

# Preparation of high-oxidation-state platinum group metal fluorides in flow systems. Synthesis of the metal hexafluorides, $\text{MF}_6$ ( $\text{M}=\text{Ru}, \text{Rh}, \text{Os}, \text{Ir}, \text{Pt}$ ), ruthenium pentafluoride tetramer, $(\text{RuF}_5)_4$ , and the novel trimer, $(\text{RuF}_5)_3$ \*

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## Abstract

The fluorination of platinum metals under anhydrous conditions in a flow system yields the volatile metal hexafluorides ( $\text{M}=\text{Ru}, \text{Rh}, \text{Os}, \text{Ir}, \text{Pt}$ ) in high yield. The flow fluorination of ruthenium also affords green  $\{\text{RuF}_5\}_4$  and bright red  $\{\text{RuF}_5\}_3$ . In the case of palladium, no volatile products were observed, the only product of the reaction being  $\text{Pd}^{\text{II}}[\text{Pd}^{\text{IV}}\text{F}_6]$ .

## Introduction

The hexafluorides of the platinum group metals are rare examples of discrete molecular compounds in unusually high oxidation states and, as such, their spectroscopic properties have been extensively studied [1]. Flow fluorinations of the platinum group metals have previously had limited success. The hexafluorides  $\text{OsF}_6$  and  $\text{IrF}_6$  can be prepared in nearly quantitative yield using reduced-pressure (*ca.* 300 mmHg) fluorine systems [2, 3]. A brief report on the flow fluorination of platinum metal suggests a very low yield of  $\text{PtF}_6$  [4], while the flow fluorination of ruthenium metal powder is reported to yield a black–green residue containing significant amounts of ruthenium dioxide from which only  $\text{RuF}_5$  may be distilled [5]. The more reactive hexafluorides ( $\text{PtF}_6$ ,  $\text{RuF}_6$  and  $\text{RhF}_6$ ) have only previously been prepared in significant quantities using specialised induction heating [6] or high-pressure fluorination techniques [7]. In this paper we report a new flow fluorination procedure which yields not only  $\text{OsF}_6$  and  $\text{IrF}_6$  in high yield, but also produces reasonable yields of  $\text{RuF}_6$ ,  $\text{RhF}_6$  and  $\text{PtF}_6$ .

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\*D. A. Boyd, J. H. Holloway and G. Stanger, *Eur. Pat.* 0 330 335 A1 (1989).

## Experimental

Figure 1 shows the apparatus used for these flow fluorinations.

In a typical experiment, the platinum metal (*ca.* 5 mmol) was loaded into a nickel boat and placed in the copper reactor. The apparatus was evacuated (1 Torr) for 16 h, flamed several times over a period of at least 1 h, filled to 1 atm with dry nitrogen, and heated at *ca.* 100 °C for a further 60 min in a stream of dry nitrogen. The metal was hydrogenated *in situ* by passing a stream of hydrogen through the line and heating the reactor to *ca.* 400 °C for 60 min. The metal was allowed to cool under a hydrogen atmosphere and then flushed completely with dry nitrogen. A fluorine/dry nitrogen mixture was passed through the line for *ca.* 60 min and the quartz traps warmed to *ca.* 100 °C to passivate their surfaces. The fluorine (Matheson, Lyndhurst, NJ) of 98% purity was freed from HF, CO<sub>2</sub>, CF<sub>4</sub> and SiF<sub>4</sub> traces by passage through a liquid-oxygen cooled U-trap (-186 °C) prior to mixing with the nitrogen. Cooling baths were placed around each trap and the reactor heated to *ca.* 600 °C. Once the reaction was complete, the fluorine flow was stopped, the line was flushed completely with dry nitrogen and the quartz traps were sealed under *ca.* 600 mmHg pressure of dry nitrogen.

