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A DFT Computational Study of the Bis-Silylation Reaction of Acetylene Catalyzed by Palladium Complexes

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Received August 3, 2001

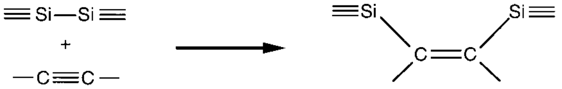
Abstract: In this paper we have investigated at the DFT(B3LYP) level the catalytic cycle for the bis-silylation reaction of alkynes promoted by palladium complexes. A model-system formed by an acetylene molecule, a disilane molecule, and the $Pd(PH_3)_2$ complex has been used. The most relevant features of this catalytic cycle can be summarized as follows: (i) The first step of the cycle is an oxidative addition involving $H_3Si-SiH_3$ and $Pd(PH_3)_2$. It occurs easily and leads to the cis $(SiH_3)_2Pd(PH_3)_2$ complex that is 5.39 kcal mol^{-1} lower in energy than reactants. (ii) The transfer of the two silyl groups to the C−C triple bond does not occur in a concerted way, but involves many steps. (iii) The cis $(SiH_3)_2Pd(PH_3)_2$ complex, obtained from the oxidative addition, is involved in the formation of the first C−Si bond (activation barrier of 18.34 kcal mol^{-1}). The two intermediates that form in this step cannot lead directly to the formation of the final bis(silyl)ethene product. However, they can isomerize rather easily (the two possible isomerizations have a barrier of 16.79 and 7.17 kcal mol^{-1}) to new more stable species. In both these new intermediates the second silyl group is adjacent to the acetylene moiety and the formation of the second C−Si bond can occur rapidly leading to the (Z)-bis(silyl)ethene, as experimentally observed. (iv) The whole catalytic process is exothermic by 41.54 kcal mol^{-1}, in quite good agreement with the experimental estimate of this quantity (about 40 kcal mol^{-1}).

Introduction

The bis-silylation of unsaturated organic compounds, which can be formally represented as the insertion of a double or triple C−C bond into a Si−Si bond, is a particularly interesting transformation which allows the simultaneous creation of two new Si−C bonds (Scheme 1). This reaction represents a convenient route to obtain bis(silyl) compounds which can represent useful intermediates in organic chemistry or can be used as building blocks for the synthesis of silicon-containing polymers. These polymeric species are nowadays attracting increasing attention, since they can be designed to possess useful chemical and physical properties such as thermal stability or the ability of transferring optical and electrical information.[1]

Experimental studies have shown that this reaction proceeds with appreciable yields only when transition metal catalysts are used and a number of examples are now available in the literature.[2,3] $Pd(PPh_3)_4$ complexes, for instance, were used by Watanabe and co-workers to add chloromethyl and methoxymethyl disilanes to allene and 1,2-butadiene.[2a,b] The reaction of organodisilanes with butadiene in the presence of various palladium complexes was also investigated by Sakurai.[2c] Hayashi and co-workers demonstrated that the bis-silylation of ethylene proceeds in the presence of platinum phosphine complexes to give 1,2-bis(silyl)ethanes.[2d] More recently the bis-silylation of α-diketones, catalyzed by palladium or platinum complexes, was examined by Yamashita et al.[2e]

Scheme 1



A particular attention has been devoted during the last two decades to the bis-silylation of C−C triple bonds.[3] The bis-silylation of acetylenic compounds was first reported by Kumada and co-workers.[3a] These authors found that the reaction of dihydrotetramethyldisilane with dimethyl acetylenedicarboxylate, in the presence of palladium(II) complexes such as $PdCl_2$-

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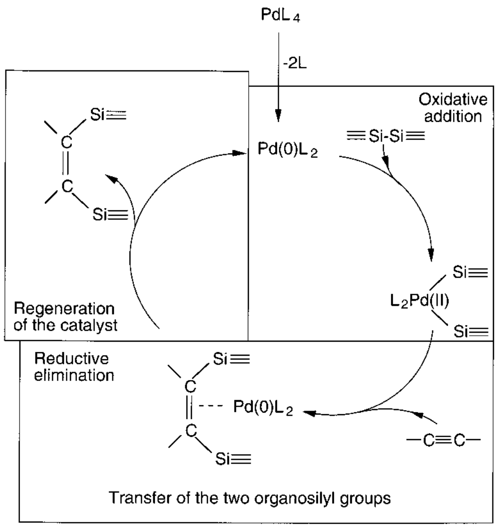
Scheme 2



L = ligand (PR_3, halogen)

