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REACTION OF POWDERED IRIDIUM WITH CHLORINE AND CARBON MONOXIDE: SOME NEW CHLOROCARBONYL DERIVATIVES OF IRIDIUM

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Summary

In a search for better methods of preparing carbonyl compounds of the transition metals the reaction of powdered iridium with carbon monoxide and chlorine under various conditions has been studied. The outcome of the reaction depends on the CO/Cl_2 ratio and on the temperature. The iridium(II) complex $Ir(CO)_2Cl$ (I) has been isolated, and its reactions with CO, $AsPh_4Cl$, PPh_3 and Cl^- ions examined. The anion $(IrCOCl_4)^-$ has been isolated as its caesium and bis(triphenylphosphine)iminium salts, and the complex $Ir_2(CO)_4Cl_6$ has been identified by mass spectrometry.

Introduction

Transition metal halides have long been known to react with carbon monoxide at atmospheric or high pressure to give halocarbonyls [1]. Reactions of iridium trihalides, $IrX_3 \cdot nH_2O$ (X = Cl, Br, I) with carbon monoxide at 150°C gave a series of iridium halocarbonyls [2], the main product being halotricarbonyliridium, $Ir(CO)_3X$ and the more unusual dihalodicarbonyliridium, which, owing to its very low stability, could be isolated as a by-product in the case of the reaction with chlorine. The reaction of Na_2IrX_6 (X = Cl, Br) with carbon monoxide at high temperature

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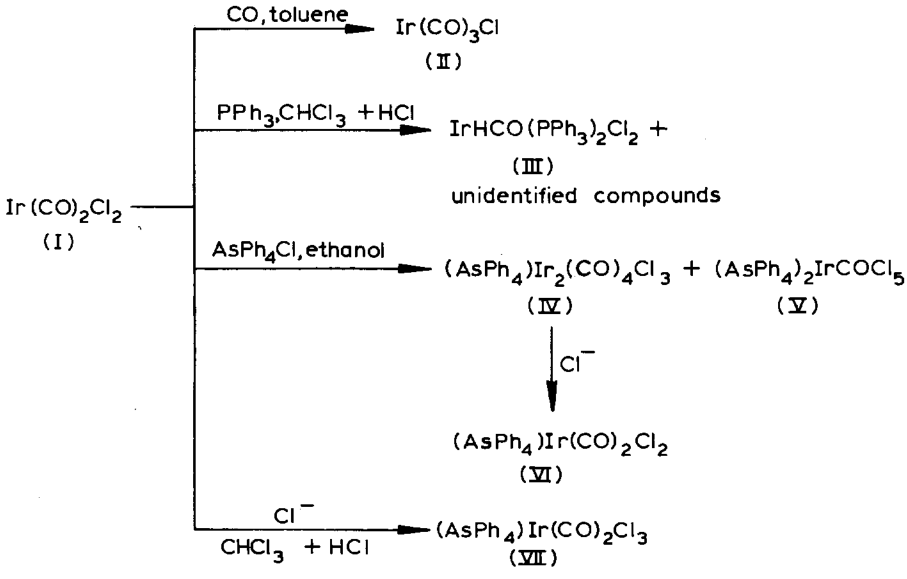
* Deceased.

(100–200°C) and pressure (150–200 atm), which is one of the traditional methods of preparing dodecacarbonyltetrairidium, gave a series of halocarbonylanions [4], which were also readily prepared from iridium trihalides by bubbling carbon monoxide into the 2-methoxyethanol solutions at 120°C [5] or from halide complexes by decarbonylation of formic acid [6]. Covalent iodocarbonyls of iridium were obtained by carbonylation of iridium tri- and tetra-iodide at 200–250°C and 250 atm [7].

Results and discussion

We obtained volatile carbonyl compounds by passing a mixture of chlorine and carbon monoxide over a layer of powdered commercial iridium at 350°C in a tubular furnace. The yields were rather poor because of the formation on the surface of the large metal grains of a thin carbon black layer which prevented a further attack. Better results were obtained by use of activated iridium obtained in situ by thermal decomposition of $(NH_4)_2IrCl_6$ at 400°C in a hydrogen atmosphere. Treatment of the activated metal with carbon monoxide and chlorine in the molar ratio 1/2 at 300°C gave a pale yellow volatile solid (yield 30%), which was identified from its elemental analysis, IR spectrum and chemical behaviour as $Ir(CO)_2Cl_2$ (I) [2,3]. It is noteworthy that higher yields can be achieved by supporting the metal on Al_2O_3; at temperature close to 100°C a yellowish-white bulky solid sublimes out. The compound, probably an adduct of formula $Ir(CO)_2Cl_2 \cdot nAlCl_3$, contains the $Ir(CO)_2Cl_2$ moiety, as indicated by the IR spectrum (ν(CO) ($CHCl_3$) 2160, 2120 cm^{-1}). Unfortunately, the large amount of $AlCl_3$ formed, prevented separation of the pure compound. Compound I is stable under an inert atmosphere, but it is quickly decomposed by most air as well as by donor solvents. It is slightly soluble in toluene and chloroform, insoluble in hydrocarbons, and fairly soluble in THF, acetone and ethanol, in which slow decomposition occurs. It was impossible to

