

Synthesis and characterisation of ruthenium carbonyl fluorides

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The oxidative fluorination of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 in anhydrous HF afforded, in solution, *cis*- $[\text{RuF}_2(\text{CO})_4]$ as the major product with $[\text{RuF}(\text{CO})_5]^+$, $[\text{Ru}_2\text{F}_4(\text{CO})_7]$, $[\{\text{RuF}(\text{CO})_4\}_2(\mu\text{-F})]^+$, *mer*- and *fac*- $[\text{RuF}_3(\text{CO})_3]^-$, $[\{\text{RuF}_2(\text{CO})_3\}_n]$ and $[\{\text{RuF}_2(\text{CO})_3\}(\mu\text{-F})\{\text{Ru}(\text{CO})_5\}]^+$ as minor products, all of which have been characterised by ^{13}C , ^{19}F and $^{13}\text{C}\{^{19}\text{F}\}$ NMR spectroscopies. Removal of the HF solvent *in vacuo* yielded tetrameric $[\{\text{RuF}_2(\text{CO})_3\}_4]$.

Recently, there has been renewed interest in fluoride as a ligand in low-oxidation-state transition-metal co-ordination chemistry.^{1–3} Particular interest in transition-metal carbonyl fluoride complexes in this laboratory has its origins in the 1970s⁴ and we have recently described the controlled fluorination of $[\text{Os}_3(\text{CO})_{12}]$ ⁵ and $[\text{Ir}_4(\text{CO})_{12}]$ ⁶ by XeF_2 in solution at room temperature and characterised the reaction intermediates and products by a combination of multinuclear NMR spectroscopic techniques. The principal product in the osmium system is *cis*- $[\text{OsF}_2(\text{CO})_4]$, which cannot be oxidised at room temperature, but which loses carbon monoxide on removal of the solvent.⁵ In contrast, for iridium, the product *fac*- $[\text{IrF}_3(\text{CO})_3]$ can be isolated on removal of the solvent, but it can also be readily oxidised by XeF_2 in solution at room temperature to iridium(v) salts.⁶ The related fluorination of $[\text{Ru}_3(\text{CO})_{12}]$ in a 1:3 metal complex: XeF_2 ratio in anhydrous HF or 1,1,2-trichlorotrifluoroethane solvent yields,⁷ on removal of solvent, the crystallographically characterised $[\{\text{RuF}_2(\text{CO})_3\}_4]$,⁸ increasing the metal complex: XeF_2 ratio to 1:4.5 gave a buff solid in which, it was claimed, on the basis of ESR and magnetic susceptibility data, oxidation to the unusual 17-electron complex $[\text{RuF}_3(\text{CO})_3]$ had occurred.⁷ We had found no comparable species during our study of the fluorination of $[\text{Os}_3(\text{CO})_{12}]$ and, consequently, have reinvestigated the fluorination of ruthenium carbonyl to identify any intermediates formed during the fluorination and to establish whether oxidation of the ruthenium(II) complex could be observed at low temperatures.

Experimental

Proton, ^{13}C and ^{19}F NMR spectroscopic studies were carried out on a Bruker AM300 spectrometer at 300.13, 75.47 and 282.41 MHz respectively and on a Varian VXR600S at the University of Edinburgh SERC Ultra-High Field NMR service at 600.0, 150.87 and 564.29 MHz respectively. Spectra were recorded on samples in FEP (perfluoroethylene-propylene copolymer) NMR tubes (outside diameter 4 mm) held coaxially in 5 mm precision glass NMR tubes containing a small quantity of $(\text{CD}_3)_2\text{CO}$ as lock substance. Proton and ^{13}C NMR spectra were referenced to external SiMe_4 and ^{19}F NMR spectra to external CFCl_3 using the high-frequency-positive convention. The IR spectra were recorded using a Digilab FTS40 spectrometer on samples as dry powders between KBr discs.

All preparative manipulations were carried out on a metal vacuum line with facilities to connect Teflon and FEP reaction vessels. Xenon difluoride was prepared by the static fluorination of xenon gas under UV irradiation at room temperature.⁹ Hydrogen fluoride (ICI) was purified by vacuum transfer, dried by repetitive fluorination at room temperature and stored in Kel-F tubes over dry BiF_5 .¹⁰ Weighed samples of $[\text{Ru}_3(\text{CO})_{12}]$ and XeF_2 were loaded, in a dry-box (<10 ppm water), into prefluorinated FEP reactors (outside diameter 4 mm, 0.5 mm

wall thickness) fitted with poly(tetrafluoroethylene) valves (Production Techniques Ltd.). After evacuation on the vacuum line, HF (*ca.* 0.3 cm³) was condensed into the reaction tube at -196°C . The HF was allowed to melt and the reaction mixture was held at *ca.* -60°C , with judicious venting of the xenon gas evolved, until no further gas evolution was observed. After the reaction was complete, either the reaction vessel was heat-sealed as described previously¹¹ for NMR studies, or the HF solvent was removed *in vacuo* to leave solid samples which were manipulated in a dry-box.

