Chemistry of Transition-metal Vapours. Part III.[1,2] Formation of Complexes with Arenes, Trifluorophosphine, and Nitric Oxide

By **R. Middleton, J. R. Hull, S. R. Simpson, C. H. Tomlinson,** and **P. L. Timms,*** School of Chemistry, University of Bristol, Bristol BS8 1TS

Pure, solid bis(cumene) and bis(*m*-di-isopropylbenzene)chromium were obtained by condensing chromium vapour with the arenes at −196°. Stable complexes $Cr(arene)(PF_3)_3$ have been made from chromium vapour, PF_3, and the vapour of benzene, hexafluorobenzene, cumene, or mesitylene; the yield of $Cr(C_6F_6)(PF_3)_3$ was poor. Condensation of iron vapour, PF_3, and C_6H_6 formed $Fe(C_6H_6)(PF_3)_2$. Manganese vapour condensed with a mixture of NO, BF_3, and PF_3 gave $Mn(NO)_3PF_3$, but nitric oxide has proved to be a dangerous reagent in metal atom reactions.

THE formation of complexes by reacting transition-metal vapours with ligands at low temperatures provides a useful alternative to conventional synthetic methods, as is now apparent in publications from several sources.[1-5] In this work we describe the preparation of some compounds of zerovalent chromium, manganese, iron, and cobalt, using arenes, trifluorophosphine, and nitric oxide as ligands.

EXPERIMENTAL

Apparatus and Techniques.—Evaporation and low temperature condensation reactions of Mn, Fe, and Co were carried out in glass or stainless steel apparatus previously described.[1,2,6]

Most reactions with chromium vapour were conducted in the apparatus of Figure (a). The metal was sublimed from a spiral of tungsten or molybdenum wire (1 mm diameter) heated by a current of 40—50 A. Molybdenum radiation shields deflected the metal vapour downwards into the bottom half of the liquid nitrogen-cooled vacuum vessel. The vapour of the compound to be condensed with the chromium vapour, was sprayed simultaneously on to the cold surface of the vacuum chamber. Reaction products with vapour pressure greater than *ca.* 0·1 Torr at 20° were pumped out of the vacuum chamber at the end of a run along with excess reactants. Less volatile products were collected more conveniently by replacing the evaporator assembly by the flask shown in Figure (b). A fast stream of nitrogen gas was used to avoid oxidation of the products during this exchange. With the apparatus re-evacuated, liquid nitrogen was put into the 2 l flask and the reaction products sublimed on to it by warming the vacuum chamber. In this way a clean separation of involatile products and unreacted chromium from volatile products was obtained.

The mass spectra of volatile products were taken on A.E.I. MS9 or MS30 instruments or on a modified Vacuum

---

[1] P. L. Timms, *J. Chem. Soc.* (*A*), 1970, 2526.

[2] Part II, P. L. Timms, *J.C.S. Dalton*, 1972, 830.

[3] P. L. Timms, *Chem. Comm.*, 1969, 1033.

[4] D. L. Williams-Smith, L. R. Wolf, and P. S. Skell, *J. Amer. Chem. Soc.*, 1972, **94**, 4042.

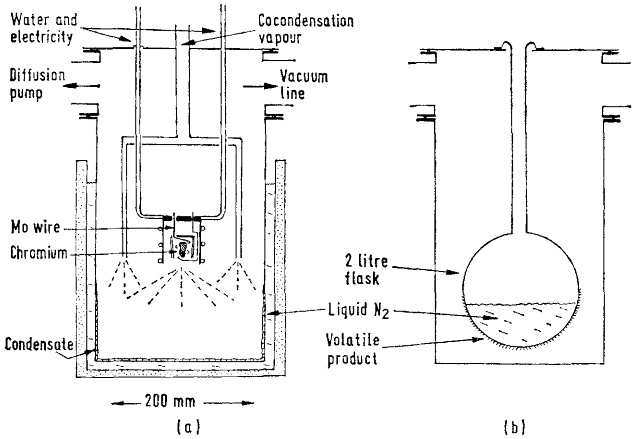
[5] E. K. von Gustorf, O. Jaenicke, and O. E. Polansky, *Angew. Chem. Internat. Edn.*, 1972, **11**, 532.

