188. *Iodocarbonyl Derivatives of Iridium.*

By L. Malatesta, L. Naldini, and F. Cariati.

The carbonylation of iridium tri- or tetra-iodide, alone or mixed with potassium iodide, gives $IrI_3(CO)_3$, $[IrI_3(CO)_2]_2$, $Ir_2I_6(CO)_3$, $[Ir_2I_6(CO)_4]^{2-}$, $[IrI_4(CO)]^-$, $[IrI_4(CO)_2]^-$, and $[IrI_5(CO)]^{2-}$. On reduction with metallic zinc the fourth and the sixth of these gave $[IrI_2(CO)_2]^-$, and the fifth and the seventh gave $[IrI_3(CO)]^-$.

$K[IrBr_5(CO)]$ and $K[IrCl_5(CO)]$ have been prepared by the action of bromine and chlorine on the corresponding iodo-derivatives.

The only iodocarbonyl compounds of iridium known until a few years ago were $IrI(CO)_3$ and $IrI_2(CO)_2$, prepared by Hieber *et al.*[1] by the action of carbon monoxide on IrI_3,H_2O at atmospheric pressure at 150°. Recently, Malatesta, and Sandroni[2] announced the preparation of $IrI_3(CO)_3$, $[IrI_3(CO)_2]_2$, $K[IrI_4(CO)_2]$, and $K_2[IrI_5(CO)]$. Soon afterwards Naldini and Brambilla[3] described the iodocarbonyliridates, $K_2[Ir_2I_6(CO)_4]$ and $K[IrI_4(CO)]$. We have completed this research, and describe here the preparation and properties of these compounds and other iridium carbonyl derivatives prepared from them.

Carbonylation of Iridium Tri-iodide. When iridium tri-iodide is treated with carbon monoxide at 250 atm. for about 18 hours followed by very slow cooling, the main product is the tri-iodotricarbonyliridium $IrI_3(CO)_3$ (I), a rather unstable substance which loses one molecule of carbon monoxide slowly in the dry state and almost immediately in solution, giving the dimeric tri-iododicarbonyliridium $[IrI_3(CO)_2]_2$ (II).

Under the same conditions, but with rapid final cooling, a mixture of (I), (II), and hexaiodotricarbonyldi-iridium $Ir_2I_6(CO)_3$ (III) is obtained. Compounds (II) and (III) are very stable both in the solid state and in solution; their infrared spectra do not show any frequencies ascribable to carbon monoxide bridges.

Carbonylation of Iridium Tri-iodide mixed with Potassium Iodide.—At 200 atm. and 200—250° a mixture of the two iodocarbonyliridates $K_2[Ir_2I_6(CO)_4]$ (IV) and $K[IrI_4(CO)]$ (V) is obtained, both of which behave in acetone as strong electrolytes. At higher temperatures compound (V) is the main product. Compound (IV) is probably formed by the action of Hieber's dicarbonyl on potassium iodide:

$$2IrI_2(CO)_2 + 2KI = K_2[Ir_2I_6(CO)_4] \quad (IV)$$

Although deriving from the d^7-configuration of iridium(II), compound (IV) is diamagnetic; this behaviour can be explained by considering it as dimeric, with a metal–metal bond. The molecular weight in acetone solution is in fact about $\frac{1}{3}$ that of $K_2[Ir_2I_6(CO)_4]$, as would be expected if the dimeric salt is completely dissociated. This compares with the molecular weight found for $K[IrI_4(CO)]$, which is half the value calculated for the monomer.

