Preparation and Characterization of Tetrakis(tricarbonyldifluororuthenium), Tricarbonyltrifluororuthenium, and Bis(tricarbonyldifluororuthenium–ruthenium pentafluoride)

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The ruthenium carbonyl fluorides, $[\{Ru(CO)_3F_2\}_4]$, $[Ru(CO)_3F_3]$, and $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ have been prepared in high yield. I.r. spectroscopy, magnetic susceptibility, and e.s.r. spectroscopy have shown that $[Ru(CO)_3F_3]$ is monomeric but that the structure of $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ is closely related to that of $[\{Ru(CO)_3F_2\}_4]$ and $(RuF_5)_4$, which have been previously characterized by single-crystal *X*-ray diffraction as fluorine-bridged tetramers.

RUTHENIUM carbonyl chlorides, bromides, and iodides are well known.[1,2] Although several carbonyl fluorides of other transition metals have been reported,[3-8] only one carbonyl fluoride of ruthenium has been unambiguously characterized.[9] We now report a study in which two different methods have been used for the preparation of carbonyl fluorides of ruthenium: (*i*) fluorination of $[Ru_3(CO)_{12}]$ with XeF_2 in Genetron 113 (1,1,2-trichlorotrifluoroethane) or anhydrous hydrogen fluoride as solvents; and (*ii*) carbonylation of ruthenium pentafluoride in a dynamic system. The reaction of $[Ru_3(CO)_{12}]$ and XeF_2 in the mole ratio 1 : 3 in Genetron 113 or HF solvents yields $[\{Ru(CO)_3F_2\}_4]$ at room temperature, whereas, in ratios greater than or equal to 1 : 4.5, $[Ru(CO)_3F_3]$ is produced. Reaction of $[Ru_3(CO)_{12}]$ in Genetron 113 with elemental fluorine[10] also yields $[Ru(CO)_3F_3]$. The considerable danger of explosion, however, led to abandonment of this method as a satisfactory preparative route. At higher temperatures a different reaction takes place. The reaction of a large excess of XeF_2 and $[Ru_3(CO)_{12}]$ at 100 °C yields the adduct $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$. This compound is also formed by carbonylation of RuF_5 at 200 °C in a flow system.

I.r. spectra of solid ruthenium carbonyl fluorides in Nujol mulls in the 400—2 500 cm^{-1} region (wavenumbers in cm^{-1})

$[\{Ru(CO)_3F_2\}_4]$	$[Ru(CO)_3F_3]$	Assignment	$[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$	Description
2 140s	2 148s	ν_1 (a_1)	2 196s	CO str.
			2 157vw	^{13}CO str.
2 060s, br	2 072s,br	ν_3 (e)	2 122ms	CO str.
1 998w(sh)	1 995w(sh)			^{13}CO str.
			722w	
652m	649w	ν_2 (a_1)	654ms	(Ru–F) str.
594m	596m	ν_4 (e)		(Ru–F) str.
532ms	544ms			(Ru–C) str. and CO bend.
502s	503ms		553ms	
484s	486w(sh)			

RESULTS

Reaction of $[Ru_3(CO)_{12}]$ *with* XeF_2 *in a* 1 : 3 *Mole Ratio: the Preparation of* $[\{Ru(CO)_3F_2\}_4]$.—The reaction of $[Ru_3(CO)_{12}]$ (1 mol) with XeF_2 (3 mol) in a Pyrex glass apparatus at room temperature using dry Genetron 113 as solvent yielded an air-sensitive, involatile, yellow solid, and carbon monoxide and xenon were liberated. The overall stoicheiometry of the reaction is represented by equation (1).

$$\tfrac{4}{3}[Ru_3(CO)_{12}] + 4XeF_2 \xrightarrow{\text{r.t.}} [\{Ru(CO)_3F_2\}_4] + 4Xe + 4CO \quad (1)$$