Results and Discussion

Triruthenium dodecacarbonyl was found to be insufficiently soluble and unreactive in simple halogenocarbons to allow an investigation of its fluorination. However, we have shown¹² that $[\text{Ru}_3(\text{CO})_{12}]$ dissolves slowly in anhydrous HF at room temperature with protonation and that this is a convenient solvent in which to investigate the fluorination of $[\text{Os}_3(\text{CO})_{12}]$.⁵ Therefore, reactions with molar ratios of 1:1 through to 6:1 XeF_2 : $[\text{Ru}_3(\text{CO})_{12}]$ in anhydrous HF were investigated; fluorination occurred at *ca.* -60°C with the liberation of xenon gas and the generation of a number of HF-soluble ruthenium complexes. In contrast to the earlier report⁷ that ruthenium carbonyl undergoes discrete stepwise fluorination at XeF_2 :metal complex ratios of 3:1 and 4.5:1 affording initially $[\{\text{RuF}_2(\text{CO})_3\}_4]$ and subsequently $[\text{RuF}_3(\text{CO})_3]$, we now find that, at ratios of >3:1 and at room temperature or below, the solutions contain unreacted XeF_2 as identified by ^{19}F NMR spectroscopy. The ruthenium complexes in solution all contain Ru^{II} (see below) and we can find no evidence for the oxidation of these complexes by XeF_2 at room temperature. The earlier evidence for $[\text{RuF}_3(\text{CO})_3]$ was limited to mainly ESR and magnetic susceptibility data and we now suggest that the claim for this complex at room temperature was in error. At ratios <3:1, ^1H NMR spectra showed the presence of unreacted $[\text{RuH}(\text{CO})_5]^+$ and $[\text{Ru}_3\text{H}(\text{CO})_{12}]^+$ ¹² indicating that the fluorination of ruthenium carbonyl is essentially the same as that of osmium carbonyl.⁵ It is important to note that the fluorination reactions occur rapidly at *ca.* -60°C whilst the protonation of ruthenium carbonyl by HF only occurs slowly at room temperature,¹² *i.e.* it is unlikely that $[\text{RuH}(\text{CO})_5]^+$ and $[\text{Ru}_3\text{H}(\text{CO})_{12}]^+$ play a significant role in these fluorination reactions.

At the 3:1 molar ratio neither XeF_2 nor protonated ruthenium species were observed in the NMR spectra and the reaction was judged to have reached completion. However, in contrast to the ^{19}F NMR spectra for the products obtained on fluorination of $[\text{Os}_3(\text{CO})_{12}]$, the room-temperature ^{19}F NMR spectrum revealed a number of broad unresolved resonances in the region associated with fluorine bound to a low-valent metal centre which sharpened only slightly on cooling. Better quality spectra could only be obtained if the species formed in the

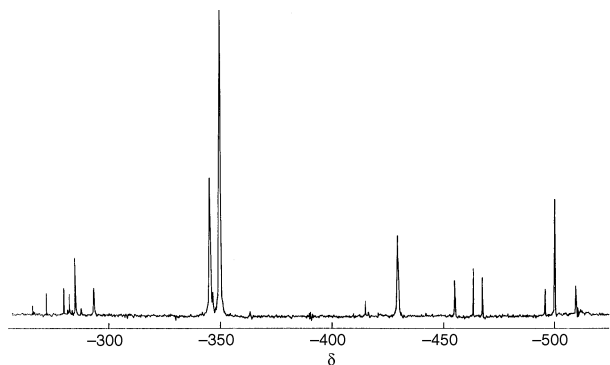


Fig. 1 The 282.41 MHz ^{19}F NMR spectrum of products from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 (1:3) in anhydrous HF at -60°C

reaction were kept cool (*ca.* -60°C) throughout and after the reaction, suggesting that the HF-soluble products may be fluxional and/or unstable at room temperature, which may account for the discrepancy with the earlier work.

