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Mechanism of the Gold(III)-Catalyzed Isomerization of Substituted Allenes to Conjugated Dienes: A DFT Study

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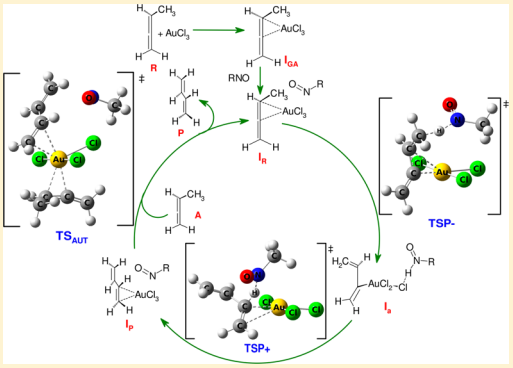
Supporting Information

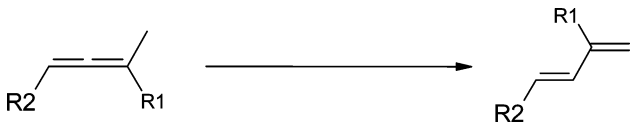
ABSTRACT: The mechanism of gold(III) [Au(III)]-catalyzed isomerization of alkyl-substituted allenes to conjugated dienes in the presence of a nitroso compound (additive) was studied quantum mechanically using hybrid density functional PBE0 with 6-31G** basis set for lighter atoms and (aug)-ccpVDZ basis set and LANL2 electron core potential for Au atom. Several pathways, involving the nitroso compound in a free or bound state to the gold−allene (GA) complex, were investigated. Calculated results reveal that the unbound nitroso compound acts as a better proton transferring agent in the isomerization process and utilizes its own nitrogen atom to carry the proton. While comparing the efficiency of other basic reagents to carry out the process, it appeared that the moderate basicity of the nitroso compound plays a crucial role to reduce the activation barrier of the reaction pathway. A similar pathway was also investigated using a gold(I) [Au(I)] catalyst and found to be less favorable than the process catalyzed by a Au(III) catalyst. All these facts agree well with the experimental reports for the reaction.



INTRODUCTION

The transformation of alkyl-substituted allene derivatives to conjugated dienes has received much attention from synthetic organic chemists for many years (Scheme 1).[1] Without any catalyst or solvent, this process was found to require high activation energy and lacked selectivity.[2] Recently, the facile isomerization of a specific class of allenes to conjugated dienes using suitable solvents and reagents was reported. Hsung and his group observed that a number of allenamide derivatives, when heated in acetonitrile solution, isomerize to 2-amido conjugated dienes.[3] This reaction may occur even at room temperature when certain organic acids are used as an additive. Though this protocol was found to be applicable to a specific class of allene derivatives for generating the 2-amido dienes, the methodology cannot be applied to carry out the isomerization of unactivated allenes to 1,3-dienes under ambient conditions. However, Ting et al. reported the isomerization of several alkyl-substituted unactivated allene derivatives to 1,3-butadiene systems under metal-catalyzed conditions.[4] Their observations revealed that Au(III) chloride[5] with an additive, nitrosobenzene, is capable to catalyze the transformation of an unactivated allene to a conjugated diene almost exclusively at room temperature.

Scheme 1



In the search for a plausible reaction mechanism, investigators encountered several confusing questions during the developmental stages of the isomerization protocol. Formerly, it was believed that the isomerization takes place through a concerted [1,3] sigmatropic migration of hydrogen. According to the Woodward−Hoffmann symmetry rule, the migration should occur in an antarafacial manner if the process takes place in a concerted way.[6] Though this proposal can explain, qualitatively, the requirement of high activation energy for the process, a discrepancy in the actual energy values, measured by theoretical and experimental methods, was pointed out by Jensen.[7] On the basis of this observation, the author proposed that an alternative pathway, other than [1,3] sigmatropic migration, should exist for the isomerization reaction of the substituted allenes to conjugated dienes. The possibility of an alternative pathway became clear when the isomerization at low temperature was observed by Hsung and his group.[3] On the basis of the experimental conditions required for this isomerization process, we have recently proposed a new bimolecular pathway that can rationalize not only the energetics of the reaction but also the stereoselectivity and regioselectivity associated with the process.[8] This mechanistic pathway may be considered as a tandem ene/retro-ene process involving two consecutive steps.

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Scheme 2

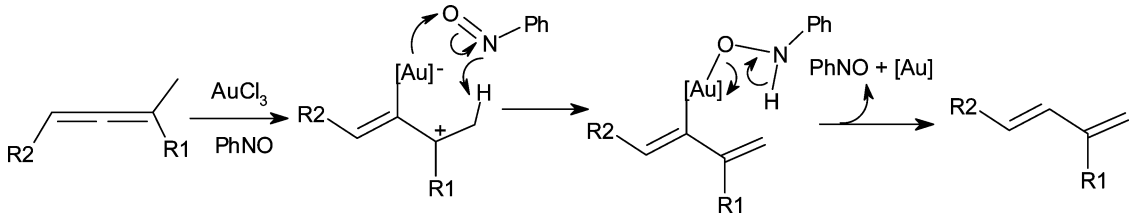

Table 1. Short Description and Global Activation Barrier (kcal mol^{-1}) for Each Pathway Shown in Scheme 3

