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Far-Infrared Spectra of Complexes of Rhodium and Iridium with π -Bonding Ligands

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The infrared spectra of the following square-planar rhodium(I) and iridium(I) halogeno complexes have been measured in the range 460–200 cm^{-1} : $[\text{RhXL}_2]_2$ ($L = \text{CO}, \text{C}_2\text{H}_4$, or cyclooctene or $L_2 = \text{norbornadiene}$ or 1,5-cyclooctadiene; $X = \text{Cl}$ or Br); $\text{RhX}(\text{CO})(\text{MR}_3)_2$ ($M = \text{P}$ or As ; $R = \text{alkyl}$ or aryl ; $X = \text{Cl}$ or Br); $\text{RhCl}(\text{C}_7\text{H}_5)(p\text{-toluidine})$ and $\text{RhCl}(\text{C}_7\text{H}_5)\{\text{M}(\text{C}_6\text{H}_5)_3\}$ ($\text{C}_7\text{H}_5 = \text{norbornadiene}$; $M = \text{P}, \text{As},$ or Sb); $\text{RhX}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ ($X = \text{Cl}$ or Br) and $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]_2$; $[\text{Ir}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ ($\text{C}_8\text{H}_{12} = 1,5\text{-cyclooctadiene}$); $\text{IrX}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ($X = \text{Cl}$ or Br). Strong bands due to metal–chlorine stretching vibrations appear in the range 310–250 cm^{-1} and the frequencies of bridging metal–chlorine stretching vibrations are about 20–40 cm^{-1} lower than those of terminal metal–chlorine stretching vibrations. Similar measurements have been made on the following octahedral rhodium(III) and iridium(III) complexes: $\text{RhX}_3\{\text{M}(\text{C}_2\text{H}_5)_3\}_3$ and $[\text{RhX}_3\{\text{M}(\text{C}_2\text{H}_5)_3\}_2]_2$ ($X = \text{Cl}$ or Br ; $M = \text{P}$ or As); $\text{RhClX}_2(\text{CO})(\text{MR}_3)_2$ ($X = \text{Cl}, \text{Br},$ or I ; $M = \text{P}$ or As ; $R = \text{C}_2\text{H}_5$ or C_6H_5); $\text{IrClXY}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ($XY = \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{H}_2, \text{HCl},$ or CH_3I) and $\text{IrBrX}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ($X = \text{Cl}$ or Br). Bands due to metal–chlorine stretching vibrations appear in the range 350–250 cm^{-1} , the frequencies depending mainly on the ligand *trans* to the chlorine atom in the complex. Ligands can be ordered according to their effect on $\nu(\text{M}-\text{Cl}_{\text{trans}})$ as follows: $\text{Cl} > \text{Br} > \text{I} \sim \text{CO} > \text{CH}_3 \sim \text{PR}_3 \sim \text{AsR}_3 > \text{H}$ (decreasing metal–chlorine stretching frequency along this series). From the pattern and frequencies of the $\text{M}-\text{Cl}$ absorption bands, it is concluded that the octahedral adducts of $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ with halogens, hydrogen, hydrogen chloride, and methyl iodide contain the addend atoms in *cis* positions.

Introduction

Metal–halogen stretching frequencies in complexes depend, *inter alia*, on the oxidation state and the coordination number of the metal, and they may be useful in making stereochemical assignments.¹ In continuation of our study² of the far-infrared spectra of octahedral metal carbonyl halides, we have examined a series of halogeno complexes of square-planar rhodium(I) and iridium(I) and of octahedral rhodium(III) and iridium(III) containing π -bonding ligands such as olefins, carbon monoxide, and tertiary phosphines and arsines. We hoped to locate the frequencies due to metal–chlorine stretching vibrations and to see if they could be used to distinguish between *cis* and *trans* isomers in both series of compounds. We also wished to compare the values of terminal and bridging MCl stretching frequencies.

Experimental Section

Infrared spectra were measured as Nujol mulls on a Grubb–Parsons double-beam grating spectrophotometer, Type DM2 (200–455 cm^{-1}), as described previously.¹ Spectra in the $\text{C}\equiv\text{O}$ stretching region were recorded as Nujol mulls and in benzene solution on a Perkin–Elmer 337 double-beam instrument (400–4000 cm^{-1}) and were calibrated against polystyrene film.

X-Ray powder photographs were taken on a Nonius–Guinier camera, using nickel-filtered $\text{CuK}\alpha$ radiation, by Mrs. V. Poon to whom we are indebted.

Microanalyses were carried out by Dr. A. Bernhardt, Max-Planck Institute für Kohlenforschung, Mülheim, Germany.

Preparation of Complexes. $[\text{RhCl}(\text{CO})_2]_2$.—This was prepared by the reaction of carbon monoxide at atmospheric pressure with rhodium(III) chloride.^{3,4}

The complexes of the formula $\text{RhCl}(\text{CO})\text{L}_2$ ($L = \text{P}(\text{C}_2\text{H}_5)_3, \text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5, \text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2, \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3, \text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3, \text{As}(\text{C}_2\text{H}_5)_3, \text{and } \text{As}(\text{C}_6\text{H}_5)_3$) were prepared by direct reaction of the appropriate ligand with $[\text{RhCl}(\text{CO})_2]_2$ ^{5,6} in some cases, the complex $[\text{RhCl}(\text{CO})_2]_2$ was prepared *in situ* by displacing cyclooctene from its rhodium(I) complex with carbon monoxide. The properties of the triethylphosphine, diethylphenylphosphine, ethyldiphenylphosphine, and triethylarsine complexes were identical with those reported recently by Chatt and Shaw,⁷ who used a slightly different method of preparation. The preparation of the tri-*p*-tolylphosphine and tri-*p*-anisylphosphine complexes will be reported in detail separately.⁸

