

Mechanism for the Reaction of a Tungsten-Germylyne Complex with α , β -Unsaturated Ketones: A DFT Study

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Abstract. In this report we present results of theoretical analysis for the reaction mechanism involving a tungsten-germylyne complex with α , β -unsaturated ketones. Three different substituents, namely H, Me and CF_3 in α -position of the unsaturated ketones have been selected to account for a variety of experimental observations. The computed results for different unsaturated ketones are in good agreement with experimental evidence and suggest that the formation of the final product can be achieved through steric as well as electronic effects.

Keywords. Tungsten-germylyne complexes; α , β -unsaturated ketones; substituent effect; density functional theory.

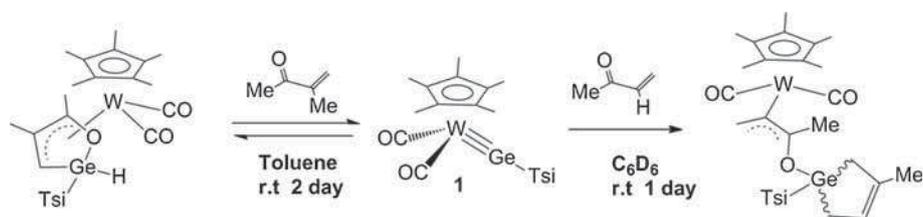
1. Introduction

Since the synthesis of the first carbyne complex in 1973,¹ this class of complexes constitutes an attractive synthetic target for research in fundamental organometallic and main-group chemistry. Since carbyne complexes bear formal metalcarbon triple bonds, the study of carbyne complexes is quite intriguing, mostly due to their unique structural parameters, bonding characteristics, and reactivity properties. This is particularly true for the application of such species in catalytic reactions.² Only recently, heavier analogues of carbyne complexes have been synthesized. For example, Power *et al.* reported a molybdenum germylyne complex as the first heavier congener of carbyne complexes in 1996.³ Subsequently, a series of heavier congeners have been synthesized between the years 2000 to 2010 by Filippou *et al.*⁴ In comparison to synthetic efforts, theoretical studies on the reactivity of such complexes are rather scarce.⁵ Fukuda *et al.* first reported that germylyne complexes react with alcohols and aldehydes at room temperature.⁶ Subsequently, Tilley *et al.* reported the reactions of an unstable cationic osmiumsilylyne complex with alkynes, resulting in product formation via addition to the $\text{Os}\equiv\text{Si}$ triple bond.⁷ More recently, Fukuda *et al.* reported a new series of reactions of **1** with α , β -unsaturated ketones involving a complete cleavage of the $\text{W}\equiv\text{Ge}$ triple bond to yield two types of η^3 -germoxyallyl

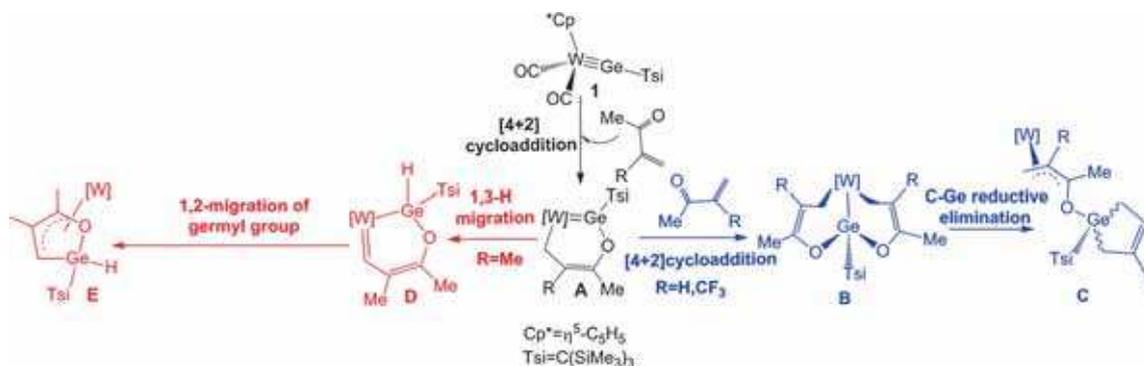
complexes, depending on the substituents in α -position of the ketones (scheme 1).⁸ Due to these experimental results, two general mechanisms were postulated in an effort to explain the formation of two η^3 -germoxyallyl species. As depicted in scheme 2, for $\text{R}=\text{H}$, the major pathway should result in an initial [4+2]-addition leading to intermediate **A**. The subsequent step for a second [4+2]-cycloaddition between a $\text{W}=\text{Ge}$ double bond and another molecule of a α , β -unsaturated ketone generates two fused six-membered rings as intermediates **B** and therefore provides the corresponding product **C**. However, for $\text{R}=\text{Me}$, the first step should also result in an initial [4+2]-addition leading to intermediate **A**. The subsequent step for a 1, 3-H migration results in the formation of a carbene complex, intermediate **D**. Finally, this intermediate then provides the corresponding product **E**.⁸ Based on these experimental results, the reaction route largely depends on whether substituents are present in α -position of the α , β -unsaturated ketones or not.