nature of reaction/mechanism			pathway	step with highest activation barrier	global activation energy (kcal mol^{-1})	shifting of global free energy of activation due to DCM	shifting of global free energy of activation due to toluene
uncatalyzed reaction	concerted unimolecular [1,3] sigmatropic process (intramolecular)		1	concerted H-migration	68.42 (68.25)[a]	−0.12	−0.06
	stepwise bimolecular ene/retro-ene process (intermolecular)		2	retro-ene step	56.53 (56.34)	1.96	1.89
gold(III)-catalyzed reaction	hydrogen transfer by nitroso compound bound to gold atom in GA complex	hydrogen transfer by using nitrogen atom Conf-1	3	proton abstraction	48.79 (48.39)	−3.6	−1.72
		hydrogen transfer by using nitrogen atom Conf-2	4	ligand substitution followed by proton abstraction	70.38 (69.54)	−2.58	−1.01
		hydrogen transfer by using oxygen atom	5	protodeauration	26.86 (27.29)	2.00	1.16
	hydrogen transfer by nitroso compound bound to allene moiety in GA comlex	hydrogen transfer by using nitrogen atom Conf-1	6	hydrogen donation	84.08 (83.79)	−0.97	−0.04
		hydrogen transfer by using nitrogen atom Conf-2	7	hydrogen donation	84.08 (83.79)	−0.97	−0.04
		hydrogen transfer by using oxygen atom	8	hydrogen donation	81.79 (81.90)	−1.48	−0.81
	hydrogen transfer by unbound (free) nitroso compound	hydrogen transfer by using nitrogen atom	9	protodeauration	20.06 (19.29)	−0.09	0.56
		hydrogen transfer by using oxygen atom	10	protodeauration	26.86 (27.29)	2.39	3.33

[a]Values in parentheses represent the energies with dispersion corrections.

Though the bimolecular mechanism can successfully rationalize uncatalyzed allene isomerization, this mechanistic pathway is unsuitable for Au(III)-catalyzed isomerization,[4] because the activation of the allenic double bond under Au catalysis generally follows a different pathway.[9] In this context, several reports on the activation of the alkyne triple bond by Au(III) toward different nucleophilic addition reactions should be noted.[10,11] A comparative analysis of the relativistic and nonrelativistic pathways for Au(III)-catalyzed nucleophilic addition of a water molecule to a triple bond is noteworthy.[10] The different reactivity of gold with respect to platinum has also been reported on the basis of frontier orbital pictures of the metal salts complexed to a representative alkyne system.[11]

A literature survey shows that the synthetic utility of the Au salt as a catalyst has grown enormously over recent decades.[9,12] Several reactions of allene derivatives under gold-catalyzed conditions have efficiently been performed with high yield and specificity.[13] Among them, the cycloisomerization of allenes, involving an intramolecular nucleophilic addition, is, by far, the most common reaction. Reported examples include the formation of oxygen (furan,[14,15] dihydrofuran,[16] dihydropyrans,[17] lactone[18]), nitrogen,[19−21] and sulfur[22,23] heterocycles along with some carbocyclic compounds.[24−26] Moreover, the transformation of an allene derivative to an acyclic conjugated system has also been reported by several researchers.[27−30] Most of these transformations involve a sigmatropic rearrangement, where a C−O or C−H bond cleavage takes place as a mandatory step. The problem of allene isomerization under the gold catalysis,[4] reported here, is also associated with the cleavage of C−H bond, which is mechanistically similar to the reaction observed by the Shi and Li group.[31] In this reaction, the conversion of (cyclopropylidenecyclohexyl)benzene to a biaryl derivative takes place through the migration of hydrogen. The proposed mechanistic pathway by Ting et al. for the allene isomerization[4] under Au(III) catalysis shows that the mandatory hydrogen migration[32] in the GA complex is assisted by a nitrosobenzene molecule bound to the Au(III) ion (Scheme 2).

A deeper insight into the mechanism reveals that nitrosobenzene may assist the hydrogen shifting process by utilizing either its nitrogen or oxygen atom in bound or unbound conditions. Our present quantum mechanical (QM) study on this isomerization determines a favorable mechanism and points out the specific role of the metal ion and nitrosobenzene during the progress of the reaction. Two other experimental observations, that a strong base such as trialkylamine is ineffective and that Au(III) is superior to Au(I) in the catalytic process of the allene isomerization, has also been investigated and rationalized properly. In designing the mechanistic pathways, we excluded the possible involvement of Au clusters[33] in the catalysis of the isomerization process. It is our belief that this investigation would give better insight into the mechanism of the allene isomerization under Au(III) catalysis and guide experimentalists in designing efficient reagents that can effectively assist the hydrogen transfer process in similar types of reactions.

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Table 2. Relative Energies (ΔE_{0K}) of the Stationary Points, the Global Activation Barrier and Shifting of Global Free Energies of Activation in Different Solvents (in kcal mol^{-1}) of Pathway 9 (#→9) and Its Modification Using Different Reagents and Catalysts (#→Ph, NMe3 or g1)

		relative energies of the stationary points on the PES of modified pathway 9							shifting of global free energy of activation due to	
Sl. no.	reactants	$I_{GA}/I_{\#\text{-}GA}$	$I_{R1}/I_{\#\text{-}R1}$	$TS_{\#}P-$	$I_{\#}a$	$TS_{\#}P+$	$I_P/I_{\#\text{-}P}$	global activation energy (kcal mol^{-1})	DCM	toluene
1	nitrosomethane + Au(III)−allene complex (#→9)	−39.70 (I_{GA})	−47.84 (I_{R1})	−35.58	−48.85	−28.79	−59.23 (I_P)	20.06 (19.29)[a]	−0.09	0.56
2	nitrosobenzene + Au(III)−allene complex (#→Ph)	−39.70 (I_{GA})	−44.51	−32.95	−44.49	−27.85	−56.30	16.66 (15.60)	1.13	1.79
3	trimethylamine + Au(III)-allene complex (#→NMe3)	−39.70 (I_{GA})	−44.31	−43.01	−69.10	−34.98	−55.16	34.12 (34.70)	6.38	3.56
4	nitrosobenzene + Au(I)−allene complex (#→g1)	−41.68	−51.00	−29.07	−31.66	−30.08	−62.50	21.93 (22.65)	7.64	4.64

[a]Values in parentheses represent the energies with dispersion corrections.

