Can $Cp_2Zr(C_2H_4)$ Easily React with Hydrosilane? Theoretical Study

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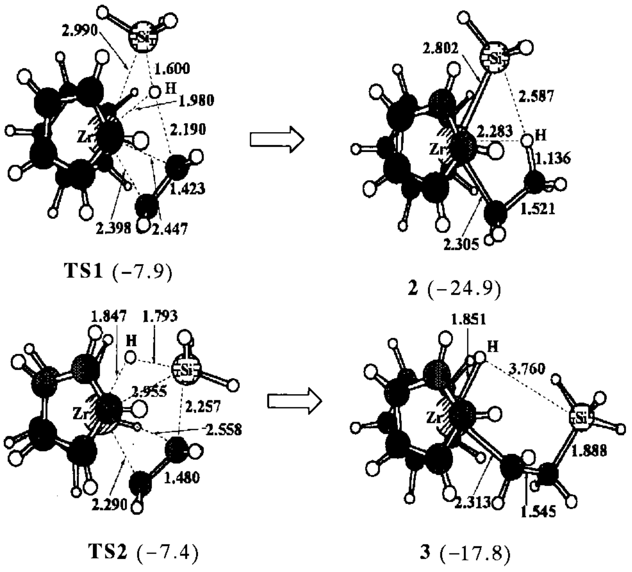
DFT calculations clearly show that a zirconocene–ethylene complex, $Cp_2Zr(C_2H_4)$, easily reacts with hydrosilane, SiH_4, to afford either $Cp_2Zr(H)(C_2H_4SiH_3)$ or $Cp_2Zr(SiH_3)(C_2H_5)$. In the transition state, the Si–H anti-bonding σ^*-orbital of SiH_4 overlaps well with the π-back donating molecular orbital between Zr d_π and C_2H_4 π^* orbitals.

The transition-metal catalyzed hydrosilylation of alkene is one of the important synthetic reactions of organosilicon compounds. In well-known Chalk–Harrod and modified Chalk–Harrod mechanisms, oxidative addition of hydrosilane to a low valent transition-metal complex occurs first, and then, alkene is inserted into either the M–H bond or the M–SiR_3 bond of a transition-metal hydride silyl complex, to afford a transition-metal alkyl silyl complex or a transition-metal alkyl hydride complex, respectively.[1] Many experimental results have been discussed in terms of these two mechanisms.[1] However, Takahashi and his collaborators experimentally proposed that both zirconocene alkene and zirconocene hydride silyl complexes are considered an active species in zirconocene-catalyzed hydrosilylation of alkene and that the zirconocene–alkene complex reacts with hydrosilane to afford either a zirconium alkyl silyl complex or a zirconium alkyl hydride complex (eqs 1 and 2).[2,3] The similar reactions were also proposed by Sonoda et al.[4] On the other hand, the usual alkene insertion into the Zr–silyl bond was also experimentally proposed in zirconium-catalyzed hydrosilylation[2,5] and carbosilylation.[4]

$$Cp_2Zr(C_2H_4) + H{-}SiR_3 \rightarrow Cp_2Zr(SiR_3)(C_2H_5) \qquad (1)$$
$$Cp_2Zr(C_2H_4) + H{-}SiR_3 \rightarrow Cp_2Zr(H)(C_2H_4SiR_3) \qquad (2)$$

If these reactions, eqs 1 and 2, easily took place, a new reaction mechanism different from traditional Chalk–Harrod and modified Chalk–Harrod mechanisms should be presented for the zirconocene-catalyzed hydrosilylation of alkene. Thus, it is very important to investigate whether these reactions easily take place or not. However, no such investigation has been reported, so far, to our best knowledge. In this communication, we wish to report theoretical investigation of the reaction between the zirconocene–ethylene complex and hydrosilane.

The DFT method was used in this work with the B3LYP functional.[6] Geometry optimization was carried out with a basis set system described below; for Zr and Si, (311/311/211) and (21/21/1) basis sets were employed, respectively, with effective core potentials (ECPs).[7] For the other atoms, 6-31G* basis set[8] was used, while a d-polarization function was omitted in the C atom of a Cp group but a p-polarization function was added to H atoms of hydrosilane.[8c] Energy changes were evaluated with a larger basis set system; for Zr and Si, (541/541/211/1)[9] and (531111/4211/1) sets[10] were used, respectively, where the ECPs[7b] were employed only for Zr. For the other atoms, 6-31G** set was used except for the Cp group in which the d- and p-polarization functions were omitted. Ethylene and SiH_4 were adopted as models of alkene and hydrosilane, respectively, to save computational time. All calculations were performed with Gaussian 98 program package.[11]



TS1 (−7.9)

2 (−24.9)

TS2 (−7.4)

3 (−17.8)

Figure 1. Optimized geometries of transition states and products of the reaction between $Cp_2Zr(C_2H_4)$ and SiH_4 Bond length in Å. In parehthses are relative energy to sum of reactants (kcal/mol).

