

A THEORETICAL STUDY
ON
THE ELECTRONIC STRUCTURES AND THE CATALYTIC REACTIONS
OF
TRANSITION METAL COMPLEXES

BY
SHIGEYOSHI SAKAKI

DEPARTMENT OF HYDROCARBON CHEMISTRY
FACULTY OF ENGINEERING
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Preface

Catalytic reactions are of interest and well studied both in the pure and applied chemistries. Catalysts are classified into following groups; (1) metals, (2) metal oxides, (3) acids and bases, (4) transition metal complexes, and (5) others. The catalyses by transition metal complexes are generally homogeneous with few exceptions and have been investigated actively during the last decade. Others are heterogeneous in most cases and have been studied for several decades.

When we consider why and how catalysts accelerate reactions, we should know how catalysts interact with reagents and how the reagents become favorable for the reaction by the interactions. In order to elucidate the above issues, we must investigate electronic structures of intermediates in which catalysts interact with reagents. While recent spectrometers such as nuclear magnetic resonance and electron spin resonance supply us information on electronic structures of intermediates, the studies with these instruments are sometimes difficult because of the low concentrations and/or the short-lives of intermediates. On the other hand, theoretical works supply us information on the above issues. Furthermore, theoretical works are also necessary in order to anticipate the abilities of catalysts and to design catalysts for our requisite reactions. Thus, catalytic chemistry requires theoretical works. Nevertheless, only a few of these works have been

reported. Theoretical works on solid catalyses are difficult due to many unsolved problems in theoretical studies of surface state of solid. Therefore, at the start, we had better perform theoretical works on homogeneous catalyses. In this field, transition metal complexes are of special interest, since they catalyze various organic reactions and also form sometimes stable organo-metal complexes which are considered as models of intermediates in catalyses.

There are three theoretical methods in the chemistry of transition metal complexes; (1) the molecular orbital (MO) method, (2) the valence bond (VB) method, and (3) the crystal field theory. The VB method has been used only in a few studies on transition metal complexes and it is not feasible for moderately large molecules even with recent high-speed computers. While the crystal field theory is useful for studying electronic structure of the central metal atom, this method can not give us information on electronic structures of ligands. On the other hand, the MO method is a useful means for studying both electronic structures of the central metal ions and ligands, and its application to large molecules is moderately easy. Thus, the MO method is the best theoretical means for the studies on catalyses by transition metal complexes, since catalytic systems contain generally many atoms, and since the reactants coordinating to the metal as ligand should be investigated. Unfortunately, however, the

MO studies have not been so popular in the chemistry of transition metal complexes as in organic chemistry.

The main theme of this thesis is a theoretical study of electronic structures of transition metal complexes and their behaviors in catalytic reactions. This thesis is divided into two parts. In part I, the author carries out semi-empirical SCF-MO studies on some transition metal complexes in order to look into the usefulness of this MO method in the chemistry of transition metals and also to investigate electronic structures of organo-transition metal complexes which are often considered as the models of intermediates in catalyses. In part II, he performs theoretical works on some homogeneous catalyses by the use of the semi-empirical SCF-MO method; specifically he studies the oxidation of olefin catalyzed by Hg(II) and Pd(II) complexes, and the hydrogen-deuterium exchange reaction of ethylene catalyzed by $\text{trans-PtHX(PR}_3)_2$.

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Numerical calculations were carried out with Facome 230-60 and 230-75 Computers of Data Processing Center in Kyoto University. To the staffs I wish to acknowledge my gratitude.

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PART I

SEMI-EMPIRICAL SCF-MO STUDIES
ON
TRANSITION METAL COMPLEXES

Chapter 1. Introduction

The MO method is widely applied in the field of organic chemistry. It is also applied in the field of the chemistry of transition metals, while its application is less popular than that in organic chemistry. Since the first attempt of the semi-empirical MO method on transition metal complexes was carried out by Wolfsberg and Helmholz,¹⁾ various MO methods have been applied to transition metal complexes; the extended Wolfsberg-Helmholz MO method (the self-consistent charge (SCC) MO method,²⁾ the self-consistent charge and configuration (SCCC) MO method,³⁾ and others⁴⁾), the zero-differential overlap (ZDO) approximated SCF-MO method (the complete neglect of differential overlap (CNDO) MO method,⁵⁾ the intermediate neglect of differential overlap (INDO) MO method,⁶⁾ and the ASMO SCF method including overlap integrals⁷⁾), the SCF- $X\alpha$ scattered wave model (SCF- $X\alpha$ -SW) method,⁸⁾ the discrete variational (DV) method,⁹⁾ and the ab initio MO method.¹⁰⁾ Electron repulsions are not considered explicitly in the Wolfsberg-Helmholz and the extended Wolfsberg-Helmholz MO methods, while they are considered explicitly in the other MO methods. The ab initio MO method is the best. However, it is difficult to apply this method to catalytic systems even with a recent high-speed computers, because catalytic systems include generally too many atoms for this method. The SCF-

X α -SW and DV methods require moderate amount of computer time for large molecules. However, their applications to transition metal complexes are few and far between, relative to those of semi-empirical SCF-MO methods. Thus, the ZDO approximated SCF-MO methods are most suitable for studies of catalytic systems including transition metal complexes.

In part I, the author carries out MO calculations on transition metal complexes by the use of the CNDO-type approximated semi-empirical SCF-MO method or the INDO-type one.

In chapter 2 of this part I, the introductory CNDO-type MO calculations are presented on some transition metal complexes such as MnO_4^- , CrO_4^{2-} , PdX_4^{2-} , and PdX_6^{2-} (X=F, Cl, and Br).

In chapter 3, semi-empirical UHF-MO calculations are carried out on iron group halides and some other similar halides. The MO method used in this thesis was found to give reasonable results on Werner type transition metal complexes, as described in chapters 2 and 3. Hereafter from chapter 4 to chapter 6, the semi-empirical SCF-MO calculations are carried out on organo-transition metal complexes.

In chapter 4, electronic structures of ferrocene and cobalticenium ion are investigated, in which transition energies, orbital energies, and charge distributions are discussed.

In chapter 5, electronic structures of Ag(I)-olefin complexes are investigated. Main interest is directed to the

coordination bonding characters of olefins.

In chapter 6, MO studies are carried out on Pt(0) and Pt(II) complexes with ethylene and acetylene. A discussion is presented on the difference in coordination bonding characters of ethylene and acetylene between Pt(0) and Pt(II) complexes.

In chapter 7, the resultant conclusions in this part I are presented.

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In Ref. 1 ~ 10, the author presents representative studies. Of course, there are many studies besides them in the above references.

Chapter 2. Preliminary Survey of MO Calculations on Transition Metal Complexes

§ 1. Introduction

Since the molecular orbital (MO) calculations of MnO_4^- and CrO_4^{2-} were presented by Wolfsberg and Helmholz,¹⁾ various MO methods have been used in the MO calculations of transition metal complexes, as described in chapter 1. However, none of them was perfectly satisfactory, because an effective method for some compounds can not always give reasonable results in other cases.

In order to re-examine the usefulness of the CNDO type MO calculations of transition metal complexes except for the estimation of the intra-atomic triplet transition, the author calculated the electronic structures of MnO_4^- , CrO_4^{2-} , PdX_4^{2-} and PdX_6^{2-} (X=halogen), since the CNDO type approximation avoids the difficulties of preserving rotation invariance and of estimating one-center exchange repulsion integrals in the INDO type one. The calculated results of the electron density, the strength of the Pd-X bond, and the electronic spectra of these complexes are presented in this chapter.

§ 2. MO method

The author starts from Roothaan's familiar closed-shell

SCF equation²⁾ and separate the Hartree-Fock matrix element, F_{rs} , into the one-electron part, H_{rs} , and the two-electron part;

$$|F_{rs} - \epsilon S_{rs}| = 0 \quad (1)$$

$$F_{rs} = H_{rs} + \sum_{t, u}^{\text{occ}} P_{tu} [(rs|tu) - 0.5(rt|su)]$$

where r, s, t , and u denote atomic orbitals (AO's) and P_{tu} is density matrix element between the AO. t and AO. u . Then, the following approximations are introduced into eq.(1): (I) The zero-differential overlap (ZDO) approximation³⁾ is introduced;

$$S_{rs} = \delta_{rs} \quad (2)$$

$$(rs|tu) = \delta_{rs} \delta_{tu} (rr|tt) \quad (3)$$

(II) The diagonal element of the one-electron part, H_{rr} , is approximated as follows;⁴⁾

$$H_{rr} = U_{rr} + \sum_{B \neq A} (B|rr) \quad (4)$$

$$U_{rr} = -I_r - (N_r - 1)(rr|rr) - \sum_{s \neq r} N_s (rr|ss) \quad (5)$$

$$(B|rr) = - \sum_s^B N_s (rr|ss) \quad (6)$$

where N_r and I_r represent the number of electrons on the AO. r in the neutral atom A, and the valence state ionization potential of the AO. r , respectively. $\sum^A$ indicates the summation on the A atom. (III) The off-diagonal element of one-electron part, H_{rs} ($r \neq s$), is approximated according to Wolfsberg and Helmholz;¹⁾

$$H_{rs} = -\frac{1}{2} K S_{rs} (I_r + I_s) \quad (7)$$

where the parameter K is taken equal to 1.1.

(IV) The one-center Coulomb repulsion integral $(rr|rr)$ and the two-center Coulomb repulsion integral $(rr|ss)$ are estimated by the Pariser's approximation⁵⁾ and the Ohno's approximation⁶⁾ respectively.

In order to calculate S_{rs} , Clementi's AO⁷⁾ and Burns' AO⁸⁾ were used for ligands and metals respectively. The same orbital exponents were used for s- and p-orbitals. The values obtained by Jaffé et al.⁹⁾ were used for the I_r and $(rr|rr)$ of ligand atoms. The values used for the metals are listed in Table 1.

The bond population or the atomic orbital bond population can not be used as the bond index in the MO method including the ZDO approximation. The bond order can not be useful for the bond index because of its rotation variable character. Thus, the author use the quantity, E_{AB} , as the bond index, which is defined as the energy contribution of the AB bond to the total energy.^{3, 18)} This quantity is represented as follows under approximations used here;

$$E_{AB} = 2 \sum_r^A \sum_s^B P_{rs} H_{rs} - 0.5 \sum_r^A \sum_s^B P_{rs}^2 (rr|ss) \\ + \sum_r^A \sum_s^B (P_{rr} - N_r) (P_{ss} - N_s) (rr|ss) \quad (8)$$

Table 1 The ionization potential (I_r) and one-center Coulomb repulsion integral (J_{rr})

		I_r	$J_{rr}^{12)}$
Cr	3d	$-20.28^{10})$ eV	14.03_{eV}
	4s	-14.73	6.80
	4p	-10.31	5.80
Mn	3d	$-21.64^{10})$	14.70
	4s	-15.35	7.09
	4p	-10.62	5.95
Pd	4d	$-8.54^{11})$	13.87
	5s	-7.60	7.46
	5p	-3.84	6.22

§ 3. Results and Discussion

MnO_4^- and CrO_4^{2-} . For the purpose of comparing our results with previous one,¹³⁻¹⁵⁾ MO's of MnO_4^- and CrO_4^{2-} were calculated. The net charge on the Mn atom in MnO_4^- was found to be 1.28 from the metal K-X ray spectra.^{13-b)} However, negative net charge on the Mn atom was obtained. This may be due to the too large electron density of the 4s and 4p orbitals of the Mn atom compared with the results of Oleari et al.¹⁴⁾ and Hillier et al.¹⁵⁾ (MnO_4^- ; 4s, 0.81 and 4p, 0.78; CrO_4^{2-} ; 4s, 0.81 and 4p, 0.78 in our results).

The highest occupied (HO) MO and the lowest unoccupied (LU) MO are considered to be represented by t_1 ^{13, 14)} and e ¹⁶⁾, respectively. Calculated results with respect to HOMO and LUMO are compared with previous ones in Fig. 1. The results of Oleari et al.¹⁴⁾ seem to be quite reasonable. However, the MO calculations by Brown et al.^{13-b)} gave a positive orbital energy for the HOMO of CrO_4^{2-} . Also, in the case of Hillier's calculation,¹⁵⁾ the representations of HOMO and LUMO are not t_1 and e , respectively, and the HOMO of CrO_4^{2-} has a positive orbital energy. In contrast to these results, our results are reasonable regarding the orbital energies and the orbital symmetries.

The calculated transition energies are given in Table 2. Our results agree well with the experimental results.

PdX_4^{2-} and PdX_6^{2-} . The author then calculated the MO's

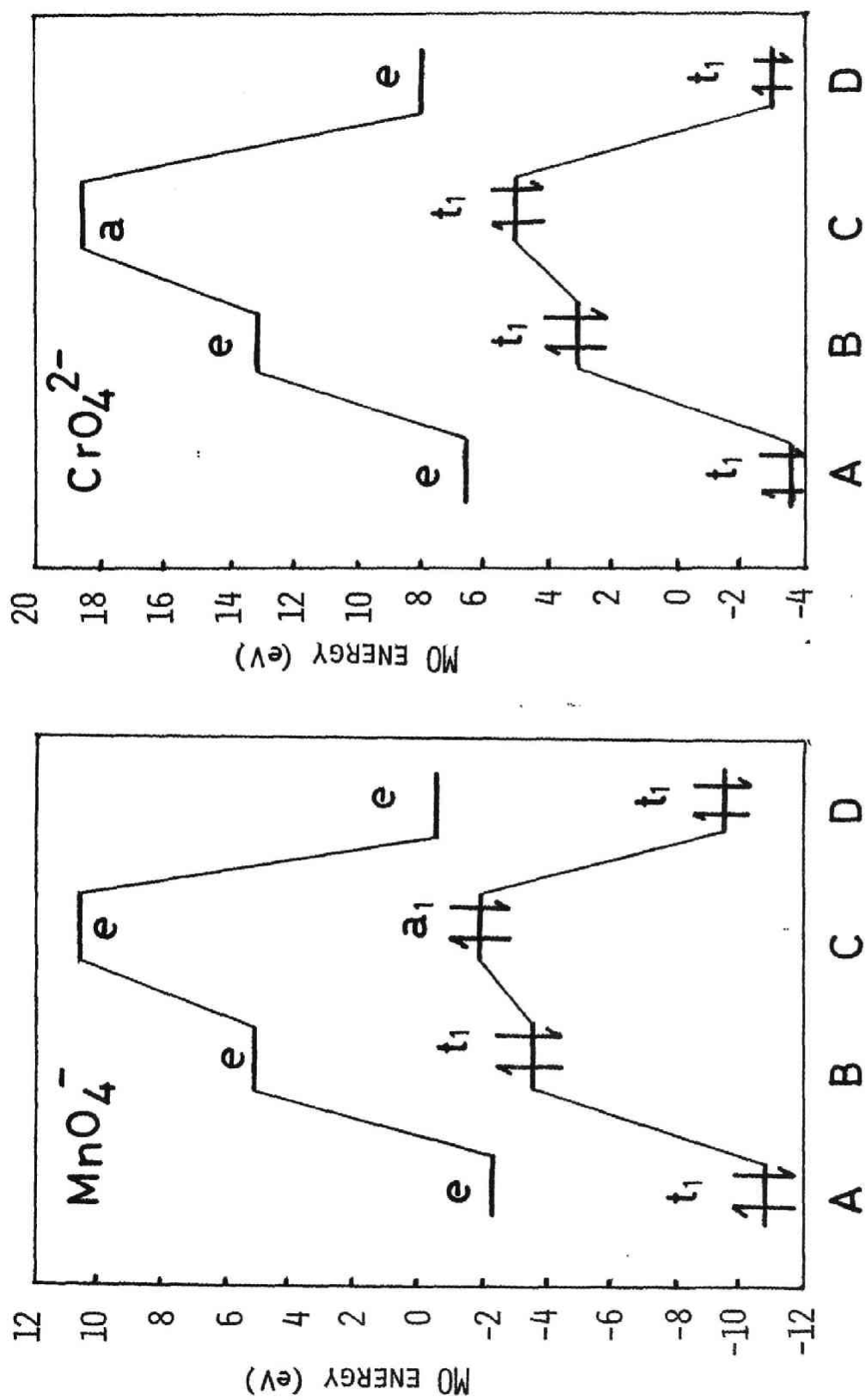


Fig. 1. HOMO and LUMO of MnO_4^- and CrO_4^{2-} by various methods.

$\uparrow\uparrow$; HOMO, —; LUMO A; Oleari et al.^{5-a)} by INDO. B; Brown et al.^{4-b)} by VE-SVF-CNDO. C; Hillier et al.⁶⁾ by ab initio, D; the author's one by CNDO.

Table 2 Transtion energies of MnO_4^- , CrO_4^{2-}
and PdCl_6^{2-}

(a) MnO_4^-

Experimentals ^{17-b)}	Calculated
1.79 eV 3T_1 or 1T_1 ^{17-a)}	1.44 eV 1T_1
2.38 1T_2	2.45 $^1T_2 + ^1E$
	3.65 1T_2
3.44 1T_1	4.27 1T_1
4.13 1T_2	4.47 1T_2

(b) CrO_4^{2-}

Experimentals ^{17-c)}	Calculated
3.00 eV 1T_1	3.36 eV 1T_1
	3.78 1T_1
3.56 1T_2	5.15 1T_2
4.65 1T_2	6.47 1T_2
5.20	6.70 1T_1

(c) PdCl_6^{2-}

Experimentals ²²⁾	Calculated
2.27 eV	3.98 eV $^1T_{1g}$
3.64	4.13 $^1T_{2g}$
	5.94 $^1T_{1u}$
5.17	6.45 $^1T_{2u}$

of PdX_4^{2-} and PdX_6^{2-} in order to examine the validity of this MO method for different types of complexes. The net charge of the Pd atom decreases with a decrease in the electronegativity of halogen, as is shown in Table 3. This tendency agrees with the results obtained by means of photoelectron spectroscopy.¹⁹⁾ However, the author obtained a negative net charge on the Pd atom due to the large electron density of 5s- and 5p-orbitals. As is shown in Table 3, the absolute value of $E_{\text{Pd-Cl}}$ is larger than that of $E_{\text{Pd-Br}}$ in PdX_4^{2-} , and PdX_6^{2-} , and the absolute value of $E_{\text{Pd-X}}$ of PdX_6^{2-} are larger than that of PdX_4^{2-} . These results agree with experimental results.²⁰⁾

Though the order of the bond strength agrees with the experimental results, it is failed to obtain reasonable transition energies of PdX_4^{2-} . The calculated transition energies seem too small for PdCl_4^{2-} (0.019 eV) and PdBr_4^{2-} (0.028 eV). Furthermore, neither is the d-d transition which is to be expected as the first transition.²¹⁾ For PdCl_6^{2-} , the calculation gives almost reasonable results, as is shown in Table 2.

As has been described above, the CNDO type MO method gives reasonable transition energies of MnO_4^- , CrO_4^{2-} and PdCl_6^{2-} , although successful results can not be obtained in PdX_4^{2-} . Also, this MO method gives us reasonable trends of electron density and bond strength for PdX_4^{2-} and PdX_6^{2-} .

Table 3 Electron Densities and $E_{\text{Pd-X}}$ of PdX_4^{2-} and PdX_6^{2-}

	Electron densities		Net Charge		$E_{\text{Pd-X}}$ (eV)	Obsd.	
	4d	5sp	on Pd			$f_{\text{Pd-X}}^{\text{a)}$	$\nu_{\text{Pd-X}}^{\text{b)}$
			Calcd.	Expt.		(mdyn/Å)	(cm ⁻¹)
PdCl_4^{2-}	8.075	2.259	-0.333	0.42	-15.882	1.355	310
PdBr_4^{2-}	8.049	2.343	-0.392	0.23	-14.688		187
PdF_6^{2-}	7.137	2.219	0.644		-19.124		
PdCl_6^{2-}	7.177	3.043	-0.220	0.72	-16.300	1.90	317
PdBr_6^{2-}	7.157	3.203	-0.360		-14.920	1.58	198

a) The force constant of Pd-X stretching vibration (Ref. 20).

b) The frequency of stretching vibration of Pd-X (Ref. 20).

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 However we can not obtain the I_r for d^5s^2 except with I_{4s} because of the lack of the observed atomic spectra.
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Chapter 3. Iron Group Fluorides and Some Other Transition Metal Halides

§ 1. Introduction

^{19}F NMR studies on open-shell iron group fluorides have revealed the existence of hyperfine interaction between the fluorine nuclei and the magnetic electrons.¹⁻⁷⁾ Also similar hyperfine interactions have been observed in ESR studies on those complexes.^{2, 8-14)} These hyperfine interactions have been explained in terms of the spin fractions on the F^- ligand.²⁻¹⁵⁾ It has been accepted that unpaired electrons have been brought into s and p orbitals of ligand by the metal-fluorine covalency (the spin delocalization (SD) mechanism)^{2, 16)} except CrF_6^{3-} and VF_6^{4-} in which spin fractions on the 2s orbital of the F^- ligand are considered to be resulted from the mixing of the excited states (the spin polarization (SP) mechanism).^{3, 10)}

Some theoretical works have been carried out on the electronic structures of these complexes.¹⁵⁻²⁰⁾ However, only a few of reports^{19,20,23)} have been presented on UHF-MO calculations of these complexes, while an UHF-MO method is suitable for calculating spin fractions. Also, UHF-MO calculations have never been reported on NiCl_6^{4-} , MnCl_6^{4-} and MnCl_4^{2-} so far as we know.

In the present work, the semi-empirical UHF-MO calculations

are carried out on open-shell iron group fluorides and some other complexes. The discussion is presented on the spin transfer mechanism, ligand effect on spin transfers, and the metal-halogen bonding natures.

§ 2. MO method, Parametrization, and Geometries of Complexes

MO method. A semi-empirical UHF-MO method is used, in which CNDO or INDO type approximations are included. The approximations used here are the same as our previous ones for the CNDO type MO method²⁵⁾ and as the Konishi's ones for the INDO type MO method²⁶⁾ respectively. Only the one-electron part of Fock matrix elements, H_{rt} , in the INDO type MO method are reiterated here;

$$H_{rr} = -I_r - (N_r - 1)\gamma_{rr} - \sum_{t \neq r}^A N_t (\gamma_{rt} - 0.5 \kappa_{rt}) - \sum_{B \neq A} \sum_s^A N_s \gamma_{rs} \quad (1)$$

$$H_{rs} = -0.5 K S_{rs} (I_r + I_s) \quad (2)$$

where AO. r is on the A atom and $\sum^A$ means the summation on the A atom. H_{rr} in the CNDO type MO method is obtained from eq(1) by neglecting κ_{rt} . For Wolfsberg-Helmholz²⁷⁾ parameter K , values of 1.0 and 0.80 are used in AO pair including d-orbital and in that including only s and p orbitals, respectively.

Parametrization. Elements of the first transition series have $d^{n-2}s^2$ configurations in their ground states except the Cr atom which contains d^5s configuration, where n represents the number of valence electrons. However, d^n and $d^{n-1}s$ configurations etc. also should be considered valence

state configurations. Thus, the arbitrariness exists in the choice of the valence state. The effects of valence state is investigated in MO calculations on NiF_6^{4-} . As described in the following section, the authors use the $d^{n-2}s^2$ valence state and d-function for d^n configuration in standard MO calculations.

For metal atoms, ionization potentials are calculated by using data of Di Sipio et al.²⁸⁾ Values of one-center Coulomb repulsion integrals are also taken from the same work.²⁸⁾ While these quantities are considered to depend on the electronic configurations of the atom, the same values are used for three different configurations since the data of Di Sipio et al. are evaluated from various electronic configurations including these three ones. For ligand atoms, values of ionization potentials and one-center Coulomb repulsion integrals are taken from Hinze's work.²⁹⁾ Values of one-center exchange repulsion integrals are adopted from Di Sipio's work³⁰⁾ for metal atoms and from Hinze's work³¹⁾ for ligand atoms.

In INDO type MO calculations, values of one-center Coulomb repulsion integrals, γ_{ds} and γ_{dp} , are evaluated from Slater-Condon parameters³⁰⁾ so as to hold rotational invariance.

Double- ζ type functions of Richardson et al.³²⁾ are used only for d-orbitals and single Slater type orbitals³³⁾ are used for s and p orbitals.

Bond Index.

The contributions of the AB bond to the

total energy, E_{AB} , is used as the bond index.^{34, 35} This quantity is represented as follows under both CNDO and INDO type approximations used here;

$$E_{AB} = \sum_r^A \sum_t^B [2 P_{rt} H_{rt} - \{ (P_{rt}^\alpha)^2 + (P_{rt}^\beta)^2 \} \gamma_{rt}] + \sum_r^A \sum_t^B (P_{rr} - N_r) (P_{tt} - N_t) \gamma_{rt} \quad (3)$$

where $P_{rt} = P_{rt}^\alpha + P_{rt}^\beta$. The first term on the right hand side represents approximately the contribution of the covalent bonding interaction and the second one does approximately that of electrostatic one. In order to investigate the metal-halogen bonding nature, the first term are divided into each AO pair terms, such as $E_{AB(s)}$, $E_{AB(p)}$, and $E_{AB(d)}$;

$$E_{AB(s)} = \sum_r^A [2 P_{rs} H_{rs} - \{ (P_{rs}^\alpha)^2 + (P_{rs}^\beta)^2 \} \gamma_{rs}] \quad (4)$$

$$E_{AB(p)} = \sum_r^A \sum_t^{B(p)} [2 P_{rt} H_{rt} - \{ (P_{rt}^\alpha)^2 + (P_{rt}^\beta)^2 \} \gamma_{rt}] \quad (5)$$

where $\sum_t^{B(p)}$ means the summation on the p-orbitals of the B atom. $E_{AB(d)}$ is also similarly defined. These quantities, $E_{AB(s)}$ and $E_{AB(p)}$ etc., represent the contribution of the s-orbital of the B atom and that of p-orbitals of the B atom to the A-B bonding interaction etc., respectively. The second one in eq(3) is not divided into each AO pair terms, since it approximately represents the electrostatic interaction and the division described above is meaningless.

Geometries. Structures of MX_6^{n-} are assumed as the rigid octahedral for simplicity, while they are slightly

distorted.^{3, 4, 6)} Structures of CuCl_4^{2-} and MnCl_4^{2-} are considered to obey D_{4h} ³⁶⁾ and T_d ¹²⁾ symmetries, respectively. Their coordinate systems are shown in Fig. 1.

§ 3. Results and Discussion

Effects of Valence State. Three MO calculations are carried out on NiF_6^{4-} by using three valence state, d^8s^2 , d^9s and d^{10} , in order to investigate the effects of valence state. NiF_6^{4-} is the most convenient for this purpose, since this compound has been well investigated experimentally^{6, 7)} and theoretically.^{16, 17, 21, 23)} Results are given in Table 1.

In calculations I ~ III, an electron density on the 3d-orbital of the nickel atom agrees well with that obtained by the ab initio MO calculation, while electron densities on the 4s and 4p orbitals are remarkably larger than those of the ab initio MO calculation.²³⁾ Generally speaking, an ab initio MO method gives an reasonable electron densities. In transition metal complexes, however, electron densities on 4s and 4p orbitals are extremely affected by the orbital expandings.³⁷⁾ Thus, the authors do not carry out parametrizations for electron densities on 4s and 4p orbitals.

On spin fractions of the 2s-orbital of the F^- ligand, f_s , the calculation III gives reasonable result, while the spin fraction on the 2p_σ-orbital of the F^- ligand, $f_{p\sigma}$, is too small relative to the experimental value.⁷⁾ On the other

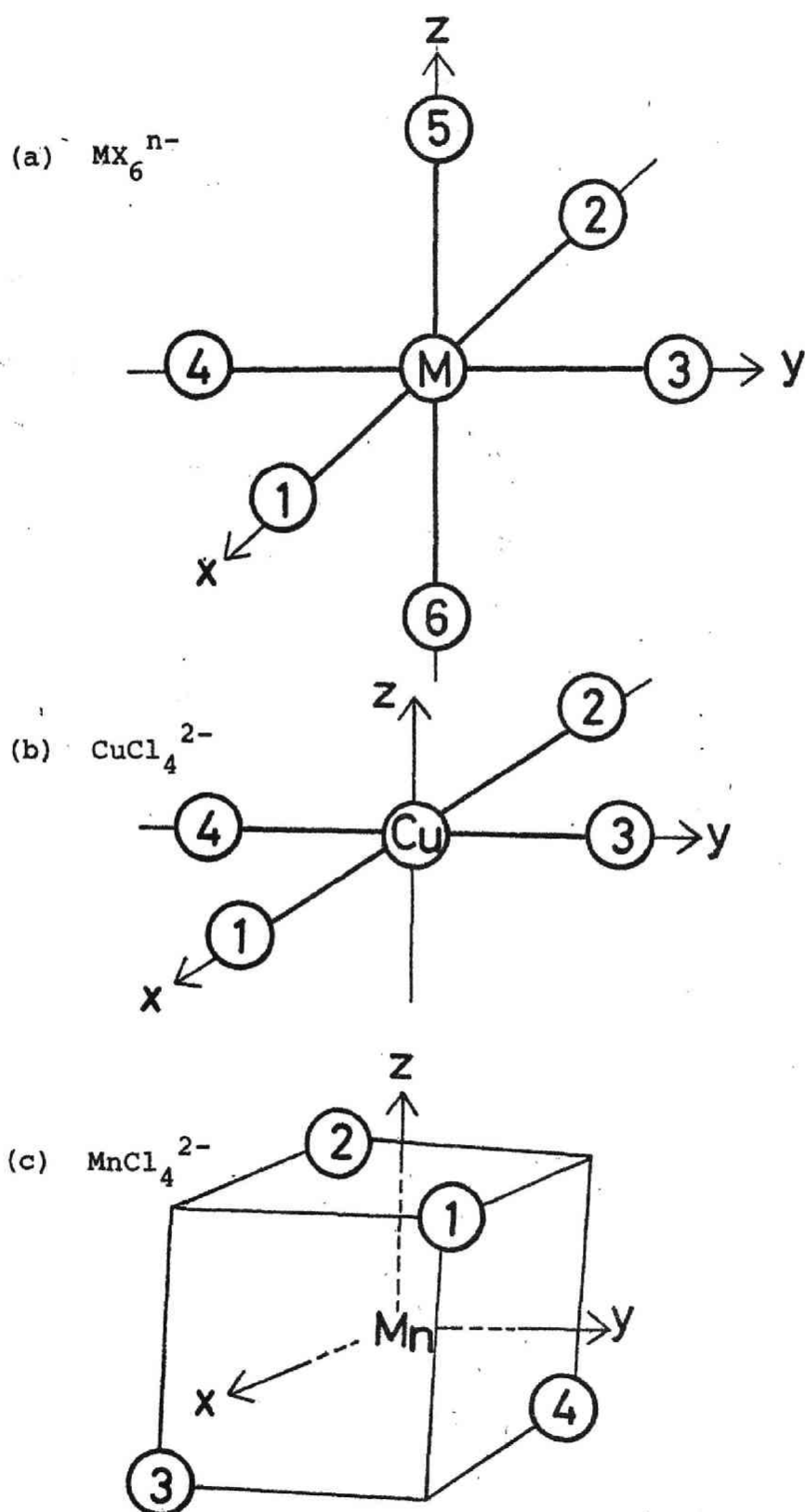


Fig. 1. Coordinate systems of MX_6^{n-} , $CuCl_4^{2-}$, and $MnCl_4^{2-}$
 $M=V(II)$, $Cr(III)$, $Mn(II)$, $Fe(III)$, and $Ni(II)$; $X=F^-$, Cl^- ,
 and Br^- .