The same reaction also occurred in Kel-F [polychlorotrifluoroethylene)] apparatus using anhydrous HF as solvent. Powder photographs of the yellow solid produced in these reactions are identical to a photograph of the product of the high-pressure carbonylation of RuF_5 supplied by Marshall *et al.*[9] and $\sin^2\theta$ values correspond with those obtained from the single-crystal *X*-ray diffraction study on $[\{Ru(CO)_3F_2\}_4]$.[9] The i.r. spectrum (see Table) is also identical to that of $[\{Ru(CO)_3F_2\}_4]$ formed by the reaction of RuF_5 with CO as reported by Marshall *et al.*[9,10]

According to the crystallographic study[9] the symmetry of the molecular unit, $[\{Ru(CO)_3F_2\}_4]$, in the solid state is D_{2d}. An i.r. spectrum based on D_{2d} symmetry, however, would be more complex than that obtained (Table). The crystallographic study indicates that the three carbonyls about each ruthenium are *facial* and that the C–O bond lengths are essentially equivalent. Local symmetry about each ruthenium atom can, therefore, be approximated to C_{3v}. This should give rise to three normal modes of vibration, A_1 and E, for the CO group. Assignment of our i.r. spectrum on this basis is straightforward. The peak in the ν(CO) region at 2 140 cm^{-1} can be unambiguously associated with A_1 and that at 2 060 cm^{-1} is, therefore,

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[1] J. A. McCleverty, *J. Organometallic Chem.*, 1973, **48**, 351.

[2] E. Benedetti, G. Braca, G. Sbrana, F. Salvetti, and B. Grassi, *J. Organometallic Chem.*, 1972, **37**, 361.

[3] D. M. Bruce, A. J. Hewitt, J. H. Holloway, R. D. Peacock, and I. L. Wilson, in preparation.

[4] T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 1973, **12**, 1437.

[5] T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 1970, **9**, 2611.

[6] D. M. Bruce, J. H. Holloway, and D. R. Russell, *J.C.S. Chem. Comm.*, 1973, 321.

[7] T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 1972, **11**, 2563.

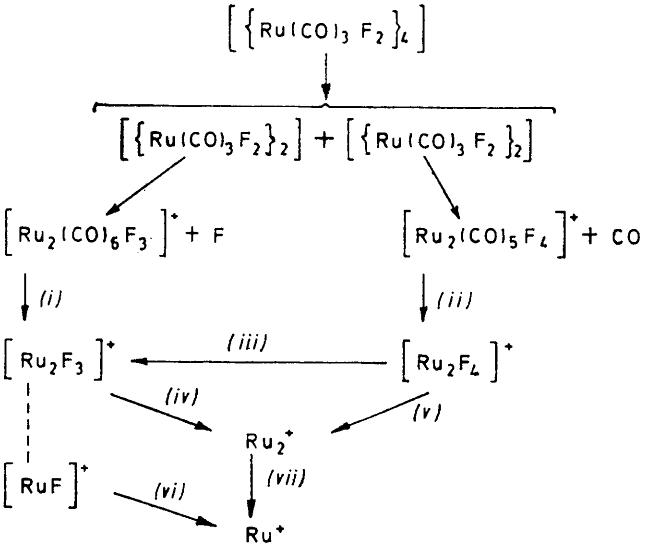
[8] T. A. O'Donnell, K. A. Phillips, and A. B. Waugh, *Inorg. Chem.*, 1973, **12**, 1435.

[9] C. J. Marshall, R. D. Peacock, D. R. Russell, and I. L. Wilson, *Chem. Comm.*, 1970, 1643.

[10] C. J. Marshall, Ph.D. Thesis, Leicester University, 1972.

attributed to the *E* mode. A more precise approach would be to regard the local symmetry about the ruthenium as C_1, in which case the *E* vibrational mode would be expected to be split into two *A* vibrational modes. Splitting was not apparent in our spectra, but the peak at 2 060 cm^{-1} is broad and it seems probable that the splitting is small. The weak band at 1 998 cm^{-1} can probably be attributed to ν(^{13}CO), the splitting being consistent with that found for gaseous CO.

