Chemistry of Transition-metal Vapours. Part I. Reactions with Trifluorophosphine and Related Compounds

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The known complexes $Cr(PF_3)_6$, $Fe(PF_3)_5$, $Co_2(PF_3)_8$, $Ni(PF_3)_4$, and $Pd(PF_3)_4$ have been formed by condensation of the corresponding metal vapours with trifluorophosphine at $-196°$. The compound $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$ was also formed in the reaction of iron with trifluorophosphine. Neither manganese nor copper gave volatile products with trifluorophosphine. Condensation of nickel vapour with chlorodifluorophosphine formed $Ni(PF_2Cl)_4$ and condensation of nickel vapour with a mixture of phosphine and trifluorophosphine formed the new compounds $Ni(PF_3)_3PH_3$ and $Ni(PF_3)_2(PH_3)_2$.

THE synthetic chemistry of gaseous atomic and molecular species stable only at high temperatures can be conveniently studied by condensation of the species with volatile reactants at very low temperatures, as shown by the work of Skell on carbon vapour.[1] Subsequently, the technique has been applied to a variety of species [2] and, most recently, to transition-metal vapours.[3,4]

In the present work, vapours of the first-row transition metals chromium–copper and palladium, have been condensed with trifluorophosphine at $-196°$ in an attempt to synthesise zero-valent trifluorophosphine complexes and related compounds. It was hoped that this procedure would provide a convenient alternative to the use of high-pressure equipment in many conventional preparations of trifluorophosphine complexes.[5]

EXPERIMENTAL

The apparatus used is shown in the Figure. Metals were evaporated from crucibles similar to those described by Olsen *et al.*[6] The crucibles were made by coatings of alumina cement being baked on a conical spiral of *ca.* 1·2 mm. diam. molybdenum wire and were insulated by a molybdenum radiation shield. The crucibles could hold *ca.* 0·7 ml. of molten metal. By passage of a current of 22 amp at 9 v through the wire the crucibles were heated to *ca.* 1800° but the power was adjusted for each metal to cause evaporation of 1—2 g. in 30 min. The crucibles were contained in an open-top water-cooled copper box to minimise the amount of heat radiated to the liquid nitrogen cooled walls of the vacuum chamber.

With the exception of iron, each of the metals evaporated was of greater than 99·8% purity. Pure iron (99·9%) was tried but mild steel containing 0·5% carbon was found to evaporate much faster as the surface of the molten metal remained free of an alumina-rich dross. Sublimation of

chromium was accompanied by slight attack on the alumina and formation of chromium oxides and lower aluminium oxides, but none of the other metals reduced the alumina.

Before a metal was vaporised the apparatus was pumped down to a pressure below 5×10^{-6} Torr. The main part of
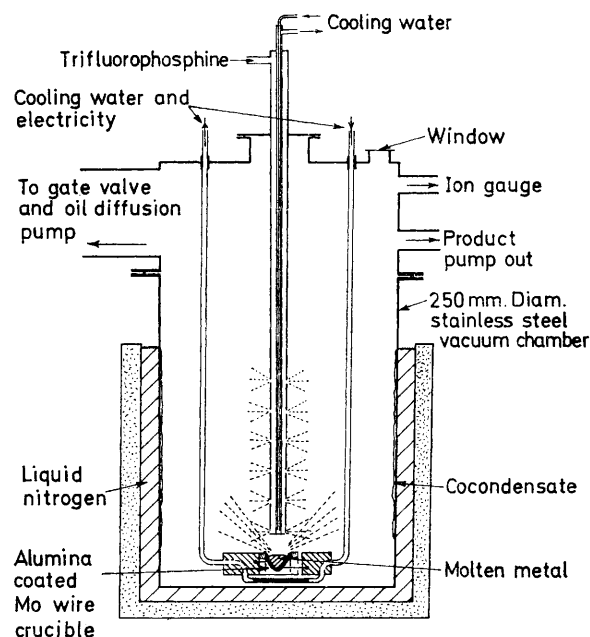
the vacuum chamber was then immersed in liquid nitrogen and evaporation of the metal commenced. Simultaneously, gaseous trifluorophosphine (99% pure) was bled into the vacuum chamber from a gas burette at a rate sufficient to give at least an 8 : 1 mole ratio of PF_3 : metal on the cold surface. The pressure rose to *ca.* 5×10^{-5} Torr when

[1] P. S. Skell and L. D. Westcott, *J. Amer. Chem. Soc.*, 1963, **85**, 1023.
[2] P. L. Timms, *Endeavour*, 1968, **27**, 133.
[3] P. L. Timms, *Chem. Comm.*, 1969, 1033.
[4] P. L. Timms, *Chem. Comm.*, 1968, 1525.
[5] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.
[6] L. O. Olsen, C. S. Smith, and E. C. Crittenden, *J. Appl. Phys.*, 1945, **16**, 425.

trifluorophosphine was admitted. If the metal ceased to evaporate while trifluorophosphine was being added, the pressure rose to at least 1.5×10^{-4} Torr showing that the metal vapour had a marked gettering action.

