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## Abstract

*Ab initio* electronic structure calculations using RHF, MP2, and CCSD(T) levels of theory have been used to investigate a reaction path for the hydrosilation reaction catalyzed by divalent titanium (modeled by TiH<sub>2</sub> and TiCl<sub>2</sub>). Optimized structures and energies are presented. All levels of theory predict a barrierless reaction path compared to a barrier of at least 55 kcal/mol at the MP2 level for the analogous uncatalyzed reactions. The use of correlated methods (MP2 or CCSD(T)) is required to obtain accurate structures and energies.

## Disciplines

Chemistry

## Comments

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## Chapter 10

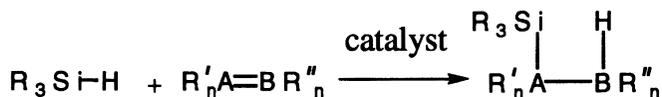
# Catalysis of the Hydrosilation and Bis-Silylation Reactions

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*Ab initio* electronic structure calculations using RHF, MP2, and CCSD(T) levels of theory have been used to investigate a reaction path for the hydrosilation reaction catalyzed by divalent titanium (modeled by  $\text{TiH}_2$  and  $\text{TiCl}_2$ ). Optimized structures and energies are presented. All levels of theory predict a barrierless reaction path compared to a barrier of at least 55 kcal/mol at the MP2 level for the analogous uncatalyzed reactions. The use of correlated methods (MP2 or CCSD(T)) is required to obtain accurate structures and energies.

The hydrosilation reaction is a general method for adding an Si-H bond across a C-C double bond. This method encompasses a wide variety of substituted alkenes, dienes, and alkynes leading to many different organosilicon products. Thus the method is very useful; indeed it is the second most important method of producing organosilanes on a large scale (1). The general hydrosilation reaction may be written as:



One of the simplest examples known experimentally is the addition of trichlorosilane to ethylene, which will occur rapidly at room temperature and give nearly 100% yields with a variety of homogeneous transition metal based catalysts (2).

Several analogous uncatalyzed reactions ( $\text{HSiCl}_3$ ,  $\text{SiH}_4$  + ethylene,  $\text{SiH}_4$  + propene) were studied previously (3); all were found to have large ( $\geq 54$  kcal/mol) barriers. Thus, the catalyst is crucial in making the process economically viable. Industrially one active catalyst is believed to be a divalent  $\text{Cp}_2\text{Ti}$  species ( $\text{Cp} = \text{C}_5\text{H}_5$ ) (1).

This paper will consider first the simplest prototypical example of a catalyzed hydrosilation reaction, in which A and B are carbon; R, R' and R'' are hydrogen and the catalyst is  $\text{TiH}_2$ . This choice of reactants and catalyst allows mapping the entire reaction path at a high level of theory. Particularly, the choice of  $\text{TiH}_2$  as the catalyst

allows the use of high-level all-electron *ab initio* wavefunctions which would not be possible if the more complex catalysts such as  $\text{TiCl}_2$  or  $\text{TiCp}_2$  were used. The significant differences between the all hydrogen calculations and calculations involving Cl substituents will be discussed.

### Computational Methods

The minimum energy reaction path connecting reactants to products was determined using all electron *ab initio* wavefunctions. The reaction paths were fully optimized using Møller-Plesset second order perturbation theory (MP2). Single-point energies were computed at the MP2 optimized stationary points using coupled cluster singles and doubles plus perturbative triples (CCSD(T)). The basis sets used were a triple- $\zeta$  quality valence for the all hydrogen reaction (4) and a double- $\zeta$  quality valence using SBKJC effective core potentials for the reactions involving chlorine (5).

The GAMESS (6) program was used for all of the RHF calculations and most of the MP2 optimizations. The Gaussian 92 suite of programs (7) was used for the remainder of the MP2 calculations and the CCSD(T) calculations.