To the best of our knowledge, there are currently no detailed theoretical studies available in the literature for these novel reactions of **1** with α , β -unsaturated ketones reported by Fukuda *et al.*⁸ Here, we report a detailed density functional theory (DFT) computational investigation of the mechanism and substituent effect of **1** with α , β -unsaturated ketones based on experimental evidence reported by Fukuda *et al.*⁸ From the results presented here, we hope to gain more insights into the factors that control the activation barriers of this

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Scheme 1. Reactions of **1** with different α , β -Unsaturated Ketones.



Scheme 2. Possible Mechanisms for the Reactions of **1** with α , β -Unsaturated Ketones.

key reaction. Furthermore, this study will also provide invaluable information to facilitate an improved understanding of the mechanisms of other related reactions.

2. Computational Methods

Geometries, energies, and first- and second-energy derivatives of all of the stationary points found here were fully optimized by density functional theory (DFT) using the GAUSSIAN 09 program suite.⁹ For DFT calculations, the M06-2X hybrid functional,¹⁰ combined with the 6-31G(d, p) basis set for all atoms except for W, which the small-core Los Alamos (LANL2TZ(f)) pseudopotentials and basis sets that include the Dunning-Huzinaga full TZ and Los Alamos ECPs plus TZ have been employed with an extra f polarization function¹¹ were selected. Vibrational frequency calculations at the M06-2X/6-31G (d, p) (LANL2TZ (f) for W) level of theory were used to characterize all of the stationary points as either minima (the number of imaginary frequencies (NIMAG=0) or transition states (NIMAG=1)). The relative energies are, thus, corrected for the vibrational zero-point energies (ZPE, not scaled). In several significant cases, intrinsic reaction coordinate (IRC)¹² calculations were performed to unambiguously connect the transition states with the reactants and the products. The solvent effect was taken into account by M06-2X/6-311++G (d, p) (LANL2TZ (f) for W) single-point calculation with integral equation formalism polarizable continuum model (IEFPCM). The radii and nonelectrostatic terms were taken from Truhlar.¹³

3. Results and Discussion

3.1 Mechanism for reaction of **1** with methyl vinyl ketone ($R = H, R2$)

To ensure simplicity in the computational studies, the Cp^* group has been replaced by the Cp group in our calculations. The corresponding energy profiles for reaction pathways **a**, **b** and **c** are shown in figure 1. The optimized geometries for the reactants, intermediates, transition states and products of the reactions along with selected key geometry parameters (e.g. bond lengths) are depicted schematically in figure 2. The free energies for these reactions are shown in table S2 (see Supplementary Information) and change relative to the starting materials, dissolved or gaseous. Unless otherwise noted, the relative energies discussed in subsequent sections refer to the value obtained in benzene as a solvent. Detailed structural parameters and energies determined here are can be found in the Supporting Information.

To introduce this study, the feasibility of the originally proposed mechanism has been evaluated. First, we have examined the reaction mechanisms between **1** and methyl vinyl ketone ($R=H, R2$) in benzene. In accordance to our calculated results, the first step for the title reaction involved the [4+2]-addition of **A-1** with one molecule of a α , β -unsaturated ketone to generate **A-2** through a six-membered transition structure **A-TS1**. Figure 1 illustrates that the free activation energy was calculated to be 14.3 kcal/mol for **A-TS1** and the free reaction energy was determined to be -5.9 kcal/mol for **A-2** with respect to the reactant. Figure 2 shows that the bond lengths of W-C and Ge-O were found to be