[6] P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 121.

Generators MM12. The last was of particular value for unstable compounds because of special inlet systems and a low source temperature. I.r. spectra were run on a Perkin-Elmer 457 instrument; n.m.r. spectra were run on a Perkin-Elmer R10 or a Varian HA100 instrument. Analysis for elements was carried out by standard microanalytical methods.

Chromium and Arenes.—The cumene and *m*-di-isopropylbenzene used were redistilled reagent grade products. About 1% each of *o*- and *p*-isomers were found by gas chromatography in the *m*-di-isopropylbenzene.

In a typical experiment, chromium (2·1 g, 40 mmol) was vaporised and condensed at −196° with cumene vapour (520 mmol) in 30 min. The vacuum apparatus was warmed to room temperature with continuous vacuum pumping to remove the excess of cumene. The sparingly volatile bis(cumene)chromium was collected on the inserted cold flask as described above. The flask was warmed to room temperature before it was taken out of the apparatus. The product was dissolved off the flask by aerated water as the cation $Cr(C_9H_{12})_2^+$ and precipitated and weighed as the iodide or the hexafluorophosphate: yield 7·6 mmol (19% on Cr). When unoxidised *bis(cumene)chromium* was required for physical measurements, it was scraped off the flask and then purified if necessary by sublimation in conventional apparatus. It was obtained as a dark yellow crystalline solid, m.p. 46° (Found: C, 51·4; H, 5·75; I, 29·7. $C_{18}H_{24}CrI$ requires C, 51·5; H, 5·70; I, 30·3%). Its mass spectrum showed major peaks at *m/e* 292 (M^+), 172 ($M - C_9H_{12}$)$^+$, 120 ($C_9H_{12}^+$), 105 ($C_8H_9^+$), and 52 (Cr^+).



(a) Apparatus for condensing chromium with other vapours at −196°; (b), a method for collecting slightly volatile reaction products

Bis(m-*di-isopropyl*)*chromium*.—Dark greenish yellow solid, m.p. 55° (Found: Cr, 10·0; C, 56·5; H, 7·3; I, 25·7. $C_{24}H_{36}CrI$ requires Cr, 10·3; C, 57·2; H, 7·15; I, 25·2%). The mass spectrum shows prominent peaks at *m/e* 376 (M^+), 214 ($M - C_{12}H_{18}$)$^+$, 162 ($C_{12}H_{18}^+$), 147 ($C_{11}H_{15}^+$), and 52 (Cr^+). *Bis*(m-*di-isopropylbenzene*)*chromium iodide* melts at 143° with some decomposition; *bis*(m-*di-isopropylbenzene*)*chromium hexafluorophosphate* is stable in air when wet but decomposes vigorously in air when dry.

Chromium, Arenes, and Trifluorophosphine.—Trifluorophosphine (Ozark Mahoning, 98% pure) was purified from chlorofluorophosphines by passage through traps on a vacuum line at −150°. It was bled as a gas into a stream of arene vapour and the mixture was condensed with chromium vapour.

The following experimental procedure for mesitylene is similar to that used with benzene and cumene. In 30 min, chromium (1·5 g, 29 mmol) was evaporated and condensed with trifluorophosphine (230 mmol) and mesitylene (78 mmol) at −196°. Unreacted trifluorophosphine and mesitylene were pumped off on warming to room temperature together with 7 mmol of $Cr(PF_3)_6$.[1] The less volatile $Cr(mesitylene)(PF_3)_3$ was then collected on the cold flask [Figure (b)]; yield 3 mmol (1·3 g). The compound forms cream-coloured needle-like crystals which decompose in air above 130° (Found: C, 24·9; H, 2·75. $C_9H_{12}CrF_9P_3$ requires C, 24·9; H, 2·75%); mass spectrum (Table 1); ^{19}F n.m.r. spectrum (CCl_3F ref.), doublet of complex multiplets 1250 Hz apart, centred at −11·1 p.p.m.

