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DICHLORO-BIS(PENTAFLUOROPHENYL)(CHELATE) COMPLEXES OF PALLADIUM(IV)

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Summary

Four organometallic palladium(IV) complexes: $Cl_2(C_6F_5)_2Pd(L—L)$ (L—L being a bidentate nitrogen-donor ligand) have been prepared by the oxidative addition of chlorine to the corresponding bis(pentafluorophenyl)palladium(II) complexes, $(C_6F_5)_2Pd(L—L)$. Some of their properties are described.

Introduction

It is known that the tendency of d^8 complexes to form oxidized adducts of d^6 configuration increases upon descending a triad or passing from right to left, within Group VIII [1,2]. Therefore, it is not surprising that the number of known palladium(IV) complexes is small. Although it was reported [3,4] that the two pentafluorophenyl groups of $BrTl(C_6F_5)_2$ could be transferred to the complex $Cl_2Pd(PPh_3)_2$ to give an organometallic palladium(IV) complex, we have shown [5] that the reaction of the thallium compound with palladium(II) complexes leads to mixtures of binuclear and mononuclear palladium(II) complexes: $[ClPd(C_6F_5)L]_2$ and $ClPd(C_6F_5)L_2$ ($L = PPh_3, PMePh_2, AsPh_3$).

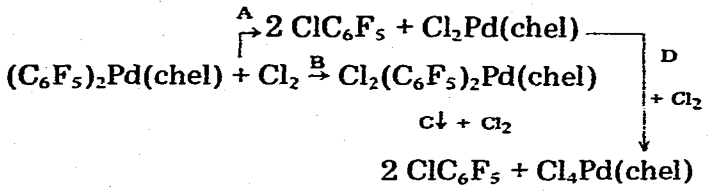
Even though phosphines appear to be incapable of stabilizing organometallic palladium(IV) complexes, it seemed possible that stable complexes might be obtained by use of appropriate ancillary ligands. Since all the known neutral palladium(IV) complexes [6] had a nitrogen donor as at least one of their ligands ($Pd(NH_3)_2Cl_4$, and $Pd(chel)Cl_4$, (chel) = en, bipy, phen), it seemed convenient to start from organometallic palladium(II) complexes $(C_6F_5)_2Pd(chel)$ in which chel is a bidentate nitrogen ligand, and to oxidize them by direct chlorination under mild conditions. Thus we describe below the results obtained with chel = ethylenediamine (en), 1,2-bipyridine (bipy), 1,10-phenanthroline (phen), 1,2-propylenediamine (pn).

Results and discussion

Preparation of dichloro-bis(pentafluorophenyl)(chelate) palladium(IV)

When palladium(II) complexes of the type $(C_6F_5)_2Pd(chel)$ in dichloromethane solution are treated with chlorine the reaction may take one of the courses in Scheme 1.

SCHEME 1



$$\begin{tikzcd} & 2\,ClC_6F_5 + Cl_2Pd(chel) \arrow[dd, bend left=60, "D", "+Cl_2"'] \\ (C_6F_5)_2Pd(chel) + Cl_2 \arrow[ur, "A"] \arrow[r, "B"] & Cl_2(C_6F_5)_2Pd(chel) \arrow[d, "C"', "+Cl_2"] \\ & 2\,ClC_6F_5 + Cl_4Pd(chel) \end{tikzcd}$$

Process A may involve either *(i)* cleavage of the Pd^{II}—C bonds by the direct action of chlorine or *(ii)* an initial oxidative addition of chlorine followed by a reductive elimination of ClC_6F_5. This process takes place when chel = *N,N,N',N'*-tetramethylenediamine and leads to palladium(II) complexes. It is not considered further in the present paper. Process B leads to the formation of organometallic palladium(IV) complexes (when chel = en, bipy, phen and pn), the first known organopalladium complexes in this oxidation state (see Table 1). Processes C and D lead to the formation of complexes of the $Cl_4Pd(chel)$ type. Process C, the cleavage of the Pd^{IV}—C bond by the excess of Cl_2, is observed in every case as a sequel of process B. Since the organometallic palladium(IV) complexes are soluble in dichloromethane, whilst the $Cl_4Pd(chel)$ complexes are insoluble in this solvent, the formation of only traces of a reddish precipitate clearly indicates the moment when the passage of the chlorine stream must be stopped. It is also necessary to remove quickly the excess of chlorine in the solution to avoid further reaction of type C.

