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Density Functional Study of the π Bond Activation at the Pd═Sn Bond of the $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ Complex. Why Do the $(H_2PC_2H_4PH_2)Pd$ and SnH_2 Counterparts Mutually Rotate?

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The activation mechanism of the π bonds, the nonpolar C≡C of C_2H_2 and the polar C═O of HCHO and the C≡N of HCN, at the Pd═Sn bond of the model complex $(H_2PC_2H_4PH_2)$-Pd═SnH_2 is theoretically examined using a density functional method (B3LYP). For the nonpolar ethyne C≡C π bond, the reaction proceeds by the homolytic mechanism supported by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis. The charge transfers, the electron donation from the ethyne π orbital to the Sn p orbital, and the back-donation from Pd dπ orbital to the ethyne π* orbital successfully occur step by step to complete the π bond breaking during the reaction. Without the rotation of the $(H_2PC_2H_4PH_2)Pd$ group, the first charge transfer from the ethyne π orbital to the Sn p orbital is too weak to break the π bond. On the other hand, for the strongly polarized formaldehyde C═O π bond, the donation of lone pair electron on the C═O oxygen to the Sn p orbital is so strong that both the nucleophilicity of the Pd atom and the electrophilicity of C═O carbon are significantly enhanced through the Pd(dπ)−Sn(pπ) orbital, and the C═O π bond is broken by the heterolytic mechanism with the electrophilic attack of the C═O carbon to the Pd atom. In this mechanism, the rotation of the $(H_2PC_2H_4PH_2)Pd$ group is not necessary. However, when the C═O π bond approaches the Sn atom in a η^2-fashion, the reaction proceeds by the homolytic mechanism with the rotation of the $(H_2PC_2H_4PH_2)Pd$ group, which is similar to the case of ethyne. In the case of hydrogen cyanide, where the C≡N π bond has to approach the Sn atom in a η^2-fashion to break its π bond, only the homolytic pathway with the rotation of the $(H_2PC_2H_4PH_2)Pd$ group exists. The first charge transfer from the substrate to the Sn p orbital plays a key role in determining the mechanism, and it is strengthened enough to break the π bond by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group in the homolytic mechanism. The potential energy surface of the activation reaction was quite smooth with a small energy barrier even in the homolytic mechanism with the rotation of the $(H_2PC_2H_4PH_2)Pd$ group due to the successive stepwise process. The ligand effects on the activation activity are also discussed.

1. Introduction and Background

The unique activities of stannylene complexes for the organic synthesis have recently been reported by many experimentalists.[1] For, example, the Pd═Sn double bond functions as a catalyst for the synthesis of the electrochemically important material stannole. The phosphine-coordinated Pd complexes, $(PR_3)_2Pd$ and $(R_2PC_2H_4PR_2)$-Pd (R = Me, i-Pr, t-Bu), catalyze the [2+2+1] cycloaddition of two ethynes and one stannylene, SnR'_2 ($R' = CH(SiMe_3)_2$ and $R'_2 = \{C(SiMe_3)_2CH_2\}_2$), to produce the stannole.[2] As we previously reported, in this reaction, the first step of the catalytic cycle is the π bond activation of ethyne at the Pd═Sn bond of the stannylene complex formed by the coordination of the stannylene to the Pd first, which proceeds along the quite smooth potential energy surface requiring a only small energy barrier, as mentioned below. On the other hand, the σ bond of water and methanol O−H is also easily broken at the Pd═Sn bond of the $(R_2PC_2H_4PR_2)$-Pd═SnR'_2 (R = i-Pr, t-Bu; $R' = CH(SiMe_3)_2$) complexes even at −40 °C to form the $(R_2PC_2H_4PR_2)Pd(H)Sn(OR'')$-$R'_2$ (R″ = H, Me) products.[3] Here, of our most interest is the behavior of the phophine ligands coordinated to the Pd during such activation reactions. According to our previous theoretical investigations[4,5] with the model

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† Institute for Fundamental Chemistry.

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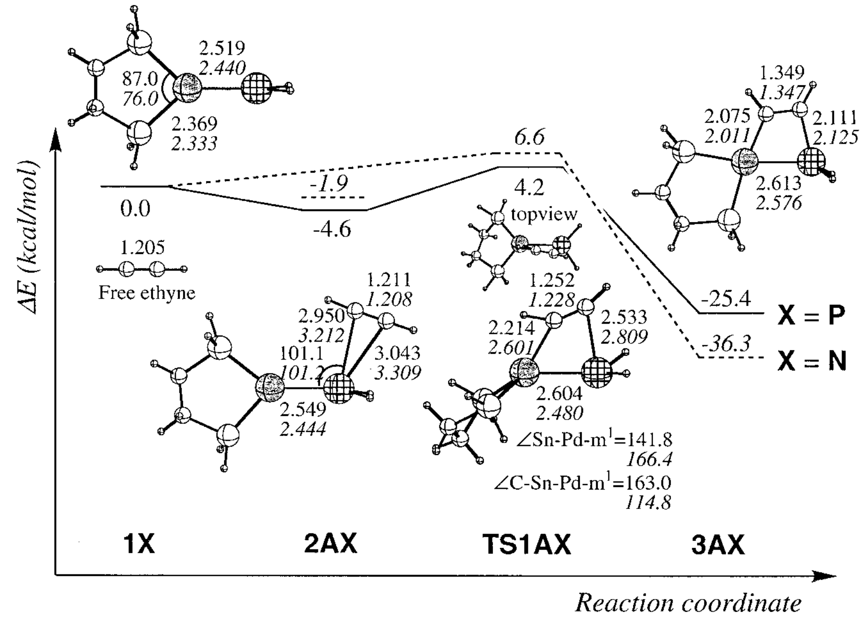
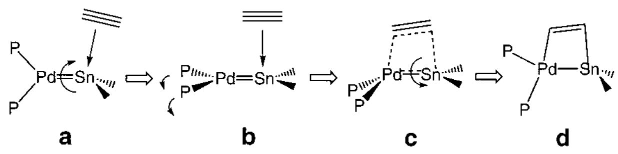


Figure 1. B3LYP/BSI potential energy surfaces (in kcal/mol) of the ethyne C≡C π bond activation at the Pd=Sn bond of the stannylene complexes $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ **1P** (normal line) and $(H_2NC_2H_4NH_2)Pd{=}SnH_2$ **1N** (dotted line), together with the optimized structures (in Å and deg) at the B3LYP/BSI level. The values in plain and italic type are for **X** = **P** and **X** = **N**, respectively. m^1 is the midpoint between two P atoms.

Scheme 1



complexes $(PH_3)_2Pd{=}Sn$ and $(H_2PC_2H_4PH_2)Pd{=}Sn$, in the case of the σ bond activation of H−H, C−H, O−H, and N−H, the phosphine-coordinated Pd counterpart never rotates around the Pd−Sn axis during the reaction, independent of the polar and nonpolar bonds. However, it rotates during the π bond activation$^{4-6}$ and only in the homolytic mechanism. We briefly summarize below our previous reports with the density functional method (B3LYP) for the nonpolar ethyne C≡C and polar formaldehyde C=O π bond activation at the Pd=Sn bond of the model complexes $(PH_3)_2Pd{=}Sn$ and $(H_2PC_2H_4PH_2)Pd{=}SnH_2$.

