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PLATINUM-MERCURY COMPOUNDS AS INTERMEDIATES TO MONO- AND DI-ARYLPLATINUM(II) COMPLEXES

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Summary

The reaction of HgR_2 (R = 2,5-$C_6H_3Cl_2$; 2,3,4- and 2,4,6-$C_6H_2Cl_3$; 2,3,4,5-, 2,3,4,6- and 2,3,5,6-C_6HCl_4 and C_6Cl_5) with $Pt(PPh_3)_3$ gives the new stable compounds $[(PPh_3)_2RPt(HgR)]$ containing Pt—Hg bonds. When R contains an *ortho* chlorine atom (R = 2,5-$C_6H_3Cl_2$; 2,3,4-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4) refluxing xylene solutions of these compounds gives the complexes $[PtR_2(PPh_3)_2]$, with simultaneous precipitation of mercury. In the other cases the initial compounds are recovered unaltered. All the compounds containing the Pt—Hg bond react readily with CF_3COOH to give a new series of compounds of formula $[Pt(O_2CCF_3)R(PPh_3)_2]$.

Introduction

The preparation of mono- and di-arylplatinum(II) complexes of the type $[PtXRP_2]$ and $[PtR_2P_2]$ is especially difficult when P is a bulky phosphine, such as triphenylphosphine, and/or R are phenyl groups with bulky *ortho* substituents. The compounds of this type cannot, as a rule, be obtained from magnesium, lithium or tetraorganotin reagents and $[PtX_2P_2]$ [1]. Organomercury compounds have also been studied as reagents for the preparation of arylplatinum(II) compounds; although the synthetic value of the reactions of organomercury compounds HgR_2 with $[PtX_2P_2]$ has been regarded as low [2], we found that the yields are considerably increased if the reaction is carried out in the molten state [3]. This makes possible the preparation of organoplatinum compounds containing bulky ligands such as PPh_3 and C_6Cl_5; in no case however, were diorgano complexes $[PtR_2(PPh_3)_2]$, obtained.

On the other hand, the action of the organomercury compounds HgR_2 on triphenylphosphine complexes of zerovalent platinum, $Pt(PPh_3)_n$ (n = 3, 4) gives the compounds $[PtR_2(PPh_3)_2]$ where the R groups are small [4]; these reactions were found to give isolable organomercury compounds with metal—

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metal bonds when either R was a strongly electronegative group (e.g. CF_3 or C_6F_5) [4] or steric crowding occurred near the intermetallic bond (e.g. R = mesityl) [5]. These results prompted us to examine the action of several bis-(polychlorophenyl)mercury compounds, containing one or two *ortho* chlorine atoms, on $Pt(PPh_3)_3$ to give compounds of the type $[(PPh_3)_2RPt(HgR)]$. We also examined the demercuriation reaction with the purpose of obtaining $[PtR_2(PPh_3)_2]$ in which R are bulky groups.

Results and discussion

Preparation of $[(PPh_3)_2RPt(HgR)]$

The compounds $[(PPh_3)_2RPt(HgR)]$ (R = 2,5-$C_6H_3Cl_2$; 2,3,4- and 2,4,6-$C_6H_2Cl_3$; 2,3,4,5-, 2,3,4,6- and 2,3,5,6-C_6HCl_4 and C_6Cl_5) were prepared by adding the appropriate HgR_2 to a solution of $Pt(PPh_3)_3$ in benzene, under nitrogen and at room temperature:

$$Pt(PPh_3)_3 + HgR_2 \rightarrow [(PPh_3)_2RPt(HgR)] + PPh_3$$

Analyses and decomposition temperatures are given in Table 1. All the compounds are stable as solids and in solution but a gradual darkening is observed under strong sunlight. This stability may be attributed to the relatively high electronegativity of the R groups as well as to the presence of at least one *ortho* chlorine atom in the benzene ring (vide infra). The compounds are readily soluble in benzene, acetone and dichloromethane, but only sparingly soluble in ethanol and hexane. Values of the molar conductivity in anhydrous acetone (18°C) correspond to non-electrolytes.

The bands of the coordinated polychlorophenyl groups appear in the IR spectra with small differences from the analogues nickel(II) compounds [6]. A band centered at 550 cm^{-1} due to triphenylphosphine enables us to assign a *cis* configuration to all the compounds [7].

