Semi-empirical SCF-MO Studies of Platinum Hydrides and the Insertion Reaction of Ethylene into the Pt(II)-H Bond

Shigeyoshi SAKAKI, Hiroshi KATO,* Hiroyoshi KANAI, and Kimio TARAMA
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606
**Department of General Education, Nagoya University, Chikusa-ku, Nagoya 464*

(Received August 19, 1974)

Semi-empirical SCF–MO calculations were carried out on *trans*-$PtHX(PH_3)_2$ (X=halogen and CN^-). The absolute value of E_{pt-H} decreases in the following order: F>Cl>Br>I>CN; this agrees with the order of the bond strength of the Pt–H bond. The electron density on the H ligand is remarkably large in all the complexes (*ca.* 1.25 e) and decreases in this order: F>Cl>Br>I>CN. An insertion reaction of ethylene into the Pt–H bond was investigated by the use of the MO method. The intermediate five-coordinate π-olefinic hydride complex has a trigonal bipyramid structure in which Cl and H ligands are positioned *trans* to each other. Three reaction paths of the insertion were investigated, and the following reaction path seems the best: The H ligand starts first to approach ethylene and then the Cl ligand starts to move to the *trans*-position of the H ligand. The reactivities of *trans*-$PtHX(PH_3)_2$ increase in this order: F<Cl<Br<I<CN. MO calculations also reveal that the catalytic ability of *trans*-$PtHX(PH_3)_2$ increases as follows in the hydrogen-deuterium exchange reaction of ethylene: F<Cl<Br<I.

The role of transition metal complexes in homogeneous catalytic reactions is currently a topic of great interest in the fields of both the pure and applied chemistry. In these catalytic reactions, isomerization and hydrogenation of olefins and acetylenes have been particularly studied, as has been reviewed recently.[1,2] It has been accepted in many catalytic isomerizations and hydrogenations that the formation of the metal-hydride (M–H) bond and its reaction with unsaturated compounds are key steps in the overall reaction.[2,3] Many transition metal hydrides have been found and several insertion reactions of olefins into M–H bonds have been reported.[4]

Stable hydride complexes of platinum(II), *trans*-$PtHX(PH_3)_2$ (X=halogen *etc.*), were prepared by Chatt and Shaw.[5] Structural studies have been carried out on *trans*-$PtHX(PEt_3)_2$ (X=Cl and Br),[6,7] and spectroscopic studies such as NMR and IR have been reported.[5,8–11] However, little theoretical study has been done, even though it is necessary in order to investigate the bonding character of the Pt(II)–H bond.

It is wellknown that ethylene reacts with *trans*-$PtHCl(PEt_3)_2$ under vigorous conditions (95°C/80 atm) to give an ethylplatinum(II) complex:[5,12]

$$trans\text{-}PtHCl(PEt_3)_2 + C_2H_4 \rightleftarrows trans\text{-}Pt(C_2H_5)Cl(PEt_3)_2 \qquad (1)$$

Several investigations have been carried out on the insertion reaction of ethylene in order to elucidate the reaction mechanism.[12–17] The suggestion has been accepted that both forward and reverse reactions proceed *via* five-coordinate π-olefinic hydride complexes.[12–13,17]

In this work, we have carried out semi-empirical SCF–MO calculations of hydride complexes of platinum(II) in order to investigate their electronic structures. Studies have also been done of the ethylene insertion reaction into the Pt(II)–H bond. We will discuss the electronic structure of the intermediate five-coordinate π-olefinic hydride complex, $PtHCl(PH_3)_2(C_2H_4)$. The ligand effects and the role of the Pt(II) ion in the ethylene insertion reaction will also be discussed. We have tried to anticipate the ligand effect on the catalytic abilities of *trans*-$PtHX(P_3R)_2$ in the hydrogen-deuterium (H–D) exchange reaction of ethylene.

MO Calculations and Geometries of Complexes

MO Calculations. The MO calculations were performed by the use of the CNDO-type MO method. This method gave reasonable results on tetrachloroplatinate, Zeise's salt, the Pt(0)-ethylene complex, the Pt(0)-acetylene complex, *etc.*[18] The approximations used in this MO method have been reported in detail elsewhere.[18] Here, let us describe important features. (1) The Fock-matrix elements are obtained by the CNDO-type approximations.[19] (2) The resonance integrals are evaluated by the Wolfsberg-Helmholz approximation,[20] where the parameter "K" is taken as 0.90 for AO pairs including a d-orbital and as 0.80 for AO pairs including only s- and p-orbitals.[18] (3) The one-center Coulomb repulsion integrals of the Pt atom are estimated by multiplying a correction factor by nonempirical values calculated by means of single Slater-type orbitals. (4) The two-center Coulomb repulsion integrals are evaluated by the use of a modified Ohno's approximation[18] for AO pairs including only one outer 6s- or 6p-orbital of the Pt atom and by the use of Ohno's original approximation[21] for the other AO pairs.