$(PEt_3)_2$, leads to α,α′-bis(dimethylsilyl)maleate. Using palladium complexes as catalysts, they also reported that fluorinated and angle-strained disilanes easily add to acetylene to give bis-silylation, while the hexamethyldisilane does not react.[3c] The bis-silylation between strained disylacycloalkanes and an acetylene molecule was independently reported by Sakurai et al.[3b] They used $PdCl_2(PPh_3)_2$ as a catalyst and observed that the reaction proceeds in good yields. Watanabe and co-workers investigated the addition of methoxymethyldisilane to phenylacetylene in the presence of various triphenylphosphine complexes of Ni, Rh, Pd, and Pt.[3e,f] They also noted that hexamethyldisylane undergoes the same reaction, but that the bis-silylated product was obtained in lower yield. These authors found that palladium and platinum complexes such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $Pt(PPh_3)_4$, are the most effective catalysts for this reaction and that the *cis*-bis-silylated product is obtained selectively (in all cases the *cis/trans* ratio is very high). A concerted transition state, where the two acetylene carbon atoms simultaneously interact with the metal and the silicon atom bonded to the methoxy group, was proposed. A direct effect of the methoxy group was indicated as the factor responsible for the observed regioselectiviity. More recently a variety of different catalysts, all based on palladium, have been tested. Ito and co-workers, for instance, showed that the system palladium(II) acetate − *tert*-alkyl isocyanide efficiently catalyzes the bis-silylation with hexaalkyldisilanes, i.e., disilanes not activated by withdrawing substituents such as alkoxy groups and halogens.[3m] $[(dcpe)Pd]_2(m-H_2)_2$ species (dcpe = 1,2-bis(dicyclohexylphosphono)ethane) were used by Fink with non-activated disilane such as $MeSiH_{2-}SiH_2Me$ and $HMe_2Si-SiMe_2H$ to obtain stable bis(silyl)palladium complexes.[3n] The X-ray crystal structure of these complexes was determined and the bis-silylation of $MeO_2C-CC-CO_2Me$ was investigated. It was found that the reaction proceeds easily to afford the cis bis-silylated product.

A schematic representation of the catalytic cycle, commonly postulated on the basis of the experimental evidence, is reported in Scheme 2 for the bis-silylation of alkynes promoted by Pd-based catalysts. The mechanism consists of three major steps: (1) The oxidative addition of disilane (Si−Si) to palladium to form bis(organosilyl)palladium complexes. (2) The transfer of two organosilyl groups to the C−C triple bond. (3) The reductive elimination and the regeneration of the catalyst.

The catalytic cycle for the insertion of C−C unsaturated bonds into Si−Si bonds has been investigated from a theoretical point of view in only a few papers. In many of the studies that appeared in the literature only the first step of the cycle (the oxidative addition) was considered in detail. Sakaki and co-workers,[4] for instance, investigated the oxidative addition of an Si-X bond (X = H, Si, C, F) to $M(PH_3)_2$ complexes (M = Pd, Pt) at the HF, MP2, and CCD levels. For disilane and $Pd(PH_3)_2$ they found that the oxidative addition occurs in a concerted way and proposed a symmetric transition state where the two Pd−Si bonds form simultaneously. However these results could be affected by the symmetry constraints used during the geometry optimization. The platinum-catalyzed bis-silylation of ethylene was studied by Sakaki and co-workers at the HF, MP2, and MP4 levels.[5] They had evidence that the rate-determining step of the process is the ethylene insertion into the $Pt-SiH_3$ bond, but, for the simple model-system used in that study, they found a very high activation energy (about 45 kcal mol^{-1}). Also, the connection between some critical points of the surface was not explained satisfactorily. More recently, Gordon studied the addition of disilane to ethylene in the absence of a catalyst using HF and MP2 methods.[6] A concerted transition state with a very high activation energy (about 50 kcal mol^{-1}) was found.

Since the mechanistic scenario for this class of reactions is still rather confused and to our knowledge no detailed and accurate theoretical studies are available on the catalyzed bis-silylation of alkynes, we have carried out at the DFT level a theoretical investigation of this reaction promoted by Pd complexes. Our aim is to shed light on the mechanistic details of the catalytic cycle given in Scheme 2 and to explain the stereochemical outcome experimentally observed. To this purpose we have chosen as a model-system an acetylene molecule reacting with the active species which forms from a $Pd(PH_3)_2$ complex and the disilane molecule $H_3Si-SiH_3$. The $Pd(PH_3)_2$ system emulates the $Pd(PR_3)_2$ species (R = Ph, Me, Et) usually involved in the real experimental system.

Computational Procedure

All of the DFT computations reported here have been performed with the Gaussian 98 series of programs[7] using the nonlocal hybrid Becke's three-parameter exchange functional denoted as B3LYP.[8] The geometry of the various critical points on the reaction surface has been fully optimized with the gradient method available in Gaussian 98 using the DZVP basis

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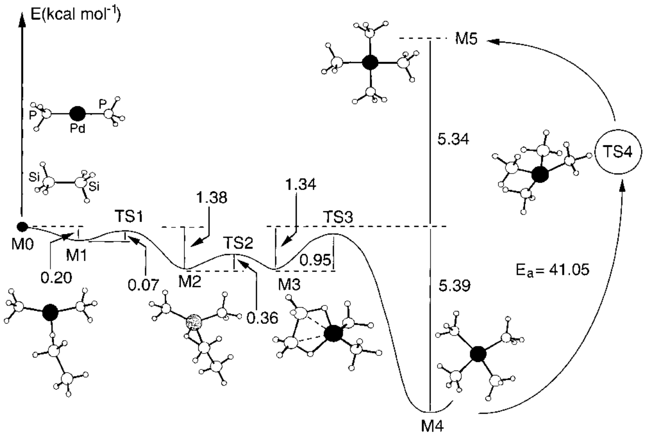

Figure 1. Energy profile for the oxidative addition step. Energies are in kcal mol^{-1}.

