

Theoretical Study of the Olefin Insertion Reaction in the Heterobimetallic Pt(H)(PH₃)₂(SnCl₃)(C₂H₄) Compound

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Ab initio MO calculations at the MP4(SDQ)//MP2 level of theory were carried out to investigate the energies and reaction mechanism for the olefin insertion reaction (first step in the olefin hydroformylation catalytic cycle) using heterobimetallic *trans*-Pt(H)(PH₃)₂(SnCl₃) as the active catalytic species. The electronic effects of SnCl₃ on the trigonal-bipyramidal intermediates formed were analyzed through the charge decomposition analysis method. The results show that the major role of the SnCl₃ ligand is to stabilize the pentacoordinated intermediates as well as to weaken the Pt–H bond *trans* to it, favoring the insertion.

Introduction

Insertion reactions of organic molecules into platinum–hydrogen and platinum–alkyl bonds have been known for many years.¹ They are introduced as fundamental steps in the field of applied inorganic chemistry, for example, in the homogeneous hydrogenation of olefins and acetylene,^{2a} hydroformylation reactions,^{2b} and olefin isomerization.^{2c} These reactions are catalyzed by a wide range of transition-metal compounds, cobalt and rhodium being the only ones used in industrial processes.³ To obtain more selective catalysts, studies of new mono- and bimetallic complexes have been carried out. Of particular interest is the combination of platinum complexes with group 14 metal halides, forming a heterobimetallic catalytic system. Among these heterobimetallic catalysts, the ones formed by the combination of platinum complexes of the [PtCl₂(PR₃)₂] type and SnCl₂ have been shown to be highly active and selective in the hydroformylation of olefins.⁴ From an experimental point of view, these systems are suitable for mechanistic studies because the presence of Pt, Sn, P, C, and H atoms in the intermediates makes the NMR studies of these different nuclei possible, as well as the isolation of possible intermediates.⁵

Despite the attractive properties of this Pt–Sn catalytic system, several questions related to this system are not yet fully understood. For example, the fact that catalytic activity is observed only in the presence of

SnCl₂ suggests that SnCl₂ plays a fundamental role in the catalytic cycle. Indeed, as was pointed out by Scrivanti et al.,^{4a} SnCl₂ can act in several ways: (I) it may behave as a Lewis acid, (II) it may be the source of SnCl₃[−], which may act as a counterion, and (III) it may act as a ligand directly bound to platinum, which is of crucial importance in catalysis, favoring the insertion, carbonylation, and hydrogenolysis processes either by stabilizing the pentacoordinated intermediates and/or stabilizing the *trans* position.

Schwager and Knifton proposed a tentative catalytic cycle,⁶ by analogy with the cobalt- and rhodium-based catalysts, in which the following steps take place: (I) insertion of the olefin into the Pt–H bond, (II) carbonylation of the Pt–alkyl intermediate formed, and (III) hydrogenolysis of the resulting acyl intermediate, which leads to the aldehydes and regeneration of the initial Pt–H species.

We believe that theoretical calculations on the elementary steps of this catalytic system can provide the necessary insight to understand how this catalyst works and possibly how modifications can be planned in order to increase both the activity and selectivity. Extensive theoretical studies have been done in the field of theoretical catalysis and have been recently reviewed by Morokuma and co-workers.^{7,8} The first step to understand the way this Pt–Sn catalyst works was recently performed by our group.⁹ We investigated the formation of the cocatalyst *trans*-Pt(Cl)(PH₃)₂(SnCl₃) through the insertion reaction of SnCl₂ into the Pt–Cl bond (Scheme 1). In that work,⁹ it was pointed out that the insertion of SnCl₂ into the Pt–Cl bond proceeds through a three-center transition state and that this reaction is followed by rapid isomerization. The analysis of the nature of the bonds showed that the SnCl₃ ligand is a stronger *trans* director than is the PH₃ group