The quantity of E_{AB}[22,23] is used as the bond index in this work; it is defined as the energy contribution of the AB bond to the total energy. Under the approximations used here, E_{AB} is written as follows;[19]

$$E_{AB} = E_{AB}^{(1)} + E_{AB}^{(2)} + E_{AB}^{(3)} \qquad (2)$$

$$E_{AB}^{(1)} = 2.0\sum_{r}^{A}\sum_{t}^{B}P_{rt}H_{rt} \qquad (3)$$

$$E_{AB}^{(2)} = -0.5\sum_{r}^{A}\sum_{t}^{B}P_{rt}^{2}\gamma_{rt} \qquad (4)$$

$$E_{AB}^{(3)} = \sum_{r}^{A}\sum_{t}^{B}(P_{rr}-N_{r})(P_{tt}-N_{t})\gamma_{rt} \qquad (5)$$

where $E_{AB}^{(1)} + E_{AB}^{(2)}$ and $E_{AB}^{(3)}$ represent approximately a covalent bonding interaction and an electrostatic one respectively. The negative value of E_{AB} indicates the bonding interaction. The larger the absolute value of E_{AB}, the greater the interaction between A and B atoms becomes.

Geometries of Complexes. trans-*PtHX(PR$_3$)$_2$*: The bond lengths of the Pt–Cl and Pt–Br were taken from X-ray studies,[6,7] while those of the other Pt–X bonds were estimated from the covalent bond radii of X's. The bond lengths of the Pt–P and Pt–H bonds were fixed as 2.268 and 1.62 Å respectively for all the complexes. While the ∠PPtCl and ∠PPtBr angles were slightly larger than 90° as a result of the steric effects of Cl and Br ligands,[6,7] ∠PPtX was assumed to be 90° in all the complexes, for the value of this angle had not been known in the other complexes. The PR$_3$ group (R=phenyl or alkyl group) was replaced by the PH$_3$ group for the sake of simplicity; its structure was assumed to be the same as that of the uncomplexed one.[24] In spite of these simplifications, MO calculations on these models gave reasonable and sufficient results to enable us to discuss the ligand effect of X, as will be described in the following section.

trans-*PtX(C$_2$H$_5$)(PH$_3$)$_2$*: Since no X-ray study had been carried out on this complex, the bond lengths of the Pt–C and Pt–Cl bonds were taken from the structure of $[Pt(CH_3)_3Cl]_4$,[24] and the Pt–P bond length was fixed in all the complexes. The bond lengths of the other Pt–X bonds were estimated in the same way as those in *trans*-PtHX(PH$_3$)$_2$. The Pt–P bond length and the structure of the PH$_3$ group were assumed to be the same as the corresponding ones in *trans*-PtHX(PH$_3$)$_2$. In these complexes, the structure of the ethyl group was taken from Ref. 24, while only the β-hydrogen atom of the ethyl group was brought slightly close to the Pt atom (β-H–Pt=2.22 Å [25] and β-H–C=1.09 Å) when the abstraction of the β-hydrogen atom was investigated.

Five-coordinate π-Olefinic Hydride Complexes and an Insertion Reaction of Ethylene into the Pt(II)–H Bond. Two types of five-coordinate intermediate complexes were investigated in the insertion reaction of ethylene into the Pt(II)–H bond; they are shown in Fig. 1. In both structures, the structure of the ethylene part was assumed to be the same as the uncomplexed one. The coordination bond of ethylene was also assumed to intercept the double bond of ethylene perpendicularly at its center, and the coordination bond distance was fixed as 2.0 Å by reference to that of Zeise's salt.[26] The A structure can be expected from the substitution reaction of *trans*-Pt(NO$_3$)H(PEt$_3$)$_2$ with ethylene which was reported by Deening *et al.*[15] The B structure has been proposed by Uguagliati *et al.*;[14] also, a similar intermediate complex has been isolated by Clark *et al.* in the insertion reaction of tetracyanoethylene with *trans*-Pt(CH$_3$)(CN)(PEt$_3$)$_2$.[16]

