984. *Pentafluorophenyl Derivatives of Transition Metals. Part IV.*[1] *Platinum*(II) *Compounds*

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Several new complexes in which pentafluorophenyl groups are σ-bonded to platinum have been prepared by treating bis(tertiary phosphine)platinum dichlorides with pentafluorophenyl-lithium or pentafluorophenylmagnesium bromide. These organoplatinum complexes are very stable, and some of their chemical properties are reported. The infrared spectra of several of the compounds were examined in the region 700—250 cm.$^{-1}$ and platinum–phosphorus stretching frequencies assigned. These bands were used to confirm isomeric character.

Following the synthesis of stable nickel(II) complexes of the types $[L_2NiRX]$ and $[L_2NiR_2]$ (R = pentafluorophenyl; L = tertiary phosphine or bipyridyl; X = Cl, Br, I, or SCN),[1] we have now prepared analogous platinum(II) compounds (Table 1). Several of the new compounds [(I), (II), (IV), (V), (VII), (VIII), and (XIII)] were obtained in the same way as their nickel(II) analogues, *i.e.*, by treating bis(tertiary phosphine)platinum halides with pentafluorophenyl-lithium or pentafluorophenylmagnesium bromide. Others were prepared by metathetical or isomerisation reactions described below.

The pentafluorophenylplatinum complexes are at least as stable thermally as their phenyl analogues, and in some cases appear to be more stable. Thus, the phenyl analogues of (I) and (IV) decompose at their melting points of 133 and 151°, respectively,[2] whereas (I) and (IV) melt at higher temperatures without decomposing. Similarly, pentafluorophenyl groups bonded to platinum are not cleaved by hydrochloric acid as readily as are phenyl groups. Whereas *cis*-$(Et_3P)_2Pt(C_6H_5)_2$ with hydrochloric acid affords *cis*-$(Et_3P)_2Pt(C_6H_5)Cl$ in 60% yield, under identical conditions *cis*-$(Et_3P)_2Pt(C_6F_5)_2$ is unaffected by the acid.

Like the phenyl complexes, the pentafluorophenyl derivatives are apparently unaffected by prolonged exposure to moist air. The infrared spectra of the new compounds show strong bands attributable to C_6F_5 absorptions near 1060 and 955 cm.$^{-1}$ which are useful in following the formation, and the reactions, of the compounds.

[1] Part III, J. R. Phillips, D. T. Rosevear, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 455.

[2] J. Chatt and B. L. Shaw, *J.*, 1959, 4020.

Nucleophilic reagents readily displace fluorine from hexafluorobenzene to form pentafluorophenyl derivatives.[3] Similar fluorine replacement reactions occur with pentafluorobenzene. In order to test how the reactivity of the perfluoroaromatic ring is affected by replacement of fluorine by platinum, compound (IV) was treated with methyl-lithium under conditions which readily bring about replacement of fluorine by methyl in hexafluorobenzene. Complex (IV) was recovered quantitatively from the reaction mixture. There was also no reaction between (IV) and methylamine, yet this reagent readily replaces fluorine atoms in hexafluorobenzene by methylamino-groups. These results suggest that the pentafluorophenyl groups withdraw electrons from platinum, thus strengthening the C–F bond in the *para*-position. In contrast, the nucleophilic reagent the sodium salt of methanethiol reacts with pentafluorophenylplatinum compounds with cleavage of fluorocarbon groups. Thus, treatment of (VII) with this reagent affords (VI) rather than a compound containing a *p*-$MeS{\cdot}C_6F_4Pt$ group. A similar cleavage of pentafluorophenyl groups from a metal occurs in reactions between $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ and sodium salts of thiols.[4]

Although the *cis*-complex (I) sublimes unchanged at 160°/0·1 mm., when heated at 230°/0·6 mm. it is converted into the *trans*-isomer (VIII). Similarly, at 175° (II) sublimes unchanged, but at 190° it is transformed into its *trans*-isomer (IX), while (III) on sublimation at 180° affords (X). Interestingly, the two compounds (V) and (VII) re-solidify immediately above their melting points as their *trans*-isomers which melt at higher temperatures (Table 1).

