

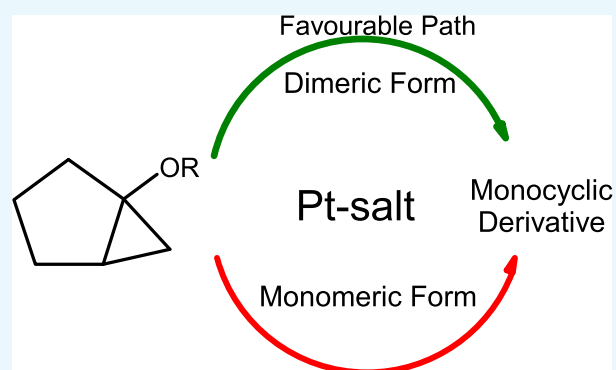
Theoretical Study on the Mechanism of Rearrangement Reactions of Bicyclic Derivatives of Cyclopropane to Monocyclic Derivatives under the Catalysis of Pt-Salt

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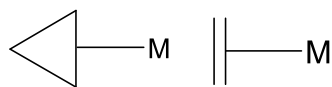
Supporting Information

ABSTRACT: In this paper, the mechanistic studies on the isomerization of hydroxyl and silyl derivatives of bicyclic cyclopropanes under the catalytic action of Zeise's salt have been reported. The catalytic activity of both the monomeric and the dimeric forms of Zeise's salt has been studied by applying the high-level quantum mechanical method. Results from this investigation reveal that the reaction goes favorably under the catalysis of the dimeric form of Zeise's salt. The calculated activation barrier for the catalytic process using Zeise's dimer reveals that the rearrangement occurs with an activation barrier of 19–25 kcal mol⁻¹. Depending on the nature of substituents present on the substrate, formation of various products has been explained. This study also includes the heteronuclear counter part of Zeise's dimer where one of the Pt-metals is replaced by palladium (Pd) and nickel (Ni) successively. The calculated activation barrier using these heteronuclear catalysts is found to be close enough to that calculated for the catalytic pathway using Zeise's dimer.



INTRODUCTION

The reactions of cyclopropane derivatives under the transition-metal catalytic conditions have got considerable attention in various fields of chemistry.¹ In many organic reactions, the cyclopropane ring system behaves like an unsaturated olefin moiety because of the similarities in their electronic structures.² As a result, the tendency of the cyclopropane system to form coordinate bonds with other transition-metal ions resembles with the property of the unsaturated compounds that acts as the π -ligand in many complex molecules for organic synthesis.^{3,4}



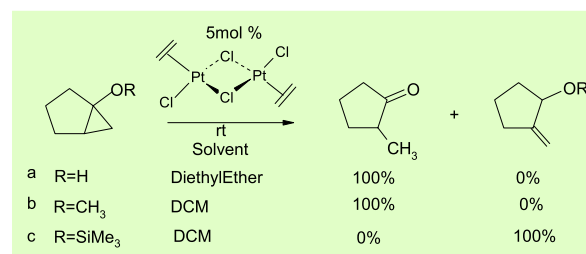
The literature survey reveals that the cyclopropane derivative when coordinated to a platinum atom, invariably undergoes an oxidative insertion reaction to produce a platinumacyclobutane derivative.⁵



Under several circumstances, the formation of this four-membered ring was detected by spectroscopic measurement, yet the instability of the ring is quite evident by its reactivity

with other groups or reagents present within the substrate or environment that leads to a variety of rearranged products. In the past few decades, several instances were noticed where the substrates are found to be mostly bicyclic in nature.⁶ In particular, if the substrate contains an oxy substituent, the ring opening and rearrangement reactions are quite facile.⁷ Thus, reports from Jennings et al. reveal the effective utilization of Zeise's salt for the ring opening reactions in conversion of several hydroxy- and alkoxy-substituted cyclopropane derivatives to methyl ketones⁸ (Scheme 1a,b). Another report by

Scheme 1. Rearrangement Reactions of Bicyclic Derivatives of Cyclopropane under the Catalysis of Zeise's Salt



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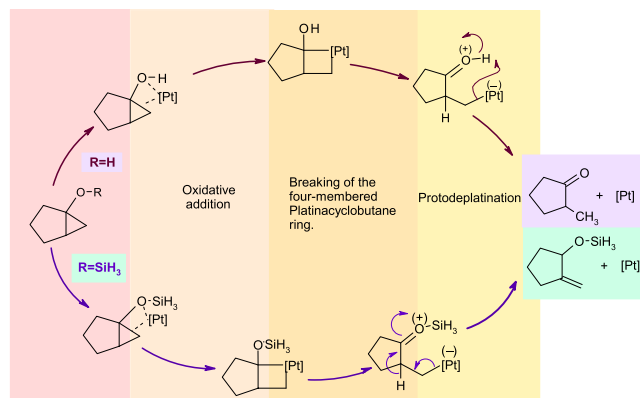
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Sonoda et al. shows an efficient catalytic isomerization of the cyclopropane derivative to allyl silyl ether at ambient temperature when the siloxy group is present on the ring junction⁹ (Scheme 1c). Madsen et al. extends such ring-opening reaction in a derivative of the natural product for the synthesis of 2-C-branched carbohydrates. Such reaction can be performed by using a variety of O-nucleophiles including alcohols, phenols, and water.¹⁰

While proposing the mechanism of these reactions, all authors assumed the involvement of a mononuclear Pt-complex for catalyzing the reaction (Scheme 2). At the very