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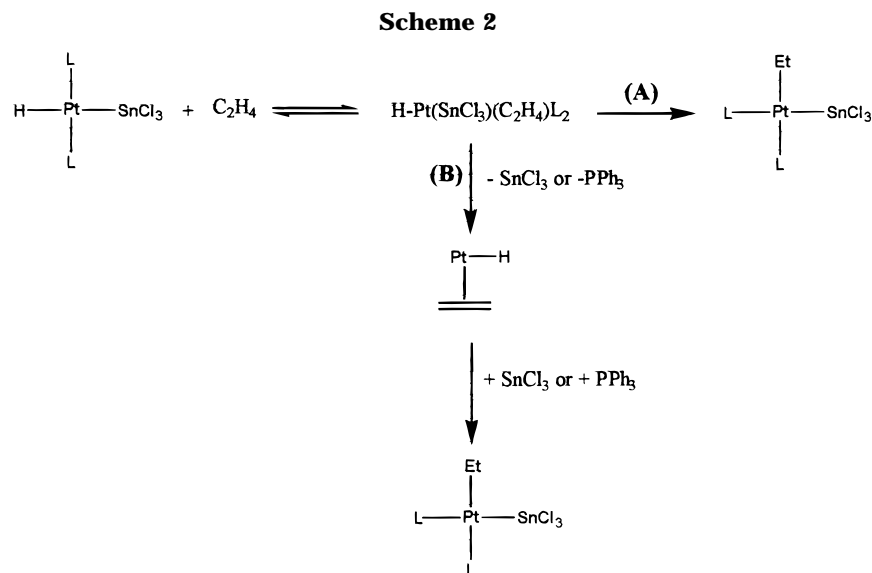
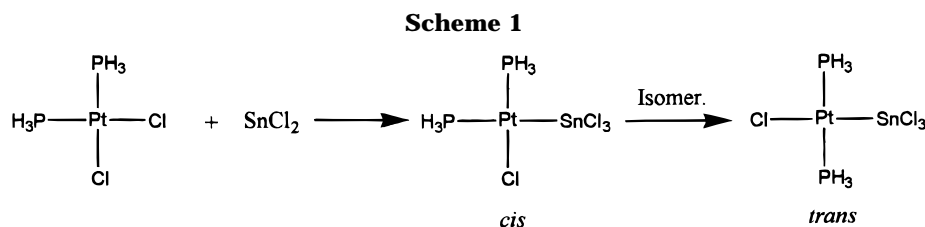
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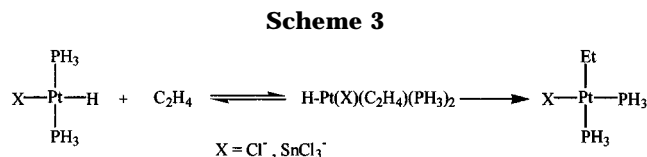
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and is capable of weakening the Pt–P bond trans to it by ca. 26 kcal/mol.

The aim of this work is to study the energetic and the reaction mechanism of the olefin insertion reaction (first step in the hydroformylation catalytic cycle) using a heterobimetallic Pt–Sn catalyst. This reaction may proceed through the two possible pathways^{4a} shown in Scheme 2.

In the course of the olefin insertion reaction, the formation of pentacoordinated species takes place, which is by itself a problem because the potential energy surface (PES) of five-coordinate molecules is very flat and rearrangements can take place very easily.¹⁰ In the present work, we will not discuss the mechanism for these intramolecular rearrangements and will focus only on the insertion reaction involving the most stable five-coordinate species present on the PES. For the interested reader, there are beautiful theoretical works dealing with the intramolecular rearrangements in five-coordinate compounds.^{11–13} There are some spectroscopic and kinetic evidences that ruled out pathway B.^{4a} Therefore, in this work we carried out *ab initio* molecular orbital calculations to investigate the energies and mechanism of the olefin insertion reaction shown in pathway A (see Scheme 2) using a model phosphine PH₃. To evaluate the energetic and electronic influence of the SnCl₃ ligand on the entire process, the calcula-



tions were performed using two distinct catalytic species, the first one without the SnCl₃ ligand and the other one with SnCl₃ (arising from the insertion reaction of SnCl₂ into the Pt–Cl bond), as exemplified in Scheme 3. Comparisons with other catalysts are made in order to assess the facility of the olefin insertion reaction promoted by the Pt–Sn catalyst compared to other well-known catalysts.

Calculations

Full symmetry unconstrained geometry optimizations were performed at the second-order Møller–Plesset perturbation (MP2) level of theory using the LANL2DZ effective core potential (ECP) and valence double- ζ basis set of Hay and Wadt¹⁴ for the Pt and Sn atoms. These include electrons in the 6s, 6p, and 5d orbitals for Pt and electrons in the 5s and 6p orbitals for Sn, which were described by the associated basis set of the form (3s3p3d)/[2s2p2d] and (3s3p)/[2s2p] for Pt and Sn, respectively. For the P, Cl, and C atoms, the split-valence basis set 6-31G(d),¹⁵ which includes a set of five d polarization functions, was used. For the hydrogen atoms, a smaller split-valence 3-21G¹⁵ basis set was used. The valence basis set for the tin atom was augmented with a set of five d polarization functions ($\alpha = 0.180$).¹⁶ All of the stationary points located on the potential energy surface were characterized as minima

