

Fluorophosphine Complexes of the Platinum Group Metals

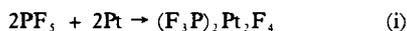
DEVELOPMENTS INVOLVING ORGANIC DERIVATIVES

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Dedicated to Henri Moissan on the occasion of the one hundredth anniversary of his discovery of the first fluorophosphine platinum complex, this review describes the recent interest, and developments in fluorophosphines as ligands for platinum group metals. The synthesis, structure, reactions, stability, and the potential of these compounds as homogeneous and heterogeneous catalysts are the main features of this article.

Looking for a way of preparing fluorine chemically, Moissan reacted phosphorus pentafluoride and platinum black (1). He was able to isolate a product of composition F_5Pt .



In 1891 he recognised the true structure of the first trifluorophosphine complex (2), see Equation (i) and Figure 1. This "failed" attempt at preparing fluorine had started the chemistry of fluorophosphines, soon after the discovery of the first carbonyl complexes by Schützenberger, in 1868 (3). Interestingly both complexes, the first PF_3 complex as well as the first CO complex, involved a platinum(II) atom, see in Figure 1.

Following the preparation by Chatt in 1949 of some further platinum(II) complexes of PF_3 , and his postulation of the similarity between trifluorophosphine and carbonyl complexes with respect to their bonding situation (4), the interest of chemists was drawn to fluorophosphines and their co-ordination compounds. Nevertheless it

took some eight years before the first organo(difluoro)phosphine and di(organo)-fluorophosphine compounds were successfully synthesised, and published by Burg (5).

With organofluorophosphines now available, their use as ligands in co-ordination chemistry has been studied intensively, and hundreds of mono-, di-, and trifluorophosphine complexes of different transition metals have been prepared (6), as indicated in Table I.

Why Examine Ligands of Formula C_nP-F_{2-n} Instead of PF_3 ?

Organofluorophosphines are compounds involving a carbon-phosphorus-fluorine (C-P-F) moiety. In contrast to other fluorophosphines, for example Si-P-F, N-P-F, P-P-F, O-P-F, S-P-F, and X-P-F (where X = halogen), they show a stable element-phosphorus bond (here C-P). The physical and chemical properties of organofluorophosphines also resemble those of

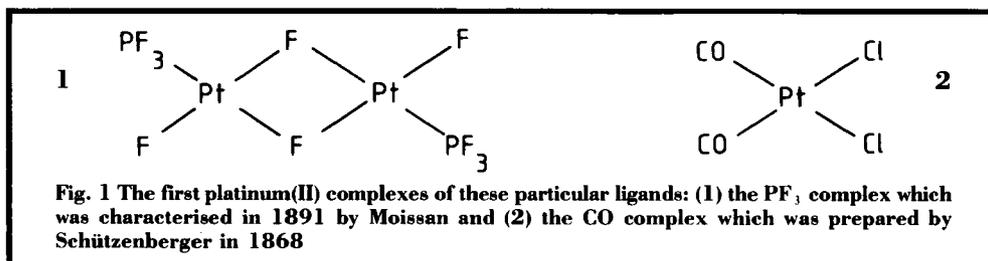


Table I								
Fluorophosphine Complexes of Transition Metals								
Ti	V	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	Cu	Zn
Zr	Nb	<u>Mo</u>	Tc	<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	Ag	Cd
Hf	Ta	<u>W</u>	Re	<u>Os</u>	Ir	<u>Pt</u>	Au	Hg

Blue typeface indicates known complexes, blue and underlining indicates known organofluorophosphine complexes (6, 7)

