Further evidence for the preference of a planar three coordinate structure for copper(I) comes from X-ray data for the solid dicyanocuprate(I) compound.[30] The configuration of the copper is found to be three-coordinate with the nitrogen of an adjacent cyanide group occupying the third position. The three cyanide ligands are bent only slightly out of plane in the crystal. The present data suggest that M–C π bonding may be sufficiently important to influence the structure of the ions and thus the tendency toward mixed-ligand complex formation. This is in contrast to the analogous mercury(II) compounds, which contain coordinated water in the nonmixed complexes and which form a great number of mixed complexes with a variety of other ligands.[31] Copper(II) also forms mixed-ligand complexes containing cyanide ions.[32] This suggests that the behavior of copper(II) and mercury(II) as compared to copper(I) may be related to a decrease in the π bond character of the M–C bond occurring when the oxidation state of the metal is increased. The difference in the intensities of the A_1 cyanide line for the ions $Hg(CN)_4^{2-}$ and $Cu(CN)_4^{3-}$ is also notable as another point of distinction between Hg(II) and Cu(I).[33] Whereas the mercury complex belongs to a group of ions having "normal" Raman intensities, the intensity of the copper(I) complex was found to be abnormally high and could not be simply treated using bond localized polarizabilities.

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[30] E. Staritzky and D. I. Walker, *Anal. Chem.*, **28**, 419 (1956).

[31] Reference 12, p. 67.

[32] D. Cooper and R. A. Plane, paper presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

[33] G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, **35**, 1027 (1961).

CONTRIBUTION FROM INORGANIC CHEMISTRY RESEARCH LABORATORIES,
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Hydrido and Carbonylhydrido Complexes of Iridium Containing Stannous Chloride

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The preparation of the complexes $IrHClXL_3$, IrH_2XL_3, $IrHClX(CO)L_2$, $IrDClX(CO)L_2$, $IrH_2X(CO)L_2$, and $IrD_2X(CO)L_2$, where X = $SnCl_3^-$ or Cl^- and L = $(C_6H_5)_3P$, are described. The infrared and n.m.r. spectra of these complexes are discussed with regard to possible structures. The results confirm the large *trans* effect of $SnCl_3^-$ as a ligand. A hydride-transfer reaction occurs between $IrCl(CO)L_2$ or $IrHCl_2(CO)L_2$ and H_2O in acetone solutions containing $SnCl_2$. The $IrHClX(CO)L_2 \cdot (CH_3)_2CO$ species initially found in this reaction loses acetone upon recrystallization. A compound corresponding to the formula $IrCl_2X(CO)L$ is also prepared.

Introduction

Hydride complexes of the transition metals have been extensively investigated, and two excellent reviews have appeared in the recent literature.[1,2] In particular, a number of investigations have been reported in which iridium is the central metal atom.[1] In connection with work recently reported in this laboratory on stannous chloride complexes of various transition metals,[3–5] the reaction of $SnCl_2$ with certain Ir(IV), Ir(III), and Ir(I) compounds was investigated. In view of the formation of a rhodium hydride species catalyzed by the presence of $SnCl_2$[6] and the ease with which iridium hydrides are formed by interaction with alcohols in the presence of triphenylphosphine,[7] it was of interest to ascertain whether $SnCl_2$ would catalyze iridium hydride formation. Furthermore, it was also of interest to determine whether $SnCl_2$ would be incorporated in the resulting complex as a trichlorostannate(II) ligand. That $SnCl_2$ promotes the interaction of iridium(III) with solvents is shown by the formation of an anionic iridium carbonyl complex, related to $[Ir_2Cl_6(SnCl_3)_4]^{4-}$,[3,5] which has been prepared in ethanol or 2-methoxyethanol in the absence of triphenylphosphine.

In all of the complexes reported in this paper, $SnCl_2$ appears to be acting as a weak σ-donor ligand, *i.e.*, $SnCl_3^-$, and exhibiting a large *trans* effect as a result of its ability to form d_π–d_π bonds with the central metal atom.[5] Lindsay, *et al.*,[8] have recently reported the characteristics of $SnCl_3^-$ as a ligand, and their results suggest weak σ-donation but a strong $d\pi$–$d\pi$ contribution to the metal–tin bond. Chatt[9,10] has shown that there is a good correlation between *trans*-effect and π-acceptor properties of a ligand in the series *trans*-Pt-

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[1] A. P. Ginsberg, *Progr. Transition Metal Chem.*, **1**, 111 (1965).

[2] M. L. H. Green, *Advan. Inorg. Nucl. Chem.*, **6**, 115 (1965).

[3] A. G. Davies, G. Wilkinson, and J. F. Young, *J. Am. Chem. Soc.*, **85**, 1692 (1963).

[4] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964).

[5] J. F. Young, R. D. Gillard, and G. Wilkinson, *ibid.*, 5176 (1964).

[6] J. F. Young, Ph.D. Thesis, University of London, July 1965.

[7] L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

[8] R. V. Lindsay, Jr., G. W. Parshall, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

[9] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

[10] J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. Ind.* (London), 859 (1958).