Carbonylation of Iridium Tetraiodide mixed with Potassium Iodide.—At 200 atm. and 200°, with a 1 : 1 iridium to potassium ratio, the dicarbonyl salt $K[IrI_4(CO)_2]$ (VI) is the main product; it is a red crystalline compound soluble in water (better if acidified with some hydrogen iodide), diethyl ether, acetone, and ethyl alcohol. Above 250°, under carbon monoxide, the salt (VI) decomposes according to the reaction:

$$4K[IrI_4(CO)_2] \longrightarrow 2K_2[IrI_5(CO)] \ (VII) + [IrI_3(CO)_2]_2 + 2CO$$

The pentaiodocarbonyliridate (VII) can also be obtained as the main product of the carbonylation of a 1 : 2 mixture of iridium tetraiodide and potassium iodide at 250° and 200 atm.

---

[1] Hieber, Lagally, and Mayr, *Z. anorg. Chem.*, 1941, **246**, 138.

[2] Malatesta and Sandroni, Internat. Conf. on Co-ordination Chem., *Chem. Soc. Special Publ.* No. 13, 1959, p. 122.

[3] Naldini and Brambilla, *Rend. Ist. Lomb. Scienze*, 1960, **94**, 742.

Reactions of the Iodocarbonyliridates.—(1) *Reduction with zinc.* The carbonyliridates (IV) and (VI), on reduction with zinc, give an anion derived from univalent iridium, which has been isolated as the tetraphenylarsonium salt: $(AsPh_4)[IrI_2(CO)_2]$ (VIII). This behaves as a strong electrolyte and shows two strong bands of about the same intensity in the infrared spectrum, suggesting that if, as is likely, the anion is planar [4] the CO groups are in the "*cis*" configuration. Reduction of the monocarbonyliodoiridates (V) and (VII) gives instead an anion, derived from bivalent iridium, which has also been isolated as the tetraphenylarsonium salt, $(AsPh_4)[IrI_3(CO)]$ (IX).

(2) *Reaction with potassium iodide and hydriodic acid, and thermal decomposition.* We tried to prepare the pentaiodoiridate, $K_2[IrI_5]$, from the tetraiododicarbonyliridate (VI) by refluxing it for 6 hours with 55% aqueous hydrogen iodide, evaporating the solution to dryness, and extracting the residue with ethyl acetate. We obtained unchanged tetraiododicarbonyliridate (VI), and the non-extractable solid was a mixture of the pentaiodocarbonyliridate (VII) and potassium iodide. The complete decarbonylation of compound (VI) did not take place, the only reactions being:

$$K[IrI_4(CO)_2] \xrightarrow{HI + KI} K[IrI_4(CO)] + CO$$

$$K[IrI_4(CO)] + KI \longrightarrow K_2[IrI_5(CO)]$$

The thermal decomposition of the pentaiodocarbonyliridate (VII) gave no better results. In fact no reaction was observed up to 250°, and at higher temperatures the compound decomposed slowly to give an insoluble residue of iridium iodide and metallic iridium. Thus the compound previously [2] thought to be $K_2[IrI_5]$ was in fact the carbonyl compound (VII).

(3) *Reaction with bromine and chlorine.* The iodocarbonyliridates (VI) and (VII), when boiled with an aqueous solution of hydrogen bromide and bromine, gave the compound $K_2[IrBr_5(CO)]$ (X), which had previously [5] been erroneously formulated as $K_2[IrBr_5]$. By analogy, the compound formulated [5] as $(AsPh_4)[IrBr_4]$ must be considered as $(AsPh_4)[IrBr_4(CO)]$. The analogous reaction of the same iodocarbonyliridates, (VI) and (VII), with aqueous hydrogen chloride and chlorine gave $K_2[IrCl_5(CO)]$ (XI), which was isolated as the tetraphenylarsonium salt.

The infrared spectra of the salts $K[IrX_5(CO)]$ ($X = Cl, Br, I$) shows a shift of the CO stretching band to lower wave-numbers in the order $Cl > Br > I$, also in accordance with the inductive power of the halogen atom.