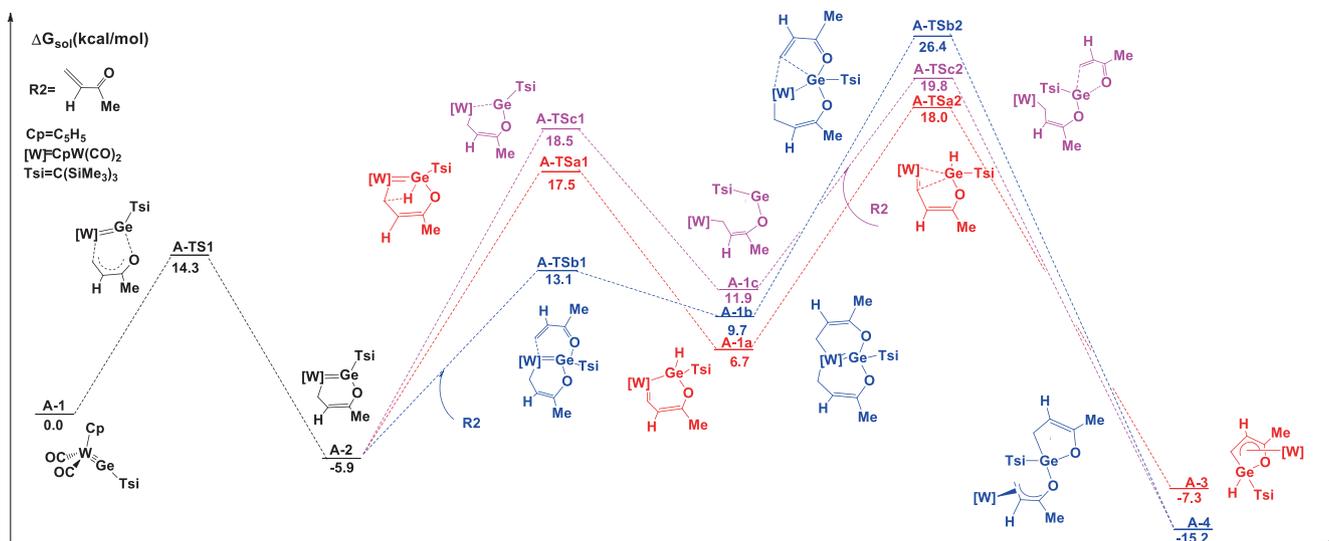


Figure 1. Energy profiles for path **a**, **b** and **c** ($R=H$); the relative energies are given in kcal/mol.

3.386 and 2.146 Å, respectively. As the reaction proceeds from **A-TS1** to **A-2**, it becomes clear that the W-C and Ge-O bonds have been fully established, with bond lengths of the W-C and Ge-O bonds now being 2.331 and 1.831 Å, respectively. After [4+2]-cycloaddition of a substrate molecule to the $W\equiv Ge$ triple bond, three possible reaction pathways could be determined from our calculations. For pathway **a**, a 1,3-H migration transition state was located, resulting in the formation of the carbene complex intermediate **A-1a**. Based on computation results obtained, the activation free energy of this step was found to be 23.4 kcal/mol with the formation of **A-1a** being an endothermic process (the free reaction energy for the **A-1a** was 12.6 kcal/mol with respect to **A-2**). A higher energy barrier found for this step indicates that this step is also rate-determining for pathway **a**. In the 1,3-H migration transition state, the H-atom connected to C is transferred to a Ge atom and the distances of the H-C and H-Ge bonds were determined to be 1.762 and 1.656 Å, respectively. Finally,

1,2-migration of the germyl group to the carbene carbon followed by coordination of the $C=C$ double bond in the oxagermacyclopentenyl ring to the unsaturated W-center results in formation of complex **A-3**. Figure 2 shows that the formed Ge-C and cleaved Ge-W bond lengths were found to be 2.136 and 3.185 Å in **A-TS2a**, respectively. The final energy barrier was determined to be 11.3 kcal/mol (transition state **A-TS2a**). These final steps are exothermic in nature totaling -14.0 kcal/mol.

In pathway **b**, a second [4+2] cycloaddition between a $W=Ge$ double bond and another molecule of a α, β -unsaturated ketone could generate intermediate **A-1b** with two fused six-membered rings as chelating moieties. Figure 2 show that the W-C and Ge-O bond lengths for the second cycloaddition transition state **A-TSb1** were 3.010 and 1.983 Å, respectively. The free activation energy of this step was endothermic in nature with 19.0 kcal/mol, together with the formation of **A-1b** also being endothermic (the free reaction energy for the **A-1b** was 15.2 kcal/mol with respect to **A-1** + **R2**).