The frequencies of the two i.r. bands in the ν(Ru–F) region of the spectrum are too high to be attributed to bridging fluorine atoms, and hence must be associated with the single terminal fluorine on each ruthenium. If local symmetry is again considered, only one i.r. band would be expected. If, however, the spectrum is interpreted on the basis of D_{2d} symmetry for the molecular unit, which would take into account coupling interactions within the tetramer, two bands would be expected. We are therefore inclined to assign the spectra as B_2 (652 cm^{-1}) and *E* (594 cm^{-1}). The three bands in the 450—550 cm^{-1} region of the spectrum can be interpreted as being due to deformation and ν(Ru–C) stretching modes. It seems reasonable to assign the band of lowest frequency, at 484 cm^{-1}, to ν(Ru–C) in keeping with previous assignments on ruthenium carbonyls.[11] Our spectrum has a close similarity to those of tricarbonyldihalogenoruthenium compounds, $[Ru_2(CO)_6X_4]$ (X = Cl, Br, or I),[12] which are dimeric and it is clear that the close similarity is due to the occurrence of approximate C_{2v} local symmetry about the *fac*-M(CO)$_3$ units within the dimers.



SCHEME 1 (*i*), −6 CO; (*ii*), −5 CO; (*iii*), −F; (*iv*), −3 F; (*v*), −4 F; (*vi*), −F; (*vii*), −Ru

Chemical analysis confirmed the empirical Ru(CO)$_3$F$_2$ formulation and, as expected, an e.s.r. signal could not be obtained from a solution of the compound in anhydrous HF at temperatures down to 77 K. The mass spectrum of $[\{Ru(CO)_3F_2\}_4]$ can be explained in terms of simultaneous fragmentation of $[Ru_2(CO)_6F_3]^+$ and $[Ru_2(CO)_5F_4]^+$ (Scheme 1). The two species presumably arise from dissociation of $[\{Ru(CO)_3F_2\}_4]$ into two $[Ru(CO)_3F_2]$ units as shown. The absence of masses greater than $[Ru_2(CO)_6F_3]^+$ in the spectrum is almost certainly due to loss of the parent $[\{Ru(CO)_3F_2\}_4]$ as it dissociates in the inlet system.

Reaction of $[Ru_3(CO)_{12}]$ *with* XeF$_2$ *in a* 1 : ⩾4.5 *Mole Ratio: the Preparation of* $[Ru(CO)_3F_3]$.—When the mole ratio of $[Ru_3(CO)_{12}]$ and XeF$_2$ was increased from 1 : 3 to 1 : ⩾4.5, reaction at room temperature in either dry Genetron 113 or anhydrous HF solvent yielded an air-sensitive buff solid. Carbon monoxide and xenon were liberated during the reaction. The overall stoicheiometry is represented by equation (2).

$$[Ru_3(CO)_{12}] + 4.5XeF_2 \xrightarrow[\text{r.t.}]{CCl_2FCClF_2\text{ or HF}} 3[Ru(CO)_3F_3] + 4.5Xe + 3CO \quad (2)$$

The formulation $[Ru(CO)_3F_3]$ for the buff solid was confirmed by analytical, e.s.r., and magnetic-susceptibility data. The magnetic susceptibility at 298 K was $\chi = 7.63 \times 10^{-8}$ m^3 kg^{-1}. The effective magnetic moment at 298 K is 1.92 B.M.* and is consistent with a ruthenium(III) ion having one unpaired electron in a trigonally distorted $^2T_2$ ground state.[13] A frozen solution of the compound in anhydrous HF at 77 K gave an e.s.r. spectrum typical of an axially symmetric species having two *g* features. No hyperfine coupling was observed and presumably any coupling to fluorine is small and lost within the linewidth (ΔH 100 G). The derived spin-Hamiltonian parameters are $g_\parallel$ 1.809 and $g_\perp$ 2.286. The e.s.r. spectrum showed that the complex is a monomeric *facial* isomer, since the *meridional* isomer would have a spectrum exhibiting three distinct *g* features.[14] In SClFO$_2$ a similar spectrum was obtained having $g_\parallel$ 1.850 and $g_\perp$ 2.237. The small shifts in $g_\parallel$ and $g_\perp$ arise from the effects of differing solvation. This has been observed previously, for example in *mer*-$[OsCl_3(PBu^n_2Ph)_3]$.[14]