DISCUSSION

The trend of the above carbonylation reaction indicates that the formation of low-valent carbonyl derivatives of iridium is more difficult from the tri-iodide than from the trichloride and tribromide. In fact, the latter give,[5] first $IrX_2(CO)_2$ and $IrX(CO)_3$ ($X = Cl, Br$), and, with longer reaction times, the pure carbonyls $Ir(CO)_4$ and $Ir(CO)_3$, which have never been obtained by carbonylation of iridium tri-iodide.

According to Hieber *et al.*[1] the reduction which usually accompanies the carbonylation reaction occurs because the formation of $COCl_2$ and $COBr_2$ makes the elimination of the halogens easier. In our opinion, the formation of $COCl_2$ and $COBr_2$, though obviously favouring the removal of chlorine, and to a lesser extent bromine, has only a minor influence on the course of the reaction. The determining factor seems instead to be the stabilisation of the low-valent states of iridium by co-ordination of the π-bonding carbon monoxide molecules, or, conversely, the destabilisation of the halogen–iridium bonds brought about by co-ordination.* This view is supported by the fact that the salt

---

* This destabilisation effect decreases from chlorine to iodine, probably because of the different electronegativities.

[4] Nyholm, *Proc. Chem. Soc.*, 1961, 294.

[5] Malatesta and Canziani, *J. Inorg. Nuclear Chem.*, 1961, **19**, 81.

$K_2[Ir_2Cl_5(CO)_4]$, in which iridium has the average oxidation number 1·5, is remarkably resistent to oxidation, whilst $K_2[Ir_2I_5(CO)_4]$, which can be obtained in solution from the former by exchange with potassium iodide, is easily oxidised.[5] It is an analogous consequence of this same fact that the tendency of carbon monoxide to react with the iridium(III) halides increases from the chloride to the iodide so much that iridium tri-iodide can absorb, in the cold, three molecules of carbon monoxide.

EXPERIMENTAL

Infrared spectra were taken on a Perkin-Elmer model 137 spectrophotometer, for Nujol mulls (see Table). The carbonylation reactions were carried out in a stainless steel pressure-vessel with a capacity of about 100 ml. The reactants were contained in a test-tube (1 × 15 cm.) inside a copper tube. Magnetic susceptibilities were measured with a Gouy balance at room temperature.

Infrared spectra of iridium complexes.

Compound	Oxidn. no. of Ir	CO stretching bands (cm.$^{-1}$)	Compound	Oxidn. no. of Ir	CO stretching bands (cm.$^{-1}$)
$IrI_3(CO)_3$	3	2178w, 2114	$K[IrI_4(CO)]$	3	2051
$[IrI_3(CO)_2]_2$	3	2123, 2087	$(AsPh_4)[IrI_4(CO)]$	3	2000
$Ir_2I_6(CO)_3$	3	2118, 2074, 2041sh	$K_2[IrI_5(CO)]$	3	2032
$(AsPh_4)[IrI_2(CO)_2]$	1	2020, 1941	$(AsPh_4)_2[IrI_5(CO)]$	3	2000
$K_2[Ir_2I_6(CO)_4]$	2	2136, 2092	$K_2[IrBr_5(CO)]$	3	2061
$(AsPh_4)_2[Ir_2I_6(CO)_4]$	2	2100, 2070	$(AsPh_4)_2[IrBr_5(CO)]$	3	2008
$K[IrI_4(CO)_2]$	3	2118, 2066	$K_2[IrCl_5(CO)]$	3	2079
$(AsPh_4)[IrI_4(CO)_2]$	3	2109, 2074	$(AsPh_4)_2[IrCl_5(CO)]$	3	2012
$(AsPh_4)[IrI_3(CO)]$	2	2000			

Tri-iodotricarbonyliridium(III), $IrI_3(CO)_3$ (I).—Finely ground iridium tri-iodide, in a test-tube, was placed in a pressure-vessel into which carbon monoxide was pumped up to a pressure of 250 atm. The vessel was kept at 100° for 18 hr., and then the temperature was slowly lowered. A dark red crystalline sublimate *A* was collected from the top of the test-tube and a brown-red product *B* from the bottom; both had the correct analysis for the required *product* (Found for *A* and *B*, respectively: I, 58·0, 57·5; Ir, 28·9, 29·3; CO, 13·0, 12·8. $C_3I_3IrO_3$ requires I, 57·9; Ir, 29·2; CO, 12·8%).