The ^{31}P NMR spectrum supports a *cis* geometry for $[(PPh_3)_2(2,3,4,6\text{-}C_6HCl_4)Pt\{Hg(2,3,4,6\text{-}C_6HCl_4)\}]$ (Fig. 1) which exhibits two main signals at δ 18.2 (P_a) and δ 34.4 (P_b) ppm (P_b *trans* to Hg). Both signals show Pt satellites, $J(Pt-P_a)$ 2535 and $J(Pt-P_b)$ 2555 Hz. The presence of Pt—Hg bond is evidenced by the $^2J(^{199}Hg-P)$ coupling of 2833 and 285 Hz for P_b and P_a respectively. The

TABLE 1

ANALYTICAL DATA OF $[(PPh_3)_2RPt(HgR)]$

R	Found (cald.) (%)		Decomposition temperature
	C	H	(°C)
2,5-$C_6H_3Cl_2$	46.9(47.55)	3.0(2.99)	150—160
2,4,6-$C_6H_2Cl_3$	45.0(44.99)	2.7(2.67)	160—170
2,3,4-$C_6H_2Cl_3$	45.3(44.99)	2.7(2.67)	170—180
2,3,4,5-C_6HCl_4	42.6(42.70)	2.4(2.39)	222—224
2,3,4,6-C_6HCl_4	42.5(42.70)	2.4(2.39)	272—275
2,3,5,6-C_6HCl_4	42.7(42.70)	2.4(2.39)	245—250
C_6Cl_5	40.5(40.62)	2.1(2.11)	285—289

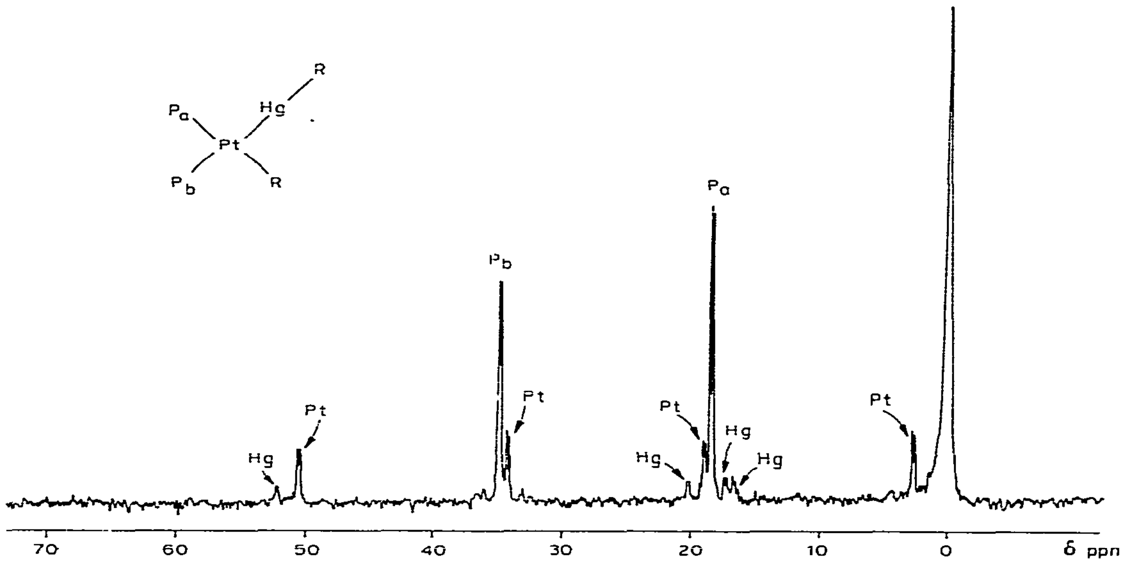

Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[(PPh_3)_2(2,3,4,6\text{-}C_6HCl_4)Pt\{Hg(2,3,4,6\text{-}C_6HCl_4)\}]$.

coupling constant $^2J(P_a—P_b)$ of 16 Hz is typical of a *cis* complex. These data indicate that the reaction of $Pt(PPh_3)_3$ with HgR_2 results in a *cis* oxidative addition of the organomercury compound to platinum. The *cis* square planar geometry of these compounds is consistent with the crystal structure of $[(PPh_3)_2(CF_3)Pt\{Hg(CF_3)\}]$ [8].