Scheme 2. Reported Mechanism of the Conversion of the Bicyclic Substrate to the Monocyclic One under Metal Complex-Catalyzed Condition



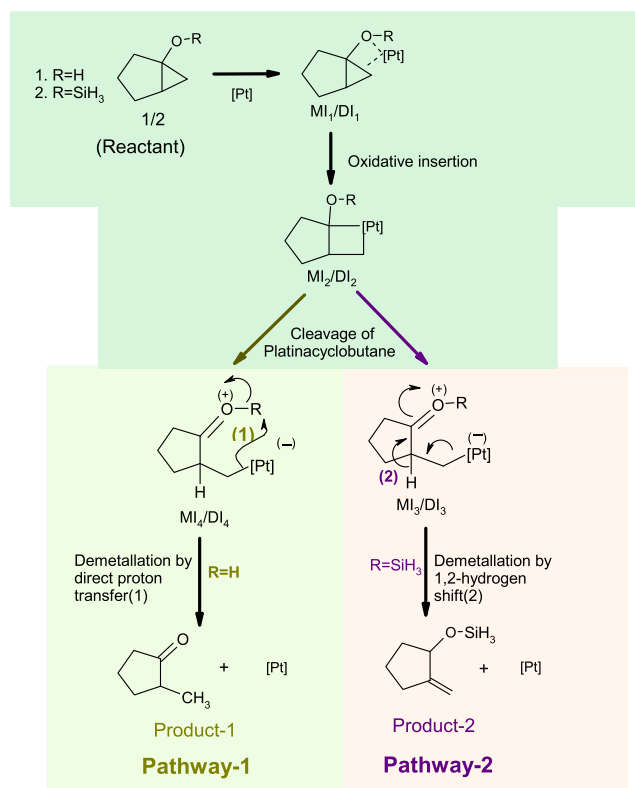
first step of the mechanisms, the Pt-metal gets inserted into the cyclopropane moiety by oxidative addition reaction to generate a four-membered platinacyclobutane ring as an intermediate.

Depending on the nature of various substituents present on the ring junction, the generated platinacyclobutane intermediate rearranges to different products. In particular, the presence of the hydroxy group at the bridge head of the bicyclic skeleton promotes the formation of keto compounds by cleavage of the Pt–C bond. During such process, the mandatory transfer of the proton from the hydroxy group at the ring junction to cyclopropane carbon was further confirmed by the deuterium labeling experiment and other NMR spectroscopy. When the silyl group is present at the ring junction of the substrate, an exocyclic double bond is formed in the product; such formation could be explained by a [1,2]-hydrogen shift between two adjacent carbon atoms present on the ring. All mechanisms proposed here utilize a single Pt-metal ion for the catalytic process; however, the experimental method reveals clearly the utilization of dimeric Zeise's salt to carry out the reaction. Our previous density functional theory (DFT) study revealed that the involvement of Zeise's dimer with the substrate provides a more favorable pathway than that observed using a single platinum atom for the rearrangement of oxaspirohexane to 3-methylenetetrahydrofuran.¹¹ Here, depending on the nature of various substituents in the bicyclic skeleton, we report our investigation on the mechanism of the reactions by using the monomeric and dimeric form of the metal catalyst and show the importance of the dimeric form (Zeise's salt) in reducing the activation barrier.

RESULTS AND DISCUSSION

To perform our mechanistic study, we have selected the bicyclo[3.1.0]hexane derivatives with hydroxy or siloxy substituents at the ring junction (1 and 2 in Scheme 3) that were previously reported in the experiment. The overview of the studied pathways is shown in Scheme 3.

Scheme 3. Overview of Plausible Mechanisms Involving the Monomeric and Dimeric Forms of the Pt-Catalyst Condition



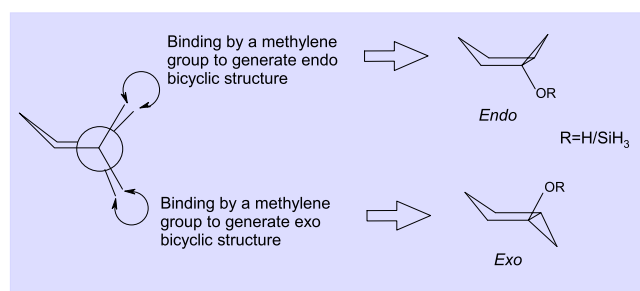
Though a single Pt atom is shown as a catalyzing element, we have studied the effect of both the monomeric and dimeric form of Zeise's salt involved in catalyzing the reaction to compare the effectiveness of the catalytic activity of monometallic and dimetallic complexes. However, representing the single and double activation process, we have used the letter "M" and "D" attached to the name of the pathways or stationary points; for example, the single activation process of pathway-1 is represented as pathway-1M, whereas the corresponding double activation process is designated as pathway-1D.

The hydroxyl derivative of the bicyclic compound (R=H in Scheme 3) furnishes 2-methylcyclopentanone (designated as pathway-1), whereas the silyl derivative of the same bicyclic structure results 2-methylene-1-siloxycyclopentane as the final product (designated as pathway-2). The first step involves the coordination of the substrate (1 or 2) to the metal center of the catalyst to form the intermediate complex MI_1/DI_1 . This step is followed by the oxidative addition of a Pt-metal ion into the cyclopropane moiety to generate four-membered platinacyclobutane intermediate MI_2/DI_2 . Opening of the platinacyclobutane ring takes place through the cleavage of the Pt–C bond to produce intermediate MI_3/DI_3 (R=SiH₃) or MI_4/DI_4 (R=H). For the hydroxyl derivative, protodeplatination

takes place in intermediate MI_4 or DI_4 by transferring a proton from the hydroxyl group to generate methylcyclopentanone as the final product (pathway-1). However, the silyl derivative MI_3 or DI_3 promotes a 1,2-hydride shift which ultimately undergoes a deplatination process to form the cyclopentane derivative with an exocyclic double bond (pathway-2).

