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NEUTRAL AND CATIONIC PENTAFLUOROPHENYLPALLADIUM(II) COMPLEXES

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Summary

Neutral and cationic pentafluorophenylpalladium(II) complexes of the types $[X(C_6F_5)Pd(AsPh_3)_2]$ (X = Br, I, CN, SCN, CNO, CH_3COO, NO_3 or O_3ClO) $[(C_6F_5)Pd(AsPh_3)_2L](ClO_4)$ (L = Py, PEt_3, PPh_3, $SbPh_3$ or $OPPh_3$), and $[(C_6F_5)PdL_3](ClO_4)$ (L = $AsPh_3$, Py, PEt_3 or PPh_3) have been prepared. Their stabilities, conductivities and IR spectra have been studied.

Introduction

We recently found a method of synthesizing $Cl(C_6F_5)Pd(AsPh_3)_2$ [1] in good yield (90%). We have now shown that this compound may be used in the preparation and study of new pentafluorophenylpalladium(II) complexes having $AsPh_3$ as one of the ligands.

Results and discussion

(a) Preparation of the complexes

The complex $[Cl(C_6F_5)Pd(AsPh_3)_2]$ has been used as starting material in two different processes.

(1) Reactions with inorganic salts MX. The metathesis with MX in acetone (in benzene, in the case of the perchlorato complex) leads to neutral organo-complexes (X being Br, I, CN, SCN, CNO, ONO_2, CH_3COO, O_3ClO) (see eqn. 1).

$$Cl(C_6F_5)Pd(AsPh_3)_2 + MX \rightarrow MCl + [X(C_6F_5)Pd(AsPh_3)_2] \quad (1)$$

(2) Reactions of the perchlorato-complex. The ligand O_3ClO of the perchlorato-complex, prepared as indicated above, can be readily displaced by neutral ligands [2] to give cationic complexes of two different types.

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TABLE 1

ANALYTICAL RESULTS

	Complex	Colour	M.p. (°C)	Λ_M (ohm^{-1} cm^2 mol^{-1})		Analysis found (calcd.) (%)			
				Acetone	Nitromethane	C	H	N	Pd
I	$Br(C_6F_5)Pd(AsPh_3)_2$	pale-yellow	160-170[a]	0.19	20.25	52.70 (52.23)	3.15 (3.13)		10.99 (11.02)
II	$I(C_6F_5)Pd(AsPh_3)_2$	yellow	170-190[a]	0.36	9.8	49.93 (49.81)	2.95 (2.98)		10.06 (10.50)
III	$CN(C_6F_5)Pd(AsPh_3)_2$	white	175-185[a]	0.14	8.78	56.90 (56.63)	3.41 (3.31)	1.43 (1.53)	10.88 (11.67)
IV	$SCN(C_6F_5)Pd(AsPh_3)_2$	white	200-220[a]	0	2.14	52.87 (53.44)	3.15 (3.20)	1.47 (1.48)	10.81 (11.27)
V	$CNO(C_6F_5)Pd(AsPh_3)_2$	white	168[b]	1.13	33.9	55.49 (55.66)	3.56 (3.26)	1.35 (1.51)	10.52 (11.46)
VI	$CH_3COO(C_6F_5)Pd(AsPh_3)_2$	white	128[b]	0.52	0.78	55.73 (55.92)	3.52 (3.52)		10.96 (11.26)
VII	$NO_3(C_6F_5)Pd(AsPh_3)_2$	pale-yellow	184[c]	1.90	12.58	53.65 (53.22)	3.14 (3.19)	1.45 (1.48)	10.66 (11.22)
VIII	$O_3ClO(C_6F_5)Pd(AsPh_3)_2$	pale-yellow	190-195[a]	112.7	86	51.26 (51.19)	3.17 (3.03)		9.48 (10.79)