At -60°C the ^{19}F NMR spectrum was dominated by a large singlet at $\delta -349.0$ and 15 minor resonances with various multiplicities (Table 1, Fig. 1). The assignment of many of these resonances may be made by comparison with data for the related osmium and iridium carbonyl fluoride complexes. In particular, we have identified that fluorine *trans* to carbonyl, fluorine *trans* to fluorine and bridging fluoride ligands at low-valent metal centres generally have characteristic ^{19}F NMR chemical shift values and that fluorine ligands in similar chemical environments have very similar chemical shifts. Additionally, all the couplings (Table 1), although slightly smaller in magnitude than those identified in the osmium and iridium systems, are indicative of *cis*- $^2J_{\text{FF}}$ interactions.

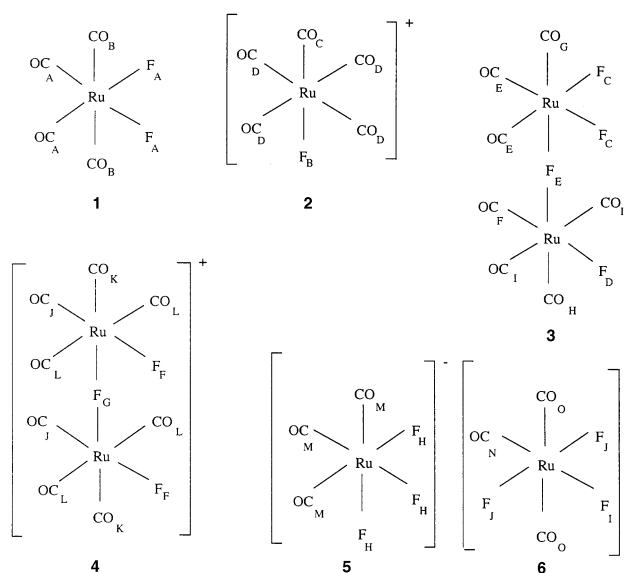
The large singlet at $\delta -349.0$ is in a region characteristic of fluoride *trans* to carbonyl at a metal centre with a ' $\text{F}_2(\text{CO})_4$ ' first co-ordination sphere and is attributed to F_A in complex **1** which is isostructural with *cis*- $[\text{OsF}_2(\text{CO})_4]$, the major species obtained from the fluorination of osmium carbonyl. Complex **1** was first postulated 19 years ago,⁴ and completes the series of complexes *cis*- $[\text{RuX}_2(\text{CO})_4]$ ($\text{X} = \text{halide}$).¹³ A low-frequency shift of *ca.* 80 ppm is indicative of a reduction in the number of fluorines bound at the metal centre and the singlet at $\delta -429.5$ is, therefore, attributed to F_B in complex **2** [we have previously reported the analogous osmium(II) complex]. A high-frequency shift of *ca.* 70 ppm is indicative of an increase in the number of fluorines bound at the metal centre. Three resonances in a 2:1:1 ratio, the doublet at $\delta -285.7$ [indicative of a ' $\text{F}_3(\text{CO})_3$ ' ligand arrangement], the doublet at $\delta -345.8$ and the doublet of triplets at $\delta -455.5$, for which the extremely low-frequency chemical shift indicates a bridging fluoride ligand, show related couplings of 61 and 85 Hz respectively, and are assigned to the three fluorine environments in $[\text{Ru}_2\text{F}_3(\mu\text{-F})(\text{CO})_7]$ **3**. The fourth analogue of a complex identified in the fluorination of osmium carbonyl, $[\text{Ru}_2\text{F}_2(\mu\text{-F})(\text{CO})_8]^+$ **4**, is identified from the doublet and triplet resonances, in a 2:1:1 ratio, at $\delta -344.9$ and -500.8 ($^2J_{\text{FF}} = 73$ Hz). Complexes **1–4** and their osmium(II) counterparts³ show a remarkable consistency in their values for $\delta(\text{F}_{\text{terminal}})$, confirming that $\delta(\text{F})$ remains a valuable tool for structural identification in this area. The synergy between the data for the osmium and ruthenium systems is poorer, however, in the $\delta(\text{F}_{\text{bridging}})$ region, where $\delta(\mu\text{-F})$ is *ca.* 40 ppm to lower frequency for ruthenium than for osmium; $\delta(\text{F}_\text{C})$ at -500.8 represents one of the lowest ^{19}F chemical shifts reported. This may indicate subtle differences in the electronic nature at the metal centres in these complexes which is supported by the smaller $^2J_{\text{FF}}$ coupling constants for ruthenium and may account for our difficulties in acquiring NMR data for the ruthenium system at room temperature.