As the starting reactant may exist in several conformational isomers, we have selected the most favorable one by constructing it from cyclopentane geometry. While constructing the bicyclic structure, we have chosen the envelope geometry of the cyclopentane ring and utilized its two adjacent eclipsed carbons to insert the cyclopropane ring for generating the bicyclic structure (Scheme 4).

Scheme 4. Construction of an Endo and Exo Bicyclic Structure from Envelope Conformation of the Cyclopentane Ring



Out of the two possible orientations of the cyclopropane structure relative to the cyclopentane ring system (exo and endo in Scheme 4), the exo orientation is found to be more stable than the endo isomer by $3.8 \text{ kcal mol}^{-1}$. With this exo isomer, the initial complex is generated by forming a Pt–O coordinate bond between monomeric or dimeric Zeise's salt and the oxygen atom of the substrate molecule. Our investigations on the energy and topology of molecular orbitals of the substrates have given us a clue about the number and orientation of metal centers that can be employed to bind with the geometry of the substrates (Figure 1).

The outermost two filled molecular orbitals [highest occupied molecular orbital (HOMO) and HOMO – 1] have almost the same energies and are suitable for making the

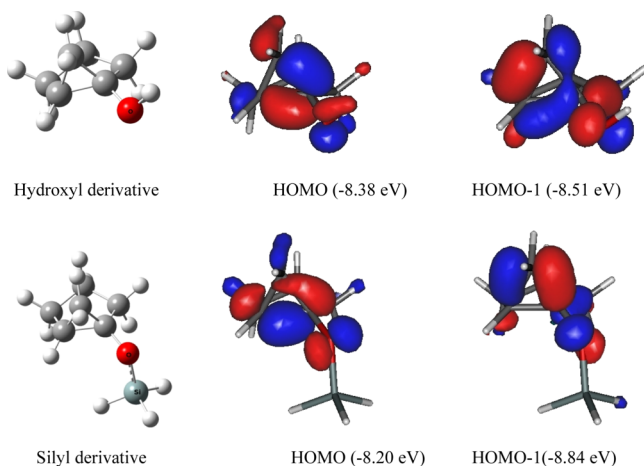


Figure 1. Structure and the outermost molecular orbitals of the bicyclic compounds.

coordinate bond with a metal center. The next molecular orbital (HOMO – 2) is situated well below of these two orbitals and may be assumed to be inert for making a coordinate bond with a metal center. Scrutiny of the topology of the outermost two molecular orbitals (Figure 1) clearly reveals that the lobes of the wave functions are largely associated with the edges of the cyclopropane moiety and with the substituent oxygen atom as well. We surmised that the electrons associated to these molecular orbitals and suitable to coordinate with maximum two metal atoms are present at the vicinity of the substrate.

Study on the Mechanism of Rearrangement of 1-Hydroxy-bicyclo[3.1.0]hexane. The potential energy surface indicating the transition states and intermediates involved in all the proposed mechanisms of pathway-1M and pathway-1D (Scheme 3) are shown in Figure 2. Pathway-1M_a (red color) is an alternative pathway diverged from pathway-1M (brown color) that shows a variation of mechanism for the transformation of the bicyclic derivative 1-hydroxy-bicyclo[3.1.0]hexane to 2-methylcyclopentanone under the catalytic action of the monomeric form of Pt-salt. Similarly, pathway-1D_a (magenta color) is another alternative pathway diverged from pathway-1D (blue color) that progress under the catalysis of the dimeric form of Zeise's salt.

Catalysis by Activation of the Substrate with One Metal Atom. The pathway-1M and pathway-1M_a (Figure 2) in which single Pt-metal is used as a catalyst follow three major steps: the first step is the formation of the four-membered platinacyclobutane intermediate, the second step is the opening of the four-membered platinacyclobutane intermediate, and the third step that is the final step involves with the protodeplatination process. The initial complex ($1MI_1$), in which the Pt-metal is coordinated to the hydroxyl oxygen of the substrate, undergoes an oxidative insertion reaction by crossing an activation barrier of $18.99 \text{ kcal mol}^{-1}$ through the transition-state $1MTS_1$, and the four-membered platinacyclobutane intermediate ($1MI_2$) is formed as a product. The ball and stick models (Figure 3) of the initial complex $1MI_1$ reveals that the distance between the hydroxyl oxygen of the substrate and the coordinated Pt-metal is 2.17 \AA .

While forming the transition structure ($1MTS_1$) in the oxidative insertion process, the shorter bond length between C3 and Pt (2.22 \AA) in comparison to that of C1–Pt (2.95 \AA) clearly indicates that the bond formation between C3 and the Pt-metal atom takes place at the early stage of the reaction. While forming the intermediate from the transition-state $1MTS_1$, the C1 atom gets the bonding electron mostly from the Pt atom and reduces its positive charge to some extent ($+0.526$ to $+0.423$). It has also been observed that C1–C3 distance of the cyclopropane moiety in the initial substrate $1MI_1$ (1.48 \AA) increases to generate the four-membered platinacyclobutane intermediate $1MI_2$ (2.34 \AA) through the distance 1.88 \AA in $1MTS_1$. Intermediate $1MI_2$ then undergoes a conformational change for the formation of the H bond and intermediate $1MI_3$ is formed through transition-state $1MTS_2$ with an activation barrier of $5.30 \text{ kcal mol}^{-1}$.