SCHEME 1



obtain accurate magnetism data because of the low stability of the compound. Qualitative data, however indicate that compound I is paramagnetic (μ_{eff} 1.6–1.7 B.M.). The IR spectrum in toluene shows two strong absorption bands at 2160, 2140 cm^{-1}, which appear to be very similar to those reported for the analogous derivative of platinum (ν(CO)2200, 2162 cm^{-1}) [8]. The reactions of the unusual compound of iridium(II) can be summarized as shown in Scheme 1.

Compound I reacts both in solid state and in toluene solution with carbon monoxide to give the known $Ir(CO)_3Cl$ (II) [2]. The expected instability of the iridium(II) complexes in the presence of donor ligand was observed when I was treated with triphenylphosphine in chloroform containing HCl, the well known $IrHCO(PPh_3)_2Cl_2$(III) [9] being along formed with unidentified products. A disproportionation reaction occurred when I was treated with $AsPh_4Cl$ in ethanol; a deep green insoluble solid separated from the solution, and was identified as $(AsPh_4)Ir_2(CO)_4Cl_3$ (IV), and the known iridium(III) carbonyl compound $(AsPh_4)_2IrCOCl_5$(V) [5,10] was isolated from the mother liquors. The nature of compound IV was confirmed by the reaction with an excess of Cl^-, for instance by boiling it in ethanol with LiCl, which gave the yellow $(AsPh_4)Ir(CO)_2Cl_2$(VI) [5] as a result of the reversible reaction

$$[Ir_2(CO)_4Cl_3]^- + Cl^- \rightleftharpoons 2[Ir(CO)_2Cl_2]^-$$

Dissolution of I in chloroform in the presence of HCl gave the new carbonyl anion $[Ir(CO)_2Cl_3]^-$, which was isolated as the tetraphenylarsonium salt (VII).

Treatment of activated iridium with carbon monoxide and chlorine (molar ratio 1/2) at 200°C in the presence of dry gaseous HCl gave the anion $(IrCOCl_4)^-$, probably as $HIrCOCl_4$. The compound was characterized as the caesium (VIII) and bis(triphenylphosphine)iminium salts (IX).

When activated iridium was treated with a mixture of 2 mol of chlorine and 1 mol of carbon monoxide at 180°C an orange compound was isolated, and was identified by mass spectrometry as the dimeric compound $Ir_2(CO)_4Cl_6$(X). Its IR spectrum (see Table 1) was closely similar to that of the analogous iodo derivative [6]. Compound X is stable only in an inert atmosphere. Reaction of X with Cl^- ions in hydrochloric acid gave the anion $[Ir(CO)_2Cl_4]^-$, which was characterized as its tetraphenylarsonium salt (XI). Probably the reaction occurs through a nucleophilic attack of Cl^- and consequent rupture of the chlorine bridges.

Experimental

$Ir(CO)_2Cl_2$ (I)

The $(NH_4)_2IrCl_6$ (3 g) is kept for 5 h in a tubular furnace under a hydrogen stream at 450°C. After removal of the NH_4Cl sublimate, a nitrogen stream is passed, the temperature is decreased to 300°C, and a stream of CO and Cl_2 in a molar ratio 1/2 (0.7 ml CO and 1.7 ml Cl_2 min^{-1}) is admitted. Immediately a pale yellow sublimate is formed. After 5 h cooling under a nitrogen stream, the sublimate is collected under nitrogen (2.15 g; yield 30%). The compound is unstable to moisture.

