

A theoretical study of platinum-catalyzed disilylation of alkene

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Abstract

Model compounds of intermediates and transition states involved in the Pt-catalyzed disilylation of alkene were optimized with the energy gradient method and the energy changes along this catalytic reaction were calculated with the ab initio MO/MP4SDQ method. The rate-determining step is the ethylene insertion into the Pt(II)–SiH₃ bond, of which the activation energy was evaluated to be much too high (45 kcal mol⁻¹). This high activation energy arises from the strong *trans*-influence of the silyl group. This result clearly indicates that the disilylation can take place for the substrate that is easily inserted into the metal–silyl bond. © 1997 Elsevier Science S.A.

Platinum and palladium-catalyzed disilylations of alkene [1–3], alkyne [4,5], diene [6], and similar compounds [7] have received considerable attention because two silyl groups can be introduced into an organic molecule at a time. In the reaction mechanism proposed for the disilylation of alkene and alkyne [2,3,5], the oxidative addition of disilane occurs first, affording the transition metal disilyl complex, then alkene or alkyne is inserted into the metal–silyl bond, and finally the Si–C reductive elimination takes place to yield a disilylated product. Although intermediates involved have not been experimentally detected in the catalytic reactions, such elementary processes as the oxidative addition of disilane to Pt(0) [8], the reductive elimination of Pt(CH₃)(SiH₃)(PR₃)₂ [9], and the alkyne insertion into the metal–silyl bond [10] have been ascertained experimentally to occur. However, there remain many important issues to be examined: for instance, (1) which is the rate-determining step? (2) how much is the activation energy? and (3) how is the transition state characterized? Proper answers to these issues are necessary to make further developments in this field.

In the present work, platinum-catalyzed disilylation of ethylene is theoretically investigated with the ab initio MO method, to provide theoretical answers to the above-mentioned issues. It is also our intention with this work to put forward the theoretical calculation of a full

catalytic cycle, since theoretical calculations on full catalytic cycles are still sparse [11,12].

Geometries were optimized with the ab initio HF energy gradient method in the ethylene insertion [13] using the effective core potentials (ECPs) for core electrons (up to 4f) of Pt [14], a (4s 4p 3d)/[3s 3p 2d] set for valence electrons of Pt [14], MIDI-3^{*} and MIDI-3 basis sets for Si and C [15] respectively, a (4s)/[2s] set [16] for H (except for H of PH₃), and MINI-1 basis set for PH₃ [15], where superscript ^{*} indicates that the d-polarization function was involved. As ascertained in our previous work [12], the *E_a* value calculated for the SCF geometry would be almost the same as that calculated for the MP2 geometry in the ethylene insertion into P*–H. In the oxidative addition and the reductive elimination, geometries were optimized with the ab initio MP2 energy gradient method, because introduction of electron correlation somewhat shifts the transition state to the reactant side in these reactions [17]. Even in the oxidative addition reaction in which introduction of electron correlation somewhat changes the TS geometry, the *E_a* value calculated for the MP2 geometry is almost the same as that calculated for the SCF geometry [16]. In MP2 optimization, a (4s 4p 3d)/[3s 3p 3d] set was used for Pt [14] with the same ECPs as above, and MIDI-4^{*}, MIDI-4, and (4s)/[2s] basis sets were employed for Si [15], C [15], and H [16] atoms respectively. Energy changes were evaluated at the MP4SDQ level, where (4s 4p 3d)/[3s 3p 3d] [14], (12s 8p 1d)/[6s 4p 1d] [16], MIDI-4^{*} [15], (9s 5p

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1d)/(3s 2p 1d) [16], and (4s)/[2s] [16] sets were used for Pt, Si, P, C, and H atoms respectively. The Gaussian 92 program [18] was used for all these calculations.

