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# BIS(PENTAFLUOROPHENYL) COMPLEXES OF PALLADIUM(II) AND OF PLATINUM(II)

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## Summary

The preparation of eight bis(pentaflurophenyl) complexes of $Pd^{II}$ and of $Pt^{II}$ with monodentate and bidentate nitrogen-donor ligands is described together with a preparation of a $Pd^{II}$ complex of 1,2-bis(diphenylphosphino)ethane. Some properties of the complexes are given.

New possibilities for assignment of *cis* or *trans* configuration are discussed which depend upon the splitting or disappearance of certain bands in the IR spectra.

## Introduction

Most of the known pentafluorophenyl derivatives of palladium(II) and of platinum(II) [1-5] are neutral complexes of the (phosphine)$_2$ M($C_6F_5$)X and (phosphine)$_2$ M($C_6F_5$)$_2$ types, or are cationic complexes [6,7] of the [(phosphine)$_2$ M($C_6F_5$)L]$ClO_4$ type.

There is only one palladium(II) derivative and one platinum(II) derivative which do not include phosphine as one of their ligands [3]: these are [(bipy)Pd($C_6F_5$)$_2$] and [(norbornadiene)Pt($C_6F_5$)$_2$]. In addition, there is a single case of a platinum(II) complex which contains a diphosphine as a ligand [($Ph_2PCH_2CH_2PPh_2$)Pt($C_6F_5$)$_2$] [1].

We describe here the preparation of new pentafluorophenyl derivatives of palladium(II) and of platinum(II) with monodentate and bidentate nitrogen ligands (py, bipy, phen, en, tmen). Furthermore, the palladium(II) complex [($Ph_2PCH_2CH_2PPh_2$)Pd($C_6F_5$)$_2$] has been prepared. All these complexes are described for the first time in this paper.

## Results and discussion

### *(a) Preparation of the complexes*

All the preparations were carried out according to eqn. 1, where M = Pd,

$$L_2MCl_2 + 2LiC_6F_5 \rightarrow L_2M(C_6F_5)_2 + 2LiCl \qquad (1)$$

$L_2$ = $2C_5H_5N$, $H_2NCH_2CH_2NH_2$, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)-ethane, or *N*, *N*, *N'* *N'*-tetramethylethylene diamine; and where M = Pt, $L_2$ = $2C_5H_5N$(*cis*), $2C_5H_5N$ (*trans*), 2,2'-bipyridine or 1,10-phenanthroline, respectively.

The starting materials were prepared according to published methods (see Experimental) and were added to an excess of $LiC_6F_5$ in ether solution at −78° In the case of the platinum complexes, $CH_2Cl_2$ was added in order to improve the solubility. Whenever the reaction took place readily at a low temperature, which was the case with all the platinum complexes, that temperature was maintained throughout so as to prevent the decomposition of the $LiC_6F_5$ [8]: when the reaction did not go to completion at a low temperature, as in the case of the palladium complexes, the temperature of the mixture was allowed to rise rapidly in order to obtain pure end-products. It is important to follow the instructions given in the Experimental section closely in order to avoid a substantial decrease in yield or even complete failure of the reaction.

The resulting solutions were evaporated to dryness and the residues were extracted with acetone The complexes were crystallized from the solutions by the addition of ethanol or benzene or by cooling to −30° As a consequence of that treatment the crystals of some of the platinum complexes contained acetone, as is clearly seen from the IR spectra The acetone can be removed either by heating the product in a drying-oven to over 120° or by recrystallization from a benzene solution.

The chlorine in the starting complexes is completely substituted in all the cases. This is shown by the disappearance of the $\nu$(M—Cl) bands from the IR spectra and by qualitative tests, which show the total absence of Cl in the new complexes.

### *(b) IR spectra*

Table 1 lists the vibrations which we have assigned to $C_6F_5$. Those near 1500, 1060 and 950 $cm^{-1}$, which are generally assigned to that group [3, 4, 6, 7, 9], appear split or broad This splitting has already been observed [9] in *cis*-complexes of the $XAu(C_6F_5)_2PPh_3$ type.