The formation of $[\text{MF}(\text{CO})_5]^+$ ($\text{M} = \text{Ru}$ or Os) in the fluorination of $[\text{M}_3(\text{CO})_{12}]$, with a higher CO to metal ratio than that of

Table 1 Fluorine-19 NMR data for the ruthenium carbonyl fluorides*

Complex	$\delta(^{19}\text{F})$	$^2J_{\text{FF}}/\text{Hz}$	Assignment
1 $[\text{RuF}_2(\text{CO})_4]$	-349.0 (s)	—	F_A
2 $[\text{RuF}(\text{CO})_5]^+$	-429.5 (s)	—	F_B
3 $[\text{Ru}_2\text{F}_4(\text{CO})_7]$	-285.7 (d)	61	F_C
	-345.8 (d)	85	F_D
	-455.5 (dt)	61, 85	F_E
4 $[\{\text{RuF}(\text{CO})_4\}_2(\mu\text{-F})]^+$	-344.9 (d)	73	F_F
	-500.8 (t)	73	F_G
5 <i>fac</i> - $[\text{RuF}_3(\text{CO})_3]^-$	-294.1 (s)	—	F_H
6 <i>mer</i> - $[\text{RuF}_3(\text{CO})_3]^-$	-272.5 (t)	55	F_I
	-495.9 (d)	55	F_J
7 $[\{\text{RuF}_2(\text{CO})_3\}_4]$	-279.6 (t)	61	F_K
	-467.8 (t)	61	F_L
8 $[\{\text{RuF}_2(\text{CO})_3(\mu\text{-F})\}\{\text{Ru}(\text{CO})_5\}]^+$	-283.4 (d)	63	F_M
	-463.7 (t)	63	F_N

* Recorded in anhydrous HF at -60°C at 282.41 MHz.



the starting material, suggests that carbonyl loss and scavenging must have occurred. The comparable hydride complexes^{12,14,15} have been observed in the protonation of the parent carbonyls where it has been suggested that metal-metal bond cleavage is associated with carbonyl loss and scavenging around the cluster.¹⁵ It is likely that a similar process may be occurring during fluorination of $[\text{M}_3(\text{CO})_{12}]$, but when $\text{M} = \text{Os}$ we found no evidence for mononuclear species with lower CO to metal ratios than that of the starting material.⁵ However, for $\text{M} = \text{Ru}$, perhaps as a fortuitous result of keeping the reaction mixture at a very low temperature throughout the fluorination process and data collection, resonances attributable to both *mer*- and *fac*- $[\text{RuF}_3(\text{CO})_3]^-$ are observed. A singlet at $\delta -294.1$, in a region characteristic of a ' $\text{F}_3(\text{CO})_3$ ' ligand arrangement, can only be rationalised in terms of the *fac* isomer **5**. The triplet and doublet resonances, in a 1:2 ratio, at $\delta -272.5$ [also indicative of the ' $\text{F}_3(\text{CO})_3$ ' arrangement] and the extremely low frequency $\delta -495.9$ (suggestive of *F trans* to *F*) showing couplings of 55 Hz can be rationalised in terms of the *mer* isomer **6**. All of these resonances have similar chemical shift values to those seen for the isostructural, neutral, iridium(III) complexes where the *mer* isomer, which contains the apparently less favourable *F trans* to *F* arrangement, isomerises to the thermodynamically favoured *fac* isomer on standing at room temperature.⁶

The assignment of the final four resonances is tentative since ruthenium analogues of all of the previously established metal carbonyl fluoride complexes have already been identified. These resonances occur in two, related, pairs: triplets at $\delta -279.6$ and -467.8 ($^2J_{\text{FF}} = 61$ Hz) and a doublet at $\delta -283.4$ and a triplet at $\delta -463.7$ ($^2J_{\text{FF}} = 63$ Hz). The multiplicities and chemical shift

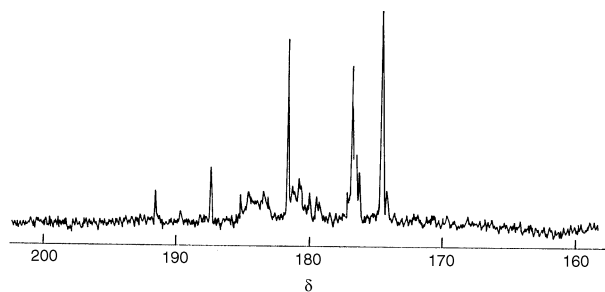


Fig. 2 The 75.47 MHz ^{13}C NMR spectrum of products from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 (1:3) in anhydrous HF at -60°C

