1.0 from ref 2 then $k_{-o}/k_2 + (K_{\mathrm{Fe(III)}}/k_2)(k_{-1} - k_o) = k'_-/k_2 = 0.037$ and using k'_- we find $k_{-o} = 1.4 \times 10^5$ M^{-1} s^{-1}; $k_{-1} = 1.6 \times 10^8$ M^{-1} s^{-1} and $k_2 = 9.2 \times 10^6$ M^{-1} s^{-1}. This latter value is in good agreement with the directly measured values[6,7] for the reaction $Tl^{2+} + Fe^{2+}$ in 1 M $HClO_4$ which have been reported as 3.3×10^6 M^{-1} s^{-1} and also as 6.7×10^6 M^{-1} s^{-1}. k_{-1} and k_{-o} are greater than k_1 and k_o, respectively, and k_{-1} is in fact only about 10 times less than the diffusion-controlled limiting rate. As this latter is of course less than that known for proton transfer and since also in all solutions $[Fe^{3+}] \leq 10^{-2}[H^+]$, the distribution of Tl(II) is between Tl^{2+} and $TlOH^+$ and that of Fe(III) is between Fe^{3+} and $FeOH^{2+}$ and is overwhelmingly determined by equilibria 7 and 8.

The large increase in rate for hydrolyzed over aquo species has been noted for many other reactions of aquohydroxy cations and has been attributed to a change of mechanism from outer-sphere electron transfer (k_o, k_{-o} paths) to either inner-sphere OH^- bridging and/or H atom transfer.

Were the k_{-1} paths taken to reflect reaction between $TlOH^+$ and Fe^{3+}, then (using $pK_2 = 4.6$) not only would the products of the reaction of $TlOH^{2+}$ and Fe^{2+} be thermodynamically unstable but also the calculated rate constants for this path would at both ionic strengths be about 10^{10} M^{-1} s^{-1}, i.e., about 10^5 times that of the water-exchange rate[9] of the iron(III)–aquo ion.

Using the equilibrium constant $k_o/k_{-o} = K_{12} = 4.4 \times 10^{-8}$ M and also using $E° = 0.74$ V for the Fe^{3+}/Fe^{2+} couples[7] we find $E°_{Tl^{3+}/Tl^{2+}} = 0.30$ V (cf. 0.30, 0.31, and 0.32 V from ref 3, 4, and 5).

We now consider the individual data from ref 2 which were used to construct (10b), all of which refer to $I = 3.0$. Here both A and B are available for a series of $[H^+]$ values. Combining and rearranging (9) and (10a) give (12) where k_{-1},

$$\frac{(0.5A - k_o)(1 + K_{\mathrm{Tl(III)}}/[\mathrm{H}^+]}{B} = \frac{K_{\mathrm{Tl(III)}}(k_1 - k_o)k_2}{k_{-o}[\mathrm{H}^+] + K_{\mathrm{Fe(III)}}(k_{-1} - k_{-o})} \qquad (12)$$

k_{-o}, and k_2 are unknown at $I = 3.0$ but $k_{-1} \gg k_{-o}$ and $k_2k_{-1}/k_{-o} = 1.92$ (see above). We make the single assumption that the ionic strength dependence of k_{-o} is the same as that we have found for k_o and calculate that at $I = 3.0$ $k_{-o} = (1.4 \times 10^5 \times 0.0078)/0.0060 = 1.82 \times 10^{-5}$ M^{-1} s^{-1}, $K_{\mathrm{Fe(III)}}k_{-1} = 1.92$ s^{-1}, $k_{-o} = 3.5 \times 10^5$ M^{-1} s^{-1}, and $k_{-1} = 3.5 \times 10^8$ M^{-1} s^{-1}. By substitution into (12) we have calculated k_2 for a series of $[H^+]$ values. These are given in Table II. They show no trend with change of $[H^+]$ from 0.4 to 2.8 M, and this demonstrates that any effects arising from different reactivities of Tl^{2+} and $TlOH^+$ with Fe^{2+} are not significant but are within the experimental error of the data.

