Journal of Organometallic Chemistry, 72 (1974) 299—303

CATIONIC PENTAFLUOROPHENYL COMPLEXES OF PLATINUM(II)

R. USÓN, P. ROYO and J. GIMENO
Department of Inorganic Chemistry, University of Zaragoza (Spain)
(Received December 10th, 1973)

Summary

The complex $[O_3ClOPt(C_6F_5)(PEt_3)_2]$ which we have prepared for the first time, is used as a precursor of a series of cationic complexes $[LPt(C_6F_5)(PEt_3)_2]ClO_4$ ($L = PEt_3$, PPh_3, $AsPh_3$, H_2O, CO, $OPPh_3$, $SPPh_3$, $HNPr_2$, py), which are easily obtained by adding L to the perchlorato complex.

Introduction

We have recently shown [1—3] that the facile substitution of the perchlorato group O_3ClO^- in perchlorato complexes by neutral or anionic ligands can be used for preparing series of new pentafluorophenyl complexes of Au^I, Au^{III} and Pd^{II} [4].

The perchlorato group of the starting complex $[O_3ClOPt(C_6F_5)(PEt_3)_2]$, which is described in this paper for the first time, is readily displaced when neutral ligands are added. Thus cationic complexes can easily be prepared; nine out of the great number of possible new complexes are given here as examples.

Results and discussion

(a). Preparation of $[O_3ClOPt(C_6F_5)(PEt_3)_2]$

Process (1) takes place when a benzene solution of *cis*-chloro(pentafluorophenyl)bis(triethylphosphine)platinum(II) is mixed with a benzene solution of silver perchlorate, at room temperature. The silver chloride precipitates immediately together with some of the complex, which is only slightly soluble in benzene. Afterwards the suspension is evaporated to dryness and dichloromethane is added to the solid residue. The complex is completely extracted and thus separated from the silver chloride, which is insoluble in the solvent. The Pt^{II} perchlorato complex is obtained by evaporating part of the dichloromethane and adding benzene.

$$Cl(C_6F_5)Pt(PEt_3)_2 + AgClO_4 \rightarrow AgCl + O_3ClOPt(C_6F_5)(PEt_3)_2 \qquad (1)$$

At room temperatures and in the absence of moisture the complex is stable enough for short periods in the solid state to be handled without any apparent change, so that the IR spectra can be taken or solutions prepared.

(b). Preparation of cationic complexes

The addition of a neutral ligand to a solution of the perchlorato complex in dichloromethane causes the facile displacement of the perchlorato ion from its coordination position. This position becomes occupied, as in process (2), by the ligand L which must possess a greater coordination capacity. We have always

$$O_3ClOPt(C_6F_5)(PEt_3)_2 + L \rightarrow [LPt(C_6F_5)(PEt_3)_2]^+ClO_4^- \qquad (2)$$

(L = PEt_3, PPh_3, $AsPh_3$, H_2O, CO, $OPPh_3$, $SPPh_3$, $HNPr_2$, py)

used an excess of ligand L rather than a stoichiometric amount. Partial evaporation of the dichloromethane followed by an addition of benzene or hexane gives causes separation of the cationic Pt^{II} complex as a white precipitate. Analyses are in reasonable agreement with the proposed formulae for each complex.

(c). Conductivities

The conductivities of the complexes are given in Table 1. They show clearly that the cationic complexes behave as 1/1 electrolytes. On the other hand, the nitromethane and acetone solutions of the perchlorato-complex also show the expected conductivities for 1/1 electrolytes, since the solvent itself displaces the coordinated perchlorato ion by birtue of its greater donor capacity. In benzene (a non donor solvent) the original complex behaves as a non conductor, which indicates the existence of a neutral complex. The measured molecular weight (684) shows that it is monomeric in chloroform.

(d). IR spectra

All the complexes show the characteristic vibrations of the triethylphosphine and pentafluorophenyl groups [5]. The perchlorato complex shows ab-

TABLE 1

CONDUCTIVITIES

Complex	Solvent	Concentration (10^{-4} × mole/l)	Conductivity ($ohm^{-1} \cdot cm^2 \cdot mole^{-1}$)
(I) $O_3ClOPt(C_6F_5)(PEt_3)_2$	Nitromethane	5.12	89.4
	Acetone	6.39	148.2
	Benzene	5.21	Nil.
(II) $[Pt(C_6F_5)(PEt_3)_3]ClO_4$	Nitromethane	5.07	77.8
(III) $[Pt(C_6F_5)(PPh_3)(PEt_3)_2]ClO_4$	Nitromethane	6.34	78.8
(IV) $[Pt(C_6F_5)(AsPh_3)(PEt_3)_2]ClO_4$	Nitromethane	5.28	89.2
(V) $[Pt(C_6F_5)(H_2O)(PEt_3)_2]ClO_4$	Nitromethane	6.60	70.8
(VI) $[Pt(C_6F_5)(CO)(PEt_3)_2]ClO_4$	Nitromethane	13.6	83.1
(VII) $[Pt(C_6F_5)(OPPh_3)(PEt_3)_2]ClO_4$	Nitromethane	6.49	87.8
(VIII) $[Pt(C_6F_5)(SPPh_3)(PEt_3)_2]ClO_4$	Nitromethane	4.72	84.3
(IX) $[Pt(C_6F_5)(HNPr_2)(PEt_3)_2]ClO_4$	Nitromethane	4.53	91.6
(X) $[Pt(C_6F_5)(py)(PEt_3)_2]ClO_4$	Nitromethane	4.99	86.3