TABLE 1

ANALYTICAL AND SPECTRAL DATA OF THE IRIDIUM COMPOUNDS

Compound	Color	Analyses (Found calcd. (%))				Infrared data ν(CO) (cm^{-1})
		C	H	Ir	Cl	
$Ir(CO)_2Cl_2$ (I)	pale yellow			60.25 (60.20)	20.20 (22.24)	2160s, 2140s (toluene)
$Ir(CO)_3Cl$ (II)	brown			61.20 (61.50)	11.60 (11.60)	2080s (Nujol)
$Ir(H)(CO)(PPh_3)_2Cl_2$ (III)	light yellow	53.74 (54.40)	3.73 (3.80)			2240m ν(Ir–H), 2020 (Nujol)
$(AsPh_4)Ir_2(CO)_4Cl_3$ (IV)	deep green	34.11 (34.08)	2.11 (2.04)		10.62 (10.77)	2090m, 2050m (Nujol)
$(AsPh_4)_2IrCOCl_5$ (V)	yellow	38.25 (38.40)	2.30 (2.56)		22.53 (22.74)	2040s (ethanol)
$(AsPh_4)Ir(CO)_2Cl_2$ (VI)	yellow	44.05 (44.17)	2.61 (2.85)		9.92 (10.06)	2030s, 1950s (Nujol) 2050s, 1970s (ethanol)
$(AsPh_4)Ir(CO)_2Cl_3$ (VII)	yellow	41.19 (42.45)	2.68 (2.70)		14.35 (14.35)	2060s, 2025s (ethanol)
$CsIr(CO)Cl_4$ (VIII)	red			32.50 (33.10)	24.01 (24.20)	2040s (Nujol)
$PPNIr(CO)Cl_4$ [a] (IX)	yellow	47.20 (47.60)	2.96 (3.30)		15.40 (15.80)	2060s (Nujol)
$Ir_2(CO)_4Cl_6$ (X)	orange	6.56 (6.75)		54.4 (54.32)	30.1 (29.92)	2140s, 2075s, 2020s (Nujol) 2140s, 2120s 2080s (toluene)
$(AsPh_4)Ir(CO)_2Cl_4$ (XI)	green yellow	41.20 (40.40)	2.55 (2.60)	24.65 (24.60)		2140(s) 2090(s) (Nujol)

[a] PPN = bis(triphenylphosphine)iminium.

$Ir(CO)_3Cl$ (II)

Compound I (0.1 g) is suspended in anhydrous toluene (30 ml) and anhydrous CO is bubbled into the stirred solution for 24 h. A brown solid separates and is filtered off under an inert atmosphere and vacuum dried.

$Ir(H)(CO)(PPh_3)_2Cl_2$ (III)

Compound I (0.04 g) is dissolved in a HCl chloroform (30 ml) (approximately 1.7×10^{-4} *M* and treated with PPh_3 (0.078 g). The solution is kept at 50°C for 1 h and its volume is than reduced to 1/3. Addition of ethanol (2 ml) gives a light yellow precipitate, which is recrystallized from chloroform and ethanol.

$(AsPh_4)Ir_2(CO)_4Cl_3$ (IV)

Compound I (0.04 g) is suspended in anhydrous ethanol (15 ml) under nitrogen, $AsPh_4Cl$ (0.054 g) is added and the mixture is stirred for 3 h. The green black precipitate is filtered off, washed with ethanol (5 ml), and vacuum dried.

$(AsPh_4)_2IrCOCl_5$ (V)

The mother liquors from the preparation of compound IV are evaporated to dryness to leave a crystalline solid, which is washed with ethanol (5 ml) to give V as yellow crystals.

$(AsPh_4)Ir(CO)_2Cl_2$ (VI)

A suspension of compound IV (0.2 g) in anhydrous ethanol (10 ml) containing LiCl (0.025 g) is refluxed for 3 h under nitrogen. The resulting clear yellow solution is concentrated to 1/3 of its volume, to give a yellow crystalline precipitate, which is recrystallized from ethanol.

$(AsPh_4)Ir(CO)_2Cl_3$ (VII)

Compound I (0.04 g) in chloroform (10 ml) is treated with a solution of $AsPh_4Cl$ (0.018 g) in ethanol (5 ml) and the mixture is then saturated with gaseous hydrochloric acid and stirred for 15 min. The yellow precipitate is filtered off, washed with hydrochloric acid 6 *N* (15 ml), and vacuum dried.

$CsIrCOCl_4$ (VIII)

A stream of $CO/Cl_2/HCl$ (432/63/5) is passed over activated iridium * (0.5 g) contained in a tubular furnace at 200°C. The yellow sublimate is washed out with dilute HCl. Addition of CsCl to the solution causes red crystals to separate.

$PPNIrCOCl_4$ (IX)

This is prepared in the same way as VIII but with final addition of PPNCl. Yellow needles are obtained.

$Ir_2(CO)_4Cl_6$ (X)

A CO/Cl_2 stream (molar ratio 1/2) is passed for 1.5 h over activated iridium * (1

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* The activated iridium is obtained from $(NH_4)_2IrCl_6$ by heating for 5 h at 450°C in a hydrogen atmosphere.

g) contained in a tubular furnace at 180°C. A orange sublimate is obtained. M^+ (70 eV) = 709.

($AsPh_4$)Ir(CO)$_2$Cl$_4$ (XI)

Compound X (0.2 g) is treated with HCl 12 *N* (5 ml) and $AsPh_4Cl$ (0.1 g). Green yellow crystals separate.

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