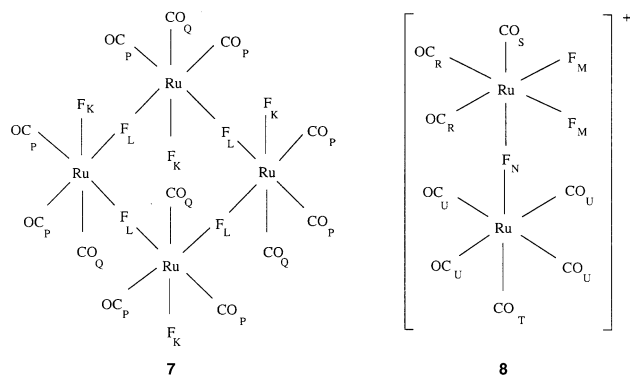


Table 2 Carbon-13 NMR data for the ruthenium carbonyl fluorides^a

Complex	$\delta(^{13}\text{C})^b$	Assignment
1	178.9(80)	CO_A
	174.5	CO_B
2	174.3(90)	CO_C
	172.4	CO_D
3^c	181.6(120)	CO_E
	178.4(110)	CO_H
	174.3	CO_I
4	178.8(110)	CO_K
	178.6(100)	CO_J
	174.4	CO_L
5	<i>d</i>	—
6	181.9(110)	CO_N
	175.0	CO_O
7^c	182.1(110)	CO_Q
8	<i>d</i>	—

^a Recorded in anhydrous HF at -50°C at 150.87 MHz. ^b $\text{trans-}^2J_{\text{FC}}$ (± 5 Hz) coupling constants in parentheses when resolved (see text); $\text{cis-}^2J_{\text{FC}}$ too small to be measured. ^c Additional carbonyl environments not assigned (see text). ^d No carbonyl assignments possible (see text).

values offer indications of reasonable assignments. By analogy with the data for F_H , F_I and F_C , the resonances at $\delta -279.6$ and -283.4 must arise from fluorine ligands co-ordinated to metal centres with ' $\text{F}_3(\text{CO})_3$ ' ligand environments whilst, by analogy to the chemical shifts for F_E and F_G , those at $\delta -463.7$ and -467.8 must arise from bridging fluoride ligands. Consequently, the coupled triplet resonances are tentatively assigned to F_K and F_L in the crystallographically characterised fluoride-bridged tetramer **7**. Alternative assignments, which would produce triplet resonances for both the bridging and terminal fluoride ligands, would include other oligomeric $[\{\text{RuF}_2(\text{CO})_3\}_n]$ formulations. However, although the dimers $[\{\text{RuX}_2(\text{CO})_3\}_2]$ ($\text{X} = \text{Cl}, \text{Br}$ or I) are well established,¹³ there are no precedents for comparable, late transition-metal bis-(fluoride-bridged) dimers and there are numerous examples of fluoride-bridged tetramers, so we prefer to assign these resonances to **7**. The final two resonances, from their multiplicity and chemical shifts, are most appropriately assigned to F_M and F_N in the novel fluoride-bridged cation **8**, a structural isomer of **4**.

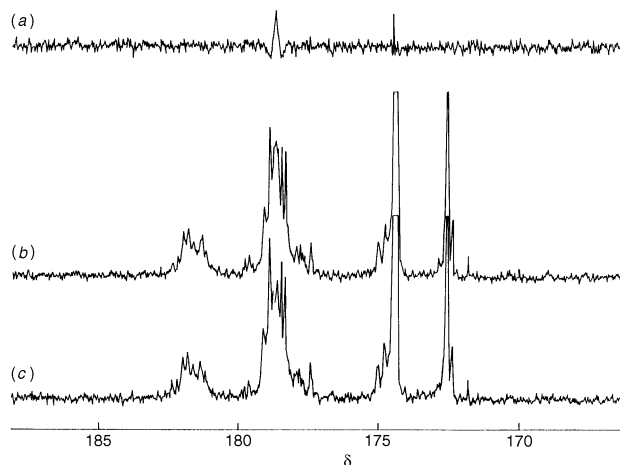


Fig. 3 The 150.87 MHz ^{13}C NMR spectra of products from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 (1:3) in anhydrous HF at -50°C : (a) difference (b) - (c), (b) selective ^{19}F -decoupled at $\delta -349.0$ and (c) fully coupled