Other Complexes.—The following complexes were prepared by literature methods: $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ⁹ $[\text{RhCl}(\text{C}_6\text{H}_4)_2]_2$ ¹⁰ $[\text{RhX}(\text{C}_8\text{H}_{12})]_2$ ($X = \text{Cl}$ or Br)¹¹ $[\text{RhCl}(\text{C}_7\text{H}_5)]_2$ ¹² $\text{RhCl}(\text{C}_7\text{H}_5)\text{L}$ ¹³ [$L = p\text{-toluidine}, \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{or } \text{Sb}(\text{C}_6\text{H}_5)_3$; $\text{C}_6\text{H}_{14} = \text{cyclooctene}$; $\text{C}_8\text{H}_{12} = 1,5\text{-cyclooctadiene}$; $\text{C}_7\text{H}_5 = \text{norbornadiene}$]; $\text{RhX}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ [$X = \text{Cl}$ or Br]¹⁴ $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]_2$ ¹⁴ $[\text{IrCl}(\text{C}_8\text{H}_{12})]_2$ ¹⁵ $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ¹⁶ $\text{IrBr}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ¹⁷ *cis*- and *trans*- $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$ ¹⁸ $[\text{RhCl}_3\text{L}_2]_2$ [$L = \text{P}(\text{C}_2\text{H}_5)_3, \text{P}(n\text{-C}_4\text{H}_9)_3, \text{or } \text{As}(\text{C}_2\text{H}_5)_3$]¹⁸ $\text{RhCl}_3(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$ ¹⁹ $\text{RhCl}_3(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ²⁰ $\text{RhCl}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ²⁰ $\text{IrCl}_3(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ²¹ $\text{IrHCl}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ²¹ $\text{IrH}_2\text{Cl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ²¹ $\text{IrClIICH}_3(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ¹⁹

$[\text{RhBr}(\text{C}_2\text{H}_4)_2]_2$.—This was obtained as an insoluble, brown powder from the reaction of ethanolic rhodium(III) chloride and

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a large excess of lithium bromide with ethylene. The infrared spectrum, which was measured immediately after the preparation, showed the presence of coordinated ethylene and the absence of metal-chlorine bonds. Owing to the instability of the complex, satisfactory analytical data could not be obtained.

RhBr(CO){P(C₂H₅)₃}₂.—The chloro complex RhCl(CO){P(C₂H₅)₃}₂ (0.3 g), lithium bromide (0.3 g), and acetone (10 ml) were heated under reflux in a nitrogen atmosphere for 3 hr. After evaporating the orange solution to dryness at 15 mm, the residue was extracted with pentane (10 ml) and cooled to -78°. The orange crystals were filtered and recrystallized from pentane; yield, 0.18 g (53%). *Anal.* Calcd for C₃₁H₃₀BrOP₂Rh: C, 34.95; H, 6.8; Br, 17.9. Found: C, 36.0; H, 6.85; Br, 17.5.

RhBr(CO){P(C₂H₅)₃}₂.—Rhodium tribromide trihydrate (0.6 g) and triphenylphosphine (8 g) were heated under reflux in 2-ethoxyethanol (50 ml) for 4 hr. The solution initially turned deep red and finally became orange. It was decanted and set aside overnight. The beautiful yellow crystals which separated were filtered, washed with ether, and dried at 25° (1 mm); yield, 0.58 g (52%). *Anal.* Calcd for C₃₇H₃₀BrOP₂Rh: C, 60.4; H, 4.1; Br, 10.9. Found: C, 60.7; H, 4.1; Br, 10.0.

cis- and trans-RhBr₃{P(C₂H₅)₃}₃. **Method A.**—*trans*-RhCl₃{P(C₂H₅)₃}₃ (0.5 g), lithium bromide (2 g), and acetone (30 ml) were refluxed under nitrogen for 5 min. The solution was evaporated to dryness at 15 mm, and the residue was recrystallized from benzene-petroleum ether (bp 80–100°), giving red needles of the *trans*-bromo complex (0.37 g, 60%). *Anal.* Calcd for C₁₈H₁₅Br₃P₃Rh: C, 31.0; H, 6.5; Br, 34.4. Found: C, 31.7; H, 6.6; Br, 34.4.

Method B.—Rhodium tribromide trihydrate (0.3 g) dissolved in deoxygenated methanol (10 ml) was cooled to -78° and treated with triethylphosphine (0.26 g) under nitrogen. The solution was stirred at -78° for 1 hr and then allowed to warm slowly to room temperature. The red-brown solution lightened in color, and a small amount of beige precipitate which formed (possibly [RhBr₃{P(C₂H₅)₃}₂]) was filtered off from the still cold solution. As the filtrate reached room temperature, a pale yellow precipitate of the *cis*-bromo complex formed. This was filtered off, washed with ethanol and ether, and dried *in vacuo* (0.1 g, 19%). It isomerized rapidly to the *trans* complex on attempted recrystallization. *Anal.* Found: C, 31.3; H, 6.65.

Evaporation of the filtrate at 15 mm, followed by recrystallization of the residue from benzene-petroleum ether (bp 80–100°) gave orange-red plates of the *trans* complex. *Anal.* Found: C, 31.4; H, 6.6; Br, 33.0.

The crystalline forms of the *trans*-bromo complex prepared by methods A and B differ, as shown by their X-ray powder patterns, but their infrared spectra (4000–200 cm⁻¹) are identical. The compound prepared by method A is isomorphous with *trans*-RhCl₃{P(C₂H₅)₃}₃ and with *trans*-RhBr₃{As(C₂H₅)₃}₃ (see below). The *cis*-bromo complex RhBr₃{P(C₂H₅)₃}₃ has a similar X-ray powder pattern to that of the *cis*-chloro complex.

cis- and trans-RhCl₃{As(C₂H₅)₃}₃.—The procedure of Chatt, Johnson, and Shaw¹⁸ was followed, but the work-up described by these authors could not be reproduced.

Rhodium trichloride trihydrate (1.6 g) was dissolved in deoxygenated ethanol (50 ml), and triethylarsine (3.5 g) was added under nitrogen. The mixture was heated to boiling for 10 min and allowed to cool. A small amount of red-brown solid was filtered off; no yellow prisms were obtained at this stage (*cf.* ref 18). The solution was evaporated to dryness at 15 mm, and the solid was extracted with five 10-ml portions of ether. The ether extract was evaporated to dryness at 15 mm and the residue recrystallized from methanol gave orange-red prisms of *trans*-RhCl₃{As(C₂H₅)₃}₃ (3.0 g, 88%). *Anal.* Calcd for C₁₈H₁₅Cl₃As₃Rh: C, 31.1; H, 6.5; Cl, 15.3. Found: C, 31.0; H, 6.5; Cl, 15.7.

