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ORIGINAL PAPER

Quantum chemical study of the mechanism of ethylene elimination in silylative coupling of olefins

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Abstract Silylative coupling of olefins differs from olefin metathesis. Although in both these reactions ruthenium catalysts play a crucial role and ethylene product is detected, ruthenium-carbene intermediate is formed only in the course of the metathesis reaction. In this study quantum chemical calculations based on the density functional theory (DFT) have been carried out in order to examine the mechanism of the silylative coupling of olefins leading to ethylene elimination. In the first step of the catalytic cycle, a hydrogen atom from the ruthenium catalytic center is transferred preferentially to the carbon atom bound to Si in a vinylsilane. This H transfer is coupled with the formation of Ru-C bond. Next, the rotation around the newly formed C-C single bond occurs so that silicon atom is placed in the vicinity of the ruthenium center. The following step involves the migration of a silyl moiety, and leads to Ru-Si bond formation, coupled with ethylene elimination. The next reaction, that is the insertion of ethylene (alkene) into Ru-Si bond, has an activation barrier almost as high as the reaction of ethylene elimination. However, the posibility of removing gaseous ethylene from the reactive mixture together with the entropic fators suggests that the insertion of alkene that is larger than C_2H_4 is the rate limiting step in the silylative coupling of olefins. It also suggests that the substituents attached to the silicon atom or the carbon atoms of an alkene by electronic and steric effects may significantly affect silyl migration and thus the effectiveness of the catalytic reaction.

Keywords Density functional calculations · Reaction mechanisms · Silylation · Silylative coupling of olefins

Introduction

Silylative coupling of olefins is an effective and efficient method for obtaining substituted vinylsilanes, making a very important class of organosilicon reagents. Experimental evidence for the migratory insertion of ethylene, [1] vinylsilane [2] and styrene [33] into the Ru-Si or Ru-H bond has indicated that the mechanism of silylative coupling of olefins (see Fig. 1) is much different from that of olefin metathesis, as it does not involve a ruthenium-carbene intermediate.

Synthetic and catalytic efforts in studies on heterocoupling of 1-alkenes, *para*-substituted styrenes, and other olefins with vinylsilanes have resulted in new methods for regioselective preparation of 1-silyl-1-alkenes as well as finctionalized vinylsilanes and such as 1-silyl-styrenes and 1-silyl-2, N(O,S) substituted ethenes, (for recent review see [4–6]). It should be noted that various ruthenium catalysts have been successfully used in the reaction (see Fig. 2).

In order to gain further insight into the reaction mechanism, to find out the rate determining step, and to examine factors affecting stability of the corresponding

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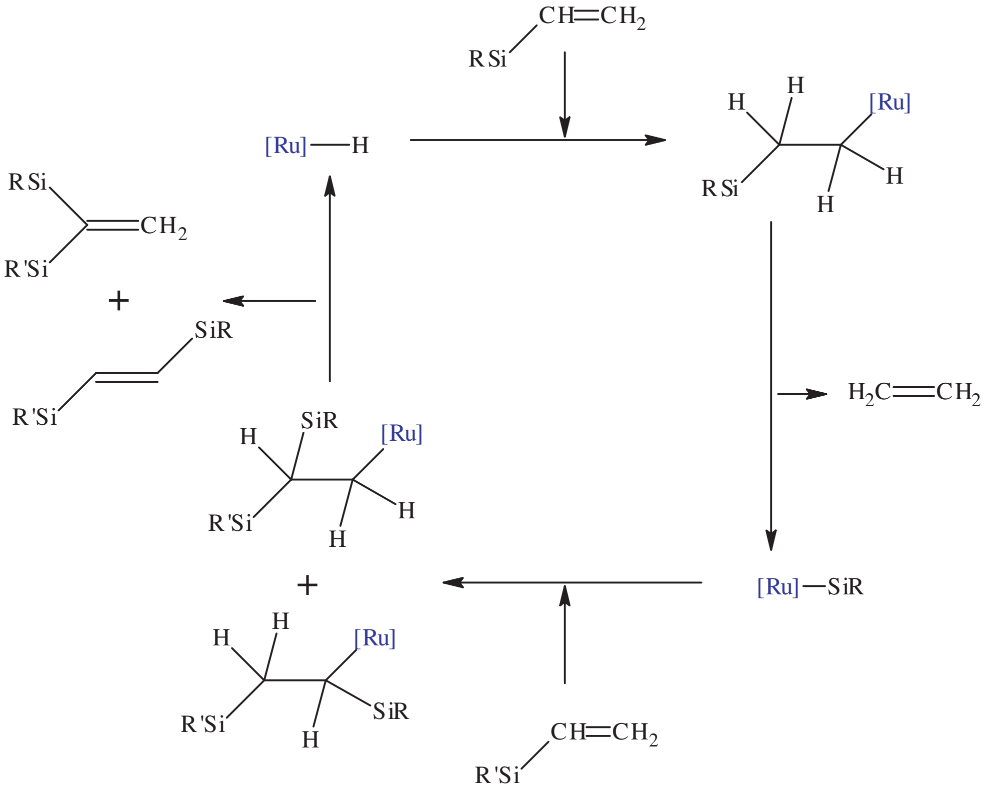
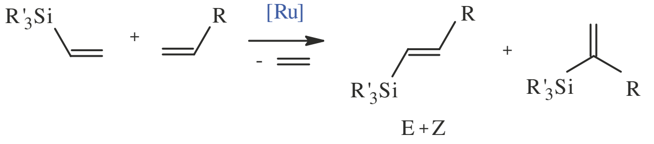