### Results and Discussion

Figure 1 shows the energy profile of the proposed catalyzed reaction for the unsubstituted system at the RHF, MP2, and CCSD(T) levels of theory. Figure 2 shows the MP2 energy profiles for each of the reaction studied. The zero of energy on the curve for each level of theory is the sum of the reactant energies at that level of theory (structures a, b, and c in Figure 3). The MP2 structures at each stationary point are given in Figure 3. Only structures for the unsubstituted reaction are shown, unless there is an important change upon Cl substitution. MP2 and CCSD(T) ZPE corrected energies are listed relative to the zero of energy in Table I.

**Unsubstituted Reaction.** It is important to note that all points on the energy plot in Figure 1 lie below the energy of the reactants, in contrast to the large barrier in the uncatalyzed reaction. Note also that there are large differences between the SCF and MP2 energy profiles, while the differences between MP2 and CCSD(T) are much smaller. So, electron correlation is essential for a correct description of this reaction surface, and MP2 is qualitatively correct. This provides some confidence in the MP2 results for the reactions containing Cl (see below).

There are two possibilities for the first step of the reaction, both of which are barrierless processes. The first, and more exothermic, is to add the  $\text{TiH}_2$  catalyst across the ethylene double bond to form the three membered ring compound shown in Figure 3d. This process is downhill in energy by 61.9 (53.4) kcal/mol at the ZPE corrected MP2 (CCSD(T)) level of theory. Note that, based on the large exothermicity and the large (0.016Å) increase in the CC bond length, structure d is a three-membered ring, not a  $\pi$  complex. Silane will then add to form the complex depicted in Figure 3e. This second barrierless addition is downhill by 6.5 (6.0) kcal/mol.

The electronic structure of  $\text{TiH}_2$  was considered in detail previously (8). Like  $\text{CH}_2$ , the ground state is a triplet, and the lowest singlet state is 21 kcal/mol higher in energy. Since  $\text{TiH}_2$  has an electronic structure similar to singlet  $\text{CH}_2$  or  $\text{SiH}_2$ , ( $s^2d^2$  vs.  $s^2p^2$ ) a reasonable expectation is that an alternative mechanism would start with an insertion of  $\text{TiH}_2$  into an Si-H bond of silane. Indeed, this occurs with no barrier to produce structure d', a Ti-Si analog of ethane. This step is downhill by 31.9 (27.8)

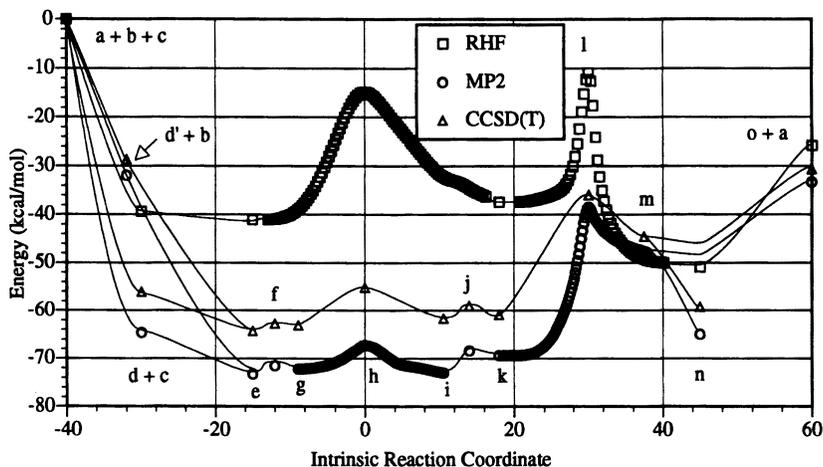


Figure 1: Energies for the Unsubstituted Reaction at RHF, MP2, and CCSD(T) Levels of Theory. (Reproduced with Permission from ref. 4. Copyright 1998 American Chemical Society)