TABLE 1

Relative intensities of some peaks in the mass spectra of $Cr(arene)(PF_3)_3$ complexes (70 eV)

	Benzene		Mesitylene		Cumene
Ion	*m/e*	Int.	*m/e*	Int.	Int.
M^+	394	16·1	436	12·5	23·2
$(M - 2PF_3)^+$	218	3·8	260	4·5	6·3
$(M - 3PF_3)^+$	130	46·3	172	64·9	100·0
Arene$^+$	78	24·1	120	7·8	8·1
PF_3^+	88	14·6		9·4	14·8
CrF^+	71	15·5		2·3	9·0
PF_2^+	69	33·1		15·6	39·1
Cr^+	52	*100·0*		*100·0*	*100·0*

$Cr(cumene)(PF_3)_3$.—Pale green solid, m.p. 47—48°; the liquid decomposes above 130° (Found: C, 24·2; H, 2·85. $C_9H_{12}CrF_9P_3$ requires C, 24·9; H, 2·75%); mass spectrum (Table 1); ^{19}F N.m.r. spectrum (CCl_3F ref.), doublet of complex multiplets 1284 Hz apart, centred at −12·7 p.p.m.

$Cr(C_6H_6)(PF_3)_3$.—Pale yellow, needle-like crystals which decompose in air above 220° (Found: Cr, 13·0; C, 18·4; H, 1·5. $C_6H_6CrF_9P_3$ requires Cr, 13·2; C, 18·4; H, 1·5%); mass spectrum (Table 1); i.r. spectrum (thin film), 3095w, 1449m, 880s, 840s, 823s, 799s cm^{-1}.

$Cr(C_6F_6)(PF_3)_3$.—The optimum conditions for forming this compound were found to be similar to those for the other arene complexes. However, the yields were very poor (1—2% on chromium) and the problem of separating the hexafluorobenzene complex from $Cr(PF_3)_6$ was more difficult than with the other arenes. Fractional sublimation proved impracticable. Instead, the mixture of $Cr(PF_3)_6$ and $Cr(C_6F_6)(PF_3)_3$ was extracted with diethyl ether in which the hexafluorobenzene complex was very soluble. The solvent was evaporated under vacuum and the solid residue redissolved in n-hexane. This solution was poured on to a 10 × 150 mm column of silica gel (Hopkin and Williams 100—200 mesh) which had been pretreated with ether and n-hexane. The $Cr(PF_3)_6$ was eluted with n-hexane and $Cr(C_6F_6)(PF_3)_3$ was then eluted with a mixture of equal volumes of n-hexane and ether. As the column was connected directly to a vacuum line through a Teflon-in-glass needle valve, the solvent was evaporated continuously and deposited $Cr(C_6F_6)(PF_3)_3$ was recovered quantitatively by vacuum line techniques (Found: C, 14·4; P, 18·2. $C_6CrF_{15}P_3$ requires C, 14·3; P, 18·5%); mass spectrum (Table 2); i.r. spectrum (Nujol and hexachlorobutadiene mulls) 1726mw, 1566m, 1559m, 1471vs, 1388m, 1317w, 1275w, 1250w, 1175m, 1130w, 1054m, 990vs, 945s, 922vs, 879vs, 850vs, 841vs, 721m, 629mw cm^{-1}.

