Fluorocarbon Platinum Complexes

By M. GREEN, R. B. L. OSBORN, A. J. REST, and F. G. A. STONE
(*Department of Inorganic Chemistry, The University, Bristol,* 8.)

FLUORO-OLEFIN complexes of rhodium,[1,2] nickel[2] and iridium[2] have recently been described; however, the nature of the bonding is not clearly understood. Herein are described some platinum–fluoro-olefin and –hexafluoroacetone complexes.

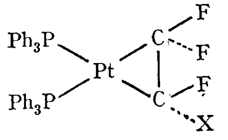
A general reaction occurs between tetrakis(triphenylphosphine)platinum and fluoro-olefins in benzene to afford colourless crystalline complexes of molecular formula $(Ph_3P)_2Pt$(fluoro-olefin). This reaction is analogous to the reaction between

$(Ph_3P)_4Pt$ with tetracyanoethylene[3] or perfluoroalkyl iodides[4] affording $(Ph_3P)_2Pt[C_2(CN)_4]$ or $(Ph_3P)_2Pt(R)_FI$, respectively.

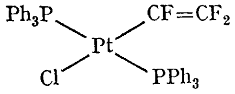
Two important points emerge from the fluorine-19 n.m.r. spectra of the complexes $(Ph_3P)_2Pt$-(fluoro-olefin). The spectrum of the hexafluoropropene complex (I; $X=CF_3$), m.p. 176—180° decomp., which has four groups of bands centred at 66·5, 107·1, 120·2, and 200 p.p.m.* (with relative integrated intensities of 3 : 1 : 1 : 1), shows a geminal F,F coupling constant of 200 c./sec. This value is of the order observed in saturated fluorocarbon systems suggesting that the perfluoropropene moiety is σ-bonded to the metal. The spectrum of complex (I; $X=F$), m.p. 218—220° decomp., shows the *X*-spectrum of an $AA'X_2X'_2$ system centred at 131·1 p.p.m. ($J(^{195}Pt-^{19}F) = 288$ c./sec., $J(^{31}P-^{19}F) = 39$ c./sec., $J(^{31}P'-^{19}F) = 29$ c./sec., and $J(^{19}F-^{19}F') = 2·5$ c./sec.,) which is field and temperature invariant. These observations are consistent with the rigid square-planar σ-bonded three-membered ring system depicted. These complexes do not show any infrared absorption corresponding to a co-ordinated double bond.

The adduct (I; $X=Cl$), m.p. 206—208° decomp., undergoes a novel molecular rearrangement on heating, just below its melting point, to afford the vinyl complex (II). The structure of (II) is assigned on the basis of its fluorine-19 n.m.r. spectrum,[5] and by the presence of a strong double-bond absorption at 1734 cm.$^{-1}$ in its infrared spectrum, which is absent in (I; $X=Cl$). This new type of rearrangement involves chlorine atom migration on to platinum to give *cis*-$(Ph_3P)_2Pt(CF{:}CF_2)Cl$, which rearranges to the observed *trans*-complex.

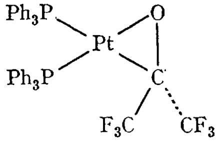
As part of a general study of the ability of hexafluoroacetone to act as a ligand towards transition metals we have found that tetrakis(triphenylphosphine)platinum reacts rapidly with hexafluoroacetone in benzene to give triphenylphosphine, and a crystalline complex $(Ph_3P)_2Pt[(CF_3)_2CO]$ (III).



(I)



(II)



(III)

The infrared spectrum of the complex showed no bands assignable to a carbonyl group π-bonded onto the metal, and the fluorine-19 spectrum showed a triplet of doublets centred at 67·8 p.p.m. with $J(^{195}Pt-^{19}F) = 71·5$ c./sec., $J(^{31}P-^{19}F) = 11·6$ c./sec., and $J(^{31}P'-^{19}F) = 1$ c./sec., which supports the illustrated structure (III). This new kind of complex is of interest in that it contains a three-membered ring involving a platinum-to-oxygen σ-bond.

(*Received, June 24th,* 1966; *Com.* 429.)

---

* Relative to CCl_3F(0·0 p.p.m.), increasing to high field.

[1] M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 1965, 6629.

[2] R. Cramer and G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 1392; G. W. Parshall and F. N. Jones, *ibid.*, p. 5356.

[3] W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, 1966, **5**, 33.

[4] D. T. Rosevear and F. G. A. Stone, to be published.

[5] A. J. Rest, D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1966, in the press.