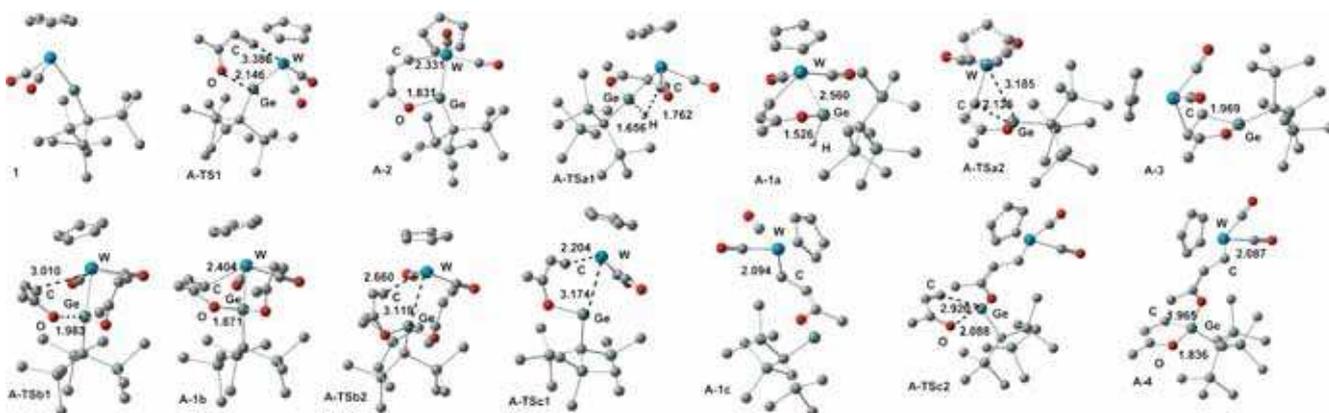


Figure 2. Selected optimized structures for the reaction of **1** and **R2**, with selected structural parameters (bond lengths in Å).

Finally, intermediate **A-1b** undergoes a GeC reductive elimination to form η^3 -allyl complexes **A-3** through **A-TSb2**. The free activation energy for this step was determined to be 16.7 kcal/mol and the free reaction energy was -17.0 kcal/mol for **A-3** with respect to **A-1b**. Overall, the potential energy surface shows that the second [4+2] cycloaddition of **A-1** is the rate-determining step for this pathway. Apart from the pathways suggested by Fukuda *et al.*,⁸ the cleavage of a WGe bond of **A-2** through **A-TSc1** generating a germylene intermediate **A-1c** would provide another possible reaction mechanism (pathway **c**). Figure 1 show that the free activation energy of this step was estimated to be 24.4 kcal/mol. Also, an endothermic process for formation of **A-1c** was found in our calculations (the free reaction energy for **A-1c** was found to be 17.8 kcal/mol with respect to **A-2**). Important to note in this context is that this step is also rate-determining. Subsequently, a [2+1] cycloaddition between a germylene unit and another molecule of α, β -unsaturated ketones generates product **A-4** through **A-TSc2**. The final energy barrier was found to be 7.9 kcal/mol and these final steps are exothermic in nature by -27.1 kcal/mol. According to our calculated results, a lower energy barrier was found for **A-TSb1** and for the whole reaction process of **R2** and **1**. In turn, this would suggest pathway **b** to be more feasible than pathway **a** and **c**. Furthermore, our calculations suggest that the major pathway for **R2** and **1** should be causing an initial [4+2]-addition resulting in the formation of an intermediate. The subsequent step for a second [4+2]-cycloaddition between a W=Ge double bond and another molecule of a α, β -unsaturated ketone generates two fused six-membered intermediates which then result in the formation of the corresponding product. Our calculated results are in good agreement with the experimental observations obtained previously.⁸

