Semi-empirical SCF-MO Studies of Electronic Structures of Pt-Ethylene and Pt-Acetylene Complexes

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A parametrization in a CNDO-type MO method is presented for Pt compounds. By the use of this parametrization, the electronic spectra of $PtCl_4^{2-}$ are calculated; they agree well with the experimental spectra in transition energies and assignments. MO calculations with this parametrization are carried out on Pt(II)–ethylene, Pt(II)–acetylene, Pt(0)–ethylene, and Pt(0)–acetylene complexes. The calculated transition energies of Zeise's salt also agree well with the experimental values. In Pt(II) complexes, electrons are donated from ethylene and acetylene to the Pt atom, while they are little donated in Pt(0) complexes. The π-bonds of ethylene and acetylene are weaker in Pt(0) complexes than those in Pt(II) complexes. These results are the consequence of the stronger π-acceptor coordination bond in Pt(0) complexes than in Pt(II) complexes. Acetylene coordinates to the Pt atom more strongly than does ethylene. The coordination bonds of ethylene and acetylene are stronger in Pt(0) complexes than in Pt(II) complexes.

The organo-transition metal complexes are very attractive in view of the metal-carbon bonding character and of the models for intermediates which exist in an organic reaction catalyzed by transition metals.[1–4] Zeise's salt[5] is one of the well-known and most investigated organo-transition metal complexes.[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 of these complexes. However, no SCF-MO calculation which explicitly includes electron-repulsion integrals has been carried out on Pt(II)–acetylene, Pt(0)–ethylene, and Pt(0)–acetylene complexes, while extended Hückel (EH) MO (noniterative) calculations have been done on them.[25,26,28,29] From the EH MO calculations, it has been proposed that the 6s orbital of the Pt atom scarcely contributes to the coordination bond of ethylene in both 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.[30a] Thus, it is necessary to re-investigate the electronic structures of Pt(II)–acetylene, Pt(0)–ethylene, and Pt(0)–acetylene complexes. Also, it is of interest to compare the coordination bonds of these complexes with each other.

In this work, parametrizations are investigated in CNDO-type MO calculations on $PtCl_4^{2-}$. By the use of the established parameters, CNDO-type MO calculations are carried out on $PtX_3(C_2H_4)^-$, $PtX_3(C_2H_2)^-$ (X=Cl, Br), $Pt(PH_3)_2(C_2H_4)$, and $Pt(PH_3)_2(C_2H_2)$. Discussions are presented of the electronic structures of these compounds, and also of the coordination bonding characters of ethylene and acetylene in these complexes.

Calculation and Geometries

Calculation. A semi-empirical SCF–MO method with CNDO-type approximations is used in this work. While the method is almost the same as in our previous works,[30] some parameters are improved: (1) In our method, the resonance integrals are evaluated by means of the Wolfsberg-Helmholz equation.[31] The value of its parameter, K, is differently adopted between the 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. While the value of K_2 is taken to be 0.80, as in our previous report,[30c] that of K_1 is determined to be 0.90 in this work, as will be described below. (2) While Ohno equation[32] was used in our previous works,[30] a modification of it which is newly presented in this work is introduced for the calculations of two-center Coulomb repulsion integrals including 6s and 6p orbitals of the Pt atom. The modification of Ohno equation is carried out for the following reason: The one-center Coulomb repulsion integrals, γ_{rt}, are calculated by the following Eq. (1) in Ohno method;

$$r_{\mathrm{rt}} = 0.5(\gamma_{\mathrm{rr}}+\gamma_{\mathrm{tt}}). \tag{1}$$

This equation can be a good approximation when the AO·r and AO·t are alike.[33] In transition metals, however, this Eq. (1) can not be successfully applied to the calculation of one-center values of $\gamma_{n\mathrm{d}(n+1)\mathrm{s}}$ and $\gamma_{n\mathrm{d}(n+1)\mathrm{p}}$, since outer s and p orbitals are very different from valence-shell d-orbitals in their expansion. As examples, Table 1 presents a comparison between those values obtained by Eq. (1) and those obtained from the atomic spectra in Ni and Pd atoms; apparently, Eq. (1) gives too large values of $\gamma_{n\mathrm{d}(n+1)\mathrm{s}}$ and $\gamma_{n\mathrm{d}(n+1)\mathrm{p}}$