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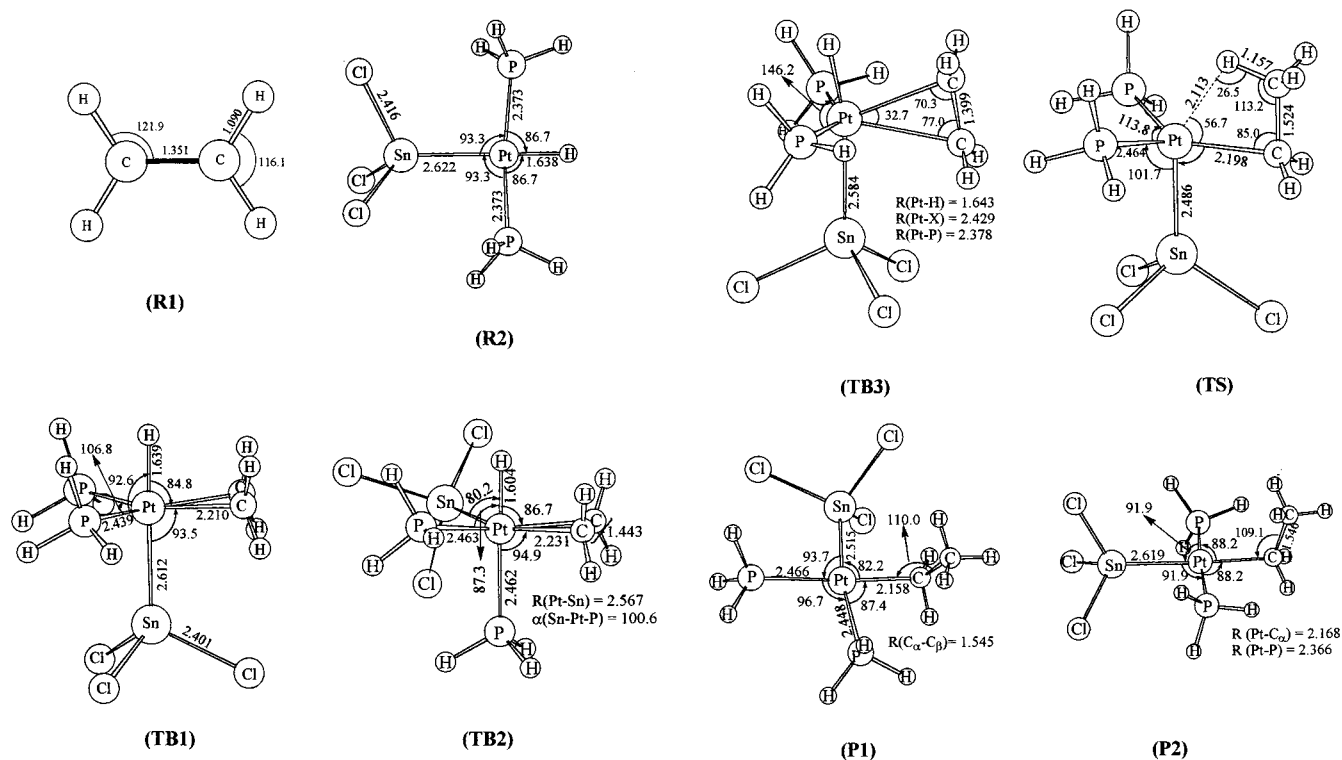


Figure 1. MP2-optimized structural parameters for the reactants (ethylene, **R1**, and *trans*-Pt(H)(PH₃)₂(SnCl₃), **R2**), pentacoordinated intermediates (**TB1**, **TB2**, and **TB3**), transition state (**TS**), and products (*cis*-Pt(PH₃)₂(SnCl₃)(ethylene), **P1**, and *trans*-Pt(PH₃)₂(SnCl₃)(ethylene), **P2**). Bond lengths are in angstroms and bond angles in degrees.

(no imaginary frequencies) or transition states (characterized by having one imaginary frequency) through harmonic frequency calculations. To obtain better energetic results, we carried out single-point calculations at the fourth-order Møller–Plesset perturbation level of theory (MP4) with single, double, and quadruple excitations MP4(SDQ) on the MP2-optimized geometries, MP4(SDQ)//MP2, using the same basis set. All calculations were performed using the GAUSSIAN94 package,¹⁷ as implemented on Silicon Graphics and Sun workstations in our laboratory.

Results and Discussion

Structural Results. The optimized structural parameters obtained for the reactants (ethylene, **R1**, and *trans*-Pt(H)(PH₃)₂(SnCl₃), **R2**), trigonal-bipyramidal intermediates (**TB1**, **TB2**, and **TB3**), transition state (**TS**), and products (*cis*-Pt(PH₃)₂(SnCl₃)(ethylene), **P1**, and *trans*-Pt(PH₃)₂(SnCl₃)(ethylene), **P2**) are shown in Figure 1. The optimized structural parameters for the same compounds with SnCl₃ replaced by Cl are shown in Figure 2. To make the structure comparisons clearer throughout the text, the symbols with primes will refer to the compounds shown in Scheme 3 with X = Cl⁻. As shown, the optimized angles of **R2**, **P1**, and **P2** around the platinum atom are a little distorted from the expected optimal value of 90° for a d⁸ square-planar compound. The calculated Pt–Sn bond distances of

2.486–2.622 Å are in good agreement with the experimental Pt–Sn values of 2.634 Å in *trans*-Pt(COPh)(SnCl₃)(PEt₃)₂,¹⁸ 2.601 Å in *trans*-Pt(H)(SnCl₃)(PPh₃)₂,¹⁹ and 2.600 Å in *trans*-Pt(H)(SnCl₃)(PCy₃)₂.²⁰ The calculated Pt–P bond distance of 2.373 Å in *trans*-Pt(H)(PH₃)₂(SnCl₃), **R2**, is longer than the experimental Pt–P distance of 2.300 Å in the parent *trans*-Pt(H)(PPh₃)₂(SnCl₃) compound.