IX	$[(C_6F_5)Pd(AsPh_3)_2py]ClO_4$	white	144[b]	123.18	95.2	53.61 (53.03)	3.32 (3.31)	1.31 (1.31)	9.09 (9.99)
X	$[(C_6F_5)Pd(py)_3]ClO_4$	white	159[c]	128.08	96.48	41.31 (41.33)	2.55 (2.48)	6.82 (6.89)	16.66 (17.43)
XI	$[(C_6F_5)Pd(AsPh_3)_2(PEt_3)]ClO_4$	white	131[c]	118.18	72.3	52.95 (52.24)	4.12 (4.11)		9.49 (9.64)
XII	$[(C_6F_5)Pd(PEt_3)_3]ClO_4$	white	95[c]	130.33	79.9	39.99 (39.63)	6.52 (6.20)		13.59 (14.63)
XIII	$[(C_6F_5)Pd(AsPh_3)_2PPh_3]ClO_4$	white	170-180[a]	107.04	74.43	57.17 (57.76)	3.70 (3.63)		7.78 (8.53)
XIV	$[(C_6F_5)Pd(PPh_3)_3]ClO_4$	white	193[c]	127.05	72.4	61.87 (62.14)	4.03 (3.91)		8.56 (9.17)
XV	$[(C_6F_5)Pd(AsPh_3)_3]ClO_4$	white	170-190[a]	130.19	75.0	55.62 (55.79)	3.55 (3.51)		7.75 (8.24)
XVI	$[(C_6F_5)Pd(AsPh_3)_2(SbPh_3)]ClO_4$	pale-yellow	140-150[a]	118.97	71.35	53.32 (53.84)	3.55 (3.39)		7.68 (7.95)
XVII	$[(C_6F_5)Pd(AsPh_3)_2(OPPh_3)]ClO_4$	white	162[b]	122.62	72.02	56.58 (57.03)	3.53 (3.59)		7.88 (8.42)

[a] Decomposes without melting. [b] Melts. [c] Melts under decomposition.

(2.1) Treatment with stoichiometric amounts of the ligand L leads to complexes with mixed ligands, as in eqn. 2.

$$O_3ClO(C_6F_5)Pd(AsPh_3)_2 + L \rightarrow [Pd(C_6F_5)(AsPh_3)_2L]ClO_4 \qquad (2)$$

($L = C_5H_5N, PEt_3, PPh_3, SbPh_3, OPPh_3$)

(2.2) The reaction with an excess of ligand L (or with a stoichiometric amount of $AsPh_3$) leads to the replacement of both the O_3ClO group and the $AsPh_3$ group, according to eqn. 3.

$$O_3ClO(C_6F_5)Pd(AsPh_3)_2 + 3L \rightarrow [(C_6F_5)PdL_3]ClO_4 + 2AsPh_3 \qquad (3)$$

(L being $C_5H_5N, PEt_3, PPh_3, AsPh_3$)

The analytical data, conductivities and melting points of the complexes are listed in Table 1. The products are crystalline and air-stable at room temperature, except for the cyano complex III, which after several days shows signs of decomposition (darkening). Acetone solutions of the acetato and the nitrato complexes (VI and VII) decompose at room temperature and precipitate metallic palladium, and their preparation must be carried out at low temperature (—20° C). The other complexes are stable, although their decomposition points are lower than those of the corresponding triphenylphosphine complexes $X(C_6F_5)Pd(PPh_3)_2$ [3].

(b) Conductivities

(1) Neutral complexes. The neutral complexes I-VII are non-conducting in acetone and in nitromethane (see Table 1). The perchlorato complex VIII in these solvents behaves as a 1/1 electrolyte because of replacement of the perchlorato group by the solvent in a process of the type shown in eqn. 2. The perchlorato complex is non-conducting in benzene.

(2) Cationic complexes. All of them behave as 1/1 electrolytes in acetone or nitromethane [4].

(c) IR spectra

All the complexes show the bands characteristic of the C_6F_5-group [5] at 1500-1490 vs, 1060-1040 s, 950-940 vs and 800-770 s cm^{-1}. The bands due to the respective ligand L and to the ligand $AsPh_3$ (except X, XII and XIV) are to be observed in all the IR spectra where they do not overlap with the absorptions of other ligands. Thus, all the complexes which have $AsPh_3$ as a ligand show, amongst others, absorptions at 470 s and 325-320 s(br) cm^{-1}; the latter conceals the absorption due to ν(Pd—Cl) expected at approx. 300 cm^{-1}. The bands due to ν(Pd—Br) and ν(Pd—I) would be found at lower frequencies [6], beyond the range of our spectrophotometer.