Table 1 Effects of valence state configurations in CNDO type MO calculations^a of NiF_6^{4-} .

Calculation		I	II	III	IV	Moskowitz ^b	obsd. ^c
Valence State		$d^8 s^2$	$d^9 s$	d^{10}	$d^8 s^2$		
d-function ^d		d^8	d^9	d^{10}	d^{10}		
Electron density	3d	8.100	8.094	8.074	8.201	8.023	
	4s	0.266	0.292	0.428	0.256	0.071	
	4p	0.518	0.576	0.843	0.502	0.060	
Spin fraction	f_s	0.22 %	0.32	0.40	0.72	0.438	0.538
	$f_{p\sigma}$	1.50 %	1.36	1.00	2.78	6.32	3.78

^a Before a single annihilation. ^b Ref. 23. ^c Ref. 7.

^d d-orbital exponents and coefficients for d^8 -configuration etc.

hand, in the calculation I, $f_{p\sigma}$ is larger than that of the calculation III, while f_s is too small. Thus, any one of three parametrizations I, II, III gives at least an unreasonable result.

When the d^8s^2 valence state and a d-function for d^{10} configuration are adopted, values of f_s and $f_{p\sigma}$ increase and become more agreeable with experimental values. (See the calculation IV in Table 1.) Since a d-function for d^{10} configuration results in large overlap integrals relative to that for d^8 configuration, the larger resonance integrals between d-orbitals of the nickel atom and s- and p-orbitals of the fluorine atom brings about larger values of f_s and $f_{p\sigma}$. It seems unreasonable at first glance that a d-function for d^{10} configuration is used in spite of the d^8s^2 valence state. However, d-functions are considered as a parameter in this work since orbital exponents and coefficients of double- ζ d-function are used in calculating overlap integrals which is necessary in the empirical Wolfsberg-Helmholz approximation. Thus, a d-function for d^n configuration and $d^{n-2}s^2$ valence state are used in the standard MO calculations.

Electron Densities. Table 2 gives electron distributions which are calculated by the INDO type MO method, in which the $d^{n-2}s^2$ valence state and a d-function for d^n configuration are used.

In NiF_6^{4-} , the INDO type MO method gives similar electron

Table 2 Electron densities and atomic charges^a

Compounds	Total density					Atomic charge		
	Metal atom		Halogen atom			Metal		Halogen
	3d	4s	4p	s	P _σ	P _π		
NiF ₆ ⁴⁻	8.138	0.251	0.465	1.922	1.945	3.991	+1.146	-0.858
NiCl ₆ ⁴⁻	8.151	0.449	0.764	1.923	1.864	3.985	+0.636	-0.773
FeF ₆ ³⁻	5.373	0.272	0.500	1.908	1.926	3.974	+1.855	-0.809
obsd. ^b							+1.33	
MnF ₆ ^{4- c}	5.190	0.212	0.429	1.922	1.954	3.985	+1.169	-0.861
MnCl ₆ ⁴⁻	5.193	0.404	0.711	1.929	1.972	3.980	+0.692	-0.782
MnBr ₆ ⁴⁻	5.190	0.444	0.760	1.936	1.852	3.980	+0.607	-0.768
CrF ₆ ⁴⁻	3.701	0.226	0.479	1.878	1.919	3.968	+1.594	-0.766
obsd. ^b							+1.53	
VF ₆ ⁴⁻	3.449	0.192	0.447	1.885	1.956	3.977	+0.913	-0.819
MnCl ₄ ²⁻	5.247	0.394	0.780	1.864	1.933	3.848	+0.579	-0.645
CuCl ₄ ²⁻	9.197	0.471	0.599	1.904	1.807	3.973	+0.732	-0.683
D-V-W ^d	9.08	0.10	0.15	1.97	1.92	3.99	+1.54	-0.88

^aThe INDO type MO method, in which the dⁿ⁻²s² valence state and d-function

for dⁿ-configuration are used. Single annihilations scarcely affect on

these results. ^bRef. 38. ^cMn-F=2.095 Å. See Footnote j of Table 3. ^eRef.39.

densities on 3d, 4s and 4p orbitals of the Ni atom, while those obtained by the former method is slightly less than those by the latter one. (Compare the results on NiF_6^{4-} in Table 2 with those of the calculation IV in Table 1.) The inclusion of one-center exchange repulsion integrals scarcely affect electron density.

In FeF_6^{3-} and CrF_6^{3-} , the net charges on the central metal ion have been obtained experimentally.³⁸⁾ Our results fairly agree with experimental values, as shown in Table 2. In NiF_6^{4-} and CuCl_4^{2-} , calculated electron densities on the 4s and 4p orbitals of the central metal ions are remarkably larger than the results of ab initio MO calculations,^{23, 39)} on which our opinion is presented in the previous paragraph. In these complexes, our smaller net charges on the central metal ion are due to the larger electron densities on 4s and 4p orbitals, relative to those of ab initio MO calculations.

In NiX_6^{4-} and MnX_6^{4-} ($\text{X}=\text{F}, \text{Cl}$ or Br), positive net charge on the central metal ion and the negative net charge on the ligand decrease in the order $\text{F} > \text{Cl} > \text{Br}$. This result is reasonable since the electronegativities of halogen decrease in this order. While electron densities on the s and p_π orbitals of the halogen scarcely depend on the kinds of halogens, those on the p_σ orbital decrease in the order $\text{F} > \text{Cl} > \text{Br}$. From this result, it is expected that the contri-

bution of halogen's p_{σ} -orbital to metal-halogen bond increases in the order $F < Cl < Br$.

In $MnCl_4^{2-}$, the net charges on the Mn and Cl atoms are smaller than those of $MnCl_6^{4-}$. This result suggests that electrons are donated from ligands to the metal ion more strongly in $MnCl_4^{2-}$ than those in $MnCl_6^{4-}$. More precise inspection of the electron densities reveals the strong electron donation in $MnCl_4^{2-}$ is resulted from the formation of strong π -bond between the Mn and Cl atoms; that is, electron densities on $3p_{\pi}$ -orbitals of the Cl^- ligand are considerably smaller than those of $MnCl_6^{4-}$, while that on the $3p_{\sigma}$ -orbital in $MnCl_4^{2-}$ is larger than that in $MnCl_6^{4-}$.

Metal-Halogen Bonding Nature. In order to investigate the metal-halogen bonding nature, E_{MX} (M=metal atom, X=halogen atom.) is divided into $E_{MX(s)}$, $E_{MX(p)}$, $E_{M(d)X}$ and $E_{M(s+p)X}$. Results are given in Table 3.

The absolute values of $E_{M(s+p)X}$ are remarkably large and do not depend so largely on the kinds of central metals, which suggests the 4s and 4p orbitals participate to the metal-halogen covalent bond to the almost same degree in all complexes. The absolute values of $E_{M(d)X}$ depend largely on the kinds of the metal atoms and increases in the order $Ni(II) < Mn(II) \sim Fe(III) < Cr(III) \sim V(II)$, which suggests the contribution of 3d-orbitals to the metal-halogen bond increases

Table 3 Metal-halogen bonding natures^a

(A) Effect of metal atom on metal-halogen covalent bond

Metal atom	Ni(II)	Fe(III)	Mn(II) ^b	Cr(III)	V(II)
$E_{M(d)X}$	-0.882 _{ev}	-1.903	-1.383	-4.909	-4.445
$E_{M(s+p)X}$	-7.042	-7.451	-6.405	-7.622	-7.229

(B) Effect of halogen atom on metal-halogen covalent bond

Halogen atom	F^b	MnX_6^{4-}		NiX_6^{4-}	
		Cl	Br	F	Cl
$E_{MX(s)}$	-5.770 _{ev}	-3.349	-2.925	-5.844 _{ev}	-3.779
$E_{MX(p)}$	-2.018	-3.793	-4.012	-2.079	-4.117

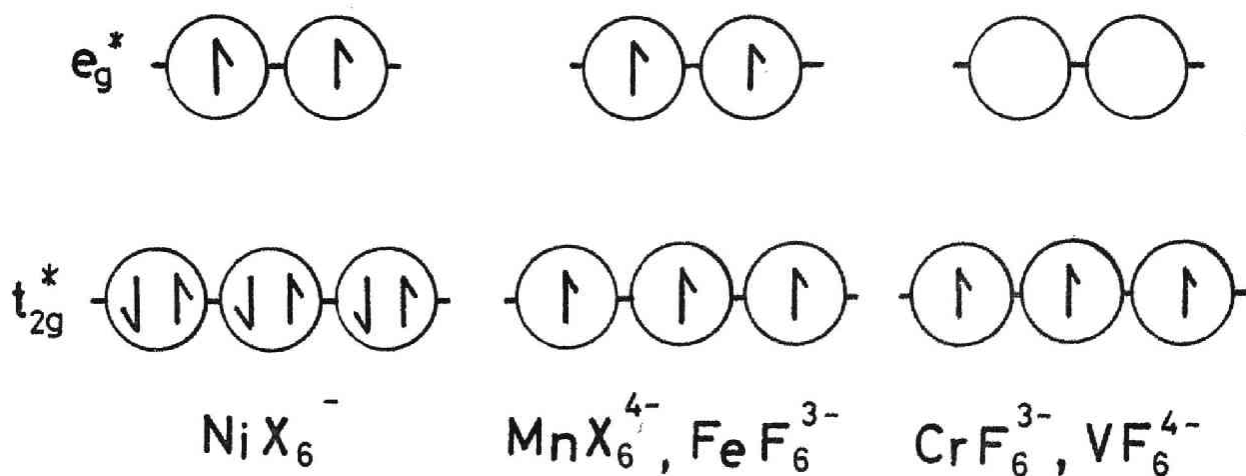
^a The INDO type MO method, in which the $d^{n-2}s^2$ valence state and the d-function for d^n -configuration are used. These data are results after a single annihilation. ^b $Mn-F=2.095 \text{ \AA}$, which is obtained from $KMnF_3$.³ While MO calculation is also carried out for $Mn-F=2.31 \text{ \AA}$, its result is not given in this table, since $2.31 \text{ \AA}$ is the Mn-F distance in NaF lattice, and since its value seems too large relative to the M-F distance in the other complexes.

in this order. This increasing order agrees with the decreasing tendency of numbers of electrons hold in the molecule; the increasing numbers of electrons results in the more electrons in anti-bonding MO's, e_g^* and t_{2g}^* , since these anti-bonding orbitals are occupied as shown in Fig. 2.

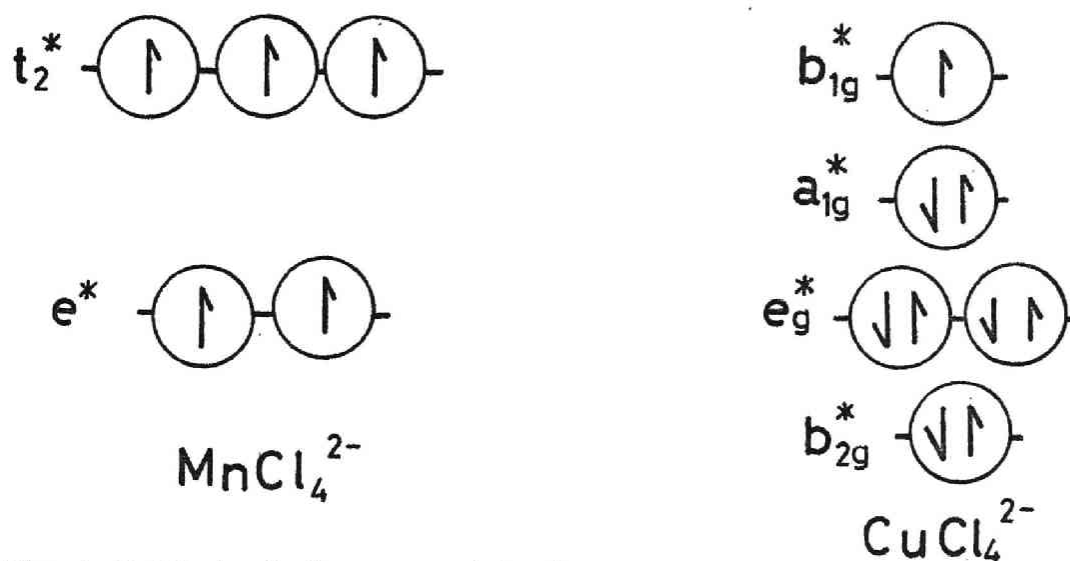
$E_{MX(s)}$ and $E_{MX(p)}$ of MnX_6^{4-} and NiF_6^{4-} are also given in Table 3. The absolute value of $E_{MX(s)}$ decreases in the order $F > Cl > Br$ and that of $E_{MX(p)}$ increases in the order $F < Cl < Br$. These results suggest that the contribution of halogen's s-orbital to metal-halogen bond decreases in the order $F > Cl > Br$ and that the contribution of halogen's p-orbital increases in the order $F < Cl < Br$. This bonding natures agree with that expected from electronegativities of halogens; as the electronegativity decreases, the s-character of the bond decreases and the p-character increases.

Spin-Fractions on the Ligands. Results are given in Table 4 and 5, compared with experimental values^{2, 4, 7, 11)} and previously calculated ones^{19, 20, 44)} In Table 4, the mark "aa" represents the results after a single annihilation proposed by Amos-Sneyder.⁴¹⁾ While the CNDO type MO method is inferior to the INDO type one as described below, results calculated by the former are also given in Table 4 for comparison.

INDO type MO calculations gives smaller values of f_s , and $f_{p_\sigma} - f_{p_\pi}$ than the CNDO type MO calculations do, in all



The e_g^* MO includes the s - and p_σ -orbitals of the ligand, and the t_{2g}^* MO does the p_π -orbitals.



The t_2^* MO includes p_σ -orbitals of ligands and the e^* MO does s - and p_σ -orbitals.

The b_{1g}^* MO includes s - and p_σ -orbitals of ligands.

Fig. 2. Schematic representations of MO's mainly contributed from metal's d -orbitals.

Table 4 Spin fractions on the F^- ligand(A) NiF_6^{4-}

	Method	f_s (%)	$f_{p\sigma} - f_{p\pi}$ (%)	M-F distance (Å)
Ours	INDO-d ⁸	0.10	0.80	2.00 ^g
	INDO-d ¹⁰	0.49	1.80	
	INDO-d ¹⁰ -aa	0.50	1.79	
Clack ^b	CNDO/II-B	0.02	0.33	1.99 ^g
	CNDO/II-G	0.15	1.39	
Brown ^c	MCZDO	—	0.46	2.00 ^g
obsd.	NMR ^d	0.538	3.78	2.00 ^g
	ESR ^e	0.490	4.51	1.99 ^g

(B) MnF_6^{4-}

	Method	f_s (%)	$f_{p\sigma} - f_{p\pi}$ (%)	M-F distance (Å)
Ours	CNDO-d ⁵	0.35	1.32	2.095 ^g
	INDO-d ⁵	0.11	0.74	
	INDO-d ⁷	0.71	1.29	
	INDO-d ⁷	0.38	1.05	2.31 ^g
	INDO-d ⁷ -aa	0.40	1.09	
Clack ^b	CNDO/II-B	0.12	1.17	2.00
	CNDO/II-G	0.34	2.25	
Brown ^c	MCZDO	—	1.98	2.00 ^g
obsd.	NMR ^g	0.52	0.18	2.00 ^g
	ESR ^e	0.47	0.80	2.00 ^g
	ESR ^e	0.41	1.30	2.31

Table 4. (Continued)

(C) FeF_6^{3-}

	Method	f_s (%)	$f_{p_\sigma} - f_{p_\pi}$ (%)	M-F distance ($\text{\AA}$)
Ours	INDO-d ⁶	0.22	2.49	1.994
	INDO-d ⁶ -aa	0.25	2.74	
	INDO-d ⁸	0.94	3.76	
Clack ^b	CNDO/II-B	0.15	7.97	1.994
	CNDO/II-G	0.44	7.38	
Brown ^c	MCZDO	—	5.14	1.910
obsd.	ESR ^e	0.763	3.3	1.994

(D) CrF_6^{3-}

	Method	f_s (%)	$f_{p_\sigma} - f_{p_\pi}$ (%)	M-F distance ($\text{\AA}$)
Ours	CNDO-d ⁴	0.0	-0.70	1.933
	INDO-d ⁴	-0.15	-1.49	
	INDO-d ⁶	-0.19	-1.79	
	INDO-d ⁶ -aa	-0.11	-1.49	
Clack ^b	CNDO/II-B	-0.003	-0.415	1.93
	CNDO/II-G	-0.01	-0.74	
Brown ^c	MCZDO	—	-4.74	1.933
obsd.	NMR ^h	-0.021	-4.90	1.933
	ESR ^e	-0.031	-4.76	1.994

Table 4 (Continued)

(E) VF_6^{4-}

	Method	f_s (%)	$f_{p_\sigma} - f_{p_\pi}$ (%)	M-F distance (Å)
Ours	CNDO-d ⁵	0.0	-0.92	1.994 ⁱ
	INDO-d ⁵	-0.17	-0.88	
	INDO-d ⁵ -aa	-0.10	-0.78	
Clack ^b	CNDO/II-B	0.0	-0.2002	1.994
	CNDO/II-G	0.0	-0.30	
obsd.	ESR ⁱ	-0.072	-2.8	1.994
	ESR ^e	-0.019	-4.15	1.994

^aThe $d^{n-2}s^2$ valence state is used in all MO calculations.

d^8 etc. represents that the d-function for d^8 -configuration is used. "aa" means the results after a single annihilation.

^bRef. 20. "B" and "G" represent that the Burns' orbital exponent and the Guterman's one are used respectively.

^cRef. 19. ^dRef. 7. ^eRef. 11. ^fW. H. Bauer, Acta Cryst., 11, 588 (1958). ^gRef. 4. ⁱRef. 2. ^jSince NMR and ESR give so

different results on $f_{p_\sigma} - f_{p_\pi}$ each others, two bond lengths of Mn-F are examined.

Table 5 Spin fractions on the Cl^- ligand^a

Compounds	f_s (%)		$f_{p_\sigma} - f_{p_\pi}$ (%)	
	calc.	obsd.	calc.	obsd.
NiCl_6^{4-}	0.33	0.58 ^b	2.10	7.3 ^b
MnCl_6^{4-}	0.37	0.4 ^c	1.50	3.9 ^c
MnCl_4^{2-}	0.25	—	-2.71 ^d	—
CuCl_4^{2-}	0.27	0.61 ^b	5.09	11.9 ^b

^aINDO type MO calculations, in which the $d^{n-2}s^2$ valence state and the d-function for d^n configuration are used. Data are after a single annihilation. In CuCl_4^{2-} , the d-function for d^{10} configuration is used. ^bRef. 40. ^cRef. 13. ^dThis value is one of before annihilation, since our coordinate system can not give spin fractions on p_σ and p_π orbitals after annihilation.

complexes. In Table 4, it is also noted that the INDO type MO method in which the $d^{n-2}s^2$ valence state and the d-function for d^n configuration (the standard parametrization) are used gives the most reasonable results.

As shown in Fig. 2, NiF_6^{4-} , MnF_6^{4-} , and FeF_6^{3-} contain $t_{2g}^6 e_g^2$ and $t_{2g}^3 e_g^2$ configurations, respectively. Metal-fluorine covalency results in positive spin fractions on 2s and $2p_\sigma$ orbitals of the F^- ligand in NiF_6^{4-} and does positive ones in 2s, $2p_\sigma$, and $2p_\pi$ orbitals in MnF_6^{4-} and FeF_6^{3-} . In these complexes, both CNDO and INDO type MO methods can give reasonable results on spin fractions, as shown in Table 4. Our results are more agreeable with experiments than the previously calculated ones.^{19, 20)} Single annihilations hardly affect values of f_s and $f_{p\sigma} - f_{p\pi}$.

In CrF_6^{3-} and VF_6^{4-} which contain t_{2g}^3 configurations as shown in Fig. 2, metal-fluorine covalency brings positive spin fractions into only two $2p_\pi$ orbitals of the F^- ligand. The spin fraction is also observed on the 2s orbital of the F^- ligand in these complexes, which is accepted to be due to the spin polarization.^{4, 10)} The CNDO type MO method fails to give spin fraction on the 2s orbital of the F^- ligand; that is, the CNDO type MO method can not give spin fraction due to the SP mechanism. The INDO type MO method can give the spin fraction on the 2s orbital of the F^- ligand. In CrF_6^{3-} , the

value of f_s is too large and the absolute one of $f_{p\sigma} - f_{p\pi}$ is too small relative to experimental values. The single annihilation, which gives almost complete eigenfunction of s^2 (See Table 7.), brings about remarkably large changes in values of f_s and $f_{p\sigma} - f_{p\pi}$. While the value of f_s is reduced by this treatment, its value after annihilation is still too large. In VF_6^{4-} , the value of f_s after annihilation agrees well with experimental value, while the value of $f_{p\sigma} - f_{p\pi}$ is too small relative to experimental value. While our results can not always agree with experiments, these are better than the results obtained by the previous CNDO/II MO method.²⁰⁾

Results for chloro complexes are given in Table 5, which are calculated by using the INDO type MO method. Calculated values of f_s fairly agrees with experimental values except for $CuCl_4^{2-}$. Values of $f_{p\sigma} - f_{p\pi}$ in chloro complexes are larger than those in fluoro complexes, which is reproduced by our calculations, while calculated values are considerably smaller than the experimental values, as shown in Table 5.

As described above, the CNDO type MO method can not give a spin fraction due to the SP mechanism, while the INDO type MO method can give it; that is, the CNDO type one is inferior to the INDO type one. It is worthwhile to compare these two methods in more detail. In Table 6, MO energies and MO coefficients are given. In NiF_6^{4-} , the CNDO type MO method gives

Table 6 Comparison between the CNDO type and INDO type MO methods

(A) NiF_6^{4-}

MO	Method ^a	ϵ (eV) ^b	Eigen vector ^c
$2t_{2g}^*$	CNDO	α 7.848 0.783	$d_{xz} - 0.311 [(1z) - (2z) + (5x) - (6x)]$
		β 7.848 0.783	" -0.311 "
	INDO	α 7.621 0.916	" -0.201 "
		β 8.818 0.952	" -0.153 "
t_{1g}	CNDO	α 6.876	$0.5 [(1z) - (2z) - (5x) + (6x)]$
		β 6.876	"
	INDO	α 4.619	"
		β 4.658	"

(B) CuCl_4^{2-}

MO	Method ^d	ϵ (eV)	Eigen vector
b_{2g}^*	CNDO	α -7.432 0.953	$d_{xy} + 0.151 [(1y) - (2y) + (3x) - (4x)]$
		β -7.432 0.953	" +0.151 "
	INDO	α -8.488 0.959	" +0.141 "
		β -8.108 0.949	" +0.157 "
a_{2g}	CNDO	α -3.390	$0.5 [(1y) - (2y) + (3x) - (4x)]$
		β -3.390	"
	INDO	α -4.229	"
		β -4.194	"

Table 6 (continued)

^aThe d^8s^2 valence state and the d-function for d^{10} -configuration are used. ^bThese positive MO energies would be due to the neglect of effects of cation and/or crystal lattice.¹⁹ The extra potential, such as crystal lattice, do not give so great effect on spin fractions.¹⁹ ^c(1z) etc. means the p_z orbital of the ligand 1. (See Fig.1.) ^dThe $d^{10}s$ valence state and the d-function for the d^{10} -configuration are used.

quite the same MO energies and almost the same MO coefficients between α -spin and β -spin MO's, while the INDO type MO method gives considerably different MO energies and MO coefficients. Also, similar results on CuCl_4^{2-} are given in Table 6. Thus, the CNDO type MO method fails to give polarization effects on MO energies and coefficients.⁴²⁾ These results reveal that the CNDO type MO method is inferior to the INDO one even in NiF_6^{4-} , in which the former method can give reasonable results on f_s and $f_{p\sigma}$ as well as the latter one.

Spin Transfer Mechanism. Spin fractions are divided into two components accordingly to the method of Nakatsuji et al.⁴³⁾; the components through the SD mechanism and the other one through the SP mechanism. Results are given in Table 7, together with expectation values of S^2 before and after a single annihilation.

In all complexes, unpaired electrons are localized in the d-orbital of the central metal ion, which supports the treatment of the ligand field theory on these complexes.

Spin fractions on the ligands are mainly contributed by the SD mechanism in NiX_6^{4-} , MnX_6^{4-} and FeF_6^{3-} . It is noted, however, that the SP mechanism considerably brings negative spin fractions on p_π orbitals of the ligand in MnX_6^{4-} . In CrF_6^{3-} and VF_6^{4-} , the SD mechanism brings about positive spin fractions on two $2p_\pi$ orbitals of the F^- ligand and the SP

Table 7 Spin appearing mechanism^a

Complex		Metal ion				Ligand ion			s ² b	
		3d _{t_{2g}}	3d _{e_g}	4s	4p	s	p _σ	p _π	ba	aa
NiF ₆ ⁴⁻	SD	0.0%	93.12%	0.0%	0.0%	0.51%	1.78%	0.0%	2.000	2.000
	SP	0.0	0.0	0.11	0.0	-0.01	0.01	0.0		
NiCl ₆ ⁴⁻	SD	0.0	92.45	0.0	0.0	0.35	2.16	0.0	2.000	2.000
	SP	0.0	0.0	0.28	0.09	-0.02	-0.05	-0.01		
FeF ₆ ³⁻	SD	96.98	85.86	0.0	0.0	1.00	3.71	0.75	8.750	8.750
	SP	0.0	0.0	0.14	0.02	-0.04	0.03	-0.01		
MnF ₆ ^{4-c}	SD	99.34	94.53	0.01	0.0	0.46	1.37	0.16	8.750	8.750
	SP	0.0	0.0	0.61	0.18	-0.06	-0.12	0.0		
MnCl ₆ ⁴⁻	SD	98.77	92.16	0.03	0.0	0.47	2.09	0.30	8.751	8.750
	SP	0.01	0.01	1.42	0.52	-0.10	-0.37	-0.02		
MnBr ₆ ⁴⁻	SD	98.81	92.24	0.04	0.01	0.39	2.20	0.29	8.752	8.750
	SP	0.02	0.02	1.77	0.66	-0.09	-0.50	-0.02		
CrF ₆ ³⁻	SD	95.76	-0.04	0.0	0.0	0.0	0.01	1.04	3.753	3.750
	SP	0.03	1.34	0.30	0.14	-0.11	-0.46	0.0		
VF ₆ ⁴⁻	SD	97.42	0.01	0.0	0.0	0.0	0.0	0.64	3.751	3.750
	SP	0.0	0.49	0.21	0.11	-0.10	-0.15	0.0		
MnCl ₄ ^{2-d}	SD	91.43	96.59	0.02	2.54	0.52	1.90 ^e		8.752	8.750
	SP	0.12	0.02	1.26	0.74	-0.27	-0.23 ^e			
		d _{x²-y²}	d _{z²}	4s	4p	3s	3p _σ	3p _π		
CuCl ₄ ^{2-f}	SD	79.00%	0.0%	0.0%	0.0%	0.27%	4.98%	0.0%	0.750	0.750
	SP	0.0	0.04	-0.21	-0.11	0.0	0.10	-0.01		

^aThe INDO type MO calculation, in which the dⁿ⁻²s² valence state

Footnote of Table 7. (Continued)

and the d-function for d^n -configuration are used. These data are spin fraction per an orbital after annihilation.

^b"aa" and "ba" mean after and before a single annihilation, respectively. ^cMn-F=2.31 Å. ^dIn $MnCl_4^{2-}$, t_{2g} and e_g should be replaced by t_2 and e , respectively. ^eThese values are spin fraction on a p-orbital. In our coordinate system, spin fractions on p-orbital after annihilation can not be divided into those on p_σ and p_π orbitals. ^fIn $CuCl_4^{2-}$, the other 3d-orbitals and 4p orbital do not have spin fractions.

mechanism induces negative spin fractions on $2s$ and $2p_{\sigma}$ orbitals of the F^{-} ligand. In $MnCl_4^{2-}$ and $CuCl_4^{2-}$, spin fractions on the ligand are mainly due to the SD mechanism, while in $MnCl_4^{2-}$ the SP mechanism considerably contributes to f_s and f_p .

The SP mechanism also induces spin fractions on $4s$ and $4p$ orbitals of the central metal ion in all complexes. Furthermore, in CrF_6^{3-} and VF_6^{4-} , its mechanism also induces positive spin fractions on $3d_{eg}$ orbitals.

Spin transfer through the SP mechanism increases $F < Cl < Br$ in MnX_6^{4-} and NiX_6^{4-} as shown in Table 7. It is interesting that this increasing order agrees with the decreasing one of spectrochemical series.

In conclusion, the INDO type MO method used here can give fairly agreeable results on spin fractions with experiments. This method is expected to be used in studies on electronic structures of open-shell transition metal complexes.

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Chapter 4. Ferrocene and Cobalticenium Ion

§ 1. Introduction

The electronic structure of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, has been of interest both theoretically and experimentally since its discovery in 1951.¹⁾

Recently, the new experimental data such as detailed analysis of optical absorption spectra¹⁻⁴⁾ and photoelectron spectra⁵⁻⁸⁾ were reported. On the other hand, the previous semi-empirical⁹⁾ and ab initio MO calculations¹⁰⁾ and the SCF X_α , SW calculations^{11, 12)} are situated on the stage of progress. The level ordering for the molecular orbitals of ferrocene is still obscure because Koopmans' theorem breaks down in this case¹⁰⁾ and the optical absorption spectra are not also explained satisfactorily by theoretical works.

In this paper, two kinds of the semi-empirical MO method are applied to calculate the electronic structures of the iso-electronic metallocene, ferrocene and cobalticenium ion. First, the parametrization of the two methods, one of which is a CNDO type method named Method I and the other of which is a INDO type method named Method II, is set up. Then the calculated results of transition energies, orbital energies and charge distributions are discussed as compared with the experimental facts.