In addition to this, in Table 1 we assign to the $C_6F_5$ groups two bands near 800 $cm^{-1}$ which appear more or less superimposed with other bands in the complexes containing phosphines. This is probably the reason why they have not been assigned before, since most of the known complexes contain phosphines. These two bands at 800 $cm^{-1}$ correspond to a symmetrical vibration and are to be observed in all the complexes with two mutually *cis* $C_6F_5$ groups At least in all the cases which are known to us [5-7], they are reduced to a single band when there is only a single $C_6F_5$ group, and disappear when the two $C_6F_5$ groups are mutually *trans*. They may therefore be of use for structural diagnosis, but this proposal can only be considered as provisional until more experimental evidence is available.

The presence of the ligand L in each complex is confirmed by the IR spectra; this can be clearly deduced from the data in Table 2.

In the complexes which contain acetone a band is observed at 1721 s $cm^{-1}$. It corresponds to $\nu$(C=O) and appears at the same frequency as in the free acetone.

TABLE 1

ABSORPTIONS ASSIGNED TO THE $C_6F_5$ GROUP IN $(C_6F_5)_2ML_2$

| | | | | |
|---|---|---|---|---|
| $(C_6F_5)_2Pt(bipy)$ | 1505s | 1065(sh)-1060s | 961(sh) 959s | 808s 798s |
| $(C_6F_5)_2Pd(bipy)$ | 1503s | 1070(sh)-1060s | 953s (br) | 795s-784s |
| $(C_6F_5)_2Pt(phen)$ | 1510s | 1069s-1063s | 959s 952s | 806 798s |
| $(C_6F_5)_2Pd(phen)$ | 1503s | 1071(sh) 1063 | 951s (br) | 795s 785s |
| *cis*-$(C_6F_5)_2Pt(py)_2$ | 1508s | 1070s-1063(s)$^c$ | 955s 950s | 806s-798s |
| *trans*-$(C_6F_5)_2Pt(py)_2$ | 1500s | 1055s-1050(s)$^c$ | 918s-942s | |
| *trans*-$(C_6F_5)_2Pd(py)_2$ | 1497s | 1053s-1010(s)$^c$ | 915s (br) | |
| $(C_6F_5)_2Pt(P—P)^a$ | 1500s | 1057s (br) | 955s (br) | *c* |
| $(C_6F_5)_2Pd(P—P)$ | 1496s | 1057s-1011s | 950s | *c* |
| $(C_6F_5)_2Pd(en)$ | 1500(sh) 1496s | *c* | 950s 915(sh) | 790s-780s |
| $(C_6F_5)_2Pd(tmen)^b$ | 1500s | *c* | 950s 916(sh) | *c* |

[a] (P—P) = $Ph_2PCH_2CH_2PPh_2$ [b] (tmen) = *N, N, N' N'*-tetramethylethylenediamine [c] Vibrations due to the ligand are also observed in this range, this does not allow any assignment to be made

TABLE 2

ABSORPTIONS ASSIGNED TO THE NEUTRAL LIGANDS IN $(C_6F_5)_2ML_2$

| | | | | | |
|---|---|---|---|---|---|
| $(C_6F_5)_2Pt(bipy)$ | 1606m | 765s | | | Ref. 10 |
| $(C_6F_5)_2Pd(bipy)$ | 1600s | 763s | | | Ref. 10 |
| $(C_6F_5)_2Pt(phen)$ | 842s | | | | Ref. 11 |
| $(C_6F_5)_2Pd(phen)$ | 845s | | | | Ref. 11 |
| *cis*-$(C_6F_5)_2Pt(py)_2$ | 1610s | 761s[a] | | 697s | Ref 10 |
| *trans*-$(C_6F_5)_2Pt(py)_2$ | 1608s | 775s[a] | 766s[a] | 692s | Ref 10 |
| *trans*-$(C_6F_5)_2Pd(py)_2$ | 1607s | 767s[a] | 757s[a] | 688s | Ref 10 |
| $(C_6F_5)_2Pt(P-P)$ | 690s | 527s | 475m | | Ref. 12 |
| $(C_6F_5)_2Pd(P-P)$ | 690m | 526s | 475m | | Ref. 12 |
| $(C_6F_5)_2Pd(en)$ | 3380s | 3320s | 1595s | | Ref 12 |
| $(C_6F_5)_2Pd(tmen)$ | 1125m | 1012m | | | Ref 12 |

[a] *trans* $Cl_2M(py)_2$ shows only a band at this range, *cis*-$Cl_2M(py)_2$ shows two bands

Were the acetone to be coordinated this band should be shifted towards lower frequency, so one must conclude that the molecule of acetone is only filling holes of the structure.

