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ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS CONTAINING PHOSPHINE AND PERCHLOROARYL LIGANDS

V *. PENTACHLOROPHENYLPLATINUM(II) COMPLEXES WITH TRIETHYLPHOSPHINE

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Summary

The preparation and characterization of the first pentachlorophenylplatinum(II) complexes of formula *cis*-[$PtX(C_6Cl_5)(PEt_3)_2$] (X = Cl, Br, I, N_3, CN, NCS, AcO, NO_3, NCO, NO_2), and *trans*-[$PtX(C_6Cl_5)(PEt_3)_2$] (X = Cl, Br, I, NCS) is described. Their diamagnetic behaviour is evidence for their square-planar geometry. *Cis* or *trans* configuration is assigned on the basis of the PMR spectra. The characterization has been completed with the study of the IR spectra. The action of HCl and Cl_2 on the compounds has also been studied.

Introduction

In continuation of our studies on pentachlorophenyl complexes of transition metals, we have prepared the first platinum compounds containing the pentachlorophenyl ligand. The greater thermodynamic and kinetic stability to be expected for Pt—C bonds than for Ni—C and Pd—C bonds could lead to somewhat different chemical properties.

The compound containing two C_6Cl_5 groups, [$Pt(C_6Cl_5)_2(PEt_3)_2$], could not be prepared, in agreement with earlier results [1—4]. This failure is probably due to a kinetic factor rather than a lower thermodynamic stability of the disubstituted compound.

The action of the C_6Cl_5MgCl or C_6Cl_5Li solutions on [$PtCl_2(PEt_3)_2$] leads to the organometallic compound only when the *cis* isomer is used as the starting compound, which may be attributed to the strong *trans* effect of the phosphines and to the lower lability of the Pt complexes. However, *trans*-[$PtCl(C_6Cl_5)(PEt_3)_2$] has been made by vacuum sublimation of *cis*-[$PtCl(C_6Cl_5)(PEt_3)_2$] at high temperature.

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[*] For Part IV see ref. 1.

Results and discussion

Preparation and properties

The action of a hot solution of C_6Cl_5MgCl in THF on solid *cis*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ leads to *cis*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ (I). Heating of I at 240°C under vacuum (0.005 mmHg) gives, after sublimation, a white product which corresponds to the isomer *trans*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ (II).

Further compounds of the type *cis*-$[PtX(C_6Cl_5)(PEt_3)_2]$ are obtained by refluxing acetone or chloroform solutions of I with an excess of the appropriate alkali metal salt (for X = Br, I, NCS, N_3, NCO) or silver salt (for X = CN, NO_2, NO_3, AcO). Similarly, alkali metal salts react with II to give *trans*-$[PtX(C_6Cl_5)(PEt_3)_2]$ in the cases examined (X = Br, I, NCS). The use of an excess of Grignard reagent or C_6Cl_5Li on *cis*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ does not give the product with two C_6Cl_5 groups, and compound I is recovered unchanged. These results are in agreement with those obtained for analogous Ni and Pd compounds [1—4].

Analytical results and melting points are given in Table 1. All the compounds are air-stable in the solid state and in solution. They are soluble in chloroform,