Although the i.r. data are similar to those observed for $[\{Ru(CO)_3F_2\}_4]$ (Table), the ν(CO) bands were shifted to higher frequency and the unambiguous monomeric nature of the compound permits the assignment of the i.r. spectrum on the basis of C_{3v} symmetry. The two strong bands in the ν(CO) region are associated with A_1 (2 148 cm^{-1}) and *E* (2 072 cm^{-1}) vibrational modes as are the bands in the ν(Ru–F) region of the spectrum, A_1 (649 cm^{-1}) and *E* (596 cm^{-1}). Again, the weak band at 1 995 cm^{-1} can probably be attributed to ν(^{13}CO). The three bands at 544, 503, and 486 cm^{-1} can be attributed to δ(Ru–C–O) deformation and ν(Ru–C) stretching modes as in the case of $[\{Ru(CO)_3F_2\}_4]$.

High-temperature Reactions of RuF$_5$ *with* CO *and* $[Ru_3(CO)_{12}]$ *with Excess of* XeF$_2$; *the Preparation of* $[\{Ru(CO)_3F_2\cdot RuF_5\}_2]$.—The reaction of RuF$_5$ with carbon monoxide in a flow system at 200 °C has been reported to yield a yellow-brown moisture-sensitive non-volatile solid of composition $[Ru(CO)F_{3.5}]$.[15] We repeated this reaction and obtained an air-sensitive involatile buff solid. I.r. spectra of the volatile products showed that CF$_2$O is

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* 1 B.M. ≈ 9.27 × 10^{-24} A m^2, 1 G = 10^{-4} T.

[11] C. O. Quicksall and T. A. Spiro, *Inorg. Chem.*, 1968, **7**, 2365.

[12] B. F. G. Johnson, R. D. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 792.

[13] B. N. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198.

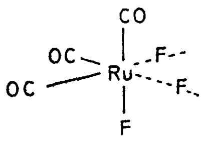
[14] A. Hudson and M. J. Kennedy, *J. Chem. Soc.* (*A*), 1969, 1116.

[15] R. D. W. Kemmitt, R. D. Peacock, and I. L. Wilson, *Chem. Comm.*, 1968, 772.

produced in the reaction. The overall stoicheiometry is represented by equation (3).

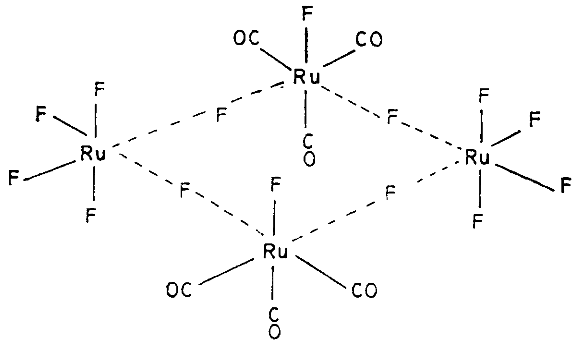
$$4RuF_5 + 9CO \xrightarrow[\text{flow system}]{200\,°C} [\{Ru(CO)_3F_2\cdot RuF_5\}_2] + 3CF_2O \quad (3)$$

Analysis of the buff solid confirmed the empirical formula, $Ru(CO)_3F_2\cdot RuF_5$. The i.r. data for the solid are summarized in the Table. The spectrum exhibited two strong features. In the carbonyl region the two strong bands at 2 196 and 2 122 cm^{-1} can be correlated with the A_1 and E vibrational modes of a *fac*-$Ru(CO)_3$ species in an octahedral environment. This points to there being an octahedral $Ru(CO)_3F_3$ unit, (I), in the molecule similar to that found in $[\{Ru(CO)_3F_2\}_4]$. The weak band at 2 157 cm^{-1} can again be attributed to $\nu(^{13}CO)$. The band at 654 cm^{-1} is close to that observed for ν_3 in salts of the $[RuF_6]^-$ anion.[16] This suggests that it might be assigned to $\nu_3(T_{1u})$ of an approximately octahedral RuF_6 unit. On this basis a tetrameric formulation, $[\{Ru(CO)_3F_2\cdot RuF_5\}_2]$, (II), seems reasonable and a satisfactory interpretation of the spectrum is possible in these terms.