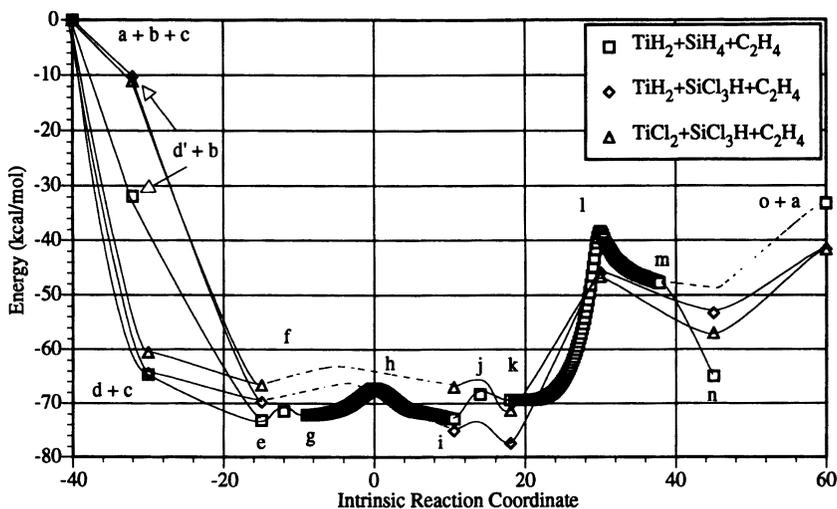
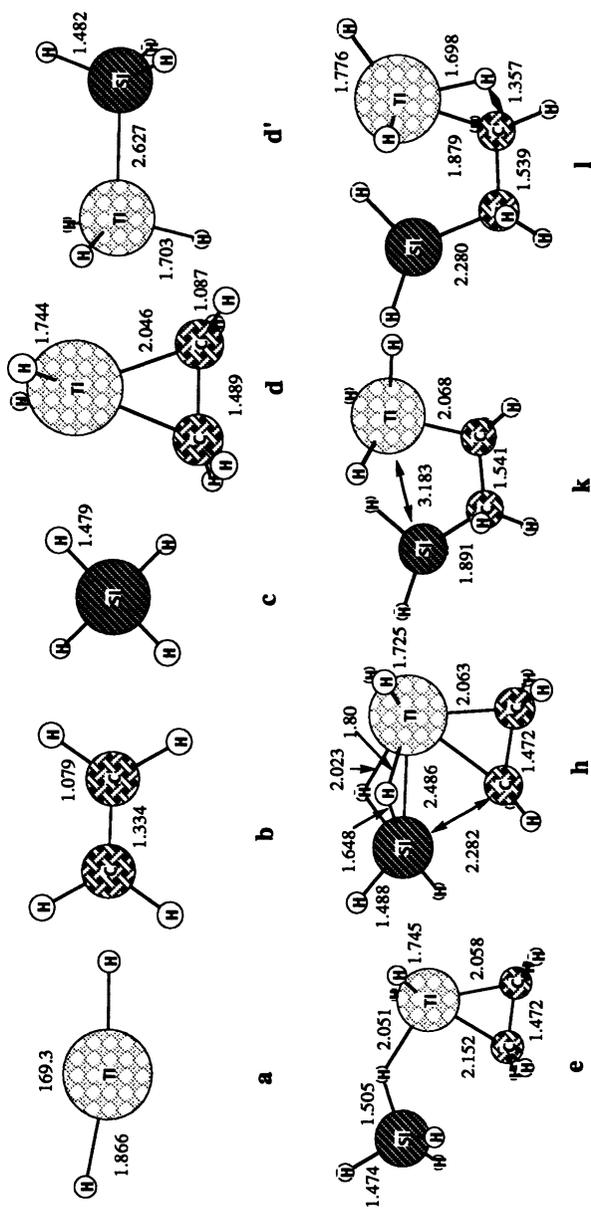


Figure 2: Energies for all reactions at the MP2 Level of Theory.