Opening of the platinacyclobutane ring then takes place by the cleavage of one Pt–C1 bond of intermediate $1MI_3$ to form intermediate $1MI_4$ by increasing the C1–Pt distance from 2.19 \AA (in $1MI_3$, Figure 4) to 3.52 – 3.52 \AA (in $1MI_4$, Figure 5). This cleavage occurs by crossing a very low activation barrier of $3.10 \text{ kcal mol}^{-1}$ through the transition-state $1MTS_3$. NBO analysis shows that during this cleavage, the C1 atom acquires more

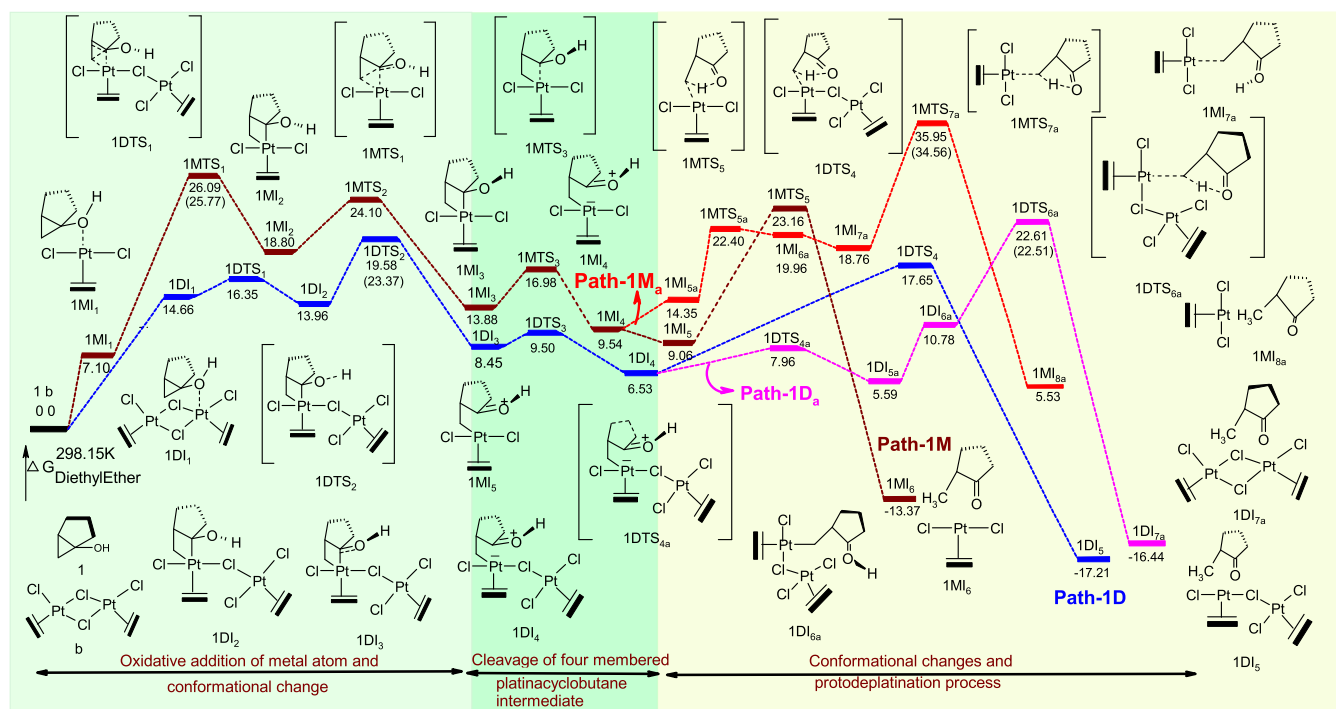


Figure 2. PES along with the thermodynamic parameters and structures of the stationary points of pathway-1M (brown color), pathway-1M_a (red color), pathway-1D (blue color), and pathway-1D_a (magenta color) under the catalytic condition of the monomeric and dimeric form of Pt-salt. Energy values that not enclosed in brackets are calculated using M06-2X functional. Values indicated in the round bracket are calculated using M06 functional.

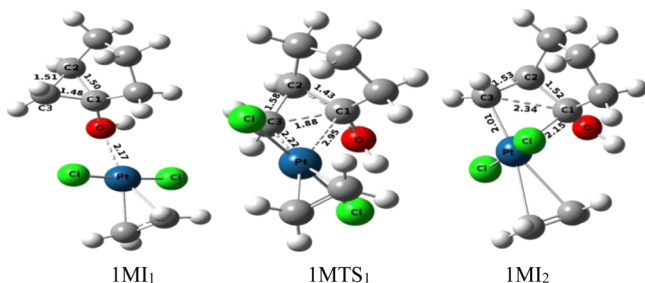


Figure 3. Ball and stick models of the stationary points during the formation of the platinacyclobutane intermediate under the catalytic condition of the monomeric form of Pt-salt.