The exchange reaction Fe(III)* + Fe(II) $\rightleftarrows$ Fe(III) + Fe(II)* also exhibits parallel paths[10] involving $FeOH^{2+}$ and Fe^{3+} as oxidants. For the unhydrolyzed path, the exchange rate (k_{22}) is 0.87 M^{-1} s^{-1} and is now used together with K_{12} derived above to test the applicability of the modified[11] Marcus equation (eq 13) to the $Fe^{2+} + Tl^{3+}$ reaction rate. ΔG_{12}* is

$$\Delta G_{12}^* = \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{[\Delta G_{12}°(1 + \alpha)]}{2} \qquad (13)$$

$$\alpha = \frac{\Delta G_{12}°}{4(\Delta G_{11}^* + \Delta G_{22}^*)}$$

here derived using $k_{12} = 6.0 \times 10^{-3}$ M^{-1} s^{-1} (k_o in eq 3). k_{11} so calculated is 4×10^3 M^{-1} s^{-1}. As expected this is less than the experimental value of 3.0×10^4 M^{-1} s^{-1} which was measured[3] under conditions where about 8%[7] of the Tl^{3+} was present as $TlOH^{2+}$. We are currently attempting to correlate rates of oxidation of other reductants by unhydrolyzed Tl^{3+}.

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Registry No. Fe^{2+}, 15438-31-0; Tl^{3+}, 14627-67-9.

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Ligand Distortions in Platinum(0) Complexes

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It is well-known that a ligand coordinated to a transition metal is distorted from its structure in the ground state.[1-10] There have been reported several theoretical studies of this matter.[11-14] The cis-bending distortion of acetylene coordinated to a metal atom has been investigated in moderate detail;[13] however that work involved a rather severe approximation, in that the metal ion was not included in the MO calculations. A semiquantitative study which included a metal ion was carried out by Nelson et al.,[14] using the extended Hückel MO method. They reported that the energy minimum brought about by the acetylene cis bending accorded with the maximum of the metal–carbon total overlap population. From this result, it is conceivable that the cis bending is induced by the strengthening of the metal–carbon bond. Blizzard et al. proposed that the cis bending should have little effect on the strength of the metal–acetylene interaction.[13] Thus, it appears that previous discussion of this issue is not conclusive.

In the present work, the electronic structures of platinum(0) complexes $Pt(PH_3)_2L$ (L = C_2H_2, C_2H_4, CS_2, CO_2) are investigated with a CNDO-type semiempirical SCF–MO method, in order to determine why the L ligand is distorted by the coordination to the platinum atom. The conclusion we reach is different from those of both Blizzard et al.[13] and Nelson et al.[14] The carbon disulfide and carbon dioxide complexes have never been investigated theoretically.

Method and Geometries

The MO method employed is a CNDO-type approximate semiempirical SCF–MO method. This method, described elesewhere,[15-17] yields successful results on the electronic spectra of tetrachloroplatinate and on the electronic structures of various third-row transition metal complexes.[16-17]