The hexafluorides OsF<sub>6</sub>, IrF<sub>6</sub> and PtF<sub>6</sub>, and the pentafluorides RuF<sub>5</sub> and PtF<sub>5</sub>, were characterised by mass spectrometry using a V.G. Micromass 16B instrument. The spectrometer was first seasoned by flushing with small amounts of elemental fluorine. Solid samples were admitted directly into the ionisation chamber on the end of a stainless-steel probe, while volatile samples were introduced through a pre-seasoned copper pipe with either a PTFE or Pyrex insulating tip, depending on the nature of the sample. Using an accelerating voltage of 4 kV and an electron energy of 70 eV, excellent spectra exhibiting the expected fragmentation patterns of OsF<sub>6</sub>, IrF<sub>6</sub> and PtF<sub>6</sub> were obtained (Table 1 and Fig. 2)

No satisfactory spectrum of RuF<sub>6</sub> could be produced because of its extreme reactivity. Samples of this material introduced through a Teflon tip gave rise only to a fragmentation pattern which could be associated with the (CF<sub>2</sub>)<sub>n</sub> chain, while those admitted via a quartz tip yielded peaks which could be attributed to the fragmentation patterns of SiF<sub>4</sub>, RuO<sub>4</sub>, WF<sub>6</sub> and (CF<sub>2</sub>)<sub>n</sub>. The SiF<sub>4</sub> and RuO<sub>4</sub> arose presumably due to the attack of the RuF<sub>6</sub> on the quartz; the WF<sub>6</sub> is assumed to result from the attack of RuF<sub>6</sub> on the tungsten filament and (CF<sub>2</sub>)<sub>n</sub> may be formed through attack on the PTFE 'O'-rings of the spectrometer.

For RuF<sub>5</sub>, fragmentation patterns due to monomeric, dimeric, trimeric and tetrameric ruthenium pentafluoride were observed as outlined in the Results section below. In order to detect the tetrameric and trimeric species, an acceleration voltage of 2 kV was used. To observe impurities and to achieve greater sensitivity for the monomeric and dimeric species higher sensitivity was achieved at 3 kV or 4 kV. Although it has been previously reported that monomeric, dimeric and trimeric derivatives of PtF<sub>5</sub> have been observed by molecular beam mass spectrometry, a signal due to PtF<sub>6</sub><sup>+</sup> is

