240. *Phosphine and Phosphite Complexes of Platinum*(II) *Fluoride.**

By J. McAvoy, K. C. Moss, and D. W. A. Sharp.

Bis-(triphenylphosphine)platinum(II) fluoride and bis-(triphenyl phosphite)platinum(II) fluoride have been prepared by the action of hydrogen fluoride on the tetra-ligandplatinum(0) derivatives. The fluorides add carbon monoxide under pressure to give dicarbonyl derivatives.

The fluorides of platinum have been the subject of a recent Paper[1] in which the existence of platinum tetrafluoride, pentafluoride, and hexafluoride is considered as well established. The report by Moissan[2] of a yellow-green difluoride was not confirmed,[1] and neither a difluoride nor a trifluoride are known. The present Paper describes the preparation of some derivatives of platinum difluoride in which there is co-ordination to the platinum from phosphorus-containing ligands.

Complexes in which other ligands are bonded to metals whilst the metal is, in turn, bonded to a fluorine atom are not well known. For platinum, it has been suggested[3]

---

* For a preliminary account of part of this work see R. D. W. Kemmitt, K. C. Moss, D. R. Russell, and D. W. A. Sharp, Preprints, Second Internat. Symp. on Fluorine Chem., 1962, p. 264.

[1] N. Bartlett and D. H. Lohmann, *J.*, 1964, 619.

[2] H. Moissan, " Le fluor et ses composes," Steinheil, Paris, 1900.

[3] R. D. Peacock, Progress in Inorganic Chemistry, 1960, **2**, 193.

that a further compound prepared by Moissan[2] should be formulated as $(PF_3)PtF_2$ with a phosphorus–platinum bond analogous to the phosphorus–nickel bond in tetrakis(trifluorophosphine)nickel(0), $Ni(PF_3)_4$. The adduct formed by the action of bromine trifluoride on platinum tetrafluoride, $PtF_4 \cdot 2BrF_3$, may be a complex in which there is interaction between lone-pairs of electrons on the bromine atom and the platinum, although it is usually considered[4] to be ionic, $[BrF_2]_2[PtF_6]$.

Bis-(triphenylphosphine) platinum(II) fluoride, $(Ph_3P)_2PtF_2$, was prepared by the action of anhydrous hydrogen fluoride on tetrakis(triphenylphosphine)platinum(0); the latter compound was prepared by the method of Malatesta and Cariello.[5] This compound, $[Ph_3P]_4Pt$, has been considered as a dihydride,[6] but recent work by Malatesta and Ugo[7] has confirmed the original formulation as a derivative of platinum(0). Present work agrees with the conclusions of Malatesta and Ugo and has, in addition, shown that chloroform is not a product of the reaction in which tetrakis(triphenylphosphine)platinum(0) is converted into bis(triphenylphosphine)platinum(II) chloride by the action of carbon tetrachloride. The reaction for the preparation of bis(triphenylphosphine)platinum(II) fluoride is, therefore,

$$(Ph_3P)_4Pt + 2HF \longrightarrow (Ph_3P)_2PtF_2 + H_2 + 2Ph_3P,$$

the other major product being hydrogen, which was not detected. The action of hydrogen fluoride as an oxidising agent is similar to its role in the fluorination of red phosphorus to phosphorus trifluoride.[8]

Bis(triphenylphosphine)platinum(II) fluoride, as normally prepared, is a white substance virtually insoluble in nonpolar solvents. The dipole moment has not, therefore, been determined. When warmed gently in a suitable solvent, it is converted into a pink form which, on successive recrystallisation, reverts to the original white derivative. Such a complex of platinum(II) should have square-planar co-ordination about the platinum, and it is suggested that, by analogy[9] with other bis(phosphine)platinum(II) halides, the original white form is the *cis*-isomer, whilst the pink form is the *trans*-isomer. In all other complexes of this type the *trans*-isomer is more strongly coloured than the *cis*.[9]

Bis(triphenyl phosphite)platinum(II) fluoride, $[(PhO)_3P]_2PtF_2$, was prepared by the action of anhydrous hydrogen fluoride on tetrakis(triphenyl phosphite) platinum(0), or by treating a methylene chloride solution of bis(triphenylphosphine)platinum(II) fluoride with triphenyl phosphite. In the latter method of preparation, the displacement of co-ordinated triphenylphosphine by triphenyl phosphite is analogous to the displacement reaction that occurs when tetrakis(triphenylphosphine)platinum(0) is treated with triphenyl phosphite.[5] As normally prepared, the phosphite complex is white, but a pink form can be obtained by heating a solution of the white form. It appears that formation of phosphine- and phosphite-platinum fluoride complexes of this type is a completely general reaction.