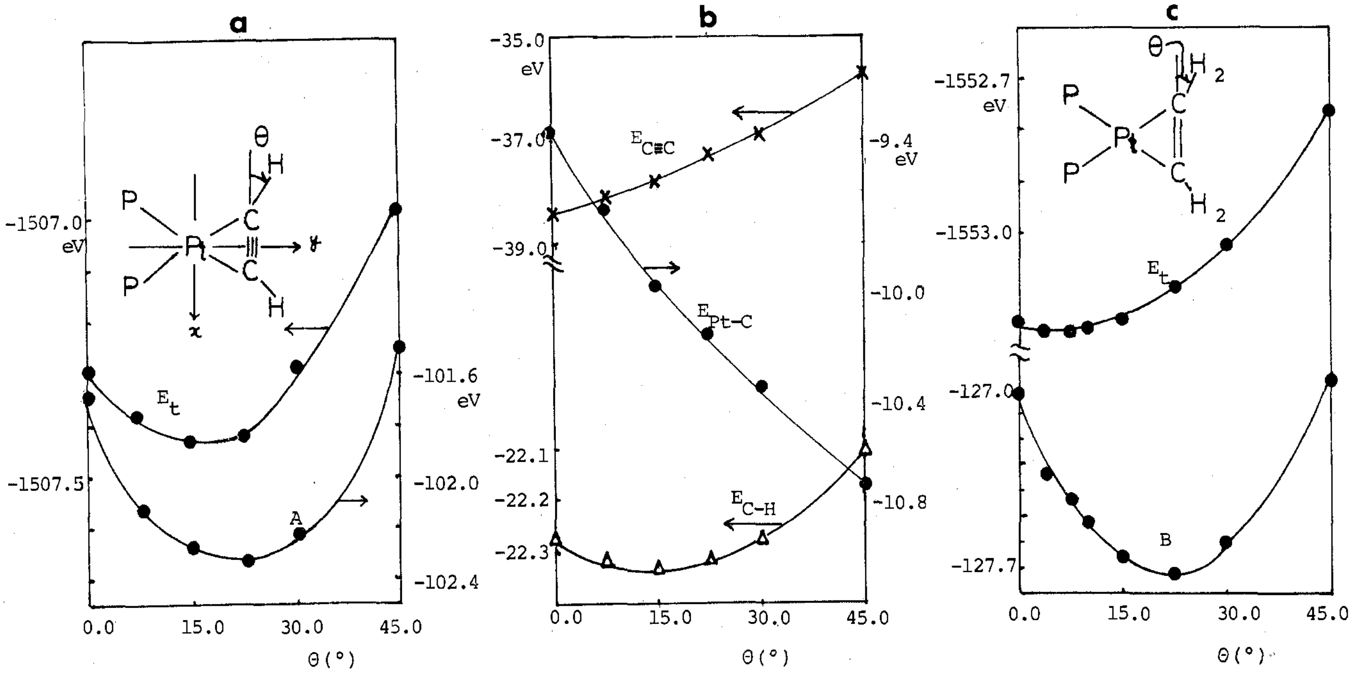


Figure 1. Total energy (E_t) and bond strength of $Pt(PH_3)_2(C_2H_2)$ and $Pt(PH_3)_2(C_2H_4)$: (a) E_t of $Pt(PH_3)_2(C_2H_2)$; (b) bond strength of the C_2H_2 complex; (c) E_t of $Pt(PH_3)_2(C_2H_4)$; A line, $2(E_{Pt-C} + E_{C-H}) + E_{C\equiv C}$; B line, $2(E_{Pt-C} + 2E_{C-H}) + E_{C=C}$. In $Pt(PH_3)_2(C_2H_4)$, bond strength changes similarly to that of $Pt(PH_3)_2(C_2H_2)$.