The residue from the ether extraction gave a mixture of yellow needles and dark red-brown prisms when recrystallized from dichloromethane-ethanol. This was separated by dissolving in dichloromethane and adding ethanol until red-brown crystals began to form. After 1 hr, these were filtered off and recrystal-

lized from dichloromethane-ethanol to give dark red-brown prisms of [RhCl₃{As(C₂H₅)₃}₂]₂ (0.21 g, 6.5%) identical with those obtained from RhCl₃ and 2 equiv of triethylarsine.¹⁸ *Anal.* Calcd for C₁₂H₁₀Cl₃As₂Rh: C, 27.0; H, 5.7; Cl, 20.0. Found: C, 27.3; H, 6.0; Cl, 19.5.

After standing overnight, the filtrate deposited an orange powder. This and the residue after removal of solvent from the filtrate were recrystallized from dichloromethane-ethanol to give yellow needles of *cis*-RhCl₃{As(C₂H₅)₃}₃ (0.1 g, 3%). *Anal.* Found: C, 29.0; H, 6.4; Cl, 15.1.

trans-RhBr₃{As(C₂H₅)₃}₃.—This was prepared similarly to *trans*-RhBr₃{P(C₂H₅)₃}₃ (method A) from excess lithium bromide and *trans*-RhCl₃{As(C₂H₅)₃}₃ as dark red needles. *Anal.* Calcd for C₁₈H₁₅As₃Br₃Rh: C, 26.1; H, 5.5; Br, 28.9. Found: C, 27.2; H, 5.7; Br, 28.4.

RhClBr₂(CO){P(C₂H₅)₃}₂.—This was prepared using the method of Heck.¹⁹ RhCl(CO){P(C₂H₅)₃}₂ (0.2 g) in dichloromethane (0.8 ml) was treated with bromine (0.8 g) in dichloromethane (0.8 ml) under nitrogen. After 1 hr solvent was removed at 15 mm and the residue was extracted with 1:1 ether-pentane (three 10-ml portions). The solution was filtered, concentrated to ca. 10 ml, and cooled to -78°. The orange powder was filtered off and recrystallized twice from methanol giving orange prisms (0.17 g, 61% yield) [$\nu(\text{C}\equiv\text{O})$ 2067 cm⁻¹ (Nujol) and 2064 cm⁻¹ (benzene)]. *Anal.* Calcd for C₁₃H₁₀P₂ClBr₂ORh: C, 27.8; H, 5.4; Br, 28.2. Found: C, 28.0; H, 5.6; Br, 28.2.

RhClI₂(CO){P(C₂H₅)₃}₂.—This was prepared similarly to the dibromo complex, using iodine in place of bromine. Red crystals were formed in methanol [$\nu(\text{C}\equiv\text{O})$ 2060 cm⁻¹ (Nujol)]. *Anal.* Calcd for C₁₃H₁₀P₂Cl₂ORh: C, 23.6; H, 5.0. Found: C, 21.9; H, 4.6.

RhCl₂(CO)₂{As(C₂H₅)₃}₂.—This was prepared similarly to the corresponding triethylphosphine complex.¹⁹ Starting from RhCl(CO){As(C₂H₅)₃}₂ and carbon tetrachloride, yellow crystals were formed (60%) [$\nu(\text{C}\equiv\text{O})$ 2071 cm⁻¹ (Nujol) and 2062 cm⁻¹ (benzene)]. *Anal.* Calcd for C₁₈H₁₅As₂Cl₂ORh: C, 27.9; H, 5.4; Cl, 19.0. Found: C, 28.1; H, 5.0; Cl, 19.5.

RhClBr₂(CO){As(C₂H₅)₃}₂.—This was prepared similarly to the corresponding triethylphosphine complex. Starting from RhCl(CO){As(C₂H₅)₃}₂ and bromine, orange crystals were formed [$\nu(\text{C}\equiv\text{O})$ 2071 cm⁻¹ (Nujol) and 2056 cm⁻¹ (benzene)]. *Anal.* Calcd for C₁₈H₁₅As₂ClBr₂ORh: C, 24.0; H, 4.7; Cl, 5.5; Br, 24.6. Found: C, 24.3; H, 4.6; Cl, 4.3; Br, 24.7.

RhClI₂(CO){As(C₂H₅)₃}₂.—This was prepared similarly to the corresponding triethylphosphine complex as red crystals [$\nu(\text{C}\equiv\text{O})$ 2050 cm⁻¹ (Nujol) and 2052 cm⁻¹ (benzene)]. *Anal.* Calcd for C₁₈H₁₅As₂Cl₂ORh: C, 21.0; H, 4.1; Cl, 4.8; I, 34.1. Found: C, 21.4; H, 4.3; Cl, 5.7; I, 34.8.

IrClBr₂(CO){P(C₂H₅)₃}₂.—IrCl(CO){P(C₂H₅)₃}₂ (0.4 g) in chloroform (20 ml) was treated with bromine (0.1 g) in chloroform (10 ml) in a nitrogen atmosphere. After 30 min, solvent was evaporated at 15 mm until the volume was ca. 10 ml. The pale yellow precipitate was filtered, washed with ether, and recrystallized from chloroform, giving 0.31 g (64%) of pale yellow crystals [$\nu(\text{C}\equiv\text{O})$ 2088 cm⁻¹ (Nujol)]. *Anal.* Calcd for C₂₇H₃₀P₂ClBr₂OIr: C, 47.2; H, 3.2; Br, 17.0. Found: C, 45.3; H, 3.2; Br, 16.5.

IrClI₂(CO){P(C₂H₅)₃}₂.—This was prepared similarly to the dibromo complex, using iodine in place of bromine. Pale orange crystals (55%) were formed in chloroform [$\nu(\text{C}\equiv\text{O})$ 2079 cm⁻¹ (Nujol)]. *Anal.* Calcd for C₂₇H₃₀P₂ClI₂OIr: C, 42.9; H, 3.1; I, 24.5. Found: C, 43.2; H, 3.1; I, 22.2.