$HX[(C_2H_5)_3P]_2$. An estimation of the *trans* effect of $SnCl_3^-$ in this way suggests that it is nearly as good a π acceptor as the cyanide group. These indications are further confirmed by the present results.

Experimental Section

Infrared spectra were determined in Nujol mulls (unless otherwise stated) using a Grubb–Parsons grating Spectromaster spectrometer. The n.m.r. spectra were determined in methylene chloride (unless otherwise stated) on a Varian Model 43100 at 56.5 Mc./sec. using the solvent as an internal calibrant. τ values are correct to the first decimal point. J values are accurate to within ±2 c.p.s., except in cases where the high-field lines are very weak. In such cases J values can only be estimated to within ±5 c.p.s. Microanalyses and molecular weights (Mechrolab osmometer at 37°) were determined by the Microanalytical Laboratory, Imperial College. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. All preparations were carried out under a nitrogen atmosphere.

Preparation of Compounds. Hydridochloro(trichlorostannato)tris(triphenylphosphine)iridium(III).—A mixture of 0.5 g. of sodium chloroiridate(III), 1 g. of anhydrous stannous chloride, and 1.9 g. of triphenylphosphine was refluxed in 40 ml. of ethanol for 1.5 hr. The resulting orange solution was filtered hot, and on cooling a yellow-orange solid separated which was subsequently filtered and washed with ethanol and ether (0.62 g., 70% based on Na_3IrCl_6).

Anal. Calcd. for $IrHCl(SnCl_3)[(C_6H_5)_3P]_3$: C, 52.1; H, 3.7; Cl, 11.4; Sn, 9.5; molecular weight, 1243. Found: C, 52.9; H, 4.1; Cl, 10.4; Sn, 8.2; molecular weight (1% in chloroform), 1119.

The presence of oxygen (2.0%) in the compound and bands in the infrared spectrum at 1115 and 723 cm.$^{-1}$ indicate the presence of triphenylphosphine oxide in this compound. Purification of the compound is difficult since successive recrystallizations with methylene chloride–ethanol mixtures result in the loss of stannous chloride with the eventual formation of the pale cream-colored chloro complex hydridodichlorotris(triphenylphosphine) iridium(III).[7]

Anal. Calcd. for $IrHCl_2[(C_6H_5)_3P]_3$: C, 61.5; H, 4.4; Cl, 6.7. Found: C, 59.0; H, 4.5; Cl, 8.8.

Its color, melting point, infrared, and n.m.r. spectra were identical with those for the compound prepared by refluxing sodium chloroiridate(IV) with excess triphenylphosphine in 2-methoxyethanol and shown by infrared and n.m.r. spectra to be the β isomer.[1]

Dihydrido(trichlorostannato)tris(triphenylphosphine)iridium(III). Method 1.—A mixture of 0.2 g. of sodium chloroiridate(IV), 0.4 g. of stannous chloride, and 0.75 g. of triphenylphosphine was refluxed in 50 ml. of 2-methoxyethanol for 1.5 hr. Half of the solvent was removed by distillation under reduced pressure during which time white crystals were formed (0.35 g., 75%). These were collected and recrystallized from methylene chloride–ethanol yielding white crystals of $IrH_2(SnCl_3)[(C_6H_5)_3P]_3$.

Anal. Calcd. for $IrH_2(SnCl_3)[(C_6H_5)_3P]_3$: C, 53.7; H, 3.9; Cl, 8.7; Sn, 9.8. Found: C, 53.8; H, 4.0; Cl, 9.0; Sn, 9.6.

Method 2.—A mixture of 0.2 g. of dihydridochlorotris(triphenylphosphine)iridium(III) and 0.4 g. of stannous chloride was refluxed in 30 ml. of acetone for 10 min. The solvent was removed *in vacuo*, and the white solid was crystallized from chloroform–ethanol. Recrystallization from chloroform–ethanol gave white crystals of $IrH_2(SnCl_3)[(C_6H_5)_3P]_3$ (*ca.* 80% yield).

Anal. Found: C, 53.8; H, 4.0; Cl, 9.9; Sn, 9.8.

The melting point, solubility, infrared, and n.m.r. spectra of the compounds prepared by both methods were identical.

Hydridochloro(trichlorostannato)carbonylbis(triphenylphosphine)iridium(III) Acetonate. Method 1.—Chlorocarbonylbis(triphenylphosphine)iridium(I) (0.2 g.)[11] was suspended in 10 ml. of acetone and on treatment with 0.4 g. of stannous chloride dissolved to give a yellow solution. After filtering, the solution was kept for 48 hr. during which time pale yellow crystals were deposited. The crystals were collected and washed with acetone, ethanol, and ether (0.11 g., 42%).

Anal. Calcd. for $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2(CH_3)_2CO$: C, 45.1; H, 3.5; O, 3.0; Cl, 13.3; Sn, 11.1. Found: C, 44.3; H, 3.4; O, 3.2; Cl, 14.6; Sn, 13.7.

Method 2.—A mixture of 0.4 g. of hydridodichlorocarbonylbis(triphenylphosphine)iridium(III)[12] and 1 g. of stannous chloride was refluxed in 60 ml. of acetone for 10 min. The yellow solution was filtered hot and then evaporated to dryness *in vacuo*. The pale yellow solid was washed with ethanol and ether to remove excess stannous chloride (yield *ca.* 50%). The compounds prepared by both methods were identical in their infrared spectra and physical properties.

