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Pentafluorophenyl Derivatives of Palladium(II)

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Solutions apparently containing $Pd(C_6F_5)_2$ *are obtained by reaction of* K_2PdCl_4 *with* C_6F_5MgBr *in THF and further addition of 1,4-dioxane (Dx). From these solutions it is possible to isolate the dioxane complexes* $Pd(C_6F_5)_2Dx_n$ *(n = 1, 2, 3) with* cis *and/or* trans *configurations, as well as* $\{Pd(C_6F_5)Dx(\mu\text{-}Cl)\}_2$*, depending on the reactant ratio. The addition of different ligands to the preceding solutions leads to the preparation of* cis *and* trans *complexes of the type* $Pd(C_6F_5)_2L_2$*, L being* $OPPh_3$*,* $OAsPh_3$*, and* NH_3*. Structural data for these compounds are obtained by IR spectroscopy and magnetic susceptibility measurements.*

Introduction

A general method for the preparation of bis-pentafluorophenyl derivatives of palladium(II) is based on the reaction of C_6F_5MgBr or C_6F_5Li with the corresponding halocomplexes, PdX_2L_2. Complexes of the type $Pd(C_6F_5)_2L_2$, where L is a mono or bidentate phosphine [1–4], 2,2′-bipyridine [2, 3], pyridine, *o*-phenanthroline, ethylenediamine, tetramethylenediamine [3], triphenylarsine, triphenylstibine, benzylamine [4], and tetrahydrothiophene [5], have been prepared this way. However, this method requires the availability of the initial halocomplexes.

In this work we follow a different route to obtain bis-pentafluorophenyl derivatives of palladium(II), starting from solutions apparently containing '$Pd(C_6F_5)_2$'. In fact, this method had already been applied to the preparation of similar compounds of cobalt(II) [6] and nickel(II) [7, 8].

Experimental

Materials

C_6F_5MgBr was prepared by the method given in ref. [9] and K_2PdCl_4 was obtained from metallic palladium [10]. Ligands were commercial grade chemicals.

Methods

Magnetic susceptibility was determined by the Gouy method at room temperature. IR spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer 457 spectrophotometer as Nujol mulls and KBr pellets. Conductivities were measured with a Phillips PW 9501/01 conductimeter. Melting points were determined on a Reichert microscope provided with heating plate.

Microanalyses

The C, H, N analyses were performed with a Perkin-Elmer 240 microanalyzer. Palladium was determined gravimetrically as dimethylglyoximate [11].

Preparation of the Complexes

Solutions starting from $2C_6F_5$ *(as* C_6F_5Br*)/1Pd (A)*

A freshly prepared and filtered solution of C_6F_5MgBr (from 1.53 ml of C_6F_5Br; 12.26 mmol) in THF (20 ml) was added to a suspension of K_2PdCl_4 (2 g; 6.13 mmol) in THF (10 ml). The reaction mixture was then refluxed and stirred for 4 h. After this time, an insoluble orange solid in an orange-yellow solution was obtained. The addition of dioxane (30 ml) separated most of the magnesium salts as dioxane complexes. After standing in the cold overnight, the solid was filtered off and a yellow solution was obtained. This solution (A) remained unaltered for several weeks when stored in the cold and under dry nitrogen.

cis-$Pd(C_6F_5)_2(\mu\text{-}Dx)$ *(I)*

15 ml of the yellow solution A were concentrated under vacuum at room temperature. The addition of hexane (20 ml) yielded a yellow solid, which was filtered and washed several times with hexane (33% yield).

cis-$Pd(C_6F_5)_2L_2$*; L =* $OPPh_3$ *(II),* $OAsPh_3$ *(III),* NH_3 *(IV)*

In separate experiments, (4.60 mmol) solutions in THF of $OPPh_3$ and $OAsPh_3$ were added to 15 ml

TABLE I. Analyses and Melting Points for the Pentafluorophenyl Palladium(II) Complexes.

No.	Complex	Analyses found (calc) %				M.P. °C
		C	H	N	Pd	
I	*cis*-Pd$(C_6F_5)_2(\mu$-Dx)	35.4	1.7	–	19.2	60(d)
		(36.3)	(1.5)		(20.1)	
II	*cis*-Pd$(C_6F_5)_2(OPPh_3)_2$	57.0	3.2	–	10.3	175
		(57.8)	(3.0)		(10.7)	
III	*cis*-Pd$(C_6F_5)_2(OAsPh_3)_2$	52.7	2.8	–	9.6	196(d)
		(53.1)	(2.8)		(9.8)	
IV	*cis*-Pd$(C_6F_5)_2(NH_3)_2$	28.8	1.1	5.5	21.2	135(d)
		(30.4)	(1.3)	(5.9)	(22.4)	
V	*trans*-Pd$(C_6F_5)_2Dx_3$	41.1	2.8	–	15.3	202(d)
		(40.9)	(3.4)		(15.1)	
VI	*trans*-Pd$(C_6F_5)_2Dx_2$	38.8	2.5	–	17.3	205(d)
		(38.9)	(2.6)		(17.3)	
VII	*trans*-Pd$(C_6F_5)_2(OPPh_3)_2$	58.1	2.9	–	10.3	180(d)
		(57.8)	(3.0)		(10.7)	
VIII	*trans*-Pd$(C_6F_5)_2(OAsPh_3)_2$	53.4	3.0	–	10.0	210(d)
		(53.1)	(2.8)		(9.8)	
IX	*trans*-Pd$(C_6F_5)_2(NH_3)_2$	29.5	1.1	5.4	21.8	145(d)
		(30.4)	(1.3)	(5.9)	(22.4)	
X	$\{Pd(C_6F_5)Dx(\mu Cl)\}_2$	28.0	2.4	–	25.5	133(d)
		(30.2)	(2.0)		(26.8)	
XI	*trans*-Pd$(C_6F_5)_2(\mu$-Dx)	36.6	1.2	–	19.7	205(d)
		(36.3)	(1.5)		(20.1)	