IrBrCl₂(CO){P(C₂H₅)₃}₂.—IrBr(CO){P(C₂H₅)₃}₂ (0.15 g) in chloroform (5 ml) was treated with chlorine (0.01 g) in carbon tetrachloride (10 ml) at 0° in a nitrogen atmosphere. After 15 min, ca. half the solvent was evaporated at 15 mm, and the pale yellow product was precipitated by addition of 15 ml of petroleum ether (bp 80–100°). It was filtered, washed with ether, and dried *in vacuo*, giving 0.13 g (80%) of the required complex [$\nu(\text{C}\equiv\text{O})$ 2085 cm⁻¹ (Nujol)]. No attempt was made at recrystallization of this complex, to avoid any possibility of

TABLE I

ABSORPTION FREQUENCIES (cm^{-1}) OF SQUARE-PLANAR COMPLEXES OF RHODIUM(I) AND IRIIDIUM(I) IN THE RANGE 460–200 cm^{-1} ^a

Compound	$\nu(\text{M-X})$	Other bands
$[\text{RhCl}(\text{CO})_2]_2$	284 vs, 274 vs	435 m, 300 sh
$[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$	273 s, 259 m, br, 250 m	399 s
$[\text{RhBr}(\text{C}_2\text{H}_4)_2]_2$	<200	393 s
$[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$	289 m, 285 m, 252 s	412 s, 334 vw
$[\text{RhCl}(\text{C}_8\text{H}_{12})_2]_2$	274 s, 254 s	382 m, 247 sh
$[\text{RhBr}(\text{C}_8\text{H}_{12})_2]_2$	<200	379 m, 250 w, 244 w
$[\text{RhCl}(\text{C}_7\text{H}_8)_2]_2$	249 vs	371 m, 356 w, 296 mw
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$	302 vs	404 s, 374 ms, 328 w
<i>trans</i> - $\text{RhBr}(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$	<200	401 s, 374 ms, 328 m
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\text{C}_6\text{H}_5\}_2$	294 s, 289 sh	382 vs, 344 ms, 242 w
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3(\text{C}_6\text{H}_5)_2\}_2$	300 s	413 ms, 344 m, 289 sh, 243 w
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	309 s	450 s, 431 s, 417 s
<i>trans</i> - $\text{RhBr}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	<200	450 s, 431 s, 417 s
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{P}(\textit{p}\text{-CH}_3\text{C}_6\text{H}_4)_3\}_2$	306 s	437 vs, 419 s, 352 m, 318 w
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{P}(\textit{p}\text{-CH}_3\text{OC}_6\text{H}_4)_3\}_2$	311 s, 306 s	446 vs, 421 vs
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{As}(\text{C}_2\text{H}_5)_3\}_2$	295 vs	339 sh, 327 m, 282 sh
<i>trans</i> - $\text{RhCl}(\text{CO})\{\text{As}(\text{C}_6\text{H}_5)_3\}_2$	~300 ^b	328 vs
$\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$	296 m	456 s, 436 m, 421 s, 408 s, 352 vw, 262 vw
$[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]_2$	303 m	455 m, 438 m, 424 m
$\text{RhBr}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$	<200	424 m, 402 s
$\text{RhCl}(\text{C}_7\text{H}_8)(\textit{p}\text{-toluidine})$	271 s	421 w, 414 m, 347 w, 316 m, 298 w
$\text{RhCl}(\text{C}_7\text{H}_8)\text{P}(\text{C}_6\text{H}_5)_3$	286 m, br	446 w, 434 w, 424 w, 269 sh
$\text{RhCl}(\text{C}_7\text{H}_8)\text{As}(\text{C}_6\text{H}_5)_3$	276 m, br	337 s, 327 s, 314 s
$\text{RhCl}(\text{C}_7\text{H}_8)\text{Sb}(\text{C}_6\text{H}_5)_3$	268 m, br	455 m
$\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	317 s, 311 sh	436 m, 420 m
$\text{IrBr}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	210 w ^c	436 m, 417 m
$[\text{IrCl}(\text{C}_8\text{H}_{12})_2]_2$	291 s, 258 m	411 s, 327 w, 245 w
C_7H_8 (norbornadiene)	...	420 s
C_8H_{12} (1,5-cyclooctadiene)	...	457 vs, 377 s

^a v, very; w, weak; m, medium; s, strong; sh, shoulder; br, broad. ^b Partly obscured by ligand absorption. ^c Assignment tentative.

disproportionation. *Anal.* Calcd for $\text{C}_{37}\text{H}_{30}\text{P}_2\text{BrCl}_2\text{OIr}$: C, 49.6; H, 3.4; Br, 8.9. Found: C, 48.0; H, 3.7; Br, 8.3.

Attempted Preparation of $\text{IrBr}_3(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$.— $\text{IrBr}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ was treated with bromine under similar conditions to those described above. A pale yellow product (slightly darker than the dichloro complex) was obtained in 84% yield. The infrared spectrum (Nujol) showed two strong $\text{C}\equiv\text{O}$ absorptions at 2030 and 2080 cm^{-1} and a medium band at 2220 cm^{-1} , presumably owing to an Ir-H stretching frequency from an iridium hydride impurity. *Anal.* Calcd for $\text{C}_{37}\text{H}_{30}\text{P}_2\text{Br}_3\text{OIr}$: C, 45.1; H, 3.1; Br, 24.3. Found: C, 45.1; H, 3.6; Br, 23.8.

Results and Discussion

Rhodium(I) and Iridium(I) Complexes.—The bands in the far-infrared spectra of a series of rhodium(I) and iridium(I) complexes are given in Table I. The dimeric halogen-bridged rhodium(I) complexes of the general formula $[\text{RhClL}_2]_2$ ($\text{L} = \text{CO}, \text{C}_2\text{H}_4, \text{cyclooctene}; \text{L}_2 = 1,5\text{-cyclooctadiene or norbornadiene}$) show, in general, two or three strong bands in the range 249–285 cm^{-1} which are absent from the spectra of the corresponding bromides and can be assigned as metal-chlorine stretching frequencies. The norbornadiene complex is exceptional in showing only one strong band due to $\nu(\text{Rh-Cl})$ at 249 cm^{-1} . The corresponding metal-bromine frequencies presumably occur below 200 cm^{-1} , the lower limit of our instrument. Our results are in general agreement with those briefly reported during the course of this work by Adams and Chandler,²² who have also located the metal-bromine

frequencies in the range 185–195 cm^{-1} in the ethylene and 1,5-cyclooctadiene complexes.

