for guiding the further experimental studies.

## 2. Computational details

The hybrid meta-GGA functional TPSSh [32] combined with the LanL2DZ basis set [33] (for gold) and 6-31G\* basis set [34–39] (for C, H, P, and O) were used for geometry optimizations and frequency calculations. As the previous report shown, for the energy computations of small gold clusters [40], the TPSSh functional together with the LAN2DZ basis set and 6-31G\* basis set were

reasonable and reliable. The mixed basis sets were denoted as 6-31G\*-LanL2DZ. Additionally, the hybrid meta-GGA functional TPSSh was utilized because of the very good metal-ligand bond energies it is reported to provide [41–46]. Based on each optimized stationary point, vibrational analysis was performed to determine its character (minimum or saddle point) and to obtain the zero-point vibrational energy (ZPVE). For each transition state, intrinsic reaction coordinate (IRC) [47,48] calculations were performed in both directions to connect the corresponding intermediates at the above level. A step of 0.1 or 0.05 amu<sup>1/2</sup> bohr was used in the IRC procedure. Wavefunction stability calculations were performed to confirm that the calculated wave functions corresponded to the ground states [49–51]. The effect of the polarized surroundings of DCE on the reaction species was evaluated at the same level. Self-consistent reaction field (SCRf) single-point energy calculations on the gas-phase-optimized structures in a DCE continuum (DCE as solvent) were carried out using Truhlar and coworkers' SMD solvation model [52]. All the above mentioned calculations were performed by using the Gaussian 09 software package [53].

For all calculations, the dispersion interaction was not taken into account, including two main reasons. One aspect, according to the compute results, the adsorption energies of the enyne on gold nanoclusters are –14.9 to 27.3 (–11.7 to 21.8) kcal/mol in the gas phase (DCE solvent), respectively, indicating that the interaction between the enyne and gold nanoclusters are chemical absorption. For another respect, in order to test the influence of dispersion correction on energy barriers, the single and double cleavage pathways of the 1,6-enyne cyclization on the Au<sub>7</sub> cluster were investigated using TPSSh functional with D3 dispersion correction [54] developed by Grimme et al. The calculated adsorption energy is –21.8 (–17.0) and activation energy of **C1** → **TS1**/**I1** is –11.7 (–9.1) in gas phase (DCE solvent), respectively, which are comparable with the results computed by TPSSh/6-31G\*-LANL2DZ (Fig. S2). To sum up, on the basis of above mentioned discuss, the dispersion correction can cause little effect on the calculate results for this studied system.

In addition, in an effort to demonstrate the reliability of computational results, the TPSS functional is employed to calculate the energies of the all geometries, including the reactants, products, intermediates and transition states. The corresponding computed results are labeled as purple color and exhibited in the potential energy profiles. By comparing the results calculated via TPSSh and TPSS, it can be demonstrated that the TPSSh used to study the energetics of small gold is reasonable and reliable in this paper.

### 3. Results and discussion

The 1,6-enyne cyclization catalyzed by the various-sized gold clusters (Au<sub>7</sub>–Au<sub>20</sub>) were studied to address the relationship between the catalytic activity and the size of gold clusters. These include planar Au<sub>7</sub>–Au<sub>10</sub>, flat cage (Au<sub>12</sub>–Au<sub>14</sub>), hollow-cage (Au<sub>16</sub>), and pyramidal (Au<sub>19</sub> and Au<sub>20</sub>). The structures of these nanoclusters (Au<sub>n</sub>, 7 < n ≤ 20) are shown in Fig. 1, and were taken from previously resolved global minimum structures, based on photoelectron spectroscopy (PES) measurements and DFT global optimizations [55–59]. Because the catalytic behavior of the small planar clusters may be different from that of the three-dimensional gold cluster, the full mechanism of the 1,6-enyne cyclization catalyzed by the Au<sub>8</sub> cluster was studied. As previously reported, the single and double cleavage pathways are the key steps of the regio-selectivity of main products for the 1,6-enyne cyclization catalyzed by the Au<sub>38</sub> nanoclusters and gold(I) complexes [30]. Hence, only the single and double cleavage pathways were investigated for the other gold structures in the present

study. In order to obtain the meaningful comparison, for all gold clusters in this study, the reaction mechanisms are identical.