Iron, Benzene, and Trifluorophosphine.—In 30 min, 25 mmol (1·4 g) of 99·9% pure iron was vaporised and condensed with benzene vapour (80 mmol) and trifluorophosphine (150 mmol) at −196°. The products of the reaction were $Fe(PF_3)_5$, $(PF_3)_3Fe(PF_2)_2Fe(PF_3)_3$,[1] and $Fe(C_6H_6)(PF_3)_2$, and they were separated by fractional condensation on a vacuum line. The least volatile, $Fe(C_6H_6)(PF_3)_2$, was collected in a 0° trap; yield 5 mmol (1·5 g); it was analysed by quantitative decomposition with 2M-HNO_3 at 60° to liberate benzene (Found: C_6H_6, 24·6%. Required C_6H_6 25·1%); mass spectrum (using MM12), peaks at *m/e* (relative intensity), 310 M^+ (1·5), 222 $(M - PF_3)^+$ (1·5), 203 $(M - PF_4)^+$ (1·4), 153 $FeFC_6H_6^+$ (1·0), 144 $FePF_3^+$ (1·4), 134 $FeC_6H_6^+$ (11·5), 88 PF_3^+ (22·5), 78 $C_6H_6^+$ (54·0), 69 PF_2^+ (100·0), 56 Fe^+ (33·0).

TABLE 2

Mass spectrum of $Cr(C_6F_6)(PF_3)_3$ (70 eV)

m/e	Probable identity	Relative intensity
502	M^+	11·4 (100) *
483	$(M - F)^+$	4·4 (18) *
464	$(M - 2F)^+$	0·5
326	$Cr(C_6F_6)PF_3^+$	0·7
307	$Cr(C_6F_6)PF_2^+$	1·5
238	$CrC_6F_6^+$	1·0
228	$Cr(PF_3)_2^+$	3·7
219	$CrC_6F_5^+$	2·0
209	$Cr(PF_3)PF_2^+$	4·0
186	$C_6F_6^+$	1·3 (7) *
159	$Cr(PF_3)F^+$	3·3
148	$C_6F_4^+$	6·8
140	$CrPF_3^+$	37·4 (85) *
129	$C_6F_3^+$	6·9
121	$CrPF_2^+$	2·6
117	$C_5F_3^+$	5·0
110	$C_6F_2^+$	2·0
98	$C_5F_2^+$	5·5
93	$C_3F_3^+$	1·9
90	CrF_2^+	4·0
88	PF_3^+	1·9
86	$C_4F_2^+$	1·0
79	C_5F^+	7·4
71	CrF^+	56·8
69	PF_2^+	15·2
52	Cr^+	*100·0* (43) *

* Approximate relative intensity at 15 eV.

Metals and Nitric Oxide.—Nitric oxide (British Oxygen 99% pure) was purified from traces of higher oxides by passage through traps at −150° on a vacuum line. Reagent grade boron trifluoride (British Oxygen 99·5% pure) was used without purification.

Although glass apparatus[2] was sometimes used for condensation of metal vapours with nitric oxide, an all metal apparatus with a high pumping speed for permanent gases[1,6] proved safer and more efficient.

$Mn(NO)_3PF_3$.—As manganese is the easiest of the transition metals to vaporise, the scale of the preparation of $Mn(NO)_3PF_3$ was not limited by the amount of the metal which could be vaporised. Rather, the scale was limited by the pressure rise in the apparatus caused by addition of nitric oxide; if the pressure rose above 0·01 Torr, oxidation of the manganese was observed.