IR spectra

The IR spectra of the four organometallic palladium(IV) complexes show bands characteristic of the C_6F_5 group, which are shown by the initial Pd^{II} complexes, at approximately 1635 m, 1510-1500 s, 1070-1060 s and 970-960 s cm^{-1}. In the Pd^{IV} complexes the latter frequency is shifted towards higher energies ($\Delta\nu \sim$ 15-18 cm^{-1}).

All the Pd^{IV} complexes show absorptions in the 400-300 cm^{-1} region, which are not present for the initial $(C_6F_5)_2Pd(chel)$ complexes and they are assigned to ν(Pd—Cl) (see Table 2). The presence of the nitrogen ligand is clearly revealed by the data shown in Table 3.

The complex bis(pentafluorophenyl)-1,2-propylenediaminepalladium(II) has been prepared for the first time. Its IR spectrum shows absorptions, characteristic of the C_6F_5 group at 1635 w, 1499 s, 949 s(br), along with two bands at 788 s and 780 s cm^{-1} which are due to the splitting of the band at ~800 cm^{-1}. This splitting was observed in the case of *cis*-$(C_6F_5)_2Pd(chel)$ [10], and corresponds to a symmetrical vibration due to two mutually *cis*-C_6F_5 groups. The presence of the pn group is confirmed by the vibrations at 3390 s, 3365 s, 3330 m

TABLE 1

ANALYTICAL DATA

Complex	M.p. (°C)	Λ_M (ohm^{-1} cm^2 mol^{-1}) in nitromethane	Analysis Found (calcd.) (%)				
			C	N	H	Pd	Cl
$Cl_2(C_6F_5)_2Pd(en)$ (II)	213-215 (dec.)	0,81	29,62 (29,42)	4,66 (4,90)	1,92 (1,54)	18,77 (18,61)	12,29 (12,40)
$Cl_2(C_6F_5)_2Pd(bipy)$ (III)	303 (dec.)	2,52	39,89 (39,58)	4,19 (4,19)	1,35 (1,20)	15,65 (15,93)	10,62 (10,62)
$Cl_2(C_6F_5)_2Pd(phen)$ (IV)	310-315 (dec.)	0,60	41,85 (41,60)	3,89 (4,05)	1,57 (1,16)	16,15 (15,38)	10,34 (10,25)
$Cl_2(C_6F_5)_2Pd(pn)$ (V)	196-198 (dec.)	0,93	30,68 (30,76)	4,66 (4,78)	2,07 (1,72)	18,35 (18,17)	11,67 (12,10)

TABLE 2

IR BANDS DUE TO ν(Pd—Cl)

Complex	Frequencies (cm^{-1})	
$Cl_2(C_6F_5)_2Pd$(en) (II)	340 s	
$Cl_2(C_6F_5)_2Pd$(bipy) (III)	344 m	352 (sh)
$Cl_2(C_6F_5)_2Pd$(phen) (IV)	344 m	354 (sh)
$Cl_2(C_6F_5)_2Pd$(pn) (V)	340 s	348 (sh)

and 3325 m due to ν(N—H) and at 1595 s and 1585 s which are assigned to $\delta(NH_2)$.

Other properties

The yellow colour of the palladium(IV) complexes is due to a charge transfer band at approximately 22000 cm^{-1}. No effort has been made to determine the extinction coefficient, because of the rapid decomposition of the complexes in dichloromethane solution, (e.g., a 1.9×10^{-4} *M* solution of $Cl_2(C_6F_5)_2Pd$(bipy) in dichloromethane goes colourless in about four hours). The complexes are non-conducting in nitromethane solution. If a few ml of an aqueous solution of potassium iodide and starch are added to dichloromethane solutions of any of the $Cl_2(C_6F_5)_2Pd$(chel) complexes a dark violet colour is immediately observed at the interface of the two solutions. This has been used as an indicator for the presence of Pd^{IV} in our complexes.

Experimental

The IR spectra were recorded on a Beckman IR 20A spectrophotometer (over the range 4000-250 cm^{-1}) using Nujol mulls between polyethylene sheets. The conductivities were measured in approximately 5×10^{-4} *M* solution with a Philips PW 9501/01 conductimeter. The C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer. To determinate Pd the samples were dissolved in fuming nitric acid and afterwards in perchloric acid, and the metal was precipitated with dimethylglyoxime [11]. Quantitative Cl analyses were performed as described by White [12], a few milligrams of sucrose being added to the samples to facilitate their combustion. The analytical results of the complexes II, III, IV

TABLE 3

IR BANDS DUE TO THE LIGAND (chel)

Complex	Frequencies (cm^{-1})		
$Cl_2(C_6F_5)_2Pd$(en) (II)[a]	3360 s	3285 s	1580 s
$Cl_2(C_6F_5)_2Pd$(bipy) (III)[b]	1600 m	765 s	
$Cl_2(C_6F_5)_2Pd$(phen) (IV)[c]	840 s		
$Cl_2(C_6F_5)_2Pd$(pn) (V)[a]	3275 s	3255 (s)	1575 s

[a] Ref. 7. [b] Ref. 8. [c] Ref. 9.

and V are given in Table 1. The palladium(II) starting complexes $(C_6F_5)_2Pd(chel)$ were prepared by methods described elsewhere: chel = en, phen [12] and chel = bipy [13].