COMPUTATIONAL METHODS

To carry out this QM calculation in a proper way, special attention was given in the choice of computational method, employed for optimizing the geometries of the species involved in the reaction pathway. Yao and his group compared several DFT and ab initio methods for assessing the ability to predict correct geometries involving gold atoms.[34] Their study revealed that several other functionals are superior to some popular hybrid functionals (such as B3LYP[35]) for predicting the results.[34] Hybrid functionals such as PBE0[36] (equivalent to PBE1PBE)[37] was found to be one of the most effective methods in handling the gold atom. On the basis of their observations, we employed this DFT functional with the basis set of (aug)cc-pVDZ for valence electrons[38] and the LANL2 effective core potential (ECP),[39] that includes the relativistic correction for describing the gold atom. Other atoms were computed using the 6-31G** basis set.[40] Dependency of energy on the dispersion problems[41] has also been measured for the species, which are involved in calculating the global activation energy, and our findings revealed that this has little effect on the total activation barrier of each pathway (Tables 1 and 2).

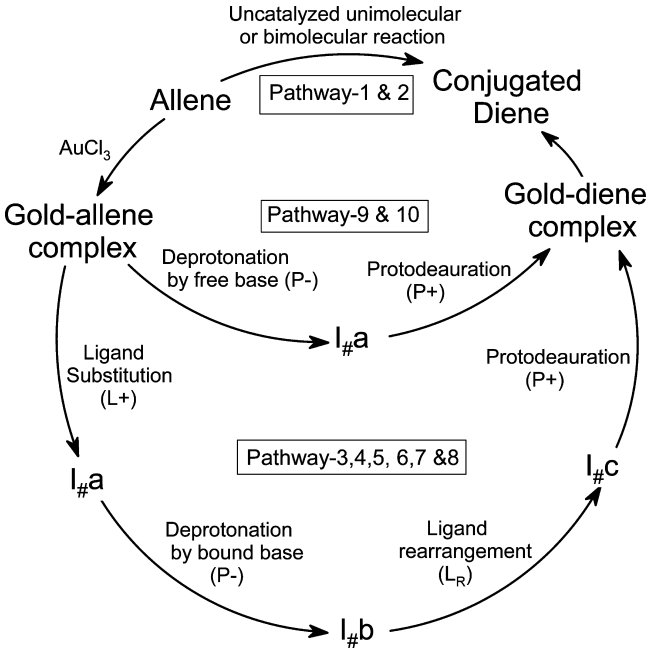
All the DFT calculations were performed with the Gaussian 09 program package.[42] Geometry optimizations of all minima and transition states (TSs) were performed at the level of theory as described in the previous paragraph. Hessian calculations for obtaining the vibrational frequencies were performed at the same level of theory as that for the geometry optimization to check whether the optimized geometrical structure is an energy minimum (with no imaginary frequency) or TS (with one and only one imaginary frequency). IRC calculations were used to check further whether the TSs connect the corresponding reactants and products. Solvent effects were also computed by the polarizable continuum model (PCM)[43] at the same level of theory using the gas-phase optimized geometries. The standard parameters for dichloromethane (DCM) and toluene, given in the Gaussian 09 package, were used for these calculations. Solvation free energies (ΔG_{DCM}, $\Delta G_{toluene}$) were calculated by adding the correction factors to the computed gas-phase relative free energies (ΔG_{298}). In addition, the dispersion correction terms for those structures, which are involved in calculating the global activation barrier, were computed using Grimme's DFT-D3[44] method with the short-range Becke−Johnson damping scheme [DFT-D3(BJ)].[45]

RESULTS AND DISCUSSION

Design of Reaction Pathways. In the present study on the mechanism of the gold-catalyzed allene isomerization, the substrate was modeled by a methylallene molecule, whereas the additive, nitrosobenzene, was approximated by nitrosomethane. The replacement of the phenyl ring by a methyl group in the nitroso compound may be an oversimplification. However, a similarity between the spatial orientation of the frontier orbitals of the nitroso group in both nitrosomethane and nitrosobenzene was observed (the orbital pictures of nitrosomethane and nitrosobenzene are given in Supporting Information (SI)). Furthermore, the low energy pathway, obtained using nitrosomethane, has been recalculated and verified using nitrosobenzene to justify our approximation.

To compare the energy requirement for the different pathways (with and without catalyst) for the allene isomerization reaction, two previously reported uncatalyzed pathways (pathways 1 and 2) were also considered[8] in addition to the present catalytic processes (Scheme 3). Energies of all the structures involved in these pathways were computed by using the present computational methods.

Scheme 3



On the other hand, the catalytic processes were considered to be initiated by the coordination of metal ion to the allenic double bond. However, our observation showed that the Au(III) chloride prefers to bind nitrosomethane over methylallene to form a coordinate bond with an energy difference of about 4.09 kcal mol^{-1} (the possible structures due

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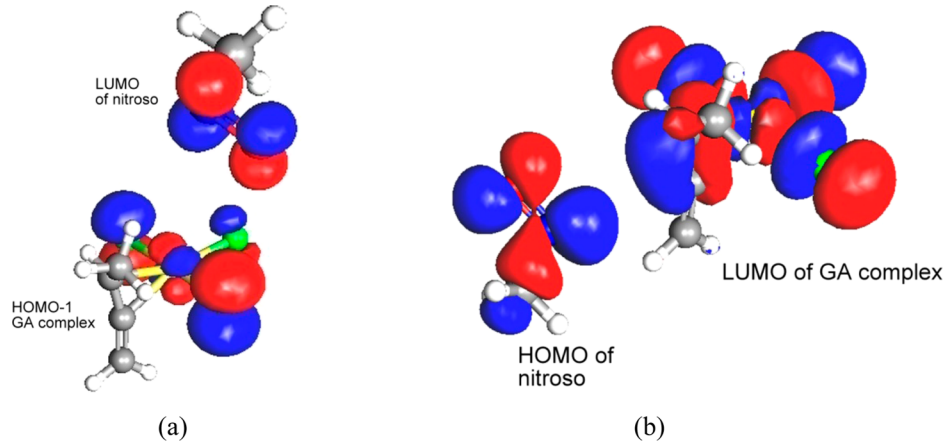
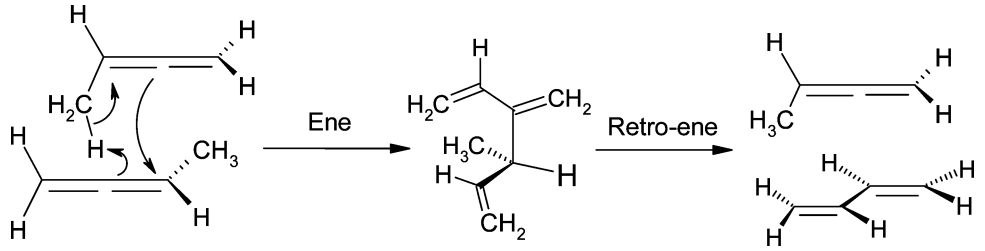


