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Theoretical study on the isomerization of propargyl derivative to conjugated diene under Au(I)-catalyzed reaction: A DFT study

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ABSTRACT

Pure and hybrid quantum mechanical calculations were performed to study the pathway of the isomerization of propargyl derivative to conjugated diene under the catalysis of Au(I) complex derived from the biphenyl-2-ylphosphine with a basic amino group on the pendant phenyl ring. It was previously proposed that a push–pull driving force operates orthogonally during the progress of the reaction. Our study reveals that this push–pull force is syn-periplanar rather than orthogonal. Steric pressure by the phosphine ligand, together with the push–pull interaction favors the transformation of η^2 to η^1 mode of Au complex. These effects are responsible for the increasing acidity of the transferring proton. The bent structure of the product suffers from the reduced steric pressure, thus favors the formation of the conjugated diene.

1. Introduction

Conjugated diene system is a useful motif employed for the generation of several synthetic and natural products [1–10] and the past decade has witnessed the development of several ambient protocols for the synthesis of diene from allene derivatives [11–17]. Recent literature survey shows that Au(III) metal ion can be employed as an effective catalyst for the isomerization of unactivated allene to conjugated diene [18–20]. Though the reaction occurs smoothly under the catalysis of Au(III) salt, a decrease in efficiency of Au(I) ion has sometimes been observed in the reaction [18,19,21]. However, a recent investigation on designed ligand reveals that Au(I) can also catalyze the process not only from an allene derivative but also from its precursor, an alkyne system (Scheme 1) [22].

The reaction pathway involves the generation of allene [23] as an intermediate and the hydrogen migration takes place under the assistance of the basic amino group present on a pendant phenyl ring [24,25] of the designed biphenyl-2-ylphosphine ligand of the Au(I) complex. While forming the product, two successive deprotonation-protodeauration reactions take place and it has been observed that the processes can go only through an intramolecular pathway rather than intermolecular one [22]. This fact reveals an association of the entropy factor in isomerization process. While interpreting the mechanistic pathway of the reaction the authors proposed that the metal atom in the alkyne complex lowers the π^* orbital of the C–C triple bond perpendicular to the metal-alkyne plane and thus exerts a pull force orthogonally on the neighboring C–H bond [22]. They have also compared it with the lowering of π^* orbital of a carbonyl group with α-hydrogen. Hence, the relative orientation of the C–H bond of the departing hydrogen atom with respect to the metal allene complex is proposed to be orthogonal (Fig. 1(a)). It has been postulated that the bound metal ion on the propargyl system in its stable geometry lowers the pk_a value of the breaking C–H bond and thus allows a soft deprotonation by the basic amino group positioned on the biphenyl ring attached to the phosphine ligand.

While investigating a similar system theoretically, our preliminary study on the transition structure geometry of the amine catalyzed deprotonation at α-carbon of a Au-bound alkyne complex reveals that the dissociating C–H σ-bond does not orient orthogonally relative to the metal-alkyne bond (Fig. 1(a)); on the contrary, the former one lies in syn-periplanar direction with respect to the later one (Fig. 1(b)). This observation, which clearly suggests that the push–pull interaction is not operated orthogonally, promote us to make a thorough investigation on the actual reaction pathway for a deeper view on the driving force associated to the reaction mechanism.

While optimizing the ligand structure of the catalyst, the investigators noticed that the simple 3′ or 5′-dimethylamino on the pendant biphenyl moiety of the ligand is very inefficient for the isomerization (entry 1 of Table 1) [22]. Replacing the dimethyl amino with a piperidine moiety (entry 2) shows an increased effi-

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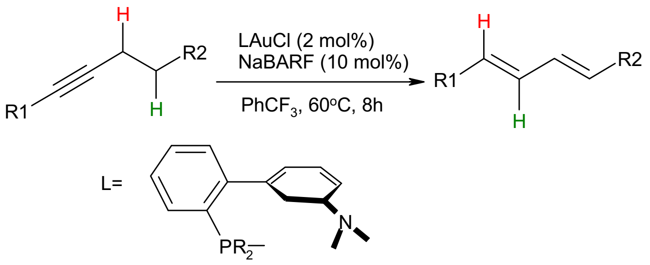
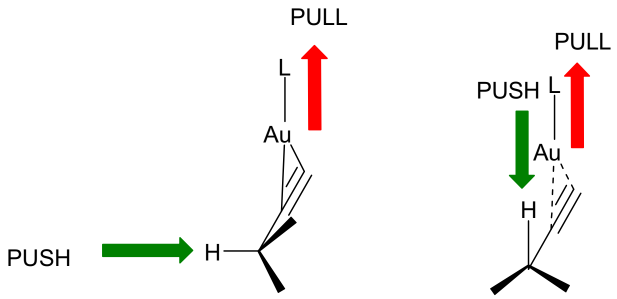


Scheme 1.