Fig. 1 Catalytic cycle for the reaction of silylative coupling of olefins

transition states, the quantum chemical calculations have been undertaken. Computational approach have already proven its usefulness in studies on problems ranging from reaction mechanisms [7–11] and catalysis, [12–17] via factors affecting molecular structure [18–24] and recognition [25–31] to applications for biological systems [32–38]. In particular, quantum mechanical calculations shed new light on mechanisms of metathesis reaction [39–42] or hydrosilylation of alkenes [43, 44]. In this study we focused on the steps leading to ethylene elimination in the course of silylative coupling of olefins, as these steps make a half of the catalytic cycle and may serve as models for the remaining reactions taking place in silylative coupling of olefins. Indeed, for the model system with R=H, the remainig half of the catalytic cycle is just the reverse path. Therefore, we consider a simple model system as a catalyst and a substrate for the reaction (see Fig. 3).

Computational methods

Trimethylvinylsilane and one of the ruthenium catalysts RuHCl(CO)(PCy$_3$)$_2$ in which two PCy$_3$ (Cy is cyclohexyl) ligands were substituted with smaller PH$_3$ were selected as



[Ru] = RuHCl(CO)(PCy$_3$)$_2$, RuCl(SiMe$_3$)(CO)(PPH$_3$)$_2$, RuHCl(CO)(PPh$_3$)$_3$, RuHCl(CO)(PCy$_3$)$_2$/CuCl, RuClSi(OEt$_3$)(CO)(PPh$_3$)$_2$

SiR'$_3$ = SiMe$_3$, Si(OEt)$_3$, SiMe$_2$Ph, (OSiMe$_3$)n

R = Ph, p-C$_6$H$_5$X (X = Me, OMe, Br), OR", SiR'$_3$, (CH$_2$)nMe, N-pyrrolidonone, 9-carbazole

Fig. 2 Silylative coupling of olefines is a convienient way of synthesis of silylalkenes

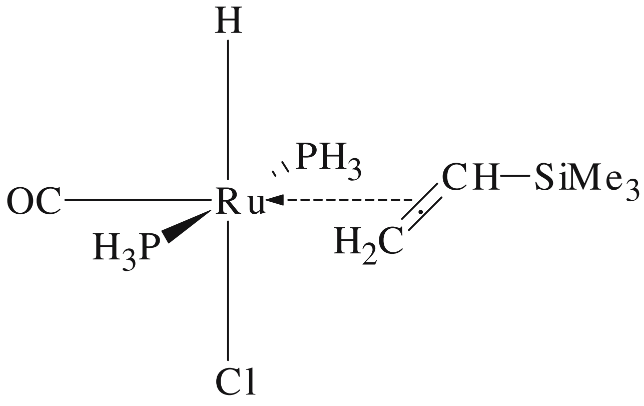


Fig. 3 The system studied on the substrate side of the vinylsilane insertion into Ru-H bond. The ruthenium catalyst [Ru]-H (left) interacting with trimethylvinylsilane (right)