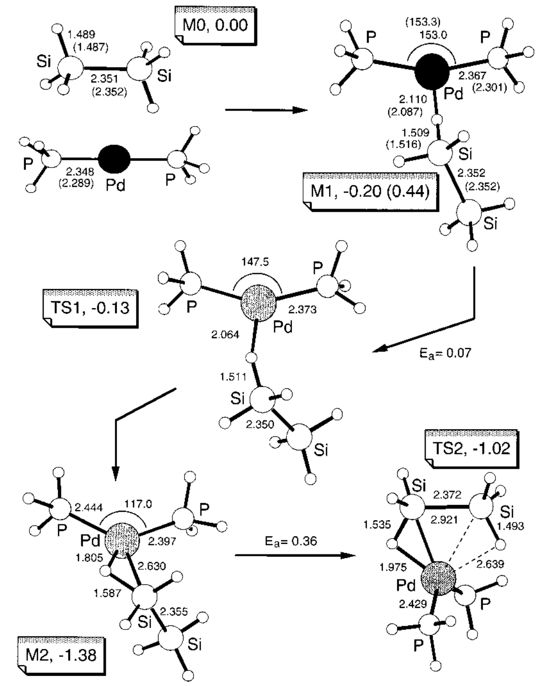

Figure 2. Schematic representation of the structures of the critical points M0, M1, TS1, M2, and TS2 located on the energy surface of Figure 1. The values (Ångstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol^{-1}) relative to reactants are reported. The absolute energy of reactants ($H_3Si{-}SiH_3 + Pd(PH_3)_2 +$ acetylene) is: −6285.87443 au (DZVP basis) and −1474.29575 au (6-311G* basis).

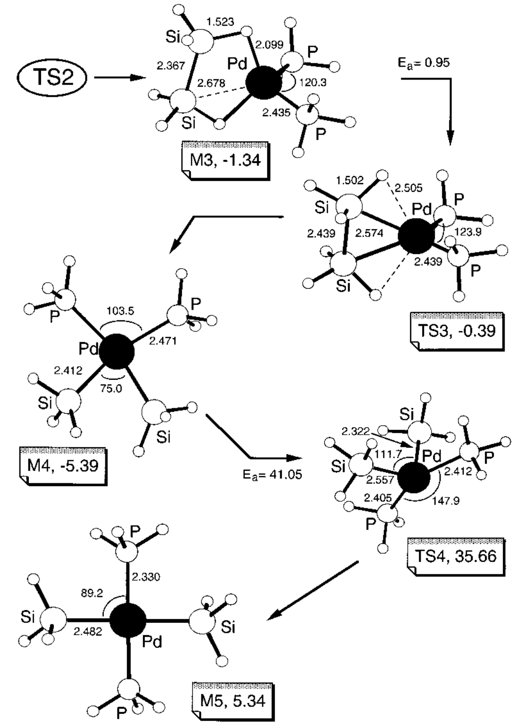

Figure 3. Schematic representation of the structures of the critical points M3, TS3, M4, TS4, and M5 located on the energy surface of Figure 1. The values (angstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol^{-1}) relative to reactants are reported.

set,[9] which is a Local Spin Density (LSD)-optimized basis set of double-ζ quality in the valence shell plus polarization functions. A computation of the harmonic vibrational frequencies has been carried out to determine the nature of each critical point. To check the reliability of the DZVP basis, the structure of the most important critical points has been re-optimized using a more accurate basis set: the metal has been described by the energy-adjusted pseudopotential basis set proposed by Preuss and co-workers[10] (**sdd** pseudopotentials in the Gaussian 98 formalism), while the 6-311G* basis has been used for all the other atoms.[11] The results obtained at this computational level, simply denoted as 6-311G*, are discussed in the Appendix.

Results and Discussion

In this section we discuss in detail the singlet potential energy surfaces associated with the various steps of the catalytic cycle for the model-system considered here. In particular we describe: (A) The oxidative addition. (B) The transfer of two silyl groups to the C−C triple bond and the regeneration of the catalyst which enters a new catalytic cycle.

A. The Oxidative Addition. The energy profile for this process is represented in Figure 1, while the structures of the various critical points located on the potential surface, with the values of the most relevant geometrical parameters, are reported in Figures 2 and 3. Figure 1 seems to indicate that the oxidative addition is a complicated process. A first complex, M1, which is only 0.20 kcal mol^{-1} lower than the reactants, forms without any barrier from the two molecules $Pd(PH_3)_2$ and H_3SiSiH_3. In M1, the interaction between the metal and the silicon atoms involves one Si−H bond which becomes slightly longer (1.509 Å) than in the isolated disilane molecule (1.489 Å). A transition state, TS1, leads to a new intermediate M2 where the interaction between the two molecules involves a three-center structure formed by palladium, silicon, and the hydrogen of one Si−H bond: here the Pd−H distance has become shorter (1.805 Å) and the Si−H distance longer (1.587 Å) than in M1. The interaction of the second silicon atom with the metal occurs in a similar way, involving a second Si−H bond (transition state TS2). This leads to a new intermediate (M3) characterized by a C_{2v} symmetry, where the two moieties $Pd(PH_3)_2$ and H_3SiSiH_3 are kept together in a cycle formed by the two Si atoms, the Pd atom, and two hydrogens simultaneously bonded