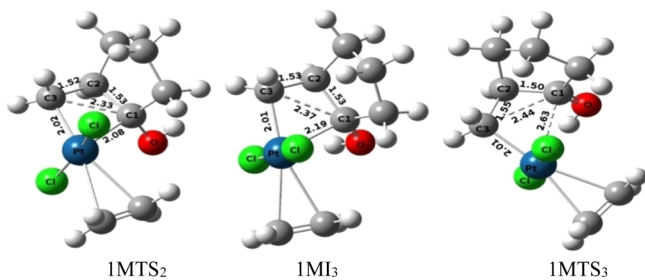


Figure 4. Ball and stick models of the stationary points during the conformational change and cleavage of the platinacyclobutane intermediate under the catalytic condition of the monomeric form of Pt-salt.

positive charge (+0.459 in 1MI₃ to +0.729 in 1MI₄ through +0.665 in transition-state 1MTS₃), whereas Pt and C3 atoms progressively get negative charge (−0.535 to −0.687 on C3 and +0.365 to +0.270 on Pt). This indicates that the opening of the platinacyclobutane ring by the cleavage of the C1–Pt

bond is mostly heterolytic in nature. After the opening of the platinacyclobutane ring, the intermediate 1MI₄ undergoes protodeplatination process. A direct proton transfer from hydroxyl oxygen to C3 carbon atom (through 1MTS₅) of pathway-1M results in the detachment of the metal atom to generate the product (1MI₆). This step requires 13.62 kcal mol^{−1} energy to overcome the activation barrier and the relative energy of this transition state is 23.16 kcal mol^{−1} for the formation of the end product 1MI₆ (C2–C1 = 1.51 Å, Figure 5). However, intermediate 1MI₅, from which the proton transferring reaction starts, differs from intermediate 1MI₄ by a small conformational orientation of the metal atom with respect to the rest of the structure. Several trials to find out the transition structure between these two conformers failed, indicating a very low energy barrier between them. Replacement of the Pt-metal by the migration of protons results in the reduction of electron density on the Pt-metal as apparent from the change of NBO charge (+0.270 to +0.429). It reveals that the delocalization of the bonding electron between the Pt and C3 atom to the C3 and H atom takes place during the protodeplatination process. Global activation barrier of pathway-1M is 26.09 kcal mol^{−1}. In an alternative pathway of protodeplatination (pathway-1M_a), the metal atom is replaced by the proton from the reactant 1MI_{7a} through the S_N2 type process (with an activation barrier of 26.41 kcal mol^{−1} through transition-state 1MTS_{7a}) to form intermediate 1MI_{8a}. To continue such pathway, a conformational change of the intermediate (1MI₄) is required through some steps, out of which one has been detected through transition-state 1MTS_{5a} (activation barrier 8.05 kcal mol^{−1}), resulting in intermediate 1MI_{6a}. Global activation barrier of pathway-1M_a is 35.95 kcal mol^{−1}. However, this pathway requires more activation energy with respect to the previous pathway-1M and thus is not

The final step of protodemetalation occurs from the intermediate $1DI_4$ through the transition state $1DTS_4$ (activation barrier $11.12 \text{ kcal mol}^{-1}$) resulting in the final product $1DI_5$ (methyl-cyclopentane and Zeise's dimer). Both the attachment of proton and the detachment of the metal center in $1DTS_4$ ($O-H = 1.36 \text{ \AA}$, $H-C3 = 1.48 \text{ \AA}$, Figure 9)

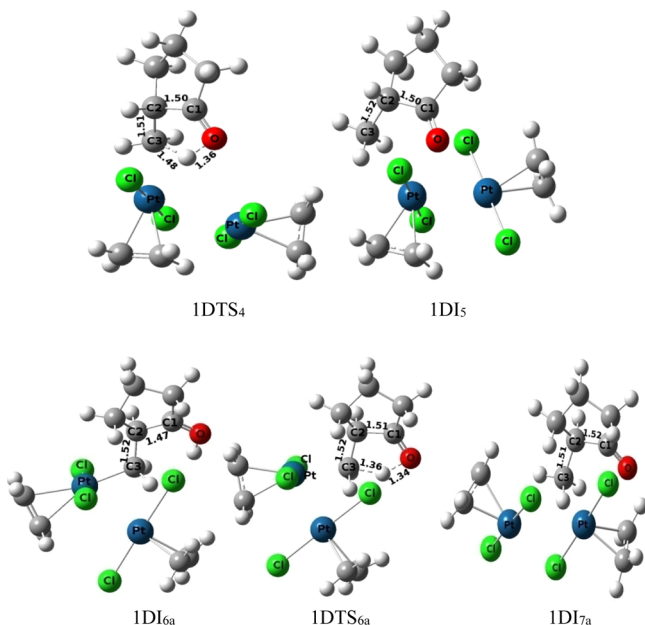


Figure 9. Ball and Stick models of the transition state and intermediate for the protodeplatination step of pathway-1D (upper) and pathway-1Da (lower) under the catalytic condition of the dimeric form of Pt-salt.

occur from the same face of the C3 atom (Figure 9). We have envisioned another possible way of protodeplatination such that the incoming proton and the eliminating Pt-metal should orient in the opposite face of the C3 atom. Such study results the divergent pathway-1Da that starts by a conformational reorganization of the cyclopentane ring through the transition structure $1DTS_{4a}$ (activation barrier $1.43 \text{ kcal mol}^{-1}$), resulting in the intermediate $1DI_{5a}$. Another conformation change of

$1DI_{5a}$ results in $1DI_{6a}$, which is necessary for the final S_N2 type mechanism for protodeplatination. Final protodeplatination occurs through transition-state $1DTS_{6a}$ ($O-H = 1.34 \text{ \AA}$, $H-C3 = 1.36 \text{ \AA}$, Figure 9) with an activation barrier of $16.08 \text{ kcal mol}^{-1}$. However, this S_N2 type protodemetalation makes the global activation barrier of pathway-1Da, $22.61 \text{ kcal mol}^{-1}$, which is larger than the global activation barrier of pathway-1D ($19.58 \text{ kcal mol}^{-1}$). This double activation process of pathway-1D is also more favorable than the previously discussed pathway-1M as revealed from Table 1, thus suggesting the involvement of two Pt metals in catalyzing the reaction.