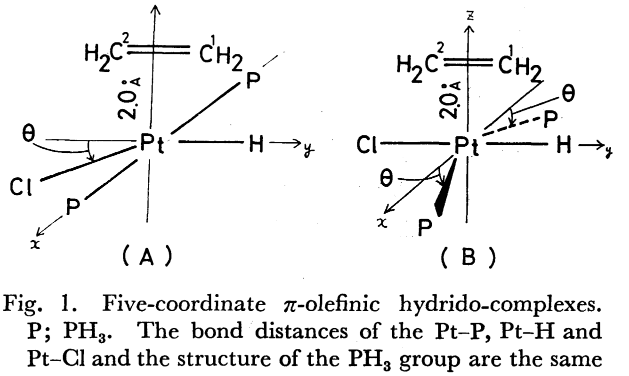


Fig. 1. Five-coordinate π-olefinic hydrido-complexes. P; PH$_3$. The bond distances of the Pt–P, Pt–H and Pt–Cl and the structure of the PH$_3$ group are the same as those in the *trans*-PtHCl(PH$_3$)$_2$.

Since the B structure was more stable than that of A, as will be described below, the insertion reaction was considered to proceed from the B structure (θ=45°); the three reaction paths shown in Fig. 2 were investigated. In the C reaction path, ethylene approaches the hydride ligand parallel with the Pt–H bond. Also, in the D reaction path, ethylene approaches the hydride ligand. In this attack, the δ angle between the coordination bond of ethylene and the z-axis increases, the other part does not vary. In the E reaction path, the hydride ligand attacks ethylene, where the δ angle between the Pt–H bond and the y-axis increases, while the other part does not vary. The states in which hydrogen atoms were displaced out of the original ethylene plane opposite to the Pt atom (10°) were investigated in two reaction paths, D and E; only the C(1)H$_2$ group was bending in the IV state, and both C(2)H$_2$ and C(2)H$_2$ groups were bending in the V state.

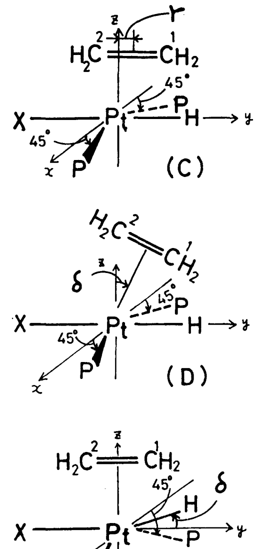


Fig. 2. Insertion reaction paths of ethylene into the Pt(II)–H bond.
P; PH$_3$. In the reaction paths C and D, the PtHCl(PH$_3$)$_2$ is the same as the state V of the five-coordinate intermediate B (Fig. 1). In the reaction path E, the H ligand transfers to ethylene and the other part is the same as the state V of the intermediate B.

Results and Discussion

Electronic Structures of trans-*PtHX(PH$_3$)$_2$.* The results are given in Table 1. The electron density on the Pt atom increases with the decrease in the elec-

Table 1. Electronic structures of *trans*-$PtHX(PH_3)_2$

	Electron density				E_{Pt-H} (eV)	$E^{(1)+(2)}_{Pt-H}$ (eV)	$E^{(3)}_{Pt-H}$ (eV)	ν_{Pt-H}[a] (cm^{-1})
	Pt	H	X	P				
F	9.710	1.289	7.658	5.217	−13.882	−12.783	−1.099	—
Cl	9.846	1.255	7.583	5.222	−13.627	−12.877	−0.750	2183
Br	9.863	1.246	7.584	5.223	−13.585	−12.890	−0.695	2178
I	9.900	1.245	7.541	5.221	−13.480	−12.850	−0.630	2156
CN	9.904	1.242	9.552[b]	5.231	−13.446	−12.833	−0.613	2041

a) Ref. 9. b) The electron density on the CN group.

tronegativity of the X ligand; *i.e.*, F<Cl<Br<I<CN. The H ligand has a remarkably large negative charge, suggesting its hydride character. The electron density on the H ligand decreases with an increase in the electron density on the Pt atom and with a decrease in the electron density on the halogen. This result seems to be similar to the alternative inductive effect;

$$\overset{\delta-}{X}\text{——}\overset{\delta+}{Pt}\text{——}\overset{\delta-}{H}$$

Scheme I.