TABLE 1

Pentafluorophenylplatinum(II) complexes

	Compound *	M. p.		Compound *	M. p.
(I)	*cis*-$(Et_3P)_2Pt(C_6F_5)Cl$	144—146°	(VIII)	*trans*-$(Et_3P)_2Pt(C_6F_5)Cl$	119—120°
(II)	*cis*-$(Et_3P)_2Pt(C_6F_5)Br$	169—170	(IX)	*trans*-$(Et_3P)_2Pt(C_6F_5)Br$	133—134
(III)	*cis*-$(Et_3P)_2Pt(C_6F_5)I$	185—186	(X)	*trans*-$(Et_3P)_2Pt(C_6F_5)I$	163—164
(IV)	*cis*-$(Et_3P)_2Pt(C_6F_5)_2$	160—161	(XI)	*trans*-$(Et_3P)_2Pt(C_6F_5)_2$	228—229
(V)	*cis*-$(Ph_3P)_2Pt(C_6F_5)Cl$	243—250 †	(XII)	*trans*-$(Ph_3P)_2Pt(C_6F_5)Cl$	285—286 (decomp.)
(VI)	*cis*-$(Ph_3P)_2Pt(C_6F_5)SMe$	194—196			
VII)	*cis*-$(Ph_3P)_2Pt(C_6F_5)_2$	243—250 †	(XIII)	$(Ph_2P{\cdot}C_2H_4{\cdot}PPh_2)Pt(C_6F_5)_2$	269—270
			(XIV)	*trans*-$(Ph_3P)_2Pt(C_6F_5)_2$	315—316

* All compounds are white, except (VI) which is yellow. † Melts and re-solidifies into *trans*-isomer.

Chatt and Shaw [2] showed that the phenyl complex *cis*-$(Et_3P)_2Pt(C_6H_5)_2$ reacts with iodine, yielding the platinic derivative $(Et_3P)_2Pt(C_6H_5)_2I_2$. In contrast, if compound (IV) is heated in a sealed tube with iodine it is isomerised to (XI). This difference may be steric in origin. If the plane of the Pt–C and Pt–P bonds is defined as the *xy*-plane in the square-planar complexes, then the ring planes of the phenyl and pentafluorophenyl groups in $(Et_3P)_2Pt(C_6H_5)_2$ and in (IV) appear from models to be constrained in positions perpendicular to the plane of the platinum dsp^2 valences. With this structure, approach of iodine along the *z*-axis of $(Et_3P)_2Pt(C_6H_5)_2$ is not hindered, but in (IV) the two pairs of fluorine atoms *ortho* to the Pt–C bond appear to prevent the bonding of iodine to the platinum on the *z*-axis.

When a suspension of (I) in light petroleum is boiled briefly in the presence of a trace of triethylphosphine, the *trans*-isomer (VIII) is produced. The phenylplatinum compound *cis*-$(Et_3P)_2Pt(C_6H_5)Cl$ is similarly isomerised, and it has been suggested [2] that the rearrangement proceeds through an ionic intermediate $[(Et_3P)_3PtC_6H_5]Cl$. The observation that

[3] J. C. Tatlow, *Endeavour*, 1963, **22**, 89.
[4] M. A. Chaudhari and F. G. A. Stone, unpublished results.

compound (IV) is not isomerised by heating with triethylphosphine supports this view, since formation of an ionic intermediate in this case is most unlikely.

During the course of this work it was important to establish the isomeric character of the pentafluorophenylplatinum compounds. A strong indication of the correct stereochemistry was frequently possible from consideration of earlier work [2] on phenylplatinum compounds, from the well-established isomeric character of the tertiary phosphine platinum halides used as starting materials, and from melting point relationships. Thus, as recorded in the Experimental section, treatment of *trans*-$(Et_3P)_2PtCl_2$ with excess of pentafluorophenyl-lithium affords *cis*-$(Et_3P)_2Pt(C_6F_5)_2$ (IV) rather than the *trans*-isomer (XI). Similarly, with phenyl-lithium the major product from the *trans*-platinum halide was *cis*-$(Et_3P)_2Pt(C_6H_5)_2$.[2] In other preparations treatment of *cis*-platinum halides with pentafluorophenyl-lithium afforded complexes assigned *cis*-configurations by analogy with the earlier results.[2] Moreover, trends in melting points between *cis*- and *trans*-isomers (Table 1) closely parallel those found earlier with analogous phenylplatinum compounds.

In order to confirm the isomer assignments made in Table 1, the proton n.m.r. and far-infrared spectra of several of the complexes were examined. The proton spectra were not first-order, but by employing the concept of virtual coupling between phosphorus atoms in *trans*-isomers [5] it was possible to confirm isomeric character in several instances. The infrared spectral results provide a distinction between the isomers.