TABLE 1. VALUES OF $\gamma_{n\mathrm{d}(n+1)\mathrm{s}}$ AND $\gamma_{n\mathrm{d}(n+1)\mathrm{p}}$[a] OF THE Ni AND Pd ATOMS

	γ_{ds}[b]	$0.5(\gamma_{\mathrm{dd}}+\gamma_{\mathrm{ss}})$	Δ_{ds}[c]	γ_{dp}[b,d]	$0.5(\gamma_{\mathrm{dd}}+\gamma_{\mathrm{pp}})$	Δ_{dp}[c]
Ni	10.09_{eV}	12.34	−2.25	8.46	11.56	−3.10
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) $\Delta_{\mathrm{ds}}= -0.5(\gamma_{\mathrm{dd}}+\gamma_{\mathrm{ss}})$, $\Delta_{\mathrm{dq}}=\gamma_{\mathrm{dp}}-0.5(\gamma_{\mathrm{dd}}+\gamma_{\mathrm{pp}})$, d) The averaged value of various types of γ_{dp}.

as compared with the corresponding values obtained from the atomic spectra. In order to improve this defect, the following modification is carried out, only when either AO·r or AO·t is an outer orbital;

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

$$14.3986/d = 0.5(\gamma_{\mathrm{rr}}+\gamma_{\mathrm{tt}}) - a_{\mathrm{r}}, \tag{3}$$

where AO·r is assumed to be an outer orbital and where R_{rt} is the distance (in Å 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 Eqs. (2) and (3) reproduce the experimental values of the one-center Coulomb repulsion integrals, such as $\gamma_{n\mathrm{d}(n+1)\mathrm{s}}$ and $\gamma_{n\mathrm{d}(n+1)\mathrm{p}}$, at $R_{\mathrm{rt}}=0.0$; for example, the values of $a_{4\mathrm{s}}$ and $a_{4\mathrm{p}}$ of the Ni atom are taken as 2.25 and 3.10 eV respectively (see Table 1). The original Ohno equation is used in the other AO pairs, in which both AO's are outer orbitals or valence ones.

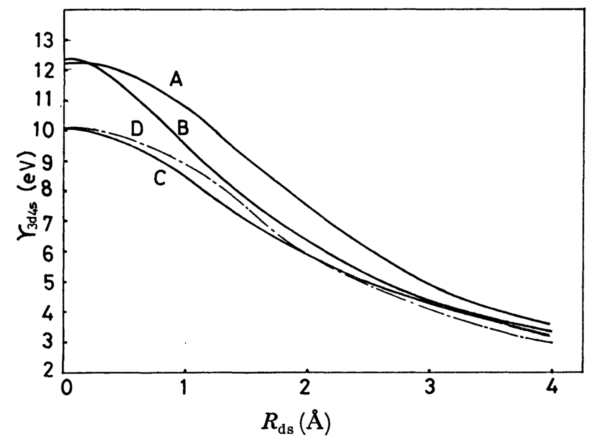

Fig. 1. Two-center Coulomb repulsion intergrals $\gamma_{3\mathrm{d}4\mathrm{s}}$[a] at various inter-atomic distances.
a) 3d; the 3d orbital of the Ni atom. 4s; the 4s orbital of the Ni atom.
A; The nonempirical value: the 3d orbital; the double-ζ type AO by Richardson *et al.* [36], the 4s orbital; the single Slater type AO by Clementi *et al.* [35].
B; Ohno's approximation.
C; The modified Ohno's approximation, Eqs (2) and (3).
D; These values are obtained by multiplying a correction factor to the nonempirical values so as to coincide the one-center value of $\gamma_{3\mathrm{d}4\mathrm{s}}$ with that obtained from atomic spectra.