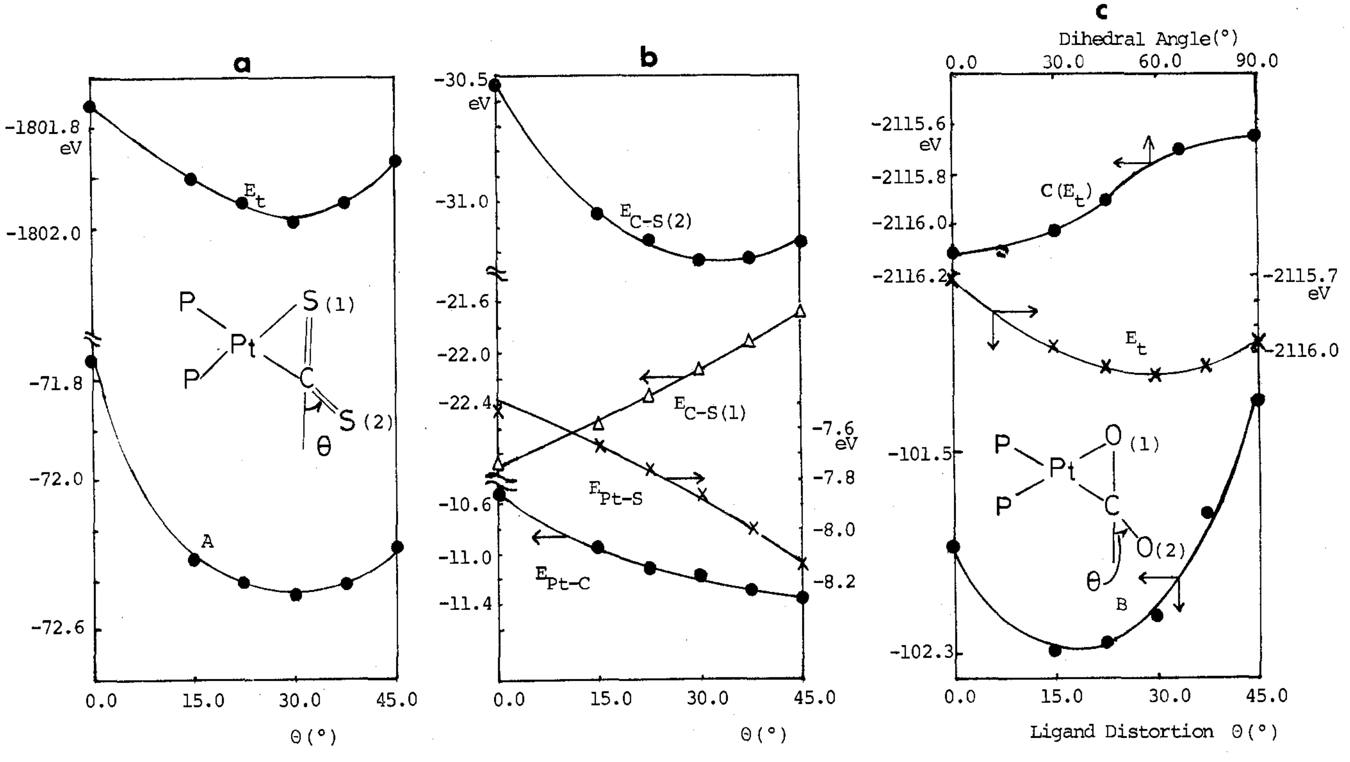


Figure 2. Total energy (E_t) and bond strength of $Pt(PH_3)_2(CS_2)$ and $Pt(PH_3)_2(CO_2)$: (a) E_t of $Pt(PH_3)_2(CS_2)$; (b) bond strength of the CS_2 complex; (c) E_t of $Pt(PH_3)_2(CO_2)$; A line, $E_{Pt-C} + E_{Pt-S(1)} + E_{C-S(1)} + E_{C-S(2)}$; B line, $E_{Pt-C} + E_{Pt-O(1)} + E_{C-O(2)} + E_{C-O(1)}$; C line, total energy as a function of the dihedral angle. In $Pt(PH_3)_2(CO_2)$, bond strength changes similarly to that of $Pt(PH_3)_2(CS_2)$.

The bond index, the E_{AB} value[18-20] used in the previous work,[15-17] is defined as the energy contribution of the AB bond to the total energy as in

$$E_{AB} = E_{AB}^{(1)} + E_{AB}^{(2)} + E_{AB}^{(3)} = 2\sum_r^A \sum_s^B P_{rs} H_{rs} - 0.5\sum_r^A \sum_s^B P_{rs}^2 \gamma_{rs} + \sum_r^A \sum_s^B (P_{rr} - N_r)(P_{ss} - N_s)\gamma_{rs}$$