The platinum atom in both bis(triphenylphosphine)platinum(II) fluoride and bis(triphenyl phosphite)platinum(II) fluoride appears to be electronically unsaturated and adds two molecules of carbon monoxide under pressure to give the complexes $L_2Pt(CO)_2F_2$ (L denotes triphenylphosphine or triphenyl phosphite). Both carbonyl derivatives show three strong infrared peaks in the metal-carbonyl region. This pattern of peaks is different from that observed[10] for the complexes $L_2Fe(CO)_2X_2$, where L is triethylphosphine, diethylphenylphosphine, or diphenylethylphosphine and X is Cl^-, Br^-, I^-, or NCS^-, and stereochemistry of the present complexes is presumably different.

---

[4] A. G. Sharpe, *J.*, 1949, 2901.
[5] L. Malatesta and C. Cariello, *J.*, 1958, 2323.
[6] J. A. Chopoorian, J. Lewis, and R. S. Nyholm, *Nature*, 1961, **190**, 529.
[7] L. Malatesta and R. Ugo, *J.*, 1963, 2080.
[8] E. L. Muetterties and J. E. Castle, *J. Inorg. Nuclear Chem.*, 1961, **18**, 148.
[9] K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 225.
[10] G. Booth and J. Chatt, *J.*, 1962, 2099.

The stability of phosphine–(metal fluorides) seems to be confined to second- and third-row transition elements. Evidence has been found[11] for stable species for rhenium, ruthenium, iridium, and palladium, but it has not been possible to prepare fluorides of this type with first-row transition elements. Attempts to introduce fluorine into bis-(n-propylphosphine)nickel(II) chloride and bis(triphenylphosphine)nickel dicarbonyl have led to complete decomposition, with nickel fluoride as the only product.

EXPERIMENTAL

Tetrakis(triphenylphosphine)platinum(0) was prepared by the method of Malatesta and Cariello.[5]

Bis(triphenylphosphine)platinum(II) *Fluoride* $(Ph_3P)_2PtF_2$.—Tetrakis(triphenylphosphine)-platinum(0) was treated with anhydrous hydrogen fluoride either in a polythene bottle immersed in a bath at −78°, or in a stainless steel bomb, or by bubbling hydrogen fluoride through a solution in benzene. There was a rapid sequence of colour changes, the mixture eventually becoming colourless. Hydrogen fluoride was removed in a stream of dry air, and the white solid product was crystallised from methylene chloride by precipitation with diethyl ether (Found: C, 57·3; H, 3·9; Pt, 25·9. $C_{36}H_{30}P_2PtF_2$ requires C, 57·1; H, 4·0; Pt, 25·7%). Bis(triphenylphosphine)platinum(II) fluoride is insoluble in non-polar solvents, but is very soluble in chloroform, methylene chloride, and nitrobenzene. If a solution in a chlorine-containing solvent is kept for some hours the solvent becomes fluorinated and bis(triphenylphosphine)platinum(II) chloride is formed. When a solution of bis(triphenylphosphine)-platinum(II) fluoride in methylene chloride is warmed gently the solution becomes red and a pink solid may be obtained. On re-treatment with methylene chloride and diethyl ether the colourless form is recovered.

Bis(triphenyl phosphite)platinum(II) *Fluoride* $[(PhO)_3P]_2PtF_2$.—Tetrakis(triphenyl phosphite) platinum(0) was prepared from tetrakis(triphenylphosphine)platinum(0) as described by Malatesta and Cariello.[5] Tetrakis(triphenyl phosphite)platinum(0) was treated with hydrogen fluoride as described for the phosphine complex and the required bis(triphenyl phosphite)-platinum(II) fluoride was precipitated from a solution in methylene chloride by the addition of n-heptane. Alternatively, 0·25 g. of triphenyl phosphite in methylene chloride was added to 0·2 g. of bis(triphenylphosphine)platinum(II) fluoride in methylene chloride, the solution stirred at room temperature for 15 min., and then added to diethyl ether to give a white precipitate (Found: C, 52·7; H, 3·8; Pt, 22·7; P, 7·7; F, 5·0. $C_{36}H_{30}O_6P_2PtF_2$ requires C, 50·7; H, 3·5; Pt, 22·9; P, 7·3; F, 4·5%). The results for carbon were always high for this complex, but the values for other elements are satisfactory. The physical properties of the phosphite complex are similar to those of the phosphine complex. When a solution in methylene chloride is warmed, a pink form of the complex results.