3.2 Mechanism for reaction of **1** with 3-methyl-3-butene-2-one (R= Me, **R3**)

A second study performed by us involved the investigation of the reaction mechanism of **1** and 3-methyl-3-butene-2-one (R=Me, **R3**) in toluene. The energy profiles for all of the reaction pathways are illustrated in figure 3. The optimized geometries for the reactants, intermediates, transition states and products of the reactions along with selected key geometry parameters (e.g. bond lengths) are depicted schematically in figure 4. Similar to **1** and **R2**, three possible pathways have been determined in our calculations. The first step for **R3** and **1** also involved the first [4+2]-addition of **B-1** with one molecule of a α, β -unsaturated ketone to generate **B-2**. The free activation energy was estimated to be 14.7 kcal/mol for **B-TS1** and the free energy of reaction was found to be -3.9 kcal/mol for **B-2** with respect to the reactant. For pathway **a**, the free activation energy for the transition state of the 1,3-H migration was determined to be 22.8 kcal/mol. The formation of **B-1a** was found to be an endothermic process (the free energy of reaction for the **B-1a** was found to be 11.8 kcal/mol with respect to **B-2**). Finally, the 1,2-migration of the germyl group to the carbene carbon followed by coordination of the C=C double bond in the oxagermacyclopentenyl ring to the unsaturated W-center results in formation of complex **B-3**. The final energy barrier was determined to be 10.1 kcal/mol with these final steps being exothermic in nature by -13.4 kcal/mol. According to our calculated results, almost the same free activation energy was found for **R2** and **R3**, indicating that the substituent (R= Me) in α -position has almost no effect on pathway **a**. A higher energy barrier was

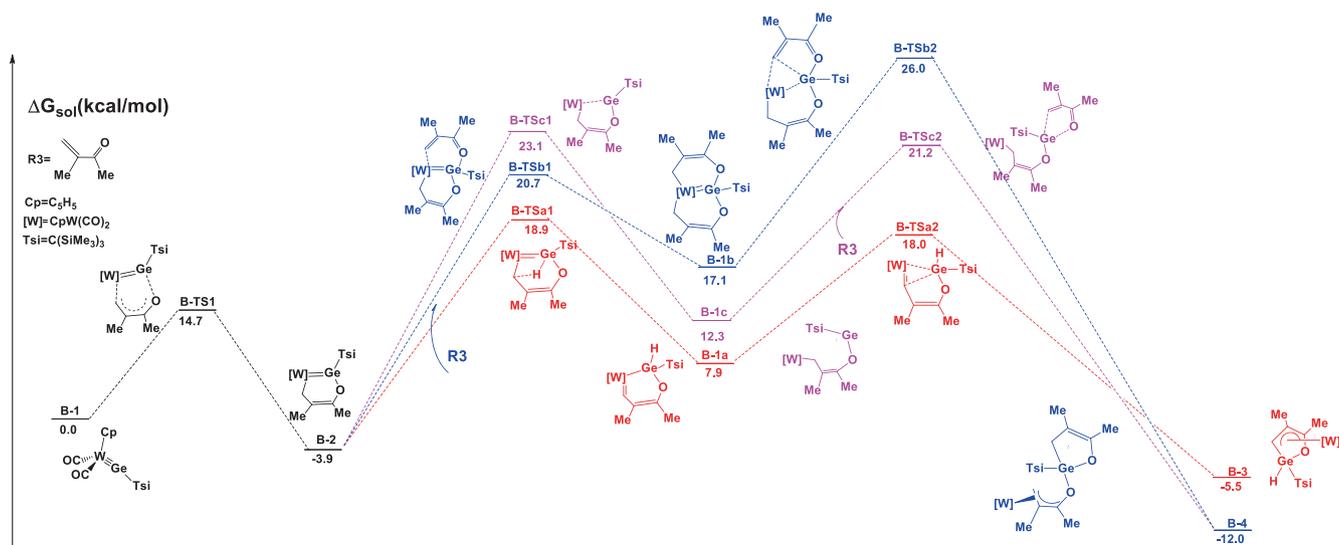


Figure 3. Energy profiles for path **a**, **b** and **c** (R=Me); the relative energies are given in kcal/mol.