Ethyne. Our calculations using the complex $(PH_3)_2Pd{=}SnH_2$ for the first process of the catalytic cycle of the stannole formation, the formation of the 1,2-metallastannete intermediate, showed the peculiar activation process with a stepwise motion of the phosphine ligands coordinated to the Pd atom as illustrated in Scheme 1. The ethyne C≡C π bond first coordinates not to the Pd but to the Sn atom of the precursor stannylene complex $(PH_3)_2Pd{=}SnH_2$ by the η^2-fashion (**a**). Here, it is of great interest that the $(PH_3)_2Pd$ and SnH_2 counterparts mutually rotate before reaching the transition state. In the intermediate (**b**), the $(PH_3)_2Pd$ group rotates around the Pd−Sn axis by about 90°, and then the interaction between ethyne and the Sn atom by the electron donation from the ethyne π orbital to the Sn p orbital is strengthened (see below) and the coordinated ethyne comes closer to the Pd atom. In the transition state (**c**), two phosphines bend down, deviating from the Pd−Sn axis to make the electron back-donation from the Pd dπ orbital to the ethyne π^* orbital facile. After passing through the transition state (**c**), the $(PH_3)_2Pd$ group further rotates to form the 1,2-palladastannete complex (**d**). When the chelate ligand, $H_2PC_2H_4PH_2$, is used instead of $(PH_3)_2$, the structure **b** does not exist as an equilibrium structure, although the reaction undergoes a similar stepwise structural rearrangement (Figure 1). These activation reactions thus proceed in a homolytic manner by the electron donation and back-donation between ethyne and the Pd=Sn.

Formaldehyde. For the activation of the strongly polarized C=O π bond of formaldehyde, there exist two reaction pathways, as presented in Figure 2. One has a homolytic mechanism and is accompanied by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis, which is similar to the case of ethyne, and the other has a heterolytic mechanism and is not accompanied by this rotation. In both mechanisms, the incoming formaldehyde first coordinates to the Sn, where only the C=O oxygen interacts with the Sn and the H−C−H plane of formaldehyde is parallel to the Pd−Sn−O plane. Another structure with the C=O coordination by the η^2-fashion does not exist as an equilibrium structure. In the transition state **TS1BP** in the homolytic mechanism, not only the $(H_2PC_2H_4PH_2)Pd$ fragment but also formaldehyde rotate. From here, the $(H_2PC_2H_4PH_2)Pd$ fragment further rotates around the Pd−Sn axis to produce the product **3BP**. On the other hand, in another transition state, **TS2BP**, in the heterolytic mechanism, the $(H_2PC_2H_4PH_2)Pd$ plane remains parallel to the C−O−Sn plane without its rotation.

In the present study, to give a definite answer to the question why the $(H_2PC_2H_4PH_2)Pd$ and SnH_2 groups mutually rotate during π bond activation by the homolytic mechanism, we further theoretically investi-

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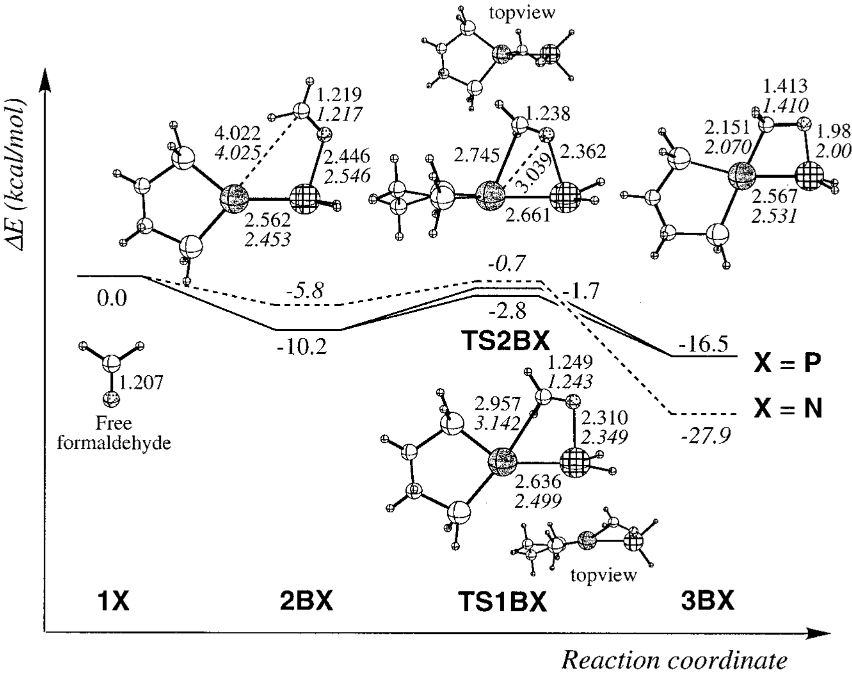

Figure 2. B3LYP/BSI potential energy surfaces (in kcal/mol) of the formaldehyde C=O π bond activation at the Pd=Sn bond of the stannylene complexes $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ **1P** (normal line) and $(H_2NC_2H_4NH_2)Pd{=}SnH_2$ **1N** (dotted line), together with the optimized structures (in Å and deg) at the B3LYP/BSI level. The values in plain and italic type are for **X** = **P** and **X** = **N**, respectively. Two pathways for **X** = **P** by the homolytic (**1P** → **2BP** → **TS1BP** → **3BP**) and heterolytic mechanism (**1P** → **2BP** → **TS2BP** → **3BP**), where the former is higher in energy than the latter, are displayed. For **X** = **N**, only the heterolytic one (**1N** → **2BN** → **TS2BN** → **3BN**) was found (see text).

gated in detail the reaction process of the π bond cleavage at the Pd=Sn bond with the density functional method (B3LYP) using the model complex $(H_2PC_2H_4PH_2)Pd{=}SnH_2$. As the π bond, two kinds of polar bonds, $C\equiv N$ of HCN and C=O of HCHO, were chosen in addition to the nonploar $C\equiv C$ of C_2H_2. Following the explanation of the calculation method in section 2, the ethyne $C\equiv C$ π bond activation is first discussed in section 3.1. The formaldehyde C=O and hydrogen cyanide $C\equiv N$ π bond activations are discussed in the subsequent sections 3.2 and 3.3, respectively. In section 3.4, the ligand effects on the activation reaction are given. Conclusions are listed in the last section.

2. Computational Details

All calculations were performed using the Gaussian98 program.[7] The calculations of the energetics as well as the geometry optimizations were carried out at the B3LYP level of theory, which consists of a hybrid Becke + Hartree−Fock exchange and a Lee−Yang−Parr correlation functional with nonlocal corrections[8] using the basis set BSI. The basis set BSI is the 6-31G(d,p) level for the H, C, N, and O atoms of ethyne, formaldehyde, hydrogen cyanide, and stannylene molecules, the 6-31G level for the C and H atoms, and the 6-31G(d) level for the P and N atoms of the spectator ligands, $H_2PC_2H_4PH_2$ and $H_2NC_2H_4NH_2$. For Pd, the triple-ζ (5s,6p,4d,1f)/[3s,3p,3d,1f] augmented by an additional single set of f orbitals with the exponent of 1.472[9] and the effective core potential (ECP) determined by Hay−Wadt[10] to replace the core electrons up to 3d and for Sn the (3s,3p)/[2s,2p] basis functions with a 5d polarization function with the exponent of 0.183[11] and the Hay−Wadt ECP[12] to replace the core electrons up to 4d were used.