Hexaiodotetracarbonyldi-iridium(III), $[IrI_3(CO)_2]_2$ (II).—Iridium tri-iodide was treated with carbon monoxide under the conditions used in the previous experiment. After being heated for 18 hr., the pressure-vessel was rapidly cooled with water. A dark red crystalline sublimate of the tricarbonyl compound (I) was observed at the top of the test-tube, and from the bottom a product *C* was collected. This, on treatment with hexane and benzene, gave an insoluble product *D*, and a solution from which brown-red crystals of *compound* (II) were obtained [Found: I, 60·4; Ir, 30·7; CO, 8·8%; *M* (cryoscopy in dibromoethane, 1·1% solution), 1197. $C_4I_6Ir_2O_4$ requires I, 60·5; Ir, 30·7; CO, 8·9%; *M*, 1258].

Hexaiodotricarbonyldi-iridium(III), $Ir_2I_6(CO)_3$ (III).—The insoluble product *D* from the previous preparation yielded (from dry ether–chloroform) dark red crystals of *compound* (III) (Found: I, 62·3; Ir, 30·9; CO, 6·8. $C_3I_6Ir_2O_3$ requires I, 61·9; Ir, 31·2; CO, 6·8%).

Potassium Hexaiodotetracarbonyldi-iridate(II), $K_2[Ir_2I_6(CO)_4]$ (IV).—Iridium tri-iodide (0·01 mole) and potassium iodide (0·01 mole) were treated with carbon monoxide at 200 atm., and the temperature was kept at 250° for 24 hr. The crude product was washed with benzene, to separate the non-ionic iodocarbonyliridium derivatives, and then treated with ether. The solid residue *E* was filtered off. The solution, on concentration, yielded orange crystals of the *product* (IV) [Found: I, 55·9; Ir, 28·6; CO, 8·0%; *M* (osmometry in acetone, 0·96% solution), 447. $C_2I_3IrKO_2$ requires I, 56·9; Ir, 28·8; CO, 8·4%; *M*, 1336]; molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 30·2 ohm^{-1}. The compound is diamagnetic.

Tetraphenylarsonium Hexaiodotetracarbonyldi-iridate(II), $(AsPh_4)_2[Ir_2I_6(CO)_4]$.—A solution of tetraphenylarsonium iodide in absolute ethanol was added to a solution of the carbonyl-iridate (IV) in ethanol. Light red crystals of the *product*, m. p. 284°, separated immediately (Found: C, 30·8; H, 1·8; I, 36·9; Ir, 18·7; CO, 5·5. $C_{26}H_{20}AsI_3IrO_2$ requires C, 30·8; H, 1·99; I, 37·6; Ir, 19·0; CO, 5·5%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 24·5 ohm^{-1}. The compound is diamagnetic.

Potassium Tetraiodocarbonyliridate(III), $K[IrI_4(CO)]$ (V).—The solid residue *E* (above) was dissolved in acetone and the solution filtered. The filtrate, on evaporation under reduced pressure, yielded dark red crystals of the *salt* (V) [Found: I, 66·1; Ir, 24·9; CO, 3·6%; *M* (osmometry in acetone, 0·92% solution), 365. CI_4IrKO requires I, 66·2; Ir, 25·0; CO, 3·6%; *M*, 767]; molar conductance (10^{-3}M-solution in acetone at 30°), 171·3 ohm^{-1}.

