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Electronic Structures of Organo-Transition-Metal Complexes

I. Silver(I)-Olefin Complexes

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By using the closed-shell SCF-MO method with the CNDO type approximation for all valence electron systems, the electronic structures of some Ag^+-olefin complexes are investigated. The calculated values of $-\Delta H$ increase with the increasing number of methyl groups on the double bond and this trend agrees with the experimental result. Also calculation reproduces many experimental results, such as the infrared, Raman, and ^{13}C NMR spectra. These experimental results are discussed on the basis of the calculated electronic structures of Ag^+-olefin complexes.

Key words: Ag^+-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 complex [3] 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], enthalpies of formation [4, 6, 7], infrared [8, 9], Raman [9] and nuclear magnetic resonance (NMR) spectra [9–12] have been measured.

Since Dewar proposed the two-way donor acceptor bond in the silver-olefin complexes, some theoretical studies have been carried out on the natures of coordination bond in such complexes; the perturbation method has been applied for the estimation of the stability of Ag^+-olefin and Ag^+-aromatic compound 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 scare. Thus, the author will calculate the MO's of six Ag^+-olefin complexes by the semi-empirical SCF–MO method, and present some discussions on the experimental results from the obtained MO's in this paper.

2. 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 4*d*-atomic orbitals of the silver atom are considered explicitly. The zero-differential overlap approximation [21] 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],

$$H_{rs} = -kS_{rs}(I_r + I_s) \tag*{(1)[2]}$$

where the parameter k is taken as 0.55. The one-center Coulomb repulsion integrals of ligand atoms are obtained by the Pariser's approximation [25] and those of the silver atom are taken from the Oleari's report [26]. The two-center Coulomb repulsion integrals are computed according to the Ohno's formula [27]. The single Slater type orbital is used for all *s*- and *p*-orbitals, and the double-ζ form is used only for the 4*d*-orbitals 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:

$$E_{\text{nucl}} = \sum_{A} \sum_{B} \sum_{r}^{\text{on A}} \sum_{s}^{\text{on B}} N_r N_s (rr|ss)\,. \tag*{(2)[2]}$$

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[1] While the one-center exchange integrals are included in the formula of Yonezawa *et al.*, the author neglects them in this calculation.

[2] For the notations used in these formulas, see Ref. [23].

Table 1. Orbital exponents (ζ_r), valence state ionization potentials (I_r) and one-center Coulomb repulsion integrals $(rr|rr)$

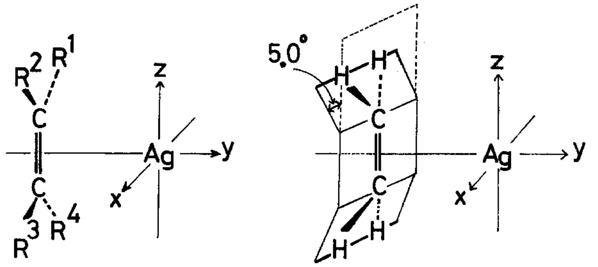
Atom	AO	ζ_r	C[a]	I_r (eV)	$(rr\|rr)$ (eV)
H	1*s*	1.0000 [31]		13.60 [33]	12.85 [33]
C	2*s*	1.5679		21.07	12.10
	2*p*	1.5679		11.27	10.93
Ag	4*d*	5.9830 [32]	0.5535 [32]	8.17 [24]	13.87 [24]
		2.6130	0.6701		
	5*s*	2.1900		7.07	7.46
	5*p*	2.1900		3.30	6.22

[a] The 4*d*-atomic orbital is represented by Basch *et al.* [32] as the linear combination of one 3*d* and two 4*d* Slater orbitals. In this work, the contribution of 3*d* Slater orbital is neglected and the 4*d*-atomic orbital is represented as the linear combination of two 4*d* Slater orbitals. Therefore strictly speeking, this 4*d*-atomic orbital is not normalized. However the contribution of the 3*d* Slater orbital is negligible small and the error induced by this approximation is very small, e.g., less than 0.2% in the case of the overlap integral between the silver atom and the carbon atom.