§ 2. Method of Calculation

The two kinds of the semi-empirical SCF MO methods, Method I

and Method II, are adopted in this calculation. Method I (complete neglect of differential overlap) type one already used in several transition-metal complexes.¹³⁾ Method II is an INDO (intermediate neglect of differential overlap) type one.¹⁴⁾ The two methods are employed for the closed shell-molecules and only Method II is used for the open shell-molecule, ferricenium ion which is the ionized species of ferrocene, by means of the unrestricted Hartree-Fock (UHF) approximation.¹⁵⁾

Only the outline of integral evaluations in the both methods is demonstrated here. The off-diagonal core integral, H_{rs} ($r \neq s$), is evaluated by the Wolfsberg-Hermholz approximation,¹⁶⁾

$$H_{rs} = -K S_{rs} (I_r + I_s) \quad (r \neq s)$$

where K is a parameter, S_{rs} is the overlap integral between AO r and AO s , and I_r is the valence-state ionization potential of AO r . Overlap integrals are calculated with the single Slater-type orbitals by Clementi and Raimondi¹⁷⁾ and especially with the double- ζ functions for metal 3d orbitals.¹⁸⁾ Overlap integrals for the metal-carbon bond in ferrocene are shown in Table 1 as the function of the d electron number. The integral values in d^8 configuration change to be small toward right with about 20 % reduction corresponding to the orbital contraction.¹⁸⁾

The one-center Coulomb repulsion integrals are obtained by the Pariser's approximation.¹⁹⁾ In Method II, the charge of the metal atoms are taken to be both neutral and single positive (abbreviated N and P respectively) as cited in Table 2. The

Table 1 Overlap integrals for the metal-carbon bond in ferrocene.

configuration	d ⁸	d ⁷	d ⁶
ζ_1	5.35	5.35	5.35
ζ_2	1.80	2.00	2.20
3d _σ (Fe) - 2s(C)	0.1577	0.1190	0.0899
3d _σ (Fe) - 2p _σ (C)	0.1532	0.1315	0.1097
3d _π (Fe) - 2p _π (C)	0.1140	0.0852	0.0637

two-center Coulomb repulsion integrals are evaluated according to the Ohno's formula.²⁰⁾ The one-center exchange integrals for Method II are derived from the data of the atomic spectra.²¹⁾

Thus the choice of the parameters in the present paper remains to be done about the value of K, the configuration of the d electron and, only in Method II, the charge of the metal atoms.

The bond lengths were taken to be Fe - C = 2.03 Å, Co - C = 2.10 Å, C - C = 1.43 Å, and C - H = 1.09 Å.²²⁾ The cyclopentadienyl (cp) ring was assumed to be planar. The symmetry of ferrocene and cobalticenium ion was set to be D_{5d} except for

Table 2 One-center Coulomb repulsion integrals for the metal atoms.

		Fe			Co		
		3d	4s	4p	3d	4s	4p
Method I ^a		15.37	7.38	6.10	16.04	7.67	6.25
Method II	N ^b	11.77	6.90	4.17	12.32	7.05	4.30
	P ^b	15.94	8.19	5.72	16.50	8.46	5.84

a L. Di Sipio, E. Tondello, F. De Michelis, and L. Oleari, Chem. Phys. Letters, 11, 287 (1971).

b N and P are the abbreviation of neutral and positive respectively where the Pariser's approximation is applied correspond to the charge of the atoms. Values are calculated from the formula by Anno and Sakai (T. Anno and Y. Sakai, Theoret. chim. Acta(Berl.), 18, 208 (1970)).

the section discussing the symmetry of ferrocene.

§ 3. Results and Discussion

The choice of the parameter is first done to fit the calculated transition energies of ferrocene to the experimental results. Then the calculated quantities with the best parameter are discussed.

Transition energies of ferrocene. Recently the detailed analysis of the ferrocene ultraviolet and visible spectra made so remarkable progress that a large number of absorption bands were able to be assigned.¹⁻⁴⁾ Therefore, the electron transition seems to be utilized as an indication of the reliability of theoretical methods.

The calculated transition energies by the two methods where the configuration interactions are further considered among limited number of singly excited configurations are presented in Tables 3-5 together with the experimental results. The electron absorption number by Armstrong et al.²⁾ is cited in the tables. The absorptions are grouped in four: singlet-triplet d-d transitions, I-III; singlet-singlet d-d transitions, IV_a-V; singlet-singlet symmetry-forbidden transitions, VI-XI; singlet-singlet symmetry-allowed charge-transfer transitions, XII and XIII.

The 3d functions of the first transition-metal atoms are scarcely affected by the electrons occupying the outer shells, i. e., the functions change according to the d electron number not to

Table 3 Singlet-singlet transition energies^a (in eV) of ferrocene by Method I

	Obsd. ^b	State	d ⁶ (K=1.1)	d ⁷ (K=1.1)	d ⁸ (K=1.1)	d ⁸ (K=0.9)
IV _a	2.70	¹ E _{1g} (a _{1g} +e _{1g})	1.57	2.25	3.16	2.15
IV _b	2.98	¹ E _{2g} (e _{2g} +e _{1g})	2.55	3.25	4.33	2.86
V	3.82	¹ E _{1g} (e _{2g} +e _{1g})	2.56	3.26	4.35	2.86
VI	4.67	CT	¹ E _{2u} 7.64 ¹ A _{1u} 7.80	6.98 7.29	6.32 6.81	6.01 5.96
VII+VIII	5.02	gerade	¹ A _{2g} 7.02	¹ E _{2g} 6.83	6.24	¹ A _{1g} 5.95
IX	5.23	¹ A _{1g} or ¹ E _{1g}	¹ E _{1g} 7.06	7.26	6.93	6.16
X+XI	5.82	gerade	¹ E _{2g} 7.45	¹ A _{2g} 7.16	6.80	6.02
XII	6.31 (0.69)	¹ A _{2u} or ¹ E _{1u}	¹ E _{1u} 7.64	7.39	6.96	6.18
XIII	6.58 (0.04)	¹ A _{2u} or ¹ E _{1u}	¹ A _{2u} 8.08	7.67	7.37	6.80

^a configuration interactions are considered among limited number of singly excited configurations. In each symmetry group several configurations are taken. The oscillator strengths are given in parentheses. ^b Ref. 1 and Ref. 2.

Table 4 Singlet-singlet transition energies^a (in eV) of ferrocene by Method II

	Obsd. ^b	State	d ⁷ P,K=0.9	d ⁷ P,K=1.0	d ⁸ P,K=0.8	d ⁸ P,K=0.9	d ⁸ N,K=0.9
IV _a	2.70	¹ E _{1g} (a _{1g} →e _{1g})	2.98	3.09	3.46	3.67	3.33
IV _b	2.98	¹ E _{2g} (e _{2g} →e _{1g})	2.19	3.09	3.56	3.91	3.42
V	3.82	¹ E _{1g} (e _{2g} →e _{1g})	2.19	3.11	3.56	3.71	3.42
VI	4.67	CT	¹ A _{1u} 3.88	4.46	3.90	4.49	3.95
			¹ E _{2u} 3.94	4.51	3.96	4.60	4.02
VII+VIII	5.02	gerade	¹ A _{2g} 4.83	5.49	4.91	6.40	5.15
IX	5.23	¹ A _{1g} or ¹ E _{1g}	¹ A _{1g} 5.87	6.32	5.40	6.35	5.17
X+XI	5.82	gerade	¹ E _{2g} 5.05	5.72	5.77	5.61	5.13
XII	6.31 (0.69)	¹ A _{2u} or ¹ E _{1u}	¹ A _{2u} 5.57 (0.65)	6.11 (0.79)	5.13 (0.15)	5.71 (0.19)	5.54 (0.43)
			¹ A _{2u} 6.03 (0.64)	6.62 (0.56)	6.09 (1.18)	6.72 (1.22)	6.25 (0.38)
XIII	6.58 (0.04)	¹ A _{2u} or ¹ E _{1u}	¹ E _{1u} 7.52 (0.09)	7.64 (0.08)	6.96 (0.001)	7.19 (0.007)	5.31 (0.02)

a See footnote a of Table 3.

b See footnote b of Table 3.

Table 5 Singlet-triplet transition energies^a (in eV) of ferrocene by the method II.

	Obsd. ^b	State	d ⁷	d ⁷	d ⁸	d ⁸	d ⁸
			P, K=0.9	P, K=1.0	P, K=0.8	P, K=0.9	N, K=0.9
I	2.35	³ E _{1g}	1.23	2.31	2.97	3.07	2.76
II	2.59 ^c	³ E _{2g}	1.23	2.31	2.99	3.32	2.76
III	2.78 ^c	³ E _{1g}	2.37	2.49	2.99	3.17	2.84

a See footnote a of Table 3.

b Ref. 1.

c Sohn et al. estimated by means of the ligand-field parameters resultant from the analysis of the spin-allowed d-d bands. See ref. 1.

the charge of atoms.¹⁸⁾ Therefore, the 3d function represented by d^8 means the expanded orbital of the neutral atom and d^6 implies that the function can be regarded as both the orbital in $3d^6 4s^2$ configuration of the neutral atom and the orbital in $3d^6$ (or $3d^6 4s$) configuration of the doubly (or singly) charged atom.

In Method I, the parameter K is first taken to be 1.1 as is in ref. 13. The influence of d number on the calculated transition energies is largest for the absorptions IV_a-V (Table 3). The calculated results with the d^7 configuration become close to the observed values for the absorptions IV_a-V , but too large for the others. Then, the dependence on the Coulomb repulsion integrals of the 3d orbital is tested. The reduction of 2 eV (or 4 eV) from the one-center Coulomb repulsion integrals of the only 3d orbitals influences merely for the absorptions XII and XIII less than for the absorptions IV_a-V . The variation of K affects all of the core-resonance integrals, H_{rs} , not only between the metal and the ligand orbitals but also among the ligand orbitals. Therefore, 0.9 is taken as K with the d^8 configuration. All kinds of the calculated transition energies became considerably close to the observed data.

In Method II, the two sets of one-center Coulomb repulsion integrals are adopted for the metal atoms (Table 2). The set N, that is derived from the spectroscopic data of the neutral atom with the Pariser's approximation,¹⁹⁾ gives slightly small values especially for the allowed CT transitions, XII and XIII (Table 4).

The set P, based on the singly positive atom, resembles the set in Method I and seems to be better for further use in the present case. A number of the combinations of the two parameter, K and the d electron number, with the set P was tested to fit to the experiment. The combination of 1.0 and d^7 was found to be best for both singlet-singlet (Table 4) and singlet-triplet (Table 5) transitions.

The two sets of the parameters are found as the best in each method. However, the assignments of transitions are different: for example, the first allowed CT band, XII, and the symmetry-forbidden bands, VII-IX. It is difficult to distinguish the difference between the two parameter sets, because the two methods are not based on the same integral parameters. Both d^8 in Method I and d^7 in Method II exceed d^6 configuration of the free atom or positive ion in the ground state. Therefore, the size of the iron 3d orbitals in ferrocene seems to be expanded from that in free regardless of charge. The fact that the Fe-C bond length of ferrocene, $2.03 \text{ \AA}$, is longer than that of $\text{Fe}(\text{CO})_5$, $1.84 \text{ \AA}$ ²³⁾ may support the present situation.

Orbital energies of ferrocene. The highest occupied molecular orbital has been discussed for a long time as to be whether e_{2g} or a_{1g} until Coutière et al. ¹⁰⁾ revealed that Koopmans' theorem breaks down in ferrocene. Now the photoelectron spectrum and the electronic configuration of the ionized molecule obtained on the basis of ESR measurements can not be used to decide immediately

the sequence of the molecular orbitals because of the different extent of the electron rearrangement which occurs upon ionization, depending on the nature of the orbital involved in the ionization process.

Orbital energies of ferrocene by the two methods are given in Table 6 together with the ab initio H-F results.¹⁰⁾ In the three methods the highest occupied orbital is neither e_{2g} nor a_{1g} , but is e_{1u} or e_{1g} , which is essentially the cyclopentadienyl π orbital. Whereas the SCF X_α SW method brings a_{1g} as the highest.¹²⁾

Ionization potentials of ferrocene calculated by Method II are compared with those obtained by both the other method and the photoelectron spectra in Table 7. Ionization potentials are given as the energy difference in total energies between the neutral molecule and the ionized radical. The agreement of values between calculation and experiment is not so good but the assignment of the first and second ionizations coincide except for the SCF X_α SW method where the sequence is reversed.¹²⁾ Of course Method II and the ab initio H-F method imply that the ground state of ferricenium ion is $^2E_{2g}$ as shown on the basis of ESR measurement.²⁴⁾

The differences between the ionization potentials mentioned above and those derived from Koopmans' theorem (cited in parentheses in the table) give the extent of the electronic rearrangement occurring upon ionization. The amounts of the electronic

Table 6 Orbital energies (in eV) of ferrocene and Cobalticenium ion

	Fe(cp) ₂			Co(cp) ₂ ⁺	
	Method I d ⁸ ,K=0.9	Method II d ⁷ ,P,K=1.0	ab initio H-F ^a	Method I d ⁹ ,K=0.9	Method II d ⁸ ,P,K=1.0
e _{1u}	-10.61	-9.53	-11.67	-15.33	-14.21
e _{1g}	-9.91	-11.68	-11.89	-15.49	-17.62
e _{2g}	-10.43	-11.59	-14.42	-16.72	-18.17
a _{1g}	-10.14	-12.39	-16.57	-18.11	-19.26
e _{2u}	-11.98	-13.91	-15.92	-16.96	-18.86
a _{2u}	-14.70	-14.40	-16.03	-19.93	-19.10
e _{2g}	-12.28	-14.60	-16.16	-19.05	-19.85

a Ref. 10.

Table 7 Comparison of the ionization potentials^a (in eV) of ferrocene calculated by the various methods with those measured by photoelectron spectroscopy

State	Method II d ⁷ , P, K=1.0	ab initio H-F ^b	SCF X _α ^c	Obsd. ^d
² E _{2g}	8.83(11.59)	8.3(14.4)	8.5	6.86
² A _{1g}	9.25(12.39)	10.1(16.6)	7.9	7.23
² E _{1g}	11.24(11.68)	11.2(11.9)	9.7	8.72
² E _{1u}	9.17(9.53)	11.1(11.7)	9.3	9.38
² E _{2u}	13.77(13.91)	— (15.9)	11.6	—
² A _{2u}	14.16(14.40)	15.5(16.0)	11.7	—

a The values calculated by the MO methods were obtained from differences in total energies as well as from Koopmans' theorem (given in parentheses).

b Ref. 10.

c Ref. 12.

d Ref. 5.

rearrangement are pretty large for both ${}^2E_{2g}$ and ${}^2A_{1g}$ states, where an electron is removed from the orbitals consisting mainly of the metal 3d orbitals, and are small for the other state where the unpaired electron distributes almost over the ligand.

Charge distribution of ferrocene. Electron density of ferrocene calculated by the present two methods given in Table 8 shows that the formal charge of iron atom is obtained to be positive but very close to zero different from the ab initio H-F result, where the iron atom has +1.23 as formal charge. The three methods have not so large discrepancy in electron density on the metal 3d orbitals, but the electron densities on the 4s and 4p orbitals by the present two methods are larger than that by the ab initio H-F method. Method II gives almost consistency of the d electron configuration between the assumption made at selecting orbital functions and the calculated result.

Symmetry of ferrocene. The equilibrium conformation of ferrocene has been proved to have both eclipsed (D_{5h}) configuration in vapor phase by the electron diffraction study ²⁵⁾ and staggered configuration (D_{5d}) in the solid state. ²²⁾ Calculation of ferrocene with D_{5h} symmetry was also performed by Method II with the same bond lengths as in D_{5d} configuration. Orbital energies, molecular orbital coefficients and transition energies are virtually identical between the two conformations. Comparison of total energy with a point charge approximation in core-core repulsion concludes that the D_{5d} conformer is more stable than the D_{5h} con-

Table 8 Charge density of ferrocene and cobalticenium ion

	Fe(cp) ₂			Co(cp) ₂ ⁺	
	Method I d ⁸ ,K=0.9	Method II d ⁷ ,P,K=1.0	ab initio H-F ^a	Method I d ⁹ ,K=0.9	Method II d ⁸ ,P,K=1.0
M	7.78	7.87	6.77	8.71	8.86
3d	6.52	7.10	6.51	7.37	8.08
4s,4p	1.26	0.77	0.25	1.34	0.78
3d _{xz} ,3d _{yz}	0.41	0.64	0.43	0.74	1.08
3d _{xy} ,3d _{x²-y²}	1.88	1.93	1.86	1.96	1.98
3d _{z²}	1.94	1.95	1.93	1.96	1.97
4s	0.37	0.39	0.00	0.39	0.38
4p _x ,4p _y	0.32	0.10	0.12	0.35	0.11
4p _z	0.25	0.18	0.01	0.26	0.19
C	4.08	4.02	4.31	4.03	3.96
2s	1.01	1.17	1.12	1.03	1.18
2p _x ,2p _y av.	0.98	0.89	1.07	0.99	0.90
2p _z	1.11	1.08	1.06	1.01	0.98
H	0.94	0.99	0.81	0.90	0.96

a Ref. 10.

former by about 1.6 kcal/mol. Therefore, a small rotation barrier seems to permit almost free rotation along the five-fold axis in the liquid state.

Cobalticinium ion. As an isoelectronic metallocene of ferrocene, cobalticinium ion, $\text{Co}(\text{cp})_2^+$, can be used to discuss further the details of the electronic structure of metallocene. A couple of electron transitions for $\text{Co}(\text{cp})_2^+$ are correlated to absorption number labeled for $\text{Fe}(\text{cp})_2$ in Table 9. For $\text{Co}(\text{cp})_2^+$, singlet-singlet d-d transitions, IV_a -V, became slightly larger and the allowed CT transition, XII, has considerably smaller value than for $\text{Fe}(\text{cp})_2$. Therefore, the intermediate transitions, should be assigned as VI-XI, can not be identified.

The parameter sets of the present two methods for $\text{Co}(\text{cp})_2^+$ were first taken as d^9 ($K=0.9$) for Method I and d^8 ($P, K=1.0$) for Method II. The number of d electron in these sets are larger by one than those for $\text{Fe}(\text{cp})_2$ corresponding to d electron increase in free atom. Calculated results satisfy the tendency of transition energy shift mentioned above.

When $\text{Co}(\text{cp})_2^+$ was given attention to be an isoelectronic metallocene of ferrocene, we might chose the same d electron number as for ferrocene. Such d electron numbers in each method, however, seem to require larger K value than 1.1, which gives still smaller values for transitions IV_a -V, than the experimental values.

The present calculation suggests that the size of the cobalt 3d orbitals in $\text{Co}(\text{cp})_2^+$ is also expanded from that in free.

Table 9 Transition energies^a (in eV) of cobalticenium ion

	Obsd. ^b	State	Method I		Method II	
			d ⁹ ,K=0.9	d ⁸ ,K=1.1	d ⁸ ,P,K=1.0	d ⁷ ,P,K=1.1
III	2.70	³ E _{1g} (e _{2g} →e _{1g})	—	—	2.23	1.68
IV _a	3.01	¹ E _{1g}	2.74	2.46	2.97	2.45
IV _b	3.27	¹ E _{2g}	3.07	2.76	2.97	2.45
V	4.13	¹ E _{1g}	3.05	2.76	3.42	2.94
		¹ A _{1u}	6.50	7.07	1.81	1.59
		¹ E _{2u}	5.28	5.89	1.92	1.70
		¹ A _{2g}	6.64	7.11	3.65	2.98
		¹ A _{1g}	4.20	4.27	6.29	6.75
		¹ E _{2g}	4.26	4.32	4.00	3.38
XII	4.71 (0.5)	¹ A _{2u} (e _{1u} →e _{1g})	5.20	5.84	5.23 (2.35)	5.03 (2.36)
		¹ E _{1u}	6.55	7.98	6.62 (0.001)	6.75 (0.001)

a See footnote a of Table 3.

b Ref. 1.

The sequences of molecular orbitals for $\text{Co}(\text{cp})_2^+$ are almost same as for $\text{Fe}(\text{cp})_2$ (Table 6). However the values of molecular orbitals were lowered throughout about 5 eV from the corresponding orbitals for $\text{Fe}(\text{cp})_2$ because of the positive charge of the whole molecule.

Electron densities on the metal orbitals in $\text{Co}(\text{cp})_2^+$ increased almost unit value from those in $\text{Fe}(\text{cp})_2$ (Table 8). Increase of electron density on the $3d_{xz}$ and $3d_{yz}$ orbitals and decrease of that on the $2p_z$ orbitals of cyclopentadienyl rings indicate that charge transfer from ligand to metal atom takes place favorably in $\text{Co}(\text{cp})_2^+$. The consistency of the d electron configuration between assumption and result is also realized for Method II.

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Chapter 5. Silver(I)-Olefin Complexes.

§ 1. Introduction

Many transition metal complexes catalyze certain reactions,¹⁾ such as isomerization, dimerization, polymerization, oxidation, hydrogenation of olefins and acetylenes. A number of organo-transition-metal complexes have been synthesized and investigated using various methods,²⁾ because these complexes were interesting as models of the intermediates of such reactions.

The Ag^+ -olefin complex³⁾ is one of the well known organo-transition-metal complexes, and its thermodynamic and spectroscopic studies have been carried out; heretofore equilibrium constants of the formation,⁴⁻⁷⁾ heat of formation,^{4, 6, 7)} infrared,^{8, 9)} Raman⁹⁾ and nuclear magnetic resonance (NMR) spectra⁹⁻¹²⁾ have been measured.

Since Dewar proposed the two-way donor acceptor bond in the silver- and platinum-olefin complexes, some theoretical studies have been carried out on the nature of coordination bond in such complexes; the perturbation method has been applied for the estimation of the stability of Ag^+ -olefin complexes^{8, 14-17)} and molecular orbitals (MO) of Ag^+ -ethylene have been obtained by the extended Hückel and ab initio MO methods.^{18, 19)} However there seems to have been no reports of systematic MO calculations on a series of Ag^+ -olefin

complexes, and theoretical interpretations of the experimental results, such as the infrared, Raman, and NMR etc., are rather scarce. Thus, the author will calculate the MO's of six Ag(I)-olefin complexes by the semi-empirical SCF-MO method, and present some discussions on the experimental results from the obtained MO's in this chapter.

§ 2. MO Calculation and Geometry

The SCF MO's are obtained by the CNDO type MO method, which has been applied to the MO calculations of MnO_4^- , CrO_4^{2-} , PdX_4^{2-} and PdX_6^{2-} (X=halogen) in a previous work.²⁰⁾

All valence orbitals including 4d-atomic orbitals of the silver atom are considered explicitly. The zero-differential overlap approximation²¹⁾ is introduced into the Roothaan's SCF equation for the closed shell molecules.²²⁾ Then the diagonal one-electron term H_{rr} in the Fock matrix element is evaluated according to the formula of Yonezawa et al.^{23)*1} The off-diagonal one-electron term H_{rs} ($r \neq s$) is calculated by the Wolfsberg-Hermholz approximation.²⁴⁾

$$H_{rs} = -k S_{rs} (I_r + I_s) \quad (1)^{*2}$$

*1 While the one-center exchange repulsion integrals are included in the formula of Yonezawa et al., the author neglects them in this calculation. For Fock-matrix elements, see chapter 2 in the part I.

where the parameter k is taken as 0.55. The one-center Coulomb repulsion integrals of ligand atoms are obtained by the Pariser's approximation²⁵⁾ and those of the silver atom are taken from Di Sipio's report.²⁶⁾ The two-center Coulomb repulsion integrals are computed according to the Ohno's formula.²⁷⁾ The single Slater type orbitals are used for all s- and p-orbitals, and the double- ζ form orbital is used only for the 4d-orbital of the silver atom. The values of the orbital exponents, ζ_r , ionization potentials, I_r , and one-center Coulomb repulsion integrals, $(rr|rr)$ are given in Table 1.

The core-repulsion energy, E_{nucl} , is approximated by;²³⁾

$$E_{\text{nucl}} = \sum_{A>B} \sum_r \sum_s^A \sum_s^B N_r N_s (rr|ss) \quad (2)^{*2}$$

As the measure of the bond strength, the two atomic part of the total energy, E_{AB} , proposed by Pople et al.²²⁾ is used, and this quantity is expressed by eq.(3), using the approximations described above.

$$E_{AB} = \sum_r^A \sum_s^B [2.0 P_{rs} H_{rs} - 0.5 P_{rs}^2 (rr|ss) + (P_{rr} - N_r)(P_{ss} - N_s)(rr|ss)] \quad (3)^{*2}$$

The distance between the silver atom and the center of the double bond of the olefin is fixed at $2.39 \text{ \AA}$ ^{*3} according to the work of Mathews et al.²⁸⁾ The olefin moieties in these complexes are supposed to be nonplanar in analogy with Zeise's salt,³⁰⁾ in which four hydrogen atoms are pushed

*2 For notations in these formulas, see Ref. 23 and chapter 2 in the part I of this thesis.

Table 1 Orbital exponent(ζ_r), valence state ionization potential(I_r) and one-center Coulomb repulsion integral ($rr|rr$)

Atom	AO	ζ_r	C^*	I_r (eV)	$(rr rr)$ (eV)
H	1s	1.0000 ³¹⁾		13.60 ³³⁾	12.85 ³³⁾
C	2s	1.5679		21.07	12.10
	2p	1.5679		11.27	10.93
Ag		5.9830 ³²⁾	0.5535 ³²⁾		
	4d	2.6130	0.6701	8.17 ²⁴⁾	13.87 ²⁴⁾
	5s	2.1900		7.07	7.46
	5p	2.1900		3.30	6.22

*The 4d atomic orbital (AO) is represented by Basch et al.³²⁾ as the linear combination of one 3d and two 4d Slater type orbitals (STO's). In this work, the contribution of 3d STO is neglected and the 4d AO is represented as the linear combination of two 4d STO's. Thus, strictly speaking, this 4d AO is not normalized. However, the contribution of the 3d STO is negligible small; e.g., less than 0.2 % in the case of the overlap integral between the Ag and C atoms.

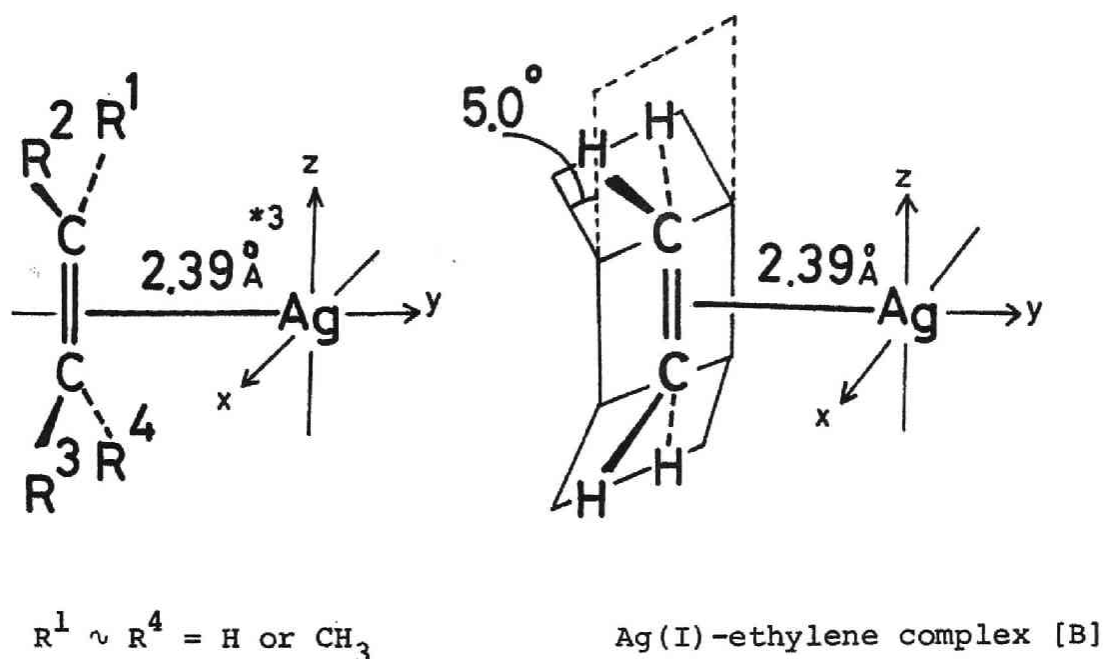


Fig. 1. Coordinate systems of Ag(I)-olefin complexes.

*3 In Ag(I)-cyclooctatetraene, the averaged Ag-olefinic carbon bond and C=C double bond lengths are estimated to be 2.49 Å and 1.37 Å, respectively.²⁸⁾ From these values, the distance between the silver atom and the center of the C=C double bond is evaluated to be 2.39 Å, assuming that the C=C double bond is perpendicular to its coordination bond.

away from the platinum ion. However in this work, the assumption is made that the olefin moiety is planar and its bond lengths are the same as those of an uncomplexed olefin²⁹⁾ due to the lack of information on the accurate configurations of these complexes. For the purpose of comparison, one nonplanar ethylene complex model has been calculated and its stability examined. Hereafter, the planar and the nonplanar ethylene complexes are named [A] and [B], respectively. These coordinate systems are shown in Fig.1.

§ 3. Results and Discussions

Heat of Formation; The heat of formation has been calculated from the difference between the total energy of the Ag^+ -olefin complex and the sum of total energies of the silver(I) ion and of the olefin. The relative values of the heat of formation to that of the Ag^+ -ethylene complex [A] are shown in Table 2, together with the values of $E_{\text{Ag-C(olefinic)}}$ and $E_{\text{Ag-C(allylic)}}$. The calculated heat of formations increase with the increasing number of methyl groups, which is good agreement with the experimental trend^{*4}. On the other hand, the absolute values of $E_{\text{Ag-C(olefinic)}}$ decrease with the increasing number of methyl groups. This suggests that the heat of formation can not only be decided by the interaction between the silver atom and the olefinic carbon atom but also by the interaction between the silver atom and another parts of olefin, which

Table 2 Heat of formations and $E_{\text{Ag-C}}$ of Ag^+ -olefin complexes

Olefin	Heat of formation		$E_{\text{Ag-C(olefinic)}}^{*3}$	$E_{\text{Ag-C(allylic)}}^{*4}$
	Calculated ^{*1}	Experimental ^{*2}		
Ethylene [A]	0.00 (eV)	0.00 (kcal/mol)	-4.57 (eV)	-
[B]	0.04		-4.64	-
Propylene	0.30	0.029	-4.55	-1.10 (eV)
trans-2-Butene	0.55	1.814	-4.44	-1.05
cis-2-Butene	0.57	1.950	-4.45	-1.04
2-Methyl-2-butene	0.80	-	-4.41	-1.06
2,3-Dimethyl-2-butene	1.00	-	-4.32	-1.06

*1 The relative value to the calculated heat of formation of the ethylene complex [A].

*2 The relative value to the experimental heat of formation of $\text{AgBF}_4:\text{C}_2\text{H}_4$ (Ref. 4).

*3 The average value of two $E_{\text{Ag-C(olefinic)}}$ in the olefin.

