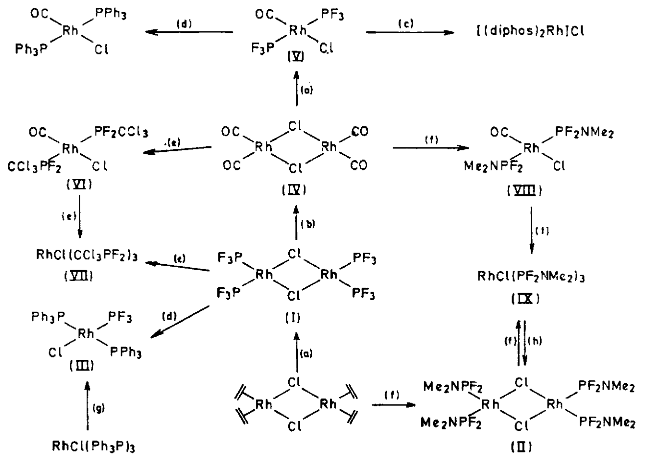
Synthesis and Ligand Exchange Studies of Fluorophosphine–Rhodium Complexes

By D. A. CLEMENT, J. F. NIXON,* and M. D. SEXTON
(*Chemical Laboratory, University of Sussex, Brighton* BN1 9QJ)

Summary Convenient syntheses and interconversions of fluorophosphine complexes of rhodium of the type (a) $L_2RhCOCl$, (b) L_3RhCl, (c) $[L_2RhCl]_2$, and (d) $L(Ph_3P)_2RhCl$ [L = fluorophosphine] are described: ^{19}F n.m.r. studies establish the *trans*-stereochemistry of (a) and (d) and in the latter case provide evidence for exchange of both types of phosphine co-ordinated to the metal.

HIGH pressure syntheses of trifluorophosphine complexes of rhodium, *e.g.* $HRh(PF_3)_4$ and $MRh(PF_3)_4$ have been reported by Kruck.[1] We now describe alternative synthetic routes to fluorophosphine–rhodium complexes under much milder conditions using metal–carbonyl or metal–olefin precursors and report n.m.r. studies which indicate exchange between co-ordinated and unco-ordinated phosphine ligands.

The reaction between trifluorophosphine and the ethylene–rhodium complex[2] $[(C_2H_4)_2RhCl]_2$ at 60° readily affords high yields of the dark red, vacuum sublimable dimer $[RhCl(PF_3)_2]_2$, (I)† which was previously obtained only in very small yield by the high-pressure reaction between $RhCl_3$ and PF_3 in the presence of copper. Yellow needles of the dimeric $[RhCl(Me_2NPF_2)_2]_2$ complex (II) are also readily obtained by this route (see Scheme).



SCHEME. (a) = an excess of PF_3; (b) = CO; (c) = diphos; (d) = Ph_3P; (e) = CCl_3PF_2; (f) = Me_2NPF_2; (g) = PF_3; (h) = heat *in vacuo*.

Treatment of (I) with an excess of trifluorophosphine does not cause bridge cleavage, and all four PF_3 groups may be replaced by carbon monoxide affording the well-known $[Rh(CO)_2Cl]_2$ complex (IV).[3] However, (I) does react with triphenylphosphine to give yellow crystals of *trans*-$RhCl(Ph_3P)_2PF_3$ (III) which is also easily made from $(PhP_3)_3RhCl$ and PF_3.[4] Similarly, the PF_3 groups are completely displaced from (I) by treatment with difluorotrichloromethylphosphine to give $RhCl(CCl_3PF_2)_3$ (VII).

Significant differences are observed in the behaviour of trifluorophosphine and the other fluorophosphines (*e.g.* R_2NPF_2 and CCl_3PF_2; R = Me or Et, $R_2 = C_5H_{10}$) towards (IV). An excess of PF_3 fails to completely displace carbon monoxide and the volatile, bright red crystalline complex *trans*-$RhCl(PF_3)_2CO$ (V) is formed almost quantitatively, whereas dialkylamino- and trichloromethyl difluorophosphines and (IV) afford either the yellow-brown carbonyl-fluorophosphine complexes *trans*-$RhCl(RPF_2)_2CO$ (IV) and (VIII) or the yellow-brown trisfluorophosphine complexes $RhCl(RPF_2)_3$ (VII) and (IX) depending on the amount of fluorophosphine used.