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

In the case of the Pt atom, unfortunately, the experimental values of $\gamma_{5\mathrm{d}\ 6\mathrm{s}}$ and $\gamma_{5\mathrm{d}\ 6\mathrm{p}}$ can not be obtained because of the lack of atomic spectra. In the Pd atom, which forms compounds similar to those of the Pt's, $a_{5\mathrm{s}}$ should be taken as 1.53 eV and $a_{5\mathrm{p}}$ 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 $a_{6\mathrm{s}}$ and 2.2—2.8 eV for $a_{6\mathrm{p}}$. From those examinations, $a_{6\mathrm{s}}=1.5$ eV and $a_{6\mathrm{p}}=2.5$ eV are chosen as the best values; they give good results on the electronic spectra of tetrachloroplatinate and Zeise's salt, as will be described in the following section.

For the Pt atom, the valence-state ionization potentials, I_{r}, are evaluated from the atomic spectra.[37] One-center Coulomb repulsion integrals, γ_{rr}, are estimated by the use of Eq. (2) in Ref. 30c. For the atoms of ligands, the values of I_{r} are taken from Hinze-Jaffé's work,[38] and those of γ_{rr} are evaluated from the same work[38] by the use of Pariser's approximation.[33] A double-ζ type d-function[39] is used for the 5d orbital of the Pt atom, while single Slater-type orbitals[35,40] are used for all the s and p orbitals. These data for the Pt atom are given in Table 2.

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 2.696	0.6331 0.5516	8.24 eV	12.42 eV
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. 37. d) The estimated values obtained by using Eq. (2) in Ref. 30-c.

Geometries. The structures of Zeise's salt[15] and its bomo analogue[18] are taken from the X-ray studies. Since the accurate structures of $\mathrm{PtX_3(C_2H_2)^-}$, (X=Cl, Br), have not been known, the bond length of the Pt–X bond is taken as equal to the corresponding one of $\mathrm{PtX_3(C_2H_4)^-}$ and the distance between the Pt atom and the center of the triple bond of acetylene is taken as equal to that of Pt(PPh$_3$)$_2$(PhC≡CPh).[24] The bond length of the C≡C triple bond is taken as equal to that of *trans*-PtCl$_2$(*p*-toluidine)[(*t*-Bu)C≡C(*t*-Bu)].[20] The ethylene and acetylene moieties are considered to be dis-

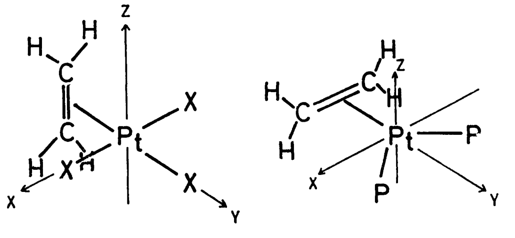

Fig. 2. Coordinate systems of Pt(II) and Pt(0) ethylene complexes.
The acetylene complexes are also the same as the above ones. X=Cl or Br, P=PH$_3$.

torted by their coordinations to the Pt atom.[2,16,20,21,24] Nevertheless, the ethylene and acetylene moieties are assumed not to be distorted because of the shortage of structural studies of these complexes. The structures of the Pt(0)–ethylene and Pt(0)–acetylene complexes are taken from the X-ray studies,[22,24] while the *cis*-bending of the CH_2 and CH groups and the small dihedral angle are neglected and PR_3 group is replaced by the PH_3 one for the sake of simplicity. These coordinate systems are shown in Fig. 2.