*4 The average value of all $E_{\text{Ag-C(allylic)}}$ in the olefin.

is supported by the bonding interaction between the allylic carbon atom and the silver atom, as shown in Table 2.

The calculated values of the heat of formation and the absolute value of $E_{\text{Ag-C}}$ in the ethylene complex [B] are larger than those in the complex [A]. That is, the nonplanar model seems more likely for the structure of ethylene in the complex.

Electron Distribution; The electron populations on silver atoms are shown in Table 3, together with π -electron densities, P_{π} , of uncomplexed olefins and quantities of transferred electron, ΔQ , from olefins. The silver(I) ion is considered to contain d^{10} configuration. The calculated results agree well with this configuration, while, compared with Basch's results ($d^{9.94} s^{0.13} p^{0.07}$ in Ag^+ -ethylene),¹⁹⁾ the 5s- and 5p-orbital electron populations obtained in this work seem to be too large. The 5s- and 5p-orbital electron populations and ΔQ increase with the increasing number of methyl groups, whereas

*4 The calculated heat of formations are compared not with the experimental values determined by the gas-chromatography technique⁷⁾ but with the ones estimated from the measurements of the dissociation pressures of these complexes,^{4, 6)} because the value determined by the gas-chromatography should include the solvation energy of the olefin by the solvent in column packing of gas-chromatograph.

Table 3 Electron populations on silver atoms, quantities of the transferred electron (ΔQ)^{*} and π -electron densities of olefinic carbon atoms in uncomplexed olefin (P_{π})

		Electron population on Ag			ΔQ	P_{π}
		4d	5s	5p		
Ethylene	[A]	9.985	0.187	0.110	0.282	1.000
	[B]	9.985	0.189	0.111	0.285	
Propylene		9.985	0.195	0.122	0.303	0.929 ^{**} 1.113
trans-2-Butene		9.985	0.202	0.130	0.317	1.035
cis-2-Butene		9.985	0.201	0.133	0.319	1.041
2-Methyl-2-butene		9.986	0.206	0.140	0.331	0.968 ^{**} 1.141
2,3-Dimethyl-2-butene		9.986	0.210	0.146	0.341	1.068

* The decrease in the electron population of olefin by the coordination to the silver ion.

** The π -electron density of the olefinic carbon atom which contains more methyl groups than the other.

the 4d-orbital electron population remains almost constant. A methyl group is known to increase the π -electron density not only by -I effect but also by hyperconjugation³⁴⁾ and this seems to results in the increase of ΔQ and the electron density on the silver atom.

In the ethylene complex [B], the 5s- and 5p-orbital electron populations and ΔQ are slightly larger than those of the complex [A]. These facts suggest that the nonplanality increases the π -electron donation from ethylene to 5s- and 5p-atomic orbitals of the silver atom.

Coordination of Olefin; The calculated bond orders of the coordination bonds and the decrease in the π -bond orders of olefins are shown in Table 4. Apparently bond orders of the σ -donor bond ($d_{\sigma}-\pi$, $s-\pi$, and $p_{\sigma}-\pi$ in Table 4) are much larger than those of the π -acceptor bond ($d_{\pi}-\pi^*$, and $p_{\pi}-\pi^*$) in all complexes. Also as shown in Table 4, the decrease in the π -bond order by the σ -donor bond, $(\Delta P_{\pi})_{\sigma}$ is much larger than that by the π -acceptor bond, $(\Delta P_{\pi^*})_{\pi}$. The largest contribution to the coordination bond is noticed in the interaction between the 5s-atomic orbital of the silver atom and π -MO of the olefin, and the next largest in that between the 5p-atomic orbital of the silver atom and the π -MO of the olefin. These facts indicate that the coordination bond is mainly contributed by the σ -donor bond in which the olefin donates its π -electron to 5s- and 5p-atomic orbitals of the silver atoms.

The coordination bond orders of the complex [B] are slightly

Table 4 The bond orders of the coordination bond in Ag^+ -olefin complexes and the change of $\text{C}=\text{C}$ π -bond order and $E_{\text{C-H(olefinic)}}$

		Bond order of coordination bond					$(\Delta P_{\pi})_{\sigma}^{\text{a)}}$	$(\Delta P_{\pi^*})_{\pi}^{\text{b)}}$	$\Delta P_{\pi}^{\text{c)}}$	$ E_{\text{C-H}} ^{\text{d)}}$
		π -acceptor		σ -donor bond						
		$d_{\pi}-\pi^*$	$p_{\pi}-\pi^*$	$d_{\sigma}-\pi$	$s-\pi$	$p_{\sigma}-\pi$				
Ethylene	[A]	0.146	0.0001	0.088	0.748	0.522	-0.122	-0.003	-0.125	-0.19 _{eV}
	[B] ^{e)}	0.148	0.001	0.090	0.751	0.526	-0.126	-0.003	-0.126	-0.19
Propylene		0.132	0.045	0.092	0.762	0.524	-0.133	-0.001	-0.134	-0.18
trans-2-Butene		0.124	0.033	0.094	0.774	0.530	-0.130	-0.007	-0.137	-0.18
cis-2-Butene		0.120	0.040	0.094	0.772	0.530	-0.130	-0.008	-0.138	-0.19
2-Methyl-2-butene		0.110	0.055	0.096	0.780	0.530	-0.134	-0.008	-0.142	-0.19
2,3-Dimethyl-2-butene		0.102	0.064	0.096	0.786	0.534	-0.133	-0.009	-0.142	-

a) The decrease in the π -bond order due to the π -electrons donation of the olefin to the silver atom defined as follows;

$(\Delta P_{\pi})_{\sigma} = (2 \sum_i^{\text{occ}} C_{i1} p_{\pi} C_{i2} p_{\pi})_{\text{complexed}} - (2 \sum_i^{\text{occ}} C_{i1} p_{\pi} C_{i2} p_{\pi})_{\text{uncomplexed}}$, where $C_{i1} p_{\pi}$ is the coefficient of the p_{π} orbital of the carbon atom 1 in MO i , and the $\text{C}=\text{C}$ double bond is formed by the carbon atom i and 2.

Table 4 (Continued)

b) The decrease in the π -bond order due to the d-electron acceptance of the olefin from the silver atom defined as follows;

$$(\Delta P_{\pi^*})_{\pi} = (2 \sum_i^{\text{occ}} C_{i1} p_{\pi^*} C_{i2} p_{\pi^*})_{\text{complexed}} - (2 \sum_i^{\text{occ}} C_{i1} p_{\pi^*} C_{i2} p_{\pi^*})_{\text{uncomplexed}}$$

where $C_{i1} p_{\pi^*}$ is the coefficient of the p_{π^*} orbital of the carbon atom 1 in MO i .

$$c) \Delta P_{\pi} = (\Delta P_{\pi})_{\sigma} + (\Delta P_{\pi^*})_{\pi}$$

d) $E_{\text{C-H}} = (E_{\text{C-H}})_{\text{complexed}} - (E_{\text{C-H}})_{\text{uncomplexed}}$, where $E_{\text{C-H}}$ represents the E_{AB} of the olefinic C-H bond.

e) In the ethylene complex [B], π -bond order (P_{π}) is defined as follows;

$$P_{\pi} = 2 \sum_i^{\text{occ}} C_{i1} p_y C_{i2} p_y, \text{ where } C_{i1} p_y \text{ is the coefficient of } 2p_y \text{ orbital of the carbon atom 1 in MO } i.$$

larger than those of the complex [A], resulting in the larger absolute value of $E_{\text{Ag-C}}$ in the complex [B]. Thus it is apparent that the interaction of ethylene with the silver atom in the complex [B] is stronger than that in the complex [A].

The Electronic Structure of the Coordinated Olefin; The coordination of an olefin to a transition metal results in a shift of C=C double bond stretching vibration ($\nu_{\text{C=C}}$) to a lower frequency from that in the uncomplexed olefin by $50\text{--}70\text{ cm}^{-1}$ for silver (I)⁹⁾ and about 150 cm^{-1} for platinum (II).³⁵⁾ A shift of $\nu_{\text{C=C}}$ ($\Delta\nu_{\text{C=C}}$) is proportional to the change in the C=C π -bond order (ΔP_{π}), as shown in Fig.2. This linear relationship between $\Delta\nu_{\text{C=C}}$ and ΔP_{π} suggests that the shift to a lower frequency of $\nu_{\text{C=C}}$ is mainly due to a decrease in the strength of the C=C π -bond. The calculation also shows that the absolute values of $E_{\text{C-H(olefinic)}}$ decrease in the silver complex by ca.0.18 eV as shown in Table 4, which is in agreement with the experimentally observed shift to a lower frequency of the olefinic C-H bond stretching vibration.⁸⁾

The ^{13}C NMR spectra of the cyclopentene and cyclohexene in aqueous silver nitrate solution reveal that the olefinic carbon resonances are shifted to higher fields, relative to those of uncomplexed cycloalkenes.¹³⁾ The most important term giving ^{13}C resonance shielding constant (σ_{p}) is the term due to the paramagnetic susceptibility. This term σ_{p} is calculated^{*5} using the approximation formula proposed by Pople.³⁶⁾ The obtained results are given in Table 5. The calculated

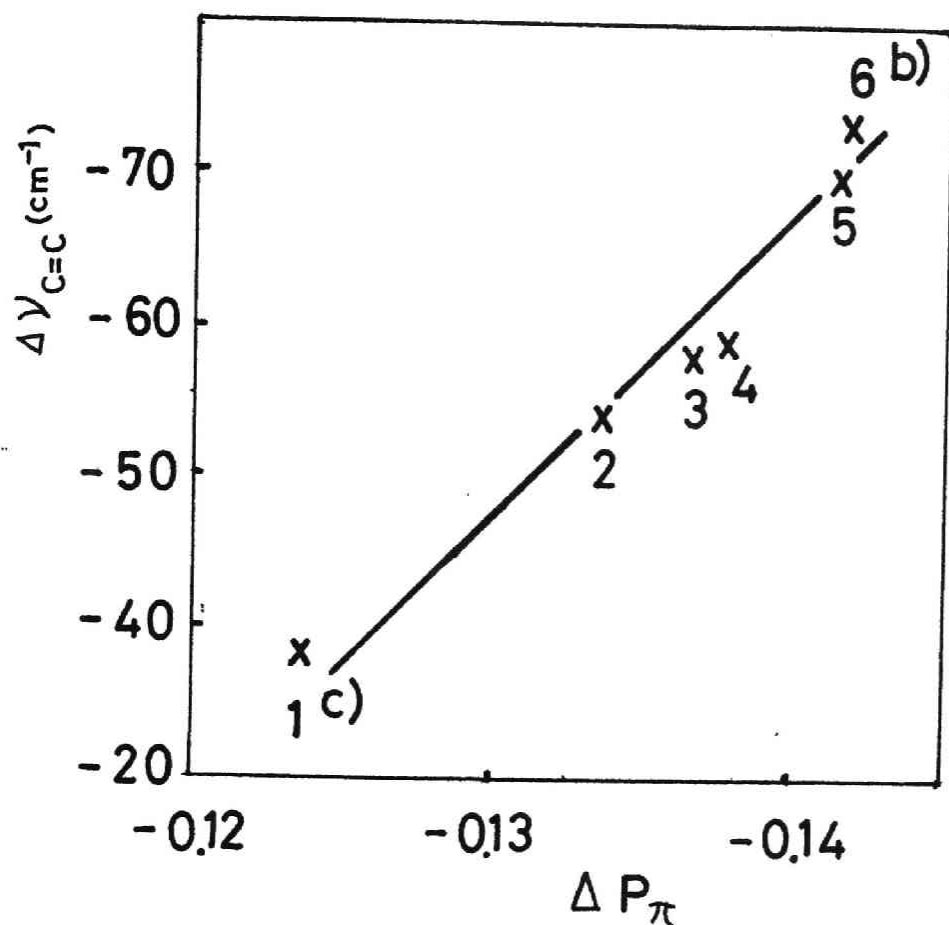


Fig. 2. The relation between the decrease in calculated π -bond order, ΔP_{π} , and the decrease in observed frequency of C=C stretching vibration, $\Delta \nu_{C=C}$.^{a)}

a) These values are taken from $\text{Ag(olefin)}_2\text{:BF}_4$ in solid (Ref. 9).

b) This value is obtained from the measurement in solution (Ref. 9).

c) This value is taken from the measurement for Ag^+ -ethylene (Ref. 3-b), therefore the points 1 and 6 may deviate from the line.

olefinic carbon resonances are shifted to higher fields in Ag^+ -olefin complexes. These shifts to higher fields ($\Delta\delta$) are attributable to the increase in δ_π^* which is due to the term, $P_{\text{AyBy}} P_{\text{AzBz}}$, as shown in Table 5. Since the decrease in the π -bond order is reflected in the increase in δ_π , and since the decrease in the π -bond order is mainly due to the π -electron donation from olefin as described before, the π -electron donation seems to be the main factor of these shifts to higher fields. On the other hand, the calculation reveals the downfield shifts for the ^{13}C resonances of the sp^3 carbon atoms in these Ag^+ -olefin complexes, and these results agree with the experimental results¹³⁾. These downfield shifts should be attributed not only one term but also two or three terms as shown in Table 5.

Transition Energy; It is expected that the $\pi-\pi^*$ transition

*5 This calculation is carried out on the assumption that the average transition energy ΔE is 8 eV in all olefins and Ag -olefin complexes.

*6 The increase in the olefinic ^{13}C resonance is mainly contributed by the term of $(Q_{\text{AB}})_{\text{xx}}$; $(Q_{\text{AB}})_{\text{xx}} = -2P_{\text{AyBy}} P_{\text{AzBz}} + 2P_{\text{AyBz}} P_{\text{AzBy}}$. For the notations in the above formula, see ref.36. The values of $\Delta\delta_\pi$ represents the change in ^{13}C NMR chemical shift due to the change in the value of $P_{\text{AyBy}} P_{\text{AzBz}}$. Since the P_{AzBz} is almost unchanged by the complex formation, $\Delta\delta_\pi$ is mainly contributed by the change of P_{AyBy} .

Table 5 The changes in ^{13}C NMR chemical shift by the complex formation

(a) The unsaturated carbon atom

Olefin		$\Delta\delta$ ^{a)}	$\Delta\delta_{(AB)_{xx}}$ ^{b)}	$\Delta\delta_{\pi}$ ^{c)}
Ethylene	[A]	+4.0 ppm	+12.0 ppm	+12.9 ppm
	[B]	+3.7	+12.0	+12.9
Propylene	^{d)} C ¹	+1.5	+11.9	+13.6
	C ²	+4.2	+12.0	+13.5
trans-2-Butene		+5.8	+11.9	+13.6
cis-2-Butene		+5.5	+11.9	+13.6
2-Methyl-2-butene	^{e)} C ¹	+5.4	+11.7	+13.4
	C ²	+6.6	+11.6	+13.4
2,3-Dimethyl-2-butene		+6.9	+11.2	+13.0

(b) The carbon atom of methyl group

Olefin		$\Delta\delta$ ^{a)}	Main Contribution
Propylene		-3.1 ppm	$(Q_{AA})_{zz}$ $(Q_{AB})_{zz}$
trans-2-Butene		-2.1	$(Q_{AA})_{yy}$ $(Q_{AA})_{zz}$ $(Q_{AB})_{zz}$
cis-2-Butene		-2.2	$(Q_{AA})_{yy}$ $(Q_{AB})_{zz}$
2-Methyl-2-butene	^{e)} C ³	-0.1	$(Q_{AA})_{yy}$
	C ⁴	-2.1	$(Q_{AA})_{yy}$
	C ⁵	-1.4	$(Q_{AA})_{yy}$ $(Q_{AA})_{zz}$
2,3-Dimethyl-2-butene		-1.4	$(Q_{AA})_{yy}$ $(Q_{AB})_{zz}$

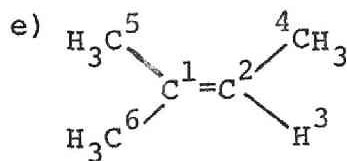
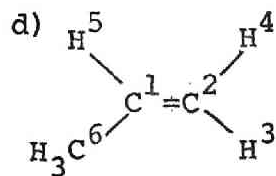
a) $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{uncomplexed}}$

b) The change in ^{13}C NMR chemical shift due to the change in

Table 5 (Continued)

the $\sum_{B \neq A} (Q_{AB})_{xx}$.

- c) The change in ^{13}C NMR chemical shift due to the change in term, $-2P_{AyBy}^P AzBz$.



energy should be changed and that the charge transfer band should appear at the formation of the transition metal complex. Unfortunately in the cases of the Ag^+ -olefin complexes, the electronic spectra have not been reported except the charge-transfer band of Ag^+ -cyclohexene.^{8, 37)} The $\pi-\pi^*$ transition energies of olefins and Ag^+ -olefin complexes are calculated and shown in Table 6. While for ethylene and propylene the $\pi-\pi^*$ transition energies are increased by the complex formation, for the other olefins it is decreased by the complex formation as in the case of Basch's results on Ag^+ -ethylene.*⁷ It is yet unknown by an experiment whether the $\pi-\pi^*$ transition band shifts to a lower frequency or to a higher one.

In Ag^+ -cyclohexene, the charge transfer band has been observed at 5.51 eV,^{8, 37)} which has been considered to have the mixed character of the charge transfer from olefin to the silver ion and the Rydberg transition in the olefin moiety.⁸⁾ The charge transfer band from π -MO of ethylene to the 5s-orbital of the silver ion is calculated as 8.25 eV in Ag^+ -ethylene complex [A]. This result is reasonable, since

7 The MO energy difference between π and π^ MO's of the olefin is decreased by the Ag^+ -olefin complex formation. However the decreasing quantities are small in the cases of ethylene and propylene, since their π -MO's have the considerably low orbital energies compared with the other olefins. This may be one reason of the higher energy shift of the $\pi-\pi^*$ transition in Ag^+ -ethylene and propylene complexes.

Table 6 $\pi-\pi^*$ transition energies and energy differences
between $\pi-$ and π^* -MO's

Olefin	Transition energy		MO energy difference ^{a)}	
	Uncomplexed	Complexed	Uncomplexed	complexed
Ethylene [A]	8.87 (eV)	9.19 (eV)	14.89 (eV)	14.88 (eV)
[B]		9.19		13.99
Propylene	7.65	7.69	13.41	12.94
trans-2-Butene	6.78	6.62	12.35	11.65
cis-2-Butene	7.15	7.09	12.71	12.15
2-Methyl-2-butene	6.60	6.43	12.10	11.38

a) MO energy difference between $\pi-$ and π^* -MO's

π -MO energy of ethylene is lower than that of cyclohexene by ca.1.5 eV. However more detail investigation of these transition energies will be carried out in the near future, since $\pi-\pi^*$ transition bands in ethylene and propylene are increased by the complex formation, which is incompatible with the Basch's result.

Although there are a few unsolved problems about the transition energy, the calculated results in this work agree with the experimental results, such as the heat of formation, infrared, Raman and NMR spectra. Thus, it is expected that this method can be satisfactorily applied in the MO calculations of other interesting organometal complexes.

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Chapter 6. Pt(II)-ethylene, Pt(II)-acetylene, Pt(0)-ethylene, and Pt(0)-acetylene Complexes

§ 1. Introduction

The organo-transition metal complexes are much attractive from viewpoints of the metal-carbon bonding character and of models for intermediates which exist in organic reaction catalyzed by transition metals.¹⁻⁴⁾ Zeise's salt⁵⁾ is one of the well-known and most investigated organo-transition metal complex.^{2, 6-17)} Besides Zeise's salt, its bromo analogue,^{2, 12-14, 17, 18)} Pt(II)-acetylene,^{19, 20)} Pt(0)-olefin^{17, 19, 21-23)} and Pt(0)-acetylene^{17, 19, 24)} complexes are also known. Some theoretical studies^{8, 25-29)} have been carried out on these complexes. However, a SCF-MO calculation which includes explicitly electron repulsion integrals has not been carried out on the Pt(II)-acetylene, Pt(0)-ethylene and Pt(0)-acetylene complexes, while the extended Hückel (EH) MO (noniterative) calculations have been done on them.^{25, 26, 28, 29)} From the EH MO calculations, it is proposed that the 6s orbital of the Pt atom scarcely contributes to the coordination bond of ethylene both in Pt(0) and Pt(II) complexes.²⁵⁾ However, CNDO type MO calculations reveal that the 5s orbital of the Ag atom mainly contributes to the coordination bond of olefin in Ag(olefin)⁺ complexes.^{30-a)}

Thus, it is necessary to re-investigate electronic structures of Pt(II)-acetylene, Pt(0)-ethylene and Pt(0)-acetylene complexes. Also it is of interest to compare coordination bonds of these complexes with each others.

In this work, parametrizations are investigated in a CNDO type MO calculations on PtCl_4^{2-} . By the use of the established parameters, CNDO type MO calculations are carried out on $\text{PtX}_3(\text{C}_2\text{H}_4)^-$, $\text{PtX}_3(\text{C}_2\text{H}_2)^-$ ($\text{X}=\text{Cl}, \text{Br}$), $\text{Pt}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$ and $\text{Pt}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$. Discussions are presented on the electronic structures of these compounds, and also on the coordination bonding characters of ethylene and acetylene in these complexes.

§ 2. MO Calculation and Geometries

MO Calculation A semi-empirical SCF-MO method with CNDO type approximations is used in this work. While the method is almost the same as the previous one,³⁰⁾ some parameters are improved: (1) In this method, resonance integrals are evaluated by the Wolfsberg-Helmholz equation.³¹⁾ The value of its parameter K is differently adopted between AO pair including d-orbitals and those including only s and p orbitals: the notation K_1 is used in the former case and the notation K_2 in the latter one. While the value of K_2 is taken as 0.80 similarly to that in the previous report,^{30-c)} that of K_1 is determined as 0.90 in this work, as described below.

(2) While the Ohno's equation³²⁾ was used in our previous works,³⁰⁾ the modified Ohno's one which is newly presented in this work is introduced for calculations of two-center Coulomb repulsion integrals including 6s and 6p orbitals of the Pt atom. The modification for the Ohno's equation is carried out from a following reason; the one-center Coulomb repulsion integrals γ_{rt} is calculated by the following eq(1) in the Ohno's equation;

$$\gamma_{rt} = 0.5(\gamma_{rr} + \gamma_{tt}) \quad (1)$$

This equation can be a good approximation when the AO.r and AO.t are alike.³³⁾ In transition metals, however, this equation (1) can not be successfully applied to the calculations of one-center values of $\gamma_{nd(n+1)s}$ and $\gamma_{nd(n+1)p}$, since outer s and p orbitals are much different from valence shell d-orbitals in expandings. As examples, Table 1 presents the comparison between those values obtained by eq(1) and those obtained from atomic spectra in Ni and Pd atoms; apparently, eq(1) gives too large values of $\gamma_{nd(n+1)s}$ and $\gamma_{nd(n+1)p}$ as compared with the corresponding ones obtained from atomic spectra. In order to improve this defect, a following modification is carried out, only when either AO.r or AO.t is an outer orbital;

$$\gamma_{rt} = 14.3986 / (d^2 + R_{rt}^2)^{1/2} \quad (2)$$

$$14.3986/d = 0.5(\gamma_{rr} + \gamma_{tt}) - a_r \quad (3)$$

, where $AO.r$ is assumed as an outer orbital and R_{rt} is the distance ($\text{\AA}$ unit) between the centers of $AO.r$ and $AO.t$. The value of a_r depends on the outer $AO.r$, which is so determined that eq(2) and (3) reproduce the experimental values of one-center Coulomb repulsion integrals, such as $\gamma_{nd(n+1)s}$ and $\gamma_{nd(n+1)p}$, at $R_{rt}=0.0$; for examples, values of a_{4s} and a_{4p} of the Ni atom are taken as 2.25 and 3.29 eV, respectively. (See Table 1.) The original Ohno's equation is also used in the other AO pairs, in which both AO's are outer orbitals or valence ones.

Figure 1 gives values of $\gamma_{3d\ 4s}$ of the Ni atom obtained by various methods. Theoretically calculated values (the line A) seem too large. The line D is obtained by multiplying a correction factor to the theoretically calculated values so as to coincide the theoretical one-center value of $\gamma_{3d\ 4s}$ with that obtained from atomic spectra. The line C obtained by using the modified Ohno's equation seems to be most agreeable with the line D in all range of R_{ds} , while the line B obtained by the original Ohno's equation is too large in the range of small R_{ds} . Thus, the modified Ohno's equation gives more reasonable value of $\gamma_{3d\ 4s}$ than the original one does.

In the case of the Pt atom, the experimental values of $\gamma_{5d\ 6s}$ and $\gamma_{5d\ 6p}$ can not be obtained unfortunately because of the lack of atomic spectra. In the Pd atom, which forms similar compounds to the Pt's ones, a_{5s} should be taken as

Table 1. Values of $\gamma_{nd(n+1)s}$ and $\gamma_{nd(n+1)p}$ ^{a)} of the Ni and Pd atoms

	γ_{ds} ^{b)}	$0.5(\gamma_{dd} + \gamma_{ss})$	Δ_{ds} ^{c)}	γ_{dp} ^{b,d)}	$0.5(\gamma_{dd} + \gamma_{pp})$	Δ_{dp} ^{c)}
Ni	10.09 eV	12.34	-2.25	8.27	11.56	-3.29
Pd	9.14 eV	10.67	-1.53	7.71	10.05	-2.34

a) $n=3$ for the Ni atom and $n=4$ for the Pd atom.

b) These values are obtained from Ref. 34.

c) $\Delta_{ds} = \gamma_{ds} - 0.5(\gamma_{dd} + \gamma_{ss})$, $\Delta_{dp} = \gamma_{dp} - 0.5(\gamma_{dd} + \gamma_{pp})$

d) The averaged value of various types of γ_{dp} .

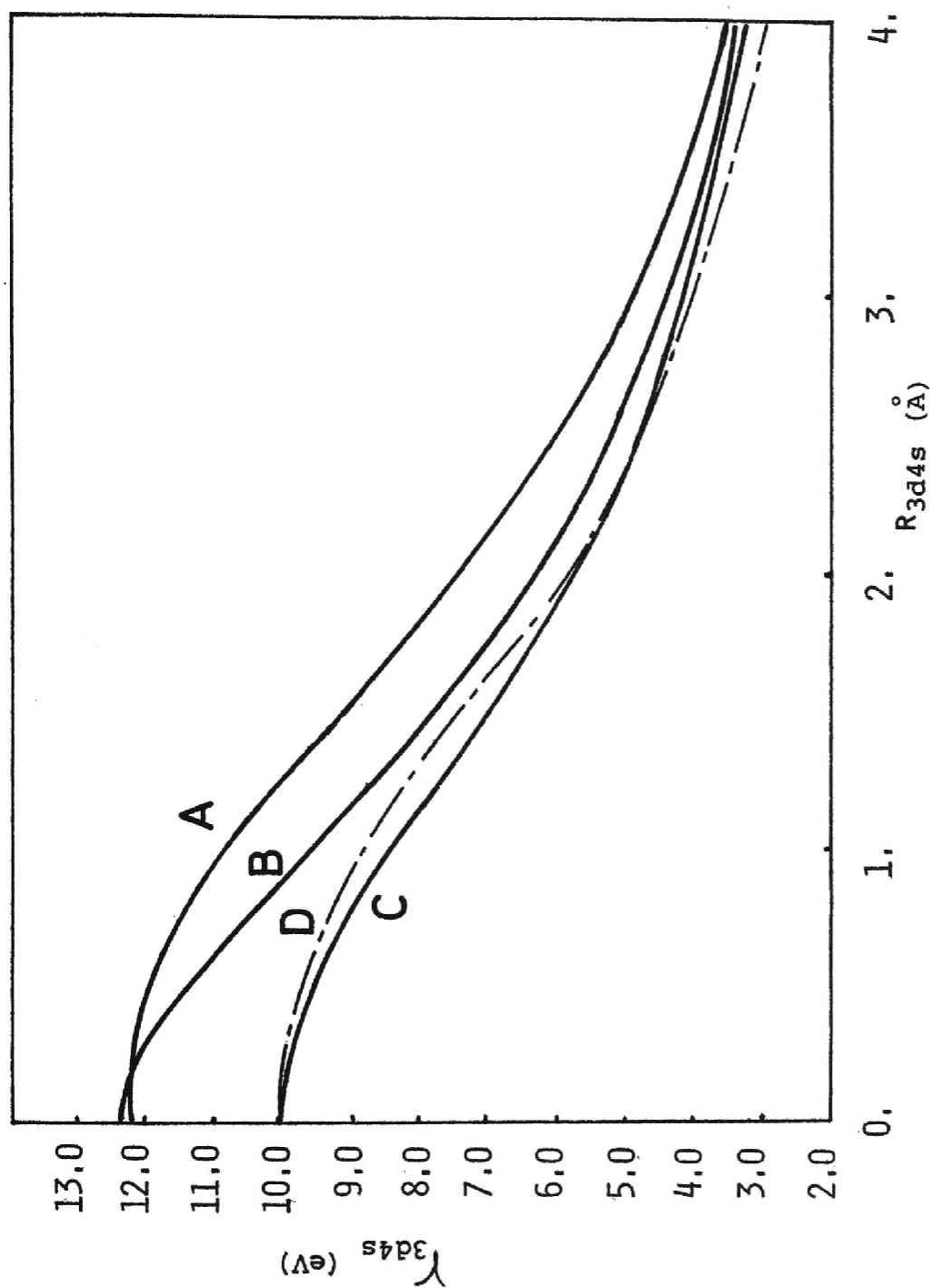


Fig. 1. Two-center Coulomb repulsion integrals V_{3d4s} at various interatomic distances.
 A; non-empirical value, 3d;double- ζ AO of Richardson et al.³⁶⁾, 4s;single Slater type AO of Clementi et al.³⁵⁾ B;The Ohno's equation, C;The modified Ohno's equation (Eq. (5) and eq.(6)) D;The scaled non-empirical values.

1.53 eV and a_{5p} as 2.34 eV. (See Table 1.) By considering these values of the Pd atom, the authors examine various values of a_r within the following regions; 1.2~1.8 eV for a_{6s} and 2.2~2.8 eV for a_{6p} . From those examinations, $a_{6s}=1.5$ eV and $a_{6p}=2.5$ eV are chosen as the best values, which give good results on electronic spectra of tetrachloro platinate and Zeise's salt, as described in the following section.

For the Pt atom, the valence state ionization potentials, I_r , are evaluated from atomic spectra.³⁷⁾ One-center Coulomb repulsion integrals, γ_{rr} , are estimated by the use of eq(2) in Ref. 30-c. For atoms of ligands, values of I_r are taken from Hinze's work³⁸⁾ and those of γ_{rr} are evaluated from the same work³⁸⁾ by use of the Pariser's approximation.³³⁾ A double- ζ type d-function³⁹⁾ is used for the 5d orbital of the Pt atom and single Slater type orbitals^{35, 40)} are used for all s and p orbitals. These data for the Pt atom are given in Table 2.