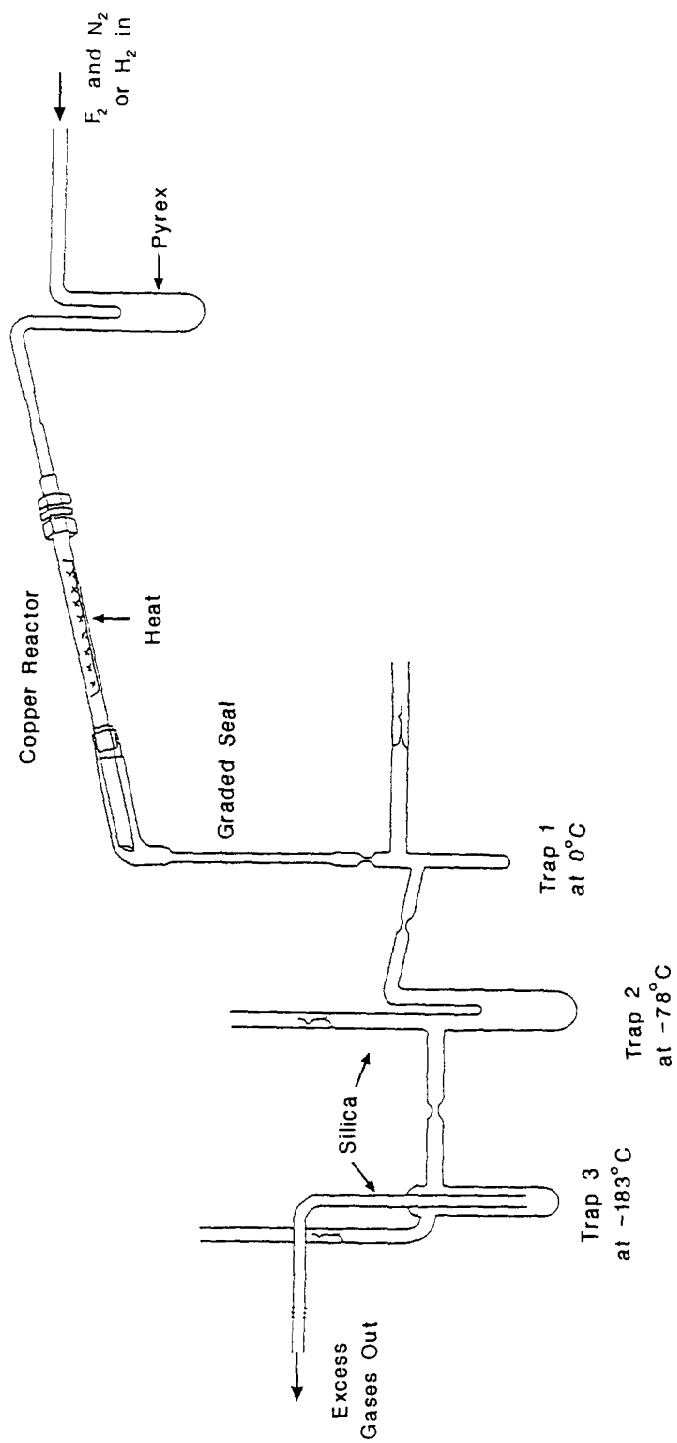
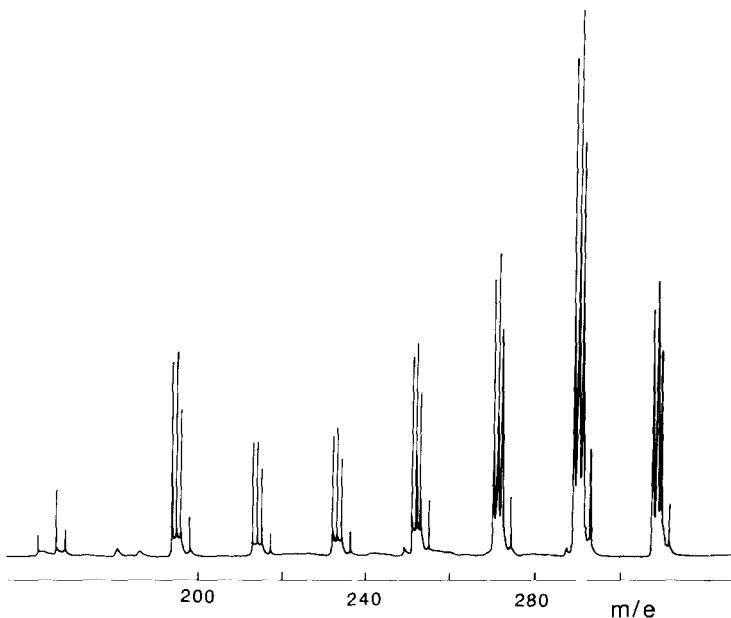


Fig. 1. Apparatus for the flow preparation of volatile and non-volatile fluorides.

TABLE 1

Relative abundancies of the ions of the hexafluorides OsF<sub>6</sub>, IrF<sub>6</sub> and PtF<sub>6</sub>

Ion	Relative abundance (%) <sup>a</sup>		
	OsF <sub>6</sub> <sup>b</sup>	IrF <sub>6</sub> <sup>b</sup>	PtF <sub>6</sub> <sup>b</sup>
M <sup>+</sup>	16.0	11.4	37.5
MF <sup>+</sup>	13.1	11.0	21.4
MF <sub>2</sub> <sup>+</sup>	27.6	28.3	23.7
MF <sub>3</sub> <sup>+</sup>	37.9	44.9	38.6
MF <sub>4</sub> <sup>+</sup>	89.4	100.0	55.3
MF <sub>5</sub> <sup>+</sup>	100.0	35.4	100.0
MF <sub>6</sub> <sup>+</sup>	15.8	9.0	50.8