the model systems for quantum chemical studies (see Fig. 3). All the molecular geometries were optimized using the density functional theory (DFT) with B3LYP-the hybrid Becke's three parameter functional [45] and Lee-Young-Parr exchange-correlation potential [46]. Two basis sets were used for geometry optimization: more flexible SDDALL basis set with Stuttgart-Dresden pseudopotentials, [47, 48] and smaller LANL2DZ basis set [49, 50]. Vibrational analyses were performed at SDDALL basis set to confirm that the geometry optimization led to a transition state or a minimum, and to calculate thermal corrections to Gibbs free energies at 298 K. Further, IRC (intrinsic reaction coordinates) calculations were performed to identify potential energy minima on both sides of the transition states. In order to check the dependence of the calculated energy barriers on the basis set used we also employed a composite basis set (BS3) in which 6-311+G(d) basis set was used for Si, P, and Cl, 6-31++G(d,p) basis set for C, O and H, [51–57] while SDD basis set (with the corresponding pseudopotential) was used for Ru. We have also inspected activation barriers for hydrogen and silyl migration in the mechanism involving two Ru centers. Due to the size of such system, instead of trimethylvinylsilane smaller molecule e.i. vinylsialne was used in computational experiment. All calculations were carried out with Gaussian03 [58].

Table 1 Relative energies (in kJ mol^{-1}) of the lowest energy chemical entities and transition states between them present in the catalytic process of silylative coupling of olefins

Structure	B3LYP/BS3
A1: vinylsilane+[Ru]-H	0.0
AB1: transition state	17.2
B1: silylethyl ruthenium complex	−9.2
BC1: transition state	59.9
C1: ethylene+[Ru]-Si	−4.2

Results and discussion

The overall picture of the reaction does not depend on the selection of the level of theory, (see Table S1 and S2 Supplementary Material) therefore, further discussion will be based on the values obtained in BS3 basis set. The number of isomeric structures is the greatest for the structures denoted as **B** (with Ru-C bond), where various conformers due to rotation about the C-C or Ru-C bond are possible. In the case of the structures denoted as **C**, the number of isomers is the lowest due to a high symmetry of ethylene molecule (D_{2h} for the isolated molecule).

Figure 4 presents relative energies of various structures that may occur in the course of the catalytic reactions of silylative coupling of olefins, while Table 1 presents relative energies calculated at the BS3 basis set for the lowest energy isomers among the chemical entities involved in the reaction (structures **A1**, **AB1**, **B1**, **BC1**, and **C1**). There are ten isomers of the [Ru]-H catalyst interacting with the vinylsilane molecule. Their relative energies are in the range from 0 to 59 kJ mol^{-1}. Five of these isomers are connected via transition states with isomeric structures of the product of a vinylsilane insertion into Ru-H bond. The lowest activation barrier for this reaction is only 17.2 kJ mol^{-1}. It suggests it is a relatively easy step in the catalytic process. Intrinsic

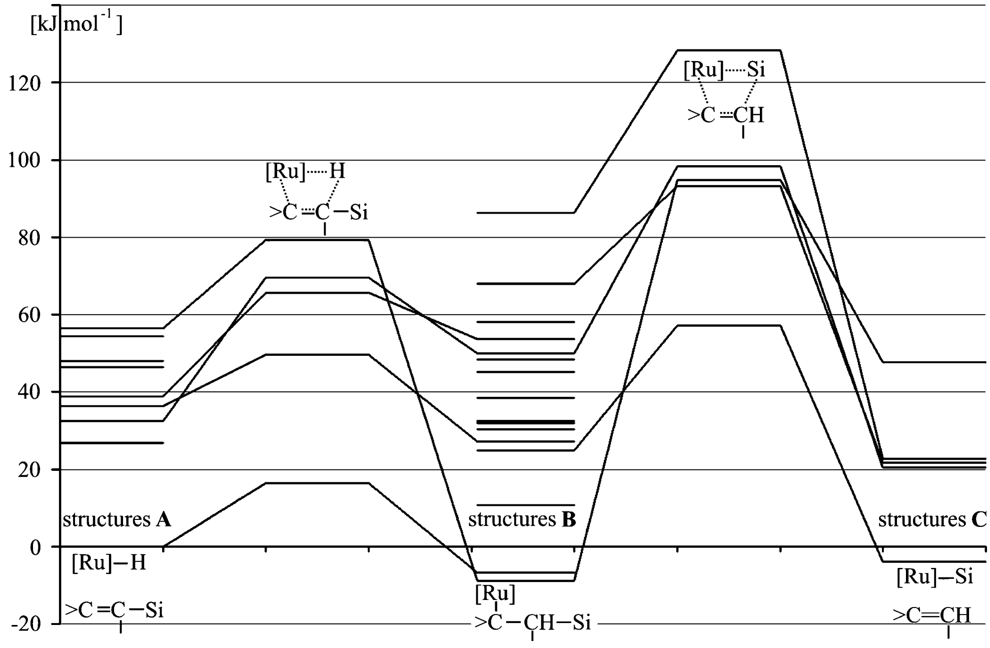


Fig. 4 Relative energies of various structures forming during silylative coupling of olefins