### *(c) Conductivities*

All the complexes behave as non-conductors in nitromethane solution ($\Lambda_M$ = 0 to 6 $ohm^{-1}cm^2mol^{-1}$).

### *(d) Magnetic susceptibilities*

All the complexes are diamagnetic as is to be expected for tetracoordinated square planar complexes of $d^8$ ions.

## Experimental

Conductivities were measured in approx 5 × $10^{-4}$ *M* solutions with a Philips PW 9501/01 conductimeter. Melting points were determined with an Reichert (Austria) apparatus provided with a microscope with polarizator and heating device. IR spectra were recorded on a Beckman IR 20 A spectrophotometer (over the range of 4000-250 $cm^{-1}$) using Nujoll mulls between polyethylene sheets. Magnetic susceptibilities were measured with a balance constructed in our Department [13]. C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. The analytical results are in reasonable agreement with the proposed formulae if the difficulties which arise from the presence of P and F in our samples are taken into account [14]. Ether solutions of pentafluorophenyllithium were prepared "in situ", according to ref. 8.

### *I Bis(pentafluorophenyl)-2,2'-bipyridineplatinum(II)*

To a solution of 27 mmol of $LiC_6F_5$ in 60 ml of dry ether, in a dry $N_2$ atmosphere and at −78° was added 1 90 g (4.50 mmol) of finely powdered $Cl_2Pt(bipy)$ [15]. Afterwards 140 ml of dry dichloromethane was added. The mixture was stirred during the night while the temperature was allowed to rise slowly to room temperature. The solution was evaporated to ≈ 75 ml and filtered. The resultant yellow precipitate was washed with 25 ml of dry $CH_2Cl_2$

and extracted with 200 ml of warm acetone. The solution was filtered and 2.9 g of a yellow compound was obtained after adding 25 ml of ethanol and evaporating the acetone. The product was identified as $(C_6F_5)_2Pt(bipy)\cdot xCO(CH_3)_2$ ($x \approx$ 0.2-0.25). Yield ≈ 92%.

Acetone was removed by heating $(C_6F_5)_2Pt(bipy)\cdot xCO(CH_3)_2$ at 120° until the weight remained constant. The final product, I, was identified as $(C_6F_5)_2Pt(bipy)$; it decomposes at 335° and is air-stable at room temperature. It is soluble in acetone, not very soluble in nitromethane, benzene and ethanol, and insoluble in petroleum ether. $\Lambda_M$ = 0.60 ohm$^{-1}$cm$^2$mol$^{-1}$. (Found. C, 38.38; H, 1.05; N, 3.80 Calcd · C, 38.55; H, 1.17; N, 4.08%.)

*II Bis(pentafluorophenyl)-1,10-phenanthrolineplatinum(II)*

To a solution of 40.5 mmol of $LiC_6F_5$ in 60 ml of dry ether at −78° was added 3.00 g (6.70 mmol) of finely powdered $Cl_2Pt(phen)$ [16] and 140 ml of dry dichloromethane. The mixture was stirred overnight while the temperature was allowed to rise slowly to room temperature. Then the solution was evaporated to 75 ml and filtered The yellowish residue was washed with 25 ml of dry $CH_2Cl_2$.

The residue was extracted with 200 ml of warm acetone and filtered. 2.6 g of a yellow compound were obtained after adding 25 ml of ethanol and evaporating the acetone. The product was filtered, washed with ethanol and air-dried. It was identified as $(C_6F_5)_2Pt(phen)\cdot xCO(CH_3)_2$ ($x \approx$ 0.75) (yield ≈ 52%)

Bis(pentafluorophenyl)-1,10-phenanthrolineplatinum(II) was obtained by heating a sample at 160° till the weight remained constant. Complex II is a yellow solid which is airstable at room temperature, soluble in acetone, not very soluble in nitromethane and dichloromethane, slightly soluble in benzene and insoluble in n-hexane and petroleum ether. It decomposes at 335°. $\Lambda_M$ imperceptible in nitromethane. (Found: C, 39.19, H, 1.05; N, 3.95. Calcd.. C, 40.63, H, 1.13; N, 3.95%.)

