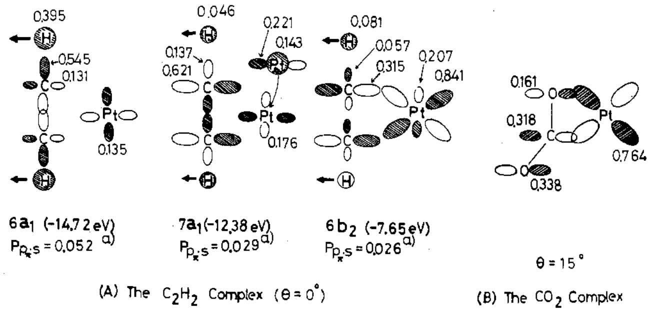

Figure 3. MO coefficients concerning with the strengthening of the X_1–R_i and X_2–R_j bonds. Superscript a signifies the partial bond order between the carbon p_π and the hydrogen 1s orbitals.

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 $E_{Pt\text{-}X_1} + E_{Pt\text{-}X_2} + E_{X_1\text{-}X_2} + \sum_i E_{X_1\text{-}R_i} + \sum_j E_{X_2\text{-}R_j} + 2E_{Pt\text{-}P}$ has a potential minimum at larger θ value than that of $E_{Pt\text{-}X_1} + E_{Pt\text{-}X_2} + E_{X_1\text{-}X_2} + \sum_i E_{X_1\text{-}R_i} + \sum_j E_{X_2\text{-}R_j}$.
(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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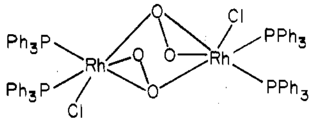
The oxygen sensitivity of $[RhCl(PPh_3)_3]$ and the dimer $[RhCl(PPh_3)_2]_2$ which derives from it, eq 1, has long been

$$2[RhCl(PPh_3)_3] \rightleftarrows [RhCl(PPh_3)_2]_2 + 2PPh_3 \qquad (1)$$

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 demonstrated[8] that the amount and rate of oxygen uptake by $[RhCl(PPh_3)_3]$ is solvent dependent, and Ph_3PO and a complex formulated as $\{[RhCl(O_2)(PPh_3)_2]_2O\}$ were isolated from oxygenated benzene and methanol solutions. Dudley et al.[9] found that benzene solutions of $[RhCl(PPh_3)_3]$ absorbed 1.50–1.75 mol of O_2 per mol of complex and that the rate of absorption was dependent on the stirring rate. These solutions deposited a red-brown precipitate which exhibited IR bands at 1094, 1120, 1190, and 850 cm^{-1} assignable to PPh_3, Ph_3PO, and coordinated O_2. The precipitate was formulated as $[RhCl(PPh_3)(Ph_3PO)O_3]\cdot C_6H_6$, and a detailed, but complicated, oxidation scheme was proposed to account for the stirring rate dependence.

Our interest in the reactions of these complexes with molecular oxygen arose from a study[10] into the mechanism of the photoinduced oxidation of coordinated ligands in *trans*-$[RhCl(CO)(PPh_3)_2]$. The original aim of the research reported herein was to clarify the nature of the final oxidation products and spectroscopically observe intermediates involved in the reactions. We have chosen to concentrate our efforts on $[RhCl(PPh_3)_2]_2$, principally because it has one less PPh_3 that can be oxidized to Ph_3PO. Success has not been achieved in characterizing the oxidation products, but we now report our spectroscopic results and propose a simple oxidation scheme for $[RhCl(PPh_3)_2]_2$.

Experimental Section

The complexes $[RhCl(PPh_3)_3]$,[11] $[RhCl(PPh_3)_2]_2$,[11] and $[RhCl(O_2)(PPh_3)_2]\cdot 2CH_2Cl_2$[7] were prepared by published procedures. Electronic absorption spectra were measured on a Cary 17 spectrophotometer using an evacuatable quartz 1-cm spectrophotometer cell. Infrared spectra were recorded on a Perkin-Elmer 621 infrared spectrophotometer using standard 0.5-mm path length NaCl solution IR cells. The electronic absorption spectral changes were recorded by first measuring the spectrum of a solution prepared by distillation of degassed solvent into the UV cell containing the complex to be examined. The cell was then opened to the atmosphere and rapidly shaken for 5–10 s, and the spectrum recorded immediately and at appropriate time intervals thereafter. The infrared spectral changes were recorded in a similar manner by filling the infrared cells in an N_2 filled glove bag with a deoxygenated solution of the complex, recording the spectrum, opening the solution to air, and recording spectra at appropriate time intervals thereafter.

