



Theoretical investigation on possible mechanisms on regioselective formation of (η^3 -siloxyallyl)tungsten complexes

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ABSTRACT

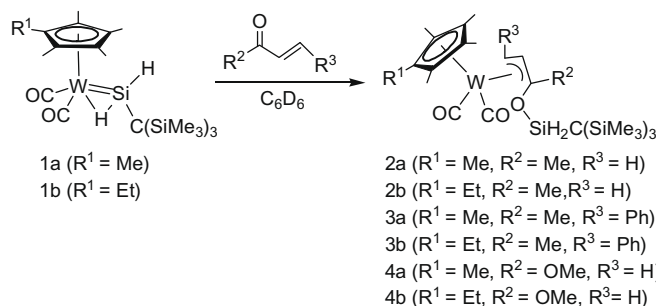
Selective formation of (η^3 -siloxyallyl)tungsten complexes by reaction of hydrido(hydrosilylene)tungsten complexes with α,β -unsaturated carbonyl compounds was reported experimentally. The mechanisms have been investigated by employing the model reaction of $[\text{Cp}(\text{CO})_2(\text{H})\text{W}=\text{Si}(\text{H})-\{\text{C}(\text{SiH}_3)_3\}]$ (**R**), derived from the original experimental complex $\text{Cp}'(\text{CO})_2(\text{H})\text{W}=\text{Si}(\text{H})-\{\text{C}(\text{SiMe}_3)_3\}$ (**1a**, $\text{Cp}' = \text{Cp}^*$; **1b**, $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$), with methyl vinyl ketone, under the aid of the density functional calculations at the b3lyp level of theory. It is theoretically predicted that the route involving migration of the hydride to silicon to afford a 16e intermediate $[\text{Cp}(\text{CO})_2\text{W}-\text{SiH}_2-\{\text{C}(\text{SiH}_3)_3\}]$ is inaccessible (route 2), supporting the proposition by experiments. Another route, via [2 + 4] cycloaddition followed by directly Si–H reductive elimination, is theoretically predicted to be accessible (route 1). In route 1, two possible paths with different attacking directions of the oxygen of methyl vinyl ketone at Si (W=Si) are put forward. The attack at the Si atom from the hydride (H1) side of the plane W–Si–H1 in **R** is found to be preferred kinetically. The regioselectivity for formation of (η^3 -siloxyallyl)tungsten complexes, where only the exo-anti isomer was obtained, is discussed based on the consideration of thermodynamics and kinetics.

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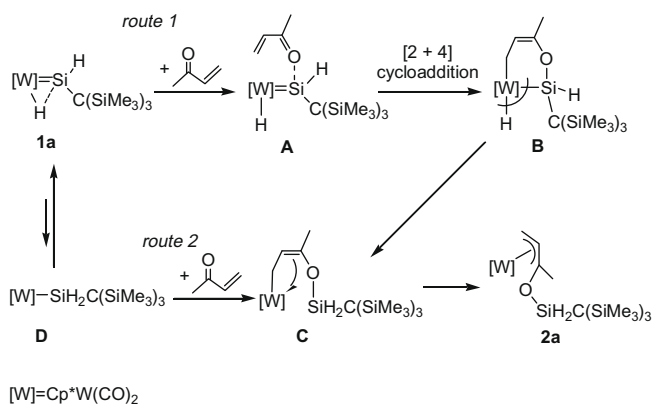
1. Introduction