The structures of the complexes $[\text{RhCl}(\text{CO})_2]_2$ and $[\text{RhCl}(1,5\text{-C}_8\text{H}_{12})_2]_2$ differ in that the angle of intersection of the planes defined by the $\text{RhCl}(\text{CO})_2$ units at the chlorine bridge is 124^o,^{23a} whereas the $\text{RhCl-C}_8\text{H}_{12}$ units are coplanar.^{23b} It has been suggested^{23a} that $[\text{RhCl}(\text{CO})_2]_2$ has intermolecular metal-metal bonds of length 3.34 Å, which are absent in $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]_2$, but reasons for the difference in structure of the two complexes are not clear. Group theory predicts that a planar RhCl_2Rh unit (D_{2h} symmetry) should show two infrared-active M-Cl vibrations of b_{2u} and b_{3u} symmetry, whereas a bent RhCl_2Rh unit (C_{2v} symmetry) should show three infrared-active M-Cl stretching vibrations ($a_1 + b_1 + b_2$). On the basis of our spectra, however, it is not possible to distinguish between these two possibilities.

A band at 435 cm^{-1} in the spectrum of $\{\text{RhCl}(\text{CO})_2\}_2$ probably arises from a $\nu(\text{Rh-CO})$ stretching mode, and bands at 399 and 393 cm^{-1} in the spectra of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ and $[\text{RhBr}(\text{C}_2\text{H}_4)_2]_2$, respectively, are probably due to an Rh-C₂H₄ stretching mode; bands in the 400- cm^{-1} region in the spectra of ethylene complexes of palladium(II) and platinum(II) have been assigned to $\nu(\text{M-C}_2\text{H}_4)$ stretching modes.²⁴

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A series of monomeric, square-planar complexes of the general formula $\text{RhCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{R}_3\text{P}$ or R_3As) is obtained either by treatment of $[\text{RhCl}(\text{CO})_2]_2$ with tertiary phosphines and arsines,⁸ or by reduction of rhodium(III) chloride complexes in ethanolic or basic media with carbon monoxide.⁷ An X-ray study²⁵ of the complex $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ together with its dipole moment of 3.15 D. in benzene solution⁵ show that this complex has the *trans* configuration (C_{2v} symmetry). The far-infrared spectra of these rhodium(I) complexes show a medium to strong band due to Rh–Cl stretching in the range 295–311 cm^{-1} , whose position varies very little with the nature of the ligand atom (P or As) in the complex, or with the substituents (ethyl or phenyl) on the ligand atom. Thus, the value of $\nu(\text{Rh}-\text{Cl})$ for $\text{RhCl}(\text{CO})\{\text{As}(\text{C}_2\text{H}_5)_3\}_2$ is only 7 cm^{-1} lower than that for $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$. The corresponding value for $\text{RhCl}(\text{CO})\{\text{As}(\text{C}_6\text{H}_5)_3\}_2$ could not be determined accurately, since the band overlaps with a band in the ligand at 328 cm^{-1} , but it is obviously close to the value of $\nu(\text{Rh}-\text{Cl})$ (309 cm^{-1}) for $\text{RhCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$. The value of $\nu(\text{Rh}-\text{Cl})$ in the rhodium(I) carbonyl complexes is about the same as that found for the anionic species *cis*- $[\text{RhCl}_2(\text{CO})_2]^-$ ²⁶ and about 40 cm^{-1} lower than that found in the isoelectronic, *trans*-planar complexes of formula PdCl_2L_2 ;²⁷ this is the effect expected for a decrease in oxidation state, provided the stereochemistry does not change.

In many of the spectra of the rhodium(I) complexes, the band due to Rh–Cl stretching shows a definite asymmetry or splitting *ca.* 5 cm^{-1} to low frequency. Solid-state splitting of the nondegenerate a_1 Rh–Cl vibration can be excluded, and we assign the extra band to the Rh–³⁷Cl vibration, with the main band being due to the Rh–³⁵Cl vibration. Chlorine isotopic splitting of the same order of magnitude has been observed in the spectra of $\text{MnCl}(\text{CO})_5$, $\text{ReCl}(\text{CO})_5$, $[(\text{C}_2\text{H}_5)_4\text{N}][\text{WCl}(\text{CO})_5]$,² and $\text{AuCl}\cdot\text{P}(\text{CH}_3)_3$.²⁷ Since the isotope ¹⁰³Rh occurs in 100% abundance, the conditions for observing the effect in rhodium(I) complexes containing only one chlorine atom are especially favorable.

The terminal M–Cl frequency of the monomeric rhodium(I) carbonyl complexes is slightly higher (*ca.* 20 cm^{-1}) than the bridging M–Cl frequency in $[\text{RhCl}(\text{CO})_2]_2$. The infrared spectra of the monomeric complexes of the formula (norbornadiene) RhClL [$\text{L} = p$ -toluidine, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, or $\text{Sb}(\text{C}_6\text{H}_5)_3$] show a band due to Rh–Cl stretching in the range 268–285 cm^{-1} , again about 20–40 cm^{-1} higher than $\nu(\text{Rh}-\text{Cl})$ in $[\text{RhCl}(\text{norbornadiene})]_2$. This difference between terminal and bridging $\nu(\text{M}-\text{Cl})$ is about the same as that observed in square palladium(II) complexes,²² and in octahedral titanium(III) and chromium(III) complexes,¹ but it is much less than that reported for the compound $[\text{PtCl}_2\text{P}(\text{C}_2\text{H}_5)_3]_2$ (87 cm^{-1})²⁸ and for di-

meric, tetrahedrally coordinated halides such as Al_2Cl_6 .²⁹ The X-ray data presently available suggest that there is little difference between bridging and terminal rhodium(I)–chlorine distances, *e.g.*, $\text{RhCl}(\text{CS})[\text{P}(\text{C}_6\text{H}_5)_3]_2$, 2.386 Å;³⁰ $[\text{RhCl}(\text{CO})_2]_2$, 2.38 and 2.33 Å^{23a} (bridging Rh–Cl bond lengths); $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$, 2.38 Å.^{23b} On the other hand, in crystalline Ga_2Cl_6 ³¹ and Au_2Cl_6 ,³² the bridging metal–halogen distances are >0.1 Å longer than the terminal metal–halogen distances. The complex $\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$, which contains monomeric, planar $\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3$ units in the crystal,³³ shows a band at 296 cm^{-1} due to a Rh–Cl stretching vibration. In organic solvents the complex loses one molecule of triphenylphosphine, and a slightly soluble, presumably dimeric complex of the formula $\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ can be isolated.¹⁴ It is surprising that $\nu(\text{M}-\text{Cl})$ for this presumed dimer is at a slightly higher frequency (303 cm^{-1}) than that for the undissociated complex, and it is possible that this complex contains a highly unsymmetrical rhodium–chlorine bridge system.