However, this result cannot be explained by hyperconjugation, since the Pt–H bond is not contributed to by hyperconjugation. Because the energy levels of the Pt's valence orbitals decrease as the X ligand goes from F^- to CN^-,[27] the electron transfer increases in this order; F<Cl<Br<I<CN, and the electron density on the H ligand decreases in this order; F>Cl>Br>I>CN.

The absolute value of E_{Pt-H} decreases in this order; F>Cl>Br>I>CN, suggesting that the strength of the Pt–H bond also decreases in this order. From the frequencies of the stretching vibration, ν_{Pt-H}, it is expected that the strength of the Pt–H bond decreases in this order; Cl>Br>I>CN,[9,11] since ν_{Pt-H} gives a measure of the strength of the Pt–H bond. Thus, our finding on the strength of the Pt–H bond agrees qualitatively with the experimental findings. The value of E_{Pt-H} is mainly contributed to by the $E_{Pt-H}{}^{(1)}$ and $E_{Pt-H}{}^{(2)}$, as is shown in Table 1; this suggests the covalent bonding character of the Pt–H bond.

Five-coordinate π-Olefinic Hydride Complexes. The various conformations of the A and B structures (see Fig. 1) were investigated, as is shown in Fig. 3 and Table 2. The increase in θ does not bring about the stabilization of the A structure, but that of the B structure, which is the most stable at $\theta=45°$. In the B structure, the steric repulsion between PH_3 and ethylene decreases greatly. However, it does not change in the A structure, while the streic repulsion between Cl and ethylene decreases. Therefore, the B structure is more favorable than the A structure for the intermediate five-coordinate complex. We will hereafter consider the insertion reaction of ethylene into the Pt(II)–H bond in the B structure.

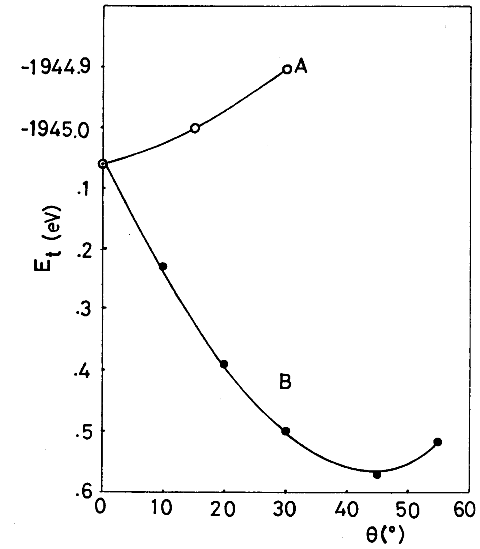


Fig. 3. Total energies of five-coordinate π-olefinic hydrido-complexes, $PtHCl(PH_3)_2(C_2H_4)$.
○: The structure A. ●: The structure B (see Fig. 1.)

An increase in θ brings about an increase in the bonding interaction between the Pt atom and ethylene in both structures, A and B; the absolute value of $E_{Pt-C(1)}+E_{Pt-C(2)}$ also increases with an increase in θ, as is shown in Table 2. In the A structure ($\theta\neq0$), the $5d_{z^2}$ and $5d_{yz}$ orbitals of the Pt atom are bonding

Table 2. Electronic structures of five-coordinate π-olefinic hydrido-complexes

	(a) Structure A			(b) Structure B[d]				
State	I	II	III	II	III	IV	V	VI
θ	0°	15°	30°	10°	20°	30°	45°	55°
$E_{Pt-C(1)}+E_{Pt-C(2)}$	−11.26	−11.46	−11.76	−11.77	−12.35	−12.89	−13.40	−13.72
E_{C-H}[a]	−0.27	−0.29	−0.31	−0.39	−0.44	−0.58	−0.62	−0.63
P_π[b]	0.86	0.86	0.85	0.84	0.82	0.81	0.79	0.78
Δq[c]	0.14	0.13	0.12	0.17	0.21	0.24	0.28	0.29

E_{AB}; eV unit. a) H=the hydride ligand of *trans*-$PtHX(PH_3)_2$. b) The π-bond order of ethylene part. c) The quantity of transferred electrons from ethylene to *trans*-$PtHX(PH_3)_2$ part. d) The state I is the same as that in the structure A.