A large negative value for E_{AB} represents the large bonding interaction between the A and B atoms. The quantities $E_{AB}^{(1)} + E_{AB}^{(2)}$ ($=E_{AB}^{(1)+(2)}$) and $E_{AB}^{(3)}$ indicate approximately the covalent and electrostatic interactions, respectively. The former is divided into AO pair terms, in order to investigate the bonding nature; e.g., the quantity $E_{Pt(d\pi)-C(p\pi)}^{(1)+(2)}$ approximately represents strength of the covalent interaction between the platinum d_π orbital and the carbon p_π. Such division is not carried out for the $E_{AB}^{(3)}$ term, since this term approximately indicates the electrostatic interaction and its

Table I. Pt-L Bonding Nature of $Pt(PH_3)_2L$ at $\theta = 0°$[a]

		$E_{d_\pi-p_{\pi_g}}{}^{(1)+(2)}$,[b] eV	$E_{sp_\sigma-p_{\pi_u}}{}^{(1)+(2)}$, eV	$E_{sp-s}{}^{(1)+(2)}$, eV	P_{π_u}[c]	P_{π_g}[d]
C_2H_2	Pt-C	−1.76	−3.06	−2.78	0.867	−0.199
CS_2	Pt-S	−1.31	−3.85	−1.53	0.557	−0.232
	Pt-C	−2.51	−2.07	−3.02		

[a] Results on the ethylene and carbon dioxide complexes are similar to these given in this table. [b] The former AO's such as d_π, sp_σ, and sp are on the platinum atom. The latter ones such as p_{π_g}, p_{π_u}, and s are on the L ligand atom. [c] The partial bond order of the π_u-type interaction in the C≡C and C=S bonds of the acetylene and carbon disulfide parts. [d] The partial bond order of the π_g-type interaction in the C≡C and C–S bonds of the acetylene and carbon disulfide parts.

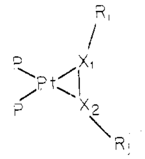
meaning is lost by the division.

Geometries of calculated complexes are shown in Figures 1 and 2. Although platinum(0) complexes often possess the triphenylphosphine ligands,[1] we employ the PH_3 group for simplicity; its sructure is taken equal to that of the free molecule.[21] The small dihedral angle observed in these complexes[1] is neglected. In $Pt(PH_3)_2L$ ($L = C_2H_2$, C_2H_4, CS_2), the Pt–P, Pt—S, Pt—C, C=S, C≡C, and C=C distances and the PPtP angle are taken from the x-ray studies.[4-6] The C—H distance is taken as equal to that of free molecule.[21] In $Pt(PH_3)_2(CO_2)$, estimated bond angles and bond distances are used,[22] since the x-ray study has not been reported. The dihedral angle is taken as zero, as ascertained from the MO calculation, shown in Figure 2c (line C).

Results and Discussion

The total energies of these complexes are given as functions of the ligand distortions in Figures 1a, c and 2a, c. The energy minima are obtained at θ_{min} = 15, 4, 30, and 30° for the acetylene, ethylene, carbon disulfide, and carbon dioxide complexes, respectively. Unfortunately, these calculated values are smaller than the observed ones of similar complexes: θ_{min} = 40° for $Pt(PPh_3)_2(PhC{\equiv}CPh)$,[4] 26° (experimentally estimated value) for $Pt(PPh_3)_2(C_2H_4)$,[7] 43.8° for $Pt(PPh_3)_2(CS_2)$,[6] and 47° for isoelectronic $Ni(PCy_3)_2(CO_2)$.[8] However, our purpose is not to reproduce correctly the degree of the ligand distortion but to investigate why the ligand is distorted by the coordination; for this purpose, our results seem sufficient.