The preparations of $(C_6F_5)_2Pd(pn)$ and the four compounds $Cl_2(C_6F_5)_2$-Pd(chel) were carried out as follows:

$(C_6F_5)_2Pd(pn)$ (I)

$Cl_2Pd(pn)$ (1.76 g, 7 mmol) was added to a solution of LiC_6F_5 (24 mmol) in 70 ml of dry diethyl ether. The mixture was stirred at —78°C for 1 h, allowed to warm to room temperature, and the stirring was continued for 5 h. The solution was evaporated to dryness and the residue was extracted with acetone (150 ml). White crystals were obtained upon concentrating the solution to a few ml. They were filtered off, and washed with hexane and water to give 1.6 g (44% yield) of complex I. It decomposes at 246°C and is non-conducting in nitromethane. It is soluble in acetone, nitromethane, benzene and dichloromethane, but insokuble in hexane and water. (Found: C, 35.51; N, 5.48; H, 2.05. calcd.: C, 35.00; N, 5.44; H, 1.97%.)

$Cl_2(C_6F_5)_2Pd(en)$ (II)

A stream of dry chlorine was bubbled for 1 h through a solution of $(C_6F_5)_2Pd(en)$ (0.5g) in 100 ml of anhydrous dichloromethane until a slight cloudiness was observed. The solution was evacuated to remove the excess of chlorine quickly and then concentrated almost to dryness. Yellow crystals precipitated, which were filtered, washed with a few drops of ether and vacuum dried to yield 0.39 g (70%) of complex II. II is air-stable; soluble in acetone, dichloromethane and nitromethane, slightly soluble in benzene and diethyl ether, and insoluble in water.

$Cl_2(C_6F_5)_2Pd(bipy)$ (III)

A solution of $(C_6F_5)_2Pd(bipy)$ (1.05 g) in 250 ml of dichloromethane was treated for approximately 20 min with dry chlorine and was then evacuated, filtered and concentrated to a few ml. Work up as for II gave complex III as yellow crystals (0.76 g, 65% yield). III is air-stable; soluble in acetone, dichloromethane and nitromethane, slightly soluble in benzene, and insoluble in water and ethanol.

$Cl_2(C_6F_5)_2Pd(phen)$ (IV)

A solution of $(C_6F_5)_2Pd(phen)$ (0.5 g) in 100 ml of dichloromethane was treated for 1 h as for II, filtered and concentrated under vacuum to approximately 10 ml. The solid was filtered off, recrystallized from dichloromethane, and vacuum-dried to yield the yellow complex IV (0.46 g, 70%). IV is air-stable; soluble in acetone, dichloromethane and nitromethane, slightly soluble in benzene and insoluble in ethanol and water.

$Cl_2(C_6F_5)_2Pd(pn)$ (V)

A solution of $(C_6F_5)_2Pd(pn)$ (0.5 g) in 100 ml of dichloromethane was treated for 1 h as for II. The resulting solution was concentrated almost to dryness to give yellow crystals, which were washed with a few drops of diethyl ether and vacuum-dried (0.35 g, 61%). V is air-stable; soluble in acetone, dichloromethane, nitromethane and benzene, slightly soluble in diethyl ether and insoluble in water.

Reaction of $(C_6F_5)_2Pd$(chel) solutions with an excess of chlorine

When the flow of the chlorine stream was continued for more than 1 h, an orange-red product was precipitated. This was identified as $PdCl_4$(chel), formed by process C. A reddish solid $PdCl_4$(bipy) was isolated when chel = bipy, (Found: C, 29.65; N, 6.53; H, 2.22. calcd.: C, 29.70; N, 6.92; H, 1.99%.) and an orange-red solid $PdCl_4$(phen) was isolated when chel = phen. (Found: C, 33.46; N, 6.50; H, 2.09. calcd.: C, 33.64; N, 6.53; H, 1.86%.)

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