POLYCHLOROPHENYL-PLATINUM(II) COMPLEXES CONTAINING TRIPHENYLPHOSPHINE

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Summary

A new method to prepare compounds of the type *trans*-[PtCl(R)(PPh$_3$)$_2$] (R = C$_6$H$_5$; 2,5-C$_6$H$_3$Cl$_2$; 2,3,4-, and 2,4,6-C$_6$H$_2$Cl$_3$; 2,3,4,5-, 2,3,4,6- and 2,3,5,6-C$_6$HCl$_4$ and C$_6$Cl$_5$) by reaction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] and HgR$_2$ in the molten state is described.

The reactions of the complexes with HCl, Cl$_2$ and I$_2$ have been examined in order to give information about the relative ease of cleavage of the various Pt—aryl bonds. The replacement of Cl by NCS suggests an associative mechanism even for the complexes in which the polychlorophenyl ligand has chlorine atoms in both *ortho* positions.

Introduction

The reactions of Grignard and organolithium reagents with halogen complexes of platinum(II), palladium(II) and nickel(II) have been widely used to prepare organometallic derivatives. However, the formation of mono- or di-organoderivatives is more difficult, particularly for platinum, when starting from [MCl$_2$P$_2$] where P is a bulky phosphine and/or when attempting to attach phenyl groups with bulky *ortho* substituents.

Eaborn et al. have recently studied the action of tetraorganotin compounds (SnMe$_3$R) on [PtCl$_2$L$_2$] (L = COD, DMSO, and others [1]), which readily gives mono- or di-organoderivatives depending on the nature of R and L. However, the tin compounds do not react, or do so only very slowly, with the bis(phosphine) complexes [PtCl$_2$P$_2$]. Even with the more reactive [Pt(CF$_3$CO$_2$)$_2$P$_2$], aryl transfer from tin to platinum is markedly less effective for P = PPh$_3$ [2].

Organomercury compounds have also been studied as reagents for the preparation of aryl-Pt^{II} compounds; thus, the action of HgPh$_2$ on solutions of [PtCl$_2$(PPhMe$_2$)$_2$] [3] or [PtCl$_2$(COD)] [1b] leads to the monophenyl derivatives. The synthetic value of the organomercury reaction has been regarded as

low [3], but we have found that it is increased considerably if the reaction is carried out in the molten state; this allow the formation of organoplatinum compounds containing bulky phosphines such as PPh_3 and organic ligands such as C_6Cl_5, which could not be obtained by the action of C_6Cl_5MgCl or C_6Cl_5Li on $[PtCl_2(PPh_3)_2]$ [4].

Results and discussion

Preparation and properties

The process consists of heating a mixture of cis-$[PtCl_2(PPh_3)_2]$ and a slight excess of HgR_2 (R = $C_6H_{5-n}Cl_n$, with n = 0—5) at a temperature near the melting point of one of the reagents (Table 1). The melt is maintained at this temperature for some 5 min, then after cooling to room temperature, the mixture is extracted with dichloromethane. The extract is concentrated and methanol is added to give a white precipitate. The HgRCl is removed from the desired compound by vacuum sublimation:

cis-$[PtCl_2(PPh_3)_2]$ + HgR_2 → trans-$[PtCl(R)(PPh_3)_2]$ + HgRCl
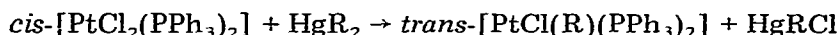
Reaction conditions are given in Table 1. A gradual decrease of the yield on increasing the number of chlorine atoms in the ring is observed.

The new compounds have been characterized by elemental analysis and IR spectra. A trans configuration is assigned to all of them on the basis of the absence of bands due to PPh_3 at 550 ± 5 cm^{-1}, which are characteristic of the compounds cis-$[PtX_2(PPh_3)_2]$ [5]. The trans configuration was also demonstrated for $[PtCl(2,5-C_6H_3Cl_2)(PEt_3)_2]$ obtained by the same method from cis-$[PtCl_2(PEt_3)_2]$ and $Hg(2,5-C_6H_3Cl_2)_2$ at 210°C. The PMR spectrum of the com-