Although transition-metal silylene complexes have developed slowly comparing with carbene complexes, extensive study on the chemistry of transition-metal silylene complexes has demonstrated that transition-metal silylene complexes as intermediates [1–24] are increasingly playing important roles in many stoichiometric and catalytic processes [25,26]. Since the first silylene complexes, $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{Si}(\text{SR})_2]\text{BPh}_4$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) ($\text{R} = \text{Et}$, $p\text{-MeC}_6\text{H}_4$) [27] were presented in 1990, considerable endeavors have focused on the synthetic methods [27–33] and structural characteristics of silylene compounds. Subsequently, exploration of reactivity for stable silylene complexes with unsaturated substrates were developed. For instance, [2 + 2]-cycloaddition was developed by reaction of cationic ruthenium silylene complexes $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiR}_2]\text{BPh}_4$ ($\text{R} = \text{Me}$ or Ph) with methyl and simple aryl isocyanates [35]. Thereafter, the first [2 + 4] cycloaddition reactions were developed, where the neutral hydrido(hydrosilylene) tungsten complexes $\text{Cp}'(\text{CO})_2(\text{H})\text{W}=\text{Si}(\text{H})-\{\text{C}(\text{SiMe}_3)_3\}$ (**1a**, $\text{Cp}' = \text{Cp}^*$; **1b**, $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$) react with α,β -unsaturated carbonyl compounds (Eq. (1)) [36]. Interestingly, η^3 -siloxyallyl complexes were produced following the [2 + 4] cycloaddition. Pos-

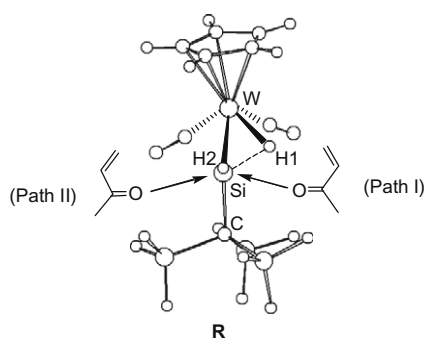
sible reaction mechanisms were proposed on the basis of experiments as shown in Scheme 1 [15], where two possible routes, route 1 and route 2, were presented. In this paper, our theoretical calculations with the aid of density functional theory (DFT) are targeted to further explore the possible mechanisms in details. Two possible site-attack modes of the oxygen of methyl vinyl ketone at the silicon atom are involved in such reaction mechanisms, as shown in Scheme 2. One path (Path I) starts with the attack of methyl vinyl ketone to the silicon atom from the hydride (H1) side of the plane W–Si–H2 in **R**, and the other path (Path II) from the opposite side of the plane mentioned above. What we want to study with interests is as follows, (i) the energies involved in the possible reaction mechanisms, (ii) whether Path I or Path II preferred? (iii) whether route 1 or route 2 more feasible? (iv) conversion of **B** to **2a**, direct or via **C**?



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Scheme 1.



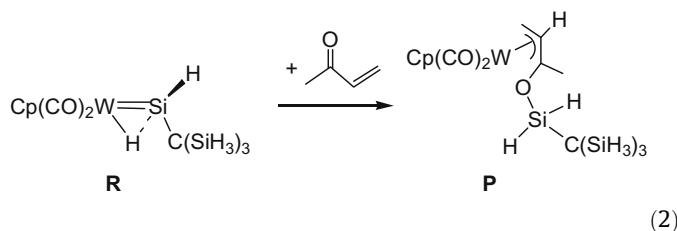
Scheme 2.

2. Computational details

Molecular geometries of the complexes were optimized without constraints via density functional theory calculations using the gradient-corrected hybrid Becke3LYP (B3LYP) [37–40] functional. Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K which include entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. Intrinsic reaction coordinates (IRCs) [41,42] were calculated for located transition states to confirm that such structures indeed connect two relevant minima. The effective core potentials (ECPs) of Hay and Wadt with a double- ζ basis set (LanL2DZ) [43–45] were used to describe W and Si. 6–31G basis set was used for H, C and O [46,47]. Polarization functions were also added for the three carbon atoms ($\zeta_d = 0.8$), O ($\zeta_d = 0.8$) in methyl vinyl ketone, the two hydrogen atoms ($\zeta_p = 0.11$) and Si ($\zeta_d = 0.262$) of silylene. All calculations were performed with the GAUSSIAN 03 software package [48].

