Low Pressure Synthesis of Trifluorophosphine Complexes of Rhodium and Iridium

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Summary A convenient low-pressure synthesis of trifluorophosphine complexes of rhodium and iridium is described, and their reactions and structures are discussed.

TRIFLUOROPHOSPHINE complexes of rhodium and iridium, such as $IrI(PF_3)_4$, $MH(PF_3)_4$, and $[M(PF_3)_4]^-$ (M = Rh or Ir), have been prepared previously by heating the metal halide and a reducing agent with PF_3 at pressures of up to 250 atm.[1–4] The ready displacement of olefins such as ethylene, cyclo-octene, or cyclo-octa-1,5-diene from their rhodium(I) and iridium(I) complexes by tertiary phosphines and arsines provides a general method for the preparation of complexes of the type $MCl(ligand)_3$,[5–8] and we now report a convenient synthesis of PF_3 complexes by a similar route.

Reaction of PF_3 at 25°:1 atm. with the cyclo-octene complex $RhCl(C_8H_{14})_2$[9] gives an 80% yield of crystalline, moderately air-stable $[RhCl(PF_3)_2]_2$,† which is readily sublimable *in vacuo* and shows a parent ion peak in its mass spectrum. The ^{19}F n.m.r. spectrum consists of two piars of doublets each surrounded by complex multiplets, centred at $\delta + 16{\cdot}25$ p.p.m. relative to internal $CFCl_3$. The doublet separation due to P–F coupling is 1300 Hz, which is of the order observed in other PF_3 complexes,[10] and J(Rh–F) is 32 Hz. Kruck's high pressure synthesis[1] gives an inseparable mixture of $Rh_2(PF_3)_8$ and $[RhCl(PF_3)_2]_2$, and passage of PF_3 (1 atm.) over a heated mixture of $RhCl_3$ and Cu powder gives $[RhCl(PF_3)_2]_2$ in only 2·6% yield.

Treatment of $IrCl(C_8H_{14})_2$[11] with PF_3 gives initially an unstable, pale yellow, low-melting crystalline solid, probably $IrCl(C_8H_{14})(PF_3)_2$. Attempted sublimation of this complex *in vacuo* causes loss of cyclo-octene and the formation of crystalline, volatile, exceedingly air-sensitive $IrCl(PF_3)_2$, which appears bronze by reflected light and dark blue when finely divided. The complex dissolves in n-pentane giving an orange solution, and the ν(P–F) bands in the i.r. spectrum are similar in pattern to those of the rhodium compound (see Table).

TABLE[a]

Selected PF_3 *complexes of* Rh *and* Ir

Compound	Colour	M.p.[b]	ν(P–F) (n-hexane)
$[RhCl(PF_3)_2]_2$	Dark Red	55–57°	944m, 926m, 917s, 906s, 875s, 860wsh.
$Hg[Rh(PF_3)_4]_2$	White	97—99°	907vs, 875m, 858wsh, 850s.
$Ph_3SnRh(PF_3)_4$	White	85° (decomp.)	930s, 905s, 877s, 845s.
$[IrCl(PF_3)_2]_n$	Bronze (see text)	76—78°	955m, 932s, 923m, 910vs, 877s.
$Hg[Ir(PF_3)_4]_2$	White	100—102°	924s, 917m, 885s, 875wsh, 861s.
$Ph_3SnIr(PF_3)_4$	White	113—114°	942s, 917s, 886sbr, 842vs.

[a] All compounds in the Table and Chart gave satisfactory elemental analyses.

[b] Sealed tube under nitrogen; uncorrected.

Both complexes react with typical bridge-splitting reagents such as Tl(acac), TlC_5H_5, Cl^-, and PPh_3 to give the expected mononuclear species (see Chart). The structure of the rhodium complex in the solid state is probably

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† This complex has been obtained independently by Dr. J. F. Nixon by treating the norbornadiene complex $[RhCl(C_7H_8)]_2$ with PF_3 (personal communication).

similar to that of $[RhCl(CO)_2]_2$[12] *i.e.* containing a non-planar halogen bridge and intermolecular Rh–Rh bonds. The iridium complex is dimeric in the vapour phase, as shown by the appearance of the parent ion at the highest *m/e* in the mass spectrum, and the solubility properties suggest that the dimeric structure is retained in solution; in the solid state, however, there are probably chains of metal atoms and possibly bridging chlorine atoms [*cf.* $IrCl(CO)_3$].[13]. The high solubility and volatility of $[IrCl(PF_3)_2]_n$ compared with $[IrCl(CO)_3]_n$ may indicate weaker Ir–Ir bonding in the PF_3 complex. In this connection, it is interesting to compare the complexes $M(CO)_2$(acac) and $M(PF_3)_2$(acac)(M = Rh or Ir); the carbonyl complexes show different colours by reflected and transmitted light and have metal–metal interactions in the solid state,[14–17] but are yellow and monomeric in solution; the PF_3 complexes are yellow-orange both by reflected and transmitted light in the solid state and in solution. Intermolecular repulsions between PF_3 groups may be responsible for this difference, and also for the failure to isolate $IrCl(PF_3)_3$.

The complex $[RhCl(PF_3)_2]_2$ is readily reduced by potassium amalgam in the presence of an excess of PF_3 to give initially the metal–metal bonded complex $Hg[Rh(PF_3)_4]_2$ as pentane-soluble crystals, and finally the potassium salt $K[Rh(PF_3)_4]$[1–3] in about 60% yield. A similar sequence of reactions occurs when $IrCl(C_8H_{14})(PF_3)_2$ is reduced under the same conditions. Preliminary studies indicate that this simple preparation of the $[M(PF_3)_4]^-$ anions provides a route to a range of new organometallic derivatives; thus reaction of $K[Ir(PF_3)_4]$ with Ph_3SnCl gives the five-co-ordinate complex $Ph_3SnIr(PF_3)_4$.

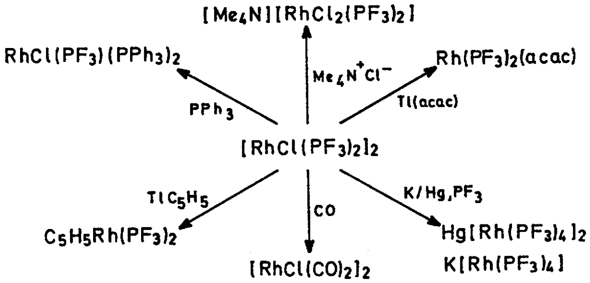

CHART. *Reactions of* $[RhCl(PF_3)_2]_2$[a].

[a] Similar reactions occur with the iridium complex.

We thank Johnson-Matthey Co. for the loan of rhodium and iridium and the National Research Council of Canada for a Fellowship (to D.J.P.).

(*Received, October 28th,* 1969; *Com.* 1637.)

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