Tetraphenylarsonium Tetraiodocarbonyliridate(III), $(AsPh_4)[IrI_4(CO)]$.—A solution of tetraphenylarsonium iodide in absolute ethanol was added to an ethanol solution of the salt (V). Red crystals of the *product* separated, m. p. 273° (Found: C, 26·9; H, 1·8; I, 45·3; Ir, 17·1; CO, 2·5. $C_{25}H_{20}AsI_4IrO$ requires C, 27·0; H, 1·8; I, 45·7; Ir, 17·3; CO, 2·5%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 24·5 ohm^{-1}.

Potassium Tetraiododicarbonyliridate(III), $K[IrI_4(CO)_2]$ (VI).—Iridium tetraiodide (0·01 mole) and potassium iodide (0·01 mole) were treated with carbon monoxide at an initial pressure of 200 atm., and the temperature was kept at 200° for 12 hr. The crude product was washed with benzene, to separate the non-ionic iodocarbonyliridium derivatives, and then dissolved in dry ether. The filtered solution was concentrated under reduced pressure, and yielded red crystals of the *salt* (VI) which were diamagnetic, and very soluble in ether, acetone, alcohol, and dilute hydriodic acid (Found: I, 63·7; Ir, 24·3; K, 4·9; CO, 7·4. $C_2I_4IrKO_2$ requires I, 63·8; Ir, 24·2; K, 4·9; CO, 7·5%); molar conductance (10^{-3}M-solution in acetone at 30°), 135 ohm^{-1}.

Tetraphenylarsonium Tetraiododicarbonyliridate(III), $(AsPh_4)[IrI_4(CO)_2]$.—A solution of tetraphenylarsonium iodide in methanol was added to a solution of the salt (VI). Red crystals of the *product* separated, m. p. 210° (Found: C, 27·1; H, 1·6; I, 35·0; Ir, 16·8; CO, 3·7%. $C_{26}H_{20}AsI_4IrO_2$ requires C, 27·4; H, 1·7; I, 34·6; Ir, 16·8; CO, 3·8%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 29·4 ohm^{-1}.

Potassium Pentaiodocarbonyliridate(III), $K_2[IrI_5(CO)]$ (VII).—Iridium tetraiodide (0·01 mole) and potassium iodide (0·02 mole) were treated with carbon monoxide at an initial pressure of 200 atm., and the temperature was kept at 240° for 12 hr. The crude product, washed with benzene as above, then with ethyl ether in order to separate a very small quantity of the salt (VI), was finally dissolved in acetone. The filtered acetone solution, on concentration under reduced pressure, yielded dark red crystals of the *salt* (VII) (Found: I, 68·0; Ir, 20·3; K, 8·6; CO, 3·2. CI_5IrK_2O requires I, 68·0; Ir, 20·6; K, 8·4; CO, 3·0%); molar conductance (10^{-3}M-solution in acetone at 30°), 242 ohm^{-1}.

Tetraphenylarsonium Pentaiodocarbonyliridate(III) $(AsPh_4)_2[IrI_5(CO)]$.—Addition of a methanolic solution of tetraphenylarsonium iodide to a methanolic solution of the salt (VII) gave, after a few minutes, brown-red crystals of the *product*, m. p. 308° (Found: C, 36·4; H, 2·3; I, 40·0; Ir, 11·5; CO, 1·7. $C_{49}H_{40}As_2I_5IrO$ requires C, 36·2; H, 2·4; I, 39·2; Ir, 11·8; CO, 1·7%), molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 56·5 ohm^{-1}.

Tetraphenylarsonium Di-iododicarbonyliridate(I), $(AsPh_4)[IrI_2(CO)_2]$ (VIII).—Some zinc powder was added to an ethanolic solution of $(AsPh_4)[IrI_4(CO)_2]$ and the solution was stirred until it became pale yellow. After filtration and concentration under reduced pressure green-yellow diamagnetic crystals, m. p. 158°, separated. The same reaction carried out with $(AsPh_4)_2[Ir_2I_6(CO)_4]$ gave an identical *product* (VIII) (Found: C, 32·9; H, 2·3; I, 28·4; Ir, 21·7; CO, 6·2. $C_{26}H_{20}AsI_2IrO_2$ requires C, 32·6; H, 2·3; I, 28·9; Ir, 21·7; CO, 6·3%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 29·4 ohm^{-1}.

