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BIS(PENTAFLUOROPHENYL)-PLATINUM(II) AND -PLATINUM(IV) COMPLEXES

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Summary

The preparation of five new platinum(II) complexes of the general formula $(C_6F_5)_2PtL_2$ ($L_2 = Ph_2AsCH_2CH_2AsPh_2$; and the *cis*- and *trans*-isomers when $L = PBu_3$ or $AsPh_3$) is described. The oxidative addition of X_2 ($X = Cl$ or Br) to some compounds of the aforementioned type leads to eight new platinum(IV) complexes $X_2(C_6F_5)_2PtL_2$ ($L = PBu_3$; $L_2 = 2,2'$ -bipyridine, 1,10-phenanthroline or $Ph_2AsCH_2CH_2AsPh_2$).

Introduction

The few pentafluorophenylplatinum(IV) complexes [1,2] belong to two types: $X_3(C_6F_5)PtL_2$ ($X = Cl$ or Br ; $L = PPh_3$ or PEt_3) and $X_2(C_6F_5)_2Pt(PEt_3)_2$ ($X = Cl$ or Br). We previously reported [3] the synthesis of platinum(II) complexes of the $(C_6F_5)_2PtL_2$ type ($L_2 = bipy$, *phen*, *py*₂-*cis* and *-trans*), which, along with several related complexes have been treated with Cl_2 , Br_2 , I_2 and CH_3I .

Results and discussion

(a) Preparation of $(C_6F_5)_2PtL_2$

The arylation of *cis*- and *trans*-isomers Cl_2PtL_2 was carried out with LiC_6F_5 (eq. 1). When L is a monodentate ligand, isomerization may take place together

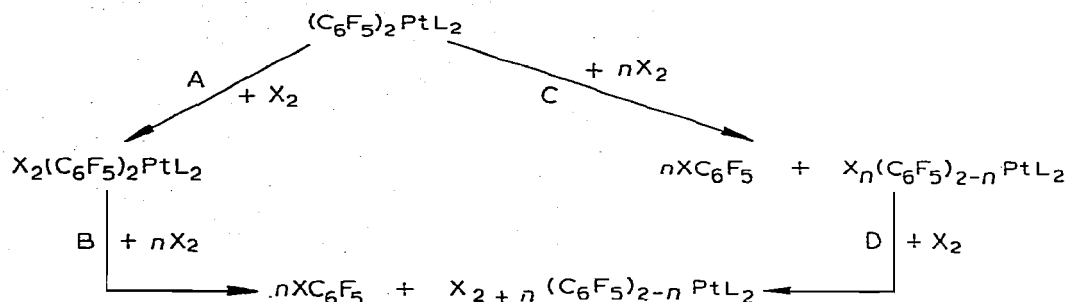
$$Cl_2PtL_2 + 2 LiC_6F_5 \rightarrow (C_6F_5)_2PtL_2 + 2 LiCl \quad (1)$$

with the displacement of the chlorine atoms. No isomerization was observed when $L = PBu_3$, whereas both the *cis*- and the *trans*-dichloro complexes led only to *cis*- $(C_6F_5)_2Pt(AsPh_3)_2$. *trans*- $(C_6F_5)_2Pt(AsPh_3)_2$ was prepared by prolonged heating of the corresponding *cis*-derivative to almost at its melting point. The analytical data for the new platinum(II) complexes are listed in Table 1.

(b) Oxidative addition of chlorine and bromine

Reaction of an excess of chlorine or bromine with platinum(II) takes place according to Scheme 1. The oxidative addition of the halogen (A) may be follow-

SCHEME 1



ed by a further reaction (B) with displacement of one or the two C_6F_5 groups, or, again, the halogen may displace one or more C_6F_5 groups (C), without causing simultaneous oxidation of the platinum. The resulting complex may finally be oxidized (D) to give the corresponding platinum(IV) complex.