For the compound *cis*-$(Et_3P)_2PtCl_2$ (C_{2v}), the isomeric character of which is firmly established, Goggin and Goodfellow [6] observed the two expected Pt–P stretching vibrations at 442 and 427 cm.$^{-1}$. Only one of the corresponding modes in *trans*-$(Et_3P)_2PtCl_2$ (skeletally D_{2h}) should be infrared-active, and these same workers observed this mode at 419 cm.$^{-1}$. In compounds of the type *cis*-$(Et_3P)_2Pt(C_6F_5)X$ (C_s) there will still be two infrared-active Pt–P stretching modes. The *trans*-isomers of this formula type have strictly C_{2v} symmetry, and as such should also in principle show two Pt–P stretching bands. However, the symmetrical stretch will not induce any significant dipole moment change provided that the two Pt–P bonds are collinear; thus, the infrared intensity associated with this vibration would be expected to be very weak. Indeed, the results summarised in Table 2 show that the *trans*-isomers have only one infrared-active Pt–P band.

TABLE 2

Correlation of isomeric character with platinum–phosphorus stretching frequencies

Composition	Stretching bands (cm.$^{-1}$) *		
	cis-Isomer		*trans*-Isomer
$(Et_3P)_2PtCl_2$	427	442	419
$(Et_3P)_2Pt(C_6F_5)Cl$	423	439	417
$(Et_3P)_2Pt(C_6F_5)Br$	418	437	412
$(Et_3P)_2Pt(C_6F_5)I$	417	433	410
$(Et_3P)_2Pt(C_6F_5)_2$	416	429	414

* Recorded as Nujol mulls held between thin Polythene discs supported on CsBr plates.

In the compounds examined, the Pt–P frequencies are lower than those in *cis*- or *trans*-$(Et_3P)_2PtCl_2$, as expected.[6]

In *trans*-$(Et_3P)_2PtCl_2$, the Pt–Cl stretching frequency occurs at 340 cm.$^{-1}$.[6] In complex (I), in which the chlorine atom is *trans* to a triethylphosphine ligand, the corresponding band has moved to 302 cm.$^{-1}$, in accord with the *trans*-directing effect of the trialkylphosphine group. When a pentafluorophenyl group is *trans* to a chlorine atom [compound (VIII)], the Pt–Cl stretch is observed at 310 cm.$^{-1}$, the relatively low wavenumber again being indicative of a strong *trans*-directing ligand in the position *trans* to the chlorine atom. For *cis*- and *trans*-$(Et_3P)_2Pt(Cl)C_6H_5$, the Pt–Cl stretching bands were at 290 and

[5] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279.
[6] P. Goggin and R. J. Goodfellow, unpublished results.

282 cm.$^{-1}$, respectively. For compounds (V) and (XII), Pt–Cl bands were at 306 and 312 cm.$^{-1}$, respectively.

Experimental

All preparations involving pentafluorophenyl-lithium [7] or pentafluorophenylmagnesium bromide [8] were carried out under nitrogen. Infrared spectra below 700 cm.$^{-1}$ were recorded with a Perkin-Elmer 221 spectrophotometer using a cæsium bromide prism. We are indebted to Professor J. S. Anderson (Oxford) for making this instrument available to us, and to Dr. Goggin for measuring the spectra. Preparation of tertiary phosphine platinum halides was as described in Gmelin's " Handbuch." [9]

Pentafluorophenylplatinum Compounds Prepared from Pentafluorophenyl-lithium.—(a) cis-*Bis(triethylphosphine)chloro(pentafluorophenyl)platinum* (I). Pentafluorophenyl bromide (430 mg., 1·74 mmoles) in diethyl ether (20 ml.) was treated at −60° with a hexane solution (1 ml.) of n-butyl-lithium (1·74 mmoles). The mixture was stirred (10 min.), and a solution of *cis*-$(Et_3P)_2PtCl_2$ (430 mg., 0·87 mmole) in dichloromethane (30 ml.) added. After warming to room temperature (1 hr.), the mixture was shaken with water, and the organic layer evaporated to dryness, giving white *needles* of (I) (437 mg., 80%) [from methanol (4 ml.)] (Found: C, 33·9; H, 4·9; Cl, 5·8; F, 15·1; P, 10·1. $C_{18}H_{30}ClF_5P_2Pt$ requires C, 34·1; H, 4·8; Cl, 5·6; F, 15·0; P, 9·8%).

