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: $[(CH_3)_4N]_2[IrCl_3(SnCl_3)_2(CO)]$.

Acknowledgments.—We are greatly indebted to E. I. du Pont de Nemours and Co. for a generous contribution to research expenses, to Albright and Wilson Ltd. for gifts of triphenylphosphine, and to Johnson-Matthey and Co., Ltd., for the loan of iridium salts. The awards of a N.A.T.O. postdoctoral fellowship (R. C. T.) and an 1851 Exhibition Overseas Science Scholarship (J. F. Y.) are gratefully acknowledged.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1., AND THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF BRISTOL, BRISTOL 8, ENGLAND

Anionic Halogenocarbonyls of Rhenium

BY E. W. ABEL, I. S. BUTLER, M. C. GANORKAR, C. R. JENKINS, AND M. H. B. STIDDARD

Received August 16, 1965

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.

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

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

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

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*.

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

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

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.

---

[1] E. O. Fischer and K. Öfele, *Z. Naturforsch.*, **14**b, 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).

TABLE I

TETRAETHYLAMMONIUM TRIHALOGENOHEPTACARBONYLDIRHENATES

$(C_2H_5)_4N^+[Re_2(CO)_7X_2Y]^-$			Found, %				Calcd., %			
X	Y	Yield, %	C	H	N	Halogen	C	H	N	Halogen
Cl	Cl	48	22.1	2.68	...	13.5	22.4	2.51	...	13.2
Cl	Br	34	20.9	2.26	...	18.8	21.2	2.37	...	17.7
Br	Br	63	19.1	2.28	1.50	26.0	19.2	2.15	1.48	15.6

TABLE II

ANIONIC HALOGENOCARBONYLS OF RHENIUM

	Compd.	Color	Infrared bands in C–O stretching region
$(C_2H_5)_4N^+$	$Re(CO)_4I_2^{-a}$	Pale yellow	2105 m, 2004 s, 1980 s, 1925 s (Nujol) 2108 m, 2000 s, 1980 s, 1925 s ($CHCl_3$)
$(C_2H_5)_4N^+$	$Re(CO)_4IBr^{-b}$	Pale yellow	2108 m, 2004 s, 1980 s, 1925 s (Nujol) 2108 m, 2002 s, 1980 s, 1925 s ($CHCl_3$)
$(C_2H_5)_4N^+$	$Re(CO)_4Br_2^-$	Pale cream	
$(C_2H_5)_4N^+$	$Re(CO)_3I_3^{2-c}$	White	2002 s, 1885 s, 1860 s (Nujol)
$(C_2H_5)_4N^+$	$Re_2(CO)_7Br_3^-$	White	2040 w, 2026 s, 1928 s, 1906 s ($CHCl_3$)
$(C_2H_5)_4N^+$	$Re_2(CO)_7Cl_2Br^-$	White	2042 w, 2024 s, 1927 s, 1904 s ($CHCl_3$)
$(C_2H_5)_4N^+$	$Re_2(CO)_7Cl_3^-$	White	2045 w, 2025 s, 1926 s, 1904 s ($CHCl_3$)
$[(CH_3)_4N^+]_2$	$Re_2(CO)_8I_2^{2-}$	White	2025 m, 1885 s (Nujol) 2027 m, 1920 s (diglyme)

[a,b,c] Conductances (measured in 10^{-3} *M* solution in $C_6H_5NO_2$) [Λ_m]: (*a*) 26.8; (*b*) 24.5; (*c*) 54.6 ohm^{-1} cm.^{2}.

After cooling, light petroleum (b.p. 40–60°) was added to the solution. The pale yellow crystals (0.55 g.), which separated, were recrystallized from chloroform and pumped at 30° (0.01 mm.) to remove possible unreacted halogenocarbonyl. The product was soluble in polar solvents and was stable to air and water. *Anal.* Calcd. for $C_{12}H_{20}I_2O_4NRe$: C, 21.1; H, 2.9 N, 2.1; I, 37.2. Found: C, 21.3; H, 3.1; N, 2.0; I, 37.0.

Tetraethylammonium Dibromotetracarbonylrhenate.—Bromopentacarbonylrhenium (0.5 g.) and tetraethylammonium bromide were heated together in diethylene glycol–dimethyl ether at 120° for *ca.* 3 hr. The resulting solution was filtered hot, and then the addition of light petroleum (b.p. 40–60°) caused precipitation of pale cream crystals. These were separated by decantation and washed with light petroleum (2 × 20 ml.). Excess solvent was removed at 20° (0.1 mm.), and finally treatment at 40° (0.1 mm.) removed possible presence of unreacted bromopentacarbonylrhenium to leave tetraethylammonium dibromotetracarbonylrhenate. *Anal.* Calcd. for $C_{12}H_{20}Br_2O_4NRe$: C, 24.4; H, 3.4. Found: C, 23.9; H, 3.4.