*III trans-Bis(pentafluorophenyl)bis(pyridine)platinum(II)*

To a solution of 16 mmol of $LiC_6F_5$ in 60 ml of dry ether at −78° was added 1.69 g (4.00 mmol) of finely-powdered *trans*-$Cl_2Pt(py)_2$ [17] and 30 ml of dry dichloromethane. The mixture was stirred overnight while the temperature was allowed to rise slowly to room temperature. Then the solution was evaporated to dryness and the residue extracted with 200 ml of warm acetone and filtered.

2.50 g of an off-white compound was obtained after adding 25 ml of ethanol and evaporating the acetone. The product was filtered, washed with ethanol and air-dried. It was identified as *trans*-$(C_6F_5)_2Pt(py)_2\cdot xCO(CH_3)_2$ (yield ≈ 90%).

The white complex $(C_6F_5)_2Pt(py)_2$ (III) was obtained by recrystallizing the compound from benzene; it is a white solid, which is air-stable at room temperature and decomposes at 265°. It is soluble in acetone, benzene and dichloromethane, not very soluble in ethanol, and insoluble in n-hexane and petroleum ether. $\Lambda_M$ imperceptible in nitromethane. (Found: C, 38.38; H, 1.45; N, 4.00. Calcd.: C, 38.44; H, 1.46; N, 4.07%.)

*IV. cis-Bis(pentafluorophenyl)bis(pyridine)platinum(II)*

To a solution of 26.4 mmol of $LiC_6F_5$ in 80 ml of ether at −78° was added 2.8 g (6.60 mmol) of finely powdered *cis*-$Cl_2Pt(py)_2$ [17] and 40 ml of dry dichloromethane. The mixture was stirred overnight while the temperature was allowed to rise slowly to room temperature. The solution was evaporated to dryness and the residue extracted with 150 ml of acetone and filtered. A white product was obtained after adding 25 ml of ethanol and evaporating the acetone. The product was identified as a mixture of IV and a small quantity of III.

To separate the isomers the mixture was treated with boiling benzene and then allowed to cool, with the result that only IV crystallized. Additional quantities of IV were obtained after partially evaporating the benzene and succesive crystallizations. The last fraction contained a mixture of III with a small amount of IV When the mixture was recrystallized from diethyl ether a product was obtained from the middle fraction for which the structural data, physical constants and analysis coincide completely with those given for III (Found. C, 4.06, H, 1.52; N, 4.06%.) 2.50 g of IV and 0.20 g of III were obtained. The yield is 55.1 for IV and 4.4% for III.

IV is a white solid which is air-stable at room temperature and decomposes at 230-235°. It is soluble in acetone and dichloromethane, not very soluble in benzene, nitromethane and diethyl ether, scarcely soluble in ethanol, and insoluble in petroleum ether. $\Lambda_M$ imperceptible in nitromethane. (Found. C, 38.04; H, 1.31; N, 4.02. Calcd.: C, 38.44, H, 1.46; N, 4.07%.)

*V Bis(pentafluorophenyl)-1,10-phenanthrolinepalladium(II)*

To a solution of 21.6 mmol of $LiC_6F_5$ in 70 ml of ether at −78° was slowly added 2.45 g of $Cl_2Pd(phen)$ [18] The mixture was stirred for 1 h at −78°, then the flask removed from the cooling bath and the temperature allowed to rise rapidly while the mixture was still stirred for three hours The ether solution was evaporated to dryness and the residue extracted with boiling acetone. V crystallized after filtering the warm acetone solution and cooling to −30° The yield can be improved by evaporating the solvent and by succesive crystallizations. The white solid was filtered, washed with ethanol and dried in vacuo. 2.79 g of V was obtained (yield 70%). V is stable at room temperature. It is soluble in acetone, nitromethane, dichloromethane and chloroform, scarcely soluble in benzene and diethyl ether, and insoluble in ethanol and water. It decomposes at 320° $\Lambda_M$ = 0.78 $ohm^{-1}cm^2mol^{-1}$ in nitromethane (Found C, 45.98; H, 1.82; N, 4.42. Calcd.. C, 46.44; H, 1.29, N, 4.51%.)