The monomeric, square-planar complex $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ has $\nu(\text{Ir}-\text{Cl})$ at 317 cm^{-1} , with a shoulder at 312 cm^{-1} , presumably due to chlorine isotopic splitting. A weak band at 210 cm^{-1} in the spectrum of the corresponding bromide may be due to the Ir–Br stretching vibration. The near identity of $\nu(\text{Rh}-\text{Cl})$ and $\nu(\text{Ir}-\text{Cl})$ in complexes of the formula $\text{MCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ($\text{M} = \text{Rh}, \text{Ir}$) suggests that there is appreciable metal–ligand bond strengthening in the iridium(I) complex which counteracts the increased mass of the metal. We² have previously noted the near identity of $\nu(\text{M}-\text{Cl})$ in the series (a) $\text{MnCl}(\text{CO})_5$ and $\text{ReCl}(\text{CO})_5$, (b) $[\text{MCl}(\text{CO})_5]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{or W}$), and (c) $\text{FeCl}_2(\text{CO})_4$ and $\text{OsCl}_2(\text{CO})_4$, and this behavior seems to be favored by the attachment of strongly π -bonding ligands to the metals. Our conclusion for the rhodium(I) and iridium(I) complexes is supported by a comparison of the $\text{C}\equiv\text{O}$ stretching frequencies (1980 and 1965 cm^{-1} , respectively).

It may be noted that the metal–chlorine and metal–diene stretching vibrations in the compounds of the formula $[\text{MCl}(\text{C}_8\text{H}_{12})]_2$ ($\text{M} = \text{Rh}$ or Ir ; $\text{C}_8\text{H}_{12} = 1,5$ -cyclooctadiene) occur at higher frequency in the iridium(I) complex than in the rhodium(I) complex, $\nu(\text{Rh}-\text{Cl})$ 274, 254 cm^{-1} ; $\nu(\text{Ir}-\text{Cl})$ 291, 258 cm^{-1} ; $\nu(\text{Rh}-\text{C}_8\text{H}_{12})$ 382 cm^{-1} ; $\nu(\text{Ir}-\text{C}_8\text{H}_{12})$ 411 cm^{-1} . This implication of stronger metal–olefin and metal–chlorine bonds in the iridium(I) compounds is in direct contradiction to recent observations¹⁵ that iridium(I)–olefin complexes are less stable than their rhodium(I) analogs and that the shift in the $\text{C}=\text{C}$ stretching frequency on coordination is *smaller* for iridium(I) than for rhodium(I). Further work is required to clarify this discrepancy; since 1,5-cyclooctadiene itself absorbs at 377

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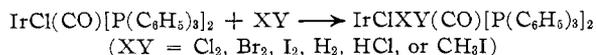
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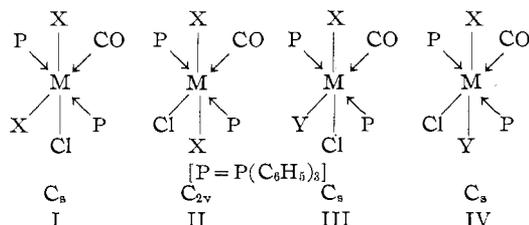
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cm^{-1} , our assignments of the metal-diene frequencies may be incorrect.

Octahedral Rhodium(III) and Iridium(III) Complexes.—Square-planar rhodium(I) carbonyl complexes of formula $\text{RhCl}(\text{CO})\text{L}_2$ are oxidized by halogens giving octahedral rhodium(III) carbonyl complexes $\text{RhClX}_2(\text{CO})\text{L}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(n\text{-C}_4\text{H}_9)_3$, or $\text{P}(\text{C}_2\text{H}_5)_3$).^{19, 20} The corresponding iridium(I) carbonyl complex $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ is oxidized not only by halogens, but by a variety of other molecules to give octahedral iridium(III) carbonyl complexes^{16, 17, 19, 21}



The addition could take place either *cis* or *trans*, and, assuming that the *trans* configuration of the tertiary phosphines is retained during the addition, there are two possible structures I and II, of C_s and C_{2v} symmetry, respectively, for the octahedral complex formed by a homonuclear addend X_2 ; in the case of a heteronuclear addend XY , both possible structures have C_s symmetry.



We have studied the far-infrared spectra of some of these complexes, and, to assist with assignments, we have also examined the spectra of *cis* and *trans* isomers of RhCl_3L_3 [$\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ or $\text{As}(\text{C}_2\text{H}_5)_3$]. The bands in the spectra are given in Table II.

trans- $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$, point symmetry C_{2v} , should show three infrared-active M-Cl modes ($2 a_1 + b_1$), whereas the *cis* isomer, point symmetry C_{3v} , should show two infrared-active M-Cl modes ($a_1 + e$). The far-infrared spectrum of the *trans* isomer shows a strong band at 342 cm^{-1} and broad, medium absorption in the range $266\text{--}238 \text{ cm}^{-1}$. These features do not appear in the spectrum of *trans*- $\text{RhBr}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$ and can be assigned to $\nu(\text{Rh-Cl})$ stretching modes. The spectrum of *cis*- $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$ shows two broad, overlapping bands centered at approximately 292 and 256 cm^{-1} , which are absent from the spectrum of the *cis*-bromide and can be assigned to the expected a_1 and e M-Cl modes. The absence of any absorption at 342 cm^{-1} suggests the assignment of this band in the *trans*-chloride as the antisymmetric b_1 mode involving principally the *trans*-chlorine atoms; the corresponding a_1 mode would not be expected to appear as a strong band, since there is only a small change in dipole moment. The M-Cl stretching vibrations at lower frequencies can therefore be assigned to motions involving chlorine atoms *trans* to tertiary phosphines. Medium absorption in the 250-cm^{-1} region in the spectrum of *trans*- $\text{RhBr}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$, which is poorly resolved from the background in our spectrum, may be