<sup>a</sup>Largest peak being taken as 100% in each case.<sup>b</sup>All spectra recorded at 70 eV, 4 kV and 70 °C.Fig. 2. Mass spectrum of PtF<sub>6</sub> (conditions: 70 eV, 4 kV, 70 °C).

also observed [8]. Our spectra also exhibited the peaks for PtF<sub>6</sub><sup>+</sup>, in addition to the expected fragmentation pattern for PtF<sub>5</sub>. No evidence for the dimer or trimer was found. This can be reasonably explained by the extreme reactivity of PtF<sub>5</sub> and its ready disproportionation to PtF<sub>6</sub> and PtF<sub>4</sub>. Rhodium pentafluoride was not examined.

The hexafluorides RuF<sub>6</sub>, OsF<sub>6</sub>, IrF<sub>6</sub> and PtF<sub>6</sub> were also characterised by gas-phase IR spectroscopy by comparison with known data [9], and IrF<sub>6</sub>

was examined by Raman spectroscopy in the solid state (94–98 K) and its spectrum successfully assigned on the basis of molecules of  $O_h$  symmetry with  $C_s$  site symmetry and a  $D_{2h}^{16} = Pnma$  space group [10]. Additionally, the hexafluorides have also been characterised by IR and UV–vis spectroscopy in inert-gas matrices and the details for  $OsF_6$ ,  $IrF_6$  and  $PtF_6$  [11], and  $RuF_6$  and  $RhF_6$  [12], have been published separately.

X-ray powder diffraction photography was used to characterise and confirm the purities of the tetrameric pentafluorides  $RuF_5$ ,  $RhF_5$  and  $PtF_5$ , and the tetrafluoride  $PtF_4$ , by comparison with data obtained previously on definitively characterised samples. The hexafluorides  $PtF_6$ ,  $IrF_6$  and  $OsF_6$  were also examined as solids at room temperature and their powder patterns were correlated with the cubic structures identified previously [10, 13].

## Results

Previous preparative procedures for the fluorination of the platinum group metals have involved the pre-fluorination of a glass and metal apparatus, the hydrogenation of the powdered metal at red heat in a (usually) porcelain crucible and the introduction of the reduced metal into the fluorination apparatus by transfer through the atmosphere. These procedures have resulted, inevitably, in both the interior of the apparatus and the reduced metal being exposed to atmospheric moisture and oxygen.

The procedures developed in the present work have resulted in the total elimination of water and oxygen and, in a number of cases, this has resulted in the products of the reaction being significantly different from those reported in earlier work. In particular, it appears that higher-oxidation-state fluorides are produced or that the highest-oxidation-state fluoride is produced in improved yield. The current work has also yielded quantitative data on the various products obtained.

For both osmium and iridium, nearly quantitative yields of the metal hexafluorides were obtained by fluorination for 1 h, as described previously [2, 3]. In all of our experiments using the new procedure, no metal remained in the nickel boat, and this preparative route may, therefore, be conveniently scaled up to procedure large quantities of these hexafluorides. Preliminary experiments without hydrogenation of the metal *in situ* and without seasoning of the quartz traps decreased the yields to *ca.* 70%, the rest being lost as oxide (e.g.  $OsO_4$ ) or deposited as ill-defined, involatile, dark residues (which are probably low-oxidation-state oxide or hydroxide species) on the apparatus walls.