Bis(triphenylphosphine)platinum(II) *Dicarbonyl Fluoride*, $(Ph_3P)_2Pt(CO)_2F_2$.—Bis(triphenylphosphine)platinum(II) fluoride (0·5 g.) was placed in a stainless-steel bomb and anhydrous hydrogen fluoride (5 ml.) added as solvent. A pressure of carbon monoxide was applied and the bomb was rocked overnight. Hydrogen fluoride was removed and the pale yellow residue was recrystallised from methylene chloride and diethyl ether (Found: C, 56·3; H, 4·0; Pt, 23·6. $C_{38}H_{30}O_2P_2PtF_2$ requires C, 56·0; H, 3·8; Pt, 24·0%). Carbon monoxide was evolved on treatment of the product with excess of pyridine; the residue after this reaction showed no carbonyl band in the infrared spectrum. 1 mole of complex gave 1·68 moles of carbon monoxide. This figure is not corrected for the solubility of carbon monoxide in the solvents used, and is taken to confirm that the complex is a dicarbonyl. The infrared spectrum showed bands at 2152, 2105, and 2083 cm.$^{-1}$.

Bis(triphenyl phosphite)platinum(II) *Dicarbonyl Fluoride*, $[(PhO)_3P]_2Pt(CO)_2F_2$.—The reaction was carried out as described for the phosphine complex. The residue was pale yellow, and was crystallised from methylene chloride–n-heptane (Found: C, 51·0; H, 4·0; P, 7·8; F, 4·7. $C_{38}H_{30}O_8P_2PtF_2$ requires C, 50·2; H, 3·3; P, 7·1; F, 4·2%). The infrared spectrum showed the same pattern as was observed for the phosphine complex. Carbonyl peaks were found at 2179, 2127, and 2092 cm.$^{-1}$.

Bis(tri-n-propylphosphine)nickel(II) chloride was prepared from tri-n-propylphosphine and

---

[11] J. McAvoy, K. C. Moss, and D. W. A. Sharp, unpublished observations.

nickel chloride.[12] A solution in methanol was treated with silver(I) fluoride. The only solid products identified were silver(I) chloride and nickel(II) fluoride—these compounds were identified by *X*-ray powder photography. Passage of anhydrous hydrogen fluoride through solutions of bis(tri-n-propylphosphine)nickel(II) chloride in diethyl ether, tetrahydrofuran, and chloroform gave only nickel fluoride. Reduction of a solution of bis(tri-n-propylphosphine)-nickel(II) chloride in tetrahydrofuran gives a hydride species.[13] Passage of hydrogen fluoride through a such a solution gave only nickel fluoride. Bis(triphenylphosphine)nickel dicarbonyl [14] was prepared by the action of triphenylphosphine on nickel carbonyl. Passage of hydrogen fluoride through solutions of bis(triphenylphosphine)nickel dicarbonyl dissolved in tetrahydrofuran and chloroform gave only nickel(II) fluoride.

Tetrakis(triphenylphosphine)platinum(0) was dissolved in carbon tetrachloride and varying concentrations were allowed to stand for periods of time ranging up to 24 hr. The solution was examined by vapour-phase chromatography but chloroform was not detected. A white precipitate that slowly formed was identified as bis(triphenylphosphine)platinum(II) chloride. A solution of tetrakis(triphenylphosphine)platinum(0) was examined by nuclear magnetic resonance spectroscopy. There was no signal that could be attributed to protons bonded to a metal.

Infrared spectra were recorded as Nujol mulls on a Grubb–Parsons DB-1/S4 spectrometer.

This work was supported in part by the U.S. Navy through the London Office of Naval Research. We thank the D.S.I.R. for a maintenance award (to J. McA.), the Chemical Society for a grant from the Research Fund, and the International Nickel Corporation and Messrs. Johnson Matthey for the loan of platinum compounds. Some preliminary work on the reactions of nickel complexes was carried out by Dr. R. D. W. Kemmitt; we acknowledge helpful discussions on the nature of the tetra(ligand)platinum derivatives with Professor J. Lewis.

CHEMISTRY DEPARTMENT, UNIVERSITY OF STRATHCLYDE,
GLASGOW C.1.

[*Received, August 10th*, 1964.]

---

[12] W. C. Davies and W. J. Jones, *J.*, 1929, 33; W. C. Davies, P. L. Pearse, and W. J. Jones, *J.*, 1929, 1262.

[13] M. L. H. Green, C. Street, and G. Wilkinson, *Z. Naturforsch.*, 1959, **14***b*, 738.

[14] V. W. Reppe and W. J. Schweckendiek, *Annalen*, 1948, **560**, 104.