Hydridochloro(trichlorostannato)carbonylbis(triphenylphosphine)iridium(III).—Recrystallization of hydridochloro(trichlorostannato)carbonylbis(triphenylphosphine)iridium(III) acetonate from chloroform–ethanol removed acetone to give $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$.

Anal. Calcd. for $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$: C, 44.1; H, 3.1; Cl, 14.1; Sn, 11.8. Found: C, 43.9; H, 3.5; Cl, 15.0; Sn, 10.9. Repeated recrystallization resulted in loss of stannous chloride giving a mixture (based on infrared spectra) of $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$ and $IrHCl_2(CO)[(C_6H_5)_3P]_2$. The analogous deuteride, $IrDCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$, was prepared by both of the above methods by the reaction of $IrCl(CO)[(C_6H_5)_3P]_2$ or $IrHCl_2(CO)[(C_6H_5)_3P]_2$ with stannous chloride in acetone containing 0.5 ml. of D_2O.

Dihydrido(trichlorostannato)carbonylbis(triphenylphosphine)iridium(III).—A mixture of 0.5 g. of dihydridochlorocarbonylbis(triphenylphosphine)iridium(III)[12] and 1 g. of stannous chloride was refluxed for 10 min. in 60 ml. of acetone. The bright yellow solution was filtered, and the filtrate was evaporated to dryness *in vacuo*. Treatment of the residue with ethanol yielded a pale yellow solid which was recrystallized from chloroform–ethanol. The pale yellow crystals were washed with ethanol and ether.

Anal. Calcd. for $IrH_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$: C, 45.7; H, 3.3; Cl, 11.0; Sn, 12.2. Found: C, 45.1; H, 3.3; Cl, 12.8; Sn, 13.9. The dideuteride was prepared in an analogous manner from dideuteriochlorocarbonylbis(triphenylphosphine)iridium(III).[12]

Dichloro(trichlorostannato)carbonyltriphenylphosphineiridium(III). Method 1.—$IrCl(CO)[(C_6H_5)_3P]_2$ (0.2 g.) was refluxed in 5 ml. of stannic chloride for 18 hr. The solution was cooled, and excess stannic chloride was removed by thorough washing with benzene. Treatment of the sticky residue with methylene chloride left a pale yellow powder which was insoluble in all common solvents (0.24 g., 88%).

Anal. Calcd. for $IrCl_2(SnCl_3)(CO)[(C_6H_5)_3P]$: C, 29.2; H, 1.9; Cl, 22.7; Sn, 15.2. Found: C, 29.1; H, 2.0; Cl, 25.0; Sn, 15.8.

Method 2.—A mixture of 0.2 g. of $IrHCl_2(CO)[(C_6H_5)_3P]_2$ and 5 ml. of stannic chloride was refluxed for 18 hr. Similar treatment of the residue as in method 1 gave $IrCl_2(SnCl_3)(CO)[(C_6H_5)_3P]$ (*ca.* 85%).

Anal. Found: C, 28.4; H, 2.1; Cl, 24.9; Sn, 14.8.

Bis(tetramethylammonium) Trichlorobis(trichlorostannato)carbonyliridate(III).—Sodium chloroiridate(IV) (0.32 g.) was dissolved in 40 ml. of ethanol in the cold. Addition of 0.35 g. of anhydrous $SnCl_2$ immediately gives a light brown precipitate of sodium chloroiridate(III). Refluxing for 5 min. redissolves the precipitate to an amber solution from which can be precipitated $[(CH_3)_4N]_4[Ir_2Cl_6(SnCl_3)_4]$.[3,5] When the solution is refluxed for a longer period (*ca.* 1 hr.), the addition of 0.12 g. of tetramethylammonium chloride in 4 ml. of methanol gives a fine yellow precipitate which is difficult to filter. The precipitate was separated by centrifuging and washed by decantation with ethanol and ether (0.43 g., 80%). The salt is insoluble in all common

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(11) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

(12) L. Vaska and J. W. DiLuzio, *ibid.*, **84**, 679 (1962).