Manganese (99·9% pure, 4 g, *ca.* 75 mmol) was vaporised from an alumina coated molybdenum spiral[1,2] in 60 min and condensed at −196° with 4·8 l of a gas mixture containing BF_3, NO, and PF_3 in a 2 : 2 : 1 mol ratio. At the end of the run, the product $Mn(NO)_3PF_3$ was separated from excess reagents by condensation in a trap at −100°. No further purification was found necessary; yield 4 mmol (0·95 g) (Found: Mn, 23·2; P, 13·5. $F_3MnN_3O_3P$ requires Mn, 23·5; P, 13·3%); m.p. (Stock ring method using a pentane thermometer) −120° ± 2°; mass spectrum (using MM12), peaks at *m/e* (relative intensity), 233 M^+ (100·0), 214 $(M - F)^+$ (8·9), 203 $(M - NO)^+$ (3·6), 184 $Mn(NO)_2PF_2^+$ (10·0), 173 $MnNOPF_3^+$ (22·2), 154 $MnNOPF_2^+$ (5·5), 145 $Mn(NO)_3^+$ (61·7), 143 $MnPF_3^+$ (5·0), 124 $MnPF_2^+$ (3·9), 115 $Mn(NO)_2^+$ (23·8), 105 $MnPF^+$ (3·3), 88 PF_3^+ (46·5), 85 $MnNO^+$ (74·6), 74 MnF^+ (37·3), 69 PF_2^+ (95·0), 55 Mn^+ (98·0); i.r. spectrum (70 mm gas cell), 1842m, 1755vs, 913m, 899sh, 894s, 667w, 665w cm^{-1}.

$Co(NO)(PF_3)_3$.—Cobalt (650 mg, 11 mmol) was vaporised and condensed at −196° with 1·5 l of a mixture containing PF_3, NO, and BF_3 in a 3 : 1 : 1 mol ratio, in 30 min. The volatile products were separated from excess reagents by a trap at −90° and then fractionated to yield 0·5 mmol (170 mg) of $Co(NO)(PF_3)_3$; the i.r. spectrum of this compound was identical to that reported by Kruck;[7] the mass spectrum showed major peaks at *m/e* 353 M^+, 265 $(M - PF_3)^+$, 235 $Co(PF_3)_2^+$, 177 $CoNOPF_3^+$. About 80 mg of a less volatile fraction was also recovered.

$Fe(NO)_2(PF_3)_2$.—Iron (1 g, 18 mmol) was vaporised and condensed with 2 l of a gas mixture containing PF_3, NO, and BF_3 in equimolar amounts, in 50 min. The volatile products were separated from reactants by a trap at −100° and were then fractionated on a low temperature distillation column to yield 1·5 mmol (470 mg) of $Fe(NO)_2(PF_3)_2$, a trace of $Fe(PF_3)_5$, and 50 mg of a mixture of less volatile compounds; the appearance and i.r. spectrum of $Fe(NO)_2(PF_3)_2$ were as reported by Kruck and Lang.[8]

RESULTS AND DISCUSSION

Bis(arene)chromium Complexes.—The normal preparation of bis(arene)chromium compounds by treating an arene with Al, $AlCl_3$, and $CrCl_3$, commonly gives very impure products with alkylated arenes which are rearranged by Friedel–Craft catalyses. Thus, 'bis(cumene)chromium' prepared this way is reported to be a liquid[9] but this in fact contains a complex mixture of bis(arene)chromium compounds including bis(toluene)-, bis(xylene)-, and bis(di-isopropylbenzene)-chromium. Pure bis(ethylbenzene)chromium has been made by this route but only under carefully controlled conditions.[10]

In this work, it was found that when chromium vapour was condensed with an excess of cumene vapour at −196° in the apparatus of Figure (a), the bis(cumene)chromium formed was a crystalline solid at room temperature. Decomposition of the compound with 2M-HNO_3 liberated only cumene. Using *m*-di-isopropylbenzene, crystalline bis(*m*-di-isopropylbenzene)chromium was formed but in this case traces of *ortho*- and *para*-isomers present in the starting material were also detected in the arene liberated

---

[7] Th. Kruck and W. Lang, *Chem. Ber.*, 1966, **99**, 3794.

[8] Th. Kruck and W. Lang, *Angew. Chem. Internat. Edn.*, 1964, **3**, 700.

[9] Gmelin, 'Handbuch der anorganische Chemie, erganzungwerk, Chrom organisch Verbindungen,' 1971.