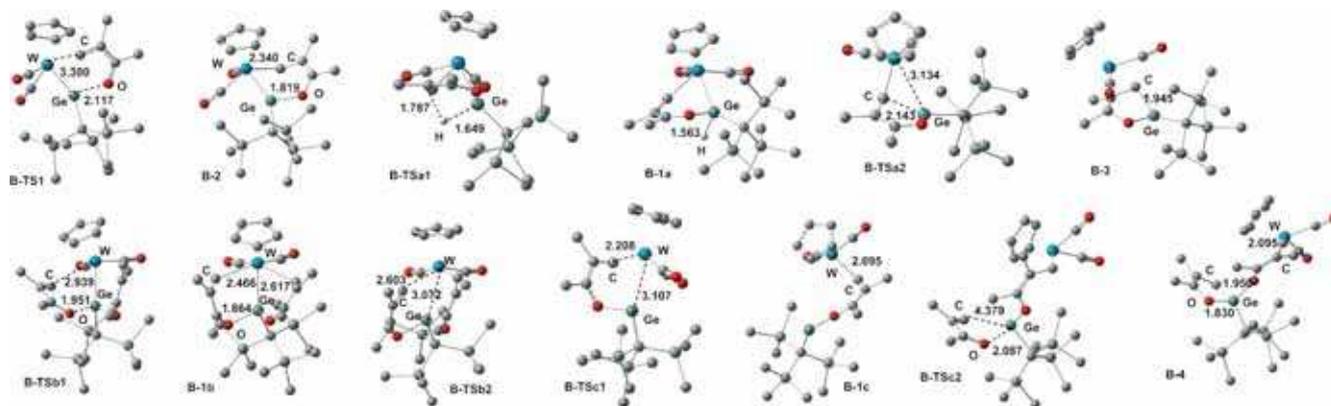


Figure 4. Selected optimized structures for the reaction of **1** and **R3**, with selected structural parameters (bond lengths in Å).

found for the 1,3-H migration step, suggesting that this step is rate-determining for pathway **a**.

In pathway **b**, the free activation energy for a second [4+2]-cycloaddition between a W=Ge double bond and another molecule of a α, β -unsaturated ketone was determined to be 24.6 kcal/mol. The free activation energy for the subsequent step of this GeC reductive elimination to form the η^3 -allyl complex **B-3** was found to be 8.9 kcal/mol. Overall, the potential energy surface shows that the second [4+2]-cycloaddition of **B-1** is the rate-determining step for this pathway. These results clearly show that a methyl substituent significantly increases the free activation energy for the second [4+2]-cycloaddition between a W=Ge double bond and another molecule of a α, β -unsaturated ketone. A higher energy barrier found for the second [4+2]-cycloaddition indicates that pathway **b** would be infeasible for the reaction of **R3** and **1**. The relatively high energy barriers found for **B-TSb1** compared to those of **A-TSa1** can mainly be attributed to the following reasons: (1) the methyl group in α -position of 3-methyl-3-buten-2-one prevents the substrate from approaching the W=Ge double bond in the intermediate **B-2** due to sterically unfavorable interactions; (2) orbital interactions of the HOMO of **A-TSa1** (figure 5) indicate that the newly formed W-C and Ge-O bonds attribute to the orbital interactions between the HOMO (**A-2**) and the LUMO (α, β -unsaturated ketone). Therefore,

the free activation energy for the [4+2]-cycloaddition between a W=Ge double bond and the α, β -unsaturated ketone is dominated by HOMO (**A-2**) and LUMO (α, β -unsaturated ketone) differential orbital energies. In general, small differential orbital energies lead to large transition state stabilization energies, and thus to lower activation energies. A methyl group in α -position would increase the LUMO energy of α, β -unsaturated ketones, which causes the second [4+2]-cycloaddition to be less feasible than a 1,3-H migration. For pathway **c**, the free activation energy for the cleavage of the W=Ge bond resulting in the formation of a germylene intermediate was found to be 27.0 kcal/mol. Subsequently, a [2+1]-cycloaddition between a germylene unit and another molecule of a α, β -unsaturated ketone yields product **B-4** through **B-TSc2**. The final energy barrier was estimated to be 8.9 kcal/mol and these final steps are exothermic in nature by -29.1 kcal/mol. Most notably due to steric effects, the major pathway for **R3** and **1** should be causing an initial [4+2]-addition resulting in the formation of an intermediate. The subsequent step for a 1,3-H migration results in the formation of the carbene complex intermediate. Finally, this intermediate then provides the corresponding product.