Results and Discussion

Parametrization. In order to investigate the 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 some typical results are given in Tables 3 and 4. (Of course, various sets of values of K_1, a_{6s}, and a_{6p} are also examined besides the three given in Table 3.)

As is shown in Table 3, the A parametrization gives remarkably large electron densities on the 6s and 6p orbitals of the Pt atom. Furthermore, this parametrization gives too small transition energies for the intra-atomic 5d→6p transition, while these are really considered to have remarkably high transition energies.[41] Thus, this parametrization is abandoned.

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

Parametrization[a]		A	B	C	D
a_{6s}[b]		0.0 eV	1.2	1.5	1.8
a_{6p}[b]		0.0 eV	2.2	2.5	2.8
Electron densities	Pt 5d	7.68	8.37	8.41	8.44
	Pt 6s	1.28	0.69	0.65	0.61
	Pt 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) $K_1=0.90$. b) Constants in Eq. (3).

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

The results on the 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 the calculations than the experimental ones, and the smaller values of a_{6s} and a_{6p} give relatively higher energies than do the larger values. 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 (3.31 eV) of ^1E_g in the D parametrization, while it is experimentally obtained at 3.76 eV. The C parametrization seems to be the best one. The electronic spectra obtained by this parametrization agree well with the experimental spectra in transition energies and assignments, although the calculated C–T bands have considerably higher transition energies and the calculated d-d band, $^1B_{1g}$, has a considerably smaller transition energy than the corresponding experimental ones.[41,42] The values of a_{6s} and a_{6p} used in the C parametrization seem reasonable in view of the a_{5s} and a_{5p} values 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 bands is obtained at 6.06 eV, and the second one at 7.28 eV, where values of 1.5 and 2.5 eV are used for a_{6s} and a_{6p}. On the other hand, in the case of $K_1=0.80$, the assignments of d-d bands can not agree with the 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 C para-

Table 4. Electronic spectra of $PtCl_4^{2-}$

Obsd[a]			Parametrization B			Parametrization C			Parametrization D		
δE[b]	ε_{max}		δE[b]	f_s		δE[b]	f_s		δE[b]	f_s	
2.62	16.3	$^1B_{1g}$[c]	1.75	0.0	$^1B_{1g}$	1.99	0.0	$^1B_{1g}$	2.27	0.0	$^1B_{1g}$
3.16	52.6	$^1A_{2g}$	3.08	0.0	$^1A_{2g}$	3.20	0.0	$^1A_{2g}$	3.29	0.0	$^1A_{2g}$
3.76	62.4	^1E_g	3.80	0.0	^1E_g	3.51	0.0	^1E_g	3.31	0.0	^1E_g
4.66	400	non-degenerate	3.95	0.0	^1E_g	4.04	0.0	^1E_g	4.07	0.0	^1E_g
			5.20	0.0	$^1A_{2g}$	4.88	0.0	$^1A_{2g}$	4.63	0.0	$^1A_{2g}$
			5.76	0.0	$^1A_{1g}+^1B_{2g}$	5.50	0.0	$^1B_{2g}$	5.28	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	{5.55	0.280	^1E_u
			6.14	0.0	$^1A_{2u}$	5.88	0.0	$^1A_{2u}$	5.66	0.0	$^1A_{2u}$
			6.23	0.0	^1E_g						
			6.60	0.0	$^1B_{2u}$	6.34	0.0	$^1B_{2u}$	6.12	0.0	$^1B_{2u}$
5.72	10900	^1E_u	7.21	0.236	^1E_u	6.97	0.258	^1E_u	6.67	0.246	^1E_u

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

metrization).

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

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

TABLE 5. CALCULATED TRANSITION ENERGIES OF ZEISE'S SALT

∂E[b]	Parametrization C f_s		Obsd[a] ∂E[b]	Obsd[a] f_s
2.39	1×10^{-4}	$^1B_1$		
3.46	4×10^{-4}	$^1B_2$		
3.71	0.023	$^1A_1$	3.72	
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. b) in eV unit.