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to the metal and the silicon. The interaction between Si and Pd is still weak (Si−Pd = 2.678 Å) and the Si−Si bond is only slightly longer (2.367 Å) than in the isolated disilane (2.351 Å). A further transition state, TS3, characterized again by a very small activation barrier (only 0.95 kcal mol^{-1}), leads to the final bis-silyl palladium complex (M4 = "active complex"), which is 5.39 kcal mol^{-1} lower than reactants. Here the Si−Si bond is definitely broken and the Pd−Si bonds are complete (the Pd−Si distances are 2.412 Å). It is important to point out that all the activation barriers which must be overcome to form the "active complex" are very small or negligible. Thus, the three transition states located for this process (in particular TS1 and TS2) and the two intermediates M1 and M2 are probably only a computational shortcoming which could be due to basis set superposition errors. The real physical meaning which stems from these results is that the bis-silyl palladium complex forms very easily and that the interaction between the two fragments occurs in a nonsymmetric way and involves first the hydrogen atoms of the two silyl groups and then the two silicon atoms to form the final Pd−Si bonds.

A second bis-silyl palladium complex (M5) has been located where the two silyl groups are not adjacent, as found in M4, but on opposite sides with respect to the metal atom. This species is the trans isomer of the bis-silyl complex and is significantly higher in energy (10.73 kcal mol^{-1}) than the cis isomer M4. A transition state, TS4, connects the cis to the trans complex. However, the isomerization process M4 → M5 is not easy since it requires the overcoming of an energy barrier of 41.05 kcal mol^{-1}.

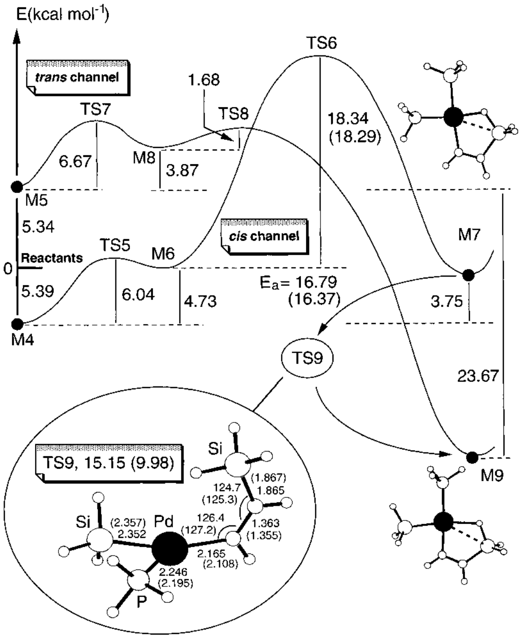

Figure 4. Energy profiles for the formation of the first C−Si bond in both the cis and trans $(SiH_3)_2Pd(PH_3)_2$ species. In the enlargement the structure of the isomerization transition state TS9 is also reported (Ångstroms and degrees).

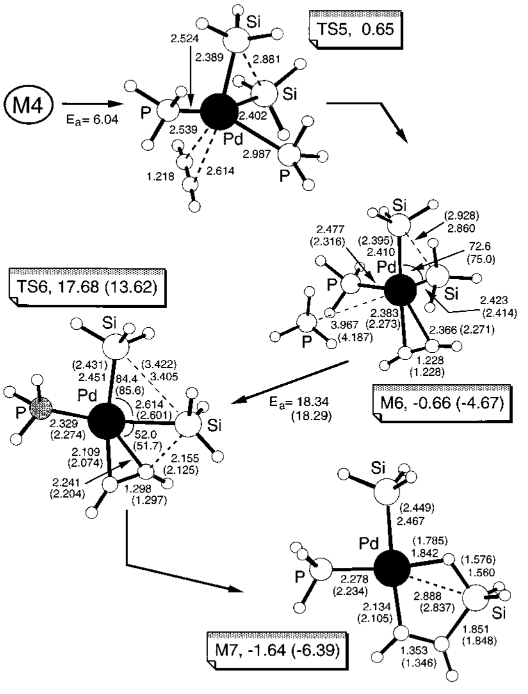

Figure 5. Schematic representation of the structures of the critical points TS5, M6, TS6, and M7 located along the cis channel of Figure 4. The values (angstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol^{-1}) relative to reactants are reported.