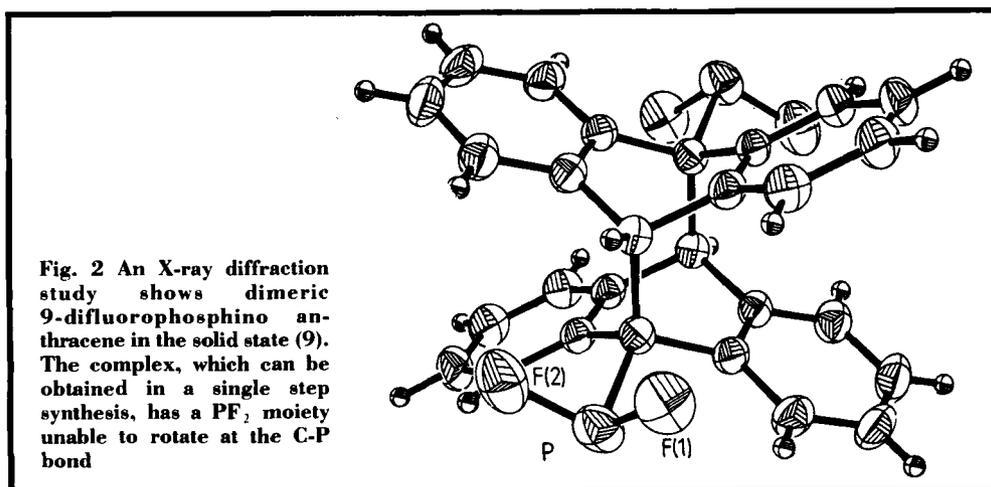
Table II			
Comparison of Bond Angles and Lengths of PF ₃ and RPF ₂			
	F-PF ₂	C-PF ₂ (Fig. 2)	Me ₂ N-PF ₂
F-P-F bond angles:	97.7°	96.3°	91.5°
P-F bond lengths:	157 pm	157–158 pm	161.0 pm

PF₃ very closely (8–10), see Table II. This has been confirmed by X-ray diffraction studies on two organofluorophosphines: the dimeric anthracene difluorophosphine, shown in Figure 2 (9), and for comparison the dimethylamino difluorophosphine (10).

One can clearly see the similarities in the bond angles of PF₃ and RPF₂ (where R = carbon bonded groups), despite strong steric hindrance,

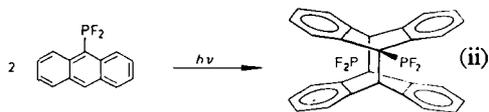
in contrast to N-PF₂ without this steric factor. In the example, Figure 2, the PF₂ moiety is unable to rotate at the C-P bond because of strong F-H "through-space" interactions.

This property serves to combine the special electronic effects of PF₃ with other characteristics of co-ordination compounds that are important in catalytic reactions, for example: stability, solubility, volatility, chirality, the bulk,



the possibility of heterogenisation, and so on.

Surprisingly, the highly sterically hindered and air-stable compound shown in Figure 2 was obtained in a single step synthesis, see Equation(ii):

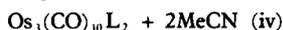
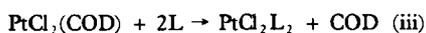


the photochemical dimerisation of difluorophosphino anthracene (9)

Methods of Preparation

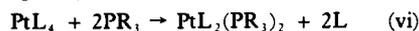
The known types of organofluorophosphine complexes of platinum group metals are given in Table III. For most of these compounds an appropriate PF_3 complex is also known.

Most of these compounds have been prepared by an exchange reaction between a labile ligand and an excess of the organofluorophosphine (7, 14, 15), that is:



where COD = 1,8-cyclooctadiene, $\text{L} = \text{RPF}_2, \text{R}_2\text{PF}$, and R = carbon bonded organic moiety.