TABLE II

ABSORPTION FREQUENCIES (CM^{-1}) OF OCTAHEDRAL COMPLEXES OF RHODIUM(III) AND IRIIDIUM(III) IN THE RANGE $460\text{--}200 \text{ CM}^{-1}$

Compound	$\nu(\text{M-X})$	Other bands
<i>trans</i> - $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$	332 s, 288 m, 256 m, br	432 m, 386 w
<i>trans</i> - $\text{RhBr}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$	a	431 s, 377 w, 318 w, 267 w, 258 sh
<i>cis</i> - $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$	305 sh, 292 s, br, 268- 256 s, 250 sh, 236 s, br	425 s, 382 w
<i>cis</i> - $\text{RhBr}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$	a	424 vs, 383 m
<i>trans</i> - $\text{RhCl}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_3$	332 vs, ^b 293 m, 274 m, 270 sh	...
<i>trans</i> - $\text{RhBr}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_3$	a	332 w
<i>cis</i> - $\text{RhCl}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_3$	298 m, 272 m, 268 m, br	338 m, 303 sh, 294 sh
$[\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_2]_2$	342 sh, 329 vs	424 w, 384 v, 232 m
$[\text{RhCl}_3\{\text{P}(n\text{-C}_4\text{H}_9)_3\}_2]_2$	332 vs, 294 m	439 m, 396 w, 256 w, 250 w, 238 m
$[\text{RhCl}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_2]_2$	327 vs, ^b 316 m	338 sh, 296 w, 284 sh, 257 m w, 250 m w, 234 m
$\text{RhCl}_3(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$	335 s, 321 vs, 270 s, br	428 m, br, 371 w, 244 m, br
$\text{RhClBr}_2(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$	313 s, $\nu(\text{M-Cl})^a$	404 s, 376 m, 332 sh, 326 sh, 269 m, 264 m
$\text{RhClI}_2(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$	307 vs, 302 sh	414 sh, 400 m, 370 w, 334 w, 238 m, br
$\text{RhCl}_3(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	341 vs, 316 s	441 w, 426 m, 417 m, 296 m, 282 m, 259 ms
$\text{RhClI}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	308 ms	420 s
$\text{RhCl}_3(\text{CO})\{\text{As}(\text{C}_2\text{H}_5)_3\}_2$	340 vs, ^b 312 vs, 284 vs, 270 vs	231 m
$\text{RhClBr}_2(\text{CO})\{\text{As}(\text{C}_2\text{H}_5)_3\}_2$	305 vs, br	340 sh, 326 vs, 266 vs, 231 m
$\text{RhClI}_2(\text{CO})\{\text{As}(\text{C}_2\text{H}_5)_3\}_2$	304 vs	324 s, 232 m
$\text{IrCl}_3(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	326 vs, 302 s	452 m, 419 s, 257 sh, 250 sh, 244 s
$\text{IrClBr}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	311 s, 302 sh, $\nu(\text{Ir-Cl})$	444 m, 426 s, 258 w, 242 ms
$\text{IrClI}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	304 sh, 296 s	430 s, 417 s, 256 ms, 236 w
$\text{IrBrCl}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	318 vs, 305 s	455 m, 424 s, 259 w
$\text{IrHCl}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	310 s, 261 vs	453 s, 424 s, 302 sh, 277 w, 254 sh, 246 sh
$\text{IrH}_2\text{Cl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	268 vs	446 vs, 431 vs, 424 vs, 299 w, 251 w, 243 w
$\text{IrClCH}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$	292 s	446 m, sh, 424 s, 258 m, br

^a $\nu(\text{Rh-Br})$ could not be located with certainty. ^b Overlaps ligand absorption.

due to the b_1 Rh-Br stretching vibration. Similar assignments of $\nu(\text{MCl})$ modes in a series of octahedral iridium(III) complexes have been made recently by Jenkins and Shaw.³⁴ It may also be noted that the single $\nu(\text{MCl})$ vibration (b_{3u}) in the spectra of *trans*-dichloroplatinum(II) complexes of D_{2h} symmetry, involving *trans*-chlorine atoms, occurs at higher frequency (*ca.* 350 cm^{-1}) than the two $\nu(\text{MCl})$ vibrations ($a_1 + b_1$) in the spectra of the corresponding *cis* compounds (*ca.* 300 cm^{-1}).²⁷

The spectra of *trans*- $\text{RhCl}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_3$ and *trans*- $\text{RhBr}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_3$ are similar to those of the corresponding triethylphosphine complexes, but both show a strong band at *ca.* 330 cm^{-1} due to a ligand mode which obscures the $b_1 \nu(\text{RhCl})$ mode in the chloride. The reason for the diffuseness of the bands due to modes of the *cis*-chlorine atoms in all of the octahedral rhodium and iridium complexes is not clear. It may be associated with the high dipole moments of the complexes (especially the *cis* complexes), which could give rise to strong intermolecular forces in the crystal lattice and complicate the modes involving the polar metal-chlorine bonds.

The dimeric, halogen-bridged, octahedral complexes $[\text{RhCl}_3\text{L}_2]_2$ ($\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(n\text{-C}_4\text{H}_9)_3$, or $\text{As}(\text{C}_2\text{H}_5)_3$) show a strong band in their infrared spectra at *ca.* 330 cm^{-1} due to terminal M-Cl stretching and weak or medium absorption, overlapping the weak background absorption, at *ca.* 240 cm^{-1} . Although this band may be due to bridging M-Cl vibrations, similar absorption appears in the spectra of *cis*- and *trans*- $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$, $\text{RhCl}_3(\text{CO})\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$, and *trans*- $\text{RhCl}_3\{\text{As}(\text{C}_2\text{H}_5)_3\}_3$. No definite assignment of bridging metal-chlorine stretching vibrations in the dimeric, octahedral, complexes of rhodium(III) is therefore possible at present.