Study on the Mechanism of Rearrangement of 1-Siloxy-bicyclo[3.1.0]hexane. The mechanism of the rearrangement of the silyl derivative of the bicyclic compound may also be considered as the composite of three separate steps. The first two steps, that is the oxidative addition of the metal atom and the cleavage of the platinacyclobutane ring are similar to that of the rearrangement of 1-hydroxy-bicyclo[3.1.0]hexane. However, the last step, that is the concerted 1,2-shift of hydrogen and the demetallation of this rearrangement differs from the step of protodemetalation of the previous path (Scheme 3). The catalysis under the monometallic and dimetallic condition of this reaction was studied, and photoelectron spectroscopy (PES) of both of them is presented in Figure 10. The mechanistic pathway under the single activation of the Pt-metal is designated here as pathway-2M (violet color in Figure 10), whereas the catalysis under double activation is designated as pathway-2D (orange color in Figure 10).

Catalytic Activity of Monometallic Complex. The initial oxidative addition of pathway-2M occurs through the transition-state $2MTS_1$ (activation barrier $18.85 \text{ kcal mol}^{-1}$) from the intermediate $2MI_1$, resulting in platinacyclobutane intermediate $2MI_2$. It has been revealed from the mechanistic pathway that this step is endergonic in nature. The distance between the oxygen atom of the siloxy group ($-OSiH_3$) and coordinated Pt-metal is 2.19 \AA in $2MI_1$ (Figure 11), and the C1–C3 bond of the cyclopropane moiety increases from 1.48 \AA in $2MI_1$ to 2.32 \AA in $2MI_2$ (through C1–C3 bond distance 1.96 \AA in $2MTS_1$) during the insertion of the Pt-metal in the cyclopropane moiety.

Table 1. Comparison of Gibbs Free Energy Barriers of the Several Segments of Different Pathways and Global Activation Energy (kcal mol^{-1})

pathway no.	relative energy required (kcal mol^{-1}) (ΔG^\ddagger)			global activation barrier	relative energy of the transition state that leads to the final product (ΔG)
	oxidative addition of the metal atom	cleavage of the platinacyclobutane ring	protode-platination		
Rearrangement of 1-Hydroxybicyclo[3.1.0]hexane					
path-1M _a (Figure 2)	18.99	3.10	26.41	35.95 (34.56) ^a	35.95
path-1M (Figure 2)	18.99	3.10	13.62	26.09 (25.77) ^a	23.16
path-1D _a (Figure 2)	1.69	1.05	16.08	22.61 (22.51) ^a	22.61
path-1D (Figure 2)	1.69	1.05	11.12	19.58 (23.37) ^a	17.65
Rearrangement of 1-Siloxy-bicyclo[3.1.0]hexane					
path-2M (Figure 10)	18.85	3.81	11.83	28.71 (28.95) ^a	28.71
path-2D (Figure 10)	18.61	3.09	12.05	25.71 (25.10) ^a	24.69

^aCalculation of the free energies was done using M06 functional.