All equilibrium structures and transitions states were optimized without any symmetry restrictions and identified by the number of imaginary frequencies calculated from the analytical Hessian matrix. The reaction coordinates were followed from the transition state to the reactant and the product by the intrinsic reaction coordinate (IRC) technique.[13] The atomic orbital (AO) population, atomic charge, and the charge of the molecule were obtained by the NBO analysis. The calculated energies relative to the free molecules, the $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ complex **1P** and the $(H_2NC_2H_4NH_2)$-$Pd{=}SnH_2$ complex **1N**, are shown. The labels for the structures **A**−**C**, for the substrates C_2H_2, HCHO, and HCN, and **P** and **N** for the $H_2PC_2H_4PH_2$ and $H_2NC_2H_4NH_2$ ligands are used, respectively.

3. Results and Discussion

3.1. Ethyne. As mentioned in the Introduction and Background, to successfully complete the ethyne π bond

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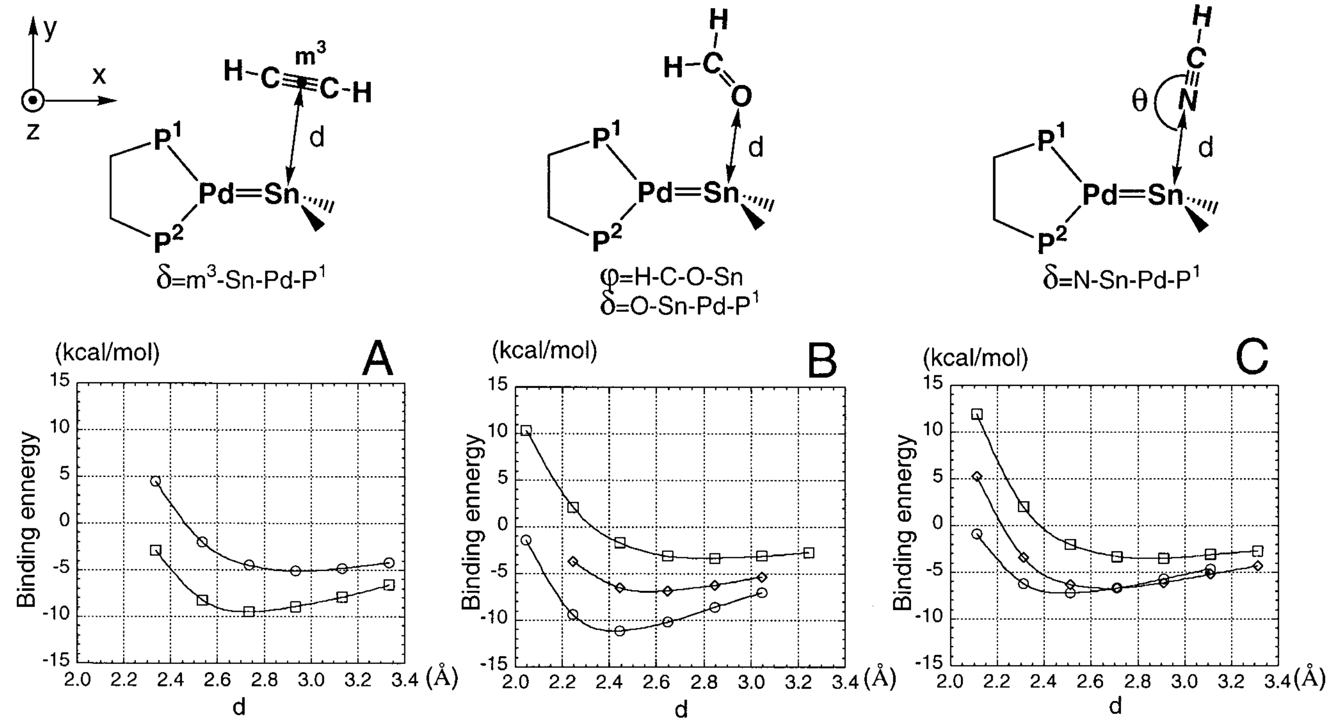
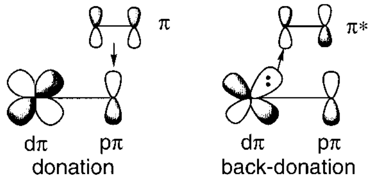
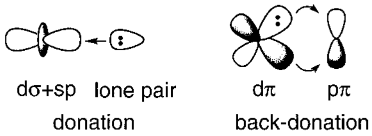


Figure 3. Plots of the binding energy of ethyne (A), formaldehyde (B), and hydrogen cyanide (C) to the Sn versus the distance (d) betweenthe Sn and substrate in **2AP** for ethyne, **2BP** for formaldehyde, and **2CP** for hydrogen cyanide. The binding energy of substrate to the Sn atom was calculated as follows; BE = $E[(H_2PC_2H_4PH_2)Pd{=}Sn(Substrate)H_2] - E[(H_2PC_2H_4PH_2)Pd{=}SnH_2] - E[Substrate]$. m^3 is the midpoint of ethyne C≡C triple bond. In A, ○: **2AP**; □: **2AP** with $\delta = 90°$. In B, ○: **2BP**; □: **2BP** with $\varphi = 90°$; ◇: **2BP** with $\varphi = 90.0°$ and $\delta = 90.0°$. In C, ○: **2CP**; □: **2CP** with $\theta = 120°$; ◇: **2CP** with $\theta = 120°$ and $\delta = 90.0°$.

breaking, the reaction in turn undergoes two kinds of charge transfers, i.e., (i) the electron donation from the ethyne π orbital to the unoccupied p orbital of the Sn, and (ii) the electron back-donation from the Pd dπ orbital to the ethyne π^* orbital with the stepwise structural rearrangement of the $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ fragment:



However, it should be noted here that both occupied Pd dπ and unoccupied Sn pπ orbitals interact with each other by the electron π back-donation from the Pd dπ orbital to the Sn pπ orbital, which significantly contributes to the Pd=Sn bonding as well as the σ donation of the lone pair electron of the Sn atom to the hybridized dσ+sp orbital of the Pd atom presented below.



As shown by the H−Sn−H plane perpendicular to the P−M−P plane in **1P**, the unoccupied pπ orbital of the Sn atom interacts with the occupied dπ orbital of the Pd atom enhanced by the small P−M−P bite angle of 87°.[14] Therefore, the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis reduces the π back-donation from the Pd dπ orbital to the Sn pπ orbital and strengthens the donation from the ethyne π orbital to the Sn p orbital. This phenomenon might be a peculiar for the π bond in which the orbital overlap with the Sn p orbital is large. Because in the case of the σ bond, such as H−H, C−H, O−H, and N−H, the activation reaction is never accompanied by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group,[4,5] independent of the polar and nonpolar bonds.