When 1—2 g. of metal had evaporated, the crucible was allowed to cool and the liquid nitrogen was removed from around the vacuum chamber. Volatile products were pumped out and handled in a glass vacuum line fitted with greaseless Viton O-ring stopcocks. Prolonged pumping was required to remove some of the less volatile trifluorophosphine–metal compounds from the vacuum chamber. It was very difficult to collect the solid, involatile residues left in a thin layer on the walls of the vacuum chamber, without them being exposed to air.

Products of sufficient volatility and stability were first characterised by use of an AEI MS10c2 mass spectrometer with a modified inlet system. ^{1}H N.m.r. spectra were run on Varian A-60 or HA-100 spectrometers, and ^{19}F n.m.r. spectra on the HA-100 or on a Perkin-Elmer R10 spectrometer. I.r. spectra (cm.$^{-1}$) were taken on a Perkin-Elmer 257 spectrometer. For the new compounds these were as follows:

$Ni(PF_3)_3PH_3$: 6 cm. gas cell; 2358m, 2218w, 1026s, 921vs, 870sh, and 850vs.

$Ni(PF_3)_2(PH_3)_2$: (a) gas cell; 2355m, 2218w, 1040m, 1012s, 889vs, and 839vs; (b) solid film at $-196°$; 2363m, 2223w, 1030m, 997s, 876s, 820vs, and 810sh.

$(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$; liquid film at 35°; 927s, 922s, 909m,sh, 890m,sh, 870m, and 857m.

Determination of the Yields of Products.—The weight of metal evaporated was found by weighing the crucible and contents before and after each experiment. The volatile products were collected and weighed and the yields given in the Results section were calculated from these two weights. However, only about 75% of the metal evaporated under high-vacuum conditions condensed on the liquid nitrogen cooled portions of the vacuum chamber, the rest condensed on internal fittings and the walls of the vacuum chamber above the liquid nitrogen level. When trifluorophosphine was sprayed into the system gas-phase intermolecular collisions undoubtedly reduced the amount of metal which condensed above the liquid nitrogen level although 15—20% was still wasted.

RESULTS

Reactions with Trifluorophosphine.—*Chromium.* The material first pumped out of the vacuum chamber was a bright blue crystalline product. This blue colour was transitory and disappeared as the material was pumped around the vacuum system to give colourless crystals, which from their mass and i.r. spectra were shown to be pure $Cr(PF_3)_6$ (8·1 g., 60%) as described by Kruck.[7]

Manganese. When trifluorophosphine and manganese vapour were condensed together at $-196°$, the pressure in the vacuum chamber was *ca.* 2×10^{-4} Torr which indicates little or no gettering action by the manganese vapour. No volatile product was obtained when the condensate was warmed although a small amount of trifluorophosphine could not be recovered even with prolonged pumping.

Iron. Two volatile products were isolated. The more volatile was obtained as faintly yellow crystals, m.p. 44°. These were identified from their mass and i.r. spectra as

$Fe(PF_3)_5$ as first made by Kruck and Prasch.[8] About 25% of the iron evaporated was recovered as this compound.

The less volatile compound formed bright red crystals [3] with a Fe:P:F ratio of 1:3·96:10·92 indicating an empirical formula FeP_4F_{11}. In the mass spectrum of the compound, the ion of highest m/e was at 778 corresponding to $[Fe_2P_8F_{22}]^+$. Prominent ions in the spectrum corresponded to loss of successive PF_3 groups down to a very abundant ion at m/e 250, $[Fe_2P_2F_4]^+$. This combined evidence showed the molecular formula was $Fe_2P_8F_{22}$ and indicated the structure $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$ analogous to $(PF_3)_3Co(PF_2)_2Co(PF_3)_3$ reported by Kruck and Lang.[9] The ^{19}F n.m.r. spectrum showed three doublets centred at δ $-0·7$, $+30·6$, and $+36·7$ p.p.m. relative to CCl_3F, with area ratios 9:1:1, confirming the $^-PF_2^-$ bridged structure. The compound $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$ is very air sensitive. Under nitrogen it melts at 34° and is stable to 150°.

About 25% of the iron evaporated was recovered as $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$. The involatile residue left in the vacuum chamber could be decomposed by strong heat with evolution of trifluorophosphine and it was partially soluble in hexane.