It is well-known that the bond distance is a very sensitive parameter in describing the trans effect, i.e., the ability of a ligand to labilize the bond trans to it. If we compare the Pt–H bond length in the compounds in which there is an X ligand trans to the hydride, it can be seen from Figures 1 and 2 that in all cases where X = SnCl₃, the Pt–H bond length is greater than when X = Cl. This result corroborates with the well-known fact that SnCl₃⁻ is a stronger trans director ligand than is Cl⁻. In fact, when SnCl₃ in compounds **TB1** and **TB2** is replaced by Cl, there is no appreciable change in the Pt–H bond length in **TB1'** and **TB2'**. This implies that the Cl ligand will not contribute with any electronic effects to labilizing the Pt–H bond or even the Pt–ethylene interaction, since the Pt–ethylene distance does not change appreciably as well. The Pt–ethylene bond distance in the pentacoordinated intermediates Pt(PH₃)₂(C₂H₄)XH is, in all cases, greater when we have X = SnCl₃ instead of Cl⁻ (see Figures 1 and 2). As we shall see later, this fact is related with the facility of the olefin insertion reaction to occur, because a short

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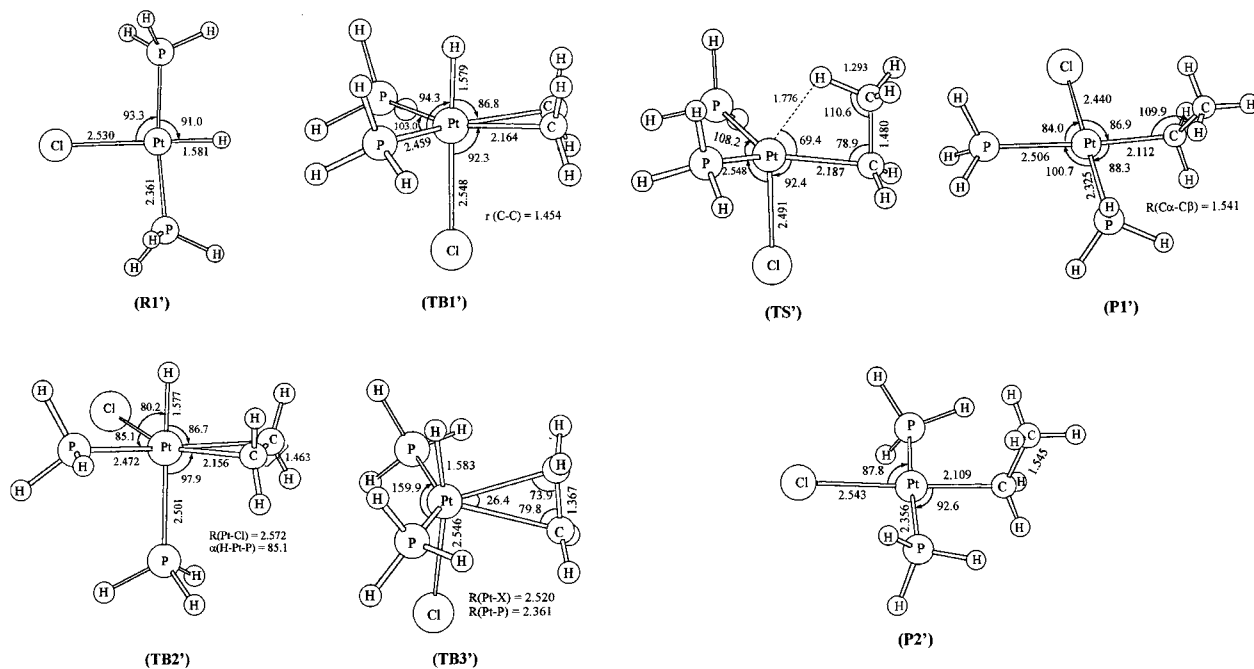


Figure 2. MP2-optimized structural parameters for the same species depicted in Figure 1 with SnCl_3 replaced by Cl.

bond distance means a strong bond energy and greater bond rotation energy, making the occurrence of such processes around the coordination sphere of the transition-metal center more difficult. The calculated geometrical parameters for the **TS** structure indicates that the formation of this structure occurs in a concerted way, where the Pt–H bond is breaking and the C–H bond is forming, leading to a four-center transition state. The C–C bond distance for the **TS** (1.524 Å) and **TS'** (1.480 Å) when compared with the C–C bond distance in free ethylene (1.351 Å) shows that the **TS** structure has C–C bond that is more like a single bond than that in the **TS'** structure. This is consistent with the fact that during the insertion reaction the olefin C–C bond gradually loses its sp^2 – sp^2 character.