**Table I: MP2 and CCSD(T) relative energies (kcal/mol) with MP2 ZPE correction**

Geometry point	TiH <sub>2</sub> +SiH <sub>4</sub> +C <sub>2</sub> H <sub>4</sub> MP2 + MP2 ZPE	TiH <sub>2</sub> +SiH <sub>4</sub> +C <sub>2</sub> H <sub>4</sub> CCSD(T) + MP2 ZPE	TiH <sub>2</sub> +SiCl <sub>3</sub> H+C <sub>2</sub> H <sub>4</sub> MP2 + MP2 ZPE	TiCl <sub>2</sub> +SiCl <sub>3</sub> H+C <sub>2</sub> H <sub>4</sub> MP2 + MP2 ZPE
a+b+c (reactants)	0	0	0	0
d'+b	-31.1	-27.8	-8.3	-10.6
d+c	-61.9	-53.4	-61.8	-59.6
e	-68.4	-59.4	-66.2	-64.9
f	-66.6	-57.8		
g	-66.6	-57.4		
h	-61.3	-49.2		
i	-67.2	-55.8	-70.0	-64.1
j	-64.0	-54.6		
k	-65.4	-56.8	-74.3	-70.5
l	-33.5	-31.1	-42.3	-44.5
m	-39.0	-37.0		
n	-59.2	-53.3	-46.9	-51.8
o+a (products)	-28.0	-25.4	-37.2	-37.2



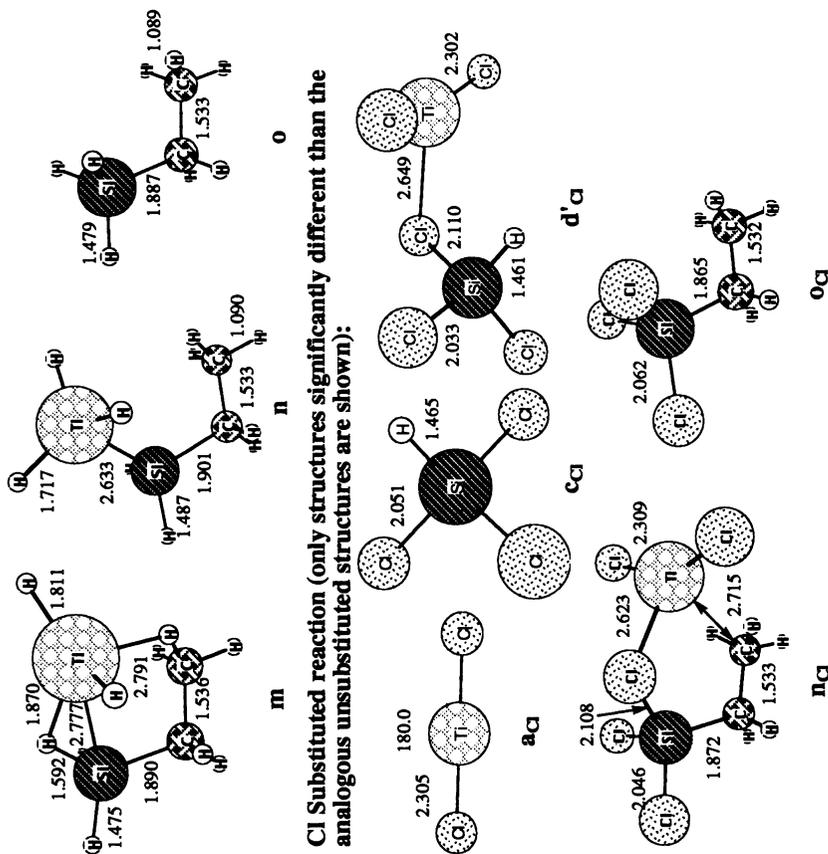


Figure 3: Significant MP2 Structures Along the Minimum Energy Reaction Path.

kcal/mol. When ethylene is added to this compound, it rearranges with no barrier to the same structure as in Figure 3e.

So, whether the catalyst adds to ethylene or silane initially, the net result after the two reactants and the catalyst have been added together is the formation of compound e, with no intervening barrier. The overall exothermicity to this point is 68.4 (59.4) kcal/mol. This very large drop in energy drives the entire reaction path down in energy. In fact, the reaction path is forced down enough that all subsequent points are below the reactants in energy.