#### 3.1. Full mechanism of 1,6-enyne cyclization catalyzed by Au<sub>8</sub> cluster

Firstly, the full mechanism of the 1,6-enyne cyclization catalyzed by the Au<sub>8</sub> cluster is studied since the planar gold clusters exhibit different catalytic behavior from the tridimensional gold clusters. As shown in Fig. 2, the adsorption of the enyne on the Au<sub>8</sub> cluster is exothermic by about 24.2 (19.9) kcal/mol in the gas phase (DCE solvent). For the planar clusters, there might be poly interactions. However, the interaction of the reactant with only one atom of the clusters is chosen throughout the study, because the bridge absorption between the clusters and reactant cannot obtain the corresponding products. The adsorption energies of the substrate (1,6-enyne) on the Au<sub>8</sub> cluster are larger than that of the Au<sub>38</sub> clusters due to the low coordinate number of the gold site in Au<sub>8</sub> cluster. Then, the formation of **I1** via 5-exo-anti-cycloisomerization is exothermic by about 5.6 (7.4) kcal/mol with about 8.5 kcal/mol of energy barrier in the gas phase (DCE solvent). The forming C1–C and C2–C bonds are 2.11 and 2.37 Å in **TS1**, respectively. The C1–C2 and C–C bonds in **TS1** are lengthened to 1.37 and 1.29 Å, respectively. These bonding variations indicate that the **I1** is formed via **TS1**. After the formation of **I1**, the single and double cleavage pathways need to overcome 10.5 (6.8) and 12.6 (8.7) kcal/mol energy to generate the products of complexes **P1** and **P2** in the gas phase (DCE solvent), respectively. The single cleavage pathway involves the formation of C–C1 bond and the cleavage of C1–C2 and C1–C bonds, while the double cleavage pathway involves the formation of C1–C bond and the cleavage of C1–C2 and C–C bonds. The energy barriers of the two pathways (Table 1) demonstrate that the single and double cleavage pathways are comparative on Au<sub>8</sub> clusters. To address the origin of the selectivity of the single and double cleavage pathways, the energy decomposition analysis (EDA) [60–62] and orbital analysis were performed by Multiwfn program [63]. The interaction energy between the Au<sub>8</sub> and substrate fragments of **TS2** (the single cleavage pathway) decreases about 24.0 kcal/mol, while that of **TS3** remains largely unchanged (Table 2). Additionally, as shown in Fig. 3, the involved orbitals that interact in **TS2** were mainly from the occupied 5d orbitals of the Au atom and the sp<sup>2</sup> orbital of the substrate fragment. The orbital interaction diagram between the Au<sub>8</sub> and the substrate fragments demonstrates that the orbital interaction in **TS3** was the donation from the sp<sup>2</sup> orbital of the substrate fragment to the unoccupied 6s and occupied 5d orbitals of the Au atom. Hence, the high energy barrier of the double cleavage pathway should be ascribed to the partially occupied d orbital of the planar gold clusters. The final step is the decomposition of **P1** and **P2** to form product and to regenerate Au<sub>8</sub> cluster. The decomposition of **P1** is endothermic by about 12.0 kcal/mol and that of **P2** is exothermic by about 15.0 kcal/mol.

The formation of **I2** via the 5-exo-syn-cycloisomerization needs to overwhelm about 16.5 (16.4) kcal/mol in the gas phase (DCE solvent) (Fig. 4). The differences of energy barriers between **TS1** and **TS4** arise from the repulsion between the hydrogen atom on the C atom and hydrogens on the C1 and C2 atoms in **TS4** (Fig. S1). The energies of **I1** and **I2** are comparable. Due to the syn configuration of the H (on C atom) and CH<sub>2</sub> group (C1 atom), only the CH<sub>2</sub> group (C1 atom) transfers from the C atom to the C atom to produce the cyclobutene intermediate **B1**. Finally, the C1–C2 bond is broken to form **P3** with an energy barrier of about 30.0 kcal/mol. Obviously, the 5-exo-syn-cycloisomerization is unfavourable kinetically.

The energy barriers of the 6-endo-cycloisomerization of **C1** are 19.0 and 15.9 kcal/mol with exothermicity of 5.9 and 8.0 kcal/mol in the gas phase and DCE solvent, respectively. The formed **I3** is

Download English Version:

<https://daneshyari.com/en/article/5392181>

Download Persian Version:

<https://daneshyari.com/article/5392181>

[Daneshyari.com](https://daneshyari.com)