Trispentafluorophenylphosphine Complexes of Rhodium, Palladium, and Platinum

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RECENT crystallographic studies have shown that in some phenylphosphine complexes of transition metals there is interaction between an *ortho*-hydrogen of the phenyl ring and the metal atom.[1,2] This observation has led us to study metal complexes of trispentafluorophenylphosphine, since the ^{19}F n.m.r. spectra of these compounds might indicate if there is a similar interaction between the *ortho*-fluorines and the metal.

Trispentafluorophenylphosphine is a very weak base; thus we find there is no protonation in concentrated sulphuric acid and complex formation does not occur with boron trifluoride even at $-78°$.

Reaction of $(C_6F_5)_3P$ (abbreviated P_F) with hydrated rhodium trichloride in refluxing ethanol gives a green crystalline solid in high yield after a few hours. This is diamagnetic ($\mu = 0 \pm 0{\cdot}3$ B.M.

at 25°) and its formula has been shown by analysis and molecular weight to be $(P_F)_4Rh_2Cl_2$, a chlorine-bridged complex of rhodium(I). The green solid has also been prepared quantitatively from P_F and tetrakis(ethylene)-$\mu\mu'$-dichlorodirhodium(I).

The phosphine ligands are easily displaced. Reaction with cyclo-octa-1,5-diene gives the bis(cyclo-octa-1,5-diene)-$\mu\mu'$-dichlorodirhodium(I), and triphenylphosphine and triphenyl phosphite give the complexes L_3RhCl [L = Ph_3P, or $(PhO)_3P$]. However, carbon monoxide gives $(P_F)_2RhCOCl$. None of these reactions is reversible.

The complex $(P_F)_2RhCOCl$ has also been prepared from P_F and $RhCl_3,xH_2O$ in refluxing β-methoxyethanol. It has one carbonyl frequency at 2004 cm.$^{-1}$ (Nujol mull), some 50 cm.$^{-1}$ higher than that observed for $(Ph_3P)_2RhCOCl$.

Liquid chlorine oxidizes $(P_F)_2RhCOCl$ to $(P_F)_2RhCOCl_3$ and $(P_F)_4Rh_2Cl_2$ to $(P_F)_4Rh_2Cl_6$. These rhodium(III) complexes are unstable in solution.

Addition of an aqueous solution of potassium tetrachloroplatinate(II) to a hot ethanolic solution of P_F gives the yellow complex $(P_F)_2PtCl_2$. The complexes $(P_F)_2MX_2$ (M = Pd or Pt; X = Cl or Br) are similarly prepared. P_F and platinous iodide in xylene gives $(P_F)_2PtI_2$. The infrared spectra (400—200 cm.$^{-1}$) of the chloride and bromide complexes exhibit only one metal halogen stretch (Table) and hence they presumably have the *trans*-configuration.

The ^{19}F n.m.r. spectra of the complexes $(P_F)_2MCl_2$ and $(P_F)_2RhCOCl$ give patterns similar to those observed for the free phosphine (Table). However, there is considerable broadening of the *ortho*-fluorine absorption in the complexes $(P_F)_2MX_2$ (M = Pd; X = Br; M = Pt; X = Br or I). On cooling a chloroform solution of the complex $(P_F)_2PtI_2$ to −20°, the *ortho*-signal sharpens and three equally spaced bands of the same intensity are observed, indicating three pairs of nonequivalent atoms (Table). The *meta*- and *para*-signals remain unchanged. At −20° the *ortho*-fluorine absorption of $(P_F)_2PtBr_2$ similarly shows three bands of equal intensity but not now equally spaced. In $(P_F)_2PtCl_2$ at −40° the two high-field *ortho*-fluorine bands merge and two peaks are observed with intensity ratio 1 : 2.

TABLE

	I.r.	^{19}F n.m.r.[a]			
	ν(M–X) cm.$^{-1}$	*ortho*	*para*	*meta*	°C
$(P_F)_2PtCl_2$	351	62·3	79·9	95·1	35°
		57·6, 66·3	79·5	94·6	−40°
$(P_F)_2PtBr_2$	255	broad	80·2	95·2	35°
		54·6, 62·9, 67·0	80·2	95·1	−20°
$(P_F)_2PtI_2$	—	broad	80·3	95·5	35°
		53·4, 60·5, 67·3	80·7	95·2	−20°
$(P_F)_2PdCl_2$	365	62·3	79·9	95·0	35°
$(P_F)_2PdBr_2$	275	broad	80·0	94·9	35°
$(P_F)_2RhCOCl$	—	62·9	81·7	95·2	35°
P_F[b]	—	67·2	85·3	97·0	—

[a] $CHCl_3$ solutions; chemical shifts in p.p.m. upfield from benzotrifluoride (internal standard) measured at 19·3 Mc./sec. The *ortho*-, *meta*-, and *para*-fluorines are always in the expected ratio 2 : 2 : 1.

[b] H. J. Emeléus and J. M. Miller, *J. Inorg. Nuclear Chem.*, 1966, **28**, 662.

These observations may be tentatively interpreted as follows. When the C_6F_5 rings rotate and the phosphine also rotates about the phosphorus to platinum bond there is equivalence of all the *ortho*-fluorines as is observed in the n.m.r. of the chloride complex at 35°. If there is no rotation about the (P–Pt) bond but the rings are still rotating one ring of the phosphine becomes nonequivalent and a 4 : 2 *ortho*-fluorine pattern results. This is observed for the chloride at −40°. If the rings and the phosphine are both stationary, three pairs of nonequivalent fluorine atoms result giving the 2 : 2 : 2 *ortho*-pattern observed in the bromide and iodide complexes at −20°. (The 4 : 2 chloride pattern could be the 2 : 2 : 2 pattern with the two bands superimposed.) The spectrum of the iodide complex on warming from −20° to 35° shows no intermediate 4 : 2 *ortho*-pattern and we attribute this to the simultaneous onset of rotation of the phosphine and the rings. The greater hindrance to rotation of the C_6F_5 rings in the bromide and iodide complexes as compared to the chloride complex is in agreement with molecular models which indicate *ortho*-fluorine steric interactions with the halogen atom. The metal itself must have some influence on the relative chemical shifts of the *ortho*-fluorines but it is not possible as yet to comment on the presence of either repulsive or attractive forces between the *ortho*-fluorine atoms and the metal.

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[1] N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1965, 237; 296.

[2] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.