TABLE I

PHYSICAL PROPERTIES OF IRIDIUM TRICHLOROSTANNATE COMPLEXES

Complex	Color[a]	M.p., °C.	$\nu_{C=O}$, cm.$^{-1}$	ν_{Ir-H}, cm.$^{-1}$	τ_H (J_{PH}, c.p.s.)[b]
α-$IrHCl_2[(C_6H_5)_3P]_3$[7,14]	y	256[c]	. . .	2193	22.4 (T, 15), 25.3 (T, 15)[d]
β-$IrHCl_2[(C_6H_5)_3P]_3$[14]	p-y	. . .	. . .	2228	29.2 (Q, 15)
$IrHCl(SnCl_3)[(C_6H_5)_3P]_3$	o-y	132–134	. . .	2155	24.7 (D, 14), 30.3 (Q, 13), 31.4 (T, 10)
$IrH_2Cl[(C_6H_5)_3P]_2$	w	172–174	. . .	(2193, 2105)[e] (2162, 2112)[e]	19.9 (T, 20), 22.3 (T, 20), 30.2 (Q, 15)
$IrH_2(SnCl_3)[(C_6H_5)_3P]_3$	w	206–207	. . .	2262, 2205	21.3 (T, 10), 23.0 (T, 10), 24.7 (Q, 20)
$IrCl(CO)[(C_6H_5)_3P]_2$[11]	y	323–325[c]	1972	. . .	. . .
$IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2\cdot(CH_3)_2CO$	p-y	199–201	2058, 2053[f]	2198, 2160	19.9 (T, 10)
$IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$	p-y	155–157	2053	2148	19.9 (T, 10)
$IrHCl_2(CO)[(C_6H_5)_3P]_2$[11]	w	315–320[c]	2024	2239	Insoluble
$IrDCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$	p-y	200–201	2056	1530[g]	. . .
$IrH_2Cl(CO)[(C_6H_5)_3P]_2$[1,12]	y	315–321[c]	2010[d,h]	2222, 2098[d,h]	17.3 (T, 15), 28.4 (T, 15)
$IrD_2Cl(CO)[(C_6H_5)_3P]_2$[12]	y	162–165	2007	1577[i]	. . .
$IrH_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$	p-y	191–193	2062[d]	2112, 2014[d]	19.9 (T, 10), 22.5 (T, 10)
$IrD_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$	p-y	205–208	2055[d]	1563[i]	. . .
$IrCl_3(CO)[(C_6H_5)_3P]_2$[11]	w	. . .	2079	. . .	. . .
$IrCl_2(SnCl_3)(CO)[(C_6H_5)_3P]$	y	270–275	2077, 2072	. . .	. . .
$[(CH_3)_4N]_2[IrCl_3(SnCl_3)_2(CO)]$[j]	y	Dec. >250	2058	. . .	. . .

[a] y = yellow; p-y = pale yellow; w = white; o-y = orange-yellow. [b] In CH_2Cl_2 solutions. Line splittings: D = doublet; T = triplet; Q = quartet. [c] Decomposes *in vacuo*. [d] In $CHCl_3$ solution. [e] See Discussion. [f] Ketone band of acetone occurs at 1716 cm.$^{-1}$. [g] ν_{Ir-D}. [h] In Nujol mull: $\nu_{C=O}$ 1997, 1983; and ν_{Ir-H} 2196, 2108 cm.$^{-1}$. [i] Low-frequency ν_{Ir-D} is obscured by triphenylphosphine bands. [j] Conductivity in dimethylformamide, 10^{-3} *M*, is 114 ohms^{-1} cm.^{2} mole^{-1}, which is in the range expected for 2:1 electrolyte.

solvents except dimethylformamide and can only be purified by reprecipitating it from a dimethylformamide solution with ethanol.

Anal. Calcd. for $[(CH_3)_4N]_2[IrCl_3(SnCl_3)_2(CO)]$: C, 11.6; H, 2.6; O, 1.7; Cl, 34.4; Sn, 25.6. Found: C, 11.1; H, 3.1; O, 2.0; Cl, 35.5; Sn, 24.7.

The same reaction takes place using 2-methoxyethanol as the solvent and the initial precipitate is reasonably pure.

Found: C, 10.5; H, 2.8; O, 1.9; Cl, 34.2.

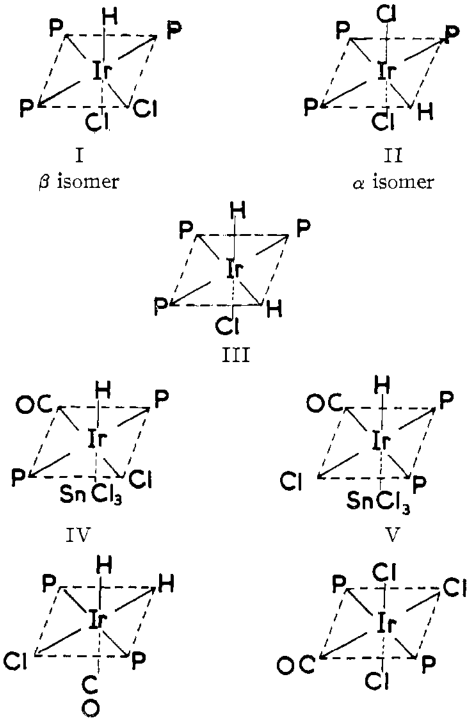
Results

The melting points, color, infrared, and n.m.r. data for the compounds discussed in the work are listed in Table I.

Discussion

α- and β-$IrHCl_2[(C_6H_5)_3P]_3$ and $IrHCl(SnCl_3)[(C_6H_5)_3P]_3$.—The n.m.r. spectrum of β-$IrHCl_2[(C_6H_5)_3P]_3$ is consistent with structure I (Figure 1) in that the hydride resonance is split by interaction with three equivalent phosphorus nuclei into a symmetrical quartet with relative intensities 1:3:3:1 and J_{PH} = 14 c.p.s., which is the magnitude of splitting expected for a hydride *cis* to three phosphine ligands.[9] The high τ value (29.2) is consistent with the hydride *trans* to a chloride as is the high Ir–H stretching frequency (2228 cm.$^{-1}$) observed in the infrared spectrum. Structure I corresponds to the β isomer[13] originally reported by Vaska as being formed by treating $IrH_2Cl[(C_6H_5)_3P]_2$ with HCl in dry ether.[14] However, we have prepared the β isomer by the method used by Vaska to form the α isomer, structure II. This discrepancy may be due to the use of slightly different reaction conditions. We have prepared the α isomer by using ethanol in place of 2-methoxyethanol as solvent.