orbitals, while these are very weak bonding orbitals in the square pyramidal complex. Ethylene donates its electrons to the $5d_{z^2}$ orbital and accepts d-electrons from the $5d_{yz}$ orbital into its π^*-MO, while it scarcely interacts with these d-orbitals in the square pyramidal complex. Of course, ethylene donates its π-electrons to the $6p_z$ orbital of the Pt atom in both the square pyramidal and trigonal bipyramidal complexes. Thus, the interaction between the Pt atom and ethylene is larger in the trigonal bipyramidal complex (A) than in the square pyramidal one; this results in the larger absolute value of $E_{Pt-C(1)}+E_{Pt-C(2)}$ in the former than in the latter. Decreases in the π-bond order of ethylene, P_π, and the quantity of transferred electrons from ethylene, Δq, suggest a greater increase in the π-acceptor bond than in the σ-donor bond, as is shown in Table 2. In the B structure, the $5d_{z^2}$ and $5d_{xz}$ orbitals of the Pt atom also become bonding orbitals. The $5d_{xz}$ orbital can not interact with ethylene, as is shown in Fig. 1. Ethylene donates its π-electrons to the $5d_{z^2}$ orbital of the Pt atom through the σ-donor bond, while it scarcely donates its π-electrons to the $5d_{z^2}$ orbital in the square pyramidal complex. The formation of this interaction brings about increases in the Δq and the $E_{Pt-C(1)}+E_{Pt-C(2)}$ and the decrease in the P_π.

TABLE 3. INSERTION REACTION OF ETHYLENE INTO Pt(II)-H BOND

(a) Reaction path C

State	I	II	III
r(Å)	0.0	0.3	0.6695
E_{total}	−1945.6	−1945.5	−1945.0
E_{C-H}[a]	−0.62	−1.27	−1.86
E_{Pt-H}[a]	−12.59	−12.23	−11.90
E_{C-C}	−29.81	−29.89	−30.27
$E_{Pt-C(1)}$	−6.65	−5.04	−3.01
$E_{Pt-C(2)}$	−6.75	−8.08	−8.66

(b) Reaction path D[b]

State	II	III	IV[c]	V[d]
δ	10°	30°	30°	30°
E_{total}	−1945.7	−1947.7	−1947.7	−1947.7
E_{C-H}[a]	−1.69	−7.83	−8.31	−8.37
E_{Pt-H}[a]	−11.82	−8.44	−8.49	−8.45
E_{C-C}	−29.61	−27.67	−27.57	−27.42
$E_{Pt-C(1)}$	−6.24	−5.68	−5.81	−5.81
$E_{Pt-C(2)}$	−7.25	−8.43	−8.49	−8.74

(c) Reaction path E[b]

State	II	III	IV[c]	V[d]
δ	10°	30°	30°	30°
E_{total}	−1946.1	−1947.7	−1947.6	−1947.6
E_{C-H}[a]	−2.40	−7.39	−7.87	−7.92
E_{Pt-H}[a]	−11.58	−9.04	−9.09	−8.94
E_{C-C}	−29.28	−27.90	−27.79	−27.68
$E_{Pt-C(1)}$	−6.21	−5.76	−5.90	−5.90
$E_{Pt-C(2)}$	−7.14	−7.75	−7.81	−8.02

E_{total} and E_{AB}; eV unit. a) H=the hydride ligand of *trans*-$PtHX(PH_3)_2$. b) The state I is the same as that in the reaction path C. c) Hydrogen atoms bonded to the C(1) atom were displaced out of the original ethylene plane opposite to the Pt atom, while the other parts are unchanged as the state III. d) Hydrogen atoms bonded to the C(1) and C(2) atoms were displaced out of the original ethylene plane opposite to the Pt atom, and the other parts were unchanged.

TABLE 4. LIGAND EFFECT OF HALOGENS IN THE INSERTION REACTION OF ETHYLENE INTO Pt(II)-H

Reaction path D, State III

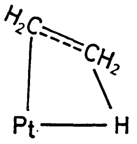
		F	Cl	Br	I	CN
Electron density	Pt	9.98	10.12	10.15	10.18	10.20
	C(1)	4.09	4.09	4.09	4.09	4.09
	C(2)	4.27	4.25	4.24	4.24	4.23
	H[a]	0.99	0.96	0.95	0.95	0.94
	E_{C-H}[a]	−7.78	−7.83	−7.84	−7.86	−7.91
	E_{Pt-H}[a]	−8.43	−8.44	−8.44	−8.42	−8.37
	E_{C-C}	−27.64	−27.67	−27.67	−27.68	−27.72
	$P_{\pi C(2)}$	1.19	1.15	1.14	1.14	1.13
	ΔQ[b]	1.13	1.20	1.22	1.22	1.24

E_{AB}; eV unit. a) H=the hydride ligand coordinating to Pt(II). b) The quantity of transferred electrons from the system $C_2H_4+H^-$ to $PtX(PH_3)_2{}^+$ part.