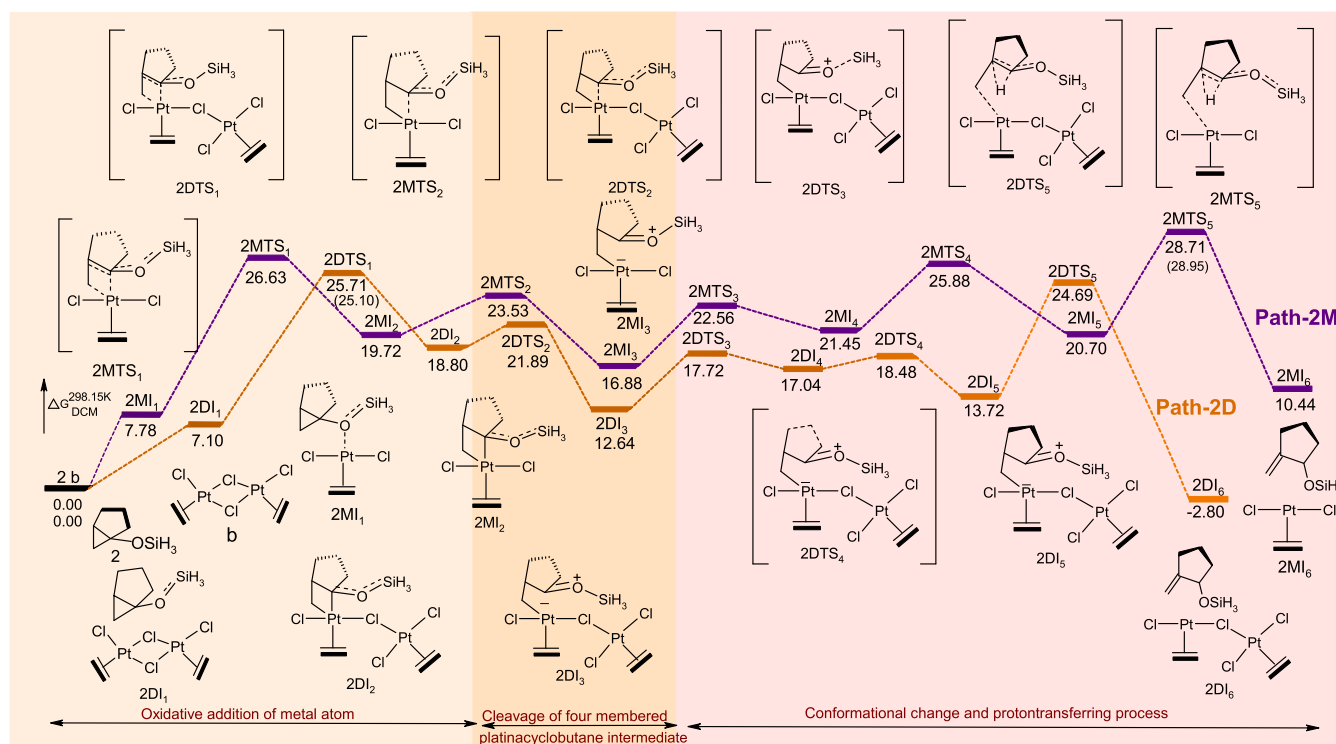


Figure 10. PES along with the thermodynamic parameters and structures of the stationary points of pathway-2M (violet color) and pathway-2D (orange color) under the catalytic condition of the monomeric and dimeric form of Pt-salt. Energy values not enclosed in brackets are calculated using M06-2X functional. Values indicated in the round bracket are calculated using M06 functional.

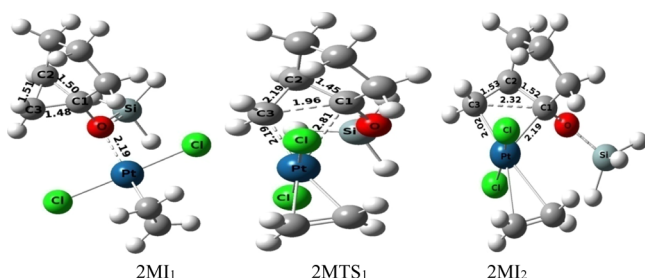


Figure 11. Ball and stick models of the stationary points during the formation of the platinacyclobutane intermediate (of the substrate 1-siloxy-bicyclo[3.1.0]hexane) under the catalytic condition of the monomeric form of Pt-salt.

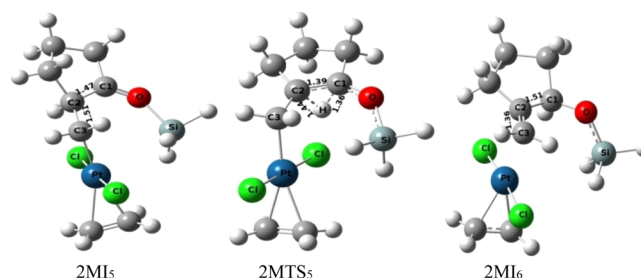


Figure 12. Ball and stick models of the stationary points of the protodeplatination step (of the substrate 1-siloxy-bicyclo[3.1.0]hexane) under the catalytic condition of the monomeric form of Pt-salt.

In the following step of C1–Pt bond cleavage, the carbon atom attached to the siloxy group (–OSiH₃) decreases the electron density around the oxygen atom and facilitates the breaking of the C1–Pt bond of the four-membered platinacyclobutane intermediate (2MI₂) to generate η^1 -complex 2MI₃ (through transition-state 2MTS₂ with an activation barrier of 3.81 kcal mol^{−1}). This heterolytic cleavage of the C1–Pt bond gives the zwitter ionic intermediate, 2MI₃, the formation of which is followed by a conformational rearrangement of the siloxy group for the formation of intermediate 2MI₄ (transition structure, 2MTS₃ with an activation barrier of 5.68 kcal mol^{−1}). There is another conformational change of the cyclopentane ring of intermediates 2MI₄ through transition structure 2MTS₄ (activation barrier 4.43 kcal mol^{−1}) to generate intermediate 2MI₅. 1,2-hydrogen shift from C2 to C1 (Figure 12) of intermediate 2MI₅, followed by a reductive elimination generates the final product 2MI₆ (transition structure 2MTS₅ with an activation barrier of

11.83 kcal mol^{−1}). The global activation barrier of pathway-2M under the catalytic condition of the monomeric form of Pt-metal is 28.71 kcal mol^{−1}.

Catalytic Activity of Dimetallic Complex. Pathway-2D (Figure 10), which consists of three major steps, also follows the mechanism similar to that of pathway-2M under the catalysis of Zeise's salt. In the first step of the mechanism, oxidative addition reaction takes place to form the platinacyclobutane intermediate (2DI₂) from the initial substrate complex, 2DI₁, by crossing an activation barrier of 18.61 kcal mol^{−1} (transition structure 2DTS₁ in which C1–Pt = 2.95 Å, C3–Pt = 2.18 Å, and C1–C3 = 1.89 Å, Figure 13). The next step is the heterolytic cleavage of the C1–Pt bond of the intermediate 2DI₂ to generate the intermediate 2DI₃ through transition structure 2DTS₂ (C1–Pt distance 2.55 Å, Figure 13) with an activation barrier of 3.09 kcal mol^{−1}. For initiating the proton shift and demetallation process, two necessary successive conformational changes have been