Electronic Effects. If we take a closer look at the trigonal-bipyramidal intermediates **TB1** and **TB2** (see Figure 1), we can observe interesting points related to basic concepts of organometallic chemistry. For example, in **TB1**, in which the hydride ligand is trans to the SnCl_3 moiety, the Pt–H bond distance of 1.639 Å is greater than the Pt–H bond distance in **TB2** (1.604 Å), where the hydride is trans to a PH_3 ligand. This suggests that SnCl_3 has a stronger trans labilizing influence than the PH_3 ligand. This fact is very important because the strong trans influence of the SnCl_3 ligand makes the **TB1** compound more reactive to olefin insertion, since the Pt–H bond in this intermediate is weaker. Indeed, as shown in Figure 1, the insertion reaction occurs in the compound where the SnCl_3 ligand is trans to the hydride (see **TS** in Figure 1). Another interesting fact when we compare **TB1** and **TB2** is that the Pt–ethylene distance of 2.210 Å in **TB1**, in which SnCl_3 is in the axial position, is smaller than the Pt–ethylene distance of 2.231 Å in **TB2**, in which SnCl_3 is in the equatorial position. This suggests that there must be some electronic factor of the SnCl_3 group influencing the Pt–ethylene interaction. The question becomes apparent: how can we explain these facts based on the molecular wave function of the complex?

Table 1. Energy Decomposition Analysis of the Five-Coordinate **TB1'**, **TB1**, and **TB2** Compounds Using the MP2 Wave Function^a

	TB1'	TB1	TB2
donation (d)	0.180 e	0.179 e	0.226 e
back-donation (b)	0.259	0.244 e	0.242 e
repulsive polarization (r)	–0.483	–0.434 e	–0.390 e
residual term (Δ)	–0.032	–0.047 e	–0.035 e
interaction energy (kcal/mol)	39.2	38.8	32.3

^a CDA was performed assuming the ethylene as the donor fragment and the $\text{Pt}(\text{H})(\text{PH}_3)_2(\text{SnCl}_3)$ as the acceptor fragment.

That is, how can we extract this chemical information from the complex MP2 wave function of these species? To do so, we analyzed the MP2 wave function of **TB1**, **TB1'**, and **TB2** through the charge decomposition analysis (CDA) method of Frenking and co-workers.²¹ The CDA method consists of using linear combination of fragment orbitals (LCFO) of properly chosen fragments A and B for the interpretation of the interactions in a molecule AB. The interaction is divided into three main contributions: (a) the mixing between the occupied orbitals of A and empty orbitals of B, which indicates the magnitude of electron donation from A to B ($A \rightarrow B$), (b) the mixing between the occupied orbitals of B with the empty orbitals of A, which gives the extent of back-donation, i.e., the electron donation from B to A ($A \leftarrow B$), and (c) the mixing between the occupied orbitals of A and the occupied orbitals of B, which indicates the extent of charge polarization in the region of bonding. This method has been shown to be very useful to explain the nature of the metal–ligand interaction.²² The results of the CDA calculations are shown in Table 1. Analysis of Table 1 shows that in **TB2**, in which SnCl_3 is in an equatorial position, the charge donation term [$\text{C}_2\text{H}_4 \rightarrow \text{Pt}(\text{H})(\text{PH}_3)_2(\text{SnCl}_3)$] is greater

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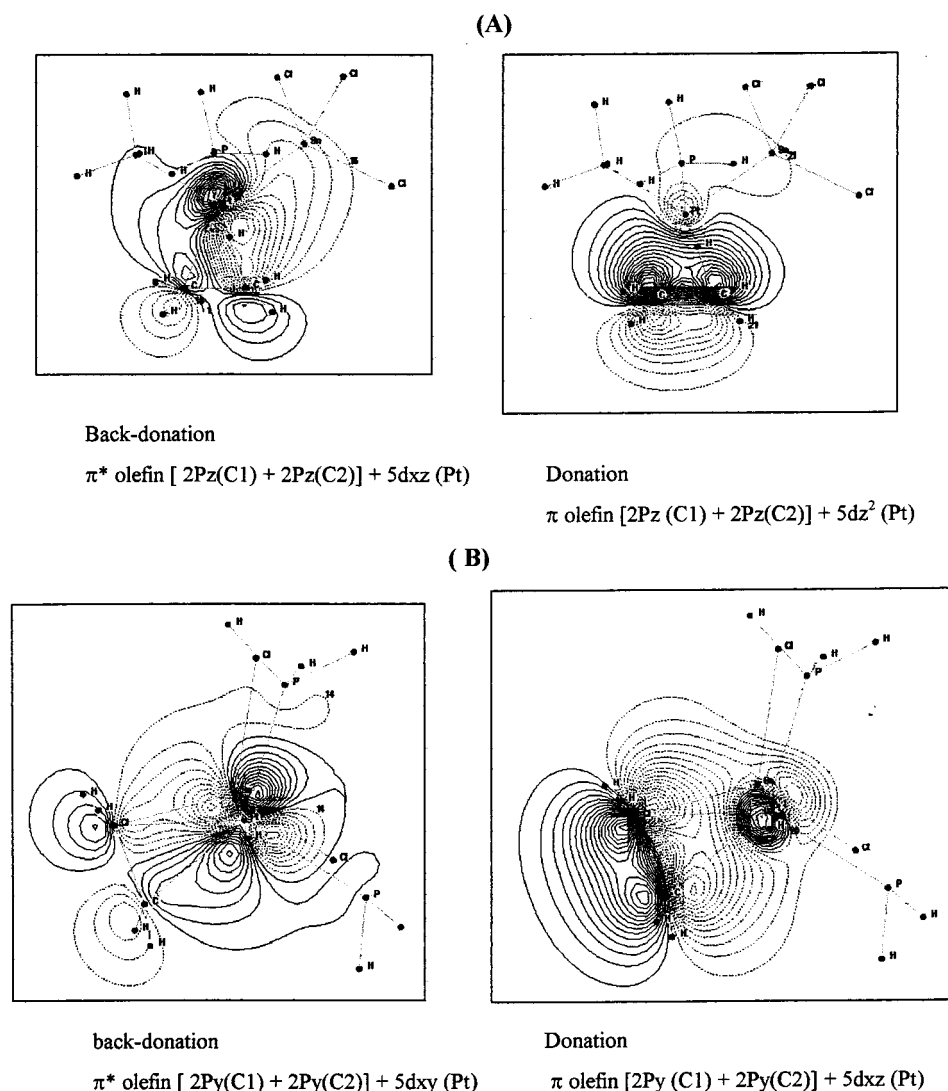