In the case of platinum(0) complexes a very large excess of organodifluorophosphine may be used to get complexes of the type PtL_4 (reduction of platinum(II) under formation of some organofluorophosphorane (16, 17), see Equation (v)). These complexes are not as stable against oxygen and moisture as their Cl_2PtL_2 analogs (17) and they may be transformed to mixed phosphine substituted complexes using tertiary phosphines (16), for example triphenylphosphine, see Equation (vi):



Bulky organic substituents involved in the fluorophosphine ligand have only a minor effect in the given preparation methods. For example two $^t\text{BuPF}_2$ or $(o,p\text{-}(\text{CF}_3)\text{C}_6\text{H}_3)_2\text{PF}$ can co-ordinate to one platinum(II) atom (18). In the case of tungsten a hexaco-ordinated species is known, that is $\text{W}(^t\text{BuPF}_2)_2$ (13). On the other hand it is impossible to co-ordinate two phosphines such as $^t\text{Bu}_2\text{PF}$ or $(\text{Me}_3\text{Si})_3\text{PF}_2$ onto one platinum(II) atom (7), but each of these ligands can co-ordinate to one metal, for example osmium or ruthenium (14). In a cluster

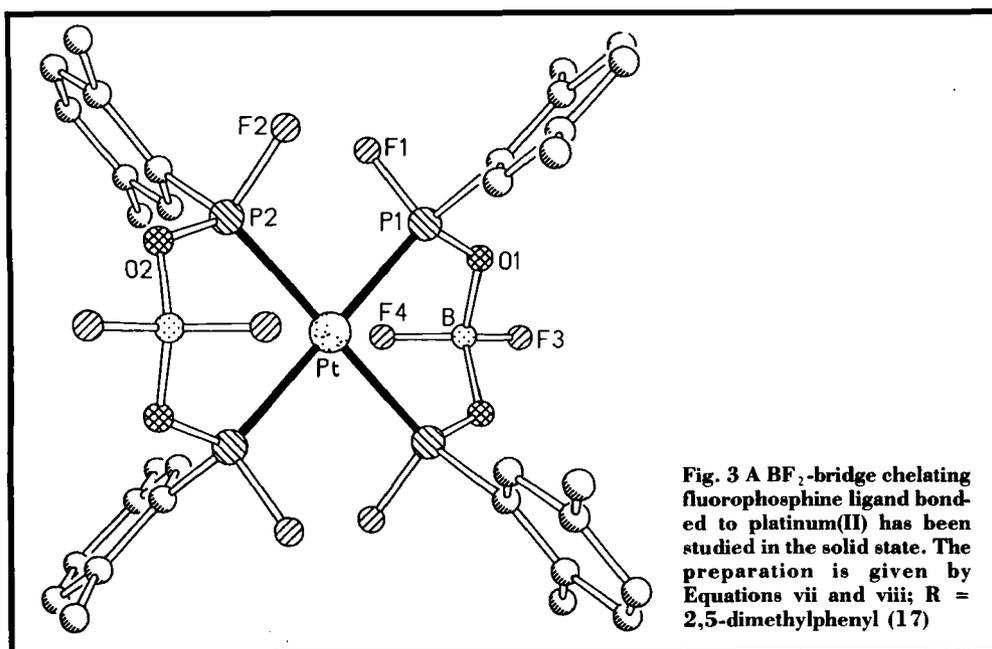


Fig. 3 A BF_2 -bridge chelating fluorophosphine ligand bonded to platinum(II) has been studied in the solid state. The preparation is given by Equations vii and viii; R = 2,5-dimethylphenyl (17)

Table III Known Types of Organofluorophosphine Complexes Involving Platinum Group Metals		
Ruthenium	Rhodium	Palladium
$Ru_3(CO)_{11}L$ $Ru_3(CO)_{10}L_2$ $Ru_3(CO)_9L_3$ $Ru_3(CO)_8L_4$ $Ru_6(CO)_{10}(P^tBu)_4L$ (11) $Ru_6(CO)_9(P^tBu)_4L_2$ (11)	$RhCp^*Cl_2L$ (12) $RhCl(PPh_3)_2L$	(a)
Osmium	Iridium	Platinum
$Os_3(CO)_{11}L$ $Os_3(CO)_{10}L_2$ $Os_3(CO)_9L_3$ $Os_3(CO)_8L_4$ $Os_3(CO)_6L_6$ $Os_6(CO)_{15}L_6$		$PtCl_2L_2$ $PtCl_2(PR_3)L$ $PtCl_2(PR_2-L)$ $PtCl(PR_3)_2(RPFO)$ $PtCl(CH_2-L)L$ PtL_4 $Pt(PR_3)_2L_2$ $Pt(AsR_3)_2L_2$ $Pt(tp)_3L$