For the purposes of the following discussion, the general form of the calculated complexes is presented in I, where X_1



I

$= X_2 = C$ and $R_i = R_j = H$ ($i = j = 1$) for the acetylene complex, $X_1 = X_2 = C$ and $R_i = R_j = H$ ($i = j = 1$ and 2) for the ethylene complex, $X_1 = C$, $X_2 = R_i = S$ ($i = 1$), and there is no R_j for the carbon disulfide complex, and $X_1 = C$, $X_2 = R_i = O$ ($i = 1$), and there is no R_j for the carbon dioxide complex. The bond strength is changed by the ligand distortion as follows (Figures 1b and 2b): (1) the absolute values of E_{Pt-X_1} and E_{Pt-X_2} monotonically increase with an increase in the ligand distortion, while that of $E_{X_1-X_2}$ monotonically decreases; i.e., the Pt–X_1 and Pt–X_2 bonds become strong and X_1–X_2 becomes weak; (2) the X_1–R_i and X_2–R_j bonds become the strongest about θ_{min}; (3) the sum of $E_{Pt-X_1} + E_{Pt-X_2} + E_{X_1-X_2} + \sum_i E_{X_1-R_i} + \sum_j E_{X_2-R_j}$, which is shown in Figures 1a, c and 2a, c, has its energy minimum about θ_{min}. The above results suggest that stabilization of the Pt–X_1, Pt–X_2, X_1–R_i, and X_2–R_j bonds induces ligand distortion and that the destabilization of the X_1–X_2 bond brought about by the ligand distortion tends to reduce the ligand distortion.[23]

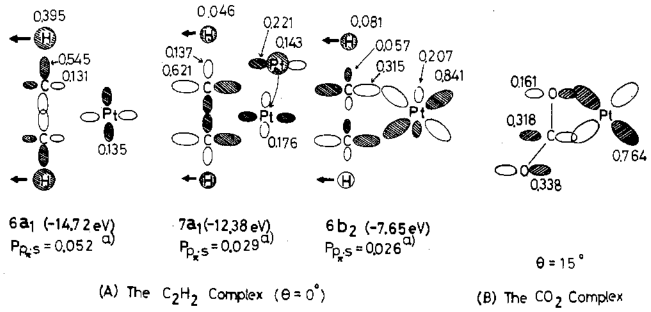
Table II. C–H Bonding Character of $Pt(PH_3)_2(C_2H_2)$[a] (eV Units)

	Complexed		Uncomplexed	
	$E_{C-H}{}^{(1)+(2)}$ (0°)	ΔE_{C-H}[b]	$E_{C-H}{}^{(1)+(2)}$ (0°)	ΔE_{C-H}[b]
s–s	−13.19	+0.03	−13.19	+0.01
p_x–s	−8.91	+0.48	−9.18	+0.38
p_y–s	−0.03	−0.66	−0.08	−0.22

[a] The p_z–s interaction hardly changes. [b] $[E_{C-H}{}^{(1)+(2)}$ at 15°] − $[E_{C-H}{}^{(1)+(2)}$ at 0°].