B. The Transfer of Two Silyl Groups to the C−C triple bond and the Regeneration of the Catalyst. To understand how the two new C−Si bonds form, we have considered in detail the reaction of the acetylene molecule with both the cis and trans isomers M4 and M5. The two corresponding reaction pathways, denoted here as cis channel and trans channel respectively, are shown in Figure 4. The structures of the various critical points are reported in Figures 5 and 6. TS5, located along the cis channel, is a transition state corresponding to the approach of the acetylene molecule to the bis-silyl palladium complex, M4. It is evident from this structure that the increasing interaction between the metal and the triple bond causes the removal of one PH_3 ligand. A significant lengthening of the corresponding Pd−P bond (2.987 Å) can be observed. TS5, which requires the overcoming of an energy barrier of 6.04 kcal mol^{-1}, leads to the intermediate, M6. Here the Pd−P bond is definitely broken, the Pd−P distance being 3.967 Å, and the two bonds between palladium and the acetylene carbons are almost completed (the two Pd−C bond distances are 2.366 and 2.383 Å, respectively). It is interesting to point out that in M6, which is 4.73 kcal mol^{-1} higher in energy than M4, the interaction between the two adjacent silicon atoms is not negligible, the Si−Si distance being 2.860 Å and the Si−Pd−Si angle 72.6°. The subsequent step corresponds to the formation of the first C−Si bond and is characterized by an energy barrier of 18.34 kcal mol^{-1} (transition state TS6). To form the new C−Si bond the silyl group, which is adjacent to the carbon atom, moves in the molecular plane toward the acetylene moiety. Both the Si−Si distance and the Si−Pd−Si angle increase, becoming 3.405 Å and 84.4°, respectively. The new forming C−Si bond is 2.155 Å in TS6, while the bond between the palladium and the silyl group involved in this transformation has become longer i.e., 2.614 Å (2.423 Å in M6). A simultaneous lengthening of the C−C bond (from 1.228 to 1.298 Å) can be observed in this transition structure. TS6 leads from M6 to a new intermediate, M7, where the first C−Si bond is complete (1.851 Å). This new bond is involved in a five-member cycle that includes the other carbon atom, the palladium, and one hydrogen atom forming a bridge between the silicon and the metal. M7 is 3.75 kcal mol^{-1} higher in energy than M4.

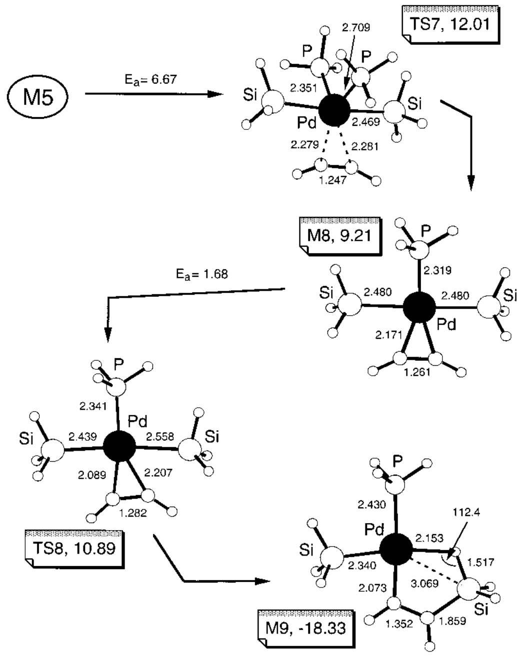

Figure 6. Schematic representation of the structures of the critical points TS7, M8, TS8, and M9 located along the trans channel of Figure 4. The values (angstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol^{-1}) relative to reactants are reported.

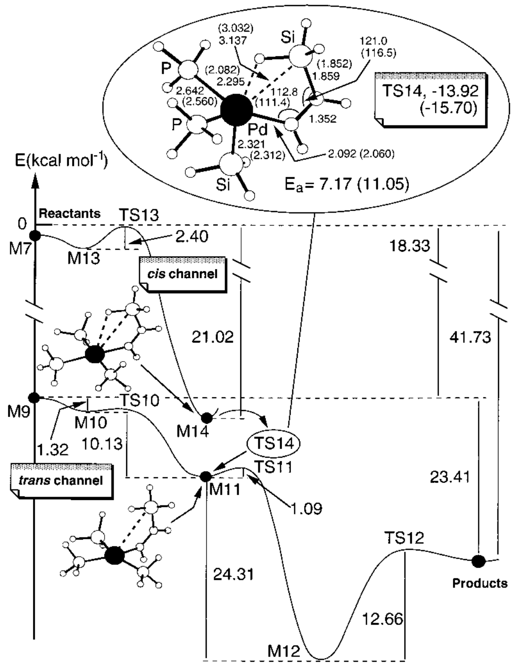

Figure 7. Energy profiles for the formation of the second C−Si bond and the regeneration of the catalyst. In the enlargement the structure of the isomerization transition state TS14 is also reported (Ångstroms and degrees).

The trans channel shows a similar trend. The first step along this reaction pathway leads from M5 to the complex, M8 between the metal and the acetylene and to the elimination of a PH_3 ligand. This complex is 3.87 kcal mol^{-1} higher in energy than M5 and its formation requires the overcoming of a barrier of 6.67 kcal mol^{-1} (transition state TS7). This value is close to that of the corresponding barrier found along the cis channel. M8 is different, in some respects, from the analogous intermediate, M6. In M6, as previously pointed out, there is a significant interaction between the two silicon atoms. In M8, the two Si atoms cannot interact since they are on opposite sides with respect to the metal atom and no interactions exist between silicon and phosphorus. As a consequence, M8 is a square-planar complex with C_{2v} symmetry. The lacking of any interactions between the ligands makes the barrier for the formation of the first C−Si bond (complex M9) much smaller (only 1.68 kcal mol^{-1} for transition state TS8) than the corresponding value found along the cis channel where some energy is required to break the Si···Si interaction. The structure of the new intermediate, M9, is very similar to that of M7. Again, the new C−Si bond belongs to a penta-atomic cycle with a bridging hydrogen atom. The most important and interesting difference between M9 and M7 is the different position of the second silyl ligand. While in M7, SiH_3 is trans to the acetylene fragment, in M9 this group is adjacent to the acetylene carbon still bonded to the metal and thus it is in the right position to form easily the second C−Si bond to obtain the final product.