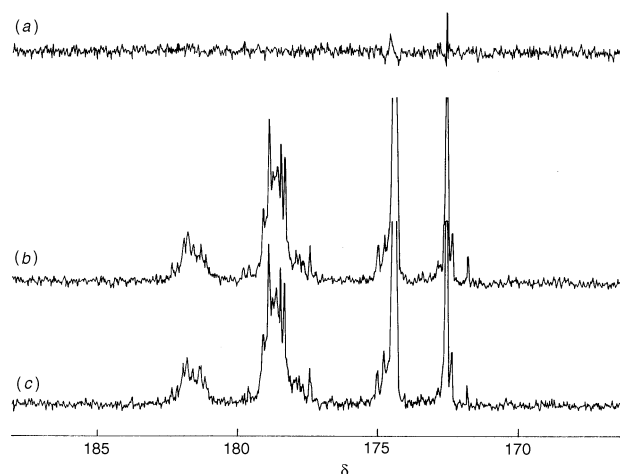


Fig. 4 The 150.87 MHz ^{13}C NMR spectra of products from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 (1:3) in anhydrous HF at -50°C : (a) difference (b) - (c), (b) selective ^{19}F -decoupled at $\delta -429.5$ and (c) fully coupled

The integration ratio for the cationic and anionic complexes is not 1:1, which indicates, as suggested in the fluorination of osmium carbonyl,⁵ the presence of other counter ions such as $[\text{HF}_2]^-$ in solution.

Confirmation of the characterisation of the carbonyl fluoride complexes of osmium and iridium has been obtained by analysing selective ^{19}F -decoupled ^{13}C NMR spectra.^{5,6} We have undertaken the same experiment for the ruthenium system. However, since we have identified from the ^{19}F NMR spectra eight ruthenium carbonyl fluoride complexes, which contain 21 different carbonyl environments, the evidence from these experiments is not as conclusive as those obtained for the osmium and iridium systems. Fourteen selective $^{13}\text{C}\{-^{19}\text{F}\}$ NMR spectra were recorded at -50°C at the EPSRC Ultra-High Field NMR service at the University of Edinburgh; data are recorded in Table 2 and representative spectra in Figs. 2-6. From our earlier experiments we note that $^2J_{\text{F trans C}}$ couplings are larger (ca. 85 Hz) than $^2J_{\text{F cis C}}$ couplings (ca. <10 Hz) and that increasing or decreasing the number of fluoride ligands bound to a metal centre has a similar (to the variation in the ^{19}F NMR data), but much smaller magnitude, high- or low-frequency effect on the ^{13}CO chemical shift. However, for ruthenium carbonyl fluorides, $\delta(^{13}\text{CO trans to F})$ occurs at a lower frequency than $\delta(^{13}\text{CO trans to CO})$, which is the opposite to that found for both osmium and iridium.

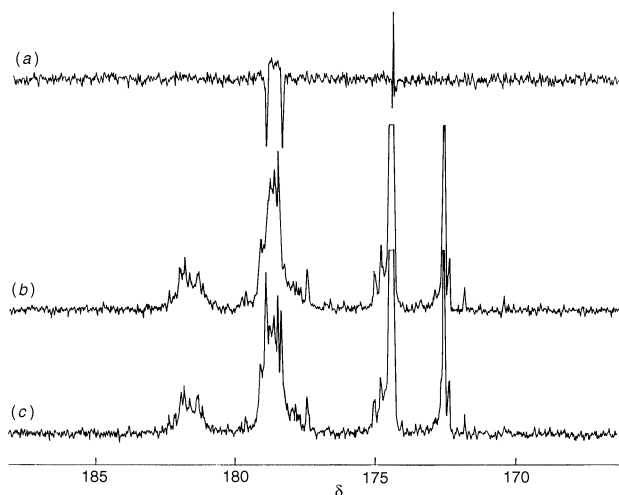


Fig. 5 The 150.87 MHz ^{13}C NMR spectra of products from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 (1:3) in anhydrous HF at -50°C : (a) difference spectrum (b) – (c), (b) selective ^{19}F -decoupled at $\delta -500.8$ and (c) fully coupled

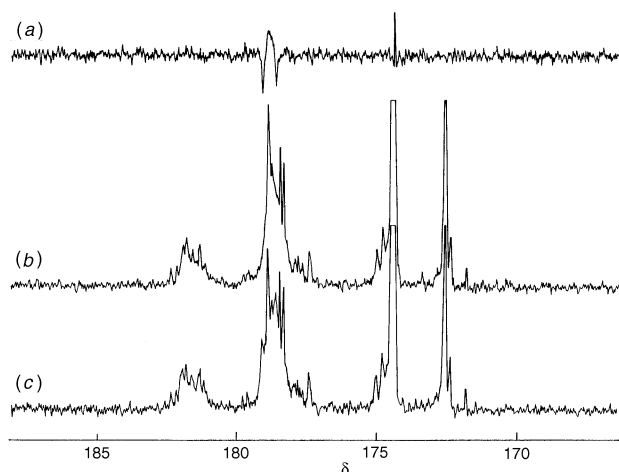


Fig. 6 The 150.87 MHz ^{13}C NMR spectra of products from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with XeF_2 (1:3) in anhydrous HF at -50°C : (a) difference spectrum (b) – (c), (b) selective ^{19}F -decoupled at $\delta -344.9$ and (c) fully coupled