Electronic Spectra of Zeise's Salt. The C parametrization gives good results for transition energies as is shown in Table 5. The transition at 3.72 eV is assigned to the d-d band. The transitions at 4.26, 4.67, and 5.16 eV are assigned to the C–T bands from the Cl^- ligand to the d-orbital of the Pt atom. Moore assigned the weak transitions at 2.71 and 2.96 eV to the spin-forbidden ones on the basis of his EH(ω) MO calculation.[8] Our calculation gives the spin-allowed d-d bands, $^1B_1$ ($d_{yz}\rightarrow d_{x^2-y^2}$), at 2.39 eV and $^1B_2$ ($d_{xy}\rightarrow d_{x^2-y^2}$) at 3.46 eV, which have very small oscillator strengths, $f_s=1\times10^{-4}$ and $f_s=4\times10^{-4}$ respectively. These results suggest that the observed weak absorptions at 2.71 and 2.96 eV can not be necessarily assigned to the spin-forbidden transitions on the basis of their small absorption coefficients. Thus, there also remains the possibility that these absorptions are spin-allowed d-d transitions.

Electron Densities of Pt–ethylene and Pt–acetylene Complexes. The results for electron densities are given in Table 6, together with the quantities of ΔQ, ΔP_π, and P_{π^*}, which are defined in the footnote of the table. In the 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 the Pt(0)–ethylene and Pt(0)–acetylene complexes, the electron densities are increased by *ca.* 0.05 e and *ca.* 0.02 e respectively. The values of ΔQ are *ca.* 0.3 e in the Pt(II) complexes, while they are nearly equal to zero in the Pt(0) complexes. This different behavior in the electron transfer between the Pt(II) and Pt(0) complexes is 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 the Pt(II) complexes, while the π-acceptor bond contributes largely to the coordination bonds in the Pt(0) complexes, as will be described below.

TABLE 6. ELECTRON DENSITIES, ΔQ[a], ΔP_π[b], AND P_{π^*}[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	Pt	5d	8.490	8.530	9.341
		6s	0.618	0.646	0.579
		6p	0.588	0.586	0.559
	C		4.125	4.125	4.181
ΔQ[a]			0.287	0.295	−0.039
ΔP_π[b]			−0.166	−0.171	−0.379
P_{π^*}[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	Pt	5d	8.495	8.541	9.362
		6s	0.610	0.635	0.574
		6p	0.603	0.590	0.571
	C		4.028	4.024	4.125
ΔQ[a]			0.289	0.302	0.004
ΔP_π[b]			−0.155	−0.160	−0.343
P_{π^*}[c]			−0.036	−0.036	−0.206

a) The quantity of transfered electrons from ethylene or acetylene to PtX_3^- or $Pt(PH_3)_2$ part. b) $\Delta P_\pi=$(P_π of complexes ethylene) — (P_π of free ethylene). ΔP_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_π is defined as the partial bond order in which π*-type interactions of ethylene or acetylene are only considered.

The absolute value of ΔP_π of $PtBr_3(C_2H_4)^-$ is larger than that of $PtCl_3(C_2H_4)^-$, suggesting that the C=C double bond of $PtBr_3(C_2H_4)^-$ is weaker than that of $PtCl_3(C_2H_4)^-$. This result agrees with the experimental finding that the ethylene part in $PtBr_3(C_2H_4)^-$ has a lower stretching vibration of the C=C double bond than that in $PtCl_3(C_2H_4)^-$.[12–14] Since the absolute value of P_{π^*} is remarkably small in the Pt(II) complexes, the decrease in the π-bond order of the ethylene part is not due to the increase in its π*-anti-bonding character, but to the decrease in its π-bonding nature.