Recall that the final desired product is ethylsilane. So, starting from compound 3e, the silyl group needs to migrate to the nearest ( $\alpha$ ) carbon, and a hydrogen needs to be transferred to the adjacent ( $\beta$ ) carbon, with the ultimate removal of the  $\text{TiH}_2$  catalyst. Therefore, the next step in the reaction is to transfer a H from the complexed silane to the Ti and to attach the Si to the  $\alpha$  C.

The first part of this step involves rotation of the silane such that there are 2 bridging hydrogens between the Si and Ti; that is e  $\rightarrow$  g via f in Figures. 1 and 3. At the MP2 level there is a small barrier (at structure f) of 1.7 kcal/mol to this process, but after the ZPE corrections are added the barrier disappears. The reaction then proceeds through transition state h with a barrier of 5.3 (8.2) kcal/mol, leading to the four-membered ring shown in Figure 3i. This ring is 5.9 (6.6) kcal/mol below the TS h. The four-membered ring can be opened up by breaking the Si-Ti bond to give the compound k. The TS for this step is shown in Figure 3j. It has a barrier height of 3.2 (1.2) kcal/mol. Compound k is 1.4 (2.1) kcal/mol below the TS j.

The final step in the process is to regenerate the catalyst by transfer of a hydrogen from Ti to C and elimination of  $\text{TiH}_2$ . The transition state for this process is shown in Figure 3l; the associated barrier height is 31.9 (25.7) kcal/mol. This TS is still 33.5 (31.1) kcal/mol lower in energy than the initial reactants. The IRC from this TS leads to the structure shown in Figure 3m which is 5.2 (5.9) kcal/mol below the TS. The structure shown in Figure 3m is not a stationary point, but it illustrates that the reaction path goes through a structure in which the  $\text{TiH}_2$  is complexed to two hydrogens. Optimization from this point leads to the insertion of  $\text{TiH}_2$  into an Si-H bond, as shown in Figure 3n. The insertion product is 25.7 (22.2) kcal/mol below the TS in energy. However, the  $\text{TiH}_2$  in Figure 3m is not tightly bound to the ethylsilane as evidenced by both the relatively long Ti-Si and Ti-H bond distances and the fact that it is a modest 11.0 (11.6) kcal/mol in energy below separated products. Thus, we do not expect a transition state for the process of simply abstracting the  $\text{TiH}_2$  to form separated products. This can occur readily due to the excess energy available to the system, since the separated products are 28.0 (25.4) kcal/mol below the reactants in energy.

Once  $\text{TiH}_2$  is removed, the process is complete with ethylsilane as the product. The overall process is exothermic by 28.0 (25.4) kcal/mol at the ZPE corrected MP2 (CCSD(T)) level of theory. This compares with the value of 29.1 kcal/mol computed by Day and Gordon at the MP2/6-311G(d,p) level of theory and a value of 27.4 kcal/mol computed by McDouall *et. al.* (9) at the MP4/6-31G(d)//HF/3-21G level of theory. There does not seem to be a good experimental  $\Delta H_0$  for this reaction, but we can estimate the value to be 28.9 kcal/mol based on the experimental heats of formation for ethylene and silane (10), and the best previous theoretical heat of formation for ethylsilane

The driving force for the entire reaction comes in the first two steps with the formation of the compound shown in Figure 3e which is 68.4 (59.4) kcal/mol below the reactants in energy and is the global minimum on the reaction surface. The first two steps in the reaction illustrate the reasons this structure is so stable. In the first

step, the electron deficient  $\text{TiH}_2$  adds to the ethylene across the  $\pi$  bond in much the same manner as the addition of  $\text{CH}_2$  to ethylene to form cyclopropane. The second step is much less exothermic and is driven mostly by the electrostatic attraction between the positively charged titanium (+0.83) and the negative hydrogen (-0.12) on the silicon.