Since the strength of the electron donation from the ethyne π orbital to the Sn p orbital is sensitively reflected in the binding energy of ethyne to the Sn, we calculated its binding energy by plotting with the variable d, as presented in Figure 3. By the rotaion of the $(H_2PC_2H_4PH_2)Pd$ group by 90° around the Pd−Sn axis, the minimum of the curvature is shifted and the distance between ethyne and the Sn atom becomes shorter by 0.214 Å. The binding energy also enlarges from 5.1 kcal/mol to 9.5 kcal/mol. Thus, the π bond of ethyne is sufficiently preactivated by the electron donation from the ethyne π orbital to the Sn p orbital, supported by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group. Also, the ethyne coordination to the Sn by its electron donation weakens the Pd=Sn bond to make the rotation of the $(H_2PC_2H_4PH_2)Pd$ group facile. This is evident from the fact that the rotation energy around the Pd−Sn axis is reduced from 9.9 kcal/mol to 6.0 kcal/mol by the coordination of ethyne to the Sn, as presented in Figure 4.

Since the Pd dπ and Sn pπ orbitals play a key role in the π bond activation as mentioned above, we also

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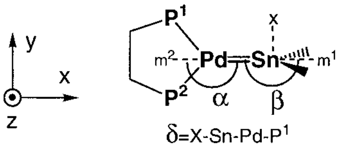
Table 1. Molecular Orbital (MO) and Total Energies and Atomic Orbital (AO) Population of the $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ Complex 1P at the B3LYP/BSI Level[a]



	total energy (hartree)	relative energy (kcal/mol)	AO population		MO energy
			Pd(d_{xy})	Sn(p_x)	Pd(d_{xy})
free SnH_2				0.000	
1P; α=180.0°, β=180.0°, δ=0.0°	−895.055027	0.0	1.769	0.341	−0.1901
1P-I; α=180.0°, β=120.0°, δ=0.0°	−895.048672	4.0	1.781	0.438	−0.1867
1P-II; α=165.5°, β=180.0°, δ=0.0°	−895.052555	1.6	1.771	0.359	−0.1782
1P-III; α=180.0°,β=180.0°, δ=90.0°	−895.039302	9.9	1.872	0.093	−0.2405
1P-IV; α=130.0°, β=180.0°, δ=90.0°	−895.036343	11.7	1.901	0.255	−0.1903

[a] m^1 and m^2 are the midpoints between two hydrogens attached to the Sn atom and between the P^1 and P^2 atoms, respectively.

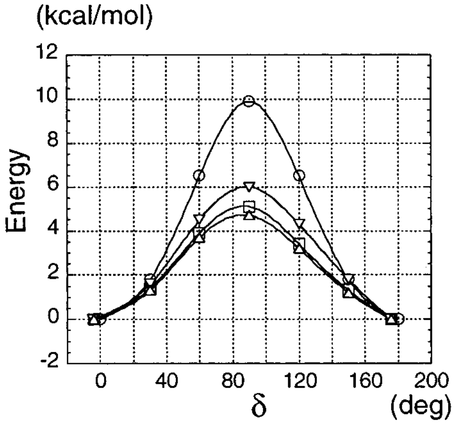


Figure 4. Rotation energy of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis. The energies are plotted versus the angle δ. For the definition of δ, see Table 1 and Figure 3. ○: **1P**; ▽: **2AP**; △: **2BP**; □: **2CP**.

followed the change in the population and the energy level of these orbitals by the deformation of the $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ fragment which is forced during the ethyne C≡C π bond activation. With the ethyne coordination to the Sn, two hydrogens attached to the Sn are bent down first and the $H_2PC_2H_4PH_2$ ligand slightly rotates around the Pd atom counterclockwise, keeping the P−Pd−P angle (see Figure 1). We artificially created in **1P** these structural deformations caused in the $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ fragment independently. On comparison with **1P** without deformation, the population and molecular orbital (MO) energy of d_{xy} slightly increased by these deformations, but it was not marked, as shown in Table 1 (**1P-I** and **1P-II**). On the other hand, the population of the Sn p_x orbital also increased in both cases. Therefore, it would be considered that the motion of the hydrogens attached to the Sn atom and the $H_2PC_2H_4PH_2$ ligand do not function to promote the ethyne coordination. These motions might be ascribed to the steric effect which comes from the ethyne coordination.

Notable changes were found when the $(H_2PC_2H_4PH_2)$Pd counterpart rotates around the Pd−Sn axis (**1P-III**). The population of the Sn p_x orbital is significantly decreased because the electron donative phosphine ligands move out of the plane of the Pd d_{xy} orbital, which would strengthen the ethyne coordination to the Sn by the electron donation from the ethyne π orbital to the Sn p orbital to efficiently weaken the ethyne π bond. As a result, the population of the Pd d_{xy} orbital increased and the molecular orbital of d_{xy} was lowered in energy. Further bend of the phosphine ligands (**1P-IV**) after the rotation deviating from the Pd−Sn axis increased the population of d_{xy} further and destabilized the molecular orbital of d_{xy} so that the electron back-donation from the Pd d_{xy} to the ethyne π* is enhanced to complete the ethyne C≡C π bond breaking. In fact, the Pd−C and Sn−C bonds are nearly formed before the $(H_2PC_2H_4PH_2)$Pd group rotates back.[5]

Thus, the merit of the rotation of the $(H_2PC_2H_4PH_2)$Pd group around the Pd−Sn axis is that both electron donation from the ethyne π orbital to the Sn p orbital and back-donation from the Pd dπ orbital to the ethyne π* orbital to break the C≡C π bond are strengthened step by step in each process. Especially, the preactivation of the π bond in the initial stage by the electron donation from the ethyne π orbital to the Sn p orbital is considered to be quite important for this homolytic mechanism, because the reaction never proceeds without the rotation of the $(H_2PC_2H_4PH_2)$Pd group.

3.2. Formaldehyde. For the C=O π bond of formaldehyde, we have found two activation pathways, which have the homolytic and heterolytic mechanism, respectively (see the Introduction and Background). The incoming formaldehyde coordinates to the Sn by the donation of the lone pair electron on the oxygen to the p orbital of the Sn, where the H−C−H plane of formaldehyde is parallel to the Pd−Sn−O plane while the pπ orbital of the C=O is perpendicular. It would be worth noting that even in the π bond activation, the heterolytic pathway, where the rotation of the $(H_2PC_2H_4PH_2)$Pd group is not accompanied, exists for such a polar C=O π bond of formaldehyde, which is similar to the case for the σ bond.[4,5]

We first followed the motion of the structure of the complex during the reactions for two pathways from **2BP** to **3BP**, i.e., a homolytic one passing through **TS1BP** and a hetrolytic one passing through **TS2BP**. The changes in the selected geometric parameters along the reaction coordinates are presented in Figure 5. The reaction can be clearly divided into three processes. In the first stage, the coordinated formaldehyde slightly rotates around the O−Sn axis, where the CH_2 part