reaction coordinate (IRC) calculations starting from the transition states for the reaction of vinylsilane insertion into Ru-H bond permitted identification of the actual species on both sides of the reaction, among a greater number of isomeric structures. On the product side, we identified 17 isomers (**B**), whose relative energies were in the range from −9.2 to 90.4 kJ mol^{-1}.

The next chemical reaction in the catalytic cycle involves a migration of the silyl moiety coupled with ethylene elimination. We have found five transition states for this reaction. The lowest energy activation barrier for the reaction of ethylene elimination is 69.1 kJ mol^{-1} as the relative energy of **BC1** transition state is 59.9 kJ mol^{-1} while the relative energy of substrates in **B1** structure is −9.2 kJ mol^{-1}. Due to a high symmetry of ethylene molecule the number of isomers (five) of [Ru]-Si catalyst interacting with ethylene is smaller than in the case of ruthenium catalyst in complex with vinylsilane (ten isomers). Relative energies of the isomeric forms of the product of this reaction are in the range from ca. −4 to 50 kJ mol^{-1}. It should be noted that the reverse reaction namely ethylene insertion into Ru-Si bond the activation barrier is 64.0 kJ mol^{-1} above that in the lowest energy complex of ethylene with the ruthenium catalyst. It means that the transition state **BC** has the highest energy in the course of the catalytic reaction. Moreover, it is difficult to identify the rate-limiting step unambigously, as the final energy barrier may well change with the nature of the acutal subsituents R and R’. On the other hand, the possibility of eliminating gaseous ethylene from the reactive mixture should favor ethylen elimination due to entropic factors.

Although experimental findings indicate that the mechanism of silylative coupling of olefins involves one ruthenium center, we also checked activation barriers for the migration of hydrogen atom and silyl moiety between two lowest energy species identified in the catalytic cycle-namely structures **B1**. The values for activation barriers were larger than 200 kJ mol^{-1}-much higher than for one center mechanism which is in line with experimental findings. Structures of transition states and potential energy minima located for the mechanism involving two Ru centers are presented as Supplementary Material.

Table 2 Relative energies (in kJ mol^{-1}) of the selected **B** conformesrs and transition states connecting them which are important for the mechanism of silylative coupling of olefins

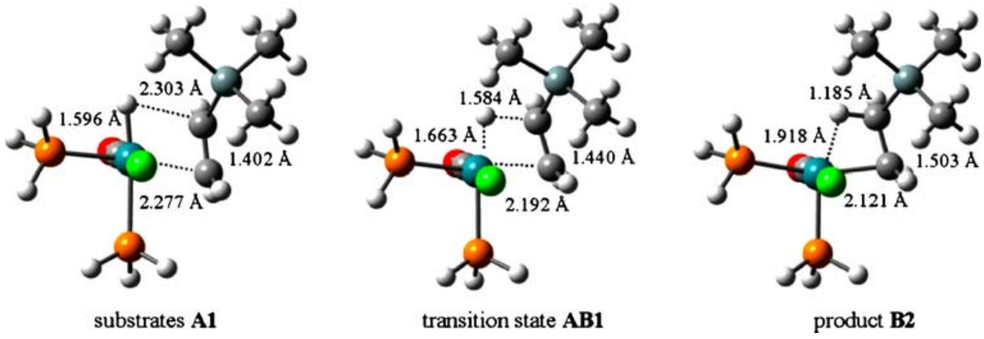
Structure	B3LYP/BS3
B1	−9.2
B2	−7.1
B4	26.0
B8	33.5
B1B8	53.6
B2B4	38.9
B2B8	46.5

Vinylsilane insertion into Ru-H bond

We have located five transition states connecting substrates and products of the reaction involving one rutenium center. The lowest energy barrier separating substrates and products is only 17.2 kJ mol^{-1}. Figure 5 presents structures involved in this reaction, as identified by IRC calculations starting form the lowest energy transition state.