TABLE 1

ANALYTICAL DATA

Compound	Found (calcd.) (%)				Melting points (°C)
	C	H	Cl or total halogen	N	
cis-$[PtCl(C_6Cl_5)(PEt_3)_2]$	29.55	4.15	30.08		207—210
	(30.13)	(4.19)	(29.74)		
cis-$[PtBr(C_6Cl_5)(PEt_3)_2]$	28.62	4.03	27.98		207—209
	(28.41)	(3.94)	(28.01)		
cis-$[PtI(C_6Cl_5)(PEt_3)_2]$	26.90	3.92	25.85		216—219
	(26.75)	(3.71)	(26.34)		
cis-$[Pt(NCO)(C_6Cl_5)(PEt_3)_2]$	31.70	4.24	24.92	2.10	218—221
	(31.55)	(4.15)	(24.52)	(1.93)	
cis-$[Pt(CN)(C_6Cl_5)(PEt_3)_2]$	31.85	4.30	25.85	1.58	212—214
	(32.26)	(4.24)	(25.12)	(1.98)	
cis-$[PtN_3(C_6Cl_5)(PEt_3)_2]$	30.08	4.17	24.81	5.84	190—192
	(29.9)	(4.15)	(24.52)	(5.81)	
cis-$[Pt(NCS)(C_6Cl_5)(PEt_3)_2]$	30.14	3.91	23.26	1.47	222—225
	(30.87)	(4.06)	(23.99)	(1.89)	
cis-$[Pt(AcO)(C_6Cl_5)(PEt_3)_2]$	32.43	4.55	24.69		156—157
	(32.45)	(4.46)	(23.96)		
cis-$[Pt(NO_2)(C_6Cl_5)(PEt_3)_2]$	30.29	4.27	23.88	1.99	198—199
	(29.72)	(4.12)	(24.39)	(1.92)	
cis-$[Pt(NO_3)(C_6Cl_5)(PEt_3)_2]$	29.08	4.05	23.66	1.98	183—182
	(29.09)	(4.04)	(23.86)	(1.82)	
trans-$[PtCl(C_6Cl_5)(PEt_3)_2]$	29.86	4.23	29.20		170—172
	(30.13)	(4.19)	(29.74)		
trans-$[PtBr(C_6Cl_5)(PEt_3)_2]$	28.94	4.20	28.22		196—199
	(28.41)	(3.94)	(28.01)		
trans-$[Pt(NCS)(C_6Cl_5)(PEt_3)_2]$	31.01	4.22	24.04	1.76	220—221
	(30.87)	(4.06)	(23.99)	(1.89)	
trans-$[PtI(C_6Cl_5)(PEt_3)_2]$	27.03	3.69	26.36		195—197
	(26.75)	(3.71)	(26.34)		

acetone, carbon tetrachloride and benzene, and slightly soluble in n-hexane and ethanol. (*Trans* isomers in general appear to be somewhat more soluble than *cis* compounds.) Their solutions in anhydrous acetone show very low conductivities in agreement with their non-electrolytic character. Magnetic measurements show diamagnetic behaviour, indicating square-planar geometry.

Cis and *trans* geometry are assigned respectively to compounds I and II and to their substitution products on the basis of PMR spectra. The substitution reactions in all cases involve retention of configuration.

PMR spectra

The methyl protons of PEt_3 for the *cis* isomers give two triplets partially overlapping, whereas for the *trans* isomers they appear as a quintet due to coupling with the protons of the methylene group and to virtual coupling with the *trans* phosphorus nucleus [5,6].

The chemical shifts of the methyl groups remain practically unchanged along the series $[PtX(C_6Cl_5)(PEt_3)_2]$ but those of the methylene groups show slight shifts towards lower fields on changing X in a sequence similar to that found for analogous Ni [7], Pd [4] and Pt [8] compounds.

IR spectra

The IR spectra of the new compounds show the bands due to PEt_3 [9] and coordinated C_6Cl_5 [4,10]. Several differences between both series of isomers are observed: the band due to the ν_6 vibration of C_6Cl_5 which appears at 1295 cm^{-1} for the *cis* isomer is observed as a split band at 1290—1300 cm^{-1} for the *trans* isomer; the band due to the ν_{19} vibration of C_6Cl_5 is overlapped with the vibration of PEt_3 that appears at 635 cm^{-1} for the *cis* isomers, whereas in the *trans* isomers the two bands are separate at 625 cm^{-1} (C_6Cl_5) and 635 cm^{-1} (PEt_3).

The bands due to the other ligands are listed in Table 2. Their positions for

TABLE 2

IR FREQUENCIES (cm^{-1}) OF PSEUDOHALIDE GROUP AND METAL HALOGEN VIBRATIONS

Compound	ν_3	δ	ν_{as}	ν-(Pt—X)	Other vibrations
cis-$[PtCl(C_6Cl_5)(PEt_3)_2]$				280m 285m	
cis-$[PtN_3(C_6Cl_5)(PEt_3)_2]$			2050vs	360m	
cis-$[PtNCS(C_6Cl_5)(PEt_3)_2]$	840m		2100vs		
cis-$[PtNCO(C_6Cl_5)(PEt_3)_2]$	1340m	595w	2240vs	340m	
cis-$[PtCN(C_6Cl_5)(PEt_3)_2]$			2140s	350m	
cis-$[PtNO_2(C_6Cl_5)(PEt_3)_2]$	1325vs	810m	1370—1385vs		540(ρ)
cis-$[PtNO_3(C_6Cl_5)(PEt_3)_2]$					1585vs(ν_4), 1285—1255vs(ν_1) 990vs(ν_2), 715m(ν_5) 800m(ν_6)^a
cis$[PtAcOO(C_6Cl_5)(PEt_3)_2]$					1630vs(ν_8), 1360s(ν_3)
trans-$[PtCl(C_6Cl_5)(PEt_3)_2]$				290m	
trans-$[PtNCS(C_6Cl_5)(PEt_3)_2]$	830m	470m	2115vs	270w	