The n.m.r. spectrum of the α isomer shows two high-field triplets at τ 22.4 and 25.3 and J_{PH} = 15 c.p.s. and is consistent with structure II in that the phosphorus nuclei *cis* to the hydride split the hydride resonance into a symmetrical 1:2:1 triplet, and the phosphorus nuclei *trans* to the hydride further split the resonance into a doublet with *J* = 164 c.p.s.[15] The smaller chemical shift of the hydride resonance and the lower Ir–H stretching frequency (2193 cm.$^{-1}$) suggest a hydride *trans* to a ligand with a larger *trans* effect than Cl^-.



I β isomer

II α isomer

III

IV

V

VI

VII

Figure 1.

When ethanolic chloroiridate(IV) solutions are refluxed with excess $(C_6H_5)_3P$ and $SnCl_2$, the complex $IrHCl(SnCl_3)[(C_6H_5)_3P]_3$ which shows a broad Ir–H stretching frequency at 2155 cm.$^{-1}$ is formed. How-

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(13) Notation due to A. P. Ginsberg, ref. 1.

(14) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 4989 (1962).

(15) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

ever, the elemental analysis and the presence of bands at 1115 and 723 cm.$^{-1}$ in the infrared spectrum suggest the presence of a small amount of coordinated triphenylphosphine oxide.[16]

The n.m.r. spectrum of $IrHCl(SnCl_3)[(C_6H_5)_3P]_3$ is much more complex than that of either of the above isomers. The weak 1:3:3:1 quartet at τ 30.3 is expected for structure I with the equatorial Cl^- replaced by $SnCl_3^-$ since the environment of the hydride is not very different from that in β-$IrHCl_2[(C_6H_5)_3P]_3$. $SnCl_3^-$ and $(C_6H_5)_3P$ act as *trans*-directing ligands, and, if either were *trans* to the hydride, the resonance would be expected to shift to lower τ values as found for the platinum phosphine hydrides.[9] However, the 1:2:1 triplet at τ 31.4, with J_{PH} = 10 c.p.s., is the most intense resonance (of the order of three to four times as intense as the quartet) and therefore is attributed to the predominant species in solution. The high τ value and the triplet structure may be explained as arising from a hydride *trans* to a chloride ligand and *cis* to two phosphorus nuclei. This condition may result if it is assumed that the phosphine *trans* to $SnCl_3^-$ is sufficiently labilized by a strong $SnCl_3^-$ *trans* effect and dissociates effectively enough in solution such that the phosphorus nuclei do not couple with the hydride. Addition of excess $(C_6H_5)_3P$ decreases dissociation and decreases the intensity of the triplet to half its original value, while simultaneously the quartet increases until the two sets of resonance are of approximately equal intensities. However, even in the presence of large excess of $(C_6H_5)_3P$ (>5 moles), it was never possible to reduce further the intensity of the triplet. The low-field doublet is extremely weak and may be due to the contaminating $(C_6H_5)_3PO$ species.

When either the α or β isomer of $IrHCl_2[(C_6H_5)_3P]_3$ is treated with $SnCl_2$ in acetone, a pale yellow solid is obtained by slow precipitation from chloroform–ethanol. The infrared spectrum of this compound shows an Ir–H stretching frequency at 2125 cm.$^{-1}$. Upon allowing the yellow filtrate to stand for a few days, a bright yellow crystalline solid separates out. These crystals show an Ir–H frequency at 2075 cm.$^{-1}$. The n.m.r. spectrum of the former compound shows a single triplet at τ 22.6 with J_{PH} = 10 c.p.s. which indicates that a phosphine ligand has been lost and that the hydride is *cis* to the remaining two phosphines and *trans* to an $SnCl_3^-$ ligand. Although the carbon and hydrogen analyses remain quite constant for different samples, the chloride and tin analyses have varied by as much as 9%. Such variation in analytical results precludes any attempt at arriving at a satisfactory empirical formula.

$IrH_2Cl[(C_6H_5)_3P]_3$ and $IrH_2(SnCl_3)[(C_6H_5)_3P]_3$.—On the basis of the infrared and n.m.r. data, the structure of $IrH_2Cl[(C_6H_5)_3P]_3$ is consistent with structure III. The n.m.r. spectrum shows two 1:2:1 triplets of equal intensity at τ 19.9 and 22.3 with J = 20 c.p.s. and a 1:3:3:1 quartet of approximately twice the intensity at τ 30.2 with J = 15 c.p.s. The hydride *cis* to the three phosphorus nuclei and *trans* to the chloride gives rise to the symmetrical quartet at high field, whereas the equatorial hydride shows a lower chemical shift since it is *trans* to a *trans*-directing ligand. The resonance due to the equatorial hydride is interpreted in the same manner as the hydride resonance in α-$IrHCl_2[(C_6H_5)_3P]_3$.