of solution A under nitrogen. After stirring for ½ h, the solution was concentrated under vacuum, and the excess of ligand was filtered off. The resulting solution was then evaporated to dryness under vacuum, and the solid residue was redissolved in THF. The addition of hexane gave the expected organocomplexes, as pale yellow ($OPPh_3$) or white ($OAsPh_3$) solids, respectively (40–50% yields).

In a separate experiment, dry NH_3 gas was slowly bubbled through 15 ml of solution A (over a time no longer than 2 min, since the presence of an excess of NH_3 produces the reduction to metallic palladium), which immediately became colorless. The solution was evaporated to dryness under vacuum and the solid residue was dissolved with THF. The addition of hexane resulted in a white solid, which was filtered and washed with the same solvent (49% yield).

Solution starting from $3C_6F_5$ (as C_6F_5Br)/1Pd (B)

The experimental procedure was similar to that used in the preparation of solution A, except for the reactant ratio: the solution of C_6F_5MgBr (from 2.29 ml of C_6F_5Br; 18.39 mmol) in THF (25 ml) was added to a suspension of K_2PdCl_4 (2 g; 6.13 mmol) in THF (15 ml) and the magnesium salts were precipitated with 40 ml of dioxane, resulting in a brown precipitate and a pale yellow solution (B).

trans-*$Pd(C_6F_5)_2Dx_3$ (V)*

20 ml of solution B were slowly evaporated under reduced pressure at room temperature, yielding white crystals of compound V (71% yield).

trans-*$Pd(C_6F_5)_2Dx_2$ (VI)*

Unlike the preceding experiment, 20 ml of solution of B were evaporated until almost dryness. By addition of hexane, a white solid resulted, which was washed several times with the same solvent and vacuum-dried for 2 h (80% yield).

trans-*$Pd(C_6F_5)_2L_2$; L = $OPPh_3$ (VII), $OAsPh_3$ (VIII), NH_3 (IX)*

The use of solution B (20 ml) instead of A leads to the *trans* isomers when following the same procedure used in the preparation of the *cis* ones. The $OPPh_3$ and $OAsPh_3$ compounds were white and they were crystallized from acetone (61 and 65% yields, respectively). The NH_3 compound was also white (57% yield).

$\{Pd(C_6F_5)_2Dx(\mu$-$Cl)\}_2$ (X)

A freshly prepared and filtered solution of C_6F_5-MgBr (from 0.38 ml of C_6F_5Br; 3.06 mmol) in THF (10 ml) was added to a suspension of K_2PdCl_4 (1 g; 3.06 mmol) in THF (20 ml). The reaction mixture was stirred and refluxed for 4 h. Afterwards, unreacted K_2PdCl_4 was removed by filtration. By addition of dioxane to the solution, an orange solid (C) in a solution of the same color (D) was obtained. The mixture was filtered and the solid C was redissolved with THF (15 ml). The addition of dioxane (5 ml) to this solution separated the magnesium salts, which were filtered off. The addition of dioxane to the filtrate led to the crystallization of the orange compound X. By treatment with dioxane, it was possible to isolate further amounts of compound X from solution D (53% yield).

trans-*Pd*$(C_6F_5)_2(\mu$-*Dx*) *(XI)*

This compound was obtained by heating *trans*-Pd$(C_6F_5)_2Dx_2$ at 135 °C under a flow of dry nitrogen.

Table I shows the analytical results and melting points of the complexes.

Results and Discussion

THF solutions containing the presumed bisorganopalladium(II) are obtained according to the following equation:

$$K_2PdCl_4 + 2C_6F_5MgBr \rightarrow \text{'}Pd(C_6F_5)_2\text{'} + MgBr_2 + MgCl_2 + 2KCl$$

where all these species should be present as THF solvates. The addition of dioxane to the solutions results in the precipitation of most of the magnesium salts as scarcely soluble magnesium complexes. The resulting solution contains mainly $Pd(C_6F_5)_2$ and the presence of small amounts of impurities do not disturb the preparative uses of the solution.