Cobalt. About 50% of the cobalt evaporated was recovered in a violet, crystalline solid product of moderate volatility with a Co:PF_3 ratio of 1:4·10. The compound thus seemed identical to the solid $[Co(PF_3)_4]_x$ reported by Kruck and Lang.[10] It was very easily decomposed by traces of water and other hydrogen-containing compounds to give $HCo(PF_3)_4$ (identified from its i.r. and mass spectra[10]). A small amount of $HCo(PF_3)_4$ was always formed along with $[Co(PF_3)_4]_x$ from cobalt vapour and trifluorophosphine. Traces of absorbed water in the stainless steel vacuum system were believed to be mainly responsible for this, but even with prolonged pumping on the system before a reaction was commenced the contamination could not be eliminated.

None of the bridged compound $(PF_3)_3Co(PF_2)_2Co(PF_3)_3$ was formed.[9] The residue on the walls of the vacuum chamber contained combined trifluorophosphine and was partially soluble in organic solvents.

Nickel. The only product of the reaction was identified from i.r. and mass spectra as $Ni(PF_3)_4$ (85%). No nickel remained on the parts of the walls of the vacuum chamber which had been cooled by liquid nitrogen. The pressure in the vacuum chamber during co-deposition of nickel and trifluorophosphine was lower than that for other metals evaporated which indicates a more efficient gettering action. Condensation of a mixture of nickel vapour and trifluorophosphine in a 2:1 mole ratio resulted in all but 3% of the trifluorophosphine being converted to $Ni(PF_3)_4$. The residue in the vacuum chamber was pure nickel.

Copper. Copper vapour appeared to have about the same gettering action for trifluorophosphine as cobalt or iron vapour. However, all the trifluorophosphine was pumped off the co-condensate on warming it to $-130°$ showing that no copper–trifluorophosphine compound of appreciable stability was formed.

Palladium. The only product formed a white crystalline solid at low temperatures melting at $-45°$ to a fairly volatile colourless liquid. As it was pumped around the vacuum system palladium was deposited. The substance was decomposed at 100° and gave palladium and trifluorophosphine

[7] Th. Kruck, *Chem. Ber.*, 1964, **97**, 2018.

[8] Th. Kruck and A. Prasch, *Angew. Chem. Internat. Edn.*, 1964, **3**, 754.

[9] Th. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, 1967, **6**, 454.

[10] Th. Kruck and W. Lang, *Z. anorg. Chem.*, 1966, **343**, 181.

in a 1 : 4 mole ratio showing that it was $Pd(PF_3)_4$ (65%) as reported by Svatos and Flagg.[11] The residue on the walls of the vacuum chamber was pure palladium.

Other Reactions.—Nickel and chlorodifluorophosphine. Nickel vapour was condensed with gaseous chlorodifluorophosphine in a 1 : 6 mole ratio at −196°. The main volatile product was a colourless liquid, but a trace of $Ni(PF_3)_4$ and a trace of a slightly volatile yellow solid were also obtained. The colourless liquid (2·5 g., 32%) was shown by its mass spectrum to be $Ni(PF_2Cl)_4$.[12] The spectrum showed a group of ions commencing at m/e 474 corresponding to $[Ni(PF_2Cl)_4]^+$ and fragment ions formed by successive loss of Cl and PF_2Cl from the parent. The [19]F n.m.r. spectrum of the liquid showed a doublet of complex form, *ca.* 1300 Hz wide, centred at +12·8 p.p.m. relative to CCl_3F. The doublet was completely symmetrical which makes it very unlikely that any of the possible isomers such as $Ni(PF_2Cl)_2(PFCl_2)(PF_3)$ was present.

The involatile residue on the walls of the vacuum chamber was partly soluble in organic solvents and contained much combined chlorodifluorophosphine.

Nickel, trifluorophosphine, and phosphine. Condensation of nickel vapour with phosphine at −196° gave no volatile product except hydrogen. Hydrogen was evolved both during the co-deposition and more rapidly on warming to room temperature. Clearly, if $Ni(PH_3)_4$ was formed at all it was extremely unstable.

Condensation of nickel vapour with a mixture of equal volumes of phosphine and trifluorophosphine also liberated some hydrogen. However, three colourless volatile products were isolated when the condensate was warmed to room temperature. The most volatile was a small amount of $Ni(PF_3)_4$. The next in order of volatility was found to be the new compound $Ni(PF_3)_3PH_3$ from its mass, i.r., and n.m.r. spectra. The mass spectrum showed the ion group assigned to $[Ni(PF_3)_3PH_3]^+$ and fragment ions corresponding to loss of PH_3 and one to three PF_3 groups. Loss of successive hydrogen atoms was observed in lighter fragment ions than $[Ni(PF_3)PH_3]^+$ but in none of higher mass. The gas-phase i.r. spectrum showed P–H stretches at 2358 and 2218 cm.[-1], a P–H deformation band at 1026 cm.[-1], and four P–F stretching bands almost identical to those reported for $Ni(PF_3)_3CO$ by Clark and Brimm.[13] The [1]H n.m.r. spectrum showed a doublet of quartets. The areas of the resonances in each quartet were in the 1 : 3 : 3 : 1 ratio expected for $Ni(PF_3)_3PH_3$ (τ 6·45, J_{H-P} = 324 Hz, $J_{H-P-P'}$ = 19·5 Hz). The [19]F n.m.r. spectrum showed a doublet of complex resonances centred at +19·8 p.p.m. relative to CCl_3F.