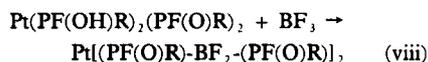
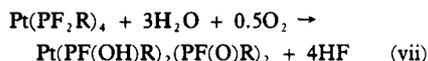
(a) Palladium complexes are claimed by Kruck but they are not yet published (13)
 L = RPF₂, R₂PF; R = carbon bonded organic moiety; Cp* = C₅Me₅; tp = CH(CH₂PPh₂)₃.
 In the case of platinum(II) complexes, some more complicated compounds are known (see below).
 For a review see (7), for further details see (14, 15).

compound, for example $Os_3(CO)_{10}L_2$, two ligands are always bonded to two different metal atoms (14, 15). Only if there are more RPF₂ ligands than metal atoms in a cluster, as in $Os_3(CO)_6L_6$, will two organodifluorophosphines be connected with one metal centre (14).

Reactions of Platinum(0) and Platinum(II) Complexes

The reactions of complexes of the type PtL_4 with water and oxygen lead to the formation of partly hydrolysed and oxidised organofluorophosphines co-ordinated to platinum(II), see Equation (vii) (17). These complexes may be reacted with boron trifluoride etherate to yield BF₃-bridged, chelating

organofluorophosphine complexes, as shown in Figure 3 on the previous page (17).



where R = a carbon bonded organic moiety.

Organofluorophosphine platinum(II) complexes are very stable compounds which do not decompose under normal conditions. These complexes are less stable only if the organic moiety is chosen from the group of multiple halogenated substituents, for example C₆F₅ or CCl₂H. This is in strong contrast to the stability of the corresponding organofluorophosphines themselves, which become more stable if they are either

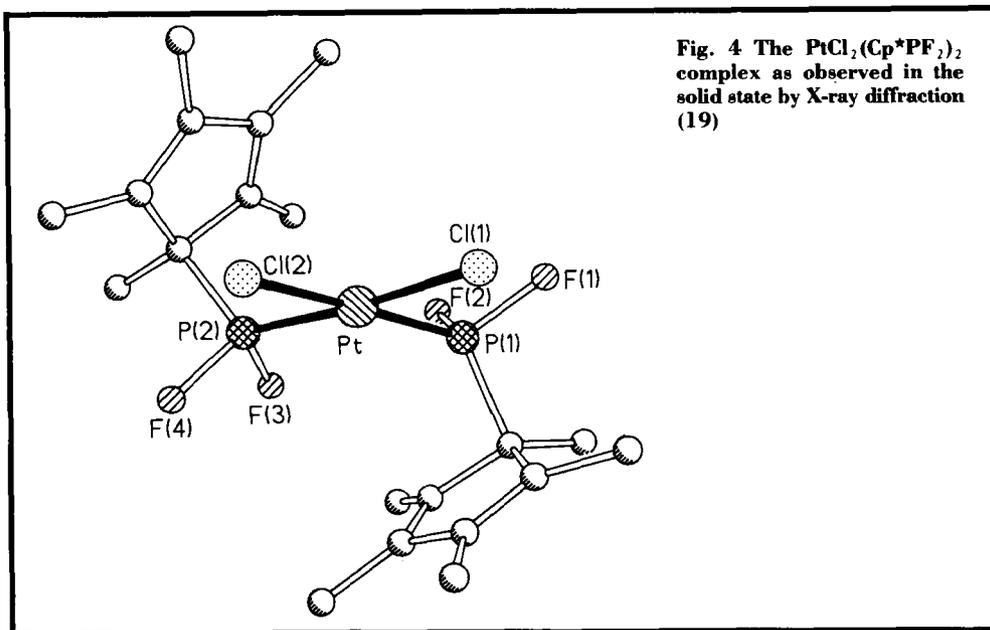


Fig. 4 The PtCl₂(Cp*PF₂)₂ complex as observed in the solid state by X-ray diffraction (19)

halogenated in the organic part or if the organic moiety shows a reasonable steric bulk.