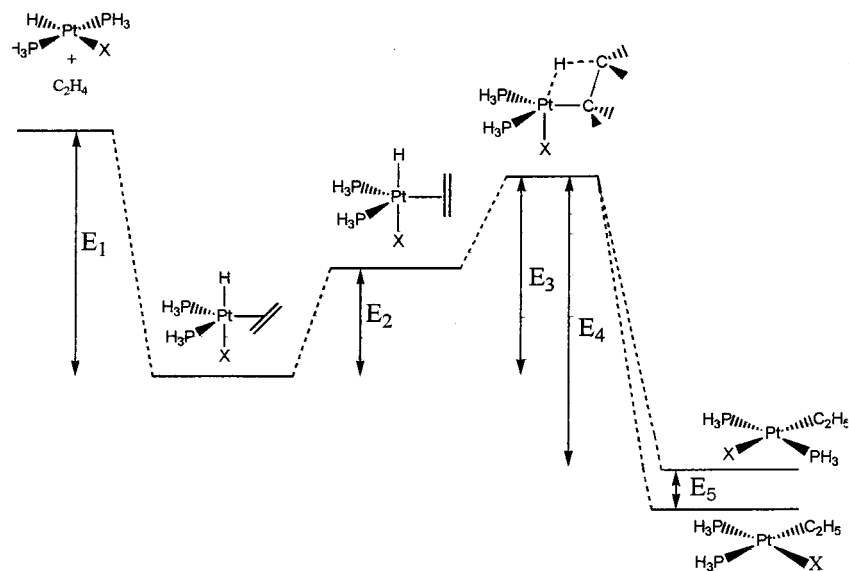
Figure 3. Contour plot for the orbitals involved in back-donation [(SnCl₃)(PH₃)₂(H)Pt → C₂H₄] and donation [C₂H₄ → Pt(H)(PH₃)₂(SnCl₃)] interactions for the pentacoordinated intermediates **TB2** (A) and **TB1** (B).

than in **TB1**, in which SnCl₃ is in an axial position. The charge back-donation term [(SnCl₃)(PH₃)₂(H)Pt → C₂H₄] has almost the same value in both compounds. This means that in **TB2** the SnCl₃ ligand is somehow drawing back electron density from the Pt atom, and so the olefin will donate more charge to the Pt(H)(PH₃)₂(SnCl₃) fragment. We can suggest from these CDA results that SnCl₃ in an equatorial position will interact more effectively with the Pt fragment. Indeed, if we compare the Pt–Sn bond distances in **TB1** and **TB2** (see Figure 1), we can see that the Pt–Sn bond distance of 2.567 Å in **TB2** is smaller than in **TB1** (2.612 Å), in which SnCl₃ is in an axial position and trans to the hydride ligand. In **TB1'**, in which SnCl₃ is replaced by Cl in an axial position, the extent of charge donation [C₂H₄ → Pt(H)(PH₃)₂Cl] is the same as in **TB1** but the charge back-donation term [Pt(H)(PH₃)₂Cl → C₂H₄] is greater than in **TB1**. This can be explained by the fact that the Cl ligand is not drawing back electron density from the Pt atom, thus, there will be more electron density (compared with **TB1**) available to be donated to the olefin. The CDA results in Table 1 also show that SnCl₃ trans to hydride stabilizes the Pt–C₂H₄ interaction more strongly, as given by the interaction energy

term shown in Table 1. The residual term (describing the mixing of the unoccupied orbitals on the fragments) is as expected for a true donor–acceptor complex.^{22c} The orbitals involved in the donation and back-donation interactions are depicted in Figure 3.