Under our conditions (room temperature, dichloromethane or benzene as solvent) the course of the reaction depended in each case upon the configuration of the starting compound and the nature of the neutral ligand. Process A occurred exclusively for $\text{L}_2 = \text{bipy}$ or $\text{PBu}_3(\text{cis})$, even with an excess of the halogen and for $\text{L} = \text{diars}$ with a stoichiometric amount of the halogen. For $\text{L}_2 = \text{phen}$ all the processes can take place, but process A could be made to predominate by use of stoichiometric amounts of X_2 , or by the rapid removal of X_2 in the case of Cl_2 . For $\text{L} = \text{py}$, the other processes could not be excluded, and mixtures of products which could not be resolved were obtained. Finally, for $\text{L} = \text{PBu}_3(\text{trans})$ or $\text{AsPh}_3(\text{cis or trans})$, no reaction took place.

The analytical data for the isolated platinum(IV) complexes are listed in Table 1.

(c) Reaction with CH_3I or I_2

No reaction was observed with CH_3I . This is in contrast with the recently reported [5] oxidative addition of CH_3I to phenyl derivatives. Reaction A seems not to take place with I_2 , though the oxidative addition A followed immediately by reductive elimination cannot be ruled out.

Isomerization frequently occurs; thus, $\text{cis}-(\text{C}_6\text{F}_5)_2\text{Pt}(\text{PBu}_3)_2$ is transformed into the trans -isomer. In the case of $\text{cis}-(\text{C}_6\text{F}_5)_2\text{PtPy}_2$ and $\text{cis}-(\text{C}_6\text{F}_5)_2\text{Pt}(\text{AsPh}_3)_2$ isomerization and simultaneous elimination lead to $\text{trans-I}_2\text{PtPy}_2$, and a mixture of $\text{trans}-(\text{C}_6\text{F}_5)_2\text{Pt}(\text{AsPh}_3)_2$ and $\text{I}(\text{C}_6\text{F}_5)\text{Pt}(\text{AsPh}_3)_2$, respectively.

No reaction was observed with $(\text{C}_6\text{F}_5)_2\text{PtbiPy}$ and $(\text{C}_6\text{F}_5)_2\text{Ptphen}$, whilst a mixture of unidentified products was obtained from $(\text{C}_6\text{F}_5)_2\text{Pt diars}$.

(d) IR spectra

The IR spectra of the platinum(II) complexes show the characteristic vibrations of the C_6F_5 group at $\sim 1500\text{s}$, 1050s and 950s cm^{-1} . The cis -isomers exhibit two additional bands at $\sim 790\text{s}$ and 780s cm^{-1} when these are not masked by absorp-

TABLE 3
INFRARED SPECTRAL DATA

Complex	Absorptions assigned to the neutral ligands (cm ⁻¹)	Ref.
<i>cis</i> -(C ₆ F ₅) ₂ Pt(PBu ₃) ₂	1205m, 1085s, 903m, 800s(br)	a
<i>trans</i> -(C ₆ F ₅) ₂ Pt(PBu ₃) ₂	1206m, 1090s, 1010s, 904s, 800s(br)	a
<i>cis</i> -(C ₆ F ₅) ₂ Pt(AsPh ₃) ₂	1580w, 1075s, 996m, 690s, 476s, 468s	a
<i>trans</i> -(C ₆ F ₅) ₂ Pt(AsPh ₃) ₂	1580w, 1075s, 998m, 692s, 475s, 468(sh)	a
(C ₆ F ₅) ₂ Ptdiars	1580w, 1082s, 998m, 690s, 465(sh), 456s	a
Cl ₂ (C ₆ F ₅) ₂ Ptbipy	1606s, 758s	13
Br ₂ (C ₆ F ₅) ₂ Ptbipy	1608s, 763s	13
Cl ₂ (C ₆ F ₅) ₂ Ptphen	851s	14
Br ₂ (C ₆ F ₅) ₂ Ptphen	845s	14
Cl ₂ (C ₆ F ₅) ₂ Pt(PBu ₃) ₂	1089s, 905m(br), 800s(br)	a
Br ₂ (C ₆ F ₅) ₂ Pt(PBu ₃) ₂	1090s, 905m(br), 900s(br)	a
Cl ₂ (C ₆ F ₅) ₂ Ptdiars	998s, 686s, 472s, 452s	a
Br ₂ (C ₆ F ₅) ₂ Ptdiars	998s, 686s, 472s, 455s	a