Preparation of $[PtR_2(PPh_3)_2]$

Sokolov et al. [4] reported that $[(PPh_3)_2(CF_3)Pt\{Hg(CF_3)\}]$ underwent demercuriation by ultraviolet light; we also observed this process on refluxing some of the compounds $[(PPh_3)_2RPt(HgR)]$ in xylene; thus, when R possesses only one *ortho* chlorine atom (R = 2,5-$C_6H_3Cl_2$; 2,3,4-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4) a rapid precipitation of mercury is observed:

$$[(PPh_3)_2RPt(HgR)] \xrightarrow[\text{reflux}]{\text{xylene}} [PtR_2(PPh_3)_2] + Hg$$

However, if R contains two *ortho* chlorine atoms (R = 2,4,6-$C_6H_2Cl_3$; 2,3,4,6- and 2,3,5,6-C_6HCl_4 and C_6Cl_5), the platinum-mercury compounds are recovered unchanged. Similar results were obtained when these reactions were carried out in benzene or THF.

These facts show that even though the electronegativity is an important factor in determining the stability of the compounds with Pt—Hg bonds, the presence of one or two chlorine atoms in the *ortho* position of the benzene ring can be the determinant factor. Thus, in the compounds $[(PPh_3)_2RPt(HgR)]$ (R = 2,4,6-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4) only the first resists the action of heat, although the electronegativity of the two R groups is very similar [9].

The reaction described enables the isolation of new diorganoderivatives of

TABLE 2

ANALYTICAL DATA OF DIFFERENT $[PtR_2(PPh_3)_2]$ COMPOUNDS

Compound	Found (calcd.) (%)			Decomposition temperature (°C)
	C	H	Cl	
$[Pt(O_2CCF_3)R(PPh_3)_2]$				
R = 2,5-$C_6H_3Cl_2$	54.0(54.01)	3.2(3.37)	7.1(7.20)	250—252
R = 2,4,6-$C_6H_2Cl_3$	51.9(52.15)	3.2(3.18)	10.3(10.49)	220—221
R = 2,3,4-$C_6H_2Cl_3$	52.6(52.15)	3.1(3.18)	10.4(10.49)	255—256
R = 2,3,4,5-C_6HCl_4	50.5(50.44)	3.2(2.98)	13.7(13.53)	248—251
R = 2,3,4,6-C_6HCl_4	50.3(50.44)	3.3(2.98)	13.8(13.53)	254—255
R = 2,3,5,6-C_6HCl_4	50.7(50.44)	2.9(2.98)	13.4(13.53)	251—254
R = C_6Cl_5	50.6(48.83)	3.1(2.79)	16.5(16.38)	249—250
$[PtR_2(PPh_3)_2]$				
R = 2,5-$C_6H_3Cl_2$	56.7(56.98)	3.6(3.58)	13.9(14.01)	227—228
R = 2,3,4-$C_6H_2Cl_3$	53.3(53.35)	3.1(3.17)	19.2(19.68)	248—250
R = 2,3,4,5-C_6HCl_4	48.8(50.15)	2.6(2.80)	23.6(24.67)	255—257
$[PtX(C_6Cl_5)(PPh_3)_2]$				
X = NCS	48.9(50.29)	2.8(2.92)	17.1(17.26)	267—269
X = NO_2	49.6(49.69)	2.9(2.97)	17.4(17.46)	240—243
X = CN	51.7(51.90)	3.1(3.03)	17.5(17.81)	275—278

platinum containing four very bulky ligands. Analyses and decomposition temperatures are given in Table 2. The compounds are diamagnetic, and non-electrolytes in anhydrous acetone. The IR spectra show the bands due to the polychlorophenyl groups [6].

A band of medium intensity at 550 cm^{-1} did not enable us to establish unequivocally the configuration of these species. However, the ^{31}P NMR spectrum showed the products to be a mixture of the *cis* and *trans* isomers. Thus, the spectrum of $[Pt(2,3,4,5\text{-}C_6HCl_4)_2(PPh_3)_2]$ in $CDCl_3$ exhibited two signals with J(Pt—P) 2111 (*cis*) and 3038 Hz (*trans*); the spectrum also indicated a greater concentration (85%) of the *cis* isomer. The compound with R = 2,5-$C_6H_3Cl_2$ showed also preponderance of the *cis* isomer (65%), whereas for R = 2,3,4-$C_6H_2Cl_3$ no *trans* isomer was detected. These facts indicate that alongside the demercuriation, an isomerization process occurs, probably caused by the vigorous conditions required for the demercuriation process.