The far-infrared spectra of the octahedral carbonyl complexes of the general formula $\text{MCl}_3(\text{CO})\text{L}_2$ [$\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, or $\text{As}(\text{C}_2\text{H}_5)_3$] are similar to those of *trans*- $\text{RhCl}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_3$, in agreement with structures I or II ($\text{X} = \text{Cl}$), with C_{2v} symmetry. The highest frequency $\nu(\text{MCl})$ vibration, assigned to the b_1 mode, occurs at *ca.* 330 cm^{-1} in both rhodium and iridium complexes. A shoulder at 302 cm^{-1} in some of the spectra is assigned to the a_1 $\nu(\text{MCl})$ mode of the chlorine *trans* to carbon monoxide.

We now discuss the infrared spectra of the octahedral iridium(III) carbonyl complexes. The dihydride $\text{IrClH}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$, obtained by addition of hydrogen to the complex $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$, shows a single band due to M-Cl stretching at 268 cm^{-1} , in reasonable agreement with a value close to 270 cm^{-1} reported during the course of our work by Vaska.³⁵ This low value is characteristic of a chlorine atom *trans* to hydrogen,^{34,36} which has a high *trans*-bond-weakening effect. This observation and the appearance of two bands due to M-H stretching vibrations at 2112 and 2200 cm^{-1} strongly favor structure I (C_s symmetry) for the dihydride, resulting from *cis* addition of hydrogen to the complex $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$.³⁷

The infrared spectrum of the hydrogen chloride adduct $\text{IrCl}_2\text{H}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ shows two bands due to M-Cl stretching vibrations at 310 and 261 cm^{-1} , which can be assigned to the a' and a'' stretching modes of chlorine atoms *trans* to carbon monoxide and hydrogen, respectively, in the octahedral molecule (III; $\text{X} = \text{H}$, $\text{Y} = \text{Cl}$) (Vaska³⁵ reports 313 and 265 cm^{-1}).

In their study of octahedral iridium(III) complexes, Jenkins and Shaw³⁴ showed that $\nu(\text{M-Cl})$ is strongly influenced by the nature of the ligand (Cl, H, or tertiary phosphine) *trans* to the chlorine atom but is very little affected by the ligands *cis* to the chlorine atom. The near identity of $\nu(\text{M-Cl})$ *trans* to CO in planar $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ and octahedral $\text{IrCl}_2\text{H}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ supports this conclusion. We find that the M-Cl stretching frequencies in the octahedral adducts of the formula $\text{IrClXY}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ ($\text{XY} = \text{Cl}_2, \text{Br}_2, \text{I}_2$, or CH_3I) fall into the order $\text{Cl}_2 > \text{Br}_2 > \text{I}_2 > \text{CH}_3\text{I}$, which favors structure I for the halogen adducts ($\text{X} = \text{Cl}, \text{Br}$, or I) and structure III for the methyl iodide adduct

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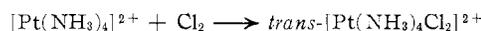
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($\text{X} = \text{CH}_3$, $\text{Y} = \text{I}$), resulting from *cis* addition of these molecules to $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$. In agreement with this, the spectrum of the complex $\text{IrBrCl}_2(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$, obtained by adding chlorine to the complex $\text{IrBr}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$, shows *two* strong bands at 318 and 305 cm^{-1} , which can be assigned to the a' and a'' $\nu(\text{M-Cl})$ modes of chlorine atoms *trans* to bromine and carbon monoxide, respectively (IV, $\text{X} = \text{Cl}$; $\text{Y} = \text{Br}$). In the alternative structure (III, $\text{X} = \text{Cl}$; $\text{Y} = \text{Br}$) of C_{2v} symmetry, we would expect to see only one strong band at *ca.* 326 cm^{-1} characteristic of chlorine *trans* to chlorine. The bands due to $\nu(\text{Ir-Br})$ modes, which should appear at *ca.* $240\text{--}260\text{ cm}^{-1}$, could not be located with certainty. All of the iridium(III) carbonyl complexes show medium bands in this region, which may be due to $\delta(\text{PIrCl})$ modes.

It has previously been suggested^{34,36} that the variations in $\nu(\text{M-Cl})$ caused by ligands *trans* to a chlorine atom ($\text{Cl} > \text{PR}_3 \sim \text{AsR}_3 > \text{H}$) are caused by inductive release of electrons from the less electronegative ligands which weakens the M-Cl bond. The results in Table II support this conclusion and suggest that the ligands can be ordered according to their effect on $\nu(\text{M-Cl}_{\text{trans}})$ as follows: $\text{Cl} > \text{Br} > \text{I} \sim \text{CO} > \text{CH}_3 > \text{PR}_3 \sim \text{AsR}_3 > \text{H}$. The far-infrared spectra also suggest that the octahedral adducts of $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ with halogens, hydrogen, and methyl iodide contain the addend atoms in *cis* positions. Similar though not so clear-cut trends appear in the spectra of the corresponding octahedral halogen adducts of $\text{RhCl}(\text{CO})\text{L}_2$ [$\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_2\text{H}_5)_3$, or $\text{As}(\text{C}_2\text{H}_5)_3$] (Table II), and it seems likely that *cis* addition occurs in these cases also. Vaska³⁵ has recently shown that the addition of hydrogen halides to $\text{IrCl}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2$ occurs *cis*, on the basis of the far-infrared spectra of the adducts.

The oxidation of platinum(II) complexes to platinum(IV) complexes is thought to occur with retention of configuration, the addend atoms being in *trans* positions in the final product,³⁸ *e.g.*



It has previously been assumed³⁹ that this idea also applies to additions to the formally analogous d^8 systems rhodium(I) and iridium(I) but this is clearly not the case. Indeed, *cis* addition may also take place in the halogenation of platinum(II) complexes, *e.g.*, the halogenation of *trans*- $\text{Pt}(\text{C}_6\text{H}_5)_2\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$ to give octahedral platinum(IV) complexes of the type $\text{PtX}_2(\text{C}_6\text{H}_5)_2\{\text{P}(\text{C}_2\text{H}_5)_3\}_2$ ($\text{X} = \text{Cl}, \text{Br}$, or I).⁴⁰

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