3.3 Mechanism for reaction of **1** with 3-trifluoromethyl-3-butene-2-one ($R = CF_3, R_4$)

According to our calculated results, steric effects rather than electronic effects play a crucial role in the formation of the product and the involvement of key intermediates of **R3**. Presumably, through substituent modification, electronic effects can be adjusted to become more significant than steric effects. We therefore focused our attention on the study of electronic effects of corresponding substituents. A trifluoromethyl group ($R = CF_3, R_4$) in α -position was selected as a model structural moiety. Energy profiles for all reaction

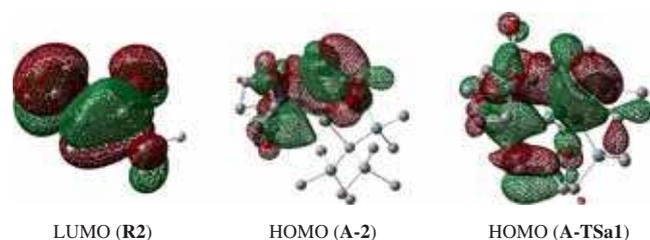


Figure 5. The orbital interactions for LUMO (**R2**), HOMO (**A-2**) and HOMO (**A-TSa1**).

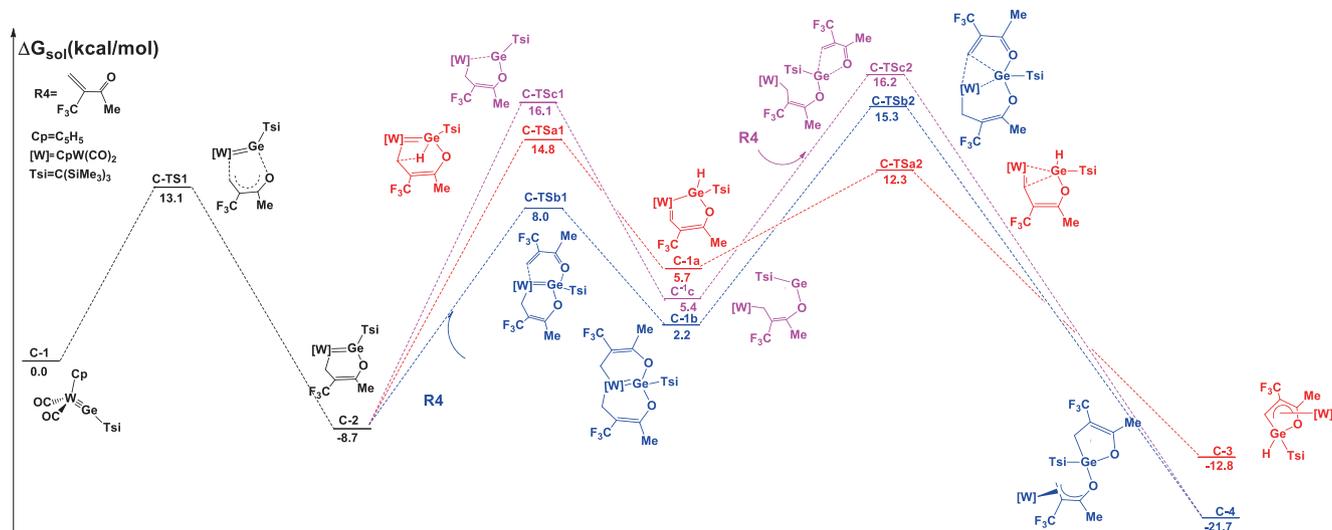


Figure 6. Energy profiles for path **a**, **b** and **c** ($R=CF_3$); the relative energies are given in kcal/mol.

pathways are illustrated in figure 6. Along with selected key geometry parameters (e.g. bond lengths), the optimized geometries for the reactants, intermediates, transition states and products of the reactions are depicted schematically in figure 7. As shown in figure 6, the free activation energy for the first [4+2]-addition step was calculated to be 13.1 kcal/mol for **C-TS1**. A lower energy barrier was found for the [4+2]-addition of **R4**, providing evidence for our hypothesis. The free activation energy for next 1,3-H migration transition state was determined to be 23.5 kcal/mol and the final energy barrier was estimated to be 6.6 kcal/mol for pathway **a**. These results indicate that the substituent ($R=CF_3$) in α -position has very little effect on pathway **a**. For pathway **b**, the activation free energy for a second [4+2]-cycloaddition between a $W=Ge$ double bond and another molecule of a α, β -unsaturated ketone was found to be 16.7 kcal/mol and the free activation energy for the final step was determined to be 13.1 kcal/mol.