TABLE 2

FREQUENCIES ASSIGNED TO L IN $[Pt(C_6F_5)L(PEt_3)_2]ClO_4$

L	ν(cm^{-1})
PPh_3	550 vs, 520 s, 500 m
$AsPh_3$	470 m
H_2O	3200-3400(br)
CO	2110 s
$OPPh_3$	1140 s, 520 m, 510(sh)
$SPPh_3$	580 s, 500 m
$HNPr_2$	3300 w, 3280 w
py	1610 m, 1210 w, 410 w

sorption bands at 1170 s, 1020 s, 850-870 s(br), 650 m and 610 m cm^{-1}, which are characteristic for the O_3ClO^- group (C_{3v}) [6]. All the cationic perchlorato complexes show absorption bands at 1100 vs(br) and 630 m cm^{-1}, which are characteristic of the ClO_4^--group (T_d) [6]. Furthermore the introduced ligands give also rise to new absorption bands, which can be assigned to internal vibrations. These bands, which are listed in Table 2, can be used qualitatively to establish the course of the reactions.

The spectra of the complexes with L = PPh_3 and $AsPh_3$ show absorptions which can be assigned to vibrations of the phenyl ring, whereas when L = H_2O a broad band is observed at 3200—3400 cm^{-1}. In the complex with L = CO a very intensive band appears at 2110 cm^{-1} and is assigned to the stretching vibration of the CO. Since the stretching vibration of the free CO molecule is at 2143 cm^{-1}, it is obvious that the bond order of the CO has diminished. This behaviour is general for end-carbonyls in metallic complexes [7].

When L = $OPPh_3$ along with bands which are characteristic of benzene ring, there appears a band at 1140 s cm^{-1}, which can be assigned to the stretching vibration P → O. This vibration which occurs in the free ligand at 1195 cm^{-1}, always falls on coordination as a consequence of the reduction of the multiple character of the P → O bond [8].

When L = $SPPh_3$, a band appears at 580 s cm^{-1} which is assigned to the stretching vibration P → S; this vibration appears in the free ligand at 637 cm^{-1}. This effect, which is similar to that observed for the oxide is in accordance with the behaviour described in ref. 9.

When L = py, absorption bands assignable to internal vibrations appear.

Finally, the spectrum of the complex with L = $HNPr_2$ shows two bands which are assigned to vibration H—N. Although free secondary amines show only one single absorption band for the stretching vibration H—N, that band splits into two when high concentrations are used, possibly because of interactions of the hydrogen bonds [10].

(e). Solubilities

The perchlorato complex is soluble in dichloromethane, chloroform, acetone and nitromethane; it is slightly soluble in benzene, but insoluble in hexane and petroleum ether. All the cationic complexes are soluble in dichloromethane, nitromethane, acetone, ethanol and methanol, slightly soluble in benzene and ethyl ether, but almost insoluble in hexane and petroleum ether.

(f). Magnetism

The magnetic susceptibilities show that the complexes are diamagnetic.

Experimental

Molecular weights were measured in chloroform with Hitachi—Perkin—Elmer model 115 osmometer and conductivities with a Metrohm A.G. Conductimeter. IR spectra were recorded on a Beckman IR 20 A spectrophotometer (over the range 4000-250 cm^{-1}) using Nujol mulls between polyethylene sheets. Magnetic susceptibilities were measured with a balance constructed in our Department [11]. C, H and N analyses were made with a Perkin—Elmer 240 microanalyzer.

All the perchlorates were white microcrystalline solids.

(I). $[O_3ClOPt(C_6F_5)(PEt_3)_2]$

A white solid precipitates when a mixture of *cis*-chloro(pentafluorophenyl)-bis(triethylphosphine)platinum(II) [12] (0.63 g; 1 mmole) and silver perchlorate (0.20 g; 1 mmole) in dry benzene is stirred at room temperature. The solution is evaporated to dryness and the solid residue is extracted with dichloromethane. The insoluble silver chloride is filtered off in the absence of air, and the dichloromethane is partially evaporated. The addition of benzene causes precipitation of complex (I), m.p. 130-132° to give yellow crystals which melt at 161-163°. (Found: C, 30.42; H, 4.55. Mol. wt., 684 (in 0.08% solution). Calcd.: C, 30. 96; H, 4.38%. Mol. wt., 697.)