Inserion Reaction of Ethylene. The results on the reaction paths and those on the ligand effect in this reaction are shown in Tables 3 and 4 respectively.

In the C reaction path, the total energy increases slightly. The absolute values of E_{C-H}, E_{C-C}, and $E_{Pt-C(2)}$ increase as the reaction proceeds from the I state to the III state, while those of $E_{Pt-C(1)}$ and E_{Pt-H} decrease. (In this paper, the H's of the Pt–H and C–H represent the hydride coordinated to the Pt atom.) These results show the increase in the C–H interaction. However, the increase in the absolute value of E_{C-C} suggests an increase in the strength of C–C bond. This rules out the C reaction path, because the C=C double bond must become a C–C single bond after an insertion reaction.

In the D reaction path, the total energy decreases as the reaction proceeds from the I state to the III state.[31] The absolute values of E_{C-H} and $E_{Pt-C(2)}$ increase in this reaction course, while those of E_{Pt-H}, E_{C-C}, and $E_{Pt-C(1)}$ decrease. These results reveal that the C–H and Pt–C(2) interactions become stronger and that the Pt–H, Pt–C(1), and C–C interactions become weaker. This situation agrees with that in the four-center-type reaction;[28])



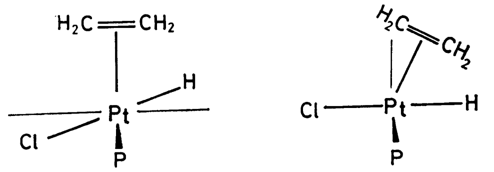
Scheme II.

Therefore, the D reaction path is reasonable for the ethylene insertion reaction.

In the E reaction path, the total energy decreases as the reaction proceeds from the I state to the III state.[31] The bonding interactions of the C–H and Pt–C(2) bonds become stronger and those of the C–C, Pt–C(1), and Pt–H bonds become weaker, similarly to those of the D reaction path, as the reaction proceeds. The E reaction path also seems reasonable.

In two reaction paths, D and E, the bending of the CH_2 group, in which hydrogen atoms are displaced out of the original ethylene plane opposite to the Pt atom, brings about increases in the absolute values of E_{C-H} and $E_{Pt-C(2)}$, and decreases in those of $E_{Pt-C(1)}$ and E_{C-C}, while it scarcely changes the total energy (see the IV and V states in Table 2). These results suggest the bending of the CH_2 groups is brought about in this reaction course; this corresponds to the C(1) and C(2) atoms becoming sp^3 character from their original sp^2 character.

It is worthwhile to investigate which ligand, ethylene or hydride, transfers in the ethylene insertion reaction. As is shown in Table 3, the II state in the E reaction path has a lower total energy, a larger absolute value of E_{C-H}, and smaller absolute value of E_{Pt-H} and E_{C-C} than that in the D reaction path; that is, the former state has a stronger C–H bonding interaction and weaker Pt–H and C–C bonding interactions than the latter one. From these results, the H ligand can be expected to transfer more easily than ethylene in the initial stage of the reaction. The following states, III—V, in the D reaction path have a larger absolute value of E_{C-H} and smaller ones of E_{Pt-H} and E_{C-C} than those in the E reaction path, while the reaction states in both reaction paths have almost the same total energies. These results suggest, at first glance, that ethylene transfers to the H ligand more favorably than the latter does to the former in the more advanced reaction states. In the E reaction path, however, the Cl ligand should also transfer, as is shown in Scheme III, as the reaction advances, since the final product is the square planar *trans*-$Pt(C_2H_5)Cl(PH_3)_2$.



The more advanced reaction state in the reaction path E

The reaction path D

Scheme III.

The transfer of the Cl ligand in the E reaction path results in almost the same intermediate state as that in the D reaction path, while the position of PH_3 is slightly different. The III—V states in the D reaction path can reasonably be considered to be more advanced reaction states in the E reaction path. Thus, our results suggest that the H ligand starts first to attack ethylene and that then the Cl ligand starts to move to the *trans*-position of the H ligand. Of course, this problem should be studied in more detail experimentally and theoretically.