Tetraphenylarsonium Tri-iodocarbonyliridate(II), $(AsPh_4)[IrI_3(CO)]$ (IX).—Some zinc powder was added to ethanolic solutions, of both $K_2[IrI_5(CO)]$ (VII) and $K[IrI_4(CO)]$ (V). After filtration and addition of tetraphenylarsonium iodide, both solutions yielded the *product* (IX), brown needles, diamagnetic, m. p. 256° (Found: C, 29·3; H, 2·4; I, 37·9; Ir, 19·4; CO, 2·8. $C_{25}H_{20}AsI_3IrO$ requires C, 30·5; H, 2·0; I, 38·6; Ir, 19·6; CO, 2·8%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 28·7 ohm^{-1}.

Potassium Pentabromocarbonyliridate(III), $K_2[IrBr_5(CO)]$ (X).—A mixture of $K[IrI_4(CO)_2]$ (VI) (8 g., 0·01 mole) and potassium bromide (1·2 g., 0·01 mole) was refluxed for ~1 hr. with 48% hydrogen bromide (50 ml.) and bromine (2 ml.) and evaporated to dryness. The residue was dissolved in the minimum amount of hot water; filtration yielded pink crystals (4 g.) of the *salt* (X). The product could be obtained in the same way from $K_3[IrI_5(CO)]$ (VII) (Found: Br, 57·8; Ir, 28·0; CO, 3·9. CBr_5IrK_2O requires Br, 57·3; Ir, 27·5; CO, 4·0%).

Tetraphenylarsonium Pentabromocarbonyliridate(III), $(AsPh_4)_2[IrBr_5(CO)]$.—From the above potassium salts, with tetraphenylarsonium bromide, pink needles of the *product* were obtained,

m. p. 293° (Found: C, 42·1; H, 2·9; Br, 27·9; Ir, 18·3; CO, 2·1. $C_{49}H_{40}As_2Br_5IrO$ requires C, 42·5; H, 2·9; Br, 28·8; Ir, 18·8; CO, 2·0%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 57·2 ohm^{-1}.

Potassium Pentachlorocarbonyliridate(III), $K_2[IrCl_5(CO)]$ (XI).—An acetone solution of $K_2[IrI_5(CO)]$ (VII) was treated with a solution of chlorine in carbon tetrachloride. The solvents were evaporated under reduced pressure, and the residue was washed with carbon tetrachloride, dissolved in ethanol, and the solution filtered. Addition of ether precipitated the *salt* (XI) as a pink crystalline diamagnetic powder, very soluble in water (Found: Cl, 36·9; Ir, 41·0; CO, 5·7. CCl_5IrK_2O requires Cl, 37·3; Ir, 40·4; CO, 5·9%).

Tetraphenylarsonium Pentachlorocarbonyliridate(III), $(AsPh_4)_2[IrCl_5(CO)]$.—From the methanolic solution of the above compound, with triphenylarsonium chloride in methanol, the *product*, m. p. 262°, was obtained (Found: C, 49·9; H, 3·3; CO, 2·3. $C_{49}H_{40}As_2Cl_5IrO$ requires C, 50·5; H, 3·4; CO, 2·4%); molar conductance (10^{-3}M-solution in nitrobenzene at 30°), 57·7 ohm^{-1}.

CENTRO DEI COMPOSTI DI CO-ORDINAZIONE DEL C.N.R.,
ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITÀ,
VIA C. SALDINI, 50, MILANO, ITALY.

[*Received, March 27th*, 1963.]