Tetraethylammonium Bromoiodotetracarbonylrhenate.—Iodopentacarbonylrhenium (0.5 g.) and tetraethylammonium bromide (0.21 g.) were heated in diethylene glycol–dimethyl ether (30 ml.) at 120° for 4 hr. After cooling, the addition of light petroleum (50 ml.) gave pale yellow crystals (0.46 g.), which were recrystallized from chloroform. Pumping at 30° (0.01 mm.) removed possible unreacted halogenocarbonyl to leave the pure product. *Anal.* Calcd. for $C_{12}H_{20}BrIO_4NRe$: C, 22.7; H, 3.2; N, 2.2; I, 20.0; Br, 12.6. Found: C, 23.1; H, 3.2; N, 2.4; I, 20.6; Br, 12.8.

The same reaction under these conditions between bromopentacarbonylrhenium and tetraethylammonium iodide produced a product with identical analyses and spectrum.

Bistetraethylammonium Triiodotricarbonylrhenate.—Iodopentacarbonylrhenium (0.5 g.) and tetraethylammonium iodide (0.4 g.) were heated in ethanol under reflux, until evolution of carbon monoxide ceased (*ca.* 8 hr.). After cooling and addition of light petroleum (50 ml.), white crystals were deposited. These were washed with chloroform and dried *in vacuo*. The bistetraethylammonium triiodotricarbonylrhenate (*Anal.* Calcd. for $C_{19}H_{40}I_3N_2O_3Re$: C, 25.0; H, 4.4; N, 3.1; I, 41.8. Found: C, 24.8; H, 4.4; N, 3.2; I, 41.8.) was totally insoluble in all common nonpolar solvents but moderately soluble in ethanol and nitrobenzene.

Tetraethylammonium Trihalogenoheptacarbonyldirhenates.—Tetraethylammonium halide (*ca.* 0.3 g.) was heated with a slight excess of halogenopentacarbonylrhenium (*ca.* 0.5 g.) in diethylene glycol–dimethyl ether (30 ml.) at 140° until the evolution of carbon monoxide ceased. The resulting mixture was filtered hot, and to the cooled solution was added 150 ml. of light petroleum (b.p. 40–60°). The white crystals which precipitated were washed with further light petroleum (2 × 20 ml.), and solvent was then removed at 20° (0.1 mm.). Subsequent treatment at 60° (0.1 mm.) for a short time ensured the removal of any unreacted halogenopentacarbonyl. Subsequent recrystallization from diethylene glycol–dimethyl ether–light petroleum gave crystals of the pure product (Table I).

Discussion

The infrared spectra of the new ions reported are given in the Table II. In the ions $Re(CO)_4XY$, X and Y can either be the same or different, and the presence of four strong infrared bands in the C–O stretching region is evidence of the C_{2v} or C_s symmetry allocated. The triiodotricarbonylrhenate ion, $Re(CO)_3I_3^{2-}$, can have either a *trans* (C_{2v}) or a *cis* (C_{3v}) structure. Ions with these two symmetries will have, respectively, three ($2A_1 + B_1$) and two ($A_1 + E$) infrared-active C–O stretching modes. The low solubility of this compound precludes the measurement of its spectrum in solution. The solid state spectrum of the compound contains three bands in the C–O stretching region, but this is not definitive evidence for a *trans* structure. It is possible that the anion has the *cis* structure and that the splitting of the E_1 band is due to solid state effects. The positions of the C–O stretching modes in the spectrum of this ion are notably lower than those of other species reported herein, owing to the presence of the double negative charge on the mononuclear anion.

The ions $Re_2(CO)_7X_2Y^-$ formed at high temperature are very insoluble, and their physical properties have been difficult to study. Analyses, however, are entirely consistent with this formulation, and structures can be considered to be based on the dihalogenooctacarbonylrheniums.[3]

The two most likely structures are represented by I and II (Figure 1). Both of these proposed structures

---

(3) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3150 (1958).