In order to investigate the role of the Pt(II) ion in the insertion reaction, a hypothetical state is studied; it is obtained by removing the $PtCl(PH_3)_2^+$ part from the III state in the D reaction path. This hypothetical state is considered to be a limiting state of the C_2H_4+ LiH reaction system in which the bond distance of Li–H is infinitely lengthened. This hypothetical state has the following characteristics: (1) The electron density on the C(2) atom is remarkably large (4.64 e); this is a result of the large electron density on its p_π orbital (1.84 e). (2) The highest occupied (HO) MO has a remarkably high orbital energy (−0.345 eV). (3) As is shown in Fig. 4, its HOMO has a non-bonding character; electrons are localized in the $2p_\pi$ orbital of the C(2) atom and the 1s orbital of the H atom. Where the Pt part exists, the MO of this type is obtained at about −10 eV and the $2p_\pi$ orbital of the C(2) atom interacts with the $5d_{z^2}$, 6s, and $6p_\pi$ orbitals of the Pt atom in the D reaction path, as is shown in Fig. 5.

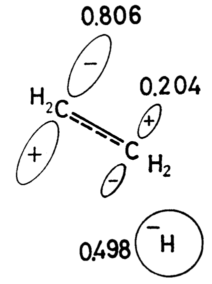


Fig. 4. AO coefficients of the HOMO of the hypothetical state, $C_2H_4+H^-$.

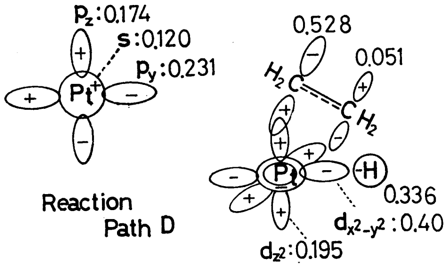
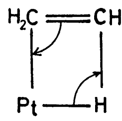


Fig. 5. AO coefficients of an important MO in the interaction between the C(2) and Pt atoms.

As a consequence of these interactions, the electron density on the $2p_\pi$ orbital of the C(2) atom, $P_{\pi C(2)}$, is remarkably reduced in $PtHX(PH_3)_2(C_2H_4)$ relative to the hypothetical state, as is shown in Table 4. Thus, it is the important role of the Pt atom to accept the excess π-electrons on the C(2) atom and to stabilize the HOMO of the hypothetical system. In other words, the insertion reaction mechanism may be represented as follows:



Scheme IV.

The ligand effects on the insertion reaction were studied in the III state of the D reaction path, as is shown in Table 4. In all the reaction systems, the electron density on the C(2) atom and the absolute value of $E_{Pt-C(2)}$ are larger than that on the C(1) atom and that of $E_{Pt-C(1)}$ respectively. The negative values of E_{C-H} in all the systems reveal the C–H bonding interaction. Its absolute value increases in this order; F<Cl<Br<I<CN, while the absolute values of $E_{\mathrm{Pt-H}}$ and $E_{\mathrm{C-C}}$ decrease in the same order. Also, the values of ΔQ, which is defined as the quantity of transferred electrons from the $C_2H_4+H^-$ part to the $PtX(PH_3)_2^+$ part, increase, and the values of $P_{\pi C(2)}$ decrease, in this order. From these results, the reactivity of *trans*-$PtHX(PH_3)_2$ in the insertion reaction can be effected to increase in the same order. This order of increase agrees with the order of increase of the *trans*-effect of the X ligand; this is consistent with the experimental results.[29]

The decreasing order of ΔQ of F>Cl>Br>I>CN is the same order as in the electron transfer from the H ligand to the Pt part in *trans*-$PtHX(PH_3)_2$. The results for ΔQ in the former case may also be due to the same reason.[27]

Hydrogen-Deuterium Exchange Reaction. *trans*-$PtHCl(PEt_3)_2$ catalyzes the H–D exchange reaction of ethylene.[30] The H–D exchange reaction is composed of two steps: the ethylene insertion into the Pt(II)–H bond, and the β-hydrogen abstraction in the Pt(II)-ethyl complexes. The transition state in the β-hydrogen abstraction is considered to be the same as that in the ethylene insertion reaction. Therefore, it is only necessary to investigate the interaction between the Pt atom and the β-hydrogen of the ethyl group in the Pt(II)-ethyl complexes. The results are given in Table 5.

TABLE 5. THE INTERACTION BETWEEN Pt AND β-H ATOMS IN *trans*-$PtX(C_2H_5)(PH_3)_2$

		F	Cl	Br	I	CN
Electron density	Pt	9.98	9.96	9.98	10.01	10.03
	β-H[a)]	0.82	0.82	0.82	0.82	0.82
$E_{\mathrm{C-H}}$[a)]		−0.60	−0.73	−0.75	−0.81	−0.80

E_{AB}; eV unit. a) H=β-H atom of ethyl group.