It is of interest to note that, when $IrH_2Cl[(C_6H_5)_3P]_3$ is prepared by Vaska's method and recrystallized from chloroform–ethanol, the first crystals to precipitate out show Ir–H stretching frequencies at 2162 and 2112 cm.$^{-1}$. If the resulting filtrate is allowed to stand for an additional period of time, a second batch of crystals precipitates out which shows Ir–H stretching frequencies at 2193 and 2105 cm.$^{-1}$, together with a small amount of the former isomer. However, if the former isomer is redissolved in methylene chloride or chloroform, isomerization occurs, and only the latter isomer can be isolated. The n.m.r. and infrared spectra of both isomers in methylene chloride are identical. In addition, identical stannous chloride complexes are obtained from either isomer.

When chloroiridate(III) solutions containing excess $(C_6H_5)_3P$ and $SnCl_2$ are refluxed in 2-methoxyethanol, $IrH_2(SnCl_3)[(C_6H_5)_3P]_3$ is formed. The n.m.r. of this compound is consistent with structure III with Cl^- replaced by $SnCl_3^-$. Thus, the quartet of the hydride *cis* to the three phosphines is shifted to lower field owing to the influence of the *trans*-directing $SnCl_3^-$ ligand, but the two triplets remain essentially unchanged except for a very small upfield shift. The fact that this complex can also be prepared directly from $IrH_2Cl[(C_6H_5)_3P]_3$ lends support to retention of configuration upon substitution. The infrared spectrum of the tin-containing complex appears to be at variance with the n.m.r. data. The $SnCl_3^-$ ligand *trans* to the equatorial hydride in structure III would be expected to lead to a decrease in the Ir–H stretching frequency rather than to the observed increase.

$IrHCl_2(CO)[(C_6H_5)_3P]_2$, $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$, and $IrDCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$.—The square-planar iridium carbonyl complex *trans*-$IrCl(CO)[(C_6H_5)_3P]_2$ is well known for the ease with which it forms octahedral iridium(III) complexes by the addition of HCl, Cl_2, H_2,[11,12] RX[17] (where RX is an active organic halide), and hydrosilanes.[18] The reaction of $SnCl_2$ with $IrCl(CO)[(C_6H_5)_3P]_2$ also forms an octahedral iridium(III) complex but in an unusual way. The iridium(I) species dissolves in acetone containing excess $SnCl_2$ to give a yellow solution from which the acetone adduct $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2(CH_3)_2CO$ can be isolated. The presence of acetone is indicated by the infrared spectrum and by the elemental analyses. The ketonic C=O stretching frequency at 1716 cm.$^{-1}$ and the asymmetric C–H stretching frequency at 1218 cm.$^{-1}$ are both indicative of uncoordi-

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[16] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960); F. A. Cotton and D. M. L. Goodgame, *ibid.*, 5267 (1960); 2298, 3135 (1961); *J. Am. Chem. Soc.*, **82**, 5774 (1960).

[17] R. F. Heck, *ibid.*, **86**, 2796 (1964).

[18] A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16 (1965).

nated acetone.[19] Moreover, the acetone is lost upon recrystallization from methylene chloride or chloroform resulting in $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$. The infrared spectrum of the acetone complex also shows two Ir—H and two C═O stretching frequencies. These doublets are presumably due to solid-state splitting since in CH_2Cl_2 each pair becomes a single peak. The n.m.r. spectrum has only one high-field line indicating that the hydride is in a single environment.

The reaction of $SnCl_2$ with $IrHCl_2(CO)[(C_6H_5)_3P]_2$ in acetone gives the identical acetone-containing complex, and upon recrystallization $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$, identical with the above-mentioned complex, is formed. It is interesting to note that such solvents as alcohols, aldehydes, and aliphatic acids do not promote the formation of the tin complex whereas acetone, ethyl methyl ketone, and ethyl acetate all promote the reaction, and the corresponding solvated complexes can be isolated. In view of Vaska's work,[7,14] which confirms the proposal that the hydride in $IrHCl_2[(C_6H_5)_3P]_3$ arises entirely from the α carbon of the solvent, the inability of ethanol to promote the formation of a hydride complex in the present work is not clear. Furthermore, if D_2O is added to the reaction mixtures of $IrCl(CO)[(C_6H_5)_3P]_2$ and $SnCl_2$ or $IrHCl_2(CO)[(C_6H_5)_3P]_2$ and $SnCl_2$ the corresponding deuteride complex $IrDCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$ is formed in both cases. $IrCl(CO)[(C_6H_5)_3P]_2$ and $IrHCl_2(CO)[(C_6H_5)_3P]_2$ are virtually insoluble in acetone, but in the presence of acetone solutions, containing $SnCl_2$ and trace amounts of H_2O or D_2O, solution is effected, and the corresponding hydride or deuteride is formed. In the case of $IrHCl_2(CO)[(C_6H_5)_3P]_2$, the $SnCl_2$ may catalyze the reduction to the square-planar iridium(I) complex which then adds $HSnCl_3$ or $DSnCl_3$ formed from $SnCl_2$ and the trace amounts of H_2O or D_2O. The fact that the reaction does not occur in ethanol suggests that the ketone or acetate in its enol form, where rapid exchange with H_2O or D_2O could occur, is responsible in some way for carrying out this novel hydrogen-transfer reaction. The mechanism by which the process occurs is not clear at the present time. Further work is now in progress on this problem. It is of interest to note here that, in all other reactions reported in this work, none of the complexes formed a solvated acetonic species nor did they form deuterides when D_2O was added to the reaction mixtures.