As a typical example of a platinum(II) complex involving a bulky substituent, the X-ray structure of PtCl₂(Cp*PF₂)₂ is shown in Figure 4 (19).

On the other hand bulky substituents involved in the phosphine ligand, such as 2,4,6-trimethylphenyl difluorophosphine, display a most interesting chemistry if

they are co-ordinated to platinum(II). PtCl₂(PF₂C₆H₂Me₃)₂, for example, splits off HCl if heated in vacuum (20) and gives a compound involving a Pt-C bond, see Figure 5.

The remaining chlorine atom in the compound shown in Figure 5 may be replaced by organic moieties using, for example, SnMe₄ or HgPh₂, and yielding the methylated or phenylated complexes, respectively.

Another most interesting aspect of

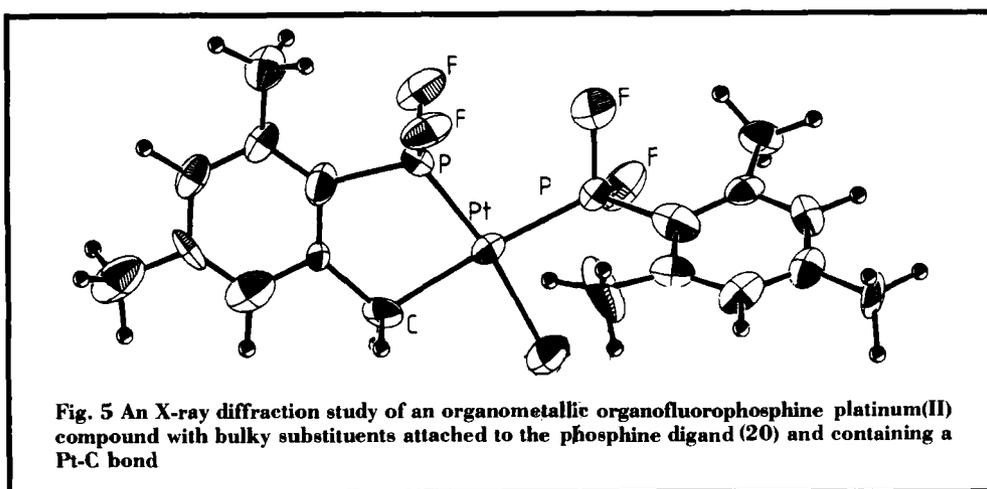


Fig. 5 An X-ray diffraction study of an organometallic organofluorophosphine platinum(II) compound with bulky substituents attached to the phosphine ligand (20) and containing a Pt-C bond

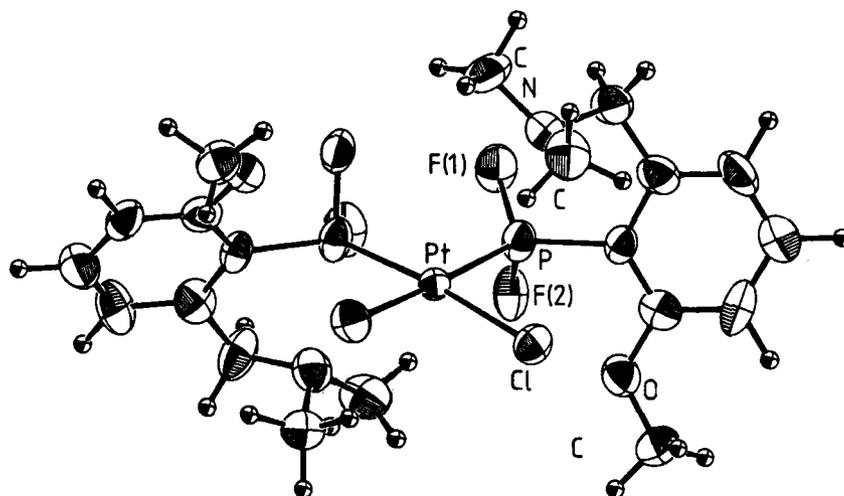


Fig. 6 A study in the solid state of the hypervalent phosphorus atom in an organofluorophosphine moiety shows the RPF_2 group in a trigonal bipyramidal co-ordination mode with one fluorine in the axial position and one fluorine in the equatorial position (21)