Figure 1. Possible interactions between (a) HOMO-1 of the the GA complex and LUMO of the nitroso compound, and (b) LUMO of the GA complex and HOMO of the nitroso compound.

Scheme 4



to the bindings of Au(III) chloride with nitrosomethane and allene are given in SI). It was also identified that the coordination of nitrosomethane with Au(III) chloride would not be a suitable starting point for this isomerization. Experimentally, it was observed that an excess of nitrosobenzene in the reaction medium arrests the reaction.[4] This observation also justifies the elimination of the possibility of the formation of initial coordination between Au(III) chloride and the nitroso compound as the suitable starting point of the reaction. Out of the two possible locations in the allene system, Au(III) prefers to bind the distal double bond over the proximal one (energy difference is 0.45 kcal mol^{-1}). It was revealed that the bond breaking process should start from the complex, in which Au(III) chloride is coordinated to the proximal double bond of the substituted allene molecule. As a result, the preferred complex (formed by coordination of Au(III) to the distal double bond) should be transformed to an energetically less favored complex (coordination between Au(III) and proximal double bond) to initiate the isomerization process. Exploration of the potential energy surface (PES) of the interconversion between two isomeric gold complexes showed that the transition between the two coordinated systems may occur by crossing two low energy barriers[46] (a detailed diagram of PES is given in SI). Measurement of the geometric parameters indicates that the length of the C−C double bond increases slightly (0.06 Å) after coordination with the metal ion, an indication of activation.

The activated GA complex then isomerizes to conjugated diene by transferring its hydrogen atom from the substituent methyl group to the central sp-hybridized carbon atom of the allene moiety. This process is considered to be assisted by a bound or an unbound (free) nitrosomethane molecule. To locate the spatial orientation of the nitrosomethane molecule with respect to the GA complex for generating the bound form, we analyzed the frontier orbital interaction of the corresponding systems (Figure 1). Orbital symmetry between HOMO-1 (which is very close in energy to HOMO; energy gap is 0.28 eV) of the GA complex and LUMO of nitrosomethane (Figure 1a) revealed the possibility of the pathways 3, 4, and 5 (Scheme 3). This interaction leads to the ligand substitution reaction as the first step of the isomerization process to generate an intermediate, in which nitrosomethane binds to the gold atom of the GA complex. On the other hand, the symmetry matching between LUMO of the GA complex and HOMO of nitrosomethane (Figure 1b) results in another possibility, where nitrosomethane binds to the allene moiety of the GA complex (pathways 6, 7, and 8, Scheme 3). Besides these binding processes, we analyzed another pathway which is assisted by the unbound (free) nitroso compound through its nitrogen or oxygen atom for transferring the proton in allene system (pathways 9 and 10, Scheme 3).

All the above approaches were finally examined individually to generate different pathways for the hydrogen migration process in the allene isomerization reaction. The global activation energies with a short description of each pathway are shown in Table 1.

The brief description of the uncatalyzed and the Au-catalyzed pathways, as listed above, for the isomerization reaction are presented in the following subsections. The most favorable pathway was then chosen on the basis of the global activation energy barrier associated with the concerned pathway.

Analysis of the Designed Pathways. *Pathways 1 and 2: Isomerization through the Concerted Sigmatropic [1,3]Shift of Hydrogen (Unimolecular Process) and Ene/Retro-Ene Tandem Reaction (Bimolecular Process).* The most straightforward uncatalyzed pathway (pathway 1) of allene isomer-

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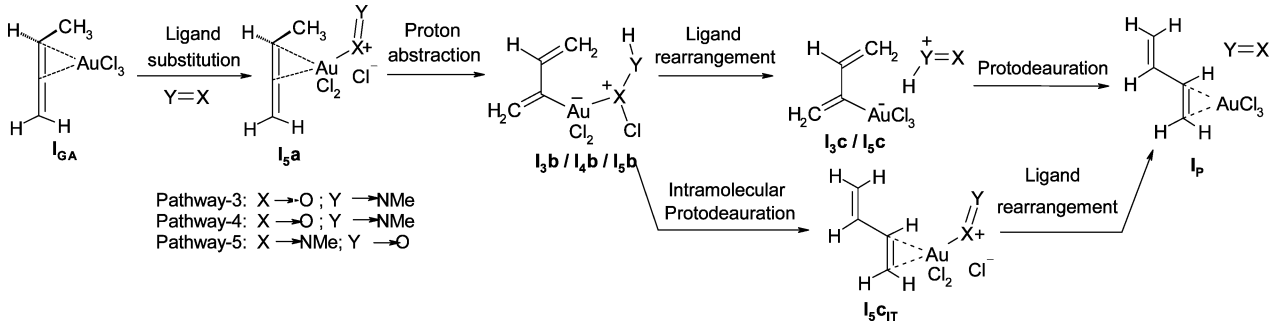
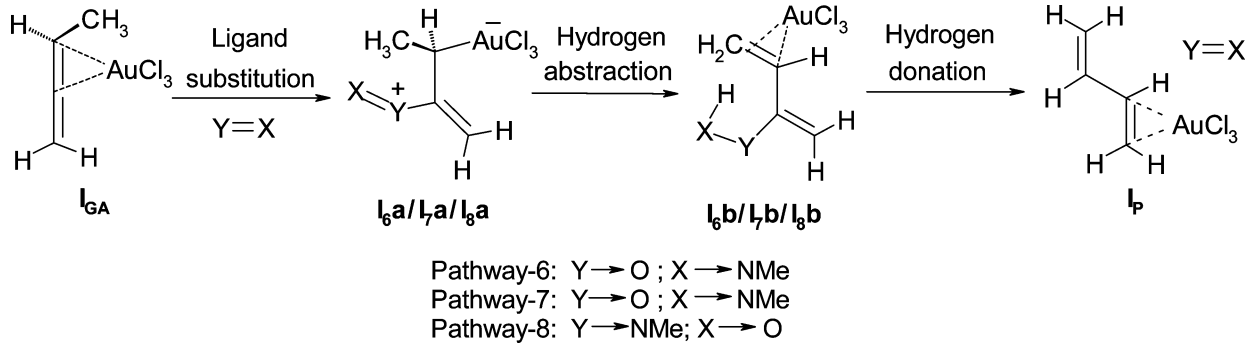
Scheme 5