Repeated recrystallization of $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$ from $CHCl_3$–C_2H_5OH mixtures leads to a gradual breakdown of the compound to form a mixture (based on infrared spectra) of $IrHCl_2(CO)[(C_6H_5)_3P]_2$ and $IrCl(CO)[(C_6H_5)_3P]_2$.

Infrared and n.m.r. spectra are consistent with structure IV for $IrHCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$ although structure V cannot be excluded. The 1:2:1 triplet with $J = 10$ c.p.s. indicates the hydride is *cis* to the two phosphines, and the low τ value (19.9) suggests the hydride is *trans* to $SnCl_3^-$. The hydride is not *trans* to the carbonyl group as indicated by the relatively high Ir–H stretching frequency (2148 cm.$^{-1}$). In the complex $IrHCl_2(CO)[(C_2H_5)_2(C_6H_5)P]_2$,[15] in which the hydride is *trans* to the carbonyl group, the Ir–H stretching frequency is very low, *i.e.*, 2008 cm.$^{-1}$. Of the nine possible isomers, these results rule out all isomers other than IV and V.

The compound $IrHCl_2(CO)[(C_6H_5)_3P]_2$ was too insoluble to record its n.m.r. spectrum; however, the very high Ir–H stretching frequency (2239 cm.$^{-1}$) indicates the hydride is *trans* to a chloride, which rules out four of the six possible isomers leaving again only structures IV and V.

$IrDCl(SnCl_3)(CO)[(C_6H_5)_3P]_2$ formed in the D_2O reactions has an Ir–D stretching frequency at 1530 cm.$^{-1}$, which agrees well with the calculated value of 1525 cm.$^{-1}$ ($\nu_{Ir-H}/\nu_{Ir-D} = 1.41$).

$IrH_2Cl(CO)[(C_6H_5)_3P]_2$, $IrD_2Cl(CO)[(C_6H_5)_3P]_2$, $IrH_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$, and $IrD_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$.—The addition of H_2 to $IrCl(CO)[(C_6H_5)_3P]_2$ gives the *cis*-dihydride species corresponding to structure VI based on infrared and n.m.r. data. The n.m.r. spectrum shows two high-field 1:2:1 triplets with $J = 15$ c.p.s. indicating that each hydride is *cis* to the two phosphorus nuclei. The τ values of 28.4 and 17.3 suggest the hydrides are *trans* to a chloride ligand and a carbonyl group, respectively. Although the splitting in the infrared spectrum of the mull could be attributed to solid-state splitting, nevertheless in $CHCl_3$ solution there are two Ir—H stretching frequencies at 2222 and 2098 cm.$^{-1}$ and a single C═O stretching frequency at 2010 cm.$^{-1}$. These results are in accord with the n.m.r. data; the low Ir–H frequency arises from the hydride *trans* to the carbonyl, and the high Ir–H frequency arises from the hydride *trans* to the chloride ligand. The preparation of $IrD_2Cl(CO)[(C_6H_5)_3P]_2$ confirms the assignment of the Ir–H stretching frequencies. The observed value of 1577 cm.$^{-1}$ for the Ir–D stretching frequency agreed quite well with the calculated value of 1575 cm.$^{-1}$. The other Ir–D frequency is obscured by the $(C_6H_5)_3P$ bands.

The addition of $SnCl_2$ to acetone solutions containing $IrH_2Cl(CO)[(C_6H_5)_3P]_2$ leads to the formation of $IrH_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$. Two 1:2:1 triplets of equal intensity at τ 19.9 and 22.5 with $J = 10$ c.p.s. suggest $SnCl_3^-$ is responsible for the downfield shift from τ 28.4 in the chloride complex to τ 22.5, and the low-field triplet has moved upfield from τ 17.3 to 19.9. Similar behavior was also observed in $IrH_2(SnCl_3)[(C_6H_5)_3P]_3$. However, the Ir–H stretching frequencies have decreased in $IrH_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$ as predicted. This is in direct contrast with the results for $IrH_2(SnCl_3)[(C_6H_5)_3P]_2$.

The preparation of $IrD_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$ was necessitated because of the difficulty in distinguishing the hydride and carbonyl bands in the tin complex. The preparation of the dideuteride allows the assignment of the bands at 2112 and 2014 cm.$^{-1}$ as being due to Ir–H stretching frequencies and the band at 2062 cm.$^{-1}$ arising from a carbonyl stretch. The high-

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[19] P. Chalandon and B. P. Susz, *Helv. Chim. Acta*, **41**, 697 (1958).

frequency Ir–D stretch occurs at 1563 cm.$^{-1}$, but the low-frequency Ir–D band is obscured by the $(C_6H_5)_3P$ band at 1428 cm.$^{-1}$. The calculated value for this Ir–D frequency is 1426 cm.$^{-1}$.