[10] V. A. Umilin, B. G. Gribov, Y. B. Zverev, B. I. Kozyrkin, and G. G. Devyatykh, *Metody Poluch. Anal. Veshchestv. Osobvi Chist., Tr. Vses. Konf.*, 1968 (publ. 1970), p. 116 (*Chem. Abs.*, 1971, **75**, 63,925).

from the chromium compound by nitric acid. The maximum yield of bis(cumene)- and bis(*m*-di-isopropylbenzene)-chromium was *ca.* 20% (on evaporated chromium), lower than that reported for bis(benzene)chromium.[3,11] Nevertheless, this seems a practical method for making small quantities of such compounds of high purity.

The Complexes Cr(arene)$(PF_3)_3$.—Condensation of chromium vapour with a mixture of an arene vapour and trifluorophosphine has been found to give the corresponding Cr(arene)$(PF_3)_3$ complex with benzene, cumene, mesitylene, and hexafluorobenzene.

Using a mol ratio of Cr : arene : PF_3 of about 1 : 6 : 6 benzene, cumene, and mesitylene each gave a 10—15% yield of Cr(arene)$(PF_3)_3$, together with similar amounts of $Cr(PF_3)_6$ and the bis(arene)chromium complexes. Only $Cr(C_6H_6)(PF_3)_3$ has been previously reported.[12] The new compounds were identified by their mass spectra and chemical analysis. Their physical properties seemed generally similar to those of the corresponding chromium arene tricarbonyls,[9] although they decomposed at somewhat lower temperatures presumably by transfer of fluorine from phosphorus to chromium.

When hexafluorobenzene and trifluorophosphine were condensed with chromium under the conditions used with the other arenes, the main product was $Cr(PF_3)_6$ but a very small amount of a solid of similar volatility to $Cr(PF_3)_6$ was also formed. The mixture was separated on a silica gel column. The mass spectrum of the minor component (Table 2) indicated the formula $Cr(C_6F_6)(PF_3)_3$; the ion at *m*/*e* 502 (M^+) was fairly prominent at 70 eV, but it became the largest peak in the spectrum at 15 eV. Ions at lower *m*/*e* all seemed derived from the parent molecule by plausible fragmentation processes although the pattern was different from that observed with other Cr(arene)$(PF_3)_3$ complexes (Table 1). The ^{19}F n.m.r. spectrum of the compound showed a singlet at +184·2 p.p.m. (CCl_3F ref.) and a doublet of complex multiplets centred at −6·1 p.p.m., spaced 1315 Hz apart. The multiplets were of similar shape to those observed with other Cr(arene)$(PF_3)_3$ compounds. The i.r. spectrum showed strong bands at 1471 and 990 cm^{-1}, probably associated with the ring stretching and C–F stretching modes of a C_6F_6 ring, and a series of bands at 922—841 cm^{-1} of similar form, but at a slightly higher frequency, than P–F stretching bands in $Cr(C_6H_6)(PF_3)_3$. The crystal habit adopted by $Cr(C_6F_6)(PF_3)_3$ (very fine yellow needles) was also like that of $Cr(C_6H_6)(PF_3)_3$.

The evidence suggests that in $Cr(C_6F_6)(PF_3)_3$, the hexafluorobenzene behaves like benzene as an effective six-electron donor. The complex is very stable. It can be heated to 100° in air without change. It is not attacked by trifluorophosphine at 1 atm. pressure at 150°. Decomposition above 250° in vacuum or attack by iodine at 100°, liberates hexafluorobenzene. It is considerably more volatile than $Cr(C_6H_6)(PF_3)_3$. Its odour is like that of hexafluorobenzene.

In view of the stability of $Cr(C_6F_6)(PF_3)_3$ it is puzzling why it is formed in such low yield. Using a wide range of different ratios of reactants, the yields did not exceed 1—2% on the chromium; $Cr(PF_3)_6$ was always formed in 15—30 fold greater abundance.