The *trans*-configuration of complexes (III), (V), (VI), and (VIII) was established by ^{19}F n.m.r. studies. (V) is an example of an $[X_3A]_2$ spin system (X = fluorine; A = phosphorus), while both (VI) and (VIII) are $[X_2A]_2$ spin systems. Analysis of the spectra is facilitated because $^1J_{PF} \gg {}^2J_{(PMP')}$, (see ref. 5 for a fuller discussion), and the resulting $^2J_{(PMP')}$ values (V) (62 Hz); (VI) (52 Hz), and (VIII) (49 Hz) are of interest because they are an order of magnitude smaller than values found in analogous *trans*-square planar platinum(II) phosphine complexes.[5] Furthermore, the magnitude of $^2J_{(PMP')}$ in the dialkylaminodifluorophosphine derivatives indicates that phosphorus rather than nitrogen is the donor atom.

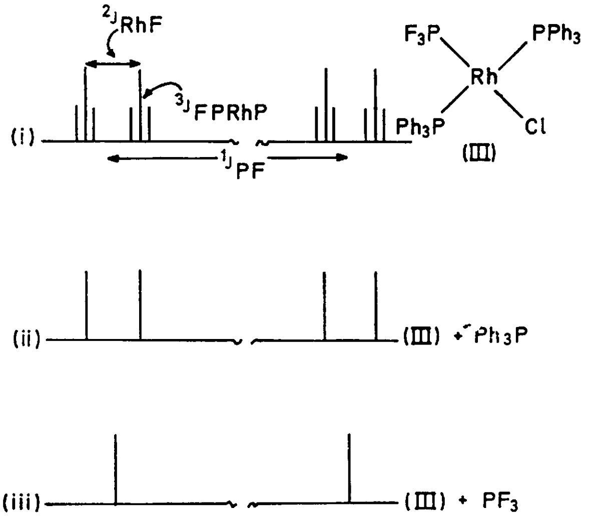


FIGURE. *Line diagram showing effect on* ^{19}F *n.m.r. spectrum of* (III) *of adding small amounts of* Ph_3P *and* PF_3.

The ^{19}F spectrum of a very carefully purified sample of (III) in benzene consists of a widely spaced doublet (coupling with phosphorus, $^1J_{PF}$ 1286 Hz) each line of which is split further into a doublet (coupling with ^{103}Rh, $^2J_{RhF}$ 32 Hz) of triplets (coupling with two equivalent phosphorus nuclei of the Ph_3P groups, $^3J_{FP}$ 7 Hz) (see Figure). Addition of

---

† The norbornadiene rhodium complex $[C_7H_8RhCl]_2$ may also be used, and Dr. M. A. Bennett (personal communication) has independently carried out the same reaction with the cyclo-octene complex $RhCl(C_8H_{14})_2$ (see following communication.)

small amounts of Ph_3P immediately leads to a collapse of the triplet pattern as free and co-ordinated Ph_3P molecules undergo exchange, but the doublet pattern due to ^{19}F–^{103}Rh is preserved (ii).

When a pressure of PF_3 is maintained above the solution of (III) the spectrum changes to a simple doublet (iii) indicating loss of ^{103}Rh–^{19}F coupling as the co-ordinated and unco-ordinated PF_3 groups undergo exchange. The fluorine chemical shift of the complex, (+ 15·4 p.p.m. ref. CCl_3F), is as expected[6,7] significantly to low-field of the free ligand. These results are of interest in connection with other exchange studies on the related $RhCl(CO)(Ph_3P)_2$ complex.[8,9]

We thank the S.R.C. for financial support for D.A.C. and M-D.S.

(*Received, October 28th,* 1969; *Com.* 1636.)

[1] T. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.
[2] R. Cramer, *Inorg. Chem.*, 1962, **1**, 722.
[3] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 211.
[4] M. A. Bennett and D. Milner, *Chem. Comm.*, 1967, 581.
[5] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.
[6] C. G. Barlow and J. F. Nixon, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 323.
[7] J. F. Nixon, *J. Chem. Soc.* (*A*), 1967, 1136.
[8] H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.*, 1960, 358.
[9] A. Wojcicki and F. Basolo, *J. Amer. Chem. Soc.*, 1961, **83**, 525.