organofluorophosphines bonded to platinum(II) has been found in the compound shown in Figure 6. In the solid state the *ortho*-substituent of the aromatic ring system ($-\text{CH}_2\text{NMe}_2$) is found to co-ordinate into the PF_2 moiety, representing the first example of an hypervalent phosphorus in this type of compound (21).

Reactions of Ruthenium and Osmium Complexes

Complexes of type $\text{M}_3(\text{CO})_{12-n}\text{L}_n$ ($\text{M} = \text{Os}, \text{Ru}, n = 1-4$; $\text{M} = \text{Os}, n = 6$) are stable compounds in the solid state, and in the case of osmium also in solution (14, 15), see Figure 7. Treatment of these complexes with trimethylamine oxide in the presence of free ligand leads to the formation of mixtures of compounds involving different numbers of ligands. Therefore one may start with $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$) and end up with all the possible complexes given above ($n = 1-6$ see Table(III) of which $n = 3$ represents the main product if an excess of amine oxide and ligand is used (14) Numbers $n > 3$ are difficult to obtain by this method, indeed $n = 5$ has never been fully characterised. Using ultraviolet light, $\text{Os}_3(\text{CO})_{12}$

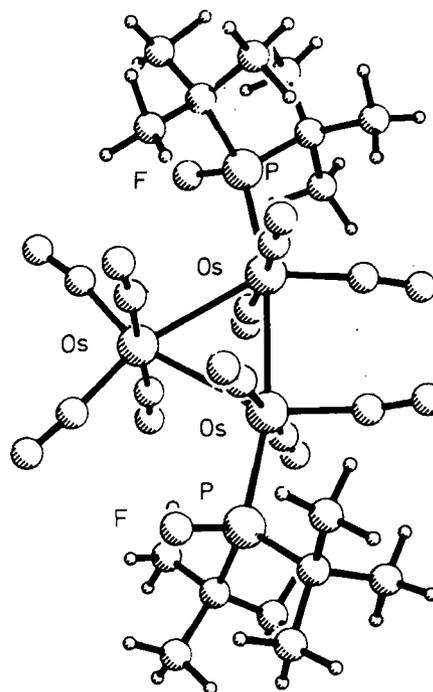


Fig. 7 A typical co-ordination mode in an osmium cluster compound, is shown for example in the solid state structure of $\text{Os}_3(\text{CO})_{10}(\text{tBu}_2\text{PF}_2)_2$ (15)

and excess ligand $n = 6$ has been found to be the major product (14).

Rhodium, Palladium and Iridium Complexes

Even though rhodium is one of the few metals showing a strong nuclear magnetic spin of $\frac{1}{2}$, which suggests that any conceivable rhodium organofluorophosphine complexes would have an interesting NMR spectra, little is known about this class of compounds (7). In the opinion of the author, organofluorophosphine complexes of rhodium as well as of iridium represent a challenge for every preparative chemist, especially with respect to possible compounds analogous to Wilkinson's and Vaska's complexes.

Palladium organofluorophosphine complexes are known to undergo some of the reactions given for platinum; however, the appropriate platinum complexes are more stable and, for this reason, have been studied in greater detail. The identity of some palladium compounds involving organofluorophosphine ligands are claimed by Kruck (13) but have not yet been published.

Properties of Complexes of Organofluorophosphines

In contrast to the more or less volatile PF_3 -complexes of transition metals, organofluorophosphine complexes are much less volatile, or non-volatile, solids; and due to the organic group they are more resistant to moisture and to air. Almost all of the known organofluorophosphine complexes of the platinum group metals may be stored for months in the solid state at room temperature, without using any protective methods, and without any changes occurring. Indeed, even in solution most of them are stable against moisture and oxygen.