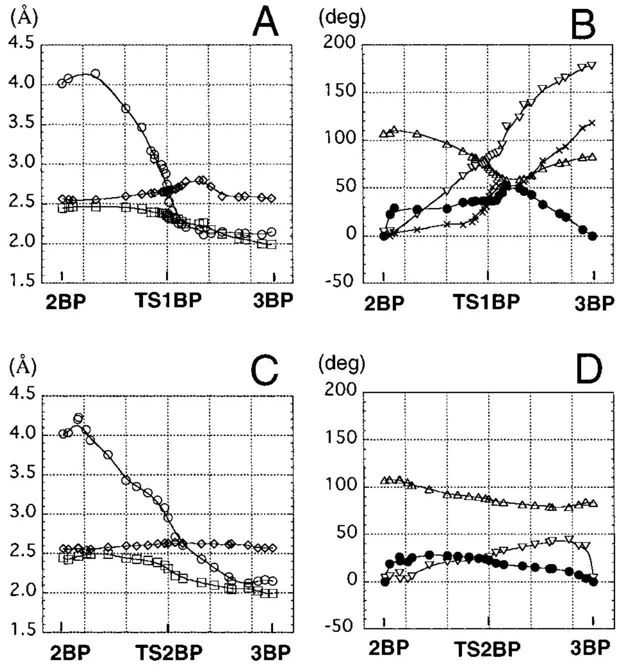


Figure 5. Changes in the geometric parameters during the C═O π bond activation of formaldehyde at the Pd═Sn bond of the $(H_2PC_2H_4PH_2)Pd$═Sn complex by the homolytic (A, B) and heterolytic (C, D) mechanism. In A and C, ○: *d*(Pd−C); ◇: *d*(Pd−Sn); □: *d*(O−Sn). In B and D, △: ∠O−Sn−Pd; ▽: ∠O−Sn−Pd−P^1; ●: ∠C−O−Sn−Pd; ×: ∠H−C−O−Sn.

deviates from the Pd−Sn−O plane to direct the C pπ orbital perpendicular to the Pd−Sn−O plane toward the Pd atom, as reflected by the increase in the C−O−Sn−Pd dihedral angle. This is a common initial motion in both homolytic and heterolytic reactions. The second process is the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis, in which the Pd−C bond is remarkably shortened and is nearly formed, for the homolytic mechanism. The C═O π orbital of formaldehyde is quickly made parallel to the Pd−Sn−O plane by its rotation just before reaching the transition state **TS1BP** in this stage, as reflected by the H−C−O−Sn dihedral angle. The O−Sn−Pd angle has a minimum around the transition state because the steric contact of formaldehyde with the phosphine ligand is reduced by the rotation of the phosphine ligand. The third process is the further rotation of the $(H_2PC_2H_4PH_2)Pd$ group to complete the reaction. The C−O−Sn−Pd dihedral angle of about 30° retained during the reaction due to the contribution of the lone pair electron of the C═O oxygen (see Figure 1) decreases with the increase in the H−C−O−Sn dihedral angle.

For the heterolytic mechanism, the rotation of the $(H_2PC_2H_4PH_2)Pd$ group does not occur. As the Pd−C distance is shortened, the dihedral angle C−O−Sn−Pd decreases, whereas the dihedral angle O−Sn−Pd−P increases. This indicates a twist of the formaldehyde C═O on the Pd−Sn axis, which is needed to weaken the electron back-donation from the Pd dπ orbital to the Sn pπ orbital and to enhance the nucleophilicity of the Pd. The O−Sn distance is shortened after passing through the transition state **TS2BP**. The O−Sn−Pd angle gradually decreases throughout the reaction due to the steric effect of the phosphine ligand, which does not rotate. It should be noted that the Pd−Sn bond distance is already elongated in **2BP** and is almost constant during the reaction, although it oscillates a little during the second rotation of the $(H_2PC_2H_4PH_2)Pd$ group in the homolytic mechanism, because the coordination of formaldehyde by the donation of the lone pair electron of the C═O oxygen to the Sn p orbital significantly weakens the back-donation from the Pd dπ orbital to the Sn pπ orbital, as mentioned in section 3.1. The small energy of only 4.7 kcal/mol required for the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis in **2BP** (Figure 4) supports this fact. However, the rotation of the $(H_2PC_2H_4PH_2)Pd$ group depends not on its easiness but on the mechanism. On the other hand, the Pd−O bond is already strong in the initial stage by the strong donation of the lone pair electron on the C═O oxygen to the Sn, as shown by the short Pd−O distance. The dihedral angle O−Sn−Pd−P^1 quickly decreases after the completion of both Pd−C and Sn−O bond formation.

The crucial factor that determines the mechanism, homolytic or heterolytic, is the strength of the electron donation of the coordinated formaldehyde to the Sn p orbital. The donation of the lone pair electron on the C═O oxygen to the Sn p orbital is strong enough to enhance the nucleophilicity of the Pd atom through the Pd(dπ)−Sn(pπ) orbital. The electron back-donation from the Pd dπ to the Sn pπ is thence significantly weakened, and the electron is localized on the Pd dπ orbital. However, if the electron donative phosphine rotates out of the Pd dπ plane, the nucleophilicity of the Pd dπ is reduced. On the other hand, the electrophilicity of the C═O carbon is also sufficiently enhanced by the electron donation from the formaldehyde oxygen to the Sn. As presented in Figure 6 A, the population increased only for the d_{xy} orbital which interacts with the Sn pπ orbital, as the distance *d* is shortened in **2BP**, although for the other d orbitals there was no marked tendency. The total charge of formaldehyde, which is positive, increases, and the negative charge of the Pd atom also increases (Figure 6C), by the electron flow from formaldehyde to the Pd through the Pd(dπ)−Sn(pπ) orbital. Thereby, the positive charge of the C═O carbon increases and the polarization of the C═O is enhanced, accumulating the negative charge on the oxygen.

However, when the formaldehyde molecule is rotated on the Pd−Sn axis to have the angle $\varphi = 90°$ in **2BP**, which corresponds to the approach of the C═O π bond to the Sn atom in the η^2-fashion, the electron donation of formaldehyde to the Sn p orbital is largely reduced, as reflected by the small binding energy of 3.3 kcal/mol at the Sn−O distance of 2.806 Å compared with 11.1 kcal/mol at the Sn−O distance of 2.446 Å for **2BP** (Figure 3B). Therefore, both the nucleophilicity of the Pd and the electrophilicity of the C═O carbon are decreased. Indeed, the population of 1.848 e for the Pd d_{xy} orbital and the negative charge of −0.163 e for the Pd atom decreased to 1.834 e and −0.136 e, respectively, as shown in Table 2. The amount of electron flow from formaldehyde to the Sn was also reduced from 0.078 to 0.045 e, and the positive charge of the C═O carbon (+0.270 e) became only slightly smaller (+0.269 e).