(a) (b)

Fig. 1. (a) Orthogonal orientation of the push–pull force for deprotonation of metal bound alkyne system as proposed previously; (b) syn-periplanar orientation of the push–pull force for deprotonation as revealed from the present theoretical study of the transition structure.

ciency of the catalysis to generate the product. However, a decrease in yield had been observed when the adamentyl system is replaced with cyclohexyl ring (entry 4). Placement of two additional methyl groups at the 3′ and 5′ position of the piperidine moiety (entry 6) results an appreciable change in the overall yield of the product. On the other hand, insertion of electron withdrawing substituent at the para position with respect to the phosphine group (entry 5) and the insertion of electron releasing methoxy group at the para position with respect to the amino group in the other phenyl ring (entry 3) also show an increase in the product yield [22]. Though, the placement of these substituents on the phenyl ring does change the acidity and basicity of the Au ion and amino group respectively by altering the electron density around them, the other changes in ligand structure are appeared to produce more prominent steric effect on the system that favors the progress of the reaction to generate the conjugated diene. Our mechanistic interpretation reveals how the steric factor along with a syn-periplanar push–pull force assists the progress of the reaction.

2. Computational methods

To characterize the actual driving forces involved in this reaction we have made a single-layered quantum chemical (DFT) and a bi-layered (DFT-PM6) oniom [26] study of the reaction. For the DFT calculation we have used LANL2DZ basis set with its ECP for Au atom [27–29] and 6-31G (d,p) basis set [30–35] for the other atoms. The hybrid functional B3LYP [36] has been used here for the present calculations. Optimization of geometries for all stationary points were performed at the level of theory as indicated. IRC calculation were further used to check whether the TSs properly connect the reactants and products. Necessary thermodynamic corrections were incorporated at the reaction temperature (60 °C) [22]. All the structures have been optimized by using Gaussian 09 package [37]. Solvent effects were computed by the Polarizable Continuum Model (PCM) [38] at the same level of theory using the gas-phase optimized structures. The standard parameters for dichloromethane (DCM) have been used, as the dielectric constant of this solvent is similar to the actual solvent (trifluorotoluene) that was used in the experimental condition. All the stationary points are plotted using relative Gibb's free energy of the corresponding system in gas phase. The energy changes due to the solvent effect for each stationary point are shown in parenthesis in Figs. 2 and 7 (all the energies of the each stationary points are given in SI as Table SI-1).

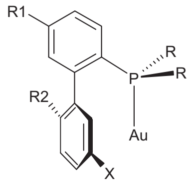
3. Results and discussion

To study whether there is any entropy contribution in the driving force of the reaction, we have chosen the inter and intra molecular isomerization of 1-butyne to 1,3-butadiene under the gold catalyzed condition and considered two proton transferring processes in common mechanistic pathway as shown in Scheme 2.

The detail PES of the two pathways is shown in Fig. 2. The pathway in red color shows the energy of the stationary points for the isomerization of metal bound 1-butyne assisted by a separate aniline base (B in Scheme 2) whereas, the green colored path represents the same transformation with the assistance of a basic dimethyl amino group present at the 3′-position of the pendant biphenyl ring of phospine ligand (B in Scheme 2). Though the former pathway (red colored) represents the proton shifting process intermolecularly the later one (green colored) shows the same process intramolecularly. Both the pathways consist of four proton transferring transition structures in which the first two transition structures (1-TS1 & 1-TS2 for intermolecular pathway and 2-TS1 & 2-TS2 for intramolecular pathway) are associated with the alkyne to allene conversion and the later two (1-TS3 & 1-TS4 for intermolecular and 2-TS3 & 2-TS4 for intramolecular pathway) are associated with the conversion of allene to conjugated diene.

At the starting point, the amino group abstracts the proton from the adjacent methyl substituent in metal bound alkyne complex

Table 1
Summary of optimization of ligand of the Au(I) salt that catalyzes the isomerization of 1-phenyl hexyne to conjugated diene as revealed from the report [22].

General structure of the catalyst	Sl. No.	Au complex with ligand L having substituent				Yield of conjugated diene (%)
		X	R	R1	R2	
	1.	NMe_2	Ad	H	H	3
	2.	$N(CH_2)_5$	Ad	H	H	19
	3.	$N(CH_2)_5$	Ad	OMe	H	35
	4.	$N(CH_2)_5$	Cy	OMe	H	4
	5.	$N(CH_2)_5$	Ad	OMe	CF_3	77
	6.	Cis-3,5-dimethylpiperidin-1-yl	Ad	OMe	CF_3	90

$N(CH_2)_5$: Piperidin-1-yl; Ad: Adamantan-1-yl; Cy: Cyclohexyl.