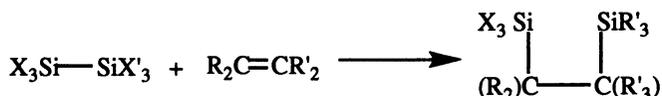
**Effect of Cl substitution.** Now consider the effect of substituting Cl atoms for hydrogens in either the catalyst or the reactants. The relevant structures are shown in Figure 3 and the potential energy curves in Figure 2. Since, as noted above, MP2 and CCSD(T) give similar results for the unsubstituted reaction, only MP2 results are reported for the reactions containing Cl. The overall features of the Cl-substituted reactions are quite similar to those for the unsubstituted case. In particular, the highest point in all cases corresponds to the separated reactants + catalyst. The proximity of the catalyst once again drives the energy strongly downhill in order to form stable intermediate complexes, and this stabilization is sufficient keep all subsequent transition states well below the reactants in energy. In view of the similarities among the reactions considered, we will only briefly discuss the essential differences:

(1) Recall that there are two alternative initiating reactions, both of which are considerably downhill without barriers. One of these corresponds to insertion of  $\text{TiH}_2$  into an Si-H bond of silane to form structure  $d'$ . However, when the substrate is  $\text{SiCl}_3\text{H}$ , this insertion (by either  $\text{TiH}_2$  or  $\text{TiCl}_2$ ) is not a barrierless process and thus does not occur. Instead, as illustrated in Figure 3, the catalyst forms a complex ( $d'$ ) in which the Ti is interacting with one of the chlorines on Si. These complexes, which are downhill by 8.3 (10.6) kcal/mol for  $\text{TiH}_2$  ( $\text{TiCl}_2$ ) will also rearrange readily to structure  $e$  when ethylene is added in the next step.

(2) In the unsubstituted reaction, Figure 2 illustrates the tendency of the catalyst to reinsert into the departing product. When  $\text{SiCl}_3\text{H}$  is used instead of  $\text{SiH}_4$ , the catalyst would have to insert into a Si-Cl bond instead of a Si-H bond. A barrier exists for this insertion, so instead a complex ( $n$ ) is formed between the departing product and the catalyst. This complex is only 9.7 (14.6) kcal/mol below the final products when the catalyst is  $\text{TiH}_2$  ( $\text{TiCl}_2$ ), so it is not difficult to remove the catalyst from the ethyltrichlorosilane product.

(3) The reaction that forms ethyltrichlorosilane is exothermic by 37.2 kcal/mol. This is the same as the exothermicity predicted earlier using the MP2/6-311G(d,p) level of theory.

**Bis-Silylation.** The addition of a Si-Si bond across a C=C bond,



is referred to as bis-silylation. Although the Si-Si single bond is fairly weak, this addition in the absence of a catalyst requires a high energy barrier, about 50 kcal/mol at the MP4/6-311G(d,p) level of theory (11). The first investigation of the catalyzed bis-silylation reaction used  $\text{TiH}_2$  as a prototype catalyst to be consistent with our previous studies of hydrosilylation (12); however, the most common catalysts for this reaction are phosphino complexes of Pt and Pd (13-18). Several potential reaction paths were explored, with the catalyst interacting first with ethylene in some cases and first with disilane in others. All structures were optimized using a triple  $\zeta$  quality basis set and Møller-Plesset second-order perturbation (MP2) theory. The results of these calculations suggest that  $\text{TiH}_2$  is such an effective catalyst for hydrosilylation that

an Si-H bond of disilane persistently adds across the C=C bond of ethylene. No transition state or route to bis-silylation (addition of Si<sub>2</sub>H<sub>6</sub> to ethylene) has been found in the presence of TiH<sub>2</sub>. This may change for a fully substituted disilane, since then there would be no Si-H bond into which the divalent Ti could insert.

## Conclusions

The results presented here clearly show that divalent titanium is an effective catalyst for the hydrosilation reaction. The simple model system using all hydrogen substituents seems to get all of the important features of the reaction pathway qualitatively correct. The effect of the substituents on the catalyst seems to be minor. More significant is the effect of substituents on the silicon with the chlorine substituted system being less prone to Ti insertion into an Si-X bond. The overall catalyzed reaction has no net barrier, because of the very stable cyclic TiX<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> intermediate. However, the energy profile of the multistep process (Figure 1) does offer the possibility of finding some of the intermediate structures if the process was carried out at low temperature.

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