Energetic Effects. Despite the fact that two distinct isomers are formed when we add C₂H₄ to the catalytic Pt(H)(PH₃)₂X species (**TB1** and **TB2** in Figure 1 and **TB1'** and **TB2'** in Figure 2), several attempts to obtain the insertion reaction in the compounds with PH₃ trans to hydride were unsuccessful. Thus, we believe that the reactive species is **TB1** for X = SnCl₃ and **TB1'** for X = Cl. Therefore, the energetic influence of the SnCl₃ ligand will be discussed considering only the pentacoordinated species where X is trans to the hydride ligand, that is, **TB1** and **TB1'**.

The energy diagram for the insertion reaction is shown in Figure 4, and the total energy of the reactants, intermediates, transition state, and products are given in Table 2. In the energy diagram shown in Figure 4, the energy differences are given in relation to the reactants (C₂H₄ and *trans*-Pt(H)(PH₃)₂X). As shown, the energy for the olefin coordination, generating the **TB1**

 ΔE MP4(SDQ)

Process	kcal/mol		Description
	X = Cl	X = SnCl ₃	
E1	-8.4 (-14.8)	-12.6(-20.1)	Stabilization energy for TB1
E2	19.0 (20.3)	9.0 (10.9)	Energy barrier for the olefin Internal rotation
E3	33.9 (35.3)	11.8 (13.9)	total Energy barrier for the insertion reaction
E4	41.1 (39.0)	23.0 (21.4)	β -hydrogen elimination barrier from P2
E5	-4.4 (-4.5)	-2.3 (-2.4)	ΔE for the isomerization cis \rightarrow trans (P1 \rightarrow P2)

Figure 4. Energy diagram (in units of kcal/mol) for the olefin insertion reaction. The energy differences are given in relation to the reactants (ethylene, **R1**, and *trans*-Pt(H)(PH₃)₂(X), **R2**). The values in parentheses are the MP2 energy differences.

Table 2. Total Energy for the Reactants, Intermediates, Transition State, and Products^a

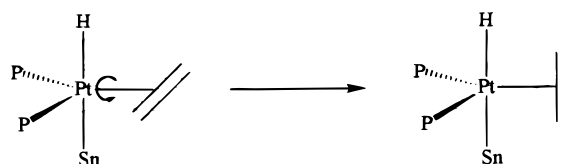
	energy (hartrees)		
	HF	MP2	MP4(SDQ)
reactants (R1 + R2)	-2263.4984 (-1341.1549)	-2264.1562 (-1341.6541)	-2264.2436 (-1341.7264)
TB1	-2263.4757 (-1341.1300)	-2264.1826 (-1341.6777)	-2264.2636 (-1341.7398)
TB2	-2263.4713 (-1341.1178)	-2264.1908 (-1341.6671)	-2264.2664 (-1341.7387)
TB3	-2263.4689 (-1341.1397)	-2264.1710 (-1341.6454)	-2264.2494 (-1341.7096)
TS	-2263.4633 (-1341.0818)	-2264.1661 (-1341.6214)	-2264.2448 (-1341.6858)
P1	-2263.5218 (-1341.1645)	-2264.2002 (-1341.6835)	-2264.2814 (-1341.7513)
P2	-2263.5206 (-1341.1777)	-2264.1964 (-1341.6907)	-2264.2778 (-1341.7583)

^a Values in parentheses are for the Pt–Cl compounds depicted in Figure 2.

trigonal-bipyramidal intermediate, is -12.6 kcal/mol, that is, the Pt–Sn catalyst stabilizes the pentacoordinated intermediates by ca. 13 kcal/mol. The olefin coordination energy in **TB1'** is ca. 8 kcal/mol. Therefore, it can be concluded that when there is a Pt–Sn bond, the increase in the stability for the olefin coordination is ca. 5 kcal/mol lower than that when the Pt–Cl bond is present. This stabilization energy makes the low-

temperature isolation of these intermediates possible for experimental studies.

For the insertion reaction to take place in the most reactive intermediates **TB1** and **TB1'**, the olefin must rotate 90° from the equatorial plane, generating the minimum energy structures **TB3** and **TB3'**, respectively, assuming a parallel orientation in relation to the Pt–H bond, as exemplified below.



As shown in Figure 4, the energy involved in this process is 9.0 kcal/mol for the pentacoordinate species having the Pt–Sn bond (**TB1**) and 19.0 kcal/mol for the Pt–Cl species (**TB1'**). The only structural difference between these two parent compounds is that a Cl ligand in Pt(H)(Cl)(PH₃)₂(C₂H₄) was replaced by a SnCl₃ in **TB1** through the insertion of SnCl₂ into the Pt–Cl bond.⁹ Therefore, on the basis of the facts described here, we conclude that the presence of SnCl₃ favors the olefin internal rotation by 10 kcal/mol, which is a crucial step for the olefin insertion reaction. Table 3 shows the comparison of our results for the olefin internal rotation

Table 3. Comparison of the Energy Barrier for the Olefin Internal Rotation Process

compound	energy (kcal/mol)
Pt(H)(Cl)(PH ₃) ₂ (C ₂ H ₄) ^a	32.3
Pt(H)(Cl)(PH ₃) ₂ (C ₂ H ₄) ^d	19.0
Rh(H)(C ₂ H ₄)(CO) ₂ (PH ₃) ^b	20.2
[Os(CO)(NO)(C ₂ H ₄)(PPh ₃) ₂] ⁺ ^c	9.5
Pt(H)(SnCl ₃)(PH ₃) ₂ (C ₂ H ₄) ^d	9.0

^a Reference 23. ^b Reference 11. ^c Reference 24. ^d Present work.