To strengthen the electron donation from the C═O π orbital to the Sn p orbital, the rotation of the $(H_2PC_2H_4PH_2)Pd$ group is necessary, as mentioned in section 3.1. As presented in Figure 3B, the binding energy of

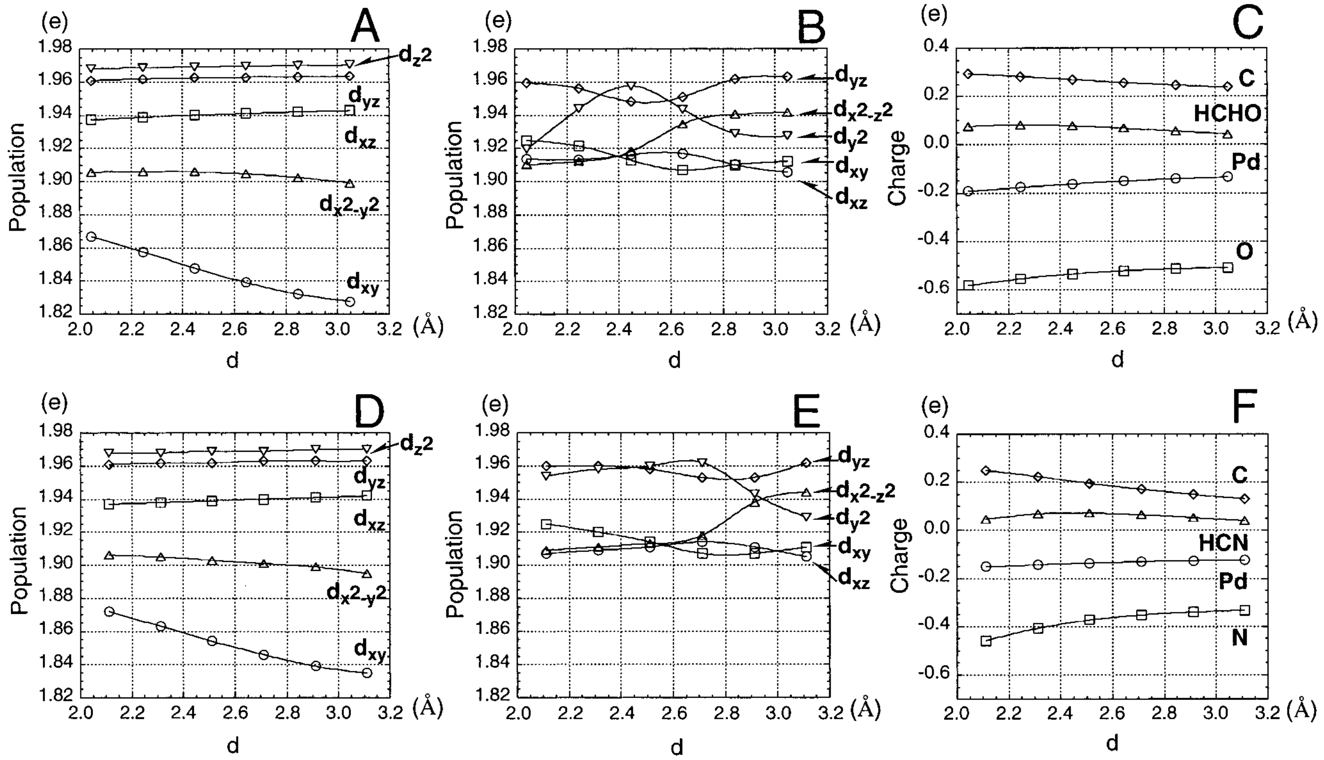


Figure 6. Plots of NBO population and charge versus the distance (*d*) between the Sn and substrate for the formaldehyde-coordinated **2BP** (A, B, C) and for the hydrogen cyanide-coordinated **2CP** (D, E, F). In B and E, δ is 90°. For the definition of d and δ, see Figure 3.

Table 2. Binding Energies and NBO Analysis of the $(H_2PC_2H_4PH_2)Pd{=}Sn(Substrate)H_2$ Complexes 2XP (X = A–C) at the B3LYP/BSI Level

	d (Å)	BE[a] (kcal/mol)	charge				AO population
			Pd	C	O, N	substrate	Pd(d_{xy})
ethyne							
2AP	2.935	−5.1	−0.123	−0.265, −0.228		0.054	1.835
formaldehyde[b]							
2BP	2.446	−11.1	−0.163	0.270	−0.535	0.078	1.848
2BP with $\varphi = 90.0°$	2.806	−3.3	−0.136	0.269	−0.532	0.045	1.834
hydrogen cyanide[b]							
2CP	2.511	−7.2	−0.136	0.196	−0.373	0.072	1.854
2CP with $\theta = 120.0°$	2.858	−3.5	−0.129	0.160	−0.349	0.058	1.831

[a] The binding energies were calculated as follows: BE = $E[(H_2PC_2H_4PH_2)Pd{=}Sn(Substrate)H_2] - E[(H_2PC_2H_4PH_2)Pd{=}SnH_2] - E[Substrate]$. [b] For the definition of φ and θ, see Figure 3.

formaldehyde to the Sn is enlarged to 6.9 kcal/mol by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group. However, now as one can easily predict, the obvious enhancement in the population for the d_{xy} orbital by the approach of formaldehyde to the Sn is not observed (Figure 6B), although the population for the d_{xy} orbital is already high without the coordination of formaldehyde, because the d_{xy} orbital is independent from the p_x orbital of the Sn by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group. Thus, the subsequent electron back-donation occurs from the highly occupied Pd dπ orbital to the formaldehyde π^* orbital to break the π bond before further rotation of the $(H_2PC_2H_4PH_2)Pd$ group. This is a typical homolytic mechanism.

3.3. Hydrogen Cyanide. We also examined the π bond activation of the other triple bond using the polar hydrogen cyanide. As presented in Figure 7, the incoming HCN similarly coordinates to the Sn first by the electron donation to the Sn p orbital with the end-on fashion, and the Pd−Sn distance is stretched to 2.560 Å in **2CP**, where the C≡N pσ orbital as well as the s orbital of the N atom occupied by the lone pair electron contributes to the coordination. The binding energy of HCN to the Sn was calculated to be 7.2 kcal/mol (Figure 3C). This is smaller by 3.9 kcal/mol compared with the case for formaldehyde, because the polarization is smaller for the C≡N π bond of hydrogen cyanide than for the C=O π bond of formaldehyde. The NBO analysis of the character of the π bond is presented in Table 3, comparing hydrogen cyanide with formaldehyde. Both σ and π electrons are more largely localized on the oxygen of formaldehyde than on the nitrogen of hydrogen cyanide, according to the sequence of the electronegativity, O (3.44) > N (3.04),[15] as shown by the atomic orbital (AO) population and the atomic charge. This is also reflected in the rotation energy of the $(H_2PC_2H_4$-

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(15) Pauling's values are presented. For example, see: *The Elements*, 3rd ed.; Emsley, J., Ed.; Oxford University Press: New York, 1998.