*VI. Bis(pentafluorophenyl)-1,2-bis(diphenylphosphino)ethanepalladium(II)*

To a solution of 11.8 mmol of $LiC_6F_5$ in 50 ml of 1,2-bis(diphenylphosphino) ethane at −78° was added 2.304 g (4.0 mmol) of $Cl_2Pd(Ph_2PCH_2CH_2PPh_2)$ [19]. The mixture was stirred for one hour at −78°. The flask was then removed from the cooling bath and allowed to reach room temperature quickly. The mixture was stirred for three hours The ether was evaporated to dryness and the residue extracted with boiling acetone. The warm acetone solution was filtered and concentrated to 25 ml. Ethanol was added drop by drop till a white precipitate was observed. The solution was then left standing at −30° overnight and 2.9 g (66% yield) of VI crystallized.

Complex VI is a white solid which is air-stable at room temperature and decomposes at 257°. It is soluble in acetone, nitromethane, dichloromethane and chloroform, not very soluble in diethyl ether and benzene and insoluble in ethanol and water. $\Lambda_M$ = 0.42 ohm$^{-1}$cm$^2$mol$^{-1}$ (Found C, 52.29; H, 2.93. Calcd.. C, 54.40; H, 2.89%.)

### *VII Bis(pentafluorophenyl)ethylenediaminepalladium(II)*

To a solution of 9 mmol of $LiC_6F_5$ in 50 ml of dry ether at −78° was added 0.71 g (3 mmol) of $Cl_2Pd(en)$ [20] The mixture was stirred at −78° for one hour, removed from the cooling bath and then stirred for four hours at room temperature. After evaporation to dryness, the residue was extracted with acetone and filtered The solution was concentrated to a few ml. LiCl was precipitated by adding benzene and filtered off. The benzene solution was evaporated to dryness, and VII crystallized after the addition of some drops of dichloromethane to the oily residue. It is a white solid which is air-stable at room temperature but decomposes at 238°. It is soluble in acetone and benzene and not very soluble in dichloromethane. $\Lambda_M$ = 5.25 ohm$^{-1}$cm$^2$mol$^{-1}$ (Found C, 33.06, H, 1.56, N, 5.43. Calcd. C, 33.59; H, 1.61, N, 5.59%.)

### *VIII trans-Bis(pentafluorophenyl)bis(pyridine)palladium(II)*

To a solution of 21 mmol of $LiC_6F_5$ in 70 ml of dry ether at −78° was added 2.348 g (7 mmol) of *trans*-$Cl_2Pd(py)_2$ [21]. The mixture was stirred for one hour at −78° and then removed from the cooling bath It was allowed to warm to room temperature and stirred for four hours The ether was evaporated to dryness and the residue extracted with boiling acetone The acetone solution was filtered and concentrated, and a few ml of ethanol added. The solution was left to stand at −30° overnight A white compound crystallized which after filtering and washing was identified as VIII It is a white solid which is stable in air at room temperature but decomposes at 252°. It is soluble in acetone, nitromethane, dichloromethane and chloroform, not very soluble in diethyl ether and benzene and insoluble in ethanol and water $\Lambda_M$ = 1.13 ohm$^{-1}$cm$^2$mol$^{-1}$. (Found. C, 44.24; H, 1.71, N, 4.59 Calcd.. C, 44.13, H, 1.68, N, 4.67%.)

### *IX Bis(pentafluorophenyl)-N,N,N′,N′-tetramethylethylenediaminepalladium(II)*

To a solution of 14 mmol of $LiC_6F_5$ in 70 ml of dry ether at −78° was added 1.17 g (4 mmol) of $Cl_2Pd(tmen)$ [22], the mixture was stirred at −78° for one hour and then removed from the cooling bath. It was then stirred for 15 h at room temperature. The mixture was evaporated to dryness and the residue extracted with warm acetone. After filtering the solution was concentrated to ≈ 10 ml; a white solid crystallized which was filtered, washed with a small quantity of alcohol and dried in vacuo. The complex was recrystallized from an acetone solution on addition of water. 1.9 g of IX was obtained (yield 85%).

IX is a white solid which is air-stable at room temperature but decomposes at 263°. It is soluble in acetone, dichloromethane, nitromethane and benzene, not very soluble in ether, slightly soluble in ethanol and insoluble in water. $\Lambda_M$ = 2.49 ohm$^{-1}$cm$^2$mol$^{-1}$. (Found: C, 39.15, H, 3.20; N, 4.79. Calcd.: C, 38.83; H, 3.20; N, 5.03%.)

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