Phosphinetris(trifluorophosphine)nickel(0), m.p. −22°, has a vapour pressure of *ca.* 7 Torr at 0°. It is stable for a few weeks at room temperature under nitrogen but it is more rapidly decomposed by air and moisture. About 10% of the nickel evaporated was recovered as this compound.

The least volatile product of the Ni + PF_3 + PH_3 reaction was a liquid which decomposed slowly above 0°. A portion of this liquid was allowed to warm to room temperature in the presence of excess of gaseous trifluorophosphine at 5 atmos. pressure. After a day the liquid had all been converted to an equimolar mixture of $Ni(PF_3)_3PH_3$ and PH_3. No $Ni(PF_3)_4$ was formed. This showed that the original liquid was $Ni(PF_3)_2(PH_3)_2$. Its [1]H n.m.r. spectrum was a doublet of quartets. The quartets were slightly distorted from a 1 : 3 : 3 : 1 pattern, probably due to second-order coupling effects which were less important in $Ni(PF_3)_3PH_3$ (τ 6·55, $J_{H-P} \approx$ 310 Hz, $J_{H-P-P'} \approx$ 19 Hz). The gas-phase i.r. spectrum of the compound, taken quickly at low pressure to avoid decomposition, showed two P–H deformation bands at 1040 and 1015 cm.[-1] and two P–F stretching bands at slightly lower frequency than those reported for $Ni(PF_3)_2(CO)_2$.[13]

Bis(phosphine)bis(trifluorophosphine)nickel(0) decomposes in a complex way at room temperature. A black solid is deposited and some hydrogen and $Ni(PF_3)_3PH_3$ are formed. The compound is slowly attacked by air. It has a very pleasant fruity smell [note that $Ni(PF_3)_2(PH_3)_2$ is likely to be very toxic]. About 15% of the nickel evaporated was recovered as $Ni(PF_3)_2(PH_3)_2$.

Several phosphine complexes of metals have been reported previously [14] and there is general agreement between their spectroscopic properties and those found for $Ni(PF_3)_3PH_3$ and $Ni(PF_3)_2(PH_3)_2$ in this work.

DISCUSSION

The reaction of gaseous metal atoms with trifluorophosphine at −196° offers a practical route to the preparation of the zero-valent complexes on a modest scale. The yields with chromium, nickel, and palladium were very good and only in the case of iron was defluorination observed and a $^-PF_2^-$ compound formed. It is not understood why defluorination did not also occur with cobalt and trifluorophosphine, but it is typical of reactions at −196° that a tiny difference in activation energy or other kinetic parameter can radically affect the course of two apparently similar reactions.

Perhaps of greater significance is the ready formation of nickel complexes with the less stable ligands chlorodifluorophosphine and phosphine. It is surprising that no 'scrambling' was observed with chlorodifluorophosphine, and it suggests that other substituted fluorophosphines might be used equally successfully. The preparation of $Ni(PF_3)_3PH_3$ and especially $Ni(PF_3)_2(PH_3)_2$ illustrates the non-equilibrium nature of reactions on the cold surface. Thus, $Ni(PF_3)_2(PH_3)_2$ was the most abundant product, although it is less stable than $Ni(PF_3)_3PH_3$ and much less stable than $Ni(PF_3)_4$, even when unreacted trifluorophosphine was present on the cold surface. There are many possibilities for the formation of new complexes by condensation of a transition-metal vapour with a mixture of two ligands, one capable of supplying a large part of the electronic requirements of the metal and the other too weak or unstable to compete with the first in conventional preparative procedures.

[11] G. F. Svatos and E. E. Flagg, *Inorg. Chem.,* 1965, **4**, 422.
[12] Th. Kruck, M. Hofler, H. Jung, and H. Blume, *Angew. Chem. Internat. Edn.,* 1969, **8**, 522.

[13] R. J. Clark and E. O. Brimm, *Inorg. Chem.,* 1965, **4**, 651.
[14] E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem. Internat. Edn.,* 1968, **7**, 136; F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.,* 1968, **90**, 3296.