The first step of the catalytic cycle is the oxidative addition of Si_2H_6 to $\text{Pt}(\text{PH}_3)_2$. As shown in Fig. 1, this step was theoretically calculated to proceed with an activation energy E_a of ca. 16 kcal mol⁻¹ and exothermicity E_{exo} of ca. 33 kcal mol⁻¹, affording *cis*- $\text{Pt}(\text{SiH}_3)_2(\text{PH}_3)_2$ [17]. The next step is the ethylene insertion into one of the Pt–SiH₃ bonds. According to Hoffmann and coworker [19], the ethylene insertion into the metal–alkyl and metal–hydride bonds can take place easily via a four-coordinate intermediate such as $\text{MLX}(\text{R})(\text{C}_2\text{H}_4)$, where M is a d⁸ metal and R is a hydride or an alkyl ligand. Actually, it was experimentally proposed [20] that ethylene substitutes one of the phosphine sites in $\text{PdPhCl}(\text{dippb})$ (dippb = 1,4-bis-(diisopropylphosphino)butane), followed by ethylene insertion into the Pt–Ph bond. Thus, we examined the ethylene insertion in the four-coordinate complex

$\text{Pt}(\text{SiH}_3)_2(\text{PH}_3)(\text{C}_2\text{H}_4)$. This insertion requires a significantly high E_a value of 45 kcal mol⁻¹, affording the product (PRO1). The transition state (TS) structure (Fig. 1) exhibits several interesting features as follows. (1) Ethylene moves toward SiH₃, and at the same time SiH₃ changes its direction toward C^β. (2) The Si–C^β distance is about 10% longer than it is in the product. (3) The Pt–C^α distance is almost the same as that in the product, indicating that the Pt–alkyl bond is already formed at the TS, preceding the formation of the Si–C^β bond. [It seems strange that the Pt–C^α distance is a little bit shorter than those of PRO3 and PRO4. One possible reason is that the Pt–C^α bond of PRO3 is a little bit weaker than that in the TS because of the agostic interaction between Pt and H atoms (remember that the Pt atom is three-coordinate at the TS because the Pt–SiH₃ bond has almost broken). However, this discussion does not lead to a completely clear reason. At the moment, we have not found the clear reason.] These features were also observed in the ethylene inser-