The band at 2110 cm^{-1} (in the cyano complex III) and the strong absorption at 2060 cm^{-1} (in the thiocyanato complex IV) can be assigned to the vibration ν(C—N). The vibrations ν(Pd—C), δ(M—C—N), etc., could not be assigned because of the presence of numerous bands due to the other ligands. Literature data [8] indicate that IV is the isothiocyanato complex (Pd/NCS). The cyanato complex V shows two absorptions at 2210 s and 605 m cm^{-1} assignable to the vibrations ν(C—N) and δ(N—C—O), respectively [9].

The acetato complex VI exhibits bands at 1610 s and 1320 s cm^{-1} which may

TABLE 2

FREQUENCIES ASSIGNED TO LIGAND L

Complex	Frequencies	Assignment
IX	1608 vs, 1215 m	internal vibrations
X	1608 vs, 1215 m, 1012 w	internal vibrations
XIII	510 s, 490 s	internal vibrations
XIV	515 s, 490 s	internal vibrations
XVII	1155 s	ν(P—O)

be assigned to ν_{as} and ν_s of the carboxyl group. The values of $\Delta\nu$, viz. 290 cm^{-1}, proves that the CH_3COO-group is monodentate [10]. The nitrato complex VII shows a band at 1888 s cm^{-1} assignable to $\nu_{as}(NO_2)$ [11], whilst the other expected bands are masked. The perchlorato complex VIII exhibits bands at 1150 s, 1015 s, 870 m, 630 mw and 610 mw cm^{-1}, characteristic of the monodentate O_3ClO group (C_{3v}) [12].

All the cationic complexes IX-XVII show a very broad band at ~1100 s cm^{-1} and an absorption at 620 ms cm^{-1} which are due to the ClO_4^--group (T_d) [12]. The presence of the ligand L can also be detected from the IR spectrum of each complex, whenever the internal vibrations are not concealed by other absorptions, as may be seen from Table 2.

The IR spectra of the complexes X, XII and XIV clearly support the absence of the $AsPh_3$ group, since they do not show the bands at 470-450 vs and 320 cm^{-1}, which are observed in the starting compound. In complex XVII, the ν(P—O) vibrations, which in the free ligand [13] are observed at 1200 cm^{-1}, are shifted towards lower energies by coordination [14].

Experimental

The C, H and N analyses were carried out on a Perkin—Elmer 240 microanalyzer; the results are in satisfactory agreement with the proposed formulae, when difficulties which arise from the presence of P and F are taken into account [15]. For the determination of Pd, the samples were dissolved in fuming nitric acid and then in perchloric acid, to precipitate the metal with dimethylglyoxime [16]. Quantitative destruction of the samples was in some cases quite difficult, and this accounts for several rather low Pd values.

The conductivities were measured in approx. 5×10^{-4} *M* solutions with a Philips 9501/01 conductimeter. The melting points were determined with a Reichert (Austria) apparatus. The IR spectra were recorded on a Beckman IR 20 A spectrophotometer (over the range 4000-250 cm^{-1}) using Nujol mulls between polyethylene sheets.

The starting compound $Cl(C_6F_5)Pd(AsPh_3)_2$, referred to below as A, was prepared according to ref. 1, and its purity was confirmed by quantitative analyses and IR spectra.

The neutral complexes I-VII were prepared by adding a slight excess of MX to an acetone solution of complex A. After several hours refluxing, the solution was evaporated to dryness, and the residue was several times washed with water to remove the soluble salts, and was finally recrystallized from dichloromethane or dichloromethane—ethanol. The yields were between 80 and 90%.

The perchlorato complex VIII was prepared by treating stoichiometric amounts of complex A with $AgClO_4$ in benzene solution. The AgCl was filtered off and hexane was added to precipitate complex VIII (86% yield).

The preparation of the cationic complexes IX-XVII was accomplished by adding ligand L to benzene solutions of the perchlorato complex. Stoichiometric amounts of the ligand were used to prepare complexes IX, XI, XIII, XV, XVI and XVII, whereas a large excess of the ligand was required for the complexes X, XII and XIV. The complexes crystallized spontaneously in some cases, whilst the complete separation of the products in other cases was accomplished by adding a few ml of hexane.

The neutral complexes I-VIII are soluble in chloroform, benzene, nitromethane and acetone, and insoluble in ethanol, hexane and water. The cationic complexes IX-XVII are soluble in acetone, chloroform and nitromethane, and insoluble in hexane and water.

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