3. Results and discussion

In this work, Cp* or C₅Me₄Et is modeled by Cp and the methyl groups attached on silicon are replaced by hydrogen atoms. Methyl vinyl ketone, employed experimentally, is chosen as a substrate. The model reaction is generated as Eq. (2), where the model reactant **R** is derived from **1a** and **P** from **2a**. Although such reactions are modeled for the purpose of reducing computer cost, the computed structural data can well reproduce the experimental parameters as discussed in the later in this paper.



The hydrido(hydrosilylene) tungsten model complex [Cp(CO)₂(H)W=Si(H)-C(SiH₃)₃] (**R**) has been optimized and structurally analyzed by a DFT calculation at the B3LYP level [49]. The structural parameters are consistent with those obtained from the X-ray crystalline structure of Cp'(CO)₂(H)W=Si(H)[C(SiMe₃)₃] (Cp' = η^3 -C₅Me₄Et) [49]. As shown in the geometrical structure of **R** (Fig. 1), an interaction of the hydride with the silicon atom is existent, supported by the structural data where the Si–H1 bond distance is 1.70 Å and the H1–W–Si angle is only 45.2°.

On the basis of the experimental observations, Tobita and coworkers proposed two possible routes, as shown in Scheme 1. In route 1, the first step (**1a** to **A**) is the binding of the reactant **1a** with methyl vinyl ketone via Si···O interaction. The second step (**A** to **B**) is a [2 + 4] cycloaddition process to make a six-membered ring. The following step (**B** to **C**) is the reductive elimination of the hydride and the silyl group from the metal center to form a new Si–H bond, and the last step (**C** to **2a**) is the isomerization from an η^1 to an η^3 -allyl complex. In route 2, they proposed hydrogen migration from the metal center to the silicon atom (**1a** to **D**) to make a 16e species. The following step (**D** to **C**) is the reaction of **D** with methyl vinyl ketone to give **C**, and then **C** rearranges to produce **2a**.

We first examine route 1 as proposed experimentally. Examining the geometrical features of **R**, one can see that methyl vinyl ketone can attack the silicon atom of **R** from two sides of the plane W–Si–H₂. Two possible reaction mechanisms are proposed. Path I starts with the attack of methyl vinyl ketone at the silicon atom from the hydride (H1) side of the plane W–Si–H₂ in **R**, and Path II from the opposite side of the plane mentioned above (Scheme 2). Selected structural parameters calculated for species involved in the two paths are illustrated in Fig. 1 and the free energy profiles for Paths I and II are given in Fig. 2.

In Path I, the first step starts with the attack of the oxygen of methyl vinyl ketone from the H1 side of the plane W–Si–H₂ in **R**, giving an intermediate (**Int1**, one model of **A**). The Si···O is calculated to be 1.97 Å in **Int1**, confirming a relative strong interaction between the two atoms. Clearly, this is due to the strong oxophilic ability of silicon atom. With the occurrence of the Si···O interaction, the Si–H1 is almost broken and the W–H1 is nearly formed. **Int1** is found to be more stable than the reactants as a result of the occurrence of the Si···O interaction. The free energy of **Int1** is higher than the reactants because of remarkable entropy decrease.

The second step is a process of [2 + 4] cycloaddition in which the W–Si moiety in **Int1** couples with methyl vinyl ketone, giving the second intermediate (**Int2**, one model of **B**). A six-membered ring is afforded. As seen in the geometry of **TS₁₋₂**, the Si–O and W–C1 bonds are being formed, the C3–O and C1–C2 are being stretched, and the C2–C3 is being shortened. It is noted that H1 in **TS₁₋₂** is moving to the bottom of the metal center. In **Int2**, the silicon atom has sp³ hybridization as a result of the formation of the Si–O σ bond. Therefore, the W–Si bond is formed as a single σ bond, making the bond longer than that in **Int1**. As is expected, H1 is pushed to the bottom of W in **Int2** as a result of the formation of W–C1 bond. **Int2** is obviously more stable than **Int1**, mainly resulting from formation of the strong Si–O bond. The free activation energy for the cycloaddition step is calculated to be 6.2 kcal/mol. The free energy change (5.6 kcal/mol) from **Int1** to **Int2** is less