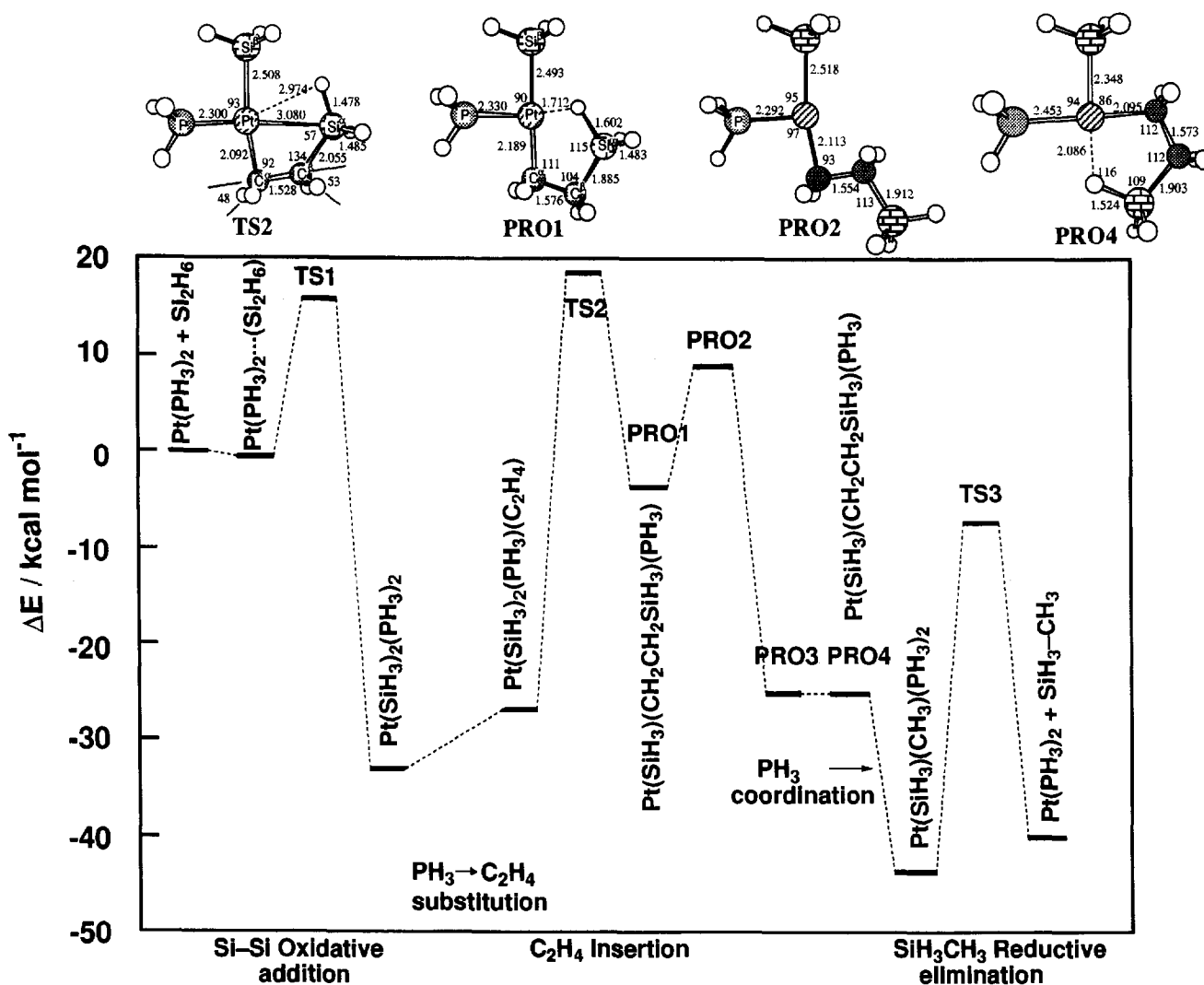


Fig. 1. Energy changes and some optimized geometries in the $\text{Pt}(\text{PH}_3)_2$ -catalyzed bis-silation of ethylene; MP4SDQ calculation.

tion into Cu–H, Cu–CH₃ [21], and Pt–H bonds [12]. These features indicate that ethylene should be activated by the unsymmetrical coordination to Pt to undergo the insertion into the metal–R bond (R = H, alkyl, etc.), as previously proposed for the nucleophilic attack on the olefin coordinating to metal [22]. The high E_a value is easily understood by considering the TS structure as follows: in the TS, the Pt–alkyl bond is already formed at the *trans* position to SiH₃, which causes significant energy destabilization because of strong *trans*-influence of alkyl and silyl groups.

In **PRO1** which is formed just after the insertion, a strong agostic interaction is formed between the Si–H bond and the Pt atom, as clearly shown by the short Pt–H distance of 1.712 Å and the long Si–H bond of 1.60 Å. Although this product is stabilized by the agostic interaction, this is not the most stable because the Pt–alkyl bond is at the *trans*-position to the Pt–SiH₃ bond. In the most stable product (**PRO4**), the *trans*-position to the most strong Pt–SiH₃ bond is vacant, and the next strongest Pt–alkyl bond is at the *trans*-position to the least strong Pt–PH₃ bond. The isomerization from **PRO1** to **PRO4** would occur after the breaking of the agostic interaction which causes the energy destabilization of ca. 22 kcal mol⁻¹ (compare **PRO1** with **PRO2** in Fig. 1). The isomerization of **PRO2** would occur very easily with no barrier, as investigated previously [12]. The final step is the Si–C reductive elimination to yield the bis-silylated product. This reductive elimination was examined on a model complex, Pt(PH₃)₂(SiH₃)(CH₃). Its E_a value was calculated to be ca. 36 kcal mol⁻¹. The reaction energy of the whole catalytic cycle was estimated to be about 33 kcal mol⁻¹ at the MP4SDQ level, considering the following reaction (Eq. (1)):



The reaction energy given in Fig. 1 (about 40 kcal mol⁻¹) is not very much different from the reaction energy of Eq. (1). Thus, it is not so bad to adopt Pt(SiH₃)(CH₃)(PH₃)₂ as a model of Pt(CH₂CH₂SiH₃)(CH₃)(PH₃)₂. The difference would be attributed to the presence of two silyl groups in SiH₃CH₂CH₂SiH₃ which would destabilize the product. Actually, the SiH₃–CH₂CH₂SiH₃ bond energy is smaller than that of SiH₃–CH₃ by ca. 5 kcal mol⁻¹ at the MP4SDQ level. A detailed theoretical investigation of the β-silyl effects is in progress now in our group.

In summary, the Pt-catalyzed disilylation of ethylene requires the significantly high E_a value at the ethylene insertion which is the rate-determining step. From this result, one should make an effort to lower the activation barrier of the insertion step by using the substrate that easily undergoes the insertion reaction.

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