Now we consider why these bonding changes occur. At $\theta = 0°$, there are strong bonding interactions of d_π–p_{π_g}, sp_σ–p_{π_u}, and sp–s between the platinum and the X_1, X_2 atoms, as are shown in Table I. It should be noted that the s orbitals of the X_1 and X_2 atoms contribute substantially to the Pt–L interaction, which suggests that the platinum, X_1, and X_2 atoms form the three-membered type of interaction and that the L ligand acts to some extent as a bidentate ligand. The strong sp_σ–p_{π_u} σ-donor and d_π–p_{π_g} π-acceptor bonds bring about a decrease in electron numbers in the π_u MO and an increase in the π_g MO, for which the P_{π_g} and P_{π_u} values give direct evidence (see Table I and its footnotes *c* and *d*). As a consequence, the hybridization of the carbon atom becomes sp^{n+1}-like from sp^n-like ($n = 1$ for acetylene, carbon disulfide, and carbon dioxide complexes; $n = 2$ for the ethylene complex). This brings about the ligand distortion, which raises the energy level of the π_u MO and lowers that of the π_g MO. These changes in MO energy levels bring about the following features. (1) The σ-donor and π-acceptor coordination bonds become strong. (2) More electrons are lost from the π_u MO and are accumulated in the π_g MO. Thus, the electron density of the platinum $5d_\pi$ orbital decreases, while that of the platinum 6s6p increases; e.g., that of the $5d_\pi$ is 1.569 at θ = 0° and 1.501 at θ = 15° and that of the 6s6p is 1.126 at θ = 0° and 1.145 at θ = 15°. Overall electron transfer occurs to the L ligand from the platinum atom. The quantity of transferred electrons increases with an increase in the L ligand distortion. (3) The contribution of the s orbital of the X_1 and X_2 atoms decreases in the X_1–X_2 bond and increases in the Pt–X_1 and Pt–X_2 bonds; e.g., for the C≡C bond of the acetylene complex, $E_{s-s} = -6.72$ eV at θ = 0° and −6.46 eV at θ = 15°, and for the Pt—C bond, $E_{sp_\sigma-s} = -2.78$ eV at θ = 0° and −3.02 eV at θ = 15°. As has been described in (1), (2), and (3), the Pt–X_1 and Pt–X_2 bonds become strong, and the X_1–X_2 bond weakens with the ligand distortion.[24]

Next, we consider the X_1–R_i and X_2–R_j bonds; $E_{X_1-R_i}$ values etc. are shown in Figures 1b and 2b. Table II gives the change in the C–H bonding nature induced by the cis bending in the acetylene complex. The C_{p_y}–H_s interaction in the complexed acetylene contributes to the C–H bond more greatly than that in the uncomplexed molecule, which shows that formation of the coordination bond with the platinum atom makes the carbon p_π (p_y) orbital more favorable to an interaction with the hydrogen atom than in the uncomplexed one. Figure 3A gives some MO schemes concerning with the C–H bond and the carbon p_π orbital. When two hydrogen atoms are pushed



(A) The C_2H_2 Complex (θ = 0°)　(B) The CO_2 Complex

Figure 3. MO coefficients concerning with the strengthening of the X_1–R_i and X_2–R_j bonds. Superscript a signifies the partial bond order between the carbon p_π and the hydrogen 1s orbitals.

away from the platinum atom, the C–H bonding interactions in the $6a_1$ and $6b_2$ MO's, as well as the C–H antibonding interaction in the $7a_1$ MO, strengthen. Since the bonding interaction is stronger than the antibonding one (see the partial bond order for this interaction given in Figure 3A), the C–H bond becomes strong relative to that at $\theta = 0°$. As the cis bending increases, the contribution of the $7a_1$ MO eventually becomes large, which would make the C–H bond weak. This situation is also seen in the ethylene complex.

In the cases of the carbon disulfide and carbon dioxide complexes, the interaction shown in Figure 3B is formed by the ligand distortion, which makes the $C–S_{(2)}$ and $C–O_{(2)}$ bonds strong. It is apparent that the d_π–p_{π_g} π-acceptor bond plays an important role.

In conclusion, besides the σ-donor and π-acceptor coordination bonds, the s orbital of the L ligand atom contributes substantially to the Pt–L interaction, which suggests a large three-membered ring type of interaction between the platinum and the L ligand. It appears that the L ligand distortion is induced by the stabilization of the $Pt–X_1$, $Pt–X_2$, $X_1–R_i$, and $X_2–R_j$ bonds; i.e., the driving forces of the L ligand distortion stem from the intraligand and the Pt–L interactions. On the other hand, the bond involved in the L ligand coordination is weakened by the distortion, by which the L ligand distortion is reduced.

Acknowledgment. MO calculations were carried out with the Facom 230-75 Computer of the Data Processing Center at Kyushu University.

Registry No. $Pt(PH_3)_2(C_2H_2)$, 36463-11-3; $Pt(PH_3)_2(CS_2)$, 60840-43-9; $Pt(PH_3)_2(C_2H_4)$, 31941-73-8; $Pt(PH_3)_2(CO_2)$, 60840-44-0.