Geometries. Structures of Zeise's salt¹⁵⁾ and its bromo analogue¹⁸⁾ are taken from X-ray studies. Since the accurate structures of $\text{PtX}_3(\text{C}_2\text{H}_2)^-$, ($\text{X}=\text{Cl}, \text{Br}$), have not been known, the bond length of the Pt-X bond is taken as equal to the corresponding one of $\text{PtX}_3(\text{C}_2\text{H}_4)^-$ and the distance between the Pt atom and the center of the triple bond of acetylene is taken equal to that of $\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})$.²⁴⁾ The bond length of the C=C triple bond is taken as equal to that of

Table 2 Ionization potential, I_r , orbital exponent, ζ_r , and one-center Coulomb repulsion integral, γ_{rr} of the platinum atom.

	ζ_r ^{a)}	C ^{b)}	I_r ^{c)}	γ_{rr} ^{d)}
5d	6.013	0.6331	8.24 eV	12.42 eV
	2.696	0.5516		
6s	2.554		9.00	7.17
6p	2.554		4.20	6.04

a) Ref.39.

b) The coefficients of the double- ζ form of the d-orbital after re-normalization, because the 3d and 4d terms of the platinum's 5d orbital are neglected in this work.

c) The calculated values from Ref.39.

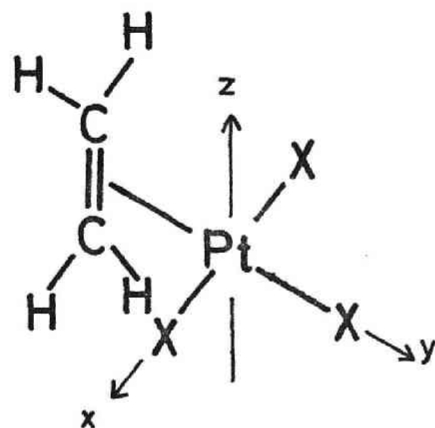
d) The estimated values obtained by using eq(2) in Ref. 30-c.

$\text{trans-PtCl}_2(\text{p-toluidine})[(\text{t-Bu})\text{C}\equiv\text{C}(\text{t-Bu})]$.²⁰⁾ The ethylene and acetylene moieties are considered to be distorted by the coordination.^{2, 16, 21)} Nevertheless, the ethylene and acetylene moieties are assumed not to be distorted because of the short of the structural studies on these complexes. The structures of $\text{Pt}(0)$ -ethylene and $\text{Pt}(0)$ -acetylene complexes are taken from the X-ray studies,^{22, 24)} while small dihedral angle and the cis-bending of CH_2 and CH groups are neglected and the PR_3 group is replaced by the PH_3 one for simplicity. These coordinate systems are shown in Fig. 2.

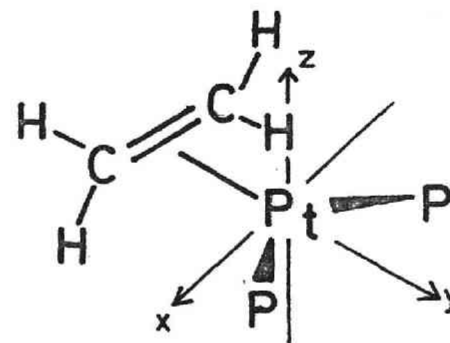
§ 2. Results and Discussion

Parametrization. In order to investigate parametrizations, MO calculations are carried out on PtCl_4^{2-} , since its electronic spectra have been well studied.^{41, 42)} In these calculations, various values of K_1 , a_{6s} and a_{6p} are examined. Only typical results are given in Table 3 and Table 4. (Of course, various sets of values of K_1 , a_{6s} and a_{6p} are also examined besides three ones given in Table 3.)

As shown in Table 3, the parametrization A gives remarkably large electron densities on 6s and 6p orbitals of the Pt atom. Furthermore, this parametrization gives too small transition energies of intra-atomic 5d+6p transition, while these are considered to hold remarkably high transition energies.⁴¹⁾



Pt(II)-ethylene complex.
X= Cl or Br.



Pt(0)-ethylene complex
P=PH₃

Fig. 2. Coordinate frames of Pt(II)-ethylene and Pt(0)-ethylene complexes

The acetylene complexes also have similar structures to the above ones.

Thus, this parametrization is abandoned.

By the use of the modified Ohno's equation, the electron densities on 6s and 6p orbitals are extensively reduced from their values obtained by the parametrization A. (See parametrizations B and D in Table 3.) Electron distributions do not depend so largely on the values of a_{6s} and a_{6p} , while electron densities on 6s and 6p orbitals slightly decrease with increasing of values of a_{6s} and a_{6p} . It should be noted that the use of the modified Ohno's equation gives remarkably high transition energies of intra-atomic 5d→6p transitions; thus, the defect in the parametrization A is overcome by the introduction of the modified Ohno's equation.

Results on electronic spectra are given in Table 4. The charge-transfer (C-T) bands (1E_u and ${}^1A_{2u}$) are obtained at higher transition energies in all calculations than the experimental ones, and the smaller values of a_{6s} and a_{6p} give relatively higher ones than the larger values do. Thus, the small values of a_{6s} and a_{6p} are abandoned. However, too large values of a_{6s} and a_{6p} result in too low transition energies (2.31 eV) of 1E_g in the calculation D, while it is obtained at 3.76 eV experimentally. The parametrization C seems to be the best one. Electronic spectra obtained by this parametrization agree well with experimental ones in transition energies and assignments, while the calculated C-T bands have considerably higher transition energies and the calculated d-d band ${}^1B_{1g}$

Table 3 Electron densities and intra-atomic 5d→6p transition energies of PtCl_4^{2-}

Parametrization ^{b)}		A	B	C	D
a_{6s} ^{a)}		0.0 eV	1.2	1.5	1.8
a_{6p}		0.0 eV	2.2	2.5	2.8
Electron densities	5d	7.68	8.37	8.41	8.44
	Pt 6s	1.28	0.69	0.65	0.61
	6p	1.20	0.63	0.60	0.57
	Cl	7.46	7.58	7.59	7.59
5d→6p transition energies					
$d_{xz}, d_{yz} \rightarrow p_z$		0.47 eV	9.14	9.66	10.18
$d_z^2 \rightarrow p_z$		0.47 eV	7.58	8.29	8.94
$d_{xy} \rightarrow p_z$		0.20 eV	11.34	10.52	10.98

a) Constants in eq(3). b) $K_1=0.90$.

Table 4 Electronic spectra of PtCl_4^{2-}

obsd. a)			Parametrization B		Parametrization C		Parametrization D	
δE	$\epsilon_{\max}$	b)	δE	b) f	δE	b) f	δE	b) f
2.62	16.3	$1B_{1g}$ c)	1.75	0.0	$1B_{1g}$	1.99	0.0	$1B_{1g}$
3.16	52.6	$1A_{2g}$	3.08	0.0	$1A_{2g}$	3.20	0.0	$1A_{2g}$
3.76	62.4	$1E_g$	3.80	0.0	$1E_g$	3.51	0.0	$1E_g$
			3.95	0.0	$1E_g$	4.04	0.0	$1E_g$
4.66	400	non-degenerate	5.20	0.0	$1A_{2g}$	4.88	0.0	$1A_{2g}$
			5.76	0.0	$1A_{1g} + 1B_{2g}$	5.50	0.0	$1B_{2g}$
			5.81	0.0	$1B_{2g}$			
5.38	8500	$1E_u + 1A_{2u}$	5.95	0.248	$1E_u$	5.73	0.284	$1E_u$
			6.14	0.0	$1A_{2u}$	5.88	0.0	$1A_{2u}$
			6.23	0.0	$1E_g$			
			6.60	0.0	$1B_{2u}$	6.34	0.0	$1B_{2u}$
5.72	10900	$1E_u$	7.21	0.236	$1E_u$	6.97	0.258	$1E_u$

a) Ref. 41. b) in eV unit. c) Ref. 42.

has considerably smaller transition energy than corresponding experimental one does.^{41, 42)} Values of a_{6s} and a_{6p} used in the parametrization C look reasonable from considering values of a_{5s} and a_{5p} of the Pd atom.

When the value of K_1 is taken as 1.0, the C-T bands have too high transition energies; the first C-T band is obtained at 6.06 eV and the second one at 7.28 eV, where 1.5 and 2.5 eV are used for a_{6s} and a_{6p} . On the other hand, in the case of $K_1=0.80$, assignments of d-d bands can not agree with experimental ones. Thus, the value of K_1 is taken as 0.90 and the following parametrizations are adopted; $a_{6s}=1.5$ eV, $a_{6p}=2.5$ eV and $K_1=0.90$ (the parametrization C).

These parametrizations are also examined in Zeise's salt. The MO calculation in which $K_1=1.0$ and the original Ohno's equation are used gives too large electron densities on outer orbitals (1.17 e on 6s and 1.85 e on 6p orbitals) and too small transition energies of intra-atomic 5d+6p transitions (about 0.3~0.9 eV). The use of the modified Ohno's equation improves these defects also in this case; intra-atomic 5d+6p transitions are obtained at ca.10 eV and see Table 6 for electron densities.

Thus, by using the parametrization C, we carry out MO calculations on Pt(II)-ethylene, Pt(II)-acetylene, Pt(0)-ethylene and Pt(0)-acetylene complexes, as described in the following sections.

Electronic spectra of Zeise's salt. The parametrization C gives good result on transition energies, which is shown in Table 5. The transition at 3.72 eV is assigned as the d-d band. Transitions at 4.26, 4.67 and 5.16 eV are assigned as the C-T bands from Cl^- ligand to the d-orbital of the Pt atom. Moore assigned the weak transitions at 2.71 and 2.96 eV as the spin-forbidden ones from his $\text{EH}(\omega)$ MO calculation.⁸⁾ Our calculation gives the spin-allowed d-d bands $^1\text{B}_1$ ($d_{yz} \rightarrow d_{x^2-y^2}$) at 2.39 eV and $^1\text{B}_1$ ($d_{xy} \rightarrow d_{x^2-y^2}$) at 3.46 eV, which hold very small oscillator strengths $f_s = 1 \times 10^{-4}$ and $f_s = 4 \times 10^{-4}$, respectively. These results suggest that the observed weak absorptions at 2.71 eV and 2.96 eV can not be necessarily assigned to the spin-forbidden transitions on the basis of their small absorption coefficients. Thus, there would also remain a possibility that these absorptions are spin-allowed d-d transitions.

Electron densities of Pt-ethylene and Pt-acetylene complexes. Results on electron densities are given in Table 6, together with quantities of ΔQ , ΔP_π , and P_{π^*} which are defined in the footnote of the table. In Pt(II) complexes, the electron density of the C atom is decreased from the value of the free ethylene by ca. 0.01 e and that of the free acetylene by ca. 0.1 e. In Pt(0)-ethylene and Pt(0)-acetylene complexes, they are increased by ca. 0.05 e and ca. 0.02 e,

Table 5 Calculated transition energies of Zeise's salt

Parametrization C'			obsd. ^{a)}	
δE	f		δE	f
2.39 eV	1×10^{-4}	1B_1		
3.46	4×10^{-4}	1B_2		
3.71	0.023	1A_1	3.72 eV	
4.37	0.024	1B_2	4.26	0.01
4.50	0.089	1B_2	4.67	0.019
4.94	0.082	1A_1	5.16	0.066
4.95	0.025	1A_1		

a) Ref. 10.

Table 6 Electron densities, $\Delta Q^a)$, $\Delta P_\pi^b)$ and $P_{\pi*}^c)$ of Pt(II) and Pt(0) complexes with ethylene and acetylene

(A) Ethylene complexes.

Compounds		$PtCl_3(C_2H_4)^-$	$PtBr_3(C_2H_4)^-$	$Pt(PH_3)_2(C_2H_4)$
Electron density	5d	8.490	8.530	9.341
	Pt 6s	0.618	0.646	0.579
	6p	0.588	0.586	0.559
	C	4.125	4.125	4.181
$\Delta Q^a)$		0.287	0.295	-0.039
$\Delta P_\pi^b)$		-0.166	-0.171	-0.379
$P_{\pi*}^c)$		-0.033	-0.034	-0.230

(B) Acetylene complexes.

Compounds		$PtCl_3(C_2H_2)^-$	$PtBr_3(C_2H_2)^-$	$Pt(PH_3)_2(C_2H_2)$
Electron density	5d	8.495	8.541	9.362
	Pt 6s	0.610	0.635	0.574
	6p	0.603	0.590	0.571
	C	4.028	4.024	4.125
$\Delta Q^a)$		0.289	0.302	0.004
$\Delta P_\pi^b)$		-0.155	-0.160	-0.343
$P_{\pi*}^c)$		-0.036	-0.036	-0.206

a) The quantity of transferred electrons from ethylene or acetylene to PtX_3^- of $Pt(PH_3)_2$ part. b) $\Delta P_\pi = (P_\pi \text{ of free ethylene}) - (P_\pi \text{ of complexed ethylene})$. ΔP_π of acetylene

Table 6 (Continued)

ethylene)-(P_π of complexed ethylene). P_π of acetylene complexes is defined as the same as that of ethylene ones, while only one π-bond (Y-axis) is considered because the other π-bond scarcely interacts with the Pt atom. c) The quantity of P_{*} is defined as the partial bond order in which π*-type interactions of ethylene or acetylene are only considered.

respectively. Values of ΔQ are ca. 0.3 e in Pt(II) complexes, while they are nearly equal zero in Pt(0) complexes. These different behaviours in the electron transfer between Pt(II) and Pt(0) complexes are due to the different character of the coordination bonds of ethylene and acetylene between these complexes; the σ -donor bond contributes mainly to the coordination bonds of ethylene and acetylene in Pt(II) complexes, while the π -acceptor bond contributes largely to the coordination bonds in Pt(0) complexes, as described below.

The absolute value of ΔP_{π} of $\text{PtBr}_3(\text{C}_2\text{H}_4)^-$ is larger than that of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$, suggesting the C=C double bond of $\text{PtBr}_3(\text{C}_2\text{H}_4)^-$ is weaker than that of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$. This result agrees with the experimental one that the ethylene part in $\text{PtBr}_3(\text{C}_2\text{H}_4)^-$ has a lower stretching vibration of the C=C double bond than that in $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ does.¹²⁻¹⁴ Since the absolute value of P_{π^*} is remarkably small in Pt(II) complexes, the decrease in the π -bond order of ethylene part is not due to the increase in its π^* -antibonding character but to the decrease in its π -bonding nature.

The values of ΔP_{π} in Pt(0) complexes are larger than those in Pt(II) complexes by ca. 0.17~0.2 e, suggesting that the C=C double and C≡C triple bonds in Pt(0) complexes are weaker than those in Pt(II) complexes. The difference in ΔP_{π} coincides well with the difference between the value of P_{π^*} of Pt(II) complexes and that of Pt(0) complexes. From this result,

roughly speaking, the stronger π -acceptor bond results in the larger increase in π^* -nature and the weaker C=C and C $\equiv$ C bonds of Pt(0) complexes than those in Pt(II) complexes.

Interaction between Pt and C atoms. In this section, the quantity of E_{AB} is used as the bond index, which means the energy contribution of the AB bond to the total energy of the molecule^{43, 44)} and is written down as follows under approximations used in this MO method³⁰⁾;

$$E_{AB} = E_{AB}^{(1)} + E_{AB}^{(2)} + E_{AB}^{(3)} \quad (4)$$

$$E_{AB}^{(1)} = 2 \sum_r^A \sum_t^B P_{rt} H_{rt} \quad (5)$$

$$E_{AB}^{(2)} = -0.5 \sum_r^A \sum_t^B P_{rt}^2 \gamma_{rt} \quad (6)$$

$$E_{AB}^{(3)} = \sum_r^A \sum_t^B (N_r - P_{rr}) (N_t - P_{tt}) \gamma_{rt} \quad (7)$$

A negative value of E_{AB} represents the bonding interaction between A and B atoms, and a larger absolute value reveals a strong interaction.

In order to investigate the bonding character, $E_{AB}^{(1)}$ and $E_{AB}^{(2)}$ are divided into each AO pair term, $E_{Ar Bs}^{(1)}$ and $E_{Ar Bs}^{(2)}$ etc., where Ar represents the AO. r on the A atom. $E_{AB}^{(3)}$ is not divided into each AO pair terms, because this term represents approximately an electrostatic energy and its meaning is lost by the division into each AO pairs.

The absolute value of E_{Pt-C} decreases in the following order; Pt(0) complexes > Pt(II) complexes, and acetylene

complexes > ethylene complexes. This result shows acetylene coordinates to the Pt atom more strongly than ethylene does and that the coordination bonds of ethylene and acetylene in Pt(0) complexes are stronger than those in Pt(II) complexes.

As shown in Table 7, $E_{\text{Pt-C}}$ is contributed largely by $E_{\text{s-}\pi}$ and $E_{\text{p}_{\sigma}\text{-}\pi}$ in Pt(II) complexes, where the former subscript, such as s and p_{σ} , means the AO of the Pt atom and the latter one the AO of the C atom. The contributions of $E_{\text{d}\pi\text{-}\pi^*}$ and $E_{\text{p}_{\pi}\text{-}\pi^*}$ are small. These results suggest that the coordination bonds of ethylene and acetylene is mainly contributed by the σ -donor bond in Pt(II) complexes, through which ethylene and acetylene donate their π -electrons to the 5d, 6s and 6p orbitals of the Pt atom. This bonding nature agrees with the proposals by Behnke et al.,⁴⁵⁾ Braterman⁴⁶⁾ and Cooper et al.⁴⁷⁾ on the coordination bond of olefin in Pt(II) complexes.

In Pt(0) complexes, the absolute values of P_{π^*} and $E_{\text{d}\pi\text{-}\pi^*}$ are much larger than those of Pt(II) complexes, while $E_{\text{d}\sigma\text{-}\pi}$ in Pt(0) complexes is smaller than that of Pt(II) complexes. These results suggest that the π -acceptor bond contributes largely to the coordination bond in Pt(0) complexes, relative to that of Pt(II) complexes. The $\text{d}\sigma\text{-}\pi$ interaction seems to be reduced by the formal d^{10} configuration of the Pt(0) atom, while this interaction is considerably large in Pt(II) complexes due to the formal d^8 configuration of the Pt(II) ion. The large absolute values of $E_{\text{s-}\pi}$ and $E_{\text{p}_{\sigma}\text{-}\pi}$ reveal that the

Table 7 Coordination bonding character of Pt(II) and Pt(0) complexes with ethylene and acetylene

Compounds	$\text{PtCl}_3(\text{C}_2\text{H}_4)^-$	$\text{PtBr}_3(\text{C}_2\text{H}_4)^-$	$\text{Pt}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$	$\text{PtCl}_3(\text{C}_2\text{H}_2)^-$	$\text{PtBr}_3(\text{C}_2\text{H}_2)^-$	$\text{Pt}(\text{PH}_3)_2(\text{C}_2\text{H}_2)$
$E_{\text{d}\sigma-\pi}$	-0.557 eV	-0.530 eV	-0.240 eV	-0.585 eV	-0.579 eV	-0.257 eV
$E_{\text{d}\pi-\pi^*}$	-0.545	-0.546	-1.844	-0.627	-0.624	-1.844
$E_{\text{s}-\pi}$	-1.368	-1.394	-1.853	-1.427	-1.880	-1.861
$E_{\text{p}\sigma-\pi}$	-1.067	-1.127	-1.239	-1.074	-1.880	-1.861
$E_{\text{s}-\text{s}}$	-0.673	-0.663	-0.876	-1.078	-1.069	-1.225
$E_{\text{p}\sigma-\text{s}}$	-1.015	-1.035	-1.184	-1.468	-1.490	-1.549
$E_{\text{Pt}-\text{C}}$	-6.547	-6.591	-8.380	-8.039	-7.698	-9.502

σ -donor bond contributes remarkably to the coordination bond in the Pt(0) complexes.

In both Pt(II) and Pt(0) complexes, the absolute values of E_{s-s} and $E_{p_{\sigma}-s}$ are remarkably large, suggesting that the large σ -bonding interaction exists between the 2s orbital of the C atom and the 6s and 6p orbitals of the Pt atom. Thus, the hybridization of the C atom of ethylene approaches from sp^2 to sp^3 and that of acetylene does from sp to sp^2 , not only due to the σ -donor and π -acceptor bond but also due to these s-s and p_{σ} -s interactions. This result also suggests that the cis-bending of the CH_2 group of ethylene and CH group of acetylene are brought about by the σ -donor bond, π -acceptor bond and these s-s and p_{σ} -s interactions.

The relative contribution of valence orbitals of the Pt atom should not be discussed by use of the bond order but by use of $E_{Ar Bs}$, since the bond order is not appropriate for the bond index due to its rotational variable character. As shown in Table 7, it is noted that the 6s orbital contributes to the coordination bond as much as the 6p orbital does, and that the contribution of the 5d orbital is one-half or one-third of those of the 6s and 6p orbitals. Our results do not agree with the proposal of Nelson et al.²⁵⁾ that the hybridization of the Pt atom is dp^2 or d^2p^2 in these complexes.

In conclusion, 6s and 6p orbitals of the Pt atom greatly contribute to the coordination bonds of ethylene and acetylene,

while the 5d orbital also considerably contributes in Pt(II) complexes. The π -acceptor bond ($d_{\pi}-\pi^*$) much contributes in Pt(0) complexes, while its contribution in the Pt(II) complexes is about one-third of that in the Pt(0) complexes. This stronger π -acceptor bond in Pt(0) complexes results in the larger electron density on the C atom, the smaller value of ΔQ , the weaker C=C and C $\equiv$ C bonds and the larger value of $E_{\text{Pt-C}}$, relative to those of Pt(II) complexes. It should be noted that strong s-s and p_{σ} -s interactions exist between Pt and C atoms besides the σ -donor and π -acceptor bonds.

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chapter 7. Summary

In part I, various modifications to the CNDO-type and INDO-type SCF-MO methods are presented, and electronic structures of transition metal complexes are investigated by the use of these methods.

In chapter 2, preliminary MO calculations are performed on MnO_4^- , CrO_4^{2-} , PdX_4^{2-} , and PdX_6^{2-} ($\text{X}=\text{F}$, Cl , and Br) by the use of the CNDO-type MO method. Calculated electronic spectra of MnO_4^- , CrO_4^{2-} , and PdCl_6^{2-} agree fairly well with experimental ones in transition energies and their assignments. Although calculated electron densities on central metal atoms are too large as compared with experimental results in MnO_4^- , PdCl_4^{2-} , and PdCl_6^{2-} , MO calculations give qualitatively reasonable results: The electron density on the Pd atom decreases in the following order; $\text{PdBr}_4^{2-} > \text{PdCl}_4^{2-} > \text{PdCl}_6^{2-}$, which agrees with experimental order. In this thesis, the quantity, E_{AB} , which is defined as an energy contribution of a AB bond to a total energy, is used as a bond index. While this quantity has been reported to be a useful bond index in organic compounds, this has not been used in transition metal compounds. This usefulness is confirmed in this chapter; that is, the following orders are obtained for the absolute value of $E_{\text{Pd-X}}$; $\text{PdCl}_6^{2-} > \text{PdCl}_4^{2-}$ and $\text{PdCl}_6^{2-} > \text{PdBr}_6^{2-}$, which are in good agreement with the order of stretching

vibration frequency of the Pd-Cl bond and that of force constant of the Pd-X bond, respectively.

In chapter 3, the CNDO-type and INDO-type UHF-MO method are used in the investigation of electronic structures of open-shell iron group fluorides and other similar transition metal halides. Calculated electron densities on central metal atoms and spin distributions are in good agreement with experimental ones. Spin fractions on the ligand are divided into two parts; one due to the spin delocalization, and the other due to the spin polarization. In almost all complexes, spin appearing on the ligand is mainly attributed to the former, while in CrF_6^{3-} and VF_6^{4-} spin fractions on 2s and $2p_\sigma$ orbitals of the ligand are due to the spin polarization, and in MnCl_6^{4-} and MnBr_6^{4-} , spin fractions on s and p_σ orbitals of the X ligand are contributed to some extent by the spin polarization. Unpaired electrons are highly localized on the d orbitals of the central metal atom, which supports the application of the crystal field theory to these complexes.

As described in chapters 2 and 3, the MO method gave reasonable results on Werner type transition metal complexes. In the following chapters 4 ~ 6, electronic structures of organo-transition metal complexes are studied by the use of the MO methods used in chapters 2 and 3.

In chapter 4, the CNDO-type MO calculations are carried out on ferrocene and cobalticenium ion which have iso-electro-

nic structures with each others and are well-known organo-metallic compounds. In ferrocene, both CNDO-type and INDO-type MO calculations give almost the same electron density on the 3d orbital of the Fe atom as that obtained from ab initio MO calculation, while electron densities on 4s and 4p orbitals of the Fe atom obtained in this work are considerably larger than those calculated by the ab initio MO method. In cobalticinium ion, calculated electron distribution is similar to that of ferrocene. In ferrocene and cobalticinium ion, electronic spectra calculated by both methods agree fairly well with experimental ones, with few exceptions.

In chapter 5, the well-known Ag(I)-olefin complexes are investigated by the CNDO-type MO method. Calculated value of $-\Delta H$ increases with the increasing number of methyl groups, which agrees with experimental results. The linear relation exists between the decrease in the calculated π -bond order of complexed olefin from that of uncomplexed one and the decrease in the stretching vibration frequency of the C=C double bond of the former from that of the latter, as shown in Fig. 2 in chapter 5. The coordination bonds of olefins are mainly contributed by the σ -donor bond, through which olefins mainly donates its π -electrons to 5s and 5p orbitals of the Ag atom. The contribution of 4d orbitals to olefin's coordination is small relative to those of 5s and 5p orbitals; especially the $d\sigma-\pi$ interaction is weak, while the $d\pi-\pi^*$

interaction is considerably strong. ^{13}C NMR chemical shift of the unsaturated carbon atom is decreased by the complex formation of olefin with the Ag(I) ion, which is interpreted in terms of the donation of olefin's π -electrons to the Ag(I) ion.

In chapter 6, theoretical studies are carried out on Pt(0) and Pt(II) complexes with ethylene and acetylene. While the MO method used in this chapter is essentially the same as the CNDO-type one used in chapters 2 ~ 5, the modified Ohno's equation is used to calculate Coulomb repulsion integrals between outer orbitals (6s and 6p orbitals) of the Pt atom and valence orbitals. The MO method with the modified Ohno's equation gives good results on electronic spectra of PtCl_4^{2-} and $\text{PtCl}_4(\text{C}_2\text{H}_4)^-$. From studies in this chapter, the σ -donor bond mainly contributes to the coordination bonds of ethylene and acetylene in Pt(II) complexes, and the π -acceptor bond also considerably contributes. In Pt(0) complexes, the π -acceptor bond contributes to the coordinations of ethylene and acetylene more extensively than that in Pt(II) complexes, and the σ -donor bond also contributes considerably, while the contribution of the σ - π interaction is remarkably small.

As described in chapters 2, 4, and 6, the MO methods used in this thesis can give good results on electronic spectra with few exceptions. In CrF_6^{3-} and FeF_6^{3-} , electron densities on the central metal atom agree well with experimental ones,

while they are too large in some cases such as MnO_4^- , PdCl_4^{2-} , and PdCl_6^{4-} . In chapters 5 and 6, studies are carried out successfully on coordination bonding characters of olefins and acetylene. Thus, the presented semi-empirical SCF-MO method is valid means for studying electronic structures of transition metal complexes, and it is expected that the MO method can give us useful information for studying catalytic reactions of transition metal complexes.

PART II

THEORETICAL INVESTIGATIONS
ON
CATALYTIC REACTIONS OF TRANSITION METAL COMPLEXES
WITH
SEMI-EMPIRICAL SCF-MO METHOD

Chapter 1. Introduction

There have been reported only a few of theoretical studies on catalytic reactions. The first attempt was carried out by Begley and Pennella,¹⁾ in which Begley et al. investigated olefin polymerization by titanium-aluminum alkyl with the extended Hückel (ω) MO method. Similar studies on Ziegler-Natta catalyst have also been reported.^{2, 3)} It should be noted that Mango and Schachtsneider⁴⁾ attempted to interpret the catalytic activity of some transition metal complexes in olefin metathesis by using Woodward-Hoffman rule. Recently the chemisorption was also theoretically investigated,⁵⁻⁸⁾ which is a very important issue in solid-phase catalysis.

As described above, theoretical studies on catalysis made a start only lately. We are far from the goal in these theoretical studies; one object is, of course, to elucidate the origin of the catalytic ability or the driving force of catalysis and the other one is to anticipate the catalytic ability (activity and selectivity) of catalysts. At the present stage, we should carry out as many theoretical studies on various catalytic reactions as possible.

In this part, theoretical studies are carried out on some reaction systems including transition metal complexes as catalyst, by means of the semi-empirical SCF-MO method used in part I.

In chapter 2 in this part, the oxymercuration and the

Wacker reaction are investigated. These reactions include the attack of nucleophiles to the olefin coordinating to the Pd(II) or Hg(II) ion as the important step. MO studies are carried out on electronic structures of Hg(II)- and Pd(II)-olefin complexes and on nucleophilic attack of OH^- to the olefin coordinating to the Pd(II) or Hg(II) ion. Main interest is directed to the reaction mechanism. Also the Markovnikoff rule in the Wacker reaction and the oxymercuration is explained by the use of the MO method.

In chapter 3, MO studies are carried out on the electronic structures of $\text{trans-PtHX}(\text{PH}_3)_2$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}, \text{or } \text{CN}^-$) which acts as catalysts in hydrogenation, isomerization, and hydrogen-deuterium exchange reactions etc. of olefins. The ethylene insertion into the Pt-H bond is investigated by the use of the MO method. This insertion reaction is considered as the key step in hydrogenation, isomerization, and hydrogen-deuterium exchange reactions etc. of olefins. A discussion is presented on the reaction mechanism and ligand effect in the insertion reaction. Also, it is tried to anticipate the ligand effect on catalytic activity of $\text{trans-PtHX}(\text{PR}_3)_2$ in the hydrogen-deuterium exchange reaction of ethylene.

In chapter 4, the resultant conclusion of this part are presented.

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Chapter 2. The oxymercuration and the Wacker reaction

§ 1. Introduction

A number of reactions of nucleophilic attack on olefins coordinated to a metal ion are well known.¹⁻³⁾ Complex formation reduces the electron density between the carbon atoms of double bond, rendering the double bond more susceptible to nucleophilic attack. This must be the first requisite for the catalytic ability of transition metal ions in nucleophilic reactions. It is, therefore, interesting from the viewpoint of catalytic chemistry to investigate the electronic structures of olefins coordinated to transition-metal ions. There have, though, been few MO studies^{4,5)} of such transition-metal olefin complexes supposed to be intermediates in catalytic reactions.