^a Own observations over L or Cl₂PtL₂.

tions due to the respective ligand. They are characteristic of the *cis*-structure [3], and are not observed in the corresponding *trans*-isomers. In the platinum(IV) complexes, the absorptions arising from the C₆F₅ group at ~1050 and 950 cm⁻¹ are shifted with respect to the corresponding platinum(II) complex by ca 10–15 cm⁻¹ towards higher energies, whilst the two bands in the 800 cm⁻¹ region are shifted by ca 10–15 cm⁻¹ towards lower energies (cf. Table 2). The dichloro-platinum(IV) complexes show bands in the 350–250 cm⁻¹ region, assignable to $\nu(\text{Pt}-\text{Cl})$ (cf. Table 2). As may be seen from Table 3, the presence of the ligand L in both the platinum(II) and platinum(IV) complexes can clearly be detected from the respective IR spectrum.

(e) Conductivities

All the complexes are non-conducting in nitromethane ($\Lambda_M = 0-12 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; cf. Table 1).

Experimental

The IR spectra (4000–250 cm⁻¹) were recorded on a Beckman IR 20A spectrophotometer using Nujol mulls between polyethylene sheets. The conductivities were measured in approx. $5 \times 10^{-4} M$ solution with a Philips PW 9501/01 conductimeter. The melting points were determined with a Reichert (Austria) apparatus provided with a microscope with polarizer and heating device. C, H and N analyses were made with a Perkin-Elmer 240 microanalyzer. Quantitative Cl and Br analyses were performed as described by White [6], a few milligrams of sucrose being added to facilitate the combustion [7].

Unless otherwise indicated, the reactions were carried out at room temperature.

Preparation of the complexes

cis-(C₆F₅)₂Pt(PBu₃)₂ (I). *cis*-Cl₂Pt(PBu₃)₂ [8] (0.65 g, 0.97 mmol) was added to a solution of LiC₆F₅ [9] (3.88 mmol) in 50 ml of anhydrous diethyl ether at

-78°C . The mixture was stirred overnight while being allowed to warm to room temperature. Subsequently moist diethyl ether (50 ml) was added to destroy residual LiC_6F_5 . The precipitate was filtered off and 10 ml of methanol was added to the filtrate. The ether was evaporated off, and the residue cooled to -30°C to give the white complex I. This was filtered off, washed with cold methanol and air-dried (0.82 g, 90.8% yield).

trans- $(\text{C}_6\text{F}_5)_2\text{Pt}(\text{PBu}_3)_2$ (II). *trans*- $\text{Cl}_2\text{Pt}(\text{PBu}_3)_2$ [8] (1.34 g, 2.0 mmol) was added to a solution of LiC_6F_5 (5.0 mmol) in 60 ml of diethyl ether. The procedure described for I yielded the white complex II (0.96 g, 51% yield). I and II are soluble in acetone, dichloromethane, diethyl ether, benzene and petroleum ether, but only slightly soluble in methanol and ethanol.

cis- $(\text{C}_6\text{F}_5)_2\text{Pt}(\text{AsPh}_3)_2$ (III). *cis*- $\text{Cl}_2\text{Pt}(\text{AsPh}_3)_2$ [10] (1.32 g, 1.5 mmol) was added to a solution of LiC_6F_5 (6.0 mmol) in 60 ml of anhydrous diethyl ether at -78°C , and the reaction and hydrolysis were carried out as for I. Since the product precipitated out, the diethyl ether was evaporated off and the residue was extracted with 200 ml of warm acetone and filtered. Addition of 20 ml of ethanol and evaporation of the acetone gave the white complex III, which was recrystallized from benzene/ethanol, filtered, washed with ethanol and air-dried (1.20 g, 70% yield). III is soluble in acetone, dichloromethane and benzene, but only slightly soluble in ethanol and diethyl ether.