A product was isolated from oxygenated toluene and CH_2Cl_2 solutions of $[RhCl(PPh_3)_2]_2$ by stirring the solutions under an oxygen purge for 3–5 days followed by precipitation with Et_2O or by evaporation of solvent on a rotary evaporator. The resultant red-brown solid was washed with Et_2O to remove any free PPh_3 and with ethanol to remove uncoordinated Ph_3PO. The elemental analysis (Galbraith Laboratories) of this product did not agree with any reasonable stoichiometry. The following results were obtained. From CH_2Cl_2 solution: Rh, 15.75; Cl, 10.99; P, 6.22; C, 47.82; H, 3.98. From benzene solution: Rh, 27.11; Cl, 10.20; P, 5.72; C, 42.02; H, 3.94. From oxidation of solid $[RhCl(PPh_3)_2]_2$: Rh, 16.74; Cl, 8.17; P, 6.41; C, 44.32; H, 3.80.

Results and Discussion

$[RhCl(PPh_3)_2]_2$ is very air sensitive, both in the solid state and in solution. The solid changes color from pink to brown after 1–2 h in air, and solutions immediately turn red-brown upon exposure and give the electronic absorption spectral changes shown in Figure 1. $[RhCl(PPh_3)_2]_2$ in degassed CH_2Cl_2 solution shows an absorption band at 457 nm (ϵ = 960). Admission of air followed by a 5–10-s shaking of the spectrophotometer cell results in complete replacement of this absorption feature by a new band at 366 nm ($\epsilon \approx 8000$) which then very slowly decreases in intensity upon standing. Absorption features characteristic of Ph_3PO simultaneously appear and grow in around 270 nm. In the 800–1300-cm^{-1} infrared spectral region, $[RhCl(PPh_3)_2]_2$ in degased CH_2Cl_2 shows a triphenylphosphine band at 1090 cm^{-1}, and exposure to air results in the spectral changes shown in Figure 2. A band assignable to coordinated O_2 appears at 851 cm^{-1}, the 1090 cm^{-1} band slowly decreases in intensity, and new bands characteristic of Ph_3PO grow in at 1117 and 1185 cm^{-1}. Similar spectral changes obtain in benzene solution. These electronic and infrared changes clearly suggest that the oxidation proceeds by a very rapid initial reaction with oxygen followed by a much slower reaction which produces Ph_3PO. The observation that Ph_3PO is produced only in the slower second step suggests that the initial rapid reaction involves formation of a dioxygen adduct.

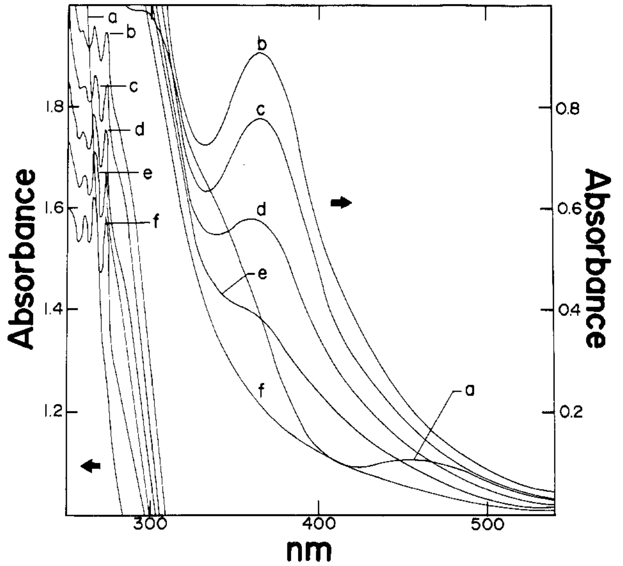


Figure 1. Electronic absorption spectral changes following exposure of a degassed CH_2Cl_2 solution of $[RhCl(PPh_3)_2]_2$ to air. Spectrum (a) was recorded prior to exposure and spectra (b–f) at the following time intervals after exposure: (b) immediately; (c) 1.5 h; (d) 4.5 h; (e) 10 h; (f) 24 h.

