Chlorinated Organic Derivatives with Ir–Hg Bonds

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The reaction of ClHgR (R = 2.5-$C_6H_3Cl_2$; 2,3,4- and 2,4,6-$C_6H_2Cl_3$; C_6Cl_5 and C_2Cl_3) with trans-*[IrCl(CO)(PPh_3)$_2$] gives the new stable compounds [(PPh_3)$_2$(CO)Cl_2Ir–HgR] which contain Ir–Hg bonds. ^{31}P NMR spectra indicate that the two phosphine are* trans *to each other in all the compounds; on the other hand, the HgR group is trans to Cl for the compounds with R = 2,5-$C_6H_3Cl_2$ and 2,3,4-$C_6H_2Cl_3$ whereas for R = C_6Cl_5 the HgR group is trans to CO. An equilibrium between the two isomers is established at room temperature for the compounds with R = C_2Cl_3 and 2,4,6-$C_6H_2Cl_3$. The complexes are probably formed by* cis *addition of ClHgR to* trans-*[IrCl(CO)(PPh_3)$_2$] followed in some cases by isomerization reactions. The action of halogens and PPh_3 on the compounds is described.*

Introduction

There is a growing interest in the synthesis of bimetallic complexes containing heteronuclear metal–metal bonds without bridging groups. The reaction of a compound of one metal in a low oxidation state with a complex or halide of the other metal offers a convenient method to prepare these complexes. The first compound with an iridium–mercury bond, [(PPh_3)$_2$(CO)Cl_2Ir–HgCl], was prepared following this method [1]. Later, other compounds of the same class have been prepared: [(PPh_3)$_2$(CO)Cl(C≡CR)Ir–Hg(C≡CR)] [2], [(PPh_3)$_2$(CS)(C_6F_5)Cl-Ir–HgCl] [3], [(PPh_3)$_2$(CO)(C_6F_5)XIr–HgX] [4] and pentacoordinated [(PPh_3)(CO)$_3$Ir–HgR] [5].

Provisional structures have been suggested based on infrared spectra and sometimes on ^{1}H NMR, but generally little is known on the stereochemistry of such compounds. This prompted us to prepare new compounds containing Ir–Hg bonds, [(PPh_3)$_2$(CO)-Cl_2Ir–HgR], where R are chlorinated organic groups, in order to examine their stereochmistry and solution behaviour with the aid of ^{31}P NMR.

Results and Discussion

The complexes [(PPh_3)$_2$(CO)Cl_2Ir–HgR] (R = 2,5-$C_6H_3Cl_2$; 2,3,4- and 2,4,6-$C_6H_2Cl_3$; C_6Cl_5 and C_2Cl_3) were prepared by adding a solution of the appropriate ClHgR in ethanol to a solution of *trans*-[IrCl(CO)(PPh_3)$_2$] in benzene at room temperature:

$$[IrCl(CO)(PPh_3)_2] + ClHgR \longrightarrow [(PPh_3)_2(CO)Cl_2Ir{-}HgR]$$

The yellow colour is rapidly discharged and after adding ethanol the products precipitate with nearly quantitative yield. It has not been possible to isolate the corresponding analogous compounds with HgR_2. The different behaviour agrees with the lower reaction rate of HgR_2 with Pt(PPh_3)$_3$ to give [(PPh_3)$_2$-RPt–HgR] [6] compared to that of ClHgR [7]. The lower positive charge on the mercury atom in the compounds HgR_2 is probably the cause for the low reactivity of these species towards [IrCl(CO)(PPh_3)$_2$].

The compounds are white and decompose prior to melting giving [IrCl(CO)(PPh_3)$_2$] and ClHgR; a similar behaviour has been reported for [IrCl(CO)(C_2F_4)-(PPh_3)$_2$] [8]. Analyses are given in Table I. The compounds are readily soluble in benzene, acetone, chloroform and dichloromethane, sparingly soluble in ethanol, and insoluble in hexane or ether. Values of the molar conductivity in anhydrous acetone (18 °C) correspond to non-electrolytes. The compounds show diamagnetic behaviour as indicated by susceptibility measurements. The IR bands of the coordinated polychlorophenyl groups show very small differences with respect to the corresponding

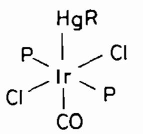
TABLE I. Analytical and ^{31}P NMR Data of [(PPh_3)$_2$(CO)-Cl_2Ir–HgR].