Overall, the fully coupled ^{13}C NMR spectrum (Fig. 2) shows four broad, overlapping, multiplets at *ca.* δ 181.5, 179.0, 174.5 and 172.5, arising from the numerous carbon monoxide ligands in complexes **1–8**. The generally sharper multiplets at δ 174.5 and 172.5 arise, predominantly, from CO *trans* to CO ligands for which the $^2J_{\text{FC}}$ couplings are small and unresolved. The shift to lower frequency results from reducing the number of fluorides co-ordinated to the metal centre; *i.e.* a chemical shift of δ 174.5 indicates a ' $\text{F}_2(\text{CO})_4$ ' metal environment whilst that of δ 172.5 indicates one of ' $\text{F}(\text{CO})_5$ '. The ^{13}C NMR data, recently reported, for the final member in this series, $[\text{Ru}(\text{CO})_6]^{2+}$ [δ 166.1 (in SbF_5)],¹⁶ also fits this trend. The higher-frequency multiplets, in descending frequency, arise from CO *trans* to F in ' $\text{F}_3(\text{CO})_3$ ' and ' $\text{F}_2(\text{CO})_4$ ' ligand arrangements. However, the data analysis is further complicated by the observation that the multiplet at δ 174.5 also contains signals arising from CO *trans* to F for complexes with a ' $\text{F}(\text{CO})_5$ ' first co-ordination sphere.

Irradiation at each ^{19}F resonance can be taken in turn. Decoupling at the intense singlet at $\delta -349.0$ (Fig. 3) changes the appearance of the multiplets at δ 179.0 and 174.5. The exact chemical shift data for CO_A and CO_B can be determined from difference spectra. However, the exact values for the $^2J_{\text{FC}}$ coupling constants cannot be determined since that for CO_B is too small to be resolved and since the signal for CO_A arises from a second-order AXX' spin system. Nevertheless, this selective-

decoupling experiment confirms the assignment for F_A to **1**. Similarly, decoupling at $\delta -429.5$ removes a large (*trans*) coupling at δ 174.3 and a smaller (*cis*) coupling at δ 172.4 (Fig. 4) where the ^{13}C resonances are readily assigned to CO_C and CO_D , respectively, in the cationic complex **2**. The first-order nature of the *trans* coupling allows the value for $^2J(\text{CO}_\text{C}-\text{F})$ (90 Hz) to be determined from a difference spectrum.

In complex **3** there are five distinct carbonyl environments, of which only three can be unequivocally assigned. Irradiation at the bridging fluoride ligand ($\delta -455.5$) removes large *trans* couplings at δ 178.4 and 181.6 which are assigned to CO_H and CO_G respectively which offers clear evidence for the variation in $\delta(^{13}\text{C})$ with ligand environment. In addition, this irradiation removes smaller *cis* couplings at δ 174.3 which may be assigned to the only CO *trans* to CO ligands, CO_I . Unfortunately, the effect of irradiating at the terminal fluorides F_C and F_D is unclear and hence an assignment for CO_E and CO_F cannot be made.

For complex **4** all three types of carbonyl ligands can be assigned by the decoupling experiments (Figs. 5 and 6). Irradiation at $\delta -344.9$ (F_F) removes a large doublet coupling at δ 178.6 (CO_J) and a smaller doublet coupling at δ 174.4 (CO_L), whilst irradiation at $\delta -500.8$ (F_C) removes a comparable coupling to CO_L (which offers further support to the assignment of the ^{19}F resonances at $\delta -344.9$ and -500.8 to complex **4**) and a large doublet coupling at δ 178.8 (CO_K). Unfortunately, neither decoupling experiment showed removal of the smaller *cis* couplings for the resonances at δ 178.6 and 178.8 (*i.e.* for F_C on CO_J and for F_F on CO_K), but this is not surprising in view of the large number of overlapping resonances in the CO *trans* to F [$\text{F}_2(\text{CO})_4$] region.