Scheme 6



ization is the concerted antarafacial migration of hydrogen from the substituent methyl group to the central sp-hybridized carbon atom. An alternative more economical process is the bimolecular stepwise pathway (pathway 2, Scheme 4) that involves an ene reaction in the first step and a retro-ene reaction in the second step (see SI for detailed PES and the structure of the stationary points for pathways 1 and 2). In agreement with our previous report,[7] the calculated activation energy barrier for both the processes (calculated with the present method) was found to be fairly high (global activation barrier for pathways 1 and 2 are 68.42 and 56.53 kcal mol^{-1}, respectively, Table 1).

Pathways 3, 4, and 5: Migration of Hydrogen by the Assistance of the Nitroso Compound Bound to the Gold Atom in the GA Complex. In pathways 3 and 4, the nitrosomethane assists the hydrogen migration in the GA complex by using its nitrogen atom as the proton carrier (Scheme 5). Before initiation of the proton abstraction step, the molecule first undergoes a ligand substitution reaction by replacing a chlorine atom from the GA complex and forms a coordinate bond between its own oxygen atom and the metal ion. Though the ligand substitution and the proton abstraction steps in both pathways (pathways 3 and 4) take place in concert, a considerable flat surface is found in the case of pathway 3 before the proton abstraction step. This flat surface corresponds to the ligand substitution step, and hence we represent the ligand substitution and proton abstraction steps in pathway 3 as two consecutive TSs (detail is given in SI). After the ligand substitution and proton abstraction steps, the resulting intermediate, $\mathbf{I_3b}$ or $\mathbf{I_4b}$, undergoes subsequent ligand rearrangement and protodeauration through a common intermediate, $\mathbf{I_3c}$. This yields the isomerized product ($\mathbf{I_P}$) as a conjugated diene, complexed with Au(III) chloride (PESs and catalytic cycles of pathways 3 and 4 are given in SI). The requirement of high energy to cross the global activation barrier (48.79 kcal mol^{-1} for pathway 3 and 70.38 kcal mol^{-1} for pathway 4, Table 1) makes these two pathways unsuitable for the isomerization process.

In the pathway 5, nitrosomethane utilizes its oxygen atom for abstracting the proton from Au-bound allene complex and its nitrogen atom for coordination with the gold atom. Unlike pathway 3 and 4, pathway 5 consists of a well-defined intermediate ($\mathbf{I_5a}$), which clearly separates the ligand substitution and proton abstraction steps during the formation of the intermediate, $\mathbf{I_5b}$. Finally, $\mathbf{I_5b}$ may follow any one of the two pathways, one of which releases the protonated nitrosomethane from gold-bound complex for the subsequent protodeauration step through $\mathbf{I_5c}$; the other one undergoes an internal proton transfer (IT) process to generate the isomerized product ($\mathbf{I_P}$). The latter pathway, IT, is less favorable than the former one due to the high energy activation barrier (see the SI for PES and full catalytic cycle). The low global activation energy (26.86 kcal mol^{-1}) of pathway 5 makes this mechanism as favorable over pathway 3 or 4 (Table 1).

Pathways 6, 7, and 8: Hydrogen Transfer by Nitrosomethane Bound to the Allene Moiety in the GA Complex. In pathways 6, 7, and 8, the isomerization process is initiated by the formation of a covalent bond between the nitrosomethane molecule and central carbon atom of the allene moiety in the GA complex (Scheme 6).

In pathways 6 and 7, the nitrosomethane molecule employs its nitrogen atom to abstract hydrogen from the methyl group of the allene moiety, complexed with Au(III), after binding itself (through a C−O covalent bond) on the central carbon atom of the allene moiety in the GA complex. Here we have assigned two different conformational approaches for nitrosomethane as pathways 6 and 7. The resulting intermediate, $\mathbf{I_6b}$ or $\mathbf{I_7b}$, then dissociates to nitrosomethane and Au(III)-complexed conjugated diene ($\mathbf{I_P}$) after giving back the captured hydrogen to the central carbon atom of the allene moiety

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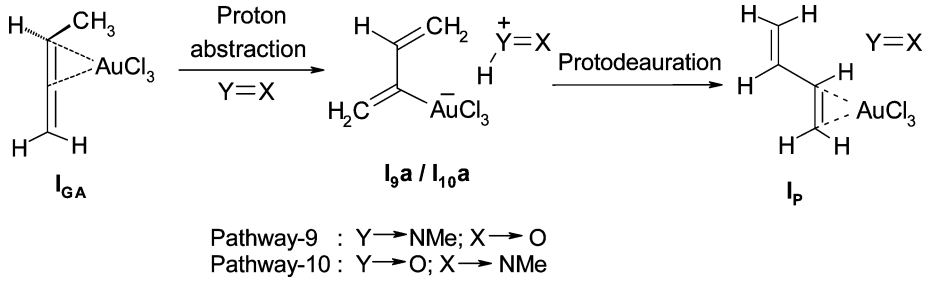
Scheme 7