The THF–dioxane solutions thus prepared behave in a different way depending on the reactant ratio ($2C_6F_6$/1Pd for solution A and $3C_6F_5$/1Pd for solution B; see Experimental), which could be understood assuming that the dioxane solvate is present in solutions A and B as the *cis* and *trans* isomer, respectively. Under this assumption, the reaction which leads to $Pd(C_6F_5)_2L_2$ (L = $OPPh_3$, $OAsPh_3$, and NH_3) could be understood as a mere substitution of dioxane by L, with retention of the *cis* or *trans* configuration of the initial solvate. However, when the ratio is $1C_6F_5$/1Pd, the compound $\{Pd(C_6F_5)Dx(\mu\text{-}Cl)\}_2$ is obtained. It is of interest to note that the solubility of this compound in the THF–dioxane mixture is close to that of the magnesium salts, making their separation difficult. Moreover, in the preparation of complex I we observed that the color of the precipitated magnesium salts was orange. These facts suggest the presence of $\{Pd(C_6F_5)Dx(\mu\text{-}Cl)\}_2$ in the precipitate, what could explain the low yield of complex I.

Most of the complexes described here are stable at room temperature under dry nitrogen, except complexes I and X, which decompose slowly. However, complexes II and III decompose slowly in the presence of air, while I and X decompose more quickly.

All the complexes are soluble in THF, dioxane (X slightly), chloroform, methanol, ethanol, and acetone. In addition, the NH_3 complexes are soluble in benzene, dichloromethane, and diethyl ether. These solutions are stable under dry nitrogen, but again complexes I and X decompose in dioxane-free solvents. All the compounds are insoluble in hexane, pentane, and cyclohexane.

The pentafluorophenyl derivatives described herein are non-conductors in acetone (conductivities 0.5–3.5 ohm^{-1} cm^2 mol^{-1} in 1.5×10^{-4}–6×10^{-4} *M* solutions) and diamagnetic in the solid so that palladium(II) is in a square-planar environment.

All the complexes show the absorptions due to the C_6F_5 group [12] at 1635(s), 1500(vs), 1050(vs), 950(vs), and 800 (s–vs) cm^{-1}.

The number of infrared bands observed for the X-sensitive mode [12] at ≅800 cm^{-1} for several bispentafluorophenyl derivatives of thallium(III) [13] and palladium(II) [3, 4] have been correlated with the symmetry of the C–M–C skeleton. The presence of two bands in this region is characteristic of a nonlinear C–M–C skeleton, while only one band is found for those derivatives for which a linear C–M–C skeleton has been proposed. Thus, the spectra of compounds I–IV exhibit two absorption bands at 800–780 cm^{-1} and accordingly we propose a *cis* configuration for them. However, compounds V–IX and XI show a single band at 760 cm^{-1}, pointing to a linear C–Pd–C skeleton, *i.e.*, with the two C_6F_5 groups in *trans* positions. On the other hand, the spectrum of complex X exhibits a single band at 800 cm^{-1}, indicating the presence of only one C_6F_5 group attached to the palladium atom.

The dioxane complexes show the bands due to this ligand [14] at approximately 1250(s), 1120(vs), 1080(s), 1050(s), 900–850 (vs; two bands), 610(s), and 300–250(s) cm^{-1}. Moreover, if the ligand had the boat rather than the chair structure, the spectra would be expected to show more absorption peaks, because of the increased number of infrared active fundamental vibrations [15]. The asymmetric C–O–C stretching vibration, present in the free ligand at 1120 cm^{-1}, appears at 1110 cm^{-1} for complex I, which indicates that dioxane acts here as a bidentate ligand [16]. Also the symmetric C–O–C stretching vibration appears shifted to 870 cm^{-1} (874 cm^{-1} in free ligand). These shifts are very small, as one could expect for a dioxane–Pd association. However, in the spectrum of complex X, besides the above-mentioned absorptions, two well discernible shoulders at 1120 and 874 cm^{-1} appear, indicating that only one of both ether oxygens is involved in bonding to palladium. The spectra of complexes V and VI are more difficult to interpret, since the band at 1110 cm^{-1} has an almost imperceptible shoulder at 1120 cm^{-1}, making doubtful any structural interpretation. The dioxane acts as bidentate ligand in complex XI, because its spectrum presents only two very sharp bands at 1110 and 870 cm^{-1}.

Characteristic vibrations of the respective ligand are present in the $OPPh_3$, $OAsPh_3$, and NH_3 complexes. Thus, in complexes II and VII the ν(P–O) frequencies are found at 1165 and 1180 cm^{-1}, respectively. Two bands are observed for complex III (at 875 and 855 cm^{-1}), as well as for complex VIII (at 890 and 870 cm^{-1}), in the As–O stretching vibration region. All these data are in agreement with those reported in the literature for this type of complexes [17–19].

In complex X, the two absorptions assignable to the $\langle Pd(\mu\text{-}Cl)_2Pd\rangle$ moiety [20–22] are located at 300(m) and 270(s) cm^{-1}, and by the same reasons discussed in ref. [4] for similar complexes, we can suggest the *trans* structure for this binuclear compound.

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