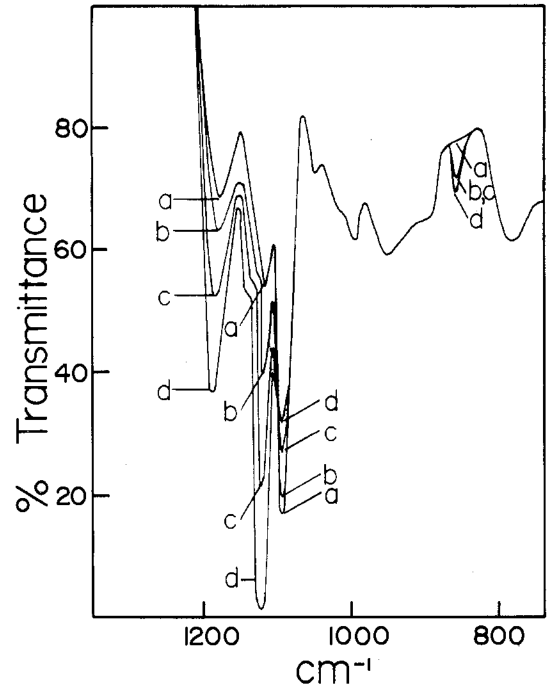
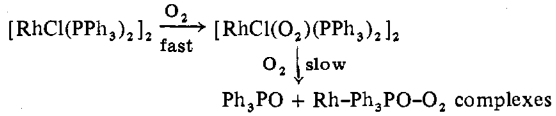


Figure 2. Infrared spectral changes following exposure of a deoxygenated CH_2Cl_2 solution of $[RhCl(PPh_3)_2]_2$ to air. Spectrum (a) was recorded prior to exposure and spectra (b–d) at the following time intervals after exposure: (b) immediately; (c) 15 min; (d) 29 h.

To test this hypothesis we prepared $[RhCl(O_2)(PPh_3)_2]_2\cdot 2CH_2Cl_2$ according to directions given by Bennett

Scheme I



$$\begin{tikzcd}[\mathrm{RhCl(PPh_3)_2}]_2 \arrow[r, "O_2", "\text{fast}"'] & [\mathrm{RhCl(O_2)(PPh_3)_2}]_2 \arrow[d, "O_2"', "\text{slow}"] \\ & \mathrm{Ph_3PO} + \mathrm{Rh\text{-}Ph_3PO\text{-}O_2}\ \text{complexes}\end{tikzcd}$$

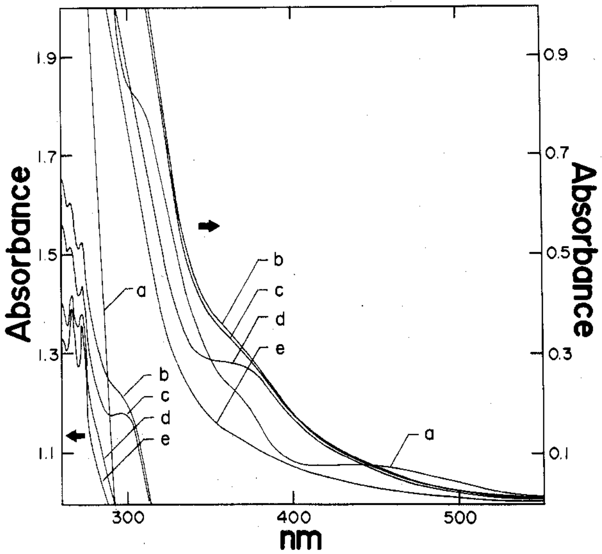


Figure 3. Electronic absorption spectral changes following exposure of a degassed CH_2Cl_2 solution of $[RhCl(PPh_3)_3]$ to air. Spectrum (a) was recorded prior to exposure and spectra (b–e) at the following time intervals after exposure: (b) immediately; (c) 15 min; (d) 4.3 h; (e) 25 h.

and Donaldson.[7] In CH_2Cl_2 solution their complex shows an absorption band at 366 nm, identical in position and shape to the spectrum resulting from the initial rapid reaction of $[RhCl(PPh_3)_2]_2$ with O_2. Further, storage of solutions of this dioxygen adduct gave infrared and electronic absorption spectral changes identical with and on the same time scale as those obtained under similar conditions during the oxidation of $[RhCl(PPh_3)_2]_2$.