Trimethylvinylsilane molecule interacts with the ruthenium catalyst most favorably in the way presented in Fig. 5 (substrates **A1**). The distances between Ru and carbon atoms of the vinylsilane are 2.277 Å, and 2.315 Å for the C atom distal to Si, and proximal to Si, respectively. In the transition state **AB1**, whose potential energy is 17.2 kJ mol^{-1} higher than the potential energy of the substrates, the hydrogen atom is transferred form the Ru atom to the C atom bearing the silyl moiety. This H transfer is coupled with the formation of Ru-C bond. Moreover, the carbon-carbon double bond in the vinylsilane elongates and becomes a single bond. Such a low value of the activation barrier indicates that the hydrogen transfer between ruthenium and carbon atoms takes place easily.

It is worth mentioning that the structure of the product of the reaction, i.e., **B2** is stabilized by an agostic interaction occurring between the ruthenium center and the hydrogen atom that was transferred during the reaction. The distance between Ru and H is only 1.918 Å, while the C-H bond is elongated to 1.185 Å. The relative energy of the structure **B2** is −7.1 kJ mol^{-1} with respect to the lowest energy substrate complex, i.e., **A1**.



substrates **A1** transition state **AB1** product **B2**

Fig. 5 Vinylsilane insertion into the Ru-H bond. The structures of the substrates, the transition state and the product have relative energies of 0.0, 17.2, and −7.1 kJ mol^{-1}, respectively. It should be noted that another conformer of the product of the reaction had even lower relative energy, i.e., −9.2 kJ mol^{-1} (*vide infra*)

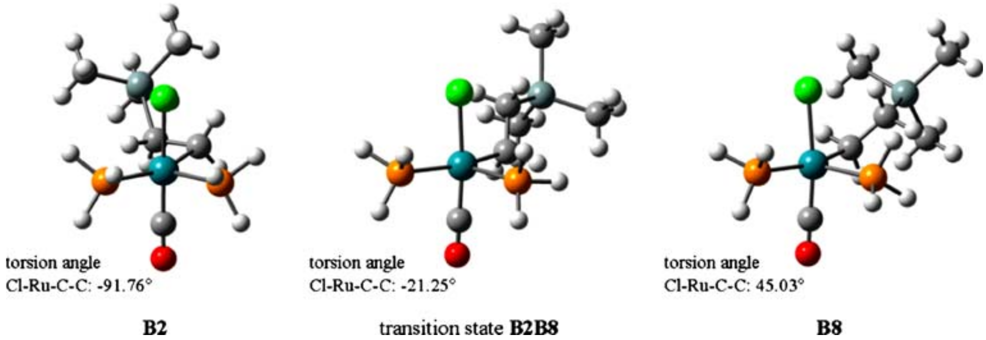


Fig. 6 The rotation around the Ru-C bond converts conformer **B2** (relative energy −7.1 kJ mol^{-1}) into conformer **B8** (relative energy 33.5 kJ mol^{-1}). The relative energy of the transition state **B2B8** amounts 46.5 kJ mol^{-1}

β-Silylethyl ruthenium complexes

The number of various isomeric structures of β-silylethyl ruthenium complexes is higher than for other compounds investigated in this study due to the fact that the rotation about carbon-carbon bond leads to various stable conformations. Indeed, we have located 17 different isomers/conformers of relative energy ranging from −9.2 kJ mol^{-1} to 90.4 kJ mol^{-1}. The structure of the product of the reaction of vinylsilane insertion into Ru-H bond, presented in Fig. 5 (**B2**), ranked second with respect to the potential energy so it does not correspond to the potential energy global minimum (**B1**) for β-silylethyl ruthenium complexes. Therefore, we searched for transition states connecting both these structures. There are two transition states **B1B8** and **B2B8**, as well as the additional potential energy minimum **B8** on the way form the structure **B2** to **B1**, see Table 2. In the first of these transitions converting **B2** to **B8** the rotation around the Ru-C bond takes place, (see Fig. 6) while in the other (converting **B8** to **B1**) the value of P-Ru-P angle increases from about 102° in **B8** to 173° in **B1** (see Fig. 7).