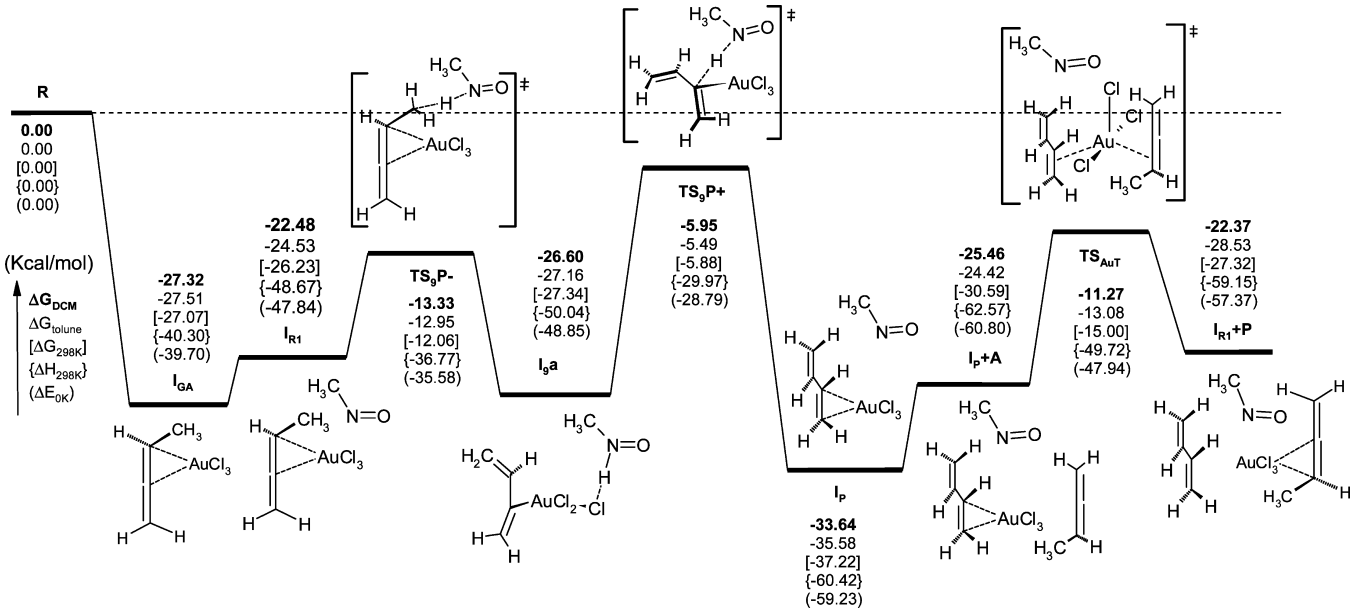


Figure 2. PES for allene isomerization catalyzed by Au(III) chloride and unbound nitrosomethane utilizing the nitrogen atom of the nitroso compound as the proton carrier (pathway 9).

through a four-membered cyclic TS. In an alternative arrangement (pathway 8), the nitrosomethane molecule utilizes its oxygen atom to abstract the hydrogen, while binding itself (through a C−N covalent bond) to the central carbon atom of the Au(III)-complexed allene moiety. Hydrogen donation, to generate the isomerized product from $\mathbf{I_8b}$, then occurs in a similar fashion by forming a four-membered cyclic TS, as found in pathways 6 and 7. The high global activation energies of these pathways (84.08, 84.08, and 81.79 kcal mol^{-1} in pathways 6, 7, and 8, respectively, Table 1), arising from the highly strained four-membered cyclic TS during the hydrogen donation, make these pathways unsuitable as a probable mechanism of the isomerization process (PES and catalytic cycles are shown in SI).

Pathway 9 and 10: Hydrogen Migration by the Assistance of Unbound Nitroso Compound in the GA Complex. In all catalytic pathways discussed so far, the nitrosomethane molecule executes proton transfer in its bound state, either to Au(III) ion or to the allene moiety in the GA complex. To investigate the catalytic process, in which the nitrosomethane is in an unbound state, pathways 9 and 10 were assigned (Scheme 7). In these pathways, a comparative investigation, on the efficiency of the basic nitrogen and oxygen atoms of the nitroso compound as the carrier of the migrating hydrogen atom, were performed. Both processes occur through a proton abstraction followed by a protodeauration step as shown in Scheme 7 (PES and catalytic cycles are given in SI).

The lower global activation energy (Table 1) of pathway 9 relative to that of pathway 10 suggests that the nitrosomethane molecule prefers to utilize its nitrogen atom over the oxygen atom as a proton carrier to achieve the isomerization reaction in GA complex. The comparison of energy requirements of pathway 9 with the other pathways (Table 1) also reveals that the free nitroso compound is more effective over the bound compound to carry out this isomerization reaction. From the PES for pathway 9 (Figure 2), it is revealed that the TS, which corresponds to the proton abstraction step ($\mathbf{TS_9P-}$), is relatively lower in energy than the TS, which represents the protodeauration step ($\mathbf{TS_9P+}$). While abstracting the proton from the Au(III)-complexed allene system by the nitrosomethane molecule, $\mathbf{TS_9P-}$ may be characterized as the late TS, as the formation of the Au−C σ bond has nearly been completed in this structure (as evident from the bond lengths shown Figure 3). However, early formation of $\mathbf{TS_9P+}$ from $\mathbf{I_9a}$, during the protodeauration step, is dictated by the small change in its Au−C σ bond distance. Finally, the product ($\mathbf{I_P}$), generated from the protodeauration step, undergoes a ligand substitution reaction with another methylallene molecule (through $\mathbf{TS_{AuT}}$) to release the conjugated diene molecule and prepare a fresh GA complex to initiate the next catalytic cycle. Previous reports[14e,20,31,32,47] suggest that the shifting of