Although a steric effect can still be detected, the trifluoromethyl group in α -position leads to a decrease of the LUMO energy of α, β -unsaturated ketones, which renders the second [4+2]-cycloaddition to be more feasible than a 1,3-H migration. Our calculated results suggest that electronic effects prevail over steric effects if a trifluoromethyl group is present as the substituent. In pathway **c**, the free activation energy for the cleavage of a $W-Ge$ bond to form a germylene intermediate was determined to be 24.8 kcal/mol with the final energy barrier being 10.8 kcal/mol. As a result of the lower energy barrier found for **C-TSb1** involving the entire reaction process for **R4** and **1** in pathway **b** was found to be more feasible than pathway **a** and **c**. These calculated results indicate that modifying the substituent on unsaturated ketones has almost no effect on the 1,3-H migration pathway. However, the effect on the second step of the cycloaddition is significant. The formation of two types of η^3 -germyoxyallyl

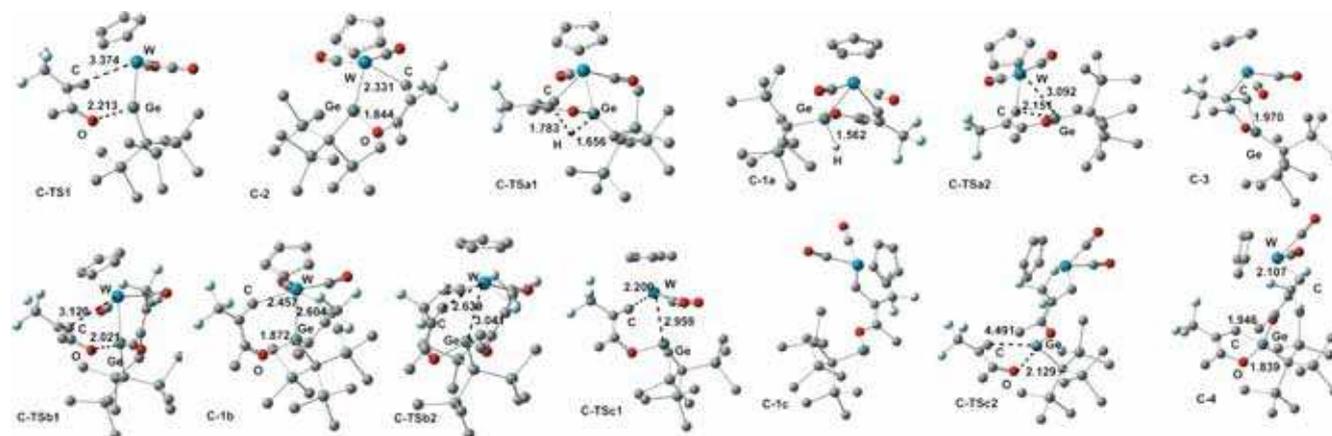


Figure 7. Selected optimized structures for the reaction of **1** and **R4**, with selected structural parameters (bond lengths in Å).

units can therefore not only be achieved through steric effects, but also through implementation of electronic effect.

4. Conclusions

In summary, this study has provided detailed theoretical calculations on the reaction trajectory and theoretical estimation of the activation energy and reaction enthalpy for the title reactions. The computational results based on the model complex and substrate show that the reaction route largely depends on the substituent in α -position. (1) For **R2** (R=H), the major pathway should be causing an initial [4+2]-addition leading to an intermediate. Subsequent steps for a second [4+2]-cycloaddition between a W=Ge double bond and another molecule of α, β -unsaturated ketone generates two fused six-membered rings as moieties in the intermediate to provide the corresponding product. (2) Due to steric effects, the major pathway for **R3** (R=Me) and **1** should be causing an initial [4+2]-addition leading to an intermediate. The subsequent step for a 1,3-H migration results in the formation of the carbene complex intermediate. Finally, this intermediate then furnishes the corresponding product. (3) When α, β -unsaturated ketones are substituted with an electron-withdrawing group (e.g. **R4**, R=CF₃), the electronic effects outweigh any steric effects resulting in an initial [4+2]-addition and leading to an intermediate. The subsequent step for a second [4+2]-cycloaddition between a W=Ge double bond and another molecule of α, β -unsaturated ketone generates two fused six-membered rings in the intermediate, resulting in the production of the corresponding product. These computational results are consistent with the experimental observations made by Fukuda *et al.*⁸ These predictions may be useful as a powerful guide for future synthetic routes and as a tool to solve potential problems in other theoretical and experimental studies.

Supplementary Information

Tables S1 and S2 are in Supplementary Information available at www.ias.ac.in/chemsci.

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