TABLE 1

ANALYTICAL DATA

$[PtCl(R)(PPh_3)_2]$ R	Analysis found (calcd.) (%)			Reaction temperature (°C)	m.p. (°C)	Yield (%)
	C	H	Cl			
C_6Cl_5	50.1 (50.17)	3.0 (2.98)	21.0 (21.17)	285	300—305 (dec)	50
2,3,4,5-C_6HCl_4	51.6 (51.95)	3.1 (3.19)	17.9 (18.27)	270	263—265	60
2,3,4,6-C_6HCl_4	50.5 (51.95)	3.1 (3.19)	18.2 (18.27)	290	310—315	60
2,3,5,6-C_6HCl_4	51.7 (51.95)	3.1 (3.19)	18.2 (18.27)	320	334—336 (dec)	50
2,3,4-$C_6H_2Cl_3$	53.7 (53.87)	3.4 (3.42)	15.0 (15.15)	275	259—261	65
2,4,6-$C_6H_2Cl_3$	52.8 (53.87)	3.3 (3.42)	14.8 (15.15)	290	323—325	70
2,5-$C_6H_3Cl_2$	55.0 (55.92)	3.6 (3.66)	11.4 (11.18)	240	296—298	80
C_6H_5	61.1 (60.56)	4.3 (4.20)	4.3 (4.26)	135	300—302 (dec)	80

pound shows a pseudoquintet ($\delta = 1.07$ ppm) which is characteristic of the *trans* compounds with triethylphosphine [6]. The IR spectra show also the bands due to the coordinated R groups not significantly different from those reported for analogous compounds [7]. Bands assignable to the vibration ν(Pt—Cl) appear in the region 280—300 cm^{-1}; a shift towards higher frequencies is observed on increasing the number of chlorine atoms on the aryl group, so that the band appears at 280 and 300 cm^{-1} for [PtCl(C_6H_5)(PPh$_3$)$_2$] and [PtCl(C_6Cl_5)(PPh$_3$)$_2$], respectively. These shifts agree with a decrease of the *trans* influence on increasing the electronegativity of the aryl groups [8].

All the compounds are stable as solids and in solution. Analytical data and decomposition temperatures are given in Table 1. Magnetic measurements reveal diamagnetic character, indicating square-planar geometry. Values of the molar conductivity (10^{-4} M) in anhydrous acetone at 18°C correspond to non-electrolytes. They are soluble in benzene, chloroform, dichloromethane, and acetone, and scarcely soluble in ethanol and ether.

Chemical reactivity

The action of HCl, Cl$_2$ and I$_2$ on the complexes and the replacement of Cl by NCS have been studied in order to examine the stability of the Pt—aryl bond and to allow comparison of the properties of the complexes with these of the analogous Ni and Pd compounds.

Action of HCl. Passage of hydrogen chloride through chloroform solutions of [PtCl(R)(PPh$_3$)$_2$] for six hours cleaves the Pt—aryl bond only for R = C_6H_5. In contrast, the analogous nickel and palladium compounds are decomposed when R contains one *ortho* chlorine atom, indicating that the Pt—R bonds are less reactive than corresponding Pd—R or Ni—R bonds. The results are also in accord with the mechanism proposed, consisting of the oxidative addition and reductive elimination [9], in cases where the ligand *trans* to the cleaved Pt—R bond has a small *trans* effect (e.g. as Cl); obviously the bulky *ortho* chlorine atoms would hinder the formation of an hexacoordinated intermediate.

Action of Cl$_2$ and I$_2$. The action of chlorine on CCl$_4$ solutions of the compounds leads to decomposition, as found for analogous Ni and Pd compounds [10,11]. These compounds remain unchanged upon the addition of a slight excess of iodine, except for R = Ph; thus, from [PtI(C_6H_5)(PPh$_3$)$_2$], obtained by a metathesis reaction [PtI$_2$(PPh$_3$)]$_2$ is obtained, and iodobenzene is detected by gas chromatography. These results agree with the difficulties found in the preparation of hexacoordinated platinum compounds with bulky ligands [12] and suggest a mechanism in which the first step is the oxidative addition of iodine forming the unstable hexacoordinated species [PtI$_3$(C_6H_5)(PPh$_3$)$_2$], and loss of phosphine followed by reductive elimination of iodobenzene finally gives the binuclear compound.