(I)

The overall validity of the spectroscopic interpretation is further justified by the bulk susceptibility, $\chi = 2.45 \times 10^{-7}$ m^3 kg^{-1} at 298 K, which yields a value of $\mu_{eff.} = 4.45$ B.M. per two Ru atoms. This strongly supports formulation (II) since each $Ru(CO)_3F_2$ unit can be regarded as $Ru^{II}(d^6)$ and each RuF_5 unit as $Ru^V(d^3)$. Thus, the paramagnetism may be imagined as deriving from two ruthenium(v) atoms in each molecule and the magnetic moment arises from a Ru^{II}/Ru^V pair. The value of $\mu_{eff.}$ so derived is entirely consistent with a $^4T_1$ ground state of Ru^V distorted by an axially symmetric crystal field.[17] Furthermore, there can be no significant antiferromagnetic interaction between ruthenium(v) ions as there is in $[(RuF_5)_4]$ ($\mu_{eff.}$ 1.795 B.M. per Ru^V ion)[18] since the experimental magnetic moment has not been reduced below the spin-only value. This means that the RuF_5 units in the tetramer cannot be adjacent to one another, again confirming structure (II).



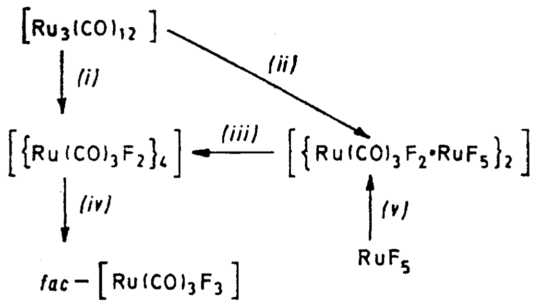
(II)

E.s.r. measurements on solutions of the compound in HF at 77 K showed only a very broad absorption extending over several thousand gauss. Broadening of this magnitude could arise from a lowering of symmetry or electron-exchange mechanisms and this is not inconsistent with the tetrameric formulation. The compound is air sensitive; exposure to traces of moisture causes immediate darkening, due to RuO_2 formation, and RuO_4 is evolved. This is typical of ruthenium(v) species.[18,19] An *X*-ray powder diffraction pattern was obtained which exhibited some similarities to that of $[\{Ru(CO)_3F_2\}_4]$. The compound was also prepared when a large excess of XeF_2 was mixed with $[Ru_3(CO)_{12}]$ in dry Genetron 113 and allowed to stand overnight at 100 °C in a Carius tube. The overall stoicheiometry of this reaction is represented by equation (4).

$$\tfrac{4}{3}[Ru_3(CO)_{12}] + 7XeF_2 \xrightarrow[100\,°C]{CCl_2FCClF_2} [\{Ru(CO)_3F_2\cdot RuF_5\}_2] + 7Xe + 10CO \quad (4)$$

DISCUSSION

A reaction scheme summarizing our preparations of ruthenium carbonyl fluorides is shown in Scheme 2.



SCHEME 2 (*i*), $3XeF_2$, r.t.; (*ii*), large excess of XeF_2, 100 °C; (*iii*), CO, 100 atm, 200 °C; (*iv*), excess of XeF_2; (*v*), CO, 200 °C

Of the three compounds formed, the structure of $[\{Ru(CO)_3F_2\}_4]$ has been shown[9] to be related to the RuF_5 tetramer,[20] three of the terminal fluorine atoms on each ruthenium being replaced by carbonyl groups. This means that there is approximately octahedral symmetry about each ruthenium in structure (I), the three carbonyls being *facial* and two equatorial fluorine atoms forming bridges with the neighbouring rutheniums. The arrangement is satisfactory not only because it permits an approximate octahedral configuration but also because it gives rise to the familiar 18-electron system favoured by many carbonyl compounds. All our physical data on the solid confirm the *X*-ray evidence and our e.s.r. data suggest that the tetramer remains intact in anhydrous HF. The tetrameric form of tricarbonyldifluororuthenium differs from those suggested

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[16] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 1959, 2762.

