

Reactions of Pentafluorosulphur Chloride and Hydrogen Fluoride with Low Valent Complexes of Some Group VIII Elements: the Preparation of $\text{PtCl}(\text{SF}_5)(\text{PPh}_3)_2$

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Summary The first metal-pentafluorosulphur(vi) complex, $\text{PtCl}(\text{SF}_5)(\text{PPh}_3)_2$ has been synthesised, and reactions of pentafluorosulphur chloride and hydrogen fluoride with some complexes of rhodium, iridium, and platinum are described.

ALTHOUGH non-metal derivatives of the pentafluorosulphur(vi) group are well known,¹ metal complexes containing metal-SF₅ bonds have not been reported.

We now find that pentafluorosulphur(vi) chloride reacts with *trans*-stilbenebistriphenylphosphineplatinum(0) in benzene solution to give a high yield of chloropentafluorosulphurbistriphenylphosphineplatinum(II) $\text{PtCl}(\text{SF}_5)(\text{PPh}_3)_2$, (I), m.p. 221–225°. The i.r. spectrum of (I) shows a band characteristic of a pentafluorosulphur group at 891 cm.⁻¹ and a band due to $\nu(\text{Pt}-\text{Cl})$ at 316 cm.⁻¹. The complex (I) is an orange solid which is stable in dry air. It is insoluble in benzene and alcohols but dissolves with decomposition in both methylene chloride and acetone, from which the platinum(IV) complex, $\text{PtCl}_2\text{F}_2(\text{PPh}_3)_2$, (II) may be isolated.

The ready decomposition of (I) in solution has precluded molecular-weight determination, but we formulate the complex as a monomer.

The i.r. spectrum (400–200 cm.⁻¹) of (II) exhibits two very strong bands at 318 and 294 cm.⁻¹. The reaction of

SF₅Cl with *trans*-PtClH(PPh₃)₂ gives only an isomer of (II), which exhibits only one strong band at 341 cm.⁻¹ in this region.

Mixed chloro-fluoro-complexes of platinum are rare.² The complex PtClF(PEt₃)₂ has been previously isolated as a by-product from the reaction of trifluoroethylene with *trans*-PtClH(PEt₃)₂,³ but we find that mixed fluoro-halogeno-complexes of this type, e.g. PtXF(PPh₃)₂, are readily formed by reaction of liquid hydrogen fluoride with halide complexes such as PtX₂(PPh₃)₂ or PtXH(PPh₃)₂, (X = Cl or Br). (The displacement of chloride and bromide by anhydrous hydrogen fluoride should be contrasted with the inability of fluoride to displace halide, (Cl, Br, or I) from platinum(IV) in aqueous solution).⁴ The reaction of anhydrous hydrogen fluoride with Pt(PPh₃)₄ has also been shown to give a platinum(II) fluoride complex, PtF₂(PPh₃)₂.⁵

So far we have been unable to isolate metal-SF₅ complexes from reactions of SF₅Cl with the complexes, *trans*-MCl(CO)(PPh₃)₂, (M = Rh or Ir). Only chloride-fluoride complexes, MCl₂F(CO)(PPh₃)₂ are formed.

Previous studies of the reactions of SF₅Cl with Ni(CO)₄ and Fe(CO)₅ have also yielded materials which contain both chlorine and fluorine.⁶

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