Flow fluorination of platinum powder yielded dense yellow–brown fumes which passed through trap 1 and condensed in trap 2 (see Fig. 1) as a deep red (almost black) crystalline solid ( $PtF_6$ ) in 60–70% yield, while a red glassy material ( $PtF_5$ ) and a fine yellow powder ( $PtF_4$ ) were found to collect in trap 1. This is in sharp contrast to earlier work [4] where only very low yields of  $PtF_6$  were obtained. After 2 h no further products were observed

emanating from the reaction zone, and it was found that there was no metal remaining in the reactor.

Previous work on the dynamic fluorination of ruthenium metal powder has always yielded black-green tars which contain significant quantities of  $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ , but from which  $\text{RuF}_5$  could be distilled [5]. The early stages of this reaction produced a pale yellow volatile material, which was recently shown to be  $\text{RuO}_4$  [14]. Using the new preparative technique, the flow fluorination of hydrogenated ruthenium metal immediately afforded green-brown fumes. A glassy green material ( $\text{RuF}_5$ ) trickled into trap 1, a bright orange-red glassy material condensed in trap 1 and a buff brown solid ( $\text{RuF}_6$ ) (40–60% yield) condensed in trap 2. After 3 h no further products were observed emanating from the reactor, and it was found that no metal remained in the reaction tube.

The red material has not been reported previously and is therefore of considerable interest. Complete characterisation has been difficult since it converts under dynamic vacuum, and at 35 °C in static vacuum, to the well-known green tetrameric  $\{\text{RuF}_5\}_4$ . However, by heating mixed samples of this red material and green  $\{\text{RuF}_5\}_4$  at 26–27 °C for 3–4 d in well-seasoned quartz apparatus, the orange-red material gradually sublimed to yield a nearly pure dark red solid. This solid is very sensitive to moisture and decomposes within 30 min even in a good dry box ( $\leq 5$  ppm water). Infrared spectra obtained for the powder between KBr discs gave bands typical of a binary transition metal fluoride [735(sh), 700(s), 660(m), 650(sh), 510(s,br)  $\text{cm}^{-1}$ ]. The mass spectra of green  $\{\text{RuF}_5\}_4$ , run at 90 °C and electron energies of 70 eV (see Fig. 3) and 50 eV, exhibit characteristic ruthenium isotope patterns centred at 102, 121, 140, 159, 178, 197, 317, 336, 355, 374, 393, 552, 571, 590, 765 and 784 amu per unit charge, which permit characterisation of the fragments associated with  $\text{Ru}^+$ ,  $\text{RuF}^+$ ,  $\text{RuF}_2^+$ ,  $\text{RuF}_3^+$ ,  $\text{RuF}_4^+$ ,  $\text{RuF}_5^+$ ,  $\text{Ru}_2\text{F}_6^+$ ,  $\text{Ru}_2\text{F}_7^+$ ,  $\text{Ru}_2\text{F}_8^+$ ,  $\text{Ru}_2\text{F}_9^+$ ,  $\text{Ru}_2\text{F}_{10}^+$ ,  $\text{Ru}_3\text{F}_{13}^+$ ,  $\text{Ru}_3\text{F}_{14}^+$ ,  $\text{Ru}_3\text{F}_{15}^+$ ,  $\text{Ru}_4\text{F}_{19}^+$  and  $\text{Ru}_4\text{F}_{20}^+$ . The mass spectrum of the red material under identical conditions yields an identical spectrum except that the peaks assigned as  $\text{Ru}_4\text{F}_{19}^+$  and  $\text{Ru}_4\text{F}_{20}^+$  are absent. In addition, although  $\{\text{RuF}_5\}_4$  does not give an ESR spectrum, due to spin-pairing in the tetrameric ring, the red material shows a broad featureless peak. This evidence, although not conclusive, strongly suggests that the red material may be a trimeric form of ruthenium pentafluoride  $\{\text{RuF}_5\}_3$  comparable to the previously reported  $\{\text{MoF}_5\}_3$  [15]. This can only be confirmed by an X-ray crystal structure analysis, but, to date, attempts to obtain a single crystal structure analysis have been unsuccessful.