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 term is expressed by Eq. (3), using the approximations described above.

$$E_{AB} = \sum_{r}^{\text{on A}} \sum_{s}^{\text{on B}} [2.0 P_{rs} H_{rs} - 0.5 P_{rs}^{2} (rr|ss) + (P_{rr} - N_r)(P_{ss} - N_s)(rr|ss)] . \qquad (3)$$ [2]

The distance between the silver atom and the center of the double bond of the olefin is fixed at 2.39 Å[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 the four hydrogen atoms are pushed 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 olefin [29] 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 frames are shown in Fig. 1.



$R^1 \sim R^4 = \text{H or CH}_3$ Etylene complex [B]

Fig. 1. Coordinate frame of Ag^+-olefin complex

3. Results and Discussions

Enthalpies of Formation. The calculated enthalpy of formation (ΔH) has been estimated 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 value of $-\Delta H$ to that of Ag^+-ethylene [A] are shown in Table 2, together with the values of $E_{\text{Ag-C(olefinic)}}$ and $E_{\text{Ag-C(allylic)}}$. The calculated values of $-\Delta H$ increase with 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 enthalpy of formation is decided not only by the interaction

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[3] In Ag^+-cyclooctatetraene, the average Ag^+-olefinic carbon and C=C double 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.

[4] The calculated enthalpies of formation are compared not with the experimental values determined by the gas-chromatography technique [7] 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 2. Enthalpies of formation (ΔH) and $E_{\mathrm{Ag-C}}$ in $\mathrm{Ag^+}$-olefin

Olefin	$-\Delta H$		$E_{\mathrm{Ag-C(olefinic)}}$[c]	$E_{\mathrm{Ag-C(allylic)}}$[d]
	Calculated[a] (in eV)	Experimental[b] (in kcal/mol)	(in eV)	(in eV)
Ethylene [A]	0.00	0.00	−4.57	—
[B]	0.04		−4.64	—
Propylene	0.30	0.029	−4.55	−1.10
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

[a] The relative value to the calculated value of $-\Delta H$ of $\mathrm{Ag^+}$-ethylene complex [A].

[b] The relative value to the experimental value of $-\Delta H$ of $\mathrm{AgBF_4{:}C_2H_4}$ (Ref. [4]).

[c] The average value of two $E_{\mathrm{Ag-C(olefinic)}}$ in the olefin.

[d] The average value of all $E_{\mathrm{Ag-C(allylic)}}$ in the olefin.

between the silver atom and the olefinic carbon atom but also by the interaction between the silver atom and the other parts of olefin, which is supported by the bonding interaction between the allylic carbon atom and the silver atom, as shown in Table 2.

The calculated value of $-\Delta H$ and the absolute value of $E_{\mathrm{Ag-C}}$ in the ethylene complex [B] are larger than those in the complex [A]. These facts suggest that the nonplanar model seems more likly for the structure of ethylene in the complex.

Electron Distribution. The electron densities on silver atoms are shown in Table 3, together with π-electron densities P_π of uncomplexed olefins and quantities of transfered electron ΔQ from the olefin. The calculated results agree well with this configuration, while, compared with Basch's results ($d^{9.94}s^{0.13}p^{0.07}$ in $\mathrm{Ag^+}$-ethylene) [19], the 5*s*- and 5*p*-orbital electron densities obtained in this work seem to be too large. The 5*s*- and 5*p*-orbital electron densities and ΔQ increase with the increasing number of methyl groups, whereas the 4*d*-orbital

Table 3. Electron populations on silver atoms, quantities of the transfered electron (ΔQ)[a] and π-electron densities of olefinic carbon atoms in uncomplexed olefin (P_π)

	Electron population on Ag			ΔQ	P_π	
	4*d*	5*s*	5*p*			
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[b]	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[b]	1.141
2,3-Dimethyl-2-butene	9.986	0.210	0.146	0.341	1.068	

[a] The decrease in the electrons of olefin by the coordination to the silver ion.

