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The mechanisms for triple gold(I)-catalyzed (4+1) cycloaddition of methylenecyclopropane with 7-naphthyl-1,3,5-cycloheptatriene: Insight into from density functional calculations

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ABSTRACT

The mechanisms of (4+1) cycloaddition for the reaction of 7-naphthyl-1,3,5-cycloheptatriene with methylenecyclopropane via triple gold(I) catalysis to generate cyclopentene have been studied by density functional theory (DFT) calculations. Free energy profiles have been calculated for the Au-, Cu- and Ag-catalyzed reactions to evaluate possibility of these cycloaddition reactions. The calculations showed that the reaction mechanism proceeds through the transformation of methylenecyclopropane to afford cyclobutene via an isomerisation, and subsequent retro-Buchner reaction takes place to give the gold(I) carbene. Finally, cyclopentene is produced catalyzed by carbene complex. On the basis of the calculations, two C—C bonds cleavage in retro-Buchner reaction was predicted to be the rate-limiting step with a free energy barrier of 27.1 kcal/mol. We also demonstrate why no reaction occurs for the other Ag, Cu and Au catalysts studied. Present calculations are consistent with the experimental observations and could provide new insights into the gold catalysis.

1. Introduction

Carbenes have attracted wide interest as one-carbon synthon in chemical synthesis [1–4], and now have been extended to the (4+1) cycloadditions [5–7], where the gold(I) carbenes are used as the C_1 component in the cycloaddition reactions. Spino et al. [8] investigated the reaction of dialkoxycyclocarbenes with dienes to form (4+1)-cycloadducts with good yields and stereoselectivities. Barluenga et al. [9] studied the (4+1) cycloaddition reactions of Fischer alkoxy(alkenyl)carbene complexes with 1,3-dienes. The carbene ligand in transfer reaction acts as a three-carbon-atom synthon, which is used as a one-carbon-atom synthon in previous synthesis. Barluenga et al. [10] reported the (4+1) cycloaddition reactions of Fischer carbene complexes with α,β-unsaturated ketones and aldehydes to generate 2,3-dihydrofurans. The reaction passes through the ring enlargement of the formylor acylcyclopropanes.

Recently, Echavarren et al. investigated 7-substituted 1,3,5-cycloheptatrienes **1** undergoing retro-Buchner reaction via gold catalysts to give carbenes **2** (Scheme 1) [11]. They proposed a novel (4+1) cycloaddition reaction of **1** with methylenecyclopropanes **3** or cyclobutenes **4** to afford cyclopentenes **5** [12]. For the reaction of **1** with **3**, gold(I) has triple catalytic role. It can isomerize **3** into **4**. In parallel, It can generate gold(I) carbenes **2** from **1**, which can cyclopropanate the cyclobutenes. Finally, gold(I) carbenes **2** can break the internal C—C bond of the bicyclo[2.1.0]pentanes to yield cyclopentenes. This reaction is seen as one carbon insertion into a double bond, which has only been obtained in rare cases for the formation of dihalocarbenes [13–15].

Experimentally, many efforts have been done to investigate the (4+1) cycloaddition of methylenecyclopropanes with 7-naphthyl-1,3,5-cycloheptatrienes by means of gold(I) catalyst, however, the whole reaction mechanisms are still unsolved, since the intermediates cannot be isolated for these catalytic reactions. Herein, the DFT calculations have been carried out to explore the reaction mechanisms of these cycloaddition reactions, and the reaction activity differences between Au, Cu and Ag catalysts, thermodynamic and dynamical properties of plausible reaction mechanisms have also been discussed.