The Wacker reaction¹⁻³⁾ and the oxymercuration^{6, 7)} are known as nucleophilic reactions to a coordinated olefin; in them Pd(II)- and Hg(II)-olefin complexes are considered to be reaction intermediates. MO calculations were carried out on Pd(II)- and Hg(II)-olefin complexes in order to investigate the electronic structures of the coordinated olefins. A discussion is presented on the catalytic activities of Pd(II) and Hg(II). Also by the use of the MO method, the author studied whether the cis-addition occurs in the oxymercuration, or whether the trans-addition does, and whether or not the

cis-addition of OH^- in the Wacker reaction is a reasonable mechanism; these issues have never been discussed theoretically. Since some works using the Iterative Extended Hückel MO method^{8, 9)} have been done to investigate the catalytic reactions, it is also the author's object to examine the possibility of applying the more accurate semi-empirical SCF-MO method to studies in the field of catalytic chemistry.

§ 2. MO Calculations and Geometries of Complexes

MO Calculations. All valence orbitals, including 5d-atomic orbitals of the Hg atom, were considered explicitly. The modified CNDO-type approximations were used; the Hartree-Fock matrix elements have been given in elsewhere.¹⁰⁾ The resonance integrals, H_{rs} ($r \neq s$), were calculated according to the Wolfsberg-Helmholz approximation;¹¹⁾

$$H_{rs} = -k S_{rs} (I_r + I_s) \quad (1)^{12)}$$

In order to determine the value of k , the MO's of ethylene, propylene, methane, carbon monoxide, and formaldehyde were calculated using various values of k . That is, as to the MO energies of ethylene and ionization potentials of these compounds, the best-fitting value of k was 0.40.¹³⁾ Hereafter, the value of k will be taken as 0.40 for all s and p orbitals. For the AO pair including the d-orbital, the value of k was determined to be equal to 0.50, thus the calculated first and second d-d transitions of PdCl_4^{2-} coincide with the

Table 1 The first and second d-d transition energies of Pd 1_4^{2-}

k	0.55	0.50	obsd.	
$1A_{2g}$	2.62 eV	2.54 eV	2.62 eV ^{a)}	2.48 eV ^{b)}
$1E_g$	3.40	3.44		2.80

a) Ref. 15. b) Ref. 16.

experimental results, as shown in Table 1.

The value of the ionization potentials, I_r , and the one-center Coulomb repulsion integrals, γ_{rr} , of ligand atoms were taken from Jaffé et al.,¹⁶⁾ while those values of the Pd atom were taken from Di Sipio et al.¹⁷⁾ Since those values of the Hg atom were not given in the paper of Di Sipio et al., the values of I_r were taken from Bach's paper¹⁸⁾ and those of γ_{rr} were estimated as follows;

$$\gamma_{rr}^{(6)} \text{ semi-emp} / \gamma_{rr}^{(5)} \text{ semi-emp} = \gamma_{rr}^{(6)} \text{ nonemp} / \gamma_{rr}^{(5)} \text{ nonemp} \quad (2)$$

where $\gamma_{rr}^{(5)}$ and $\gamma_{rr}^{(6)}$ represent the one-center Coulomb repulsion integrals of a fifth-row element and a sixth-row element, which belong to the same group in the periodic table, respectively. The subscripts "semi-emp" and "nonemp" indicate the semi-empirical value and the nonempirical value of γ_{rr} , respectively. $\gamma_{rr}^{(N)} \text{ nonemp}$ (N=5 or 6) was calculated using

Clementi's AO,¹⁹⁾ and $\gamma_{rr}^{(5)}$ semi-emp was taken from Di Sipio's paper.¹⁷⁾ Then the $\gamma_{rr}^{(6)}$ values used in this work were obtained from the values of $\gamma_{rr}^{(6)}$ semi-emp by applying the least-squares method and by imposing the restrictive condition¹⁷⁾ that the values of $\gamma_{rr}^{(6)}$ varied linearly with the atomic number. In order to calculate the overlap integrals, a single Slater-type orbital^{19, 20)} was used for all s- and p-orbitals; the double- ζ type form orbital²¹⁾ was used only for the d-orbitals of metal atoms. The values of the AO exponents, ζ_r , I_r and γ_{rr} of the Pd and Hg atoms are listed in Table 2.

The author uses the quantity of E_{AB} as the bond index,²²⁻²⁴⁾ which is defined as the contribution of the AB bond to the total energy; it is written, by the use of approximations used in this work, as follows;

$$E_{AB} = E_{AB}^{(1)} + E_{AB}^{(2)} + E_{AB}^{(3)} \quad (3)^{12)}$$

$$E_{AB}^{(1)} = 2 \sum_r^A \sum_s^B P_{rs} H_{rs} \quad (4)^{12)}$$

$$E_{AB}^{(2)} = -0.5 \sum_r^A \sum_s^B P_{rs}^2 (rr|ss) \quad (5)^{12)}$$

$$E_{AB}^{(3)} = \sum_r^A \sum_s^B (P_{rr} - N_r) (P_{ss} - N_s) (rr|ss) \quad (6)^{12)}$$

where $\sum^A$ represents the summation on the A atom.

Geometries of Pd(II)- and Hg(II)-olefin Complexes . Because of the lack of knowledge of the accurate configurations of these compounds, the configurations of the olefin moieties

Table 2. Orbital exponents, ζ_r , valence state ionization potentials, I_r , and one-center Coulomb repulsion integrals, γ_{rr} , of Pd and Hg atoms.

Atom	AO	$\zeta_r^a)$	$C^b)$	I_r	γ_{rr}
Pd		5.983	0.5264	8.17 eV ^{c)}	13.87 eV ^{c)}
		2.613	0.6373		
		2.190		7.07	7.46
		2.190		3.30	6.22
Hg		6.436	0.6667	15.66 d)	13.53 e)
		3.032	0.5401		
		2.649		10.44	7.40
		2.649		5.00	6.31

a) The double- ζ form AO's are used only for d orbitals (Ref. 21).

b) Since the author neglects the contribution of 3d orbital in the case of the Pd atom and those of 3d and 4d orbitals in the case of the Hg atom, the 4d orbital of the Pd atom and the 5d orbital of the Hg atom are re-normalized.

c) Ref. 17. d) Ref. 18. e) The estimated values with eq. 2.

in these complexes were assumed to be the same as those of the corresponding free olefins.²⁵⁾ The distances between the metal atom and the center of the double bond were fixed as 2.31 Å for the Hg(II) complexes.⁴⁾ The metal-olefin coordination bond was assumed to intercept the double bond perpendicularly at its center. The coordinate systems for these complexes are given in Fig.1.

Models for the Oxymercuration and the Wacker Reaction. In the oxymercuration, both cis- and trans-addition products were formed from the strained olefins, such as norbornene and bicyclo-[2,2,2]-oct-2-ene,^{7, 26-29)} although only a trans-addition product was formed from nonstrained olefins.⁶⁾ Therefore, it is meaningful to shed some light on the course of the addition using a MO method. Since mercurinium ions

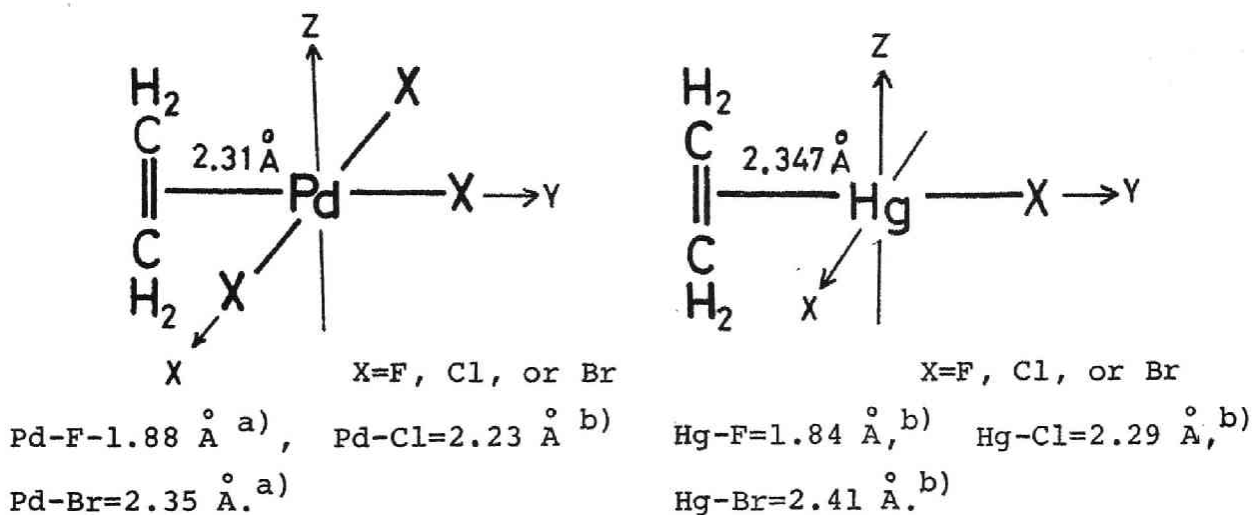


Fig. 1. The coordinate systems of Pd(II) and Hg(II)-ethylene complexes.

a) The estimated value. b) Ref. 25. (See CH_3HgX for Hg-X bond lengths.)

have been postulated as intermediates in oxymercuration of olefins,^{6, 30)} the author assumed both cis- and trans-oxymercurials were derived from a common mercurinium ion, and calculated the MO's of the models for cis- and trans-addition (See Fig. 2.). In order to investigate effects of ligands and reactants, the author calculated MO's of reaction systems, such as $\text{Hg}(\text{C}_2\text{H}_4)^{2+} + \text{OH}^-$, $\text{HgCl}(\text{C}_2\text{H}_4)^+ + \text{OH}^-$, $\text{HgCl}(\text{C}_3\text{H}_6)^+ + \text{OH}^-$, $\text{HgCl}(\text{cis-2-C}_4\text{H}_8)^+ + \text{OH}^-$, and $\text{HgCl}(\text{trans-2-C}_4\text{H}_8)^+ + \text{OH}^-$, in which OH^- was assumed to approach olefin in the trans position of Hg(II) (See Fig. 3.), since the trans-oxymercurials were formed in general.

In the case of the Wacker reaction, an oxypalladate intermediate has not been observed. However, its existence has been postulated on the basis of kinetic studies,³¹⁻³⁵⁾ and the step of its formation from Pd(II)-olefin complex has been considered to be the rate-determining step. The models for these intermediates are shown in Fig. 3.

In order to investigate the selectivity in the Wacker reaction³⁴⁾ and the oxymercuration⁶⁾ the author carried out MO calculations of models described in Fig. 4.

§ 3. Results and Discussion

Pd(II)- and Hg(II)-ethylene Complexes. The electron densities, the π -bond order, P_π ,³⁷⁾ the π^* -bond order, P_{π^*} ,³⁷⁾ the quantities of transferred electrons from ethylene to

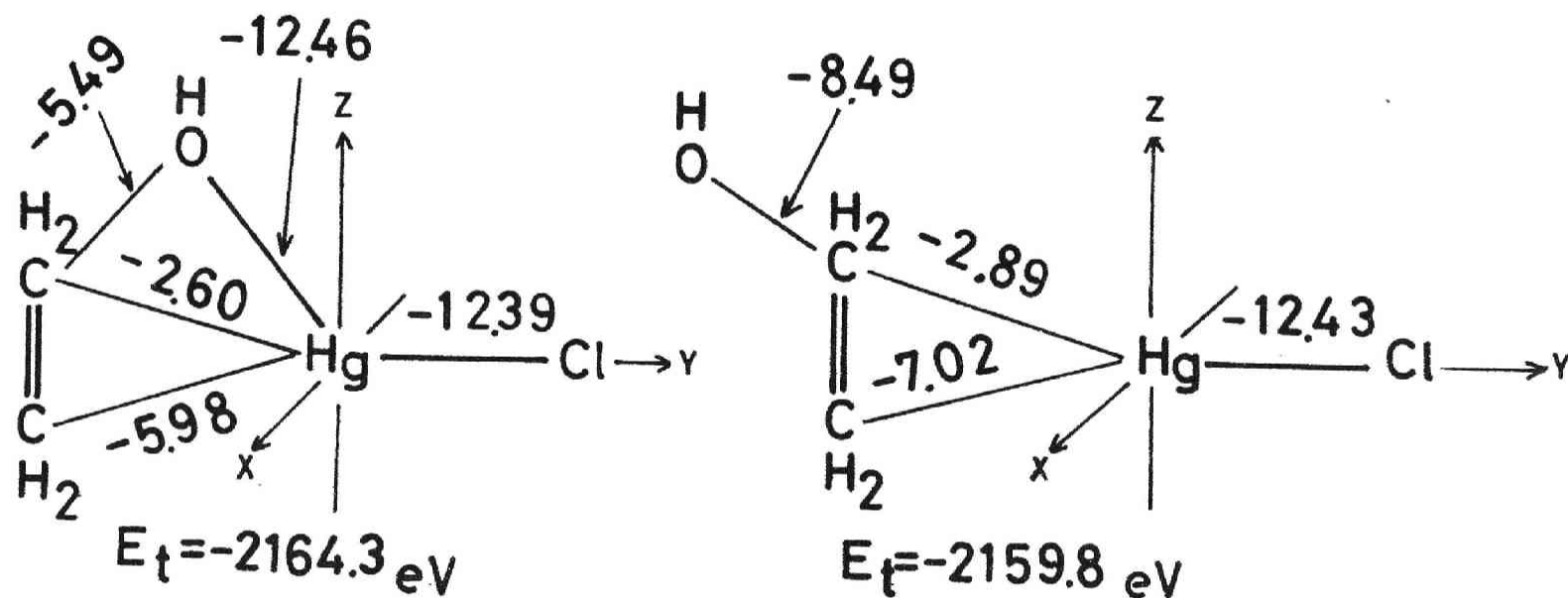
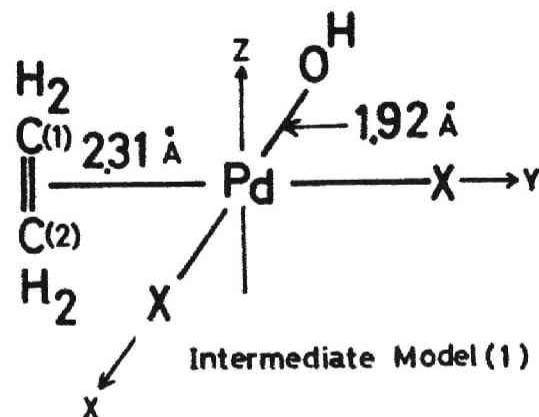


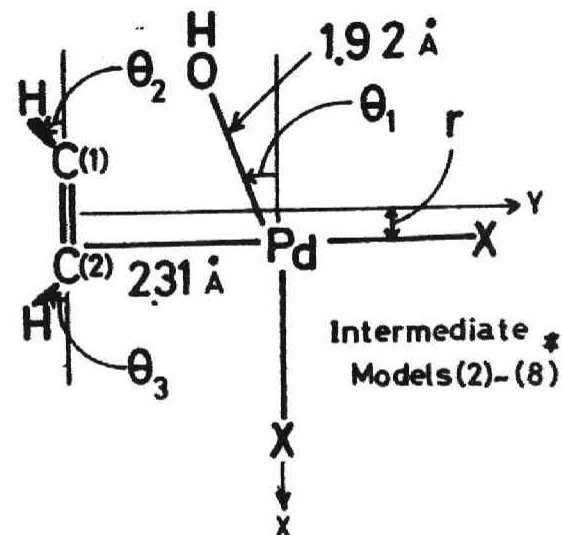
Fig. 2. The values of $E_{AB}^{a)}$ in the cis- and trans-addition in Oxymercuration.

a) eV. unit. b) The relative position of OH^- to ethylene is the same as that of the cis-addition system. $\text{C-O} = 1.72 \text{ \AA}$ and $\text{Hg-O (cis-addition)} = 2.03 \text{ \AA}$

(A) Intermediate Models in Wacker Reaction



Model	2	3	4	5	6	7	8
$r(\text{\AA})$	0.0	0.0	0.0	0.0	0.3	0.3	0.3
θ_1	0°	15°	30°	30°	30°	30°	30°
θ_2	0°	0°	0°	0°	7.5°	15°	15°
θ_3	0°	0°	0°	0°	0°	0°	7.5°



(B) Intermediate Model in Oxymercuration

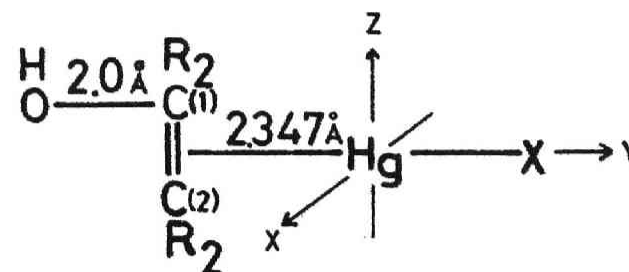


Fig. 3. Intermediate models of Wacker reaction and Oxymercuration.

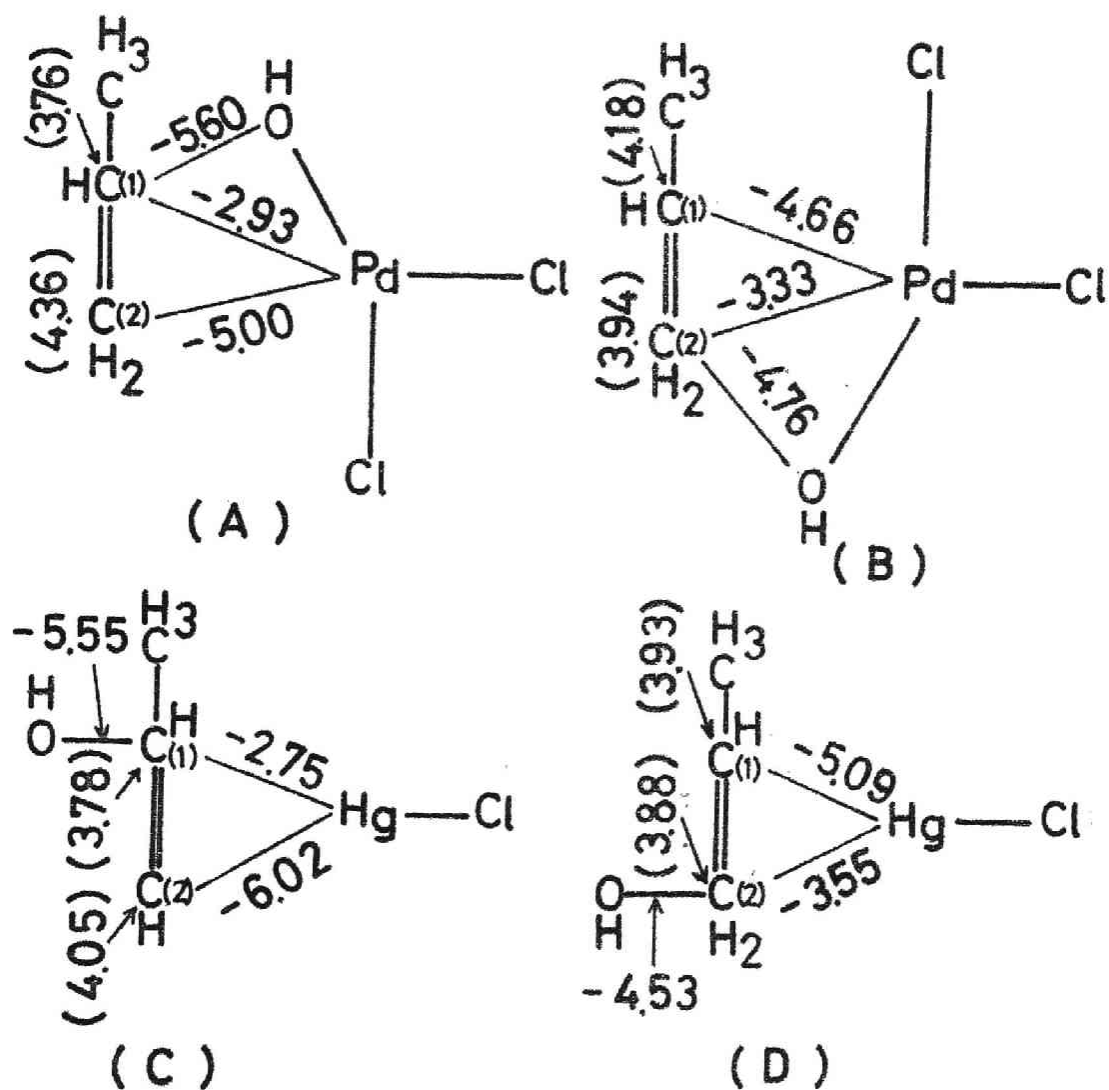


Fig. 4. The values of $E_{AB}^{a)}$ and electron densities in Wacker reaction and oxymercuration of propylene.

a; eV. unit. in parenthesis; electron density on atom.

For configurations A and B, see the model 4 in Fig. 3.

For configurations C and D, see the model for oxymercuration in Fig. 3.

metal-ligand part, ΔQ , are shown in Table 3. The electron densities on the Pd and Hg atoms increase with the decrease in the electronegativity of the halogen atom, except in the case of $\text{HgCl}(\text{C}_2\text{H}_4)^+$ or $\text{HgBr}(\text{C}_2\text{H}_4)^+$. The electron density on the C atom is decreased by the coordination as follows; free ethylene > coordinated ethylene to Pd(II) > coordinated ethylene to Hg(II). It is notable that this decreasing order agrees with the increasing reactivity for the nucleophile; i.e., the nucleophilic attack of OH^- in the Wacker reaction slowly proceeds,³¹⁻³⁵⁾ and that in the oxymercuration proceeds very fast,³⁾ while the reaction can not occur in the absence of Pd(II) and Hg(II).

The values of ΔQ in the Hg(II)-complexes are larger than those in the Pd(II)-complexes, while the values of P_π and P_{π^*} are smaller than those in the Pd(II)-complexes. The coordination bond orders are shown in Table 4. The π -acceptor bond orders, $P_{d\pi-\pi^*}$, in the Pd(II)-complexes are greater than those in the Hg(II)-complexes; this agrees with the larger values of P_{π^*} in the Pd(II)-complexes relative to those values in the Hg(II)-complexes. While in Pd(II)-complexes the contributions of the d-orbitals are remarkably large, their contributions are very small in the Hg(II)-complexes, in which the 6s and 6p orbitals of Hg(II) mainly contribute to the coordination bond. The small contribution of the 5d atomic

Table 3. The Electronic Structures of Pd(II)- and Hg(II)-ethylene Complexes.

Compounds	Electron Density		Carbon	P_{π} a)	P_{π^*} b)	ΔQ c)
	Metal d	sp				
C_2H_4			4.133	1.000	0.0	0.0
$PdF_3(C_2H_4)^-$	8.076	1.418	4.083	0.884	-0.009	0.240
$PdCl_3(C_2H_4)^-$	8.015	2.014	4.080	0.870	-0.012	0.252
$PdBr_3(C_2H_4)^-$	7.975	2.164	4.078	0.864	-0.013	0.259
$Hg(C_2H_4)^{2+}$	9.983	0.751	3.974	0.654	-0.002	0.734
$HgF(C_2H_4)^+$	9.931	1.010	4.050	0.806	-0.003	0.429
$HgCl(C_2H_4)^+$	9.942	1.282	4.044	0.807	-0.003	0.426
$HgBr(C_2H_4)^+$	9.944	1.376	4.045	0.813	-0.003	0.414

a) π -bond order of C=C double bond.

b) See the footnote (37).

c) The quantity of transferred electron from olefin to metal.

Table 4. The coordination bond orders of Pd(II)- and Hg(II)-ethylene complexes.

	π -acceptor $P_{d\pi-\pi^*}$	$P_{d\sigma-\pi}$	σ -donor $P_{s-\pi}$	$P_{p\sigma-\pi}$
$PdF_3(C_2H_4)^-$	0.131	0.235	0.256	0.282
$PdCl_3(C_2H_4)^-$	0.144	0.267	0.232	0.310
$PdBr_3(C_2H_4)^-$	0.147	0.273	0.229	0.319
$Hg(C_2H_4)^{2+}$	0.062	0.088	0.630	0.201
$HgF(C_2H_4)^+$	0.072	0.115	0.439	0.294
$HgCl(C_2H_4)^+$	0.060	0.110	0.327	0.259
$HgBr(C_2H_4)^+$	0.074	0.104	0.370	0.344

- a) $P_{d\pi-\pi^*}$ represents the bond order matrix element between d_{π} orbital of the metal atom and π^* -MO of ethylene, and the others such as $P_{d\sigma-\pi}$ etc., represent similar bond order matrix elements.

orbitals of Hg(II) is considered to be due to the $5d^{10}$ configuration of Hg(II) as well as Ag(I)-ethylene complex.^{10-b,39)}

The Oxymercuration. The results are given in Fig.2. It may be seen from a comparison of the total energy that the cis-attack system is more stable than the trans-attack system. The absolute value of E_{C-O} in the cis-attack system is smaller than that in the trans-attack system, probably because of the interaction of the O atom with the Hg atom in the cis-attack system, while there is no interaction between the O and Hg atoms in the trans-attack system. On the other hand, the bonding interaction between the O and Hg atoms contributes to the larger stabilization of the cis-attack system, suggesting that the mercurinium ion is stabilized by the coordination of the nucleophile. Our results agree with the mechanism proposed by Bach et al.²⁹⁾: (a) if the concentration of the nucleophile is sufficient, or if the solvent coordinates to Hg(II) to interfere with the coordination of the nucleophile, the trans-attack may occur, since the nucleophile in the trans-position interacts with the C atom of olefin more strongly than that in the cis-position; and (b) the mercurinium ion which is formed from a strained olefin, such as norbornene, is relatively short-lived and is likely to react with the intimate nucleophile coordinated to the mercurinium ion nearest to the olefin, since there is a remarkable bonding interaction between the C and O atoms, though this

interaction is weak relative to that in the trans-attack system. In this case, the cis-attack may occur preferably.

The calculated results of the models in Fig. 3 are given in Table 5, together with the results on the interaction of OH^- with free ethylene and on the interaction of OH^- with the ethylene coordinated to the PdCl_3^- anion.⁴⁰⁾ The values of $E_{\text{C-O}}^{(41)}$ are negative in all cases, suggesting a bonding interaction between the C atom of ethylene and the O atom of OH^- . The absolute values of $E_{\text{C-O}}$ increase in the following order; free ethylene < $\text{PdCl}_3(\text{C}_2\text{H}_4)^- < \text{HgCl}(\text{C}_2\text{H}_4)^+ < \text{Hg}(\text{C}_2\text{H}_4)^{2+}$. Those results suggest that the nucleophilic attack of OH^- on ethylene is accelerated by Pd(II) and Hg(II), and that the acceleration by Hg(II) is larger than that by Pd(II), which agrees well with the catalytic behaviour of Hg(II)³⁸⁾ and Pd(II).³⁵⁾ Compared with the absolute values of $E_{\text{C-O}}^{(1)}$, $E_{\text{C-O}}^{(2)}$, and $E_{\text{C-O}}^{(3)}$ in $\text{C}_2\text{H}_4 + \text{OH}^-$ system, those of $E_{\text{C-O}}^{(1)}$ and $E_{\text{C-O}}^{(3)}$ are largely increased in $\text{PdCl}_3(\text{C}_2\text{H}_4)^- + \text{OH}^-$ system, and the values of $E_{\text{C-O}}^{(1)}$ and $E_{\text{C-O}}^{(2)}$ are also increased in the $\text{Hg}(\text{C}_2\text{H}_4)^{2+} + \text{OH}^-$ and $\text{HgCl}(\text{C}_2\text{H}_4)^+ + \text{OH}^-$ systems. Since $E_{\text{AB}}^{(1)}$ and $E_{\text{AB}}^{(2)}$ indicate approximately the contribution of covalent interaction to the total energy, the existence of Hg(II) and Pd(II) may cause an increase in the covalent bonding ability of ethylene with OH^- . From the results that the electron density on the C atom in ethylene complexes decreases in the following order; free ethylene > $\text{PdX}_3(\text{C}_2\text{H}_4)^- > \text{HgX}(\text{C}_2\text{H}_4)^+$

Table 5. The nucleophilic attack of OH^- to olefin coordinating to Hg(II) .

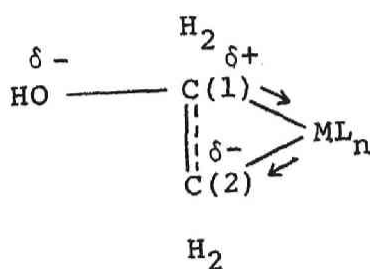
Reaction systems	Electron density			b)			(1)			(2)			(3)			$E_{\text{Hg-C(1)}}$ $E_{\text{Hg-C(2)}}$	
	Metal	C(1) a)	C(2)	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$	$E_{\text{C-O}}$
$\text{C}_2\text{H}_4 + \text{OH}^-$		3.914	4.290	-3.013	-1.961	-0.479	-0.572										
$\text{Hg}(\text{C}_2\text{H}_4)^{2+} + \text{OH}^-$	11.599	3.944	3.836	-5.427	-3.548	-1.672	-0.207	-2.540	-3.870								
$\text{HgCl}(\text{C}_2\text{H}_4)^+ + \text{OH}^-$	11.506	3.894	4.013	-4.936	-3.051	-1.277	-0.607	-3.157	-5.788								
$\text{PdCl}_3(\text{C}_2\text{H}_4)^- + \text{OH}^-$ c)	10.114	3.851	4.105	-3.832	-2.243	-0.617	-0.972	-2.206	-5.254								

$\text{HgCl}(\text{trans-2-C}_4\text{H}_8)^+ + \text{OH}^-$	11.586	3.807	3.910	-5.169	-2.935	-1.081	-1.153	-3.193	-5.319								
$\text{HgCl}(\text{cis-2-C}_4\text{H}_8)^+ + \text{OH}^-$	11.588	3.806	3.907	-5.172	-2.931	-1.078	-1.163	-3.192	-5.310								

a) See Fig. 3-b. b) The E_{AB} value of the bond C(1)-O (eV unit.).

c) The relative position of the OH^- anion to ethylene is the same as that in $\text{Hg}(\text{C}_2\text{H}_4)^{2+} + \text{OH}^-$ system (See Fig. 3-b).