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

electron density remains almost constant. A methyl group is known to increase the π-electron density not only by $-I$ effect but also by hyperconjugation [34] and this seems to result in the increase of ΔQ and the electron density on the silver atom.

In the ethylene complex [B], the $5s$- and $5p$-orbital electron densities 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

Table 4. The bond orders of the coordination bond in Ag^+-olefin complexes, and the changes in C=C π-bond orders and $E_{C-H(olefinic)}$ by the complex formation

Olefin	Bond order of coordination bond					$(\Delta P_\pi)_\sigma$[a]	$(\Delta P_{\pi^*})_\pi$[b]	ΔP_π[c]	$\Delta\lvert E_{C-H}\rvert$[d]
	π-acceptor		σ-donor						
	$d_\pi - \pi^*$ (in eV)	$p_\pi - \pi^*$ (in eV)	$d_\sigma - \pi$ (in eV)	$s - \pi$ (in eV)	$p_\sigma - \sigma$ (in eV)	(in eV)	(in eV)	(in eV)	(in eV)
Ethylene [A]	0.146	0.0001	0.088	0.748	0.522	−0.122	−0.003	−0.125	−0.19
[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	0.532	−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-electron donation of the olefin to the silver atom defined as follows;

$$(\Delta P_\pi)_\sigma = \left(2\sum_i^{\text{occ}} C_{i^1p_\pi} C_{i^2p_\pi}\right)_{\text{complexed}} - \left(2\sum_i^{\text{occ}} C_{i^1p_\pi} C_{i^2p_\pi}\right)_{\text{uncomplexed}},$$

where $C_{i^1p_\pi}$ is the coefficient of the p_π orbital of the carbon atom 1 in MO i, and the C=C double bond is formed by the carbon atom 1 and 2.

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

$$(\Delta P_{\pi^*})_\pi = \left(2\sum_i^{\text{occ}} C_{i^1p_{\pi^*}} C_{i^2p_{\pi^*}}\right)_{\text{complexed}} - \left(2\sum_i^{\text{occ}} C_{i^1p_{\pi^*}} C_{i^2p_{\pi^*}}\right)_{\text{uncomplexed}},$$

where $C_{i^1p_{\pi^*}}$ 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] $\Delta E_{C-H} = (E_{C-H})_{\text{complexed}} - (E_{C-H})_{\text{uncomplexed}}$, where E_{C-H} represents the E_{AB} value of the olefinic C—H bond.

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

$$P_\pi = 2\sum_i^{\text{occ}} C_{i^1p_y} C_{i^2p_y},$$

where $C_{i^1p_y}$ is the coefficient of $2p_y$ orbital of the carbon atom 1 in MO i.

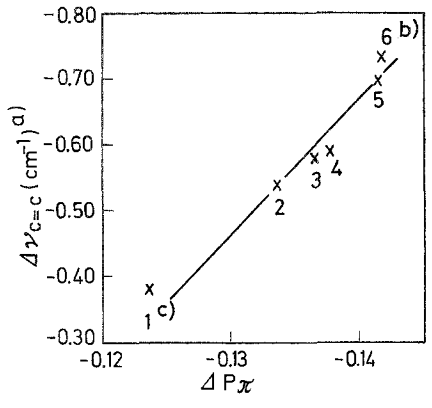

Fig. 2. The relation between ΔP_π and $\Delta\nu_{C=C}$. *1* ethylene, *2* propylene, *3* *trans*-2-butene, *4* *cis*-2-butene, *5* 2-methyl-2-butene, *6* 2,3-dimethyl-2-butene. *a* These values are taken from Ag(olefin)$_2$:BF$_4$ in solid (Ref. [9]). *b* This value is obtained from the measurement in solution (Ref. [9]). *c* This value is taken from the measurement for Ag$^+$-C$_2$H$_4$ (Ref. [3b]), therefore the points 1 and 6 may deviate from the line

in that between the 5*p*-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 5*s*- and 5*p*-atomic orbitals of the silver atom.

