The Formation of Complexes from Transition-metal Vapours

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Summary Condensation of vapours of transition elements with vapours of inorganic and organic compounds at −196° provides a practical synthesis of some metal complexes.

THE first-row transition elements from chromium to copper can be vaporized easily under high vacuum at temperatures in the range 1300°—1700°. The vapours contain almost exclusively monatomic species.[1] This communication describes a new practical synthesis of transition-metal complexes using the metal vapours as reagents.

The metals were vaporized from an alumina-coated, resistively heated, conical spiral of molybdenum wire mounted in the centre of a highly evacuated stainless-steel chamber, the walls of which were cooled in liquid nitrogen. About 2 g. of the vapour of a metal was condensed on the cold walls in a 30 min. run. During vaporization of the metal, an excess of the vapour of an inorganic or organic compound which might combine with the metal atoms was also sprayed into the chamber and condensed immediately. The pressure in the chamber remained below 1×10^{-4} torr so there were few gas-phase intermolecular collisions. Finally, the vacuum chamber was warmed to room temperature and any liberated volatile compounds were continuously pumped out, purified, and characterised.

Condensation of the transition-metal vapours with an excess of trifluorophosphine gave good yields of trifluorophosphine complexes in several cases. Chromium and nickel vapours formed the known compounds $Cr(PF_3)_6$ and $Ni(PF_3)_4$[2] in yields of 70% and 100%, respectively. With iron vapour, about 25% of the metal was recovered as the known $Fe(PF_3)_5$,[2] while another 25% appeared as a slightly volatile, red crystalline, diamagnetic compound, which was shown by analysis and its mass spectrum to be $Fe_2P_8F_{22}$. The mass spectrum (prominent ions, parent, and parent minus 1—6 PF_3 groups) and ^{19}F n.m.r. spectrum (CCl_3F ref., doublet δ −0·7, doublet δ −30·6, doublet δ +36·7 p.p.m., area ratio 9:1:1) were very similar to those reported by Kruck[3] for $(PF_3)_3Co(PF_2)_2Co(PF_3)_3$. This indicated the iron compound was $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$, with an iron–iron bond and two PF_2 bridging bonds. It melted at 34° and seemed thermally stable, although very air-sensitive. Trifluorophosphine and cobalt vapour gave a 50% yield of violet $Co_2(PF_3)_8$[2] together with some less volatile, unstable compounds which have not been characterised. No $(PF_3)_3Co(PF_2)_2Co(PF_3)_3$ was formed. Neither manganese nor copper vapour formed a volatile compound with trifluorophosphine.

Condensation of chromium vapour with a large excess of benzene vapour produced a 60% yield of dibenzenechromium. The analogous reaction with iron vapour formed a solid which exploded on being warmed to −50°. Addition of cyclopentadiene to the iron–benzene co-condensate at −196° followed by warming to room temperature gave a 40% recovery of the iron as ferrocene. Warming the iron–benzene co-condensate from −196° to 0° in an atmosphere of hydrogen caused reduction of part of the benzene to cyclohexane. These observations are consistent with the presence of a highly reactive iron–benzene complex, perhaps dibenzeneiron.

Iron and nickel vapours condensed with a six-fold molar excess of cyclopentadiene vapour formed ferrocene and π-cyclopentadienyl-π-cyclopentenylnickel in about 60% and 80% yields, respectively.

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[1] B. Siegel, *Quart. Rev.*, 1965, **19**, 77.

[2] For a review, see Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

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