R	Found (Calcd.) (%)		δ_P (ppm) relative to TMP	^{2}J (P–Hg) in Hz
	C	H		
2,5-$C_6H_3Cl_2$	44.6(44.43)	2.9(2.86)	–159.2	319
2,3,4-$C_6H_2Cl_3$	42.9(43.15)	2.6(2.69)	–159.5	328
2,4,6-$C_6H_2Cl_3$	42.8(43.15)	2.5(2.69)	–154.4 [a]	181
			–159.0	320
C_2Cl_3	40.9(40.84)	2.7(2.63)	–155.2 [a]	208
			–159.0	320
C_6Cl_5	41.0(40.80)	2.4(2.38)	–155.0	140

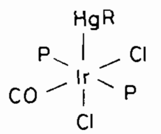
[a]Mixture of *2A* and *2B* configurations (see text).

diorganomercury derivatives. A high frequency shift of the CO band, *ca.* 2040 cm^{-1}, with respect to $[IrCl(CO)(PPh_3)_2]$ is observed in all compounds, in accord with an increase of the oxidation state of iridium.

Reaction of a ClHgR compound with *trans*-$[IrCl(CO)(PPh_3)_2]$ can give rise to six isomers; but if the two phosphine ligands remain *trans*, then only two isomers are possible:



2A



2B

Some disagreement exist in the literature as to the stereochemistry of the products formed by the addition of diatomic molecules (X–Y) to planar *trans*-$[IrCl(CO)(PPh_3)_2]$. Thus, although the action of halogens, hydrogen halides, alkyl halides and mercury halides has been reported to be *trans* stereospecific [9], further studies show that the addition of hydrogen halides to square planar iridium(I) complexes is stereospecifically *cis* in benzene solutions, but mixtures of *cis* and *trans* products are obtained in benzene/methanol solutions [10]. On the other hand it has been established that the addition of molecular hydrogen to *trans*-$[IrCl(CO)(PPh_3)_2]$ proceeds through *cis* addition [11] as also described in the reaction of gaseous hydrogen halides with solid $[IrCl(CO)(PPh_3)_2]$ [12].

^{31}P NMR of the new compounds show only one signal due to the phosphine ligands, thereby excluding isomers other than *2A* or *2B*. The chemical shift of the phosphorus atoms varies significantly among the compounds $[(PPh_3)_2(CO)Cl_2Ir–HgR]$ (Table I). Thus, for R = Cl (obtained according to [1]), 2,5-$C_6H_3Cl_2$ and 2,3,4-$C_6H_2Cl_3$, δ_P = 159 ppm, whereas for R = C_6Cl_5 $\delta_P = -155$ ppm. Both signals appear at room temperature for R = C_2Cl_3 and 2,4,6-$C_6H_2Cl_3$; in these complexes the signal at $\delta_P = -155$ ppm is broad suggesting the existence of a dynamic process. Furthermore all the compounds show Hg satellites which indicate the presence of Ir–Hg bonds. The coupling constants, $^2J(^{199}Hg–^{31}P)$ (Table I), are similar to those reported for the triazenido compounds with iridium–mercury bonds [13].

According to X-ray diffraction studies [14], $[(PPh_3)_2(CO)Cl_2Ir–HgCl]$ possesses the *2B* configuration and its chemical shift is $\delta_P = -159.5$ ppm; accordingly an identical configuration may be attributed to compounds with similar δ_P: $[(PPh_3)_2(CO)Cl_2Ir–Hg(2,5\text{-}C_6H_3Cl_2)]$ and $[(PPh_3)_2(CO)Cl_2Ir–Hg(2,3,4\text{-}C_6H_2Cl_3)]$. On the other hand the compound with R = C_6Cl_5 may be assigned to the *2A* configuration.

A gradual decrease of the signal at $\delta_P = -159$ ppm and at the same time an increase in the intensity of the signal at $\delta_P = -155$ ppm is observed on cooling the $CDCl_3$ solutions of the complexes $[(PPh_3)_2(CO)Cl_2Ir–HgR]$ (R = 2,4,6-$C_6H_2Cl_3$ and C_2Cl_3) (Fig. 1). This suggests that an equilibrium between the isomers *2A* and *2B* is established. Interestingly, none of the compounds with R = Cl, 2,5-$C_6H_3Cl_2$; 2,3,4-$C_6H_2Cl_3$ and C_6Cl_5 undergo isomerization processes on varying the temperature of their solutions, indicating that such processes depend very strongly on the nature of the ligands.

An analogous result has been obtained by Collman [9] on studying the action of ZBr (Z = H, CH_3CO) on $[IrCl(CO)(PPh_3)_2]$; an equilibrium mixture of isomers *2A* and *2B* is obtained, whereas the reactions carried out with ZCl (Z = H, CH_3CO) lead only to the *2B* isomer. It has been suggested that the observed mixtures of *cis* and *trans* products may result from stereoselectivity in the original oxidative addition reaction, followed by consequent isomerization reactions.