A further point is important in the mechanistic scenario that characterizes this catalytic process. While the transformation M4 → M7 is endothermic by 3.75 kcal mol^{-1}, the process M5 → M9 is significantly exothermic (23.67 kcal mol^{-1}) and M9 is 16.69 kcal mol^{-1} lower in energy than M7. Also, a transition state (TS9) has been located for the isomerization process M7 → M9. From M7 it is possible to reach the more stable intermediate M9 by overcoming a barrier of 16.79 kcal mol^{-1}. This indicates that this transformation can occur easily at room temperature. From the schematic representation of the transition state TS9 given in Figure 4, it is evident that the isomerization M7 → M9 corresponds to a rotation around the Pd−C bond. The rotation causes the breaking of the Pd−H interaction on one side (the SiH_3 side on the molecular plane P−Pd−Si) and the formation of a similar interaction on the other side (the PH_3 side). It is worth comparing this activation energy to that computed for the isomerization M4 → M5 (41.36 kcal mol^{-1}). In that case, the transformation involves a change of hybridization on the metal atom, which explains the much higher value found for the barrier.

Both intermediates M9 and M7 can coordinate again the phosphine ligand previously expelled and form two new intermediates M10 and M13, respectively, where the PH_3 group now slightly interacts with the metal atom (the Pd−P distance is 3.782 Å in M10 and 4.334 Å in M13). We shall demonstrate that from both these intermediates it is possible to complete the catalytic cycle and obtain a product with the stereochemical features experimentally observed. The two paths, which originate from M9/M10 and M7/M13 are an extension of the trans and cis channel respectively, and are depicted in Figure 7. The structures of the various critical points located along them are represented in Figures 8, 9, and 10.

Along the trans channel M10 easily transforms to a new intermediate, M11. A negligible barrier of 0.12 kcal mol^{-1} (transition state TS10) is required. In this new species, the definitive formation of the Pd−P bond has caused the opening of the five-member cycle (the Pd−H distance, which was 2.173 Å in M10 and 2.262 Å in TS10, has become 3.806 Å). In a subsequent transition state (TS11), the silyl group, moves toward the carbon bonded to the metal to form the second C−Si bond. The increasing interaction between carbon and silicon (the C−Si distance is now 2.217 Å) has the effect of weakening both the Pd−C and Pd−Si bonds which become 2.140 and 2.437 Å

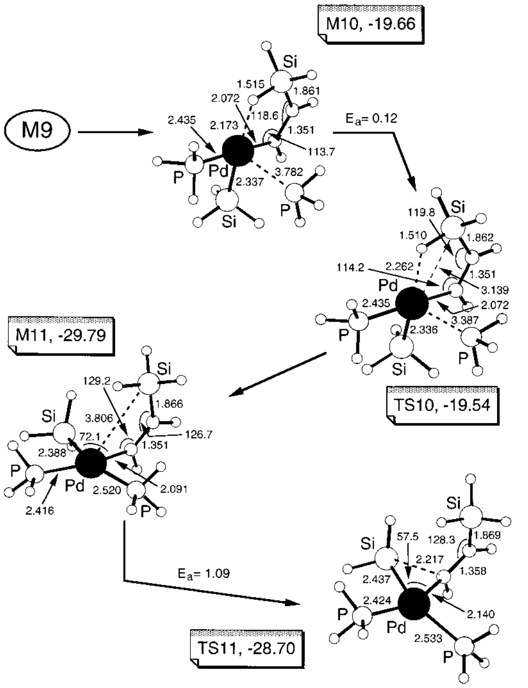

Figure 8. Schematic representation of the structures of the critical points M10, TS10, M11, and TS11 located on the energy surface of Figure 7. The values (angstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol^{-1}) relative to reactants are reported.

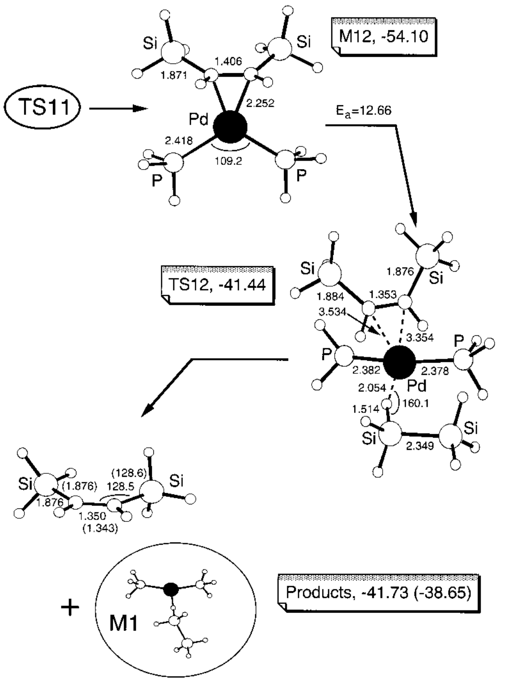

Figure 9. Schematic representation of the structures of the critical points M12, TS12, and of the final product located on the energy surface of Figure 7. The values (angstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol^{-1}) relative to reactants are reported.