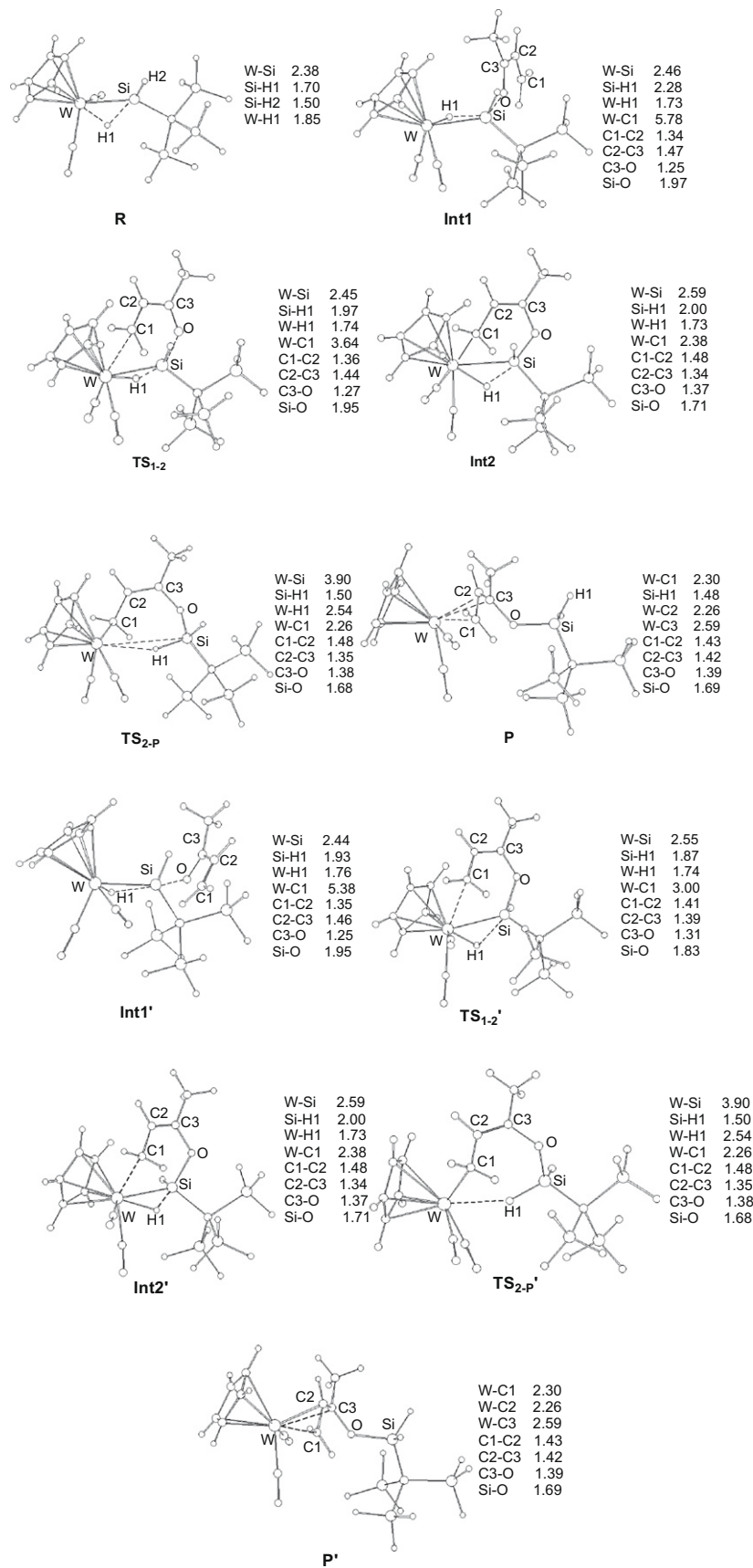


Fig. 1. Selected structural parameters (Å) calculated for species involved in Paths I and II.