The coordination bond orders of the complex [B] are slightly larger than those of the complex [A], resulting in the larger absolute value of E_{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 ($\nu_{C=C}$) to a lower frequency from that in the uncomplexed olefin by 50–70 cm^{-1} for silver (I) [9] and about 150 cm^{-1} for platinum (II) [35]. A shift of $\nu_{C=C}$($\Delta\nu_{C=C}$) is proportional to the change in the C=C π-bond order (ΔP_π), as shown in Fig. 2. This linear relationship between $\Delta\nu_{C=C}$ and ΔP_π suggests that the shift to a lower frequency of $\nu_{C=C}$ is mainly due to a decrease in the strength of the C=C π-bond. The calculation also shows that the absolute values of $E_{C-H(olefinic)}$ 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 the shielding constant of ^{13}C resonance is 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 olefinic carbon resonances are shifted to higher fields in Ag$^+$-olefin complexes.

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[5] This calculation is carried out on the assumption that the average transition energy is 8 eV in all olefins and Ag$^+$-olefin complexes.

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

Unsaturated Carbon Olefin		$\Delta\delta^{a}$ (in ppm)	$\Delta\delta_{(AB)_{xx}}{}^{b}$ (in ppm)	$\Delta\delta_{\pi}{}^{c}$ (in ppm)
Ethylene	[A]	+4.0	+12.0	+12.9
	[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

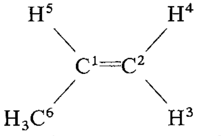
Methyl Carbon Olefin		$\Delta\delta^{a}$ (in ppm)	Main contribution
Propylene		−3.1	$(Q_{AA})_{zz}{}^{f}\ (Q_{AB})_{zz}$
trans-2-Butene		−2.1	$(Q_{AA})_{yy}\ \ (Q_{AA})_{zz}\ (Q_{AB})_{zz}$
cis-2-Butene		−2.2	$(Q_{AA})_{yy}\ (Q_{AB})_{zz}$
2-Methyl-2-butene[e]	C^3	−0.1	$(Q_{AA})_{yy}$
	C^4	−2.1	$(Q_{AA})_{yy}\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

[a] $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free}}$.

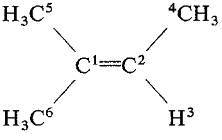
[b] The change in ^{13}C NMR chemical shift due to the change in the $\sum_{B \neq A} (Q_{AB})_{xx}$.

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

[d]



[e]



[f] For these terms, see Ref. [36].

These shifts to higher fields ($\Delta\delta$) are attributable to the increase in δ_{π}[6] which is due to the term of $P_{AyBy}P_{AzBz}$, 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 results [13]. These downfield shifts should be attributed not only to one term but also to two or three terms as shown in Table 5.

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[6] The increase in the olefinic ^{13}C resonance is mainly contributed by the term of $(Q_{AB})_{xx}$; $(Q_{AB})_{xx} = -2P_{AyBy}P_{AzBz} + 2P_{AyBz}P_{AzBy}$ where A and B represent the olefinic carbon and the neighboring atoms, respectively. 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 $P_{AyBy}P_{AzBz}$. Since the P_{AzBz} is almost unchanged by the complex formation, $\Delta\delta_{\pi}$ is mainly contributed by the change in P_{AyBy}.

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

Olefin	Transition energy		MO energy difference[a]	
	Uncomplexed (in eV)	Complexed (in eV)	Uncomplexed (in eV)	Complexed (in eV)
Ethylene [A]	8.87	9.19	14.89	14.88
[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 π- and π^*-MO's.

Transition Energy. It is expected that the $\pi-\pi^*$ transition 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 the 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 5*s*-orbital of the silver ion is calculated as 8.25 eV in Ag^+-ethylene complex [A]. This result is reasonable, since the 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 enthalpy 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.

The calculations have been carried out by the FACOM 230–60 Computer in the Data Processing Center at Kyoto University.

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[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.

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