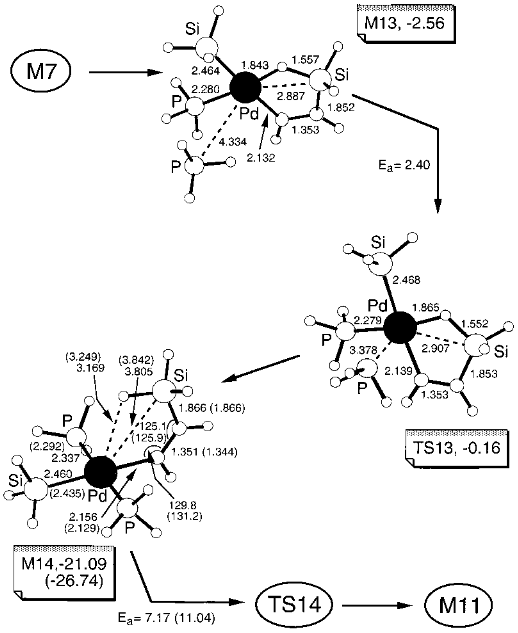

Figure 10. Schematic representation of the structures of the critical points M13, TS13, and M13 on the energy surface of Figure 7. The values (angstroms and degrees) of the most relevant geometrical parameters and the energies (kcal mol—^{1}) relative to reactants are reported.

respectively. The migration of the silyl group results in the formation of the intermediate M12 (C_s symmetry) where the product of the reaction (bis(silyl)ethene in our model system) is still coordinated to the metal atom. This intermediate is 35.76 kcal mol^{-1} lower in energy than the complex M9 and 54.10 kcal mol^{-1} lower than reactants. The configuration of the double bond of the bis(silyl)ethene moiety in this intermediate is already determined. It corresponds to a Z (or cis) configuration in agreement with the experimental evidence. A final barrier of 12.66 kcal mol^{-1} (transition state TS12) is required to release the product ((Z)-bis(silyl)ethene) and to regenerate the catalyst in the form of the complex M1 (last step of the cycle). This final step is endothermic by 12.37 kcal mol^{-1} in agreement with the fact that the regenerated catalyst M1 has an unsaturated metal coordination sphere. However, it is reasonable to believe that M1 leads immediately to the cis complex M4 which enters a new catalytic cycle. The whole catalytic process is exothermic by 41.73 kcal mol^{-1}. This value is in good agreement with that of about 40 kcal mol^{-1} estimated on the basis of thermochemical considerations.[3e] It is worth noting that these computations agree very well with the experimental results obtained by Murakami and co-workers in ref 3o. These authors studied the reaction of a bis(trialkylsilyl)palladium complex with alkynes and were able to isolate a [bis(trialkylsilyl)alkene]palladium complex which was characterized by X-ray diffraction and NMR techniques. The structure of this species is very similar to that of M12 determined in the present study. The midpoint of the double bond coordinates one site of a trigonal geometry with the double bond in the molecular plane, as found for M12 in our computations. Furthermore, it was observed that the final product of the reaction was the bis-silylated olefin and the starting bis(trialkylsilyl)palladium complex which was regenerated. This species also was characterized by X-ray diffraction. Its structure (a square planar coordination) is very close to that of the cis complex M4 that corresponds, in our mechanistic scheme, to the active catalytic species. The extension of cis channel is similar in the first part to the trans pathway. A transition state (TS13) leads from M13 to a new intermediate complex (M14), by overcoming a small barrier of 2.40 kcal mol^{-1}. As previously observed in M11, the formation of the Pd−P bond determines in M14 the opening of the penta-atomic cycle formed by the metal, the two carbon atoms, the Si atom and the hydrogen bonded to silicon (the Pd−H distance, which

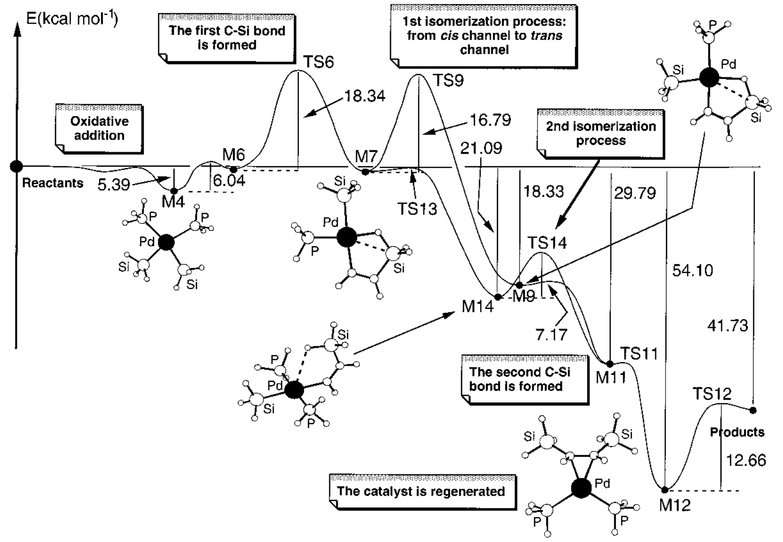

Figure 11. Energy profile for the whole catalytic cycle.

is 1.843 and 1.865 Å in M13 and TS13 respectively, becomes 3.169 Å in M14). M14 is an isomer of the intermediate M11. However, while in M11 the second silyl group is adjacent to the carbon atom (a decreasing of the Si−Pd−C angle places the SiH_3 group close enough to the acetylene carbon to form the second Si−C bond), in M14 it lies on the opposite side with respect to the palladium atom. This indicates that in the latter case the formation of the second C−Si bond cannot occur so easily as previously described for M11 and more complex structural modifications are required to place the silyl group in the right position. A further investigation of the potential surface has pointed out the existence of a further critical point connecting the cis to the trans channel i.e., the transition state TS14 which allows the isomerization M14 → M11. This structural change requires a barrier of 7.17 kcal mol^{-1} and represents an alternative and competitive way to close the catalytic cycle.