Replacement by NCS. The action of an excess of KNCS on acetone solutions of the complexes gives *trans*-[Pt(NCS)(R)(PPh$_3$)$_2$] for R = C_6H_5, 2,5-$C_6H_3Cl_2$ 2,3,4-$C_6H_2Cl_3$ and 2,3,4,5-C_6HCl_4. However, after 24 h using DMSO as solvent, total replacement is obtained for R = 2,4,6-$C_6H_2Cl_3$, partial for R = 2,3,4,6-C_6HCl_4 and 2,3,5,6-C_6HCl_4, and no replacement at all for R = C_6Cl_5.

While it is accepted that square-planar platinum complexes normally react by an associative mechanism [13], it has been recently argued that a dissociative

mechanism may be involved for complexes containing bulky substituents, such as cis-[PtBr(mesityl)(PEt$_3$)$_2$] [14,15]. Our results, based only on the nature of the products formed, are consistent with an associative process. The two paths (one via solvolysis and the other by direct action of NCS) can operate when there are no chloro substituents (R = C$_6$H$_5$) or only one in the *ortho* position (R = 2,5-C$_6$H$_3$Cl$_2$; 2,3,4-C$_6$H$_2$Cl$_3$ and 2,3,4,5-C$_6$HCl$_4$). When there are two *ortho* chlorine atoms (R = 2,4,6-C$_6$H$_2$Cl$_3$; 2,3,4,6-, 2,3,5,6-C$_6$HCl$_4$ and C$_6$Cl$_5$) the reaction must proceed via the solvolytic path since it only occurs in DMSO. The increasing difficulty of replacing of Cl by NCS on raising the electronegativity of R by increasing the number of chlorine atoms on the ring shows the influence exerted by this group on the departure of the chloride ligand.

Experimental

General

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer and samples were prepared as KBr disks or Nujol mulls. C, H determinations were carried out at the Instituto de Química Bio-Orgánica de Barcelona.

Starting materials

cis-[PtCl$_2$(PPh$_3$)$_2$] was prepared as described by Jensen [16]. Hg(C$_6$H$_5$)$_2$ was made by symmetrization of Hg(C$_6$H$_5$)O$_2$CCH$_3$ with EDTA [17] and Hg(C$_6$Cl$_5$)$_2$ by the action of a THF solution of C$_6$Cl$_5$MgCl on HgCl$_2$ [18]. The other organomercury compounds were obtained by metallation of the corresponding polychlorobenzenes with Hg(O$_2$CCF$_3$)$_2$ [19].

Preparation of the compounds [PtCl(R)(PPh$_3$)$_2$]

All these were prepared by the following general method. A mixture of 1.0 mmol of cis-[PtCl$_2$(PPh$_3$)$_2$] and 1.0 mmol of HgR$_2$ contained in a test tube was heated on a silicone oil bath for 5 min at the temperature given in Table 1; under these conditions the mixture melts. After cooling to room temperature the mass was extracted with dichloromethane. Addition of methanol to the extract precipitated [PtCl(R)(PPh$_3$)$_2$] and HgRCl. The latter was removed by vacuum sublimation (130°C; 0.05 mmHg). Yields are given in Table 1.

Replacement of halogen by NCS

To a solution of 1 mmol of [PtCl(R)(PPh$_3$)$_2$] in 100 ml of acetone was added an excess of KNCS, and the mixture was refluxed for 24 hours. After cooling, the solution was evaporated to dryness. The residual solid was washed with H$_2$O and recrystallized from dichloromethane and methanol. Yield 80—85%.

R = C$_6$H$_5$: m.p. 268—269°C (dec) IR: NCS bands 2090, 830 cm^{-1}. R = 2,5-C$_6$H$_3$Cl$_2$: m.p. 266—267°C (dec); Anal. Found (calcd.): Cl, 7.59 (7.67) %; IR; NCS bands 2090, 840 cm^{-1}. R = 2,3,4-C$_6$H$_2$Cl$_3$: m.p. 262°C (dec); Anal. Found (calcd.): Cl, 11.1 (11.09) %; IR: NCS bands 2080, 840 cm^{-1}. R = 2,3,4,5-C$_6$HCl$_4$: m.p. 252—253°C (dec); Anal. Found (calcd.): Cl, 17.03 (17.28) %; IR: NCS bands 2085, 840 cm^{-1}.

[Pt(NCS)(2,4,6-C$_6$H$_2$Cl$_3$)(PPh$_3$)$_2$] was prepared analogously in DMSO solution at 50°C. m.p. 263—265°C (dec); Anal. Found (calcd.): Cl, 10.98 (11.09) %; IR: NCS bands 2080, 840 cm^{-1}.

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