$> \text{Hg}(\text{C}_2\text{H}_4)^{2+}$, the absolute values of $E_{\text{C-O}}^{(3)}$ should be affected to this order, since $E_{\text{C-O}}^{(3)}$ represents approximately the electrostatic energy and since the O atom has a negative charge. However, the absolute values of $E_{\text{C-O}}^{(3)}$ increase in the following order: $\text{Hg}(\text{C}_2\text{H}_4)^{2+} + \text{OH}^- < \text{C}_2\text{H}_4 + \text{OH}^- < \text{HgCl}(\text{C}_2\text{H}_4)^+ + \text{OH}^- < \text{PdCl}_3(\text{C}_2\text{H}_4)^- + \text{OH}^-$; this trend disagrees with the decreasing trend of electron density on the ethylene carbon atom in Hg(II)- and Pd(II)-ethylene complexes. This disagreement is a result of the difference in the polarization of the ethylene part between the Pd(II)- and Hg(II)-systems (see Table 5.). The π -acceptor bond contributes to the coordination bond in the Pd(II)-ethylene complex, while it scarcely contributes in Hg(II)-ethylene complex. Therefore the electron transfer shown in Scheme [I] is more feasible in Pd(II)-complexes than in Hg(II)-complexes, which leads to a higher polarization, a smaller electron density on the C(1) atom, and a larger absolute value of $E_{\text{C-O}}^{(3)}$ in the Pd(II)-complexes than in the Hg(II)-complexes.



Scheme [I]

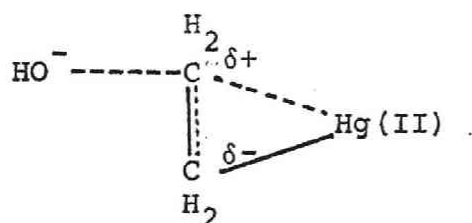
(In the Scheme [I], M and L represent a metal and a ligand, respectively, and "→" indicates the direction of electron transfer.) Therefore, the trend of $E_{C-O}^{(3)}$ is not the same as that of the electron density of the C atom in the Pd(II)- and Hg(II)-complexes. That is, the high catalytic activity of Hg(II) is not due to the electrostatic energy, while it is probably important in the long range interaction.

The absolute value of $E_{C-O}^{(3)}$ in the $HgCl(2-C_4H_8)^+$ system is remarkably large, probably because of the large positive charge on the olefinic carbon atom of butene coordinated to Hg(II).⁴²⁾ In these cases, the polarization is small.

When the mercurinium ion has an anion ligand, the absolute value of E_{C-O} is smaller than that of the system containing no anion ligand.

The absolute values of E_{C-O} for various reactants increase in the following order (See Table 5 and Table 6.); the C(β) atom of $CH_3CH=CH_2 < C_2H_4 < trans-2-C_4H_8 < cis-2-C_4H_8 < the C(\alpha) atom of CH_3CH=CH_2$ in $HgCl(olefin)^+ + OH^-$ system. The rate constants for the oxymercuration have been reported to increase in the following order;³⁸⁾ $trans-2-C_4H_8 < C_2H_4 < cis-2-C_4H_8 < CH_3CH=CH_2$. The obtained results do not agree with this order. However it has been shown by these MO calculations that the reactivity of $cis-2-C_4H_8$ is higher than that of $trans-2-C_4H_8$.

The results given in Table 5 reveal the following aspect of the structure of the intermediate in the oxymercuration; (1) The electron density on the C(1) atom is larger than that on the C(2) atom except in the case of $\text{Hg}(\text{C}_2\text{H}_4)^{2+} + \text{OH}^-$. (2) The absolute value of $E_{\text{Hg}-\text{C}(1)}$ is larger than that of $E_{\text{Hg}-\text{C}(2)}$. These situations are shown in the following picture, which agrees well with the situation usually assumed;⁷⁾



Scheme [II]

In the above scheme, "——" and "----" represent the strong interaction and the weak one respectively.

Wacker Reaction. The calculated results on 1v5 intermediate models are given in Table 6. From the 1 intermediate to the 5 intermediate, the values of E_{total} and $E_{\text{C-O}}$ decrease gradually; this shows the increases in the stability of the intermediate models and in the strength of the C(1)-O bond. These results suggest that this reaction model is reasonable for the Wacker reaction. The electron densities on the Pd and C(1) atoms decrease in the course of this, while that of the C(2) atom increases. From the above results,

Table 6. The electronic Structures of Intermediate Models^{a)}
in Wacker Reaction.

Intermediate		1	2	3	4	5	
$E_{\text{total}}^{\text{b)}$	F	-2581.5	-2581.5	-2582.7	-2583.0	-2593.7	
	Cl	-2234.5	-2234.5	-2235.7	-2234.2	-2235.7	
	Br	-2125.7	-2125.8	-2126.9	-2127.3	-2129.4	
Electron Density on Pd	F	9.563	9.562	9.541	9.537	9.518	
	Cl	9.890	9.882	9.871	9.894	9.933	
	Br	9.968	9.956	9.949	9.965	10.015	
Electron Density on C	F	C(1)	4.084	4.085	4.027	3.890	3.358
		C(2)	4.084	4.086	4.147	4.325	4.403
	Cl	C(1)	4.081	4.084	4.026	3.884	3.808
		C(2)	4.081	4.085	4.147	4.323	4.406
	Br	C(1)	4.077	4.079	4.022	3.883	3.808
		C(2)	4.077	4.085	4.146	4.323	4.400
$E_{\text{C(1)-O}}^{\text{b)}$	F	0.346	0.379	-0.245	-5.321	-16.083	
	Cl	0.327	0.378	-0.225	-5.212	-11.217	
	Br	0.249	0.302	-0.229	-5.266	-11.330	

(Table 6 . Continued)

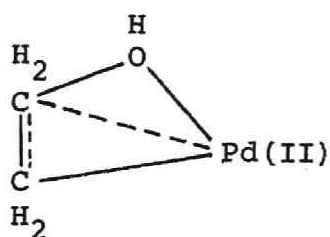
Intermediate		1	2	3	4	5
F	$E_{\text{Pd-C}(1)}^{\text{b)}$	-3.935	-3.922	-3.536	-2.818	-0.027
	$E_{\text{Pd-C}(2)}$	-3.935	-3.960	-4.203	-5.251	-6.713
Cl	$E_{\text{Pd-C}(1)}$	-3.901	-3.910	-3.670	-3.055	-1.935
	$E_{\text{Pd-C}(2)}$	-3.901	-3.876	-3.979	-4.668	-6.377
Br	$E_{\text{Pd-C}(1)}$	-3.873	-3.860	-3.549	-3.097	-2.007
	$E_{\text{Pd-C}(2)}$	-3.873	-3.894	-3.971	-4.592	-6.277
$E_{\text{Pd-O}}^{\text{b)}$	F	-16.928	-16.859	-15.492	-15.246	-13.653
	Cl	-15.493	-15.451	-15.224	-13.848	-12.335
	Br	-15.266	-15.235	-14.978	-13.717	-10.324
$P_{\pi}^{\text{c)}$	F	0.888	0.888	0.878	0.730	0.527
	Cl	0.878	0.878	0.873	0.727	0.513
	Br	0.873	0.871	0.867	0.722	0.504

a) See Fig.3.

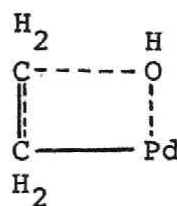
b) eV. unit

c) π -bond order of C=C double bond.

ethylene can be said to be polarized by the approach of OH^- . Proceeding from the 1 intermediate to the 5 intermediate, the absolute values of $E_{\text{Pd-C}(1)}$, $E_{\text{Pd-O}}$, and P_π decrease, whereas that of $E_{\text{Pd-C}(2)}$ increases; i.e., the bonds of $\text{C}(1)\text{-O}$ and $\text{Pd-C}(2)$ become stronger, although the bonds of $\text{Pd-C}(1)$, Pd-O , and $\text{C}=\text{C}$ become weaker, relative to those of the 1 intermediate. These results, pictured in Scheme [III], agree with the cis-type four-center reaction speculated by Henry³²⁾ and Jira et al.³³⁾ (See Scheme [IV].)



Scheme [III]



Scheme [IV]

The results for the 6~8 intermediate models (Fig. 3) are given in Table 7. The bending of $\text{C}(1)\text{H}_2$ group opposite to Pd(II) makes the total energy more negative, suggesting that the system is more stabilized and that the $\text{C}(1)$ atom changes from sp^2 to sp^3 . Also, this bending brings about decreases in the absolute values of $E_{\text{Pd-C}(1)}$ and P_π and increases in the absolute values of $E_{\text{C}(1)\text{-O}}$ and $E_{\text{Pd-C}(1)}$, which reveal that the reaction more proceeds from the 5 intermediate. However,

Table 7 The cis-bending of CH_2 group of intermediate,^{a)}
 $\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{OH})^-$ in Wacker reaction

Intermediate	5	6	7	8
E_{total}	-2235.7 eV	-2235.7 eV	-2238.6 eV	-2235.2 eV
$E_{\text{C(1)-O}}$	-11.22	-12.59	-13.68	-13.89
$E_{\text{Pd-C(1)}}$	-1.94	-1.87	-1.83	-1.74
$E_{\text{Pd-C(2)}}$	-6.38	-6.43	-6.14	-6.87
$E_{\text{Pd-O}}$	-12.34	-12.26	-11.92	-12.00
P_{π}	0.513	0.491	0.475	0.443

a) See Fig. 3.

the bending of the $C(2)H_2$ group destabilizes the system, while the absolute values of $E_{C(1)-O}$ and $E_{Pd-C(2)}$ are increased and those of $E_{Pd-C(2)}$ and P_π are decreased. Therefore, hardly any cis-bending of the $C(2)H_2$ group occurs. These results are considered to be due to the polarization of ethylene, which is expected to be enhanced by the π -acceptor bond with $Pd(II)$, as has been shown in Scheme [I]; the $C(2)$ atom should have sp^2 character to obtain the electron through the π -acceptor bond, leading to no cis-bending of its protons.

Then the change from the 1 intermediate to the 5 intermediate were investigated in detail. The values of the Fock-matrix elements, F_{rr} , are shown in Fig. 5-A, together with the sum of the values of the density matrix elements between the $d_{x^2-y^2}$ orbital of the Pd atom and the s , p_x and p_y orbitals of the O atom, and those between the d_{xy} orbital and the s , p_x , and p_y orbitals of these atoms (Fig. 5-B). There is a remarkable increase in the value of $F_{d_{xy}d_{xy}}$ and a decrease in the value of $F_{d_{x^2-y^2}d_{x^2-y^2}}$, while there are little changes in the other F_{rr} . These remarkable changes are due to the moving of OH^- in the xy plane and suggest the change in the Pd-O bonding character. As is shown in Fig. 5-B, the contribution of the d_{xy} orbital to the Pd-O bond increases, although that of $d_{x^2-y^2}$ decreases in the reaction course. In other words, OH^- attacks the $C(1)$ atom, interacting with the d_{xy} orbital, as has been proposed by Cossee et al.^{9, 43)}

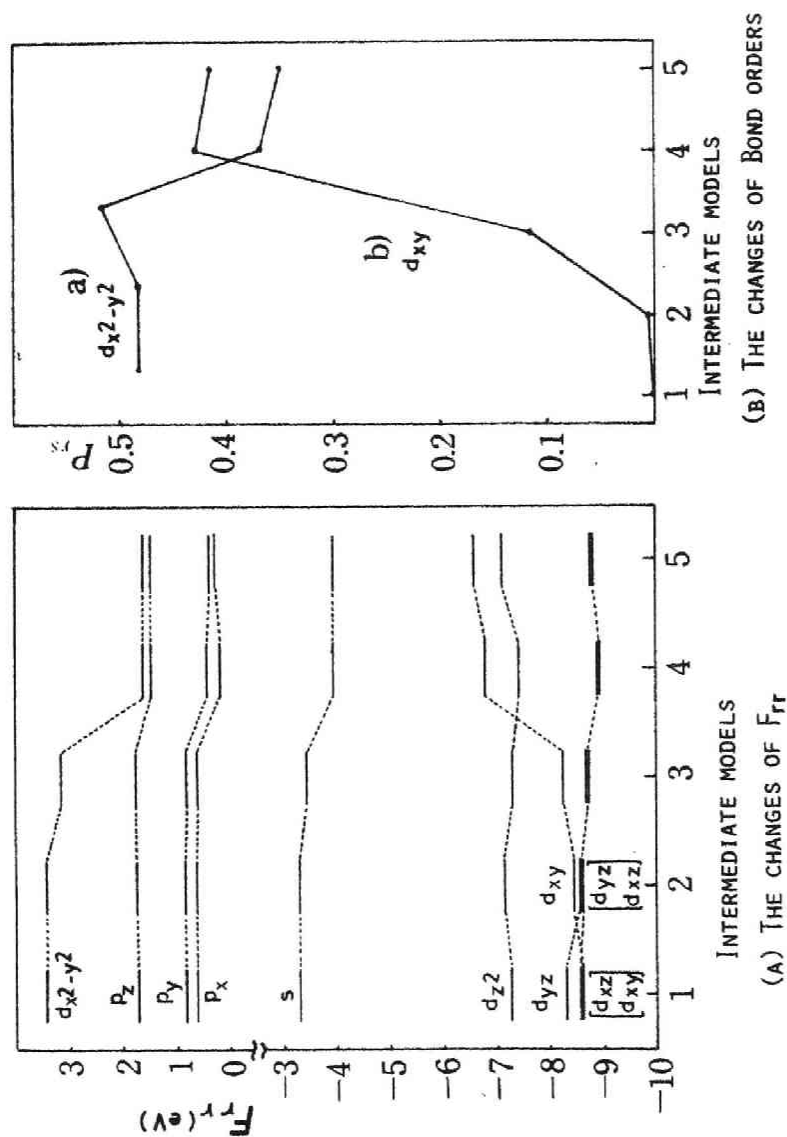
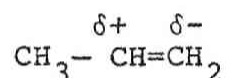


Fig. 5. Changes in values of F_{rr} and P_{rr} in the Wacker reaction.
 r = valence orbitals of the Pd atom.

Markovnikoff Rule in These Reactions.

We calculated the MO's of the models for the nucleophilic attack on propylene; the results are given in Fig.4 and Table 8. In both the Pd(II)- and Hg(II)-systems, the attack on the C(1) atom gives a lower total energy than the attack on the C(2) atom, which reveals that the former attack is superior to the latter attack. Also, the absolute values of $E_{C(1)-O}$ of models [A] and [C] are greater than those of models [B] and [D]. It is obvious from Table 8 that this difference is a result of the difference of $E_{C-O}^{(3)}$, suggesting that this selectivity is determined by the electrostatic energy. The carbon atom attacked by OH^- is positively charged in both Pd(II)- and Hg(II)-systems (see Tables 5 and 6 and Fig.4.), and the propylene is polarized by the hyperconjugation of the methyl group, as follows,



Scheme [V]

Therefore, the attack on the C(α) atom is superior to the attack on the C(β) atom, since the former attack causes the same polarization, while the latter attack causes an inverse polarization.

As has been described above, the semi-empirical SCF-MO method using the modified CNDO approximation gives fruitful results; this encourages us to apply this method to studies of the other catalytic reactions.

Table 8 Nucleophilic attack of OH^- anion to propylene

State ^{a)}	$\text{PdCl}_2(\text{OH})(\text{C}_3\text{H}_6)^-$		$\text{HgCl}(\text{C}_3\text{H}_6)^+ \text{OH}^-$	
	A	B	C	D
E_{total}	-2426.6 eV	-2426.3 eV	-2353.0 eV	-2352.6 eV
$E_{\text{C-O}}$	-5.596	-4.756	-5.545	-4.528
$E_{\text{C-O}}^{(1)}$	-3.674	-3.793	-3.063	-2.923
$E_{\text{C-O}}^{(2)}$	-0.618	-0.660	-1.175	-1.185
$E_{\text{C-O}}^{(3)}$	-1.305	-0.303	-1.307	-0.420
P_{π}	0.669	0.718	0.531	0.535

a) See Fig. 4.

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- 37) Although in the complex the notations π - and π^* -MO's of olefin lose their physical meanings, the author use terminologies in the local sense of olefin for simplicity. These terms, P_π and P_{π^*} , are defined as follows;
- $$P_\pi = 2 \sum_{\pi}^{\text{occ}} C_{\pi^1} p_Y C_{\pi^2} p_Y, \quad P_{\pi^*} = 2 \sum_{\pi}^{\text{occ}} C_{\pi^*1} p_Y C_{\pi^*2} p_Y$$
- where $C_{\pi^1} p_Y$ and $C_{\pi^*1} p_Y$ represent the MO coefficients of p_Y orbitals on C(1) atom in π -MO and π^* -MO, respectively.
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case for comparison with the oxymercuration.

- 41) These E_{C-O} and $E_{C-O}^{(1)}$ etc., represent the values of E_{AB} $E_{AB}^{(1)}$ etc., of the bond C(1)-O, respectively (in eV unit and see Fig. 3.).
- 42) In Hg(II)-complexes, the unsaturated C atom of 2-C₄H₈ has a smaller electron density than that of C₂H₄; i.e., 3.993 in HgCl(cis-2-C₄H₈)⁺, 3.995 in HgCl(trans-2-C₄H₈)⁺ and 4.048 in HgCl(C₂H₄)⁺.
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Chapter 3. Platinum hydrides and their reaction with ethylene.

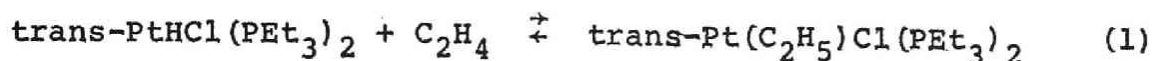
§ 1. Introduction

The role of transition metal complexes in homogeneous catalytic reactions is currently a topic of great interest in both fields of pure and applied chemistries. In those catalytic reactions, isomerization and hydrogenation of olefins and acetylenes have been particularly studied, as 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 known and the several insertion reactions of olefins into a M-H bond have been reported.⁴⁾

Stable hydride complexes of platinum(II), trans-PtHX-(PH₃)₂ (X=halogen etc.) were prepared by Chatt and Shaw.⁵⁾ Structural studies have been carried out on trans-PtHX(PEt₃)₂ (X=Cl and Br)^{6, 7)} and spectroscopic studies such as NMR and IR have been reported.^{5, 8-11)} However, a theoretical study has been little done, while it is necessary in order to investigate the bonding character of the Pt(II)-H bond.

It is well-known that ethylene reacts with trans-PtHCl-(PEt₃)₂ under a vigorous condition (95°/80 atm) to give an

ethylplatinum(II) complex;^{5, 12)}



Several works 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.^{12-14, 16, 17)}

In this chapter, the author has carried out semi-empirical SCF-MO calculations on hydride complexes of platinum(II), in order to investigate their electronic structures. Studies have been also done on the ethylene insertion reaction into the Pt(II)-H bond. A discussion is presented on the electronic structure of the intermediate five-coordinate π -olefinic hydride complex, $\text{PtHCl}(\text{PH}_3)_2(\text{C}_2\text{H}_4)$. The ligand effects and the role of the Pt(II) ion in the ethylene insertion reaction are also discussed. It has been tried to anticipate the ligand effect on the catalytic abilities of $\text{trans-PtHX}(\text{PR}_3)_2$ in the hydrogen-deuterium (H-D) exchange reaction of ethylene.

§ 2. MO calculations and Geometries of Complexes.

MO calculations. MO calculations were performed by the use of the CNDO type MO method. This method gave reasonable results on tetrachloroplatinate, Zeise's salt, Pt(0)-ethylene complex and Pt(0)-acetylene complex etc.¹⁸⁾ Approximations used in this MO method are reported in detail else-

where.¹⁸⁾ Here, several important features are described as follows: (1) Fock-matrix elements are obtained by the CNDO type approximations.¹⁹⁾ (2) 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) One-center Coulomb repulsion integrals of the Pt atom are estimated by multiplying a correction factor to nonempirical values calculated with single Slater type orbitals.¹⁸⁾ (4) Two-center Coulomb repulsion integrals are evaluated by the use of the modified Ohno's approximation¹⁸⁾ for AO pairs including only one outer 6s- or 6p-orbital of the Pt atom and by the use of the original Ohno's approximation²¹⁾ for the other AO pairs.

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

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

$$E_{AB}^{(1)} = 2.0 \sum_r^A \sum_t^B P_{rt} H_{rt} \quad (3)$$

$$E_{AB}^{(2)} = -0.5 \sum_r^A \sum_t^B P_{rt}^2 \gamma_{rt} \quad (4)$$

$$E_{AB}^{(3)} = \sum_r^A \sum_t^B (P_{rr} - N_r) (P_{tt} - N_t) \gamma_{rt} \quad (5)$$

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} means the bonding interaction. The larger the absolute value of E_{AB} is, the greater the interaction between A and B atoms becomes.

Geometries of Complexes. Trans-PtHX(PR₃)₂: The bond lengths of the Pt-Cl and Pt-Br were taken from X-ray studies^{6,7)} and those of the other Pt-X bonds were estimated from the covalent bond radii of X. The bond lengths of the Pt-P and Pt-H were fixed as 2.268 Å and 1.62 Å⁶⁾ for all complexes, respectively. While the angle $\angle\text{PPtCl}$ and $\angle\text{PPtBr}$ were slightly larger than 90° due to the steric effects of Cl and Br ligands,^{6,7)} $\angle\text{PPtX}$ was assumed to be 90° in all complexes, for the value of this angle had not been known in the other complexes. The PR₃ group (R=phenyl or alkyl group) was replaced by the PH₃ group for simplicity, whose structure was assumed to be the same as that of uncomplexed one.²⁴⁾ In spite of these simplifications, MO calculations on these models gave reasonable and enough results to discuss the ligand effect of X, as described in the following section.

Trans-PtX(C₂H₅)(PH₃)₂: Since an X-ray study had not been carried out on this complex, the bond lengths of the Pt-C and Pt-Cl were taken from the structure of [Pt(CH₃)₃Cl]₄,²⁴⁾ and the Pt-C bond length was fixed in all complexes. The bond lengths of the other Pt-X were estimated in the same way as those in trans-PtHX(PH₃)₂. The Pt-P bond length and the structure of the PH₃ group were assumed to be the same as correspondings in trans-PtHX(PH₃)₂. In these complexes, the

structure of 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 ($\beta\text{-H-Pt}=2.22 \text{ \AA}$,²⁵⁾ and $\beta\text{-H-C}=1.09 \text{ \AA}$) 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, which are shown in Fig. 1. In both structures, the structure of 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 $2.0 \text{ \AA}$ by reference to that of Zeise's salt.²⁶⁾ The structure A is expected from the substitution reaction of $\text{trans-Pt}(\text{NO}_3)\text{H}(\text{PEt}_3)_2$ with ethylene, which was reported by Deening et al.¹⁵⁾ The structure B has been proposed by Uguagliati et al.¹⁴⁾ and also a similar intermediate complex has been isolated by Clark et al. in the insertion reaction of tetracyanoethylene with $\text{trans-Pt}(\text{CH}_3)(\text{CN})(\text{PEt}_3)_2$.²⁷⁾

Since the structure B was more stable than that of A, as described below, the insertion reaction was considered to proceed from the structure B ($\theta=45^\circ$) and three reaction paths were investigated as shown in Fig. 2. In the reaction path C, ethylene approaches the hydride ligand in parallel with the Pt-H bond. Also in the reaction path D, ethylene approaches

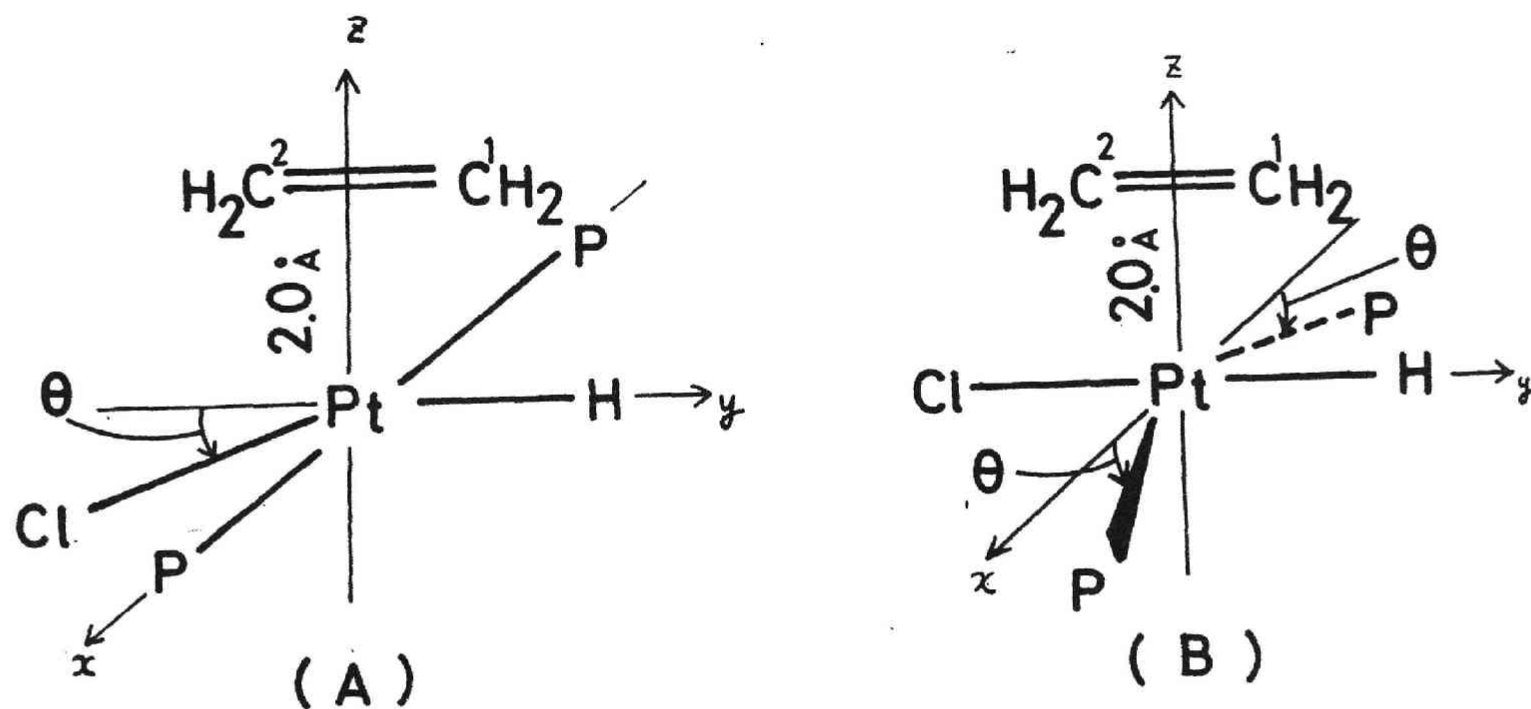


Fig. 1. Five-coordinate π -olefinic hydride complexes.

$P=PH_3$, 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 $trans-PtHCl(PH_3)_2$, respectively.

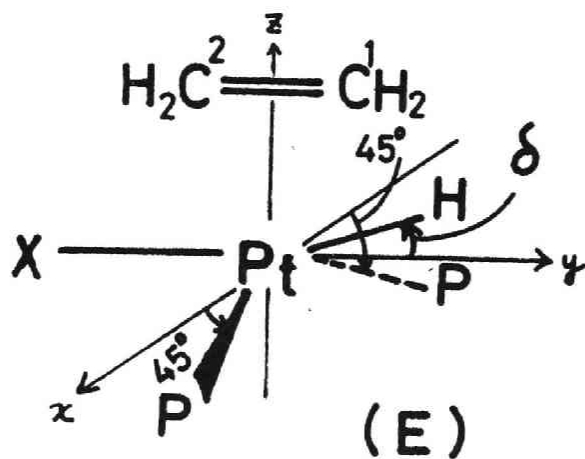
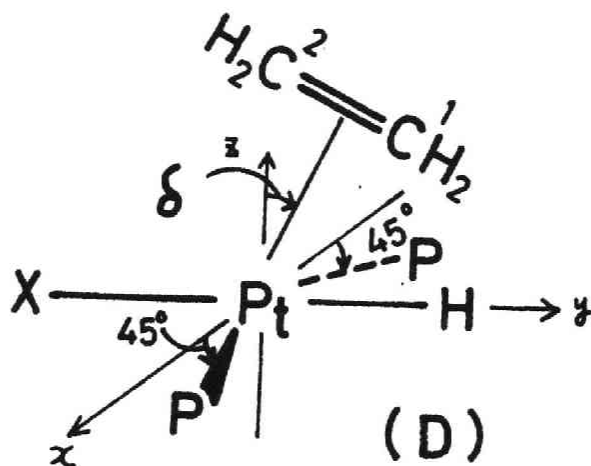
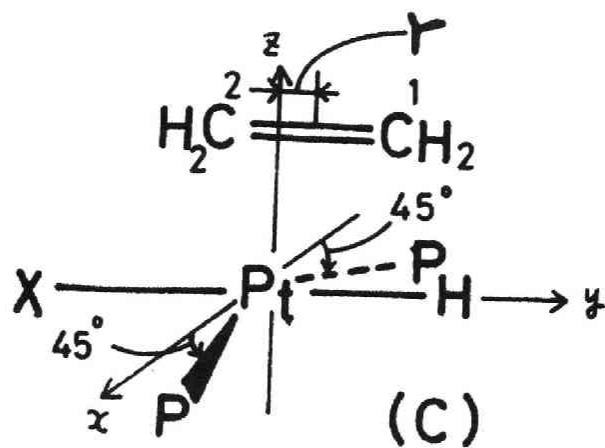
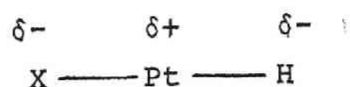


Fig. 2. Insertion reaction paths of ethylene into the Pt-H bond $P=PH_3$. The structure of $PtX(PH_3)_2$ part is the same as the corresponding one of the intermediate complex B (Fig. 1.).

the hydride ligand. In this attack, the angle δ between the coordination bond of ethylene and the z-axis increases, and the other part is not changed except for the states IV and V. In the reaction path E, the hydride ligand attacks ethylene, where the angle δ between the Pt-H bond and the y-axis increases and the other part does not change except for the states IV and V. The states in which the CH_2 group of ethylene was pushed away opposite to the Pt atom (10°) were investigated in both reaction paths D and E; only the $\text{C}(1)\text{H}_2$ group was bending in the state IV and both $\text{C}(1)\text{H}_2$ and $\text{C}(2)\text{H}_2$ groups were bending in the state V.