[17] B. N. Figgis, M. Gerloch, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.* (*A*), 1968, 2086.

[18] J. H. Holloway and R. D. Peacock, *J. Chem. Soc.*, 1963, 527.

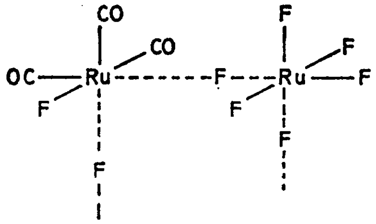
[19] M. A. Hepworth, R. D. Peacock, and P. L. Robinson, *J. Chem. Soc.*, 1954, 1197.

[20] J. H. Holloway, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1964, 644.

for the chloro- and iodo-analogues [12] and the reported [21] structure of the bromo-compound which are dimeric, although the overall octahedral arrangement about the ruthenium atoms is much the same.

Tetrameric structures amongst transition-metal pentafluorides are common whereas some of the related pentachlorides are dimeric [*e.g.* $(MoF_5)_4$, *cf.* $(MoCl_5)_2$]. In the ruthenium carbonyl fluoride system the tricarbonyl difluoride is tetrameric and all the evidence points to $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ having a similar structure while the tricarbonyl dichloride is dimeric. This suggests the possibility of a general tetrameric structural preference for carbonyl fluorides but a dimeric arrangement for the related carbonyl chlorides for certain metals. In particular it may well be that investigation of molybdenum and tungsten carbonyl fluorides will reveal structures related to $[\{Ru(CO)_3F_2\}_4]$.

Formulation of the compound of empirical formula $Ru(CO)_3F_2{\cdot}RuF_5$ as a tetrameric unit $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ cannot be definitive without a full single-crystal *X*-ray diffraction investigation. However, our i.r. and magnetic evidence in favour of the tetrameric formulation is particularly good and it is further strengthened by the e.s.r. and *X*-ray powder data. Furthermore, the close correlation between the ν(Ru–F) vibrational frequency, at 654 cm^{-1}, with that of $[RuF_6]^-$ salts [16] and the high value of the ν(CO) stretching frequencies in $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ compared with $[\{Ru(CO)_3F_2\}_4]$, point to the compound possessing a degree of ionic character. The molecule can perhaps be regarded as a tetramer composed of $[Ru(CO)_3F]^+$ and $[RuF_6]^-$ units in which the fluorine bridges are significantly unsymmetrical {the (Ru–F) bridging bonds in $[RuF_6]^-$ being shorter than those in the $[Ru(CO)_3F]^+$ unit, (III)}.



(III)

The existence of two differing oxidation states within the same compound has already been observed in the related rhenium carbonyl fluoride, $[Re(CO)_5F{\cdot}ReF_5]$. Again the strongly contrasting stabilising influence of the carbonyl and fluoride ligands can be clearly seen. Preliminary investigations on other transition metals [22] suggest that this phenomenon could be common in carbonyl fluoride systems.

Of the carbonyl fluorides we have prepared $[Ru(CO)_3F_3]$ is exceptional in that all evidence points to it being monomeric. Its relation to $[\{Ru(CO)_3F_2\}_4]$ and $[\{Ru(CO)_3F_2{\cdot}RuF_5\}_2]$ lies in the approximately octahedral symmetry and the *facial* arrangement of the carbonyls about the ruthenium. It is clear that the *facial* arrangement in the monomer, as in the other ruthenium carbonyl fluorides, is determined by the π acidity of the CO ligand. Most other examples of non-carbonyl-containing monomeric ruthenium(III) compounds [23,24] are *meridonal* isomers. Notable exceptions are $[RuCl_3(NPhH_2)_3]$ and $[Ru(py)_3Cl_3]$ [23] and in addition the osmium chloride derivative $[OsCl_3(PBu^n{}_2Ph)_3]$,[14] which have all been shown by e.s.r. measurements to have *facial* geometries. The existence of a 17-electron, monomeric, *facial*-$[Ru(CO)_3F_3]$ compound is, therefore, not without parallels in ruthenium and osmium chemistry.