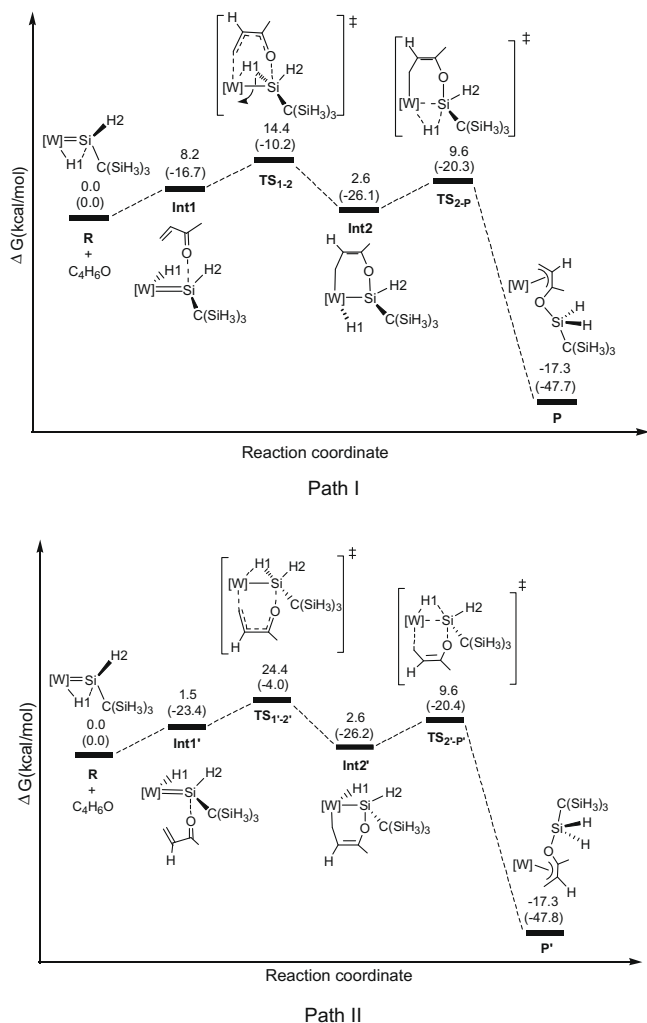


Fig. 2. Two possible free energy profiles for the model reaction of **R** with methyl vinyl ketone involved in route 1. The free energies and relative energies (in parentheses) are given in kcal/mol.

than the electronic energy change (9.4 kcal/mol), arising from formation of the six-membered metallacycle. The last step is the transformation from a six-membered metallacycle to an η^3 -substituted allyl tungsten complex. This process features three structural changes, (i) formation of Si–H1, (ii) Si–H1 bond moving far away from the metal center, and (iii) η^3 -substituted allyl coordination. The barrier in free energy for the step is calculated to be 7.0 kcal/mol, and our results of calculations confirmed that the product **P** is indeed much more stable than **Int2**. Strong W-(η^3 -allyl) interaction, Si–H formation and relief of steric hindrance as the moiety $-\text{SiH}_2\text{C}(\text{SiH}_3)_3$ moving away from the metal center contribute to the stability of **P**. In geometry of **P**, C1–C2 (1.43 Å) and C2–C3 (1.42 Å) are shorter than the C–C single bond of ethane (1.54 Å) and longer than the C–C double bond of ethylene (1.34 Å), confirming the η^3 -allyl coordination mode. W–C3 is longer than W–C1 and W–C2 as a result of the steric hindrance between the carbonyl ligand and the oxygen atom of the siloxy group, which is well in agreement with the experimental observations. It can be drawn from the pathway shown in Path I that (i) the overall reaction is favorable thermodynamically and (ii) the rate-determining step is the [2 + 4] cycloaddition.