§ 3. Results and Discussion

Electronic Structures of $\text{trans-PtHX}(\text{PH}_3)_2$. The results are given in Table 1. The electron density on the Pt atom increases with the decreasing of the electronegativity of the X ligand; i.e., $\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{CN}$. The H ligand has a remarkably large negative charge, suggesting its hydride character. The electron density on the H ligand decreases with increasing electron density on the Pt atom and with decreasing electron density on the halogen. This result seems to be similar to the alternative inductive effect;



Scheme [I]

However, this result can not be explained by hyperconjugation,

Table 1. Electronic structures of trans-PtHX(PH₃)₂

	Electron density				$E_{\text{Pt-H}}$	$E_{\text{Pt-H}}^{(1)+(2)}$	$E_{\text{Pt-H}}^{(3)}$	$\nu_{\text{Pt-H}}^{\text{a)}$
	Pt	H	X	P				
F	9.710	1.289	7.658	5.217	-13.882 _{eV}	-12.783 _{eV}	-1.099 _{eV}	—
Cl	9.846	1.255	7.583	5.222	-13.627	-12.877	-0.750	2183 _{cm} ⁻¹
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.

since the Pt-H bond is not contributed by hyperconjugation. Because energy levels of Pt's valence orbitals decrease as the X ligand goes from F^- to CN^- ,²⁷⁾ the electron transfer increases in the order $F < Cl < Br < I < CN$ and the electron density on the H ligand decreases in the order $F > Cl > Br > I > CN$.

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

Five-coordinate π -olefinic hydride complexes. The various conformations of the structures A and B (See Fig. 1.) are investigated, as shown in Fig. 3 and Table 2. The increase in θ does not bring about the stabilization of the structure A, but that of the structure B which is the most stable at $\theta=45^\circ$. In the structure B, the steric repulsion between PH_3 and ethylene decreases largely. However, it does not change in the structure A, while the steric repulsion between Cl and ethylene decreases. Therefore, the structure B is more favorable than

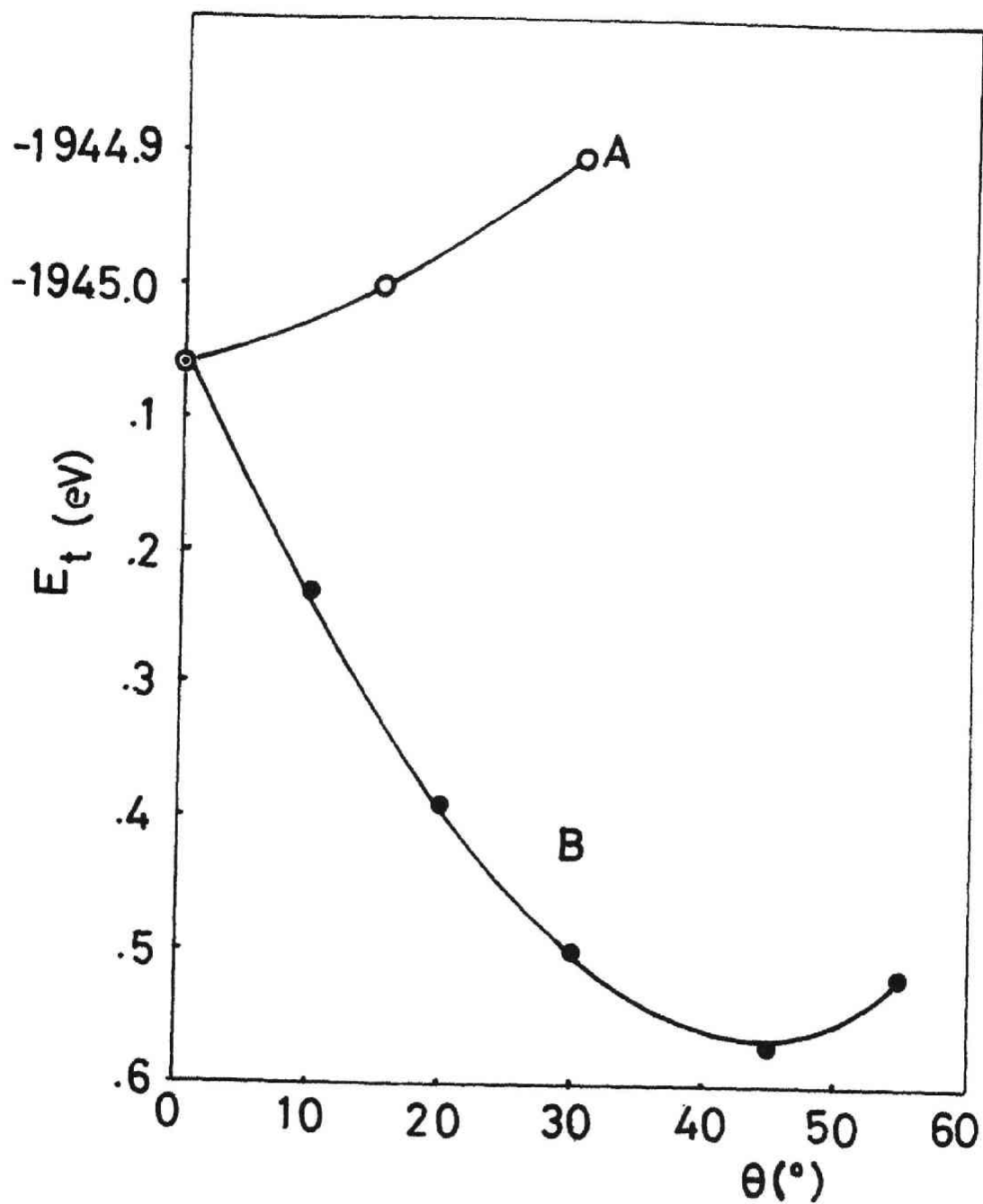


Fig. 3. Total energies of five-coordinate π -olefinic hydride complexes, $\text{PtHCl}(\text{PH}_3)_2 (\text{C}_2\text{H}_4)$.

; the structure A, ; the structure B (See. Fig. 1.)

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

(a) Structure A.

State	I	II	III
θ	0°	15°	30°
$E_{\text{Pt-C}(1)} + E_{\text{Pt-C}(2)}$	-11.26	-11.46	-11.76
$E_{\text{C-H}}$ a)	-0.27	-0.29	-0.31
P_π b)	0.86	0.86	0.85
Δq c)	0.14	0.13	0.12

(b) Structure B. d)

State	II	III	IV	V	VI
θ	10°	20°	30°	45°	55°
$E_{\text{Pt-C}(1)} + E_{\text{Pt-C}(2)}$	-11.77	-12.35	-12.89	-13.40	-13.72
$E_{\text{C-H}}$ a)	-0.39	-0.44	-0.58	-0.62	-0.63
P_π b)	0.84	0.82	0.81	0.79	0.78
Δq c)	0.17	0.21	0.24	0.28	0.29

E_{AB} ; eV unit. a) H= the hydride ligand of trans-PtHX(PH₃)₂.
 b) The π -bond order of ethylene part. c) The quantity of transferred electrons from ethylene to trans-PtHX(PH₃)₂ part.
 d) The state I is the same as that in the structure A.

the structure A for the intermediate five-coordinate complex. The author hereafter considers the insertion reaction of ethylene into the Pt(II)-H bond in the structure B.

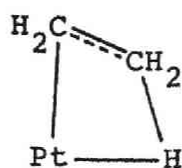
An increase of θ brings about the increase of the bonding interaction between the Pt atom and ethylene both in the structures A and B; the absolute value of $E_{\text{Pt-C}(1)} + E_{\text{Pt-C}(2)}$ increases with increase of θ , as shown in Table 2. In the structure A ($\theta \neq 0$), the $5d_z^2$ and $5d_{yz}$ orbitals of the Pt atom are bonding orbitals, while these are very weak bonding ones in the square pyramidal complex. Ethylene donates its electrons to the $5d_z^2$ orbital and accepts d-electrons from $5d_{yz}$ 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 $6p_z$ orbital of the Pt atom both in 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 that in the square pyramidal one, which results in the larger absolute value of $E_{\text{Pt-C}(1)} + E_{\text{Pt-C}(2)}$ in the former than that in the latter. Decreases in a π -bond order of ethylene, P_π , and a quantity of transferred electrons from ethylene, Δq , suggest more increase of the π -acceptor bond than that of the σ -donor bond, as shown in Table 2. In the structure B, 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 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 the increases in the Δq and the $E_{Pt-C(1)} + E_{Pt-C(2)}$ and the decrease in the P_{π} .

Insertion Reaction of Ethylene. Results on the reaction paths and those on the ligand effect in this reaction are shown in Table 3 and Table 4, respectively.

In the reaction path C, the total energy increases slightly. Absolute values of E_{C-H} , E_{C-C} and $E_{Pt-C(2)}$ increase as the reaction proceeds from the state I to III, while those of $E_{Pt-C(1)}$ and E_{Pt-H} decrease. (In this paper, 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 the increase in the strength of the C-C bond. This result rules out the reaction path C, because the C=C double bond must become a C-C single bond after an insertion reaction.

In the reaction path D, the total energy decreases as the reaction proceeds from the state I to III. 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 of the four-center type reaction;²⁸⁾



Scheme [II]

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

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

In both reaction paths D and E, the bending of the CH₂ group, in which the CH₂ group is pushed away 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-H} , $E_{Pt-C(1)}$ and E_{C-C} , while it scarcely changes the total energy. (See the states IV and V in Table 2.) These results suggest the bending of the CH₂ group is brought about in this reaction course, which corresponds to that the C(1) and C(2) atoms become sp³ character from their original sp² character.

It is worthwhile to investigate which of ethylene or hydride anion transfers in the ethylene insertion reaction. As shown in Table 3, the state II in the reaction path E has a lower total energy, a larger absolute value of E_{C-H} and

Table 3. Insertion reaction of ethylene into Pt(II)-H bond.

(a) Reaction path C.

State	I	II	III
$r(\text{\AA})$	0.0	0.3	0.6695
E_{total}	-1945.6	-1945.5	-1945.0
$E_{\text{C-H}}^{\text{a)}$	-0.62	-1.27	-1.86
$E_{\text{Pt-H}}^{\text{a)}$	-12.59	-12.23	-11.90
$E_{\text{C-C}}$	-29.81	-29.89	-30.27
$E_{\text{Pt-C(1)}}$	-6.65	-5.04	-3.01
$E_{\text{Pt-C(2)}}$	-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
$E_{\text{C-H}}^{\text{a)}$	-1.69	-7.83	-8.31	-8.37
$E_{\text{Pt-H}}^{\text{a)}$	-11.82	-8.44	-8.49	-8.45
$E_{\text{C-C}}$	-29.61	-27.67	-27.57	-27.42
$E_{\text{Pt-C(1)}}$	-6.24	-5.68	-5.81	-5.81
$E_{\text{Pt-C(2)}}$	-7.25	-8.43	-8.49	-8.74

Table 3 (continued)

(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
$E_{\text{C-H}}^{\text{a)}$	-2.40	-7.39	-7.87	-7.92
$E_{\text{Pt-H}}^{\text{a)}$	-11.58	-9.04	-9.09	-8.94
$E_{\text{C-C}}$	-29.28	-27.90	-27.79	-27.68
$E_{\text{Pt-C(1)}}$	-6.21	-5.76	-5.90	-5.90
$E_{\text{Pt-C(2)}}$	-7.14	-7.75	-7.81	-8.02

E_{total} and E_{AB} ; eV unit. a) H=the hydrido ligand of trans-PtHX(PH₃)₂. b) The state I is the same as that in the reaction path C. c) The C₍₁₎H₂ group is pushed away from the Pt atom, while the other parts are unchanged as the state III. d) Both C₍₁₎H₂ and C₍₂₎H₂ groups are pushed away from the Pt atom and the other parts are unchanged.

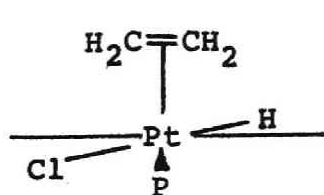
Table 4. Ligand effect of halogens in the insertion reaction of ethylene into Pt(II)-H.

Reaction path D, State III.

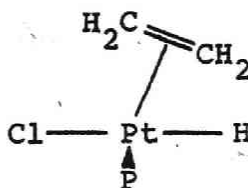
		F	Cl	Br	I	CN
	Pt	9.98	10.12	10.15	10.18	10.20
Electron	C(1)	4.09	4.09	4.09	4.09	4.09
density	C(2)	4.27	4.25	4.24	4.24	4.23
	H ^{a)}	0.99	0.96	0.95	0.95	0.94
E_{C-H}	^{a)}	-7.78	-7.83	-7.84	-7.86	-7.91
E_{Pt-H}	^{a)}	-8.43	-8.44	-8.44	-8.42	-8.37
E_{C-C}		-27.64	-27.67	-27.67	-27.68	-27.72
$P_{\pi C(2)}$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

E_{AB} ; eV unit. a) H=the hydride ligand coordinating to the Pt(II) ion. b) The π -electron density on the 2p orbital of the C(2) atom. c) The quantity of transferred electron from the system $C_2H_4 + H^-$ to $PtX(PH_3)_2^+$ part.

smaller absolute ones of $E_{\text{Pt-H}}$ and $E_{\text{C-C}}$ than that in the reaction path D does; that is, the former state has a stronger C-H bonding interaction, weaker Pt-H and C-C bonding interactions than the latter one does. From these results, it is expected that the H ligand transfers more easily than ethylene does in the initial stage of the reaction. The following states III ~ V in the reaction path D has a larger absolute value of $E_{\text{C-H}}$ and smaller ones of $E_{\text{Pt-H}}$ and $E_{\text{C-C}}$ than those in the reaction path E do, while 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 reaction path E, however, the Cl ligand should also transfer as shown in Scheme [III] as the reaction more advances, since the final product is the square planar trans-Pt(C₂H₅)Cl(PH₃)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 reaction path E results in almost the same intermediate state as that in the

reaction path D, while the position of PH_3 is slightly different. The state III ~ V in the reaction path D are reasonably considered to be more advanced reaction states in the reaction path E. Thus, our results suggest that the H ligand starts first to attack ethylene and then the Cl ligand starts to moves 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, which is obtained by removing the $\text{PtCl}(\text{PH}_3)_2^+$ part from the state III in the reaction path D. This hypothetical state is considered to be a limiting state of the reaction system, $\text{C}_2\text{H}_4 + \text{LiH}$ in which the bond distance of Li-H is infinitely lengthened. This hypothetical state has following characteristics: (1) The electron density on the C(2) atom is remarkably large (4.64 e), which is owing to 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 shown in Fig. 4, its HOMO has a non-bonding character, in which electrons are locarized in the $2p_\pi$ orbital of the C(2) atom and the 1s orbital of the H atom. Where the Pt part exists, this type MO is obtained at about -10 eV and the $2p_\pi$ orbital of the C(2) atom interacts with $5d_{z^2}$, 6s and $6p_z$ orbitals of the Pt atom in the reaction path D, as shown in Fig. 5. As the consequence of these interactions, the electron density on the

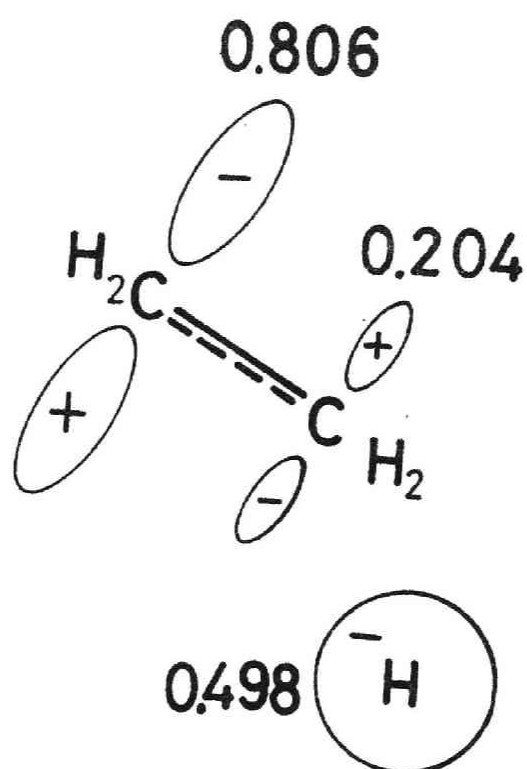


Fig. 4. AO coefficients of the HOMO of the hypothetical state, $\text{C}_2\text{H}_4 + \text{H}^-$.

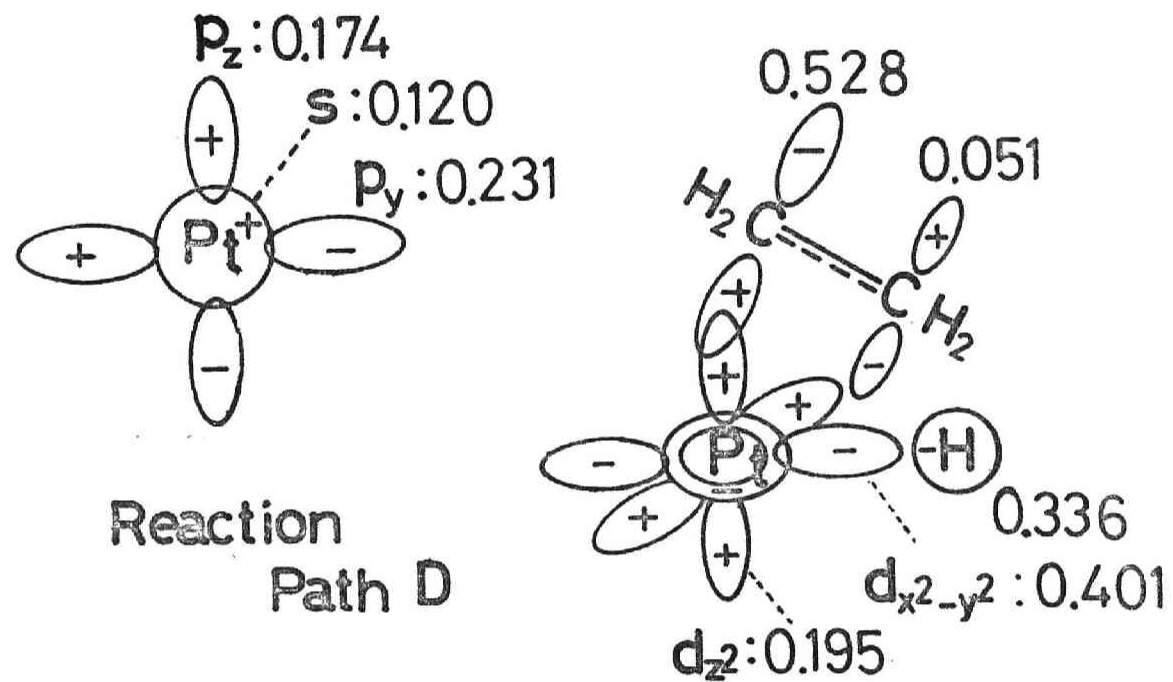
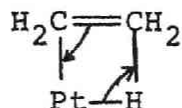


Fig. 5. AO coefficients of an important MO in the interaction between the C(2) atom and Pt atom.
The state V in the reaction path D.

$2p_{\pi}$ 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 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 is represented as follows;



Scheme [IV]

Ligand effects on the insertion reaction are studied in the state III of the reaction path D, as shown in Table 4. In all 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 systems reveal the C-H bonding interaction. Its absolute value increases in the order $F < Cl < Br < I < CN$, while the absolute value of E_{Pt-H} and E_{C-C} decrease in the same order. Also, the values of ΔQ which is defined as quantity of transferred electrons from $C_2H_4 + H^-$ part to $PtX(PH_3)_2^+$ part increases and the value of $P_{\pi C(2)}$ decreases in this order. From these results, it is expected that the reactivity of $trans-PtHX(PH_3)_2$ in the insertion reaction increases in the same order. This increasing order agrees with the increasing one of trans-effect of the X ligand, which is consistent with experimental results.²⁹⁾

The decreasing order of ΔQ as $F > Cl > Br > I > CN$ is the same order of the electron transfer from the H ligand

to the Pt part in trans-PtHX(PH₃)₂. The result on ΔQ in the former case would be also due to the same reason as that in the latter one.²⁷⁾

Hydrogen-Deuterium Exchange Reaction. Trans-PtHCl-(PEt₃)₂ catalyzes the H-D exchange reaction of ethylene.³⁰⁾ The H-D exchange reaction is composed of two steps, i.e., 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. Results are given in Table 5.

The absolute value of E_{Pt-H} increases in the order F < Cl < Br < CN < I, as shown in Table 5. The β-hydrogen atom is abstracted easily as follows; F < Cl < Br < CN < I. As described previously, the ligand effect on reactivity in the ethylene insertion increases in the order F < Cl < Br < I < CN. Therefore, the catalytic ability of trans-PtHX(PR₃)₂ in the H-D exchange reaction increases F < Cl < Br < I, while it is difficult to determine which of the iodo- or cyano-complex is more active.

Table 5. The interaction between Pt and β -H atoms
in $\text{trans-PtX}(\text{C}_2\text{H}_5)(\text{PH}_3)_2$.

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

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

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

Going from F to CN^- , the values of P_{rr} of the Pt atom increase and those of P_{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 forth term, since the $P_{rr}-N_r$ is negative in these cases. The change in the value of the third term is less than that of the forth one which is mainly due to the change in values of γ_{rs} . Thus, the values of F_{rr} decreases due to the forth term as follows; $F > Cl > Br > I > CN$. This result is not owing to our approximations but to 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.

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Chapter 4. Summary

In part II, the semi-empirical SCF-MO calculations are carried out on catalytic systems including transition metal complexes as catalysts.

In chapter 2, the oxymercuration and the Wacker reaction are investigated. In both reactions, it is the key step that a nucleophile attacks olefin coordinating to the Hg(II) or Pd(II) ion. MO calculations are carried out on this step, which suggests that the nucleophilic attack of the OH⁻ anion to ethylene is accelerated by the presences of Hg(II) and Pd(II) ions and that the acceleration by the Hg(II) ion is larger than that by the Pd(II) ion. These results agree with experimental ones. In the oxymercuration, it is of interest which of the two, cis-attack or trans-attack occurs. From MO calculations, following results are obtained; (1) the nucleophile coordinates to the Hg(II) ion to stabilize the mercurinium ion, and (2) the nucleophile in the trans-attack interacts more strongly with ethylene in the mercurinium ion than that in the cis-attack, while the interaction in the cis-attack is also considerably large. Thus, the cis-attack occurs when the mercurinium ion is relatively short-lived and is stabilized by the coordination of nucleophile to the Hg(II) ion, since the mercurinium ion is likely to react with the nearest nucleophile which coordinates to the Hg(II) ion, and

since the nucleophile in the cis-attack considerably interacts with ethylene. In the other cases, the trans-attack occurs, since the nucleophile in the trans-attack interacts more strongly with ethylene than that in the cis-attack.

In the Wacker reaction, it has been proposed without any direct evidence that the cis-attack of the OH^- anion occurs via the four-center type reaction mechanism. This mechanism is supported by the MO calculations in chapter 2.

In both the Wacker reaction and the oxymercuration, it is shown by MO calculations that the nucleophilic attack of the OH^- anion to propylene occurs at the α -carbon atom more favorably than that at the β -carbon atom, which is explained in terms of the electrostatic interaction.

In chapter 3, platinum hydrides and their reactions with ethylene are studied. In platinum hydrides, $\text{trans-PtHX}(\text{PH}_3)_2$, the electron density on the H atom and the bond strength of the Pt-H decrease in the following order $\text{F} > \text{Cl} > \text{Br} > \text{I} > \text{CN}$. The ethylene insertion into the Pt-H bond is investigated. MO calculations show the five-coordinate π -olefinic hydride complex which is an intermediate in this insertion has a trigonal bipyramidal structure in which Cl and H ligands are positioned trans to each others. This structure is more stable than the square pyramidal structure and the trigonal bipyramidal one A (See Fig. 1 in chapter 3) from following reasons; (1) the smaller steric repulsion between ethylene and phosphine,

and (2) the stronger coordination bond of ethylene in the complex B, relative to those in the complex A and the square pyramidal complex. An interesting issue is whether ethylene or the hydride ligand transfers in the ethylene insertion. From MO calculations, the hydride ligand approaches ethylene more favorably than ethylene does, via the four-center type reaction mechanism. In other words, ethylene insertion into the Pt-H bond is considered as the nucleophilic attack of the hydride ligand to ethylene coordinating to the Pt atom. Thus, the ethylene insertion is very similar to the nucleophilic attack of the OH^- anion to ethylene in the Wacker reaction. In the insertion reaction, the important role of the Pt atom is to accept excess electrons accumulated on the C atom of ethylene as shown in Table 4 in chapter 3. MO calculations reveal that reactivities of $\text{trans-PtHX(PH}_3)_2$ in the ethylene insertion increase in the following order; $\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{CN}$. They also indicate that catalytic abilities of these complexes increase in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$, in the hydrogen-deuterium exchange reaction of ethylene.

As described above, the semi-empirical SCF-MO method is valid means for studies on catalytic chemistry. This method can be useful for confirming the reaction mechanism whose direct evidence can not be obtained experimentally, and for investigating the electronic structure of the intermediate in catalysis. Furthermore, the studies in this part suggest the possibility of predicting catalytic activity and selectivity.

General Conclusion

MO studies in the chemistry of transition metal complexes are not so popular as those in organic chemistry. Also, in catalytic chemistry, only a few of those works have been reported, although MO studies are necessary in various cases of these fields. In this thesis, the author has attempted to carry out MO studies on electronic structures and catalytic reactions of transition metal complexes by the use of the semi-empirical SCF-MO method.

In part I of this thesis, MO studies have been carried out successfully on transition metal complexes. Calculated transition energies agree fairly well with experimental values in MnO_4^- , CrO_4^{2-} , PdCl_6^{2-} (chapter 2 in part I), ferrocene, cobalticenium ion (chapter 4 in part I), PtCl_4^{2-} , and PtCl_3^- (C_2H_4) $^-$ (chapter 6 in part I).

In CrF_6^{3-} and FeF_6^{3-} , calculated electron densities on the central metal atoms agree fairly well with experimental values (chapter 3 in part I). While in some cases such as MnO_4^- , CrO_4^{2-} , PdCl_4^{2-} and PdCl_6^{2-} , MO calculations give too large electron densities on the central metal atoms, the qualitatively reasonable results are obtained; the electron density on the Pd atom decreases in the order $\text{PdBr}_4^{2-} > \text{PdCl}_4^{2-} > \text{PdCl}_6^{2-}$, which agrees with experimental order (chapter 2 in part I). Also in MX_6^{n-} and $\text{trans-PtHX}(\text{PH}_3)_2$ ($\text{M}=\text{Ni(II)}$, Mn(II) , and Cr(III) ; $\text{X}=\text{F}$, Cl , Br , I , and CN), MO calculations

give reasonable results on electron densities; that is, the electron density on the central metal atom in MX_6^{n-} decreases in the order $F > Cl > Br$, and that on the Pt atom in $trans-Pt-HX(PH_3)_2$ decreases in the order $F > Cl > Br > I > CN$, which seems reasonable by considering the electronegativity of halogen (chapter 3 in part I and chapter 3 in part II).

The author has confirmed in chapter 2 in part I and chapter 3 in part II that the quantity, E_{AB} , can be used as the bond index in transition metal complexes. This quantity is defined as the energy contribution of the AB bond to the total energy. Using this quantity, the reasonable results on bond strength are obtained; for example, the Pd-X bond strength in PdX_4^{2-} and PdX_6^{2-} decreases in the order $Pd-Cl > Pd-Br$ and $Pd(IV)-X > Pd(II)-X$ (chapter 2 in part I), and the Pt-H bond strength in $trans-PtHX(PH_3)_2$ decreases in the order $F > Cl > Br > I > CN$ (chapter 3 in part II). These results qualitatively agree with experimental ones.

Coordination bonding characters have been studied successfully by the use of the MO method; in $Ag(I)$ -olefin complexes (chapter 5 in part I), the σ -donor bond mainly contributes to the coordination of olefin, in which π -electrons of olefin are mainly donated to 5s and 5p orbitals of the Ag atom, while the contribution of the π -acceptor bond is small. In $Pt(II)$ complexes with ethylene and acetylene (chapter 6 in part I), the σ -donor bond also makes the main contribution to the coordi-

nations of ethylene and acetylene, while the π -acceptor bond contributes to some extent. While the $d\sigma-\pi$ interaction is very small in Ag(I)-olefin complexes, this interaction considerably large in Pt(II) complexes. In Pt(0) complexes with ethylene and acetylene (chapter 6 in part I), the contribution of the π -acceptor bond is remarkable as well as the σ -donor bond, while the $d\sigma-\pi$ interaction is very small.

In part II, theoretical studies are carried out on the catalytic reactions of transition metal complexes with the MO method used in part I. In this part, a main discussion is presented on the reaction mechanism: In the oxymercuration, it is discussed which occurs more favorably, the cis-attack or trans-one; the cis-attack occurs when the mercurinium ion is relatively short-lived and is stabilized by the coordination of nucleophile to the Hg(II) ion. In other cases, the trans-attack occurs. In the Wacker reaction, MO calculations supply us information to support the cis-type four-center reaction mechanism proposed by Henry from his kinetic studies. In the ethylene insertion into the Pt-H bond of $\text{trans-PtHX}(\text{PH}_3)_2$, which is not a catalytic reaction by itself but an important elementary reaction in catalytic isomerization and hydrogenation etc. of olefins, MO calculations reveal that the intermediate five-coordinate π -olefinic hydride complex has a trigonal bipyramidal structure in which Cl and H ligands are positioned trans to each others. It is also suggested

from MO calculations that the H ligand starts first to approach ethylene, and that then the Cl ligand starts to move to the trans-position of the H ligand in this insertion; i.e., ethylene does not attack the H ligand.

Besides the reaction mechanism, effects of metal and ligand on catalytic activities are also investigated: The nucleophilic attack of OH^- to ethylene is accelerated by the presences of the Pd(II) and Hg(II) ions and the acceleration by the latter is larger than that by the former. These results agree well with experimental results. In the insertion reaction of ethylene into the Pt-H bond, MO calculations show that the reactivity of trans-PtHX(PH₃)₂ increases as follows; $\text{F} < \text{Cl} < \text{Br} < \text{I} < \text{CN}$. In the hydrogen-deuterium exchange reaction of ethylene, it is suggested from MO calculations that the catalytic activity of trans-PtHX(PH₃)₂ increases in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$.

In both the Wacker reaction and the oxymercuration of propylene, the nucleophile attacks the α -carbon atom more favorably than that does the β -carbon atom. This experimental result is reproduced by the MO calculations and is explained in terms of the electrostatic interaction. Thus, the MO method used in this thesis is useful in studying the selectivity.

As described above, the semi-empirical SCF-MO method supply us various important information of electronic structures of transition metal complexes; electron density, electronic

spectra, and coordination bonding characters. Also, the MO method is shown to be a useful means in catalytic chemistry of transition metal complexes and it is effective in elucidating following points of issues; (1) to investigate the electronic structure of the intermediate complex in catalytic reaction in which it is generally difficult to isolate intermediates and also to investigate experimentally their electronic structures, (2) to verify whether the reaction mechanism, in which experimental evidence is hard to obtain, is reasonable or not, and (3) to anticipate the catalytic abilities (activity and selectivity) of transition metal complexes. Thus, the MO method should be applied to catalytic chemistry in various cases. It should supply us with interesting and meaningful information, and lead to the further development of catalytic chemistry.