The absolute values of ΔP_π in the Pt(0) complexes are larger than those in the Pt(II) complexes by *ca.* 0.17—0.2 e, suggesting that the C=C double and C≡C triple bonds in the Pt(0) complexes are weaker than those in the Pt(II) complexes. Between the Pt(0) and Pt(II) complexes, the difference in the values of ΔP_π coincides well with the difference in the value of P_{π^*}. Therefore, roughly speaking, it can be said that the stronger π-acceptor bond results in the larger increase in the π*-nature and the weaker C=C and C≡C bonds in the Pt(0) complexes than in Pt(II) complexes.

TABLE 7. COORDINATION BONDING CHARACTER OF Pt(II) AND Pt(0) COMPLEXES WITH ETHYLENE AND ACETYLENE

Compounds	$PtCl_3(C_2H_4)^-$	$PtBr_3(C_2H_4)^-$	$Pt(PH_3)_2(C_2H_4)$	$PtCl_3(C_2H_2)^-$	$PtBr_3(C_2H_2)^-$	$Pt(PH_3)_2(C_2H_2)$
$E_{d_\sigma-\pi}$	−0.557 eV	−0.530 eV	−0.240 eV	−0.585 eV	−0.579 eV	−0.257 eV
$E_{d_\pi-\pi^*}$	−0.545	−0.546	−1.844	−0.627	−0.624	−1.753
$E_{s-\pi}$	−1.368	−1.394	−1.853	−1.427	−1.461	−1.861
$E_{p_\sigma-\pi}$	−1.067	−1.127	−1.239	−1.074	−1.102	−1.221
E_{s-s}	−0.673	−0.663	−0.876	−1.078	−1.069	−1.225
$E_{p_\sigma-s}$	−1.015	−1.035	−1.184	−1.468	−1.490	−1.549
E_{Pt-C}	−6.547	−6.591	−8.380	−7.360	−7.698	−9.502

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] it is written as below under approximations used in this MO method.[30]

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

$$E_{AB}^{(1)} = 2\sum_{r}^{A}\sum_{t}^{B} P_{rt}H_{rt} \tag{5}$$

$$E_{AB}^{(2)} = -0.5\sum_{r}^{A}\sum_{t}^{B} P_{rt}{}^{2}\gamma_{rt} \tag{6}$$

$$E_{AB}^{(3)} = \sum_{r}^{A}\sum_{t}^{B} (N_r - P_{rr})(N_t - P_{tt})\gamma_{rt} \tag{7}$$

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

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

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

As is shown in Table 7, E_{Pt-C} is contributed to largely by the $E_{s-\pi}$ and $E_{p_\sigma-\pi}$ in the Pt(II) complexes, where the former subscript, such as s and p_σ, indicates the AO of the Pt atom, and the latter one the AO of the C atom. The contributions of $E_{d_\pi-\pi^*}$ and $E_{p_\pi-\pi^*}$ are small. These results suggest that the coordination bonds of ethylene and acetylene are mainly contributed to by the σ-donor bond in the 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] Braterman,[46] and Cooper *et al.*[47] with regard to the coordination bond of olefin in Pt(II) complexes.

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

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

The relative contribution of valence orbitals of the Pt atom should be discussed not in terms of the bond order but in terms of E_{ArBs}, since the bond order is not appropriate for the bond index because of its rotational variable character. As is shown in Table 7, the 6s orbital contributes to the coordination bond as much as the 6p orbital does, and 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, the 6s and 6p orbitals of the Pt atom contribute greatly to the coordination bonds of ethylene and acetylene, while the 5d orbital also considerably contributes to the Pt(II) complexes. The π-acceptor bond (d_π-π^*) contributes much to the 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≡C bonds, and the larger value of E_{Pt-C}, relative to those of the Pt(II) complexes. It should be noted that strong s-s and p_σ-s interactions exist between the Pt and C atoms besides the σ-donor and π-acceptor bonds.

These calculations were carried out by the Facom 230-60 and 230-75 computers of The Data Processing Center of Kyoto University.

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