The CCl_4 solutions of $[PtR_2(PPh_3)_2]$ are stable towards HCl, Br_2 and I_2. It was not possible to displace triphenylphosphine by other, smaller and more basic phosphine such as PEt_3, $PEtPh_2$, PMe_2Ph and dpe.

Preparation of $[Pt(O_2CCF_3)R(PPh_3)_2]$

Bimetallic compounds with metal—metal bonds are frequently decomposed by trifluoroacetic acid [5] or silver trifluoroacetate [10]. The complexes studied in this work showed such behaviour. Thus, treatment of benzene solutions of $[(PPh_3)_2RPt(HgR)]$ with an excess of CF_3COOH caused cleavage of the Pt—Hg bond according to:

$$[(PPh_3)_2RPt(HgR)] + CF_3COOH \rightarrow [Pt(O_2CCF_3)R(PPh_3)_2] + Hg + HR$$

This reaction enables the preparation in good yields of a new series of compounds $[Pt(O_2CCF_3)R(PPh_3)_2]$ (see Table 2 for elemental analyses and melting points).

The marked lability of the trifluoroacetate ligand leads to ready metathetical reactions of the complexes $[Pt(O_2CCF_3)R(PPh_3)_2]$. Thus, the action of a slight excess of the alkali metal salts of the anions CN^-, NO_2^-, and NCS^- on acetone solutions of $[Pt(O_2CCF_3)(C_6Cl_5)(PPh_3)_2]$ gives the corresponding $[PtX(C_6Cl_5)(PPh_3)_2]$, compounds which cannot be prepared by displacement of chloride from $[PtCl(C_6Cl_5)(PPh_3)_2]$ [3].

Experimental

Chemical analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona. The $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 Fourier Transform spectrometer for $CDCl_3$ solutions using 85% H_3PO_4 as external reference. Infrared spectra were recorded on a Beckman IR-20 A spectrophotometer.

Starting materials

$Pt(PPh_3)_3$ was prepared according to [11]. $Hg(C_6Cl_5)_2$ was made by the action of THF solution of C_6Cl_5MgCl on $HgCl_2$ [12]. The other organomercury compounds were obtained by metallation of the corresponding polychlorobenzenes with $Hg(O_2CCF_3)_2$ [13].

Preparation of $[(PPh_3)_2RPt(HgR)]$

All these were prepared by the following general method: A mixture of $Pt(PPh_3)_3$ (1.0 mmol) and HgR_2 (1.0 mmol) was dissolved in benzene (50 ml) under nitrogen at room temperature and the resulting solution was concentrated to dryness. The residue was washed with benzene and recrystallized from dichloromethane/methanol (Yield about 70—80%).

Preparation of $[PtR_2(PPh_3)_2]$ (R = 2,5-$C_6H_3Cl_2$; 2,3,4-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4)

$[(PPh_3)_2RPt(HgR)]$ (1.0 mmol) was dissolved in xylene (50 ml). After a few minutes of reflux heating the initially colourless solution turned red, then the red colour was discharged and mercury separated. This was filtered off, and the filtrate was concentrated to dryness. The residue was recrystallized from dichloromethane/methanol (Yield about 80—90%).

Preparation of $[Pt(O_2CCF_3)R(PPh_3)_2]$

The compounds were prepared in good yields (90—95%) by adding CF_3COOH (1 ml) to a solution of the appropriate $[(PPh_3)_2RPt(HgR)]$ (1 mmol) in benzene (25 ml), whereupon mercury immediately separated. The filtered solution was concentrated to dryness and the residue washed with hexane and recrystallized from dichloromethane/methanol.

Preparation of $[PtX(C_6Cl_5)(PPh_3)_2]$ (X = NCS, NO_2, CN)

A slight excess of alkali metal salt (KNCS, KNO_2 or KCN) was added to a solution of $[Pt(O_2CCF_3)(C_6Cl_5)(PPh_3)_2]$ (0.2 g) in acetone (25 ml). The mixture was left at room temperature for 4 h and then concentrated under reduced pressure. The solids which separated were recrystallized from dichloromethane/methanol (Yield about 90%).

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