Zirconium ethylene complex, $Cp_2Zr(C_2H_4)$ **1**, reacts with SiH_4 to afford the zirconium alkyl silyl complex, $Cp_2Zr(SiH_3)(C_2H_5)$ **2** through the transition state TS1, as shown in Figure 1. In TS1, the hydrogen atom of hydrosilane approaches ethylene, and the Si–H bond to be broken in the reaction is slightly lengthened to 1.60 Å from the equilibrium distance (1.481 Å). Consistent with this lengthening of the Si–H bond, the H atom of hydrosilane is considerably distant from the C atom of ethylene ($R_{(C-H)}$ = 2.19 Å), indicating that the C–H bonding interaction is little formed in TS1. Interestingly, the C=C double bond of ethylene somewhat shortens to 1.423 Å from that (1.471 Å) of $Cp_2Zr(C_2H_4)$, probably because ethylene is moved to a new position from the best position for the interaction with the Zr center by approach of hydrosilane. All these features clearly show that TS1 is reactant-like. This result is consistent with a very small activation barrier (0.2 kcal/mol by the DFT method and 0.8 kcal/mol by the MP4(SDQ) method). On the other hand, the zirconium alkyl hydride complex, $Cp_2Zr(H)(C_2H_4SiH_3)$ **3**, is formed from **1** through the transition state TS2. In TS2, the silyl group approaches ethylene, and the Si–H bond to be broken is significantly lengthened to 1.79 Å. The Si–C distance (2.257 Å) is about 0.35 Å longer than that of **3**, indicating that the Si–C bond is considerably formed in this transition state. The C=C double bond of ethylene somewhat lengthens to 1.48 Å. Also, it should be noted that the Si atom seems to take five-coordinate hypervalency. This transition state is considered to be less reactant-like than TS1. The activation barrier is small (5.0 kcal/mol by the DFT method and 4.9 kcal/mol by the MP4(SDQ) method), too.

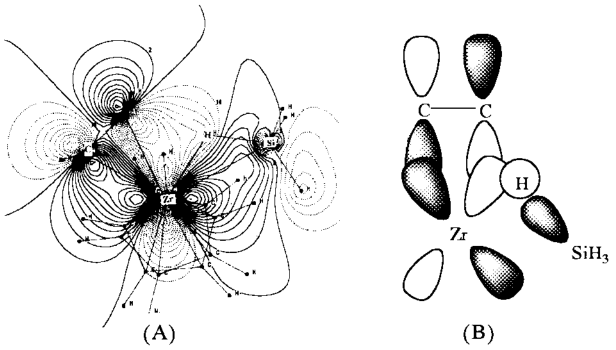


Figure 2. Contour map of HOMO and its schematical representation of the reaction between $Cp_2Zr(C_2H_4)$ and SiH_4
Solid lines: positive, dotted lines; negative

To investigate what type of interaction participates in these transition states, HOMOs of TS1 and TS2 are inspected, and that of TS1 is shown as an example in Figure 2(A). These HOMOs mainly consist of the π-back donating interaction between zirconium d_π and ethylene π* orbitals, into which the Si–H anti-bonding σ*-orbital of hydrosilane mixes in a bonding way, as schematically displayed in Figure 2(B). From this feature, one might understand that the reaction between $Cp_2Zr(C_2H_4)$ and SiH_4 is similar to σ-bond metathesis. To form this type of HOMO, the π-back donation must be strong. Actually, the π-back bondion is very strong in $Cp_2Zr(C_2H_4)$; for instance, the ethylene moiety of this complex is negatively charged by –0.71e to a much greater extent than that (–0.14e) in $PtCl_2(PH_3)(C_2H_4)$.[12]

In conclusion, the present calculations clearly show that the reaction between $Cp_2Zr(C_2H_4)$ and SiH_4 easily occurs with a small activation barrier to afford either $Cp_2Zr(H)(C_2H_4SiH_3)$ or $Cp_2Zr(SiH_3)(C_2H_5)$ and that not only Chalk–Harrod and modified Chalk–Harrod mechanisms but also a new mechanism involving the reaction between $Cp_2Zr(C_2H_4)$ and SiH_4 should be taken into consideration in the zirconocene-catalyzed hydrosilylation of alkene.[13]

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Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

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12 $Cp_2Zr(C_2H_4)$ is also considered to be a Zr(IV)–metallacycle complex. However, further investigation is necessary to show which, Zr(II)–ethylene complex or Zr(IV)– metallacycle complex, is correct representation.
13 To complete the catalytic cycle of which active species is **1**, **2** and **3** must react with ethylene to afford hydrosilylated product, C_2H_5–SiH_3, and $Cp_2Zr(C_2H_4)$. Also, they would react with hydrosilane to provide C_2H_5–SiH_3 and $Cp_2Zr(H)(SiH_3)$. Our calculations indicated that these reactions can occur with moderate activation barriers. S. Sakaki, T. Takayama, and M. Sugimoto, to be published.