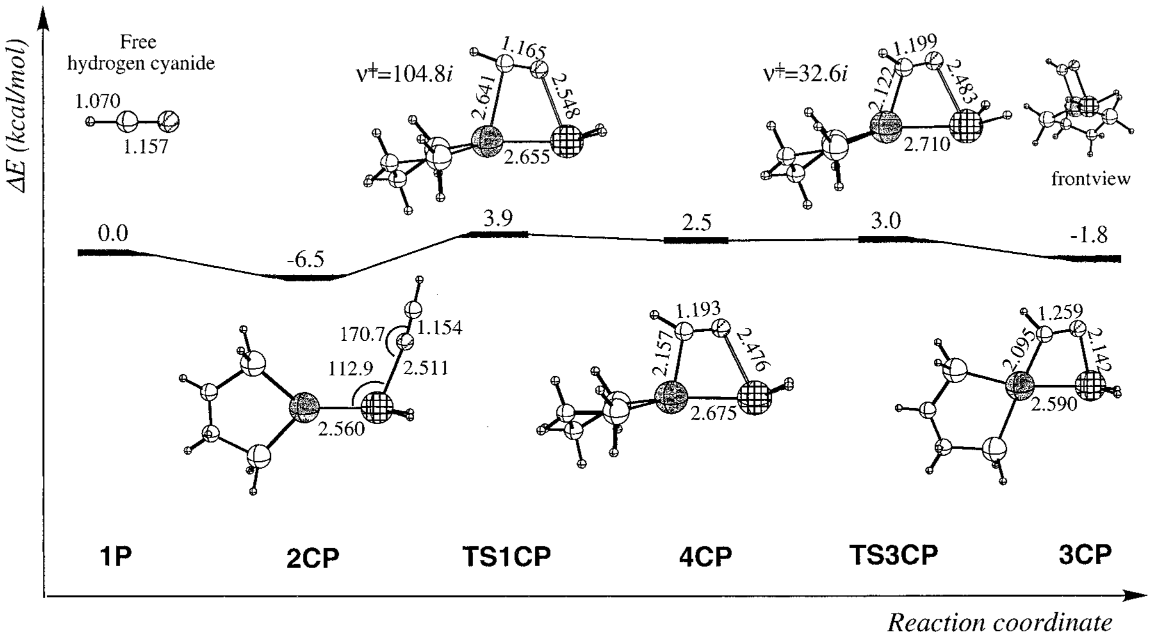

Figure 7. B3LYP/BSI potential energy surface (in kcal/mol) of the hydrogen cyanide C≡N π bond activation at the Pd=Sn bond of the stannylene complex $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ **1P**, together with the optimized structures (in Å and deg) at the B3LYP/BSI level. The imaginary frequencies (cm^{-1}) for the transition states **TS1CP** and **TS3CP** are shown.

Table 3. NBO Analysis of the Free Formaldehyde and Hydrogen Cyanide at the B3LYP/BSI Level

	C=O, C≡N		AO population			atomic charge	
	occup.	% C	C(pπ)	O, N(pπ)	O, N(pσ)	C	O, N
$H_2C{=}O$	σ: 2.00	35.6	0.709	1.284	1.591	0.221	−0.492
	π: 2.00	33.6					
HC≡N	σ: 2.00	41.8	0.917	1.077	1.527	0.075	−0.309
	π: 2.00	45.9					

$PH_2)Pd$ group around the Pd−Sn axis in **2CP** (5.1 kcal/mol), which is larger by 0.4 kcal/mol than that in **2BP** (Figure 4). However, the nucleophilicity of the Pd atom is similarly enhanced by the approach of the HCN molecule to the Sn atom. The population of the d_{xy} orbital and the negative charge of the Pd atom in **2CP** gradually increase, as the distance (d) between the Sn atom and the HCN molecule becomes smaller (Figure 6 D,F) and reaches 1.854 e and −0.136 e, respectively, at 2.511 Å (see Table 2). However, for the C≡N π bond activation, the C−N−Sn angle (θ) must become small enough to direct the C≡N π orbital toward the Pd and Sn atoms in the intermediate **2CP**, which reduces the electron donation from the coordinated HCN to the Sn. This is the essential reason the reaction proceeds by the homolytic mechanism as mentioned below. At θ = 120°,[16] the binding energy of HCN becomes 3.7 kcal/mol smaller and the distance (d) between the Sn and HCN is stretched to 2.858 Å (Figure 3C). Both the nucleophilicity of the Pd and the electrophilicity of the HCN carbon are not enhanced enough to heterolytically activate the π bond as shown by their atomic charges (see Table 2). Therefore, the activation proceeds homolytically with the support of the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis passing through the transition state **TS1CP**.

When the $(H_2PC_2H_4PH_2)Pd$ group rotates by 90° around the Pd−Sn axis in **2CP** with θ = 120°, the coordination of HCN by the electron donation from the C≡N π orbital to the Sn p orbital is strengthened to promote the activation as shown by the binding energy of 6.7 kcal/mol (Figure 3C), which is larger by 3.2 kcal/mol than that without the rotation of the $(H_2PC_2H_4PH_2)Pd$ group, because the electron back-donation from the Pd dπ orbital to the Sn pπ orbital is reduced as mentioned in sections 3.1 and 3.2. It was found that after the rotation of the $(H_2PC_2H_4PH_2)Pd$ group the HCN carbon approaches the Pd atom, decreasing both angles N−Sn−Pd and C−N−Sn, as presented in Figure 8.

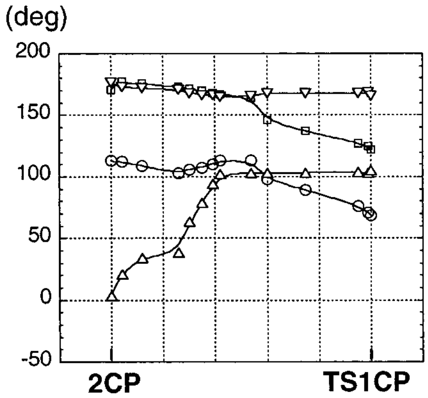

Figure 8. Changes in the geometric parameters during the C≡N π bond activation of hydrogen cyanide at the Pd=Sn bond of the $(H_2PC_2H_4PH_2)Pd{=}Sn$ complex. ○: ∠N−Sn−Pd; □: ∠C−N−Sn; ▽: ∠Sn−Pd-m^4; △: ∠N−Sn−Pd−P^1. m^4 is the midpoint between the P^1 and P^2 atoms (see Figure 3).

The subsequent electron back-donation to the C≡N π^* orbital occurs from the highly occupied Pd d_{xy} orbital (see Figure 6E). It should be noted here that the intermediate **4CP** was located at a local minimum, where the Pd−C distance of 2.157 Å is only 3% stretched compared with that in the product **3CP**, indicating that the formation of the Pd−C bond is already almost

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[16] This value comes from the C−N−Sn angle of the transition state **TS1CP**.

Table 4. NBO Analysis of the Stannylene Complexes $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ 1P and $(H_2NC_2H_4NH_2)Pd{=}SnH_2$ 1N, at the B3LYP/BSI Level

	Pd−Sn bond						AO population	
	distance (Å)	occup.	% Pd	% s	% p	% d	Pd(dπ)	Sn(pπ)
1P[a]	2.519	σ: 1.908	18.2	97.7	0.3	2.0	1.769	0.341
		π: 1.965	89.3	0.0	0.0	100.0		
1N	2.440	σ: 1.930	21.1	94.8	0.3	4.9	1.621	0.440
		π: 1.991	80.9	0.0	0.5	99.5		

[a] Reference 5.

completed at this moment. The product **3CP** is formed from **4CP** passing through the transition state **TS3CP** by further rotation of the $(H_2PC_2H_4PH_2)Pd$ group. The Sn−N bond formation is also completed in this step.