In Path II, the first intermediate **Int1'** (the other model of **A**) is afforded where the attack of the oxygen in methyl vinyl ketone to the silicon atom is from the other side of the plane W–Si–H2

in **R**. It is found that **Int1'** is more stable than **Int1** as a result of the fact that the steric hindrance involved in the latter is greater than that in the former. This step is preferred over the corresponding one involved in Path I thermodynamically both in electronic energy and in free energy. Similar to the second step in Path I, the second step in Path II is the [2 + 4] cycloaddition where the W–Si couples with methyl vinyl ketone to produce a six-membered ring intermediate (**Int2'**, the other model of **B**). Our results of calculations confirmed that **Int2'** is the enantiomer of **Int2**, giving them almost identical energies. Comparing the two cycloaddition steps, **Int1'** to **Int2'** in Path II and **Int1** to **Int2** in Path I, the free activation energy calculated for the former step (22.9 kcal/mol) is much higher than that for the latter step (6.2 kcal/mol), indicating the [2 + 4] cycloaddition is more favorable kinetically in Path I than in Path II. It is concluded by comparing the two paths that Path I is preferred over Path II kinetically.

Route 2 was proposed to start with the first conversion of the reactant **1a** to the intermediate **D**, where the hydride completely moves to the silicon atom to give a 16e species. For theoretically examining the feasibility of the route, we attempted to optimize the complex, $\text{Cp}(\text{CO})_2\text{W}-\text{SiH}_2\text{C}(\text{SiH}_3)_3$, a model of **D**, at the same B3LYP level of theory. But our calculations show that the reactant (**R**) is always obtained instead of giving the model complex of **D**, supporting the experimental proposition that route 2 is quite inaccessible. As for the transformation **B** \rightarrow **C** \rightarrow **2a** in route 1, the transition state from $\text{Cp}(\text{CO})_2\text{WCH}_2\text{CH}=\text{CMeOSiH}_2\text{C}(\text{SiH}_3)_3$, a model of **C**, to the product **P**, a model of **2a**, cannot be located. Instead, the transition state from **Int2** (or **Int2'**) to **P**, a model step derived from **B** to **2a**, was located, and **C** is calculated to be even less stable than **B**, suggesting the final product **2a** is produced directly from **B** while not through the intermediate **C**.

We previously theoretically studied the relative stability of the η^3 -allyl transition metal complexes [50–52]. For the model d^4 - $\text{CpMoL}_2(\eta^3\text{-allyl})$ ($\text{L} = \text{Cl}^-$ and PH_3), the endo isomer was found to be preferred over the exo isomer if L is a weak π acceptor or a π donor, while the exo isomer becomes more stable if L is a strong π acceptor. For example, the exo isomer of the model d^4 - $\text{CpMoCO}_2(\eta^3\text{-allyl})$ is more stable than the endo isomer by 1.0 kcal/mol since the competition for backbonding interactions of Mo–CO and Mo– η^3 -allyl makes the endo isomer less favorable [52]. As a result, the Mo–CO of the exo isomer becomes shorter than that of the endo isomer. The four possible isomers studied here were optimized and shown in Fig. 3, together with the relative electronic energies and selected bond distances. The two exo isomers are

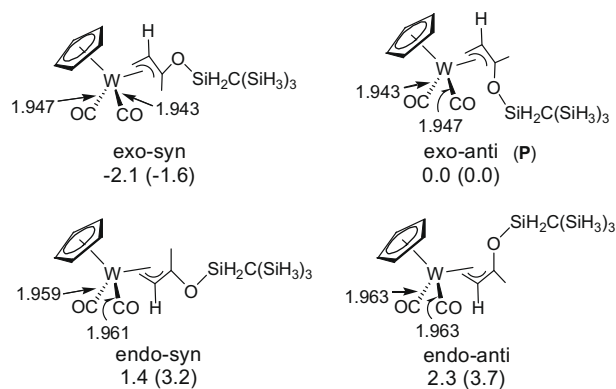


Fig. 3. B3LYP optimized geometric structures of the model product **P** and its three possible isomers, together with selected bond distances and relative energies. The relative energies of four possible isomers where Cp is replaced by Cp^* are given in parentheses. The bond distances are given in Å, and the relative energies are given in kcal/mol.