No volatile product was isolated when hexafluorobenzene was condensed with chromium vapour at −196°. The condensate exploded mildly on warming above −50°. A more violent explosion resulted when a mixture of benzene and hexafluorobenzene was condensed with chromium, and the condensate was subsequently exposed to traces of air at room temperature.* Thus, it seems that trifluorophosphine has a very important role in stabilising the hexafluorobenzene complex.

Iron, Benzene, and Trifluorophosphine.—The main volatile product of condensing iron vapour with an excess of an equimolar mixture of benzene and trifluorophosphine was a red solid, $Fe(C_6H_6)(PF_3)_2$. The formula was indicated from the mass spectrum and chemical analysis. The ^{19}F n.m.r. spectrum showed a doublet of multiplets 1305 Hz apart centred at −0·35 p.p.m. (CCl_3F ref.), and the ^1H n.m.r. spectrum showed a singlet at τ 4·58, supporting the identification. A related compound Fe(toluene)$(PF_3)_2$ has recently been reported by Williams-Smith, Wolf, and Skell[4] from the reaction of iron atoms with toluene at −196° and subsequent addition of trifluorophosphine (see below).

The volatility of $Fe(C_6H_6)(PF_3)_2$ is similar to that of $Cr(C_6H_6)(PF_3)_3$, but the iron compound is much less stable. Large crystals decompose in air about 50° and in powder form the compound is pyrophoric. Benzene was displaced from the complex by treatment with carbon monoxide at 1 atm. pressure at 20°. In its mass spectrum, the parent molecular ion $Fe(C_6H_6)(PF_3)_2^+$, was found to be of much lower abundance relative to fragment ions than with Cr(arene)$(PF_3)_3$ complexes.

Condensation of iron vapour with benzene at −196° gives an explosive material.[3] When trifluorophosphine was condensed on to the iron–benzene condensate at −196° and the mixture warmed slowly to room temperature, there was no explosion and a small yield (4% on the iron) of $Fe(C_6H_6)(PF_3)_2$ was obtained together with some $Fe(PF_3)_5$. However, when the experiment was repeated but with addition of carbon monoxide instead of trifluorophosphine, a mild explosion occurred on warming to room temperature and no iron carbonyls were recovered.

Metal Vapours and Nitric Oxide.—Nitric oxide has a vapour pressure of *ca.* 0·005 Torr at −196°. It is thus a difficult ligand to use in co-condensation reactions with metal vapours when high vacuum has to be maintained. In an effort to reduce the vapour pressure, the nitric oxide used in reactions with metal vapours was mixed with an equal volume of boron trifluoride, a compound which complexes weakly with nitric oxide in the condensed phase at low temperatures and which is relatively inert towards metal atoms.

---

* *Note added in proof.* Further investigation has shown that air-stable $Cr(C_6F_6)(C_6H_6)$ is also formed from Cr + C_6H_6 + C_6F_6.

[11] P. L. Timms, *J. Chem. Educ.*, 1972, in the press.

[12] Th. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53.

The series $M(NO)_n(PF_3)_{4-n}$.—Mixed nitrosyl trifluorophosphine complexes of cobalt, $Co(NO)(PF_3)_3$,[7] and iron, $Fe(NO)_2(PF_3)_2$,[8] have been described by Kruck and Lang. These compounds form part of a series $M(NO)_n(PF_3)_{4-n}$, of which $Mn(NO)_3PF_3$ and $Cr(NO)_4$ have not been characterised previously. It was hoped that metal vapour reactions would provide a method for completing the series.

To test the method, cobalt and iron vapours were each condensed with a mixture of boron trifluoride, nitric oxide, and trifluorophosphine at —196°. On warming to room temperature, 5—10% of each metal was recovered as $Co(NO)(PF_3)_3$ and $Fe(NO)_2(PF_3)_2$ respectively; the compounds were identified by their i.r. spectra and mass spectra. With both metals, small amounts of less volatile products of higher molecular weight were also formed but these have not been fully characterised.