(b) cis-*Bis(triethylphosphine)bis(pentafluorophenyl)platinum* (IV). From an experiment similar to that in (a) above, using twice the quantities of pentafluorophenyl bromide and n-butyl-lithium, *prisms* of (IV) (92%) were obtained (Found: C, 38·1; H, 4·2; F, 24·2; P, 8·2. $C_{24}H_{30}F_{10}P_2Pt$ requires C, 37·7; H, 3·95; F, 24·8; P, 8·1%).

(c) trans-*Bis(triethylphosphine)chloro(pentafluorophenyl)platinum* (VIII). In an experiment similar to that in (a) above, *trans*-$(Et_3P)_2PtCl_2$ (860 mg., 1·74 mmoles) treated with pentafluorophenyl-lithium (1·74 mmoles) afforded *complex* (VIII) as white plates (668 mg., 62%) (from methanol–water) (Found: C, 34·1; H, 4·7; Cl, 5·4; F, 15·1; P. 9·8. $C_{18}H_{30}ClF_5P_2Pt$ requires C, 34·1; H, 4·8; Cl, 5·6; F, 15·0; P, 9·8%), together with (IV) (20 mg., 1·5%) and recovered dichloride (170 mg.).

Treatment of *trans*-$(Et_3P)_2PtCl_2$ with an excess of pentafluorophenyl-lithium gave (IV) (59%) (from benzene), identified by its infrared spectrum, m. p., and analysis (Found: C, 37·9; H, 3·7; F, 23·3; P, 8·1%).

(d) cis-*Bis(triphenylphosphine)bis(pentafluorophenyl)platinum* (VII). Finely powdered *cis*-$(Ph_3P)_2PtCl_2$ (1·37 g., 1·74 mmoles) was added to pentafluorophenyl-lithium (3·5 mmoles) [from pentafluorophenyl bromide (0·86 g.) and butyl-lithium solution (2 ml.) in ether (50 ml.) at 0°]. The mixture was stirred (18 hr.) and filtered. The filtrate was evaporated to give *complex* (VII) (0·75 g., 41%) (from benzene) (Found: C, 54·9; H, 3·1; F, 18·0; P, 5·9. $C_{48}H_{30}F_{10}P_2Pt$ requires C, 54·7; H, 2·9; F, 18·0; P, 5·9%). The mother liquor was taken to dryness, giving cis-*bis(triphenylphosphine)chloro(pentafluorophenyl)platinum* (V) (0·71 g., 44%) (from benzene–methanol) (Found: C, 54·8; H, 3·2; Cl, 3·7; F, 10·6; P, 6·6. $C_{42}H_{30}ClF_5P_2Pt$ requires C, 54·7; H, 3·3; Cl, 3·8; F, 10·3; P, 6·7%).

(e) 1,2-*Bis(diphenylphosphino)ethanebis(pentafluorophenyl)platinum* (XIII). A mixture of finely powdered *cis*-$(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)PtCl_2$ (540 mg., 0·81 mmole) and pentafluorophenyl-lithium (1·74 mmoles) [from pentafluorophenyl bromide (430 mg.) and butyl-lithium (1 ml.) in ether (50 ml.)] was stirred for 3 days at room temperature, and filtered. The filtrate was evaporated, affording white *needles* of (XIII) (630 mg., 84%) (from benzene–methanol) (Found: C, 49·2; H, 2·8; F, 20·7; P, 6·6. $C_{38}H_{24}F_{10}P_2Pt$ requires C, 49·2; H, 2·6; F, 20·5; P, 6·7%).

Reaction Between Pentafluorophenylmagnesium Bromide and cis- *and* trans-*Bis(triethylphosphine)platinum Dichloride.*—Pentafluorophenylmagnesium bromide was prepared from magnesium (100 mg., 4 mg.-atoms), ether (2 ml.), and pentafluorophenyl bromide (1 g., 4 mmoles), the reaction mixture having been heated under reflux with stirring for 30 min. to dissolve the magnesium. A hot saturated solution of *cis*-$(Et_3P)_2PtCl_2$ (1 g., 2 mmoles) in benzene (100 ml.) was added, and the mixture stirred (30 min.), and shaken with water. The organic layer was separated and evaporated, affording white crystals of (II) (1·13 g., 83%) (from ethanol) (Found:

[7] P. L. Coe, R. Stephens, and J. C. Tatlow, *J.*, 1962, 3227.
[8] M. Hellmann, E. Peters, W. J. Pummer, and L. A. Wall, *J. Amer. Chem. Soc.*, 1957, **79**, 5654; 1960, **82**, 4846.
[9] Gmelin's " Handbuch," Vol. 68, 1957, part D, pp. 344—347.