found to be more stable than the two endo isomers, consistent with the situation in $d^4\text{-CpMoCO}_2(\eta^3\text{-allyl})$. As the structural data show, the W–CO bond distances of the exo isomers are shorter than those of the endo isomers. Considering the fact that Cp^* was employed in experiments, we also optimized the geometric structures of four possible isomers where Cp is replaced by Cp^* . The relative energies of the four possible isomers are also given in parentheses in Fig. 3. It can be seen from Fig. 3 that the relative energies of the model isomers containing Cp and those containing Cp^* have the same trend. That is, the relative stability is in the same order, exo-syn > exo-anti (**P**) > endo-syn > endo-anti.

As our results of calculations confirm, the four possible isomers have approximate electronic energies, indicating the transformation from exo-anti isomer to the other three isomers is available thermodynamically. However, experiments confirmed only the exo-anti isomer was obtained, suggesting this transformation is not thermodynamic-controlled. The kinetic factors should be considered. Generally, there are two possible transformation modes for isomerization of $\eta^3\text{-allyl}$ metal complexes. One is the rotation of $\eta^3\text{-allyl}$ around the metal center, and the other is through an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ mode. As our previous study indicated, the latter isomerizing mode is preferred over the former one [51], suggesting the former isomerizing mode can be ruled out. As for the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ mode for the isomerization of **P**, the intermediate in $\eta^1\text{-form}$, a model of **C**, is calculated to be much less stable than **P** by 24.5 kcal/mol. Clearly, the activation energy from **P** to the intermediate in $\eta^1\text{-form}$ is at least larger than 24.5 kcal/mol. Therefore, we predict that the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ mode for the isomerization of **P** is inaccessible due to the high barrier from $\eta^3\text{-form}$ to $\eta^1\text{-form}$. In summary, the fact that the sole product was obtained is due to the kinetic inaccessibility, although the isomerization is thermodynamically accessible.

4. Conclusions

Tobita and coworkers experimentally proposed the mechanisms for selective formation of ($\eta^3\text{-siloxyallyl}$)tungsten complexes by reaction of hydrido (hydrosilylene)tungsten complexes with α,β -unsaturated carbonyl compounds. Two routes, route 1 and route 2, were offered. Our computational results indicate that route 2 is quite inaccessible since the complex $\text{Cp}(\text{CO})_2\text{W-SiH}_2\text{C}(\text{-SiH}_3)_3$, a model of **D**, cannot be located. For route 1, two possible pathways, Path I and Path II, have been proposed in terms of the two different attack directions of the oxygen of methyl vinyl ketone at the silicon atom. Path I is found to be favored over Path II since the highest barrier in free energy for the former (14.4 kcal/mol) is apparently lower than that for the latter (24.4 kcal/mol). The reactions of hydrido (hydrosilylene)tungsten complexes with α,β -unsaturated carbonyl compounds to produce ($\eta^3\text{-allyl}$)tungsten complexes are found to be favored thermodynamically, and the rate-determining step is the process of [2 + 4] cycloaddition where the W–Si moiety couples with the terminal carbon and oxygen of methyl vinyl ketone to afford a six-membered metallacyclic intermediate.

Additionally, the regioselectivity for formation of ($\eta^3\text{-siloxyallyl}$)tungsten complexes, where only the exo-anti isomer was obtained, is discussed based on the consideration of thermodynamics and kinetics. The four possible isomers are calculated to have similar relative energies, suggesting the isomerizations may be accessible thermodynamically. However, such isomerizations are predicted theoretically to be inaccessible kinetically since the transformation from **P** to the intermediate in $\eta^1\text{-form}$ needs to experience a high activation energy. The two exo isomers are found to be slightly more stable than the two endo isomers, which is in agreement with our previous study on the relative stabilities of

exo and endo isomers derived from the model complex $d^4\text{-CpMoCO}_2(\eta^3\text{-allyl})$.

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