From the results obtained it is not possible to ascertain whether the addition of ClHgR to Vaska's complex is *cis* or *trans*, but the easy isomerization of

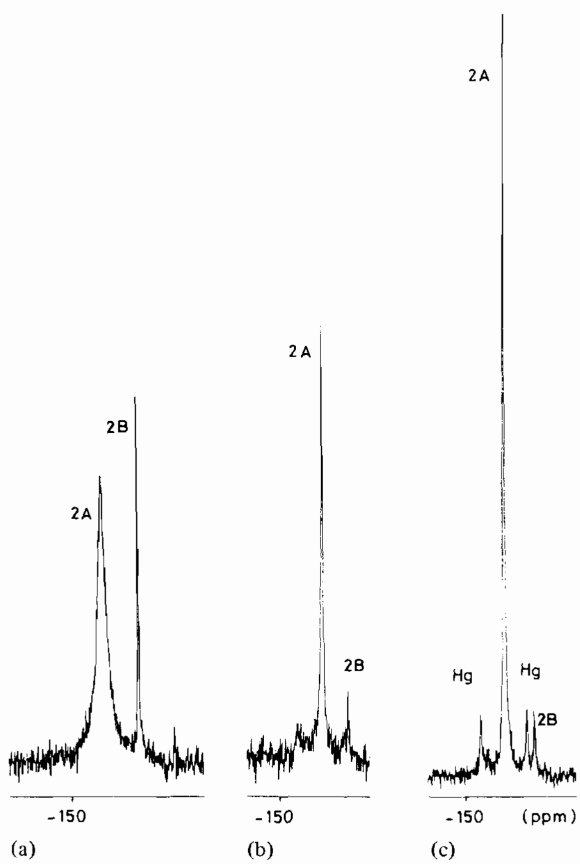


Fig. 1. Variable temperature ^{31}P NMR spectra of $[(PPh_3)_2(CO)Cl_2Ir–Hg(C_2Cl_3)]$: (a) +37 °C (b) 0 °C (c) –50 °C.

2A to *2B* (for R = 2,4,6-$C_6H_2Cl_3$ and C_2Cl_3) on raising the temperature may indicate a *cis* addition followed by the isomerization. This isomerization is total for R = Cl, 2,5-$C_6H_3Cl_2$ and 2,3,4-$C_6H_2Cl_3$ even at low temperature. On the other hand, it nearly does not occur for R = C_6Cl_5 but if the spectrum is run at +37 °C, a very weak signal ($\delta_P = -159$ ppm) is observed, indicating the beginning of an isomerization process.

The action of a number of reagents on the $CHCl_3$ solutions of the compounds prepared was examined in order to study the stability of the Ir–Hg bond. A slight excess of iodine or bromine leads in all cases to the cleavage of the bond, in agreement with the results of Nyholm for [$(PPh_3)_2(CO)Cl_2$-Ir–HgCl] [1], whereas a slight excess of triphenylphosphine only immediately cleaves the bond for R = Cl, 2,5-$C_6H_3Cl_2$ and 2,3,4-$C_6H_2Cl_3$. Only partial cleavage was observed for R = 2,4,6-$C_6H_2Cl_3$ and C_2Cl_3 and no change was observed for R = C_6Cl_5. The addition of a larger excess of PPh_3 causes finally the cleavage of the Ir–Hg bond for these last three compounds. This different behaviour may be related to the identity of the ligands attached to Hg. Thus, the presence in R of two bulky chlorine atoms in ortho to the Hg–C bond may render difficult the approach of PPh_3 to the iridium atom; on the other hand, it is well known that an increase in the electronegativity of R exerts a major effect on the stability of the metal–metal bond [15].

Experimental

Chemical analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona. $^{31}P-\{^1H\}$ NMR were obtained on a Varian XL-200 and Bruker WP 80 SY FT spectrometers as $CDCl_3$ solutions using TMP as external reference. IR spectra were recorded on a Beckman IR 20A spectrophotometer.

Starting Materials

[$IrCl(CO)(PPh_3)_2$] was obtained by a standard method [16] and the compounds RHgCl were prepared by refluxing an equimolar solution of HgR_2 and $HgCl_2$ in xylene [17].

Preparation of [$(PPh_3)_2(CO)Cl_2Ir$–HgR]

A solution of ClHgR (1.1 mmol) in ethanol (25 ml) was slowly added at room temperature to [$IrCl(CO)(PPh_3)_2$] (1.0 mmol) dissolved in benzene (50 ml). After stirring for 1 h white crystals were obtained on adding ethanol. These were recrystallized from benzene/hexane. Yield about 90%.

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