Manganese vapour condensed with a mixture of boron trifluoride, nitric oxide, and trifluorophosphine at —196°, gave only one volatile product, a green liquid. The mass spectrum and chemical analysis of this product indicated the formula $Mn(NO)_3PF_3$. The i.r. spectrum of the vapour showed two bands at 1842 and 1755 cm^{-1} only slightly shifted from the two N–O stretching bands in the known $Mn(NO)_3CO$ [13] (1823 and 1734 cm^{-1}), together with bands in the P–F stretch region, supporting the structure. The compound was stable at ordinary temperatures in an inert atmosphere but was very readily oxidised by air. When liquid $Mn(NO)_3PF_3$ was exposed to carbon monoxide at 1 atm. pressure at 20°, rapid replacement of trifluorophosphine by carbon monoxide took place and $Mn(NO)_3CO$ was formed almost quantitatively.

When manganese vapour was condensed with nitric oxide and trifluorophosphine in the absence of boron trifluoride, the condensate exploded violently on warming a little above —196° and nitrogen was liberated.

Condensation of chromium vapour with an equimolar mixture of nitric oxide and boron trifluoride at —196° gave a red condensate. On warming to room temperature a little nitrogen was evolved but no volatile product containing chromium was detected. The residue in the apparatus at room temperature was a red, chromium-rich solid, insoluble in organic solvents. The i.r. spectrum of the solid showed no N–O stretching bands. It thus seems that no stable compound $Cr(NO)_4$ was formed; if any $Cr(NO)_4$ was formed at —196° it must have decomposed with oxidation of the chromium and evolution of nitrogen well below room temperature. As was the case with manganese, condensation of chromium and nitric oxide in the absence of boron trifluoride, resulted in a powerful explosion.

Other Attempted Reactions with Nitric Oxide.—Sabherwal and Burg [14] reported the formation of $Co(NO)_3$ by a photolysis reaction. Attempts to make this compound by direct condensation of cobalt vapour with nitric oxide in the presence or absence of boron trifluoride, have been only partially successful. Under all conditions, a black, involatile, cobalt-rich solid was left in the apparatus which was not soluble in organic solvents [contrast $Co(NO)_3$]. However, the i.r. spectrum of the solid (Nujol mull) showed only two strong bands at 1879 and 1755 cm^{-1}; these were in the N–O stretch region but shifted from the values of 1860 and 1795 cm^{-1} reported for $Co(NO)_3$. It seems that the solid must have contained some terminal CoNO groups as in $Co(NO)_3$, but perhaps only on the surface of cobalt metal particles, *i.e.* chemisorbed NO.

In an attempt to make $Co(C_6H_6)NO$, analogous to $Ni(C_5H_5)NO$, cobalt vapour, benzene, and nitric oxide were condensed at —196°. All the benzene was recovered unchanged at the end of the experiment and the solid residue was identical to the black material obtained by condensing cobalt and nitric oxide. When a related experiment was tried, in which chromium vapour was condensed with nitric oxide, boron trifluoride, and benzene in an attempt to make $Cr(C_6H_6)(NO)_2$, the condensate exploded violently at *ca.* —30°.

Thus, nitric oxide has proved itself to be a dangerous ligand in metal condensation reactions. It is not clear what role boron trifluoride plays in reducing the explosion hazard in some cases, *e.g.*, in the manganese, nitric oxide, trifluorophosphine system, but it is certainly not wholly effective and great care must be exercised.

We thank Dr. G. M. Gibson for helpful suggestions and the S.R.C. for both research support and a C.A.P.S. studentship (with Albright and Wilson) to one of us (R. M.).

[2/1954 *Received*, 17*th August*, 1972]

---

[13] C. G. Barraclough and J. Lewis, *J. Chem. Soc.*, 1960, 4842.
[14] I. H. Sabherwal and A. B. Burg, *Chem. Comm.*, 1970, 1001.