Conclusions

In this paper we have investigated at the DFT(B3LYP) level the bis-silylation reaction of alkynes catalyzed by palladium complexes. To this purpose, a model-system formed by an acetylene molecule, a disilane molecule and a $Pd(PH_3)_2$ complex has been used. The most relevant results obtained in the present study are schematically represented in Figure 11, where the energy profile of the whole catalytic cycle is reported. These results can be summarized as follows:

(i) The first step of the catalytic cycle (oxidative addition) is an easy process. A cis $(SiH_3)_2Pd(PH_3)_2$ complex (M4), which is 5.39 kcal mol^{-1} lower in energy than reactants, forms with almost no barrier. A trans $(SiH_3)_2Pd(PH_3)_2$ species also exists, which is 10.73 kcal mol^{-1} higher than M4. However, the isomerization from the cis to the trans complex requires the overcoming of a large energy barrier (about 41.36 kcal mol^{-1}). Thus, the existence of the trans complex is very unlike on energy grounds.

(ii) The transfer of the two silyl groups to the C−C triple bond does not occur in a concerted way (as one could suggest to explain the stereochemical outcome of the reaction), but involves many steps.

(iii) The cis $(SiH_3)_2Pd(PH_3)_2$ complex (M4) represents the real active form of the catalyst and is involved in the formation of the first C−Si bond. The main energy barrier required by this process to reach the intermediate M7 amounts to 18.34 kcal mol^{-1}. M7 is characterized by a cyclic structure involving the acetylene moiety, the silyl group bonded to carbon and the metal. In this intermediate, the second silyl group and the acetylene fragment are placed on opposite sides with respect to the palladium atom. Thus the formation of the second Si−C bond is not an easy process and needs further significant structural modifications.

(iv) The intermediate, M7, has two possibilities: (a) It can isomerize rather easily to a new intermediate, M9, which is 16.79 kcal mol^{-1} lower in energy and immediately transforms to a new complex M11 to complete the catalytic cycle. (b) Alternatively, it can transform to a new species M14 that subsequently isomerizes to M11. Both isomerization processes, which connect the cis to the trans channel, have the effect of placing the second silyl group and the acetylene moiety in adjacent positions to make possible the formation of the second C−Si bond. They also play a key-role in determining the stereochemical output of the reaction. The Z configuration of the C−C double bond in the final product is naturally obtained in this way, in agreement with the results of the experimental investigations.[3]

(v) The barrier for the isomerization M7 → M9 is 16.79 kcal mol^{-1}, while that for the isomerization M14 → M11 occurs more easily since it requires only 7.17 kcal mol^{-1}. Thus, at least for the simple model-system investigated here, the transformation M7 → M14 → M11 represents the most convenient path to close the catalytic cycle.

(vi) The exothermicity of the whole catalytic process is 41.73 kcal mol^{-1}, a value which is in good agreement with the experimental estimate of this quantity (about 40 kcal mol^{-1}).

Appendix

To validate the results obtained with the DZVP basis set, we have recomputed the energy and the structures of the most relevant critical points using the more accurate basis set described in the computational section (6-311G* basis). The critical points that we have again investigated are: **M0** (reactants), **M1**, **M6**, **TS6**, **M7**, **TS9, M14, TS14,** and the bis(silyl)ethene product. The energy values and those of the geometrical parameters are reported in parentheses in Figures 2, 4, 5, 9, and 10. The changes for the activation barriers required for the formation of the first C−Si bond (**M6** → **TS6**) and for the two isomerization processes (**M7** → **TS9** and **M14** → **TS14**), which represent the two key-steps of the catalytic cycle, are not significant. The three barriers vary from 18.34 16.79 and 7.17 kcal mol^{-1} to 18.29 16.37 and 11.05 kcal mol^{-1}, respectively. A similar trend has been observed for the exothermicity of the reaction that becomes 38.65 kcal mol^{-1} at the 6-311G* level (41.73 kcal mol^{-1} with the DZVP basis). The two basis sets also provide similar geometrical parameters, as it is evident from the comparison between the two sets of values reported in the figures. In all cases, the variation of the bond distances on passing from the DZVP to the 6-311G* level is less than 0.06 Å and the change in the bond angles less than 3°. All these results (energy and geometry) indicate that the DZVP basis is adequate for describing this kind of reaction.

Acknowledgment. We would like to thank C.N.R. and M.U.R.S.T. (Progetto Nazionale “Stereoselezione in Sintesi Organica: Metodologie ed Applicazioni”) and Bologna University (funds for selected research topics) for the financial support of these researches.

Supporting Information Available: Supporting information has been provided for this journal article. **Table S1:** Total energies and Cartesian coordinates of the various critical points computed at the B3LYP level with the DZVP basis set. **Table S2:** Total energies and Cartesian coordinates of the various critical points computed at the B3LYP level with the 6-311G* basis set. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0118892