Structure **B2** is stabilized by the agostic interaction C-H···Ru, while conformer **B8** is not. Thus the comparison of the relative energies of conformers **B2** (−7.1 kJ mol^{-1}) and **B8** (33.5 kJ mol^{-1}) may serve as an indication that the energetic effect of the agostic interaction observed in structure **B2** is ca. 40 kJ mol^{-1}. This value suggests that this agostic interaction is of moderate energy as the agostic interaction energy ranges from about 4 kJ mol^{-1} to almost 250 kJ mol^{-1} [59–63].

The second chemical reaction in the catalytic cycle studied involves the migration of a silyl moiety and starts in the conformation **B4**. Thus, we have investigated the transition that leads from structure **B2** to **B4** (see Fig. 8). IRC calculations verified that the transition state **B2B4** connects these structures. Its relative energy amounts to 38.9 kJ mol^{-1}. During the conversion from the conformer **B2** into the conformer **B4** the rotation about C-C bond occurs, so that the value of the torsion angle Ru-C-C-Si decreases from 129° in **B2** to 53° in **B4**.

Ethylene elimination

Structure **B4** of β-silylethyl ruthenium complex with a relative energy of 26.0 kJ mol^{-1} is the substrate for the reaction of ethylene elimination coupled with the migration of a silyl group from the silylethyl moiety to the ruthenium center. In this structure the distance between the ruthenium and silicon atoms is 3.636 Å. In the lowest energy transition state for this reaction (structure **BC1**) the silyl moiety migrates from the carbon atom to the ruthenium center. The distance between Ru and Si becomes shorter, i.e., 3.233 Å, while the distance between the carbon atom and Si elongates from 1.921 Å in **B4** to 2.047 Å in **BC1**. The transition state **BC1** connecting the

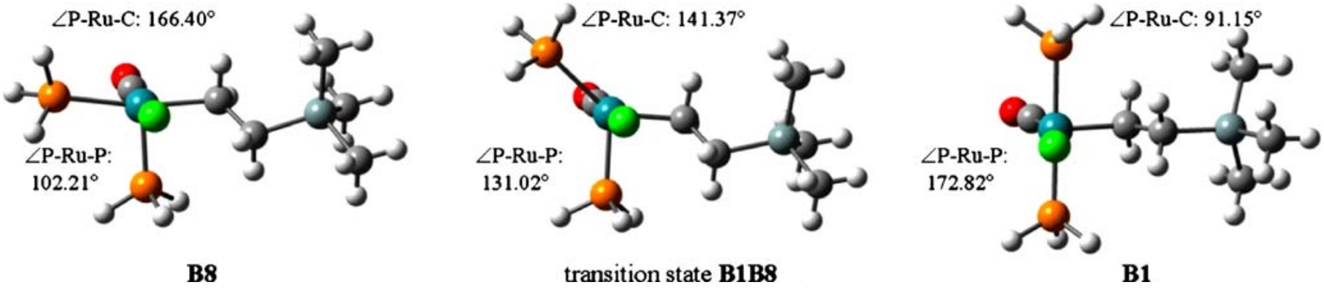
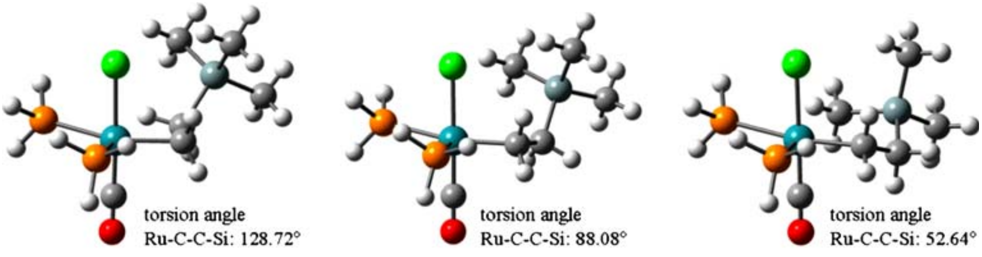


Fig. 7 The increase in the value of the P-Ru-P angle re-shapes the first coordination sphere of Ru atom and converts structure **B8** (relative energy 33.5 kJ mol^{-1}) into structure **B1** (relative energy −9.2 kJ mol^{-1}). The transition state **B1B8** connecting these structures has relative potential energy of 53.6 kJ mol^{-1}