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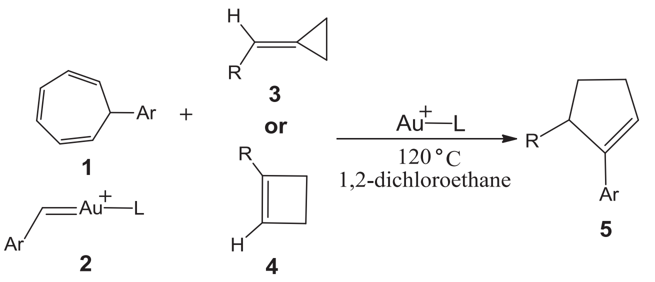
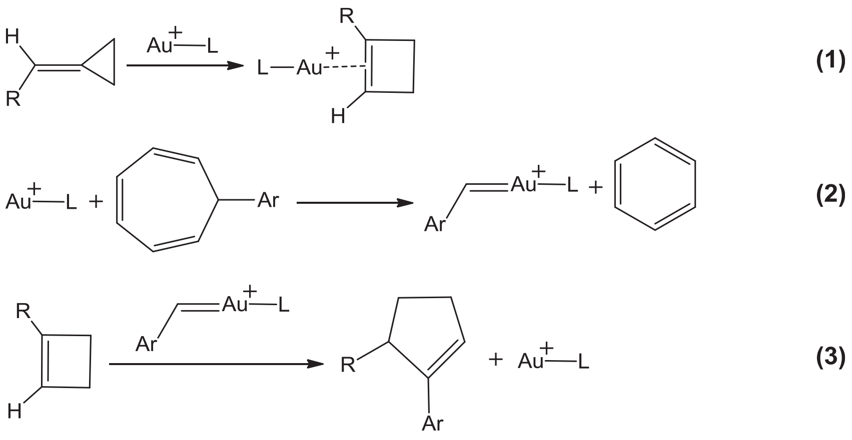


Scheme 1. The (4+1) cycloaddition between **1** and methylenecyclopropanes **3** or cyclobutenes **4** to form cyclopentenes **5**.

2. Computational details

All species in present calculations were optimized via the DFT calculations at the hybrid B3LYP level [16–19], and this method has been used in previous studies on the Au-catalyzed reactions [20–26]. The 6-31G(d) basis set was selected for the C and H atoms, while the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) [27,28] were used for the Au and P atoms. In addition, the polarization functions were added for Au(ζ_f) = 1.050, Ag(ζ_f) = 1.611, Cu(ζ_f) = 3.525 and P(ζ_d) = 0.387 [29]. Frequency calculations were used to confirm the stationary points as minima or transition states. In order to validate the



Scheme 2. The mechanisms for the cycloaddition of methylenecyclopropanes with 7-naphthyl-1,3,5-cycloheptatrienes proposed by Echavarren and coworkers [12].

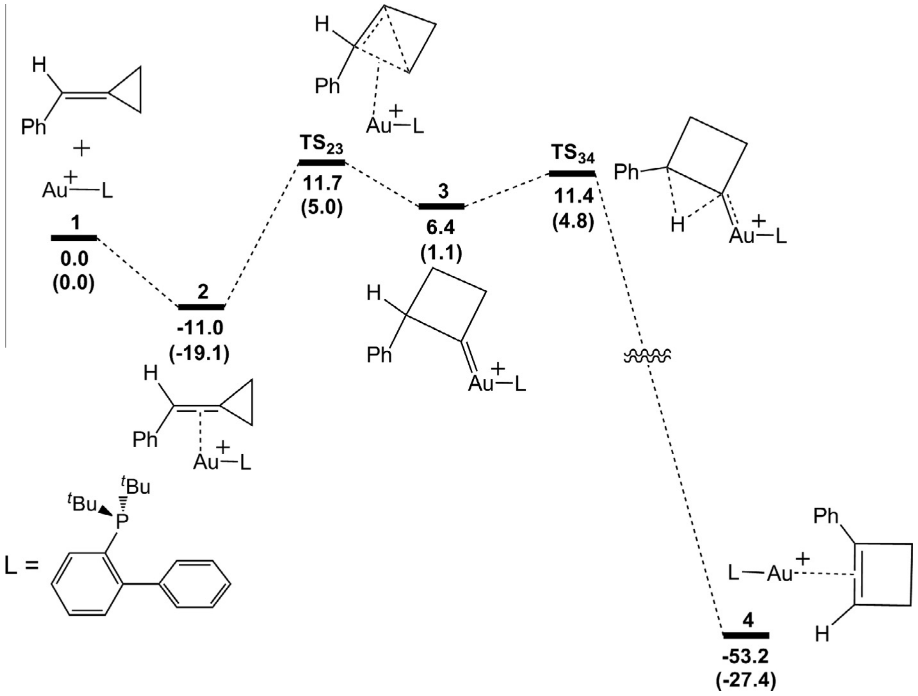


Fig. 1. Free energy profiles calculated for the formation of the η^2-cyclobutene–gold(I) complex **4** from methylenecyclopropane via ring expansion catalyzed by gold(I) catalyst. The relative free energies and relative energies (in parentheses) are given in kcal/mol.