The solubility of organofluorophosphine complexes of these metals is influenced by the organic group bonded to the phosphorus and by the general bonding state on the metal. Dichloromethane or other polar solvents are perfectly capable of dissolving reasonable amounts of most of these complexes. It is possible, however, to use hydrophobic or hydrophilic organic moieties to increase or decrease the

solubility of a given co-ordination state in a given solvent. For example, using dichloromethane as the solvent the solubility of complexes of the type $\text{Cl}_2\text{Pt}(\text{PF}_2[\text{o},\text{o}-\text{R}_2\text{C}_6\text{H}_3])_2$ increases in the following order: $\text{R} = \text{MeO} < \text{Me} < \text{PhO} < \text{H} < \text{C}_{16}\text{H}_{33}\text{O}$ (7).

In some dozens of X-ray determinations of organofluorophosphine complexes of transition metals a somewhat shorter metal-phosphorus bond length has always been observed, compared with that of the appropriate triorganophosphine co-ordination compound (7). In the case of platinum(II) complexes, the Pt-P bond length correlates with the ^{31}P - ^{195}Pt coupling constant in the NMR spectra of these compounds (7, 21). Both indicate a strong metal-phosphorus interaction, which is reflected in strong chemical and physical bonding of the organofluorophosphine to the metal.

Heterogenisation of Complexes of Organofluorophosphines

One main synthetic route to organofluorophosphines first developed by Lines and Centofanti (22) and then optimised by the author (7, 23) involves lithiation of an aromatic ring system, and treatment of this product with PF_2Cl , which is a gas. (PF_3 may also be used but gives insufficient yields). It has been shown that this method is useful for transforming polystyrol to PF_2 -functionalised polystyrol, which readily yields platinum(II) complexes on treatment with $\text{PtCl}_2(\text{COD})$ (7).

PF_2 -functionalised polystyrol should also be a good starting material for other transition metal complexes, especially for the platinum metals.

Outlook

The investigations on fluorophosphine complexes started with the hope in finding some interesting new compounds which would become as relevant for catalytic processes as some particular CO complexes. The high sensitivity of compounds involving PF_3 to moisture and oxygen has destroyed the initial optimism. As organofluorophosphines are readily available and are much less sensitive to wet air this optimism may return. In addition, the possibility of

heterogenisation of active complexes by standard organic reactions may increase the interest of industrial chemists.

Heterogenisation may not only find application in catalytic reactions, one should also keep in mind the strong bonding of the platinum group metals to organofluorophosphines, a property which may be useful in the recovery of these expensive metals from solutions and mixtures in organic solvents, by absorption using polymeric organofluorophosphines.

Lastly, $\text{Pt}(\text{PF}_3)_4$ has been used for the preparation of special platinum metal catalysts by thermal decomposition (24). Because of the high toxicity and volatility of PF_3 , which is split off during this reaction, it may be better to use organofluorophosphine ligands instead.

Acknowledgements

The author is indebted to Professors B. F. G. Johnson, P. G. Jones, Dr. D. Schomburg and Dr. R. Schmutzler. Figures are reprinted with permission of journals and/or authors.

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Precious Metals Science and Technology

In 1985, to commemorate the centenary of the founding of Tanaka Kikinzoku Kogyo K.K., a reference book entitled "Science of Precious Metals" was published in Japan (see *Platinum Metals Rev.*, 1986, **30**, (2), 62).

Now the English language version, "Precious Metals Science and Technology", containing several additional chapters has been published by the International Precious Metals Institute.

Edited by L. S. Benner, T. Suzuki, K. Meguro and S. Tanaka and consisting of some 800 pages including 500 figures and tables, this translation will be a valuable addition to the literature.

Further details, including price and availability, may be obtained from: International Precious Metals Institute, 4905 Tilghman Street, Suite 160, Allentown, Pennsylvania 18104, U.S.A.