(II). $[Pt(C_6F_5)(PEt_3)_3]ClO_4$

Triethylphosphine (0.3 ml; 2 mmole) is added to a solution of complex (I) (1 mmole) in dichloromethane. The mixture is stirred for two hours at room temperature. Partial evaporation of the dichloromethane and the addition of hexane gives complex (II), m.p. 226-228°. (Found: C, 35.03; H, 5.76. Calcd.: C, 35.34; H, 5.51%.)

(III). $[Pt(C_6F_5)(PPh_3)(PEt_3)_2]ClO_4$

PPh_3 (0.52 g; 2 mmole) is added to a solution of 1 mmole of complex (I) in dichloromethane and the subsequent procedure is as for (II). Complex(III) has m.p. 206-208°. (Found: C, 44.81; H, 5.45. Calcd.: C, 45.05; H, 4.68%.)

(IV). $[Pt(C_6F_5)(AsPh_3)(PEt_3)_2]ClO_4$

By the same procedure, 0.60 g (2 mmole) of $AsPh_3$ and 1 mmole of complex (I) in dichloromethane gave complex (IV), m.p. 198-200°. (Found: C, 43.51; H, 5.13. Calcd.: C, 43.07; H, 4.48%.)

(V). $[Pt(C_6F_5)(H_2O)(PEt_3)_2]ClO_4$

H_2O (1 ml) is added to a solution of 1 mmole of complex (I) in dichloromethane, and the procedure as for (II) gave complex (V), m.p. 148—150°. (Found: C, 30.81; H, 4.60. Calcd.: C, 30.21; H, 4.47%.)

(VI). $[Pt(C_6F_5)(CO)(PEt_3)_2]ClO_4$

Dry carbon monoxide is passed through a solution of 1 mmole of complex (I) in dichloromethane for two hours. Partial evaporation of the dichloromethane and addition of ethyl ether gives complex (VI), m.p. 158-160°. (Found: C, 31.07; H, 4.65. Calcd.: C, 31.44; H, 4.13%.)

(VII). $[Pt(C_6F_5)(OPPh_3)(PEt_3)_2]ClO_4$

By the procedure described for (II), 0.54 g (2 mmole) of $OPPh_3$ and 1 mmole of complex (I) in dichloromethane gave complex (VII), m.p. 155-157°. (Found: C, 45.31; H, 5.28. Calcd.: C, 44.31; H, 4.61%.)

(VIII). $[Pt(C_6F_5)(SPPh_3)(PEt_3)_2]ClO_4$

Analogously, 0.58 g (2 mmole) of $SPPh_3$ and 1 mmole of complex (I) gave complex (VIII), m.p. 183-185°. (Found: C, 43.75; H, 5.05. Calcd.: C, 43.59; H, 4.53%.)

(IX). $[Pt(C_6F_5)(HNPr_2)(PEt_3)_2]ClO_4$

Analogously, 0.5 ml (4.5 mmole) of $HNPr_2$ and 1 mmole of complex (I) gave complex (IX), m.p. 114-116°. (Found: C, 35.77; H, 5.98; N, 1.58. Calcd.: C, 36.08; H, 5.63; N, 1.75%.)

(X). $[Pt(C_6F_5)(py)(PEt_3)_2]ClO_4$

Analogously, 0.2 ml (2 mmole) of pyridine and 1 mmole of complex (I) gave complex (X), m.p. 151-153°. (Found: C, 36.07; H, 4.79; N, 1.62. Calcd.: C, 35.36; H, 4.50; N, 1.80%.)

References

1 R. Usón, P. Royo and A. Laguna, Syn. Inorg. Metalorg. Chem., 3 (1973) 237.
2 R. Usón, P. Royo and A. Laguna, Rev. Acad. Cienc. Zaragoza, XXVIII (1973) 71.
3 R. Usón, P. Royo, A. Laguna and J. Garcia, Rev. Acad. Cienc. Zaragoza, XXVIII (1973) 67.
4 R. Usón, P. Royo and J. Forniés, Syn. Org. Metalorg. Chem., 2 (1974), in press.
5 D.A. Long and D. Steele, Spectrochim. Acta, 19 (1961) 1955.
6 B.J. Hathaway and A.E. Underhill, J. Chem. Soc., (1961) 3091.
7 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, 3rd ed., 1973, p. 687.
8 F.A. Cotton, R.D. Barnes and E. Bannister, J. Chem. Soc., (1960) 2199.
9 M.G. King and G.P. McQuillan, J. Chem. Soc. A, (1967) 898.
10 L.J. Bellamy, The infrared spectra of complex molecules, Methuen, 1966, p. 308.
11 F. Gomez Beltran and J. Alvarez, Rev. Acad. Cienc. Zaragoza, XXII (1967) 151.
12 D.T. Rosevear and F.G.A. Stone, J. Chem. Soc., (1965) 5275.