The same product was obtained from *trans*- $\text{Cl}_2\text{Pt}(\text{AsPh}_3)_2$ [10] and LiC_6F_5 .

trans- $(\text{C}_6\text{F}_5)_2\text{Pt}(\text{AsPh}_3)_2$ (IV). Complex III (0.50 g, 0.43 mmol) was heated to 240°C for 24 h, and the resulting brown solid was washed with a few ml of dichloromethane (though part of the compound was soluble in it). The white complex IV (0.30 g, 60% yield) is soluble in acetone and benzene, and slightly soluble in methanol and ethanol.

$(\text{C}_6\text{F}_5)_2\text{Pt}(\text{diars})$ (V). $\text{Cl}_2\text{Pt}(\text{diars})$ [11] (1.60 g, 2.12 mmol) was added to a solution of LiC_6F_5 (8.48 mmol) in 60 ml of anhydrous diethyl ether at -78°C and the reaction and the hydrolysis were carried out as before. Addition of 15 ml of methanol to the ether solution and subsequent evaporation of the ether afforded the white complex V (1.92 g, 88.9% yield). The solubility was similar to that of I and II.

$\text{Cl}_2(\text{C}_6\text{F}_5)_2\text{Pt}(\text{bipy})$ (VI). Cl_2 was passed for 1 h through a stirred suspension of $(\text{C}_6\text{F}_5)_2\text{Pt}(\text{bipy})$ [3] (0.35 g, 0.51 mmol) in 50 ml of dichloromethane. The excess of Cl_2 was taken off under vacuum, 10 ml of ethanol were added, and the dichloromethane was evaporated off. The yellow complex VI was filtered off, washed with ethanol, and recrystallized from acetone/ethanol (0.30 g, 77% yield).

$\text{Br}_2(\text{C}_6\text{F}_5)_2\text{Pt}(\text{bipy})$ (VII). A stirred suspension of $(\text{C}_6\text{H}_5)_2\text{Pt}(\text{bipy})$ (0.40 g, 0.58 mmol) in 40 ml of dichloromethane was instantaneously dissolved on adding 14 ml of a 0.95 N solution of Br_2 in the same solvent. The formation of a precipitate was observed after approx. 90 min and the yellow complex VII was filtered off after 6 days stirring. It was washed with dichloromethane and air-dried (0.31 g, 62.8% yield).

$\text{Cl}_2(\text{C}_6\text{F}_5)_2\text{Pt}(\text{phen})$ (VIII). Cl_2 was bubbled through a stirred suspension of $(\text{C}_6\text{F}_5)_2\text{Pt}(\text{phen})$ [3] (0.30 g, 0.42 mmol) in 50 ml of dichloromethane until the precipitate was completely dissolved (~ 2 min). The solution was filtered and the excess of Cl_2 was sucked off under vacuum. After addition of 5 ml of ethanol, the dichloromethane was evaporated until a slight precipitate formed. The

solution was then set aside for 5 min and the resulting yellow complex was immediately filtered off, washed with ethanol and air-dried (0.12 g, 33.6% yield). Successive crystallizations of the filtrate yielded crystals with a chlorine proportion higher than the calculated value.

$Br_2(C_6F_5)_2Ptphen$ (IX). A stirred suspension of $(C_6F_5)_2Ptphen$ [3] (1.42 g, 2.07 mmol) in 60 ml of dichloromethane was immediately dissolved on adding 10 ml of a 0.95 N Br_2 solution in the same solvent. The formation of an orange-yellow precipitate was observed after a few minutes. IX was filtered off after further 2 days stirring, washed with dichloromethane, and air-dried (1.2 g, 69% yield). VI, VII, VIII and IX are soluble in acetone, and slightly soluble in dichloromethane, benzene, methanol and ethanol.

$Cl_2(C_6F_5)_2Pt(PBu_3)_2$ (X). Cl_2 was bubbled for 20 min through a solution of *cis*- $(C_6F_5)_2Pt(PBu_3)_2$ (0.24 g, 0.25 mmol) in 25 ml of dichloromethane. The excess of Cl_2 was sucked off, 10 ml of methanol were added, whereupon the dichloromethane was evaporated. Cooling the solution to $-30^\circ C$ gave complex X, which was filtered off, washed with cold methanol and air-dried (0.2 g, 80% yield). Solubilities as for I and II.