Efforts to prepare volatile rhodium fluorides in dynamic systems have not previously been very successful. The hexafluoride has not been obtained in a flow system and attempts to prepare the pentafluoride by direct fluorination of the metal powder at low temperatures have produced only small quantities. Our flow fluorination of rhodium metal was much slower than that of osmium, iridium, platinum or ruthenium and 30% of the metal remained unreacted in the nickel boat even after 12h. As in the case of the fluorination of

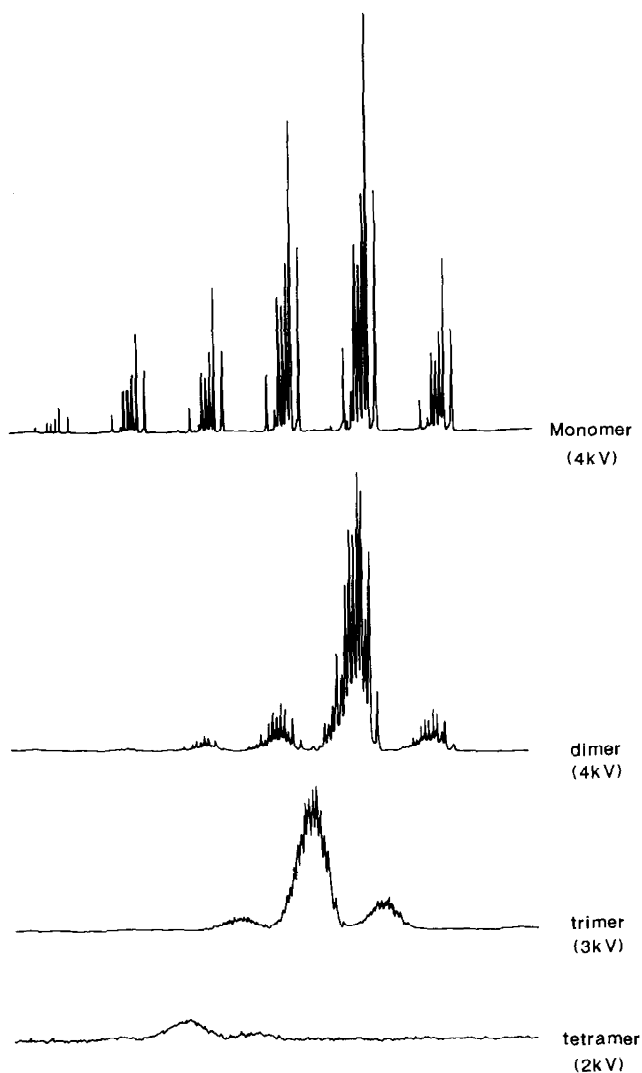


Fig. 3. Mass spectrum of  $\text{RuF}_5$  (conditions: 70 eV, 90 °C).

ruthenium powder, the fluorination of rhodium gave a red glassy material ( $\text{RhF}_5$ ) in trap 1 and a red-brown powder ( $\text{RhF}_6$ ) in trap 2.

The flow fluorination of palladium metal gave no volatile products, the nickel boat containing a black solid which was analysed chemically as  $\text{Pd}^{\text{II}}[\text{Pd}^{\text{IV}}\text{F}_6]$ .

## Conclusions

Flow fluorinations using careful experimental procedures, *in situ* drying and hydrogenation of the metal ( $M = \text{Ru}, \text{Rh}, \text{Os}, \text{Ir}, \text{Pt}$ ) and well-seasoned

quartz glassware, conveniently affords the highly reactive platinum group metal hexafluorides in preparative quantities and high yields. The flow fluorination of ruthenium metal yields green tetrameric  $\text{RuF}_5$  and a dark red glassy material believed to be trimeric  $\text{RuF}_5$ , as well as  $\text{RuF}_6$ .

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