C, 32·0; H, 4·5; Br, 11·8; F, 14·4; P, 9·2. $C_{18}H_{30}BrF_5P_2Pt$ requires C, 31·9; H, 4·5; Br, 11·8; F, 14·0; P, 9·1%).

No reaction occurred between pentafluorophenylmagnesium bromide and *trans*-bis(triethylphosphine)platinum dichloride, other than decomposition of the Grignard reagent under vigorous conditions.

cis-*Bis(triethylphosphine)iodo(pentafluorophenyl)platinum* (III).—A sample (178 mg., 0·26 mmole) of (II) in acetone (10 ml.) was treated with sodium iodide (50 mg., 0·33 mmole) in the same solvent (5 ml.). After boiling, solvent was removed and the residue washed with hot water (2 × 20 ml.), affording *complex* (III) (170 mg., 89%) (from benzene–methanol) (Found: C, 29·8; H, 4·3; F, 13·2; I, 17·5; P, 8·4. $C_{18}H_{30}F_5IP_2Pt$ requires C, 29·8; H, 4·2; F, 13·1; I, 17·5; P, 8·5%).

Treatment of cis-*Bis(triethylphosphine)bis(pentafluorophenyl)platinum with Hydrochloric Acid.*—A sample (128 mg., 0·16 mmole) of (IV) in benzene (15 ml.) was treated with hydrochloric acid in ether (1 ml.; 0·16N) for 30 min. The mixture was evaporated and the residue recrystallised (benzene), to give (IV) (120 mg., 94%), identified by its m. p. In a parallel reaction involving *cis*-$(Et_3P)_2Pt(C_6H_5)_2$, *cis*-$(Et_3P)_2Pt(C_6H_5)Cl$ was prepared (60%) in agreement with earlier work.[2]

Reaction Between cis-*Bis(triphenylphosphine)bis(pentafluorophenyl)platinum and the Sodium Salt of Methanethiol.*—A sample (180 mg., 0·17 mmole) of (VI) was added to a suspension of the sodium salt, made by bubbling methanethiol through tetrahydrofuran (20 ml.) containing sodium (30 mg., 1·3 mg.-atoms). The mixture was refluxed (5 min.), solvent removed, and the residue shaken with benzene and water. The organic layer was dried and evaporated, to give the *methylthio-complex* (VI) (156 mg., 98%) (from benzene–methanol) (Found: C, 55·5; H, 3·8; F, 10·3; P, 6·75; S, 3·2. $C_{43}H_{33}F_5P_2PtS$ requires C, 55·3; H, 3·6; F, 10·2; P, 6·65; S, 3·4%).

Treatment of cis-*Bis(triethylphosphine)bis(pentafluorophenyl)platinum with Methyl-lithium.*—Complex (IV) (216 mg.) in benzene (40 ml.) was treated with methyl-lithium (0·4 ml. of a 5·25% ether solution), and the mixture refluxed (20 min.). Addition of methanol caused vigorous effervescence; starting material (IV) (208 mg., 96%) (identified by m. p. and infrared spectrum) was recovered.

Isomerisation Reactions.—Conversion of *cis*-complexes into their *trans*-isomers on sublimation was described earlier. *trans*-Compounds were identified either by melting point (if known), by analysis, or by far-infrared studies: (IX) crystallised from methanol (Found: C, 32·1; H, 4·4. $C_{18}H_{30}BrF_5P_2Pt$ requires C, 31·9; H, 4·5%); (X) crystallised from benzene–methanol (Found: C, 29·8; H, 4·3. $C_{18}H_{30}F_5IP_2Pt$ requires C, 29·8; H, 4·2%); (XII) crystallised from benzene–methanol (Found: C, 54·6; H, 3·0. $C_{42}H_{30}ClF_5P_2Pt$ requires C, 54·7; H, 3·3%).

A sample (90 mg., 0·12 mmole) of (IV) in benzene (4 ml.) was heated (90°; 20 hr.) with iodine (60 mg., 0·24 mmole) in a sealed tube. Solvent and iodine were removed and the residue extracted with benzene to give *prisms* of (XI) (86 mg., 95%) (from benzene–methanol) (Found: C, 37·7; H, 4·2; F, 24·8; I, 0·0; P, 8·1. $C_{24}H_{30}F_{10}P_2Pt$ requires C, 37·7; H, 3·95; F, 24·8; P, 8·1%). The experiment was repeated without iodine and gave only starting material (IV).

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