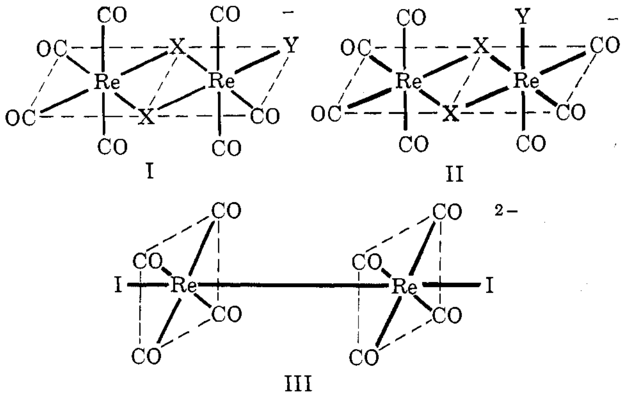

Figure 1.

have C_s symmetry, and in each case seven ($5A' + 2A''$) infrared-active stretching modes are expected. The low solubility of these salts, however, prevents the measurement of satisfactory solution spectra, and only four clear maxima could be distinguished in dilute solutions in chloroform.

The reaction of iodide ions with decacarbonyldirhenium produced a compound with a remarkably simple spectrum containing two bands in the C–O stretching region (Table I). This compound presumably contains the ion $Re_2(CO)_8I_2^{2-}$, with structure III, and is completely analogous to the product of the reaction of decacarbonyldimanganese.[2] Yields of this material were exceedingly small, and only moderately satisfactory analyses could be obtained. The ion does not appear to be stable in most solvents, and, on standing, many extra bands appear in the infrared spectra, presumably owing to decomposition or isomerization.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS

Chelate and Bridge Complexes of Metal Carbonyl Compounds with a Ditertiary Phosphine: A Study of Their Formation and Interconversion

BY ROGER J. MAWBY, DONALD MORRIS, ERLIND M. THORSTEINSON, AND FRED BASOLO

Received July 23, 1965

The reactions of the compounds $Co(NO)(CO)_3$ and $Fe(NO_2)(CO)_2$ with a severalfold excess of the diphosphine 1,2-bis(diphenylphosphino)ethane (diphos, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) are shown to yield, in toluene or tetrahydrofuran solution, fairly long-lived intermediates $Co(NO)(CO)_2$(diphos) and $Fe(NO)_2(CO)$(diphos) in which the diphosphine is only attached to the metal by one phosphorus atom. These intermediates are slowly converted to the chelate complexes $Co(NO)(CO)$(diphos) and $Fe(NO)_2$(diphos) at rates which are *independent* of the free diphosphine concentration. Similar results have been obtained for $CH_3Mn(CO)_5$ which is converted, *via* an intermediate believed to be $CH_3COMn(CO)_4$(diphos), to the chelate complex $CH_3COMn(CO)_3$(diphos). Use of metal:diphosphine molar ratios of 2:1 yields complexes of the type $[Co(NO)(CO)_2]_2$(diphos), in which the diphosphine acts as a bridge between two metal atoms. These complexes can also be converted to the corresponding chelate complexes by reaction with excess diphosphine, but at a rate which is *dependent* on the free diphosphine concentration. The unsymmetrical bridge complex, $Fe(NO)_2(CO)$(diphos)$Co(NO)(CO)_2$, has been isolated and characterized.

Introduction

The diphosphine, 1,2-bis(diphenylphosphino)ethane (diphos, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$), has been found[1,2] to form a wide variety of complexes with transition metals in which one or more molecules of the diphosphine are attached to the metal by both phosphorus atoms (*i.e.*, chelate complexes).

In the formation of metal complexes with polydentate chelating ligands it is usually impossible to observe the presence of intermediates in which one or more donor atoms are not attached to the metal. It would appear that the rate-determining step for these reactions is the attack on the metal atom by the first donor atom and that subsequent attack by the remaining donor atom or atoms is too fast to allow the observation of an intermediate.

While studying the reactions of various metal carbonyl compounds with uni- and bidentate nucleophiles, it was observed that the reactions of some of these compounds with the diphosphine mentioned above did not follow the pattern of a single rate-determining step followed by a fast second step. This prompted further investigations of these reactions, which are described in this paper.

During the course of this work several new complexes of the diphosphine were prepared, in some of which the diphosphine was chelated to a single metal atom (chelate complexes), while in others the diphosphine acted as a bridge between two metal atoms (bridge complexes). It was even possible to prepare a hetero-metal bridge compound.

Experimental Section

Preparation of Starting Materials.—The diphosphine, 1,2-bis(diphenylphosphino)ethane, was prepared by the method described by Chatt and Hart.[1] The preparation of $CH_3Mn(CO)_5$ from $Mn_2(CO)_{10}$ (a gift from the Ethyl Corporation) was carried

---

[1] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).
[2] A. G. Osborne and M. H. B. Stiddard, *ibid.*, 4715 (1962).