$Br_2(C_6F_5)_2Pt(PBu_3)_2$ (XI). 1 ml of a 1 N Br_2 solution in CCl_4 was added to a solution of *cis*- $(C_6F_5)_2Pt(PBu_3)_2$ (0.24 g, 0.25 mmol) in 25 ml of dichloromethane. After 12 h stirring, 5 ml of methanol were added and the yellow crystals of XI were obtained upon evaporating the dichloromethane. It was filtered off, washed with cold methanol and air dried (0.23 g, 84% yield). Solubilities as for I and II.

$Cl_2(C_6F_5)_2Pt diars$ (XII). The addition of a solution of 0.475 mmol of Cl_2 in CCl_4 to a stirred solution of $(C_6F_5)_2Pt diars$ (0.482 g, 0.475 mmol) in 20 ml of benzene gave a yellow precipitate. The solution was stirred for 12 h and the resulting complex XII was filtered off, washed with benzene, and dried at $120^\circ C$ to remove benzene and crystallization (0.39 g, 75% yield).

$Br_2(C_6F_5)_2Pt diars$ (XIII). On addition of 0.510 mmol of Br_2 in CCl_4 to a stirred solution of $(C_6F_5)_2Pt diars$ (0.518 g, 0.510 mmol) in 25 ml of benzene the Br_2 disappeared and a bright-yellow solid separated. This was isolated by the above procedure (0.48 g, 82% yield). XII and XIII are soluble in acetone and dichloromethane and slightly soluble in benzene, methanol and ethanol.

Reaction with I_2 . Solutions or suspensions of bis(pentafluorophenyl) compounds in toluene were treated for 8–10 h under reflux with an excess of I_2 . The resulting insoluble complexes were filtered off and recrystallized from acetone/ethanol. When the resulting complexes were soluble the toluene was evaporated, the residue extracted with acetone, and the compound finally isolated by addition of ethanol and subsequent evaporation. When L = py a black product (probably $I_4Pt py_2$ [12]) was obtained, which during the recrystallization was transformed into *trans*- $I_2Pt py_2$. The resulting complexes were identified by quantitative analysis and IR spectroscopy.

Reaction with CH_3I . Suspensions of bis(pentafluorophenyl) derivatives in CH_3I were stirred for 24 h, and the complexes were recovered by evaporating off the CH_3I . The identities of the complexes were confirmed by quantitative analyses and IR spectroscopy.

References

- 1 P. Royo, *Rev. Acad. Ciencias Zaragoza*, 27 (1972) 235.
- 2 R. Usón, P. Royo y J. Gimeno, *Rev. Acad. Ciencias Zaragoza*, 28 (1973) 355.
- 3 R. Usón, J. Forniés, J. Gimeno, P. Espinet and R. Navarro, *J. Organometal. Chem.*, 81 (1974) 115.
- 4 D.T. Rosevear and F.G.A. Stone, *J. Chem. Soc.*, (1965) 5275.
- 5 R. Uson, J. Forniés, P. Espinet and J. Garín, *J. Organometal. Chem.*, 105 (1976) C25.
- 6 D.C. White, *Microchim. Acta*, (1961) 449.
- 7 Rudolf Bock, "Aufschlussmethoden der anorganischen und organischen Chemie", Verlag Chemie, 1972, p. 110.
- 8 G.B. Kauffman, *Inorg. Synth.*, 7 (1963) 245.
- 9 P.L. Coe, R. Stephens and J.C. Tatlow, *J. Chem. Soc. A*, (1962) 3227.
- 10 *Gmelins Handbuch*, 68 (1957) 356.
- 11 G.W. Watt and J.E. Cuddeback, *J. Inorg. Nucl. Chem.*, 33 (1971) 259.
- 12 *Gmelins Handbuch*, 68 (1957) 583.
- 13 J.R. Durig, B.R. Mitchell, D.W. Sink, J.N. Willis, Jr. and A.S. Wilson, *Spectrochim. Acta, Part A*, 23 (1967) 1121.
- 14 J.R. Ferraro and N.R. Walker, *Inorg. Chem.*, 4 (1965) 1382.