[a] We have been unable to identify the ν_3 mode because of overlapping with vibrations of the phosphine which occur in the same zone.

the case of the ligands NCS, NCO and NO_2 is evidence of coordination to the metal through the nitrogen atom [11].

Action of hydrogen chloride

Gaseous HCl in chloroform solution does not cleave the Pt—C bond in the new compounds, in agreement with the results for analogous Ni and Pd compounds [2,4]. For the compounds of the type *cis*-$[PtX(C_6Cl_5)(PEt_3)_2]$, replacement of X by Cl occurs except for X = I and CN. Similarly, substitution occurs when X = Br or NCS, but not when X = I for the isomers *trans*-$[PtX(C_6Cl_5)(PEt_3)_2]$.

Action of chlorine

A steam of gaseous Cl_2 at 0°C passed into chloroform solutions of I and II brings about complete decomposition within a few minutes with formation of C_6Cl_6 and $[PtCl_4(PEt_3)_2]$. Partial decomposition occurs when a stoichiometric amount of Cl_2 (in CCl_4) is used.

Experimental

The preparation of the solution of C_6Cl_5MgCl and C_6Cl_5Li, and the subsequent reaction of those with *cis*-$[PtCl_2(PEt_3)_2]$ were carried out under dry oxygen-free nitrogen. The *cis*-$[PtCl_2(PEt_3)_2]$ was prepared by a published method [12].

Preparation of cis-$[PtCl(C_6Cl_5)(PEt_3)_2]$

A mixture of C_6Cl_6 (2.84 g, 10 mmols), Mg (0.48 g, 20 mmols) and THF (15 ml) and C_2H_5MgBr as initiator was refluxed for 30 min. The hot solution was added to solid *cis*-$[PtCl_2(PEt_3)_2]$ (2.5 g, 5 mmols) and the mixture refluxed with stirring for 5 h. The resulting solution was evaporated under reduced pressure until a syrup remained, and 20 ml of chloroform and 30 ml of 6 *N* aqueous HCl were added. The compound separated on concentrating the organic layer. Yield after recrystallization from ethanol 60%.

Preparation of trans-$[PtCl(C_6Cl_5)(PEt_3)_2]$

When *cis*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ (0.5 g) was heated under vacuum (0.005 mmHg) at 240°C in a sublimation apparatus, *trans*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ collected on the cold finger. Yield after recrystallization from ethanol 90%.

Preparation of the compounds $[PtX(C_6Cl_5)(PEt_3)_2]$

Method (a). A solution of *cis*-$[PtCl(C_6Cl_5)(PEt_3)_2]$ (0.5 g, 0.7 mmols) in acetone (20 ml) was heated under reflux for 6 h with an excess of the appropriate alkali metal salt (KI, LiBr, KSCN, KNCO, NaN_3) and a several drops of water. The product was recrystallized from ethanol and washed with water. Yield 95%. *Trans* isomers were prepared similarly.

Method (b). cis-$[PtCl(C_6Cl_5)(PEt_3)_2]$ (0.5 g, 0.7 mmols) in 20 ml of acetone or chloroform was treated with an excess of the silver salt, at room temperature for 15 min for X = NO_2, NO_3 and AcO; and under reflux, with protection from light, for 20 h for X = CN. The compounds were recrystallized from ethanol and washed with water. Yield 95%.

Analyses

C, H and N determinations were carried out at the Instituto de Química Orgánica de Barcelona (C.S.I.C.). Halogens were determined by Schöniger's method.

IR spectra were recorded on a Beckman IR 20A spectrophotometer purged with dry air. Samples were prepared as Nujol mulls between polyethylene films and as pressed KBr discs. PMR spectra were obtained on a 60 MHz Perkin—Elmer R-12A. $DCCl_3$ was used as solvent and TMS as internal standard.

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