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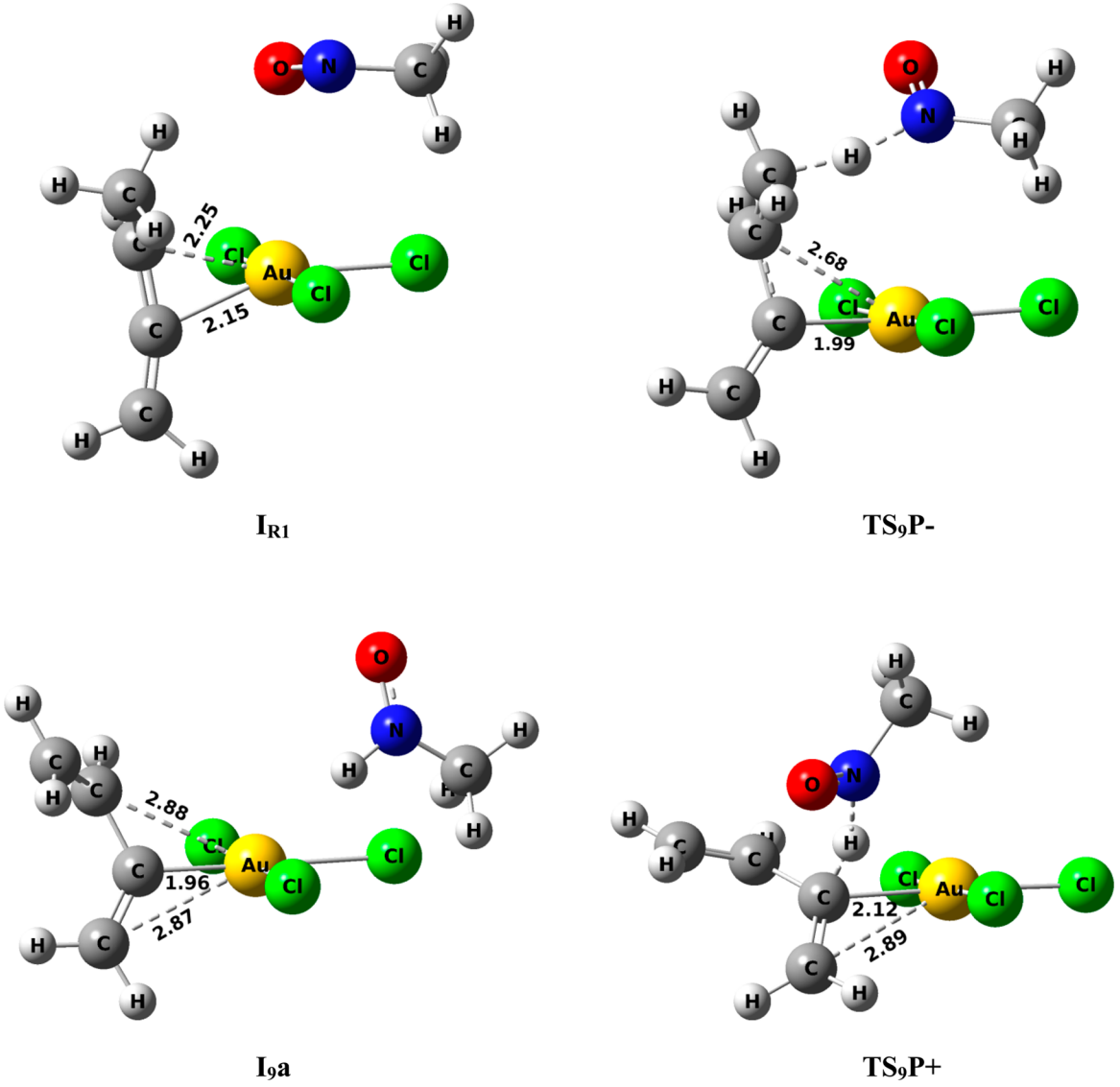

Figure 3. Relevant intermediates and transition structures for pathway 9 (I_{R1} and TS_9P- correspond to the proton abstraction step whereas the I_9a and TS_9P+ correspond to the protodeauration step).

hydrogen in several Au-catalyzed reactions can occur by crossing a low energy barrier with the assistance of an external molecule. Our results also reveal that the mechanism of the concerned reaction preferably follows a hydrogen shift through the assistance of an unbound nitroso compound (Table 1).

Factors Influencing the Minimum Energy Pathway. Several factors, such as the nature of the substituent in the additive, oxidation state of the catalytic Au atom or the change of solvent, may influence the energetics of pathway 9. We investigated the effects of these factors, and the results are summarized in Table 2 (the variation of PES is given in SI). Most of them can be rationalized by using the chemical intuition or correlating with the experimental observations as discussed in the following subsections.

Effect of the Phenyl Group of Nitrosobenzene. A more realistic PES can be obtained when nitrosomethane, in pathway 9, is replaced by nitrosobenzene, the actual additive used in the experiments.[4] The relative energies of the species, involved in pathway 9 using nitrosobenzene (Sl. no. 2 in Table 2, #→Ph), reveal that the reactivity pattern is similar to that obtained by using nitrosomethane (Sl. no. 1 in Table 2, #→9). However, a small variation in the activation energy is observed due to the impact of the phenyl group, having different electronic properties, in the nitroso compound (for pictorial comparative study of reaction pathways, see SI). The lowering of global activation barrier in the presence of nitrosobezene (Sl. no. 2 in Table 2, #→Ph), with respect to the pathway 9 for nitrosomethane (Sl. no. 1 in Table 2, #→9), is observed here. The TS ($TS_{Ph}P-$), which is involved in the proton abstraction process, requires slightly excess energy for nitrosobenzene. This is quite logical, as the lone pair of nitrogen is being more involved in phenyl ring in stabilizing the resonating structure of nitrosobenzene. However, the protodeauration process ($I_{Ph}a \rightarrow TS_{Ph}P+$) is more facile, as the captured lone pair of nitrogen in $I_{Ph}a$ is released to generate the isomerized product ($I_{Ph\text{-}P}$) in this process, thus allowing it to be stabilized by resonance again. Due to the reduction of the activation barrier of the later step, the global activation barrier is reduced to 16.66 kcal mol^{-1} for nitrosobenzene (Table 2).