The absolute values of $E_{\mathrm{Pt-H}}$ increase in this order: F<Cl<Br<CN<I, as is shown in Table 5. The β-hydrogen atom is abstracted easily as follows: F<Cl<Br<CN<I. As has been described previously, the ligand effect on the reactivity in the ethylene insertion increases in this order: F<Cl<Br<I<CN. Therefore, the catalytic ability of *trans*-$PtHX(PR_3)_2$ in the H–D exchange reaction increases: F<Cl<Br<I; it is difficult to determine which is more active, the iodo- or the cyano-complex.

These calculations were carried out with Facom 230-75 Computer of the Data Processing Center in Kyoto University.

The authors are grateful to Professor Akio Yamamoto for his creative suggestion. They also wish to thank Dr. Hideyuki Konishi for his help with calculations.

References

1) R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, **73**, 21 (1973).

2) F. R. Hartley, *ibid.*, **69**, 799 (1969).

3) R. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272, 3533 (1966).

4) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).

5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1962**, 5075.

6) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Crystallogr*, **13**, 246 (1960).

7) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

8) J. Powell and B. L. Shaw, *J. Chem. Soc.*, **1965**, 3879.

9) P. W. Atkins, J. C. Green, and M. L. H. Green, *J. Chem. Soc. (A)*, **1968**, 2275.

10) R. R. Dean and J. C. Green, *ibid.*, **1968**, 3047.

11) H. C. Clark and H. Kurosawa, *J. Organometallic Chem.*, **36**, 399 (1972).

12) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. (A)*, **1968**, 190.

13) H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, **89**, 529 (1967).

14) P. Uguagliati and W. H. Baddley, *ibid.*, **90**, 5446 (1968).

15) A. J. Deening, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, **1970**, 598.

16) H. C. Clark and R. J. Puddephatt *Inorg. Chem.*, **10**, 416 (1971).

17) A. J. Deening, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. Dalton*, **1973**, 1850.

18) S. Sakaki, H. Kato, and T. Kawamura, This Bulletin, **48**, 195 (1975).

19) S. Sakaki and H. Kato, *ibid.*, **46**, 2227 (1973).

20) H. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

21) K. Ohno, *Theoret. Chim. Acta*, **2**, 219 (1964).

22) M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

23) S. E. Ehrenson and S. Seltzer, *Theoret. Chim. Acta*, **20**, 17 (1971).

24) "Tables of Interatomic Distances and Configuration in Molecules and Ions," by L. E. Sutton, The Chem. Soc., London, (1958).

25) β-H–Pt=2.876 Å in the equilibrium distance.

26) M. Black, R. H. B. Mais, and P. G. Owston, *Acta Crystallogr*, **B25**, 1753 (1969).

27) Under the approximations used here, a diagonal Fock matrix element is written as follows:

$$F_{rr}=-I_r+\gamma_{rr}+(0.5p_{rr}-N_r)\gamma_{rr}+\sum_{s\neq r}(p_{ss}-N_s)\gamma_{rs}$$

Going from F to CN^-, the values of P_{rr} of the Pt atom increase and those of F_{ss} and γ_{rs} decrease, where r and s represent the valence orbitals of the Pt atom and those of the X ligand respectively. The increase in P_{rr} raises the value of F_{rr} through the third term on the right-hand side. However, the decreases in P_{ss} and γ_{rs} reduce the F_{rr} through the fourth term, since the $P_{rr}-N_{rr}$ is negative in these cases. The change in the value of the third term is less than that of the fourth one, mainly because of the change in the values of γ_{rs}. Thus, the values of F_{rr} decrease as a result of the fourth term as follows: F>Cl>Br>I>CN. This result is not because of our approximations but because of the fundamental nature of the X ligand; the atom which has contracted valence orbitals raises the energy of an electron of the other atom through the electronic repulsion integrals, relative to the atom whose orbitals expand largely.

28) S. Sakaki, H. Kato, H. Kanai, and K. Tarama, This Bulletin, **47**, 377 (1974).

29) R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3534 (1966).

30) R. A. Schunn, *Inorg. Chem.*, **9**, 2567 (1970).

31) It has not been ascertained that the MO method used here can give a correct energy difference between the initial state (*trans*-$PtHCl(PH_3)_2+C_2H_4$) and the interacting state ($PtHCl(PH_3)_2(C_2H_4)$). While Table 3 gives us a negative activation enthalpy, it should be studied in more detail.