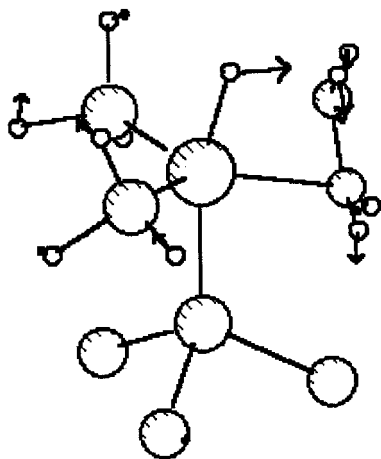


Figure 5. Normal mode exhibiting one negative eigenvalue of the Hessian matrix. The figure shows the hydride migration from the Pt atom to the ethylene.

process with other results for osmium-, rhodium-, and platinum-based catalysts. Once the olefin is parallel to the Pt–H bond, it is then able to insert into the Pt–H bond. The insertion reaction of ethylene into the Pt–H bond proceeds through the formation of a four-center transition state **TS** having an imaginary frequency of 145i cm⁻¹ and **TS'** with a negative frequency of 129i cm⁻¹ (see Figure 1), in which the migration of the hydride ligand from the metal to ethylene occurs (see Figure 5).

Thorn and Hoffmann²³ have carried out extended Hückel calculations on olefin insertion in the parent five-coordinate Pt compound Pt(H)(Cl)(PH₃)₂(C₂H₄). They found no easy insertion pathway; that is, the ethylene insertion reaction is a high-energy process. Our MP4-(SDQ) results agree with this argument, since we found the total energy barrier for the insertion reaction to be 33.9 kcal/mol using Pt(H)(Cl)(PH₃)₂(C₂H₄), **TB1'** compound. However, as shown in Figure 3, the results show that the presence of a Pt–Sn bond makes the process easier with a total insertion barrier of 11.8 kcal/mol, that is, 22 kcal/mol lower than when we have the Pt–Cl bond.

The direct product from the insertion reaction is **P1** for the Pt–Sn compound and **P1'** for the Pt–Cl compound. However, these compounds can isomerize, producing the more stable products **P2** and **P2'**, respectively, in which the phosphines are in a trans position. The energy differences between these products are given in Figure 4. An inspection of Figure 4 also shows that the activation energy for the opposite process, that is,

β -hydrogen elimination (which dissociates the product into the Pt(H)(C₂H₄) compound), from the direct products **P1** and **P1'** is 23.0 and 41.1 kcal/mol, respectively. If we divide these values by the energy required for the olefin insertion reaction (11.8 for **TB1** and 33.9 for **TB1'**), we have a β -elimination/insertion ratio of 2.0 and 1.2 for the Pt–Sn and Pt–Cl compounds, respectively. This means that the energy required for β -hydrogen elimination is 2 times greater than the energy barrier necessary for the olefin insertion reaction. The fact that this catalyst stabilizes the metal–alkyl product formed is another interesting property of this Pt–Sn catalyst.

Conclusion

In this work, we evaluated the energies and reaction mechanism for the olefin insertion reaction into the Pt–H bond (first step of the olefin hydroformylation catalytic cycle) using a heterobimetallic catalyst, *trans*-Pt(H)(PH₃)₂(SnCl₃), at the MP4(SDQ)/MP2 level of theory. All stationary points located on the potential energy surface were fully optimized. The transition-state structure obtained indicates that the reaction proceeds through a four-center transition state with the migration of the hydride ligand to ethylene. The occurrence of the Pt–Sn bond stabilizes the pentacoordinated intermediates formed by ca. 13.0 kcal/mol. The main effect of the SnCl₃ ligand is to stabilize the trigonal-bipyramidal intermediates as well as to labilize the Pt–H bond trans to it, favoring the olefin coordination and insertion reaction. The electronic effects of SnCl₃ on the pentacoordinated intermediates were assessed through the charge decomposition analysis (CDA). This procedure shows that SnCl₃ in the axial position and trans to the hydride ligand favors the Pt–ethylene interaction by 38.8 kcal/mol. The SnCl₃ ligand in the equatorial position is more effective in drawing back electron density from the Pt atom. The olefin internal rotation proceeds with a small barrier of 9.0 kcal/mol, with the total energy required for the insertion reaction being only 11.8 kcal/mol. Our results showed that the energy barrier for the opposite process (β -hydrogen elimination) is 2 times greater than the energy barrier for the olefin insertion reaction.

Of course, there is still much work to be carried out with this heterobimetallic catalyst, for example, analysis of the electronic effects due to ligand substitution, solvent effects, evaluation of selectivity, etc. Studies on the other steps of the catalytic cycle will continue in our laboratory and will be available in future publications.

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