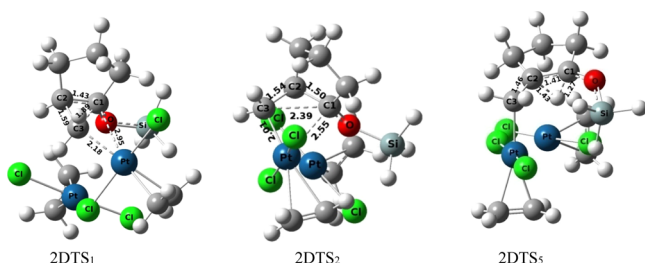


Figure 13. Ball and stick models of the stationary points of the substrate (1-siloxy-bicyclo[3.1.0]hexane) under the catalytic condition of the dimeric form of Pt-salt.

occurred through the transition structures 2DTS₃ and 2DTS₄ and the associated intermediate 2DI₄ in between them. The first conformational change is responsible for altering the orientation of the $-\text{OSiH}_3$ group from the syn- to antiposition (transition structure 2DTS₃ with an activation barrier of 5.08 kcal mol⁻¹) for the formation of intermediate 2DI₄. The next one flips the envelope structure of the cyclopentane ring from one conformation to other generating the intermediate 2DI₅ (through transition-state 2DTS₄, with an activation barrier of 1.44 kcal mol⁻¹). The last mandatory step consists of two nuclear movements in which the 1,2-hydrogen shift occurs from C2 to C1 and the detachment of the catalytic metal center from C3 to generate intermediate 2DI₆. The activation barrier associated to the last step is 12.05 kcal mol⁻¹ through the transition structure 2DTS₅. The global activation barrier of pathway-2D is 25.71 kcal mol⁻¹. However, the overall comparison between pathway-2M and pathway-2D shows that the global activation barrier of the latter pathway (25.71 kcal mol⁻¹) is more favorable than the former one (28.71 kcal mol⁻¹, Table 1).

From the previous discussion, it is clear that one of the two Pt atoms of Zeise's dimer is actively involved in the catalytic process. It participates in oxidative addition with the cyclopropane ring, consequently involved in the bond-making and bond-breaking process throughout the course of the rearrangement reaction. The second Pt provides some secondary support by coordination with various substituents having the donor atom present in the substrate. To study the role of other transition metals of the same group, we replaced second Pt by Pd and Ni in Zeise's dimer and recalculated the global activation barrier of the most favorable pathway. The calculated global activation barrier suggests that heteronuclear Zeise's dimer bearing one Pt-atom replaced by Pd or Ni may generate processes which have a comparable catalytic activity such as homonuclear Zeise's dimer.

CONCLUSIONS

In summary, our DFT study reveals that the formation of monocyclic derivatives from the substrate 1-hydroxy-bicyclo[3.1.0]hexane and 1-siloxy-bicyclo[3.1.0]hexane takes place in three major steps under catalytic conditions of monomeric and dimeric forms of Pt-salt. The first step undergoes the oxidative addition process for the formation of the platinacyclobutane intermediate which is followed by the cleavage of the Pt–C bond to open up platinacyclobutane as a second step. The final step is protodeplatination to generate the end products. Comparison of the energy barriers associated to different pathways reveals that double activation by the two Pt metal atoms leads to the energetically more favorable

mechanism to form the products. The energy barriers associated to the pathway-1D and 2D (19.58 and 25.71 kcal mol⁻¹) are quite reasonable to explain the room temperature conditions required for the rearrangement. Outcome of our study on the catalytic activity of heteronuclear Zeise's dimer where one of the Pt atoms is replaced by Pd or Ni may provide importantly to the synthetic chemist to develop a new catalytic system with multimetallic complexes.

COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 09 computational program package.¹² Geometry optimization of all species¹³ was performed using M06-2X functional¹⁴ in the DFT method. The 6-31G(d,p) basis set¹⁵ was employed for all nonmetal atoms and the LANL2DZ basis set¹⁶ was employed for the Pt atom. The computational method has been found reliable to study this ring-opening reaction and rearrangement reactions.¹⁷ Frequency calculations at the same level of theory were performed to obtain the gas phase free energies and to confirm each stationary point to be either a minimum (no imaginary frequency) or a transition structure (only one imaginary frequency). Intrinsic reaction coordinate calculations were carried out to confirm the connection of each transition state to its corresponding reactants and products.¹⁸ Single-point self-consistent reaction field calculations based on the polarizable continuum model were used for examining the solvation effect in gas-phase optimized structures.¹⁹ To obtain more accurate energies of the stationary points, single-point calculations were performed using the LANL2TZ basis set and effective core potential (ECP) with f polarization function for the metal center.²⁰ Diethylether for 1-hydroxy-bicyclo[3.1.0]hexane and dichloromethane for 1-siloxy-bicyclo[3.1.0]hexane were used as the solvent. The natural bond order (NBO) analysis was carried out using the NBO program, where the basis set is 6-31G(d,p) for nonmetal atoms and LANL2DZ (ECP) for metals are employed.²¹ All energies, reported in the Results and Discussion section, are relative free energies (ΔG^\ddagger) at 298.15 K. The global activation barrier was recalculated by optimizing the relevant stationary points using M06 functional.²²

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02344.

PES of all pathways, Cartesian coordinates, absolute energies, frequencies, and detailed thermodynamic parameters of all computed stationary points along with the structure in the ball and stick model (PDF)

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Notes

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