$IrCl_3(CO)[(C_6H_5)_3P]_2$ and $IrCl_2(SnCl_3)(CO)[(C_6H_5)_3P]$.—The observation that $IrCl_3(CO)[(C_6H_5)_3P]_2$ of structure VII is inert to substitution by hydrogen with alcoholic potash as reagent[15] may explain the fact that the compound prepared by treating Cl_2 with $IrCl(CO)[(C_6H_5)_3P]_2$ did not react with $SnCl_2$ under the usual conditions employed in our studies.

Moreover, in an attempt to prepare $IrCl_2(SnCl_3)(CO)[(C_6H_5)_3P]_2$ by treating stannic chloride with $IrCl(CO)[(C_6H_5)_3P]_2$ or $IrHCl_2(CO)[(C_6H_5)_3P]_2$, a compound whose analysis corresponds to $IrCl_2(SnCl_3)(CO)[(C_6H_5)_3P]$ is formed. It appears that one phosphine ligand is lost to give an apparently five-coordinate iridium(III) species although octahedral coordination may well be achieved through chloride bridging. The insolubility of this compound has prevented any further investigation.

$[(CH_3)_4N]_2[IrCl_3(SnCl_3)_2(CO)]$.—It is also found that stannous chloride will promote the interaction of iridium and an alkanolic solvent in the absence of triphenylphosphine. During the preparation of $Ir_2Cl_6(SnCl_2\cdot solvent)_4$ in ethanol solution it was found that prolonged refluxing led to the formation of a carbonyl species which could be precipitated as a tetramethylammonium salt: $[(CH_3)_4N]_2[IrCl_3(SnCl_3)_2(CO)]$.

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Anionic Halogenocarbonyls of Rhenium

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The action of halide ions upon decacarbonylrhenium and the halogenocarbonylrheniums has been investigated. The anions $Re(CO)_4I_2^-$, $Re(CO)_4IBr^-$, $Re(CO)_4Br_2^-$, $Re(CO)_3I_3^{2-}$, $Re_2(CO)_7Cl_3^-$, $Re_2(CO)_7Cl_2Br^-$, $Re_2(CO)_7Br_3^-$, and $Re_2(CO)_8I_2^{2-}$ are reported and their structures discussed.

Introduction

The direct replacement of carbonyl groups in metal carbonyls by halide ions has previously been reported for the hexacarbonyls of chromium, molybdenum, and tungsten[1] and for the carbonyl and halogenocarbonyls of manganese.[2] We now report the corresponding replacement reactions for the carbonyl and halogenocarbonyls of rhenium.

Results

Reaction of halide ions upon halogenopentacarbonyls of rhenium for a limited reaction time resulted in the formation of the dihalogenotetracarbonylrhenates.

$$\left.\begin{array}{l}\mathrm{Re(CO)_5X + Y^-}\\ \mathrm{Re(CO)_5Y + X^-}\end{array}\right\rangle \longrightarrow \mathrm{Re(CO)_4XY^- + CO}$$

Prolonged reaction times resulted in the elimination of a further molecule of carbon monoxide and formation of the triiodotricarbonylrhenate ion.

$$\mathrm{Re(CO)_5I + 2I^- \longrightarrow Re(CO)_3I_3^{2-} + 2CO}$$

At higher temperatures (over 140°) the interaction of halide ions and halogenopentacarbonylrheniums gave ions of formula $Re_2(CO)_7X_2Y^-$.

Two possible routes for the formation of these compounds involve either initial formation of the dimeric tetracarbonyl halide and subsequent attack by halide ion or *vice versa*.

$$\mathrm{Re(CO)_5X \xrightarrow{heat} Re_2(CO)_8X_2 + 2CO \xrightarrow{Y^-} (Re_2(CO)_7X_2Y)^- + CO}$$

$$\mathrm{Re(CO)_5X \xrightarrow{Y^-} (Re(CO)_4XY)^- + CO \xrightarrow{Re(CO)_5X} (Re_2(CO)_7X_2Y)^- + 2CO}$$

Decacarbonyldimanganese and halide ions are known[2] to react to produce the ions $Mn_2(CO)_8X_2^{2-}$. The corresponding reaction of iodide ions with decacarbonyldirhenium gives only a very poor yield of a product which is believed to be $Re_2(CO)_8I_2^{2-}$.

Experimental Section

Tetraethylammonium Diiodotetracarbonylrhenate.—Iodopentacarbonylrhenium (0.5 g.) and tetraethylammonium iodide (0.26 g.) were heated in ethanol (20 ml.) under reflux for 4 hr.

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[1] E. O. Fischer and K. Öfele, *Z. Naturforsch.*, **14b**, 763 (1959); *Chem. Ber.*, **93**, 1151 (1960); E. W. Abel, M. A. Bennett, and G. Wilkinson, *Chem. Ind.* (London), 442 (1960); E. W. Abel, I. S. Butler, and J. Reid, *J. Chem. Soc.*, 2068 (1963).

[2] E. W. Abel and I. S. Butler, *ibid.*, 434 (1964); R. J. Angelici, *Inorg. Chem.*, **3**, 1099 (1964).