Complexes **5–8** are all very minor components in the system and data from the decoupling experiments are not conclusive, particularly when the carbonyl resonances are expected to have second-order character; CO_M , CO_P , CO_R . Irradiation at F_H changes the shape of the multiplet at δ 181.5 but no definitive assignment for CO_M is possible. Irradiation at F_I removes doublet couplings at δ 181.9 and 175.0 which are assigned to CO_N and CO_O respectively; irradiation at F_J also affects these resonances, but the magnitude of the coupling constants cannot be resolved. Irradiation at F_K removes a large doublet coupling at δ 182.1, assigned to CO_Q , but although irradiation at F_L also changes the shape of the broad resonance at δ 181.5, no definitive assignment for CO_P is possible.

Removal of the solvent from any of the 3:1 molar ratio reaction mixtures, those held at -60°C during the spectroscopic investigations and those warmed to room temperature, affords a pale yellow, moisture-sensitive, solid identified as the crystallographically characterised $[\{\text{RuF}_2(\text{CO})_3\}_4]$ by IR spectroscopy. This polymerisation of the major, solution-stable, species *cis*- $[\text{RuF}_2(\text{CO})_4]$ with the loss of CO is analogous to that observed in the related osmium system. This fluorination of $[\text{Ru}_3(\text{CO})_{12}]$ to give, mainly, *cis*- $[\text{RuF}_2(\text{CO})_4]$ is comparable to oxidations with the heavier halogens (X_2 ; $\text{X} = \text{Cl}$, Br or I) which also give *cis*- $[\text{RuX}_2(\text{CO})_4]$. These complexes also polymerise with loss of CO to afford oligomeric complexes $[\text{Ru}_2\text{X}_4(\text{CO})_6]$, $[\text{Ru}_3\text{X}_6(\text{CO})_{12}]$ and the polymer $[\{\text{RuX}_2(\text{CO})_2\}_n]$.¹³ We note that to polymerise the *cis*- $[\text{RuX}_2(\text{CO})_4]$ complexes, particularly for the heavier halogens, elevated temperatures are generally required, which indicates that the fluoride complex exhibits greater carbonyl lability and may offer scope for the further development of low-valent ruthenium fluoride chemistry.

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References

- 1 K. G. Caulton, O. Eisenstein, J. T. Poulton, M. P. Sigalas and W. E. Streib, *Inorg. Chem.*, 1994, **33**, 1476.
- 2 R. G. Bergman, P. Burger and J. E. Veltheer, *J. Am. Chem. Soc.*, 1995, **117**, 12478.
- 3 M. Ahlgren, M. Haukka and T. A. Pakkanen, *J. Chem. Soc., Dalton Trans.*, 1996, 1972.
- 4 D. M. Bruce and J. H. Holloway, *Transition Met. Chem.*, 1978, **3**, 317 and refs. therein.
- 5 S. A. Brewer, J. H. Holloway and E. G. Hope, *J. Chem. Soc., Dalton Trans.*, 1994, 1067.
- 6 S. A. Brewer, A. K. Brisdon, J. H. Holloway, E. G. Hope, L. A. Peck and P. G. Watson, *J. Chem. Soc., Dalton Trans.*, 1995, 2945.
- 7 A. J. Hewitt, J. H. Holloway, R. D. Peacock, J. B. Raynor and I. L. Wilson, *J. Chem. Soc., Dalton Trans.*, 1976, 579.
- 8 C. J. Marshall, R. D. Peacock, D. R. Russell and I. L. Wilson, *Chem. Commun.*, 1970, 1643.
- 9 J. H. Holloway, *Chem. Commun.*, 1966, 22.
- 10 K. O. Christe, W. W. Wilson and C. J. Schack, *J. Fluorine Chem.*, 1978, **11**, 711.
- 11 W. W. Dukat, J. H. Holloway, E. G. Hope, P. J. Townson and R. L. Powell, *J. Fluorine Chem.*, 1993, **62**, 293.
- 12 S. A. Brewer, J. H. Holloway and E. G. Hope, *J. Fluorine Chem.*, 1995, **70**, 167.
- 13 B. F. G. Johnson, R. D. Johnston and J. Lewis, *J. Chem. Soc. A*, 1969, 792.
- 14 J. Knight and M. J. Mays, *J. Chem. Soc. A*, 1970, 711.
- 15 A. J. Deeming, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, 1970, 2967.
- 16 C. Wang, B. Bley, G. Balzer-Jöllenbeck, A. R. Lewis, S. C. Siu, H. Willner and F. Aubke, *J. Chem. Soc., Chem. Commun.*, 1995, 2071.

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