Effectiveness of Nitroso Compound over Tertiary Amine as the Proton Transfer Agent. That the nitroso compound is more effective to carry out the isomerization reaction in the

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unbound condition may raise the possibility of the effectiveness of other basic reagents to assist the same pathway of the isomerization process. However, an experimental report[4] suggested that organic bases such as trialkylamine, instead of a nitroso compound, are ineffective to carry out the reaction under similar condition. To understand the role of the nitroso compound precisely, we studied the full proton transfer pathway using trimethylamine as a proton transfer agent. The energy change of the stationary points, when trimethylamine assists the proton transfer process (Sl. no. 3 in Table 2, #→NMe3), shows that the proton abstraction step ($\mathbf{I_{NMe3\text{-}R1}} \rightarrow \mathbf{TS_{NMe3}P-}$) occurs with a very low activation energy (1.3 kcal mol^{-1}). However, the stabilized intermediate ($\mathbf{I_{NMe3}a}$) has to cross a huge energy barrier ($\mathbf{I_{NMe3}a} \rightarrow \mathbf{TS_{NMe3}P+}$, activation energy barrier is 34.12 kcal mol^{-1}) to produce the isomerized product ($\mathbf{I_{NMe3\text{-}P}}$). From our study, it appears that the activity of a reagent for proton transfer process in the Au(III)-catalyzed allene isomerization depends not only on its proton abstraction power (basicity) but also on its effectiveness to protodeaurate the central carbon atom of the allene system. Trialkylamine, being a strong base, abstracts a proton more effectively ($\mathbf{I_{NMe3R1}} \rightarrow \mathbf{TS_{NMe3}P-}$) but does not readily return the captured proton to terminate the process smoothly. However, the nitroso compound is quite effective in the total process for its inherent, optimized basic nature to complete the isomerization reaction, thus moderately balancing the activation energies of the proton abstraction and the releasing processes.

Comparison of the Catalytic Power between Au(III) and Au(I) in Allene Isomerization. An experimental report[4] also revealed that the allene isomerization, under Au(I) catalysis, results in an incomplete conversion of allene to conjugated diene. It may be assumed that the most favorable mechanistic pathway is unsuitable for Au(I)-catalyzed allene isomerization because of the lack of availability of a proper acidic proton from the weakly activated allene system due to the lower oxidation state of gold. Calculated results show that all the stationary points of this isomerization reaction, under Au(I) catalysis (Sl. no. 4 in Table 2, #→g1), reside in higher relative energy states than those observed under Au(III) catalysis (Sl. no. 2 in Table 2, #→Ph). The higher value of the global activation energy, required for Au(I) catalysis (21.93 kcal mol^{-1}) in comparison to that of the Au(III) catalysis (16.66 kcal mol^{-1}) under similar condition, reveals that the allene isomerization reaction may occur with a much slower rate under Au(I) catalysis. Thus, the calculated results agree nicely with the experimental findings.

Effect of Solvents on the Reaction Pathway. PCM solvation corrections for all stationary points, identified so far, have been carried out by using DCM and toluene as solvents. The results (Tables 1 and 2) indicate a very small change in the free energies of activation due to the incorporation of this effect. The maximum shift in free energies of activation for DCM and toluene is 7.64 and 4.64 kcal mol^{-1}, respectively (Table 2). However, this shifting was found for the Au(I)-catalyzed pathway (Sl. no. 4 in Table 2, #→g1), where the whole complex is positively charged. For the other pathways, only a little change was noted (Tables 1 and 2), thus suggesting that the incorporation of solvent affects the reaction pathway only slightly. However, the experimental report[4] stated a significant solvent-dependence of the reaction, such that the isomerization observed in DCM is completely quenched in toluene. This suggests a stronger interaction with the solvent than the PCM methods are normally capable of modeling well.

CONCLUSION

In summary, the first step of the Au(III)-catalyzed isomerization of substituted allene to conjugated diene is considered as the activation of the allene molecule by Au(III) ion through the formation of a coordinate bond between the unsaturation of allene and the metal ion. The very next step is the migration of the hydrogen atom from the substituent alkyl group of the allene moiety to its central sp-hybridized carbon atom. This migration has been considered to be assisted by an additive, a nitroso compound, either in its bound state with the GA complex or in its unbound form. Energy profiles of the possible pathways show that the metal-bound nitroso compound prefers to utilize its oxygen atom to carry the migrating hydrogen, while attaching itself to the metal ion by employing its own nitrogen (pathway 5). Other possible pathways, involving Au−O coordination (pathways 3 and 4), are found to be energetically less favorable. The nitroso compound may also be involved in the proton transfer process by binding itself to the allene moiety of the GA complex (pathways 6, 7, and 8). However, a high activation barrier due to the formation of a four-membered cyclic TS, while donating the hydrogen to allene carbon, makes it energetically unfavorable for the reaction. In an unbound condition, the nitroso compound may transfer the proton by utilizing its nitrogen or oxygen atom (pathways 9 and 10). However, pathway 9, which employs the nitrogen atom of the nitroso compond as the carrier of a proton, is identified as the energetically most favored pathway for this isomerization reaction. Further investigation reveals that the moderate basic behavior of the nitroso compound makes it more efficient than the other strongly basic agents, such as trialkylamines, to carry out the reaction. Being more basic, the trialkylamines form a stabilized conjugate acid after capturing the proton, thus prohibiting the reaction to go further by following the protodeauration process. These facts agree well with the reported experimental results. In agreement with the experiment, our calculation also suggests that Au(I) is not very effective to carry out the isomerization smoothly under similar conditions.

ASSOCIATED CONTENT

Supporting Information

PES of the isomerization of Au−allene complex by shifting the gold ion from the distal to the proximal double bond in substituted allene, PES of all other studied pathways, Cartesian coordinates, absolute energies, frequencies, and thermodynamic parameters for each computed stationary point along with the ball and stick model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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