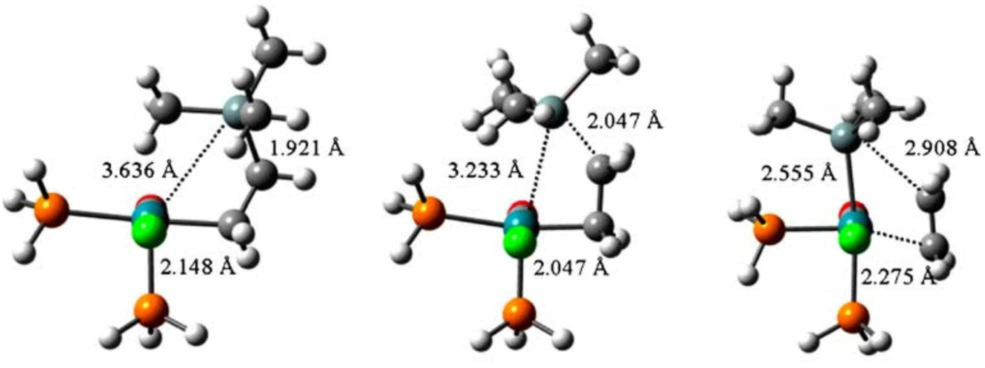
B2 transition state **B2B4** **B4**

Fig. 8 The rotation around the carbon-carbon bond converts structure **B2** (relative energy −7.1 kJ mol^{-1}) into structure **B4** (relative energy 26.0 kJ mol^{-1}). The transition state **B2B4** connecting the two minima **B2** and **B4** has a relative energy of 38.9 kJ mol^{-1}

substrate and the products for this reaction has a relative energy of 59.9 kJ mol^{-1} (see Fig. 9). However, the lowest energy structure on the substrates side of the reaction has a relative energy of −9.2 kJ mol^{-1}. Thus the activation barrier for the reaction of ethylene elimination amounts to 69.0 kJ mol^{-1}. IRC calculations starting from the transition state **BC1** led to the structure **C1** on the product side of the reaction. In this structure the bond between Ru and Si is formed, for which the interatomic distance amounts to 2.555 Å. The relative energy of the structure **C1** of the ruthenium catalyst interacting with ethylene molecule amounts to −4.2 kJ mol^{-1} and is only slightly higher than the energy of the lowest energy form among structures **B** (relative energy of structure **B1** equals −9.2 kJ mol^{-1}). These values indicate that the activation barrier for the alkene insertion into Ru-Si bond is 64.0 kJ mol^{-1} for ethylene. Therefore, the rate determining step in the catalytic process of silylative coupling of olefins can be alkene insertion into Ru-Si bond or the reverse reaction e.i. ethylene elimination. However, the possibility of elimination of gaseous ethylene from the reactive mixture, together with entropic factors e.i. production of a gaseous product, should favor ethylene elimination over alkene insertion. Thus the nature of actual substituents attached to vinyl moiety or silicon atom is likely to affect relative energies of structures **B** and **C** and, in turn, determine if alkene insertion into Ru-Si bond or alkene elimination from β-silylethyl ruthenium complex is rate-limiting step in the catalytic cycle.

Conclusions

The results obtained suggest that depending on the actual nature of substituents attached to vinyl moiety or Si atom, the rate determining step can be the insertion of an alkene into the Ru-Si bond coupled with the silyl moiety migration from Ru to C atoms, or alternatively the reverse reaction e.i. alkene elimination from β-silylethyl ruthenium complex. In our calulations at BS3 basis set on model systems the energy barriers were 69, and 64 kJ mol^{-1} for the forward and the reverse reactions. However, the possibility of removing gaseous ethylene from the reactive mixture, together with entropic factors, is most likely to facilitate ethylene elimination. This in turn would suggest that the rate limiting step is alkene insertion. It also suggests that substituents attached to the vinyl moiety, or to silicon atom, by electronic and by steric effects may modify the ease of the alkene insertion into the Ru-Si bond. Interestingly, both catalytic complexes [Ru]-H and [Ru]-SiMe$_3$ have similar energy, which agrees well with the experimental finding that the ruthenium complex with -H or -SiR$_3$ in the first coordination sphere of ruthenium, are almost equally efficient and effective in the catalytic process.



B4 transition state **BC1** **C1**

Fig. 9 The migration of the silyl moiety from carbon atom to the ruthenium center results in ethylene elimination. The relative energies of structures **B4**, **BC1**, and **C1** are 26.0, 59.9, and −4.2 kJ mol^{-1}, respectively

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