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(22) The Pt–P bond distance is taken equal to that of the carbon disulfide analogue. The Pt–C and C–O distances are equal to the corresponding ones of the acetylene analogue and the free molecule, respectively. The Pt–O distance is assumed to be equal to the Pt–C distance.
(23) The Pt–P bond becomes strong with an increase in the cis bending in this calculation. Since the d orbital of the phosphorus atom is not included in this calculation, the π-acceptor bond of the phosphine ligand is neglected. If the π-acceptor bond is included, this interaction becomes weak with the L ligand distortion, since the electron transfer from the platinum atom to the L ligand part increases with an increase in the distortion as described in the following paragraph of the text. When the σ-donor bond mainly contributes to the Pt–P bond, the Pt–P bond becomes strong with the ligand distortion. When the π-acceptor one mainly contributes, the Pt–P one becomes weak. In general, the π-acceptor interaction is considered to be large in the Pt–P bond. On the other hand, Norman proposed that it is small: J. K. Norman, Jr., *J. Am. Chem. Soc.*, **96**, 3327 (1974). The question of which of the σ-donor or π-acceptor bond mainly contributes should be investigated in more detail. Even if the Pt–P bond is included in the present consideration, the discussion is unchanged except that the stabilization of the Pt–P bond acts as the driving force and that the value of $E_{Pt-X_1} + E_{Pt-X_2} + E_{X_1-X_2} + \sum_i E_{X_1-R_i} + \sum_j E_{X_2-R_j} + 2E_{Pt-P}$ has a potential minimum at larger θ value than that of $E_{Pt-X_1} + E_{Pt-X_2} + E_{X_1-X_2} + \sum_i E_{X_1-R_i} + \sum_j E_{X_2-R_j}$.
(24) The X_1–X_2 bond weakening is mainly due to the weakening of the X_1–X_2 π-bonding and s–s interactions.

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An Infrared and Electronic Spectral Study of the Reactions of $[RhCl(PPh_3)_2]_2$ and $[RhCl(PPh_3)_3]$ with Molecular Oxygen

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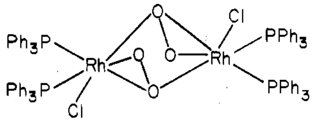
The oxygen sensitivity of $[RhCl(PPh_3)_3]$ and the dimer $[RhCl(PPh_3)_2]_2$ which derives from it, eq 1, has long been

$$2[RhCl(PPh_3)_3] \rightleftarrows [RhCl(PPh_3)_2]_2 + 2PPh_3 \tag{1}$$

noted.[1] Solutions of either complex rapidly absorb oxygen and turn red-brown, and solid $[RhCl(PPh_3)_2]_2$ decomposes within hours following exposure to air. Traces of oxygen have been reported[2-4] to greatly enhance the catalytic ability of $[RhCl(PPh_3)_3]$ in a variety of reactions, and the complex has been shown[5,6] to serve as an oxidation catalyst. The mechanism of oxidation of the complexes and the nature of their final oxidation products have never been fully elucidated, and a variety of conflicting reports have appeared.

In one of the first descriptions of $[RhCl(PPh_3)_3]$, a compound formulated as $[RhCl(O_2)(PPh_3)_2]\cdot0.5CH_2Cl_2$ was isolated when solutions were exposed to oxygen.[1] A complex of similar composition, $[RhCl(O_2)(PPh_3)_2]_2\cdot2CH_2Cl_2$, was obtained by Bennett and Donaldson[7] from concentrated, oxygen-saturated solutions of $[RhCl(PPh_3)_3]$ and was fully characterized by a complete crystal structure analysis which showed the unusual dimeric, dioxygen bridged structure, I. In



I

contrast, other workers[8,9] have instead isolated products arising from oxidation of PPh_3. Augustine and Van Peppen