A red-brown powder can be isolated from solutions of $[RhCl(PPh_3)_2]_2$ which have been exposed to oxygen for several days by precipitation with Et_2O or by solvent evaporation. This powder can be reprecipitated from CH_2Cl_2/Et_2O solutions, but a crystalline sample has not been obtained. The UV spectrum of this product in CH_2Cl_2 solution is identical with the final spectrum obtained from exposure of $[RhCl(PPh_3)_2]_2$ solutions to oxygen, and the IR spectrum shows bands at 1185 and 1118 cm^{-1}, assignable to Ph_3PO, and a band at 850 cm^{-1} attributable to coordinated O_2. Satisfactory elemental analysis corresponding to any reasonable stoichiometry has not been obtained even though several carefully washed and reprecipitated samples were analyzed.

The spectral changes detailed above for $[RhCl(PPh_3)_2]_2$ and $[RhCl(O_2)(PPh_3)_2]_2$ indicate that oxidation of $[RhCl(PPh_3)_2]_2$ proceeds by very rapid formation of Bennett and Donaldson's dioxygen adduct, or an adduct which derives from their complex in solution, which then slowly decomposes to form Ph_3PO and $Rh–Ph_3PO–O_2$ complexes, Scheme I. Since $[RhCl(PPh_3)_2]_2$ has been shown[12,13] to not dissociate to three-coordinate $[RhCl(PPh_3)_2]$ to any significant extent in solution, the initial fast reaction must occur between O_2 and the dimer. The slow decomposition to Ph_3PO most likely proceeds through an intramolecular process similar to that proposed[14] for the $[Pt(PPh_3)_4]$ catalyzed oxidation of PPh_3.

The spectral changes which obtain during oxidation of $[RhCl(PPh_3)_3]$ are similar to those observed for $[RhCl(PPh_3)_2]_2$. A degassed 7×10^{-5} M CH_2Cl_2 solution of $[RhCl(PPh_3)_3]$ shows an absorption band at 445 nm which upon exposure to O_2 is rapidly replaced by an absorption shoulder at 365 nm, Figure 3. This shoulder over a period of hours decreases in intensity and Ph_3PO features simultaneously appear near 270 nm. The infrared spectral changes are virtually identical with those observed for $[RhCl(PPh_3)_2]_2$. Although the spectral changes obtained for the two complexes are similar, the relatively lower intensity of the 365-nm shoulder in the spectrum resulting from the reaction of $[RhCl(PPh_3)_3]$ with O_2 suggests that the oxidation pathways may not be entirely the same. Further, the very rapid initial reaction of $[RhCl(PPh_3)_3]$ with O_2 and our observation that a fivefold excess of PPh_3 does not inhibit the oxidation indicate that the reaction does not proceed entirely through $[RhCl(PPh_3)_2]_2$, and direct reaction of O_2 with $[RhCl(PPh_3)_3]$ is suggested.

Finally, we have observed that the oxidation products of $[RhCl(PPh_3)_3]$ and $[RhCl(PPh_3)_2]_2$ can be readily converted back to $[RhCl(PPh_3)_3]$ simply by refluxing ethanol solutions of the products with excess PPh_3 under a nitrogen atmosphere.

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Registry No. $[RhCl(PPh_3)_2]_2$, 14653-50-0; $[RhCl(PPh_3)_3]$, 14694-95-2; O_2, 7782-44-7.

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Crystal Structure of $Cs_2LiFe(CN)_6$ by Neutron Diffraction

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The structure of a series of isomorphous compounds of the general formula $Cs_2LiM(CN)_6$, where M = Mn, Fe, and Co, has been determined.[2] These studies suggested a relation between the M–C bond distance and the amount of π back-bonding. It was found that the σ and π contributions affected the M–C bond by approximately the same amount. The high symmetry of the crystals of these salts has also permitted a detailed vibrational analysis.[3,4] Since these salts do not suffer any of the disorder problems associated with other Prussian Blue analogues[5,6] and since the high symmetry