EXPERIMENTAL

Starting Materials.—Dodecacarbonyl-*triangulo*-triosmium was obtained from Strem Chemicals Inc. of Danvers, Massachussetts, U.S.A. Its purity was monitored by i.r. and Raman spectroscopy. Xenon difluoride was prepared by pressure synthesis in a nickel vessel at 300 °C with the starting ratio Xe : F_2 equal to 2 : 1. It was purified by repeated trap to trap sublimation in a dynamic vacuum and checked for purity by i.r. spectroscopic examination of the vapour and Raman spectroscopy on the solid. Ruthenium pentafluoride was prepared and purified as described previously.[18] Carbon monoxide was supplied by Air Products and was dried by passing over KOH and P_2O_5. Genetron 113 (1,1,2-trichlorotrifluoroethane) was obtained from Fluka A.G. and was purified by distillation from P_2O_5.

Reactions.—Reactions were carried out using vacuum techniques in glass or Kel-F [polychlorotrifluoroethylene] apparatus. The compounds $[Ru_3(CO)_{12}]$ and RuF_5 were loaded into the reaction vessels in a nitrogen-circulating dry-box (Lintott Engineering Limited, Horsham, Essex). Xenon difluoride was added from glass containers by sublimation in a dynamic vacuum or by direct loading in a dry-box.

(a) XeF_2 *with* $[Ru_3(CO)_{12}]$. In each reaction the calculated amount of XeF_2 required for the reaction was added to $[Ru_3(CO)_{12}]$ (*ca.* 0.15 g) partially dissolved in Genetron 113 or anhydrous HF (*ca.* 3 cm^3). The reactants were allowed to stand at room temperature until gas evolution had ceased. Reactions were complete within 1 h. The course of reaction was interrupted periodically by cooling to liquid-nitrogen temperature. The volatile products, xenon and carbon monoxide, were removed at −80 °C. On completion of the reaction the solvent was removed by distillation under a static vacuum.

(b) CO *with* RuF_5. Carbon monoxide was passed over RuF_5 contained in a Pyrex U tube equipped with TF2/13 Rotaflo Teflon-barrelled valves at 200 °C. Unchanged CO was burned at the end of the reaction train.

(c) XeF_2 *with* $[Ru_3(CO)_{12}]$ *in a Carius tube.* Xenon difluoride (0.3 g) was mixed with $[Ru_3(CO)_{12}]$ (0.1 g) in a predried Pyrex Carius tube in the dry-box. Dry Genetron 113 was condensed into the tube which was then sealed under vacuum. The Carius tube was allowed to stand at 100 °C overnight.

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[21] S. Merlino and G. Montagnoli, *Acta Cryst.*, 1968, **B24**, 424.

[22] A. J. Hewitt, J. H. Holloway, S. Misra, and I. L. Wilson, unpublished work.

[23] J. Chatt, G. J. Leigh, and A. P. Storace, *J. Chem. Soc.* (*A*), 1971, 1380.

[24] L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1771.

X-*Ray Diffraction Measurements.*—*X*-Ray diffraction studies were made by the powder technique. Specimens were mounted in evacuated Pyrex capillaries and photographed on a Philips 11.64 cm diameter camera with Cu-K_α filtered radiation.

Spectroscopic Methods.—I.r. spectra of pulverized solid Nujol mulls sandwiched between KBr plates were recorded using a Perkin-Elmer 225 grating spectrometer. E.s.r. measurements were made on samples in Kel-F tubes using a Varian E3 spectrometer. Mass spectra were obtained on an A.E.I. MS9 spectrometer.

Magnetic-susceptibility Measurements.—These were carried out using a standard Gouy balance.

Analyses.—These were determined by a commercial analyst (Found: C, 15.0; F, 16.45. Calc. for $[\{Ru(CO)_3F_2\}_4]$: C, 16.1; F, 17.0. Found: C, 15.45; F, 24.8. Calc. for $[Ru(CO)_3F_3]$: C, 14.9; F, 23.6. Found: C, 8.20; F, 31.6. Calc. for $[\{Ru(CO)_3F_2 \cdot RuF_5\}_2]$: C, 8.60; F, 31.8%).

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