The potential energy surface of this stepwise activation of the $C{\equiv}N$ π bond by the homolytic mechanism is quite smooth, although the energy of 10.4 kcal/mol is required to pass the transition state **TS1CP**, as presented in Figure 7. Since the Pd−Sn distance is already stretched enough in the initial stage of the reaction by the coordination of hydrogen cyanide to the Sn, only a slight energy of 0.5 kcal/mol is required for the second rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis (**4CP** → **3CP**). The heterolytic pathway without the rotation of the $(H_2PC_2H_4PH_2)Pd$ group found for formaldehyde did not exist.

3.4. Effects of the Ligand. The electronic character of the P atom of the ligand, which coordinates to the Pd by the donation of its lone pair electron to the Pd dπ orbital, would affect the property of the Pd dπ orbital. On the basis of this assumption, we examined the reactivity of the $H_2NC_2H_4NH_2$ ligand for the selected nonpolar ethyne $C{\equiv}C$ and polar formaldehyde $C{=}O$ π bonds comparing with the $H_2PC_2H_4PH_2$ ligand. Since the electronegativity is larger for N (3.04) than for P (2.19)[15] and the bite angle is smaller by 11° for N than for P in the stannylene complex, the electron back-donation from the Pd dπ orbital to the Sn pπ orbital would be stronger for N than for P. The NBO analysis for both stannylene complexes $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ **1P** and $(H_2NC_2H_4NH_2)Pd{=}SnH_2$ **1N** gave results in accordance with our prediction as shown in Table 4. The π bonding of $Pd{=}Sn$ by electron back-donation from the Pd dπ orbital to the Sn pπ orbital is stronger for N than for P. The population of the Sn pπ orbital is larger by 0.099 e for N than for P, while that of the Pd dπ orbital is smaller by 0.148 e for N. The π bond is less polarized and the π electron is more largely localized on the Sn atom for N than for P. This electronic effect of the ligand was reflected in the potential energy surface of the reaction, as presented in Figure 1 for ethyne and Figure 2 for formaldehyde.

The ethyne- and formaldehyde-coordinated intermediates for the $H_2NC_2H_4NH_2$ ligand, **2AN** and **2BN**, are less stable in energy than the corresponding **2AP** and **2BP** for the $H_2PC_2H_4PH_2$ ligand, because the electron donation from the substrate to the Sn p orbital is weakened by the strong back-donation from the Pd dπ orbital, which is highly occupied due to the strong electron donative N atom, to the Sn p orbital, as shown by the distance between the substrate and the Sn atom, which is longer for **2AN** and **2BN** than for **2AP** and **2BP**, respectively. Therefore, the potential energy surfaces for the $H_2NC_2H_4NH_2$ ligand are shifted up compared with those for the $H_2PC_2H_4PH_2$ ligand, although the products **3AN** and **3BN** are lower in energy by about 11 kcal/mol than the corresponding products **3AP** and **3BP**, respectively.

In the case of ethyne, the ethyne-coordinated complex **2AN** is not on the potential energy surface of the activation reaction and is connected neither to the reactant **1N** nor to **TS1AN** (Figure 1). As shown by the dihedral angle C−Sn−Pd−m^1 of the transition state **TS1AN**, which is much smaller than 180°, just after the $(H_2PC_2H_4PH_2)Pd$ group starts to rotate around the Pd−Sn axis to break the strong electron back-donation from the Pd dπ to the Sn pπ, ethyne approaches the $Pd{=}Sn$ bond. In **TS1AN**, both Pd−C and Sn−C distances are much longer compared with those for **TS1AP**. Although we followed up the reaction coordinates, the $(H_2PC_2H_4PH_2)Pd$ group never completely rotated even after passing through the transition state **TS1AN** due to the strong interaction between the Pd dπ and Sn pπ orbitals. For formaldehyde, the intermediate **2BN** was located at the local minimum between the reactant **1N** and the transition state **TS2BN** for the heterolytic pathway. However, we did not find the homolytic pathway, which needs the rotation of the $(H_2PC_2H_4PH_2)Pd$ group to break the Pd(dπ)−Sn(pπ) interaction, for the strongly electron donative $H_2NC_2H_4NH_2$ ligand.

4. Concluding Remarks

The activation mechanism of the π bonds of nonpolar ethyne $C{\equiv}C$ and polar formaldehyde $C{=}O$ and hydrogen cyanide $C{\equiv}N$ at the $Pd{=}Sn$ bond of the model $(H_2PC_2H_4PH_2)Pd{=}SnH_2$ complex was theoretically examined using a density functional method (B3LYP). For the nonpolar ethyne $C{\equiv}C$ π bond, the reaction proceeds by the homolytic mechanism and is accompanied by the rotation of the $(H_2PC_2H_4PH_2)Pd$ group around the Pd−Sn axis. Without this rotation, the activation reaction never proceeds. The charge transfers, the electron donation from the ethyne π orbital to the Sn p orbital and the back-donation from the Pd dπ orbital to the ethyne π* orbital, successfully occur step by step to complete the π bond breaking during the reaction. Although the first charge transfer from the ethyne π orbital to the Sn p orbital is too weak to break the π bond without the rotation of the $(H_2PC_2H_4PH_2)Pd$ group, it is significantly enhanced by its rotation. On the other hand, for the strongly polarized formaldehyde $C{=}O$ π bond, the donation of the lone pair electron on the $C{=}O$ oxygen to the Sn p orbital is so strong that both the nucleophilicity of the Pd atom and the electrophilicity of the $C{=}O$ carbon are significantly enhanced through the Pd(dπ)−Sn(pπ) orbital. The $C{=}O$ π bond is also more largely polarized to accumulate the negative charge on the oxygen by this electron donation. Therefore, the $C{=}O$ π bond is broken by the heterolytic mechanism with the electrophilic attack of the $C{=}O$ carbon to the Pd atom. In this mechanism, the rotation of the $(H_2PC_2H_4PH_2)Pd$ group is not necessary, and if the electron donative phosphine rotates out of the Pd dπ plane, the nucleophilicity of the Pd dπ is reduced. However, when the $C{=}O$ π bond approaches the Sn atom in a η^2-fashion, the reaction proceeds by the homolytic mechanism supported by the rotation of the ($H_2PC_2H_4PH_2$)Pd group, which is similar to the case of ethyne, because the first electron donation from the C≡O π orbital to the Sn p orbital is weak without its rotation. In the case of hydrogen cyanide, only the homolytic pathway with the rotation of the ($H_2PC_2H_4PH_2$)Pd group exists, since the C≡N π bond has to approach the Sn atom in a η^2-fashion to break the π bond.

Thus, the first charge transfer from the substrate to the Sn p orbital plays a key role in determining the mechanism. In the homolytic mechanism, the preactivation by the electron donation from the π orbital to the Sn p orbital supported by the rotation of the ($H_2PC_2H_4PH_2$)Pd group is quite important, which is considered to be peculiar for the π bond activation since we did not find the same for the σ bond activation.[4,5] The potential energy surface of each activation reaction was quite smooth, with a small energy barrier, even in the homolytic mechanism due to the consecutive stepwise process. The activation activity was also affected by the effects of the ligand. Use of the more electron donative ligand, $H_2NC_2H_4NH_2$, which directly influences the Pd dπ orbital, reduced the activation activity.

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Supporting Information Available: Listings giving the optimized Cartesian coordinates of all equilibrium structures and transition states presented in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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