Synthesis and Characterisation of Osmium Carbonyl Fluorides

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The oxidative fluorination of $[Os_3(CO)_{12}]$ with XeF_2 in anhydrous HF afforded, in solution, *cis*-$[Os(CO)_4F_2]$ as the major product with $[Os(CO)_5F]^+$, $[Os_2(CO)_7F_4]$ and $[Os_2(CO)_8F_3]^+$ as minor products, all of which have been characterised by ^{13}C, ^{19}F and $^{13}C-\{^{19}F\}$ NMR spectroscopies. Removal of the HF solvent *in vacuo* yielded the tetrameric $[\{Os(CO)_3F_2\}_4]$.

There has been considerable interest in transition-metal centres stabilised by only reducing carbonyl and oxidising fluoride ligands, but the unambiguous assignment of the structures of such complexes has been difficult.[1–5] We have had considerable success in using XeF_2 as a fluorinating agent for low-valent transition-metal systems and have prepared and structurally characterised $Re(CO)_5F{\cdot}ReF_5$,[6] $[Re(CO)_6][Re_2F_{11}]$[6,7] and $[Ir(CO)_2(COF)(PEt_3)_2F][BF_4]$.[8] The related $[\{Ru(CO)_3F_2\}_4]$ has also been structurally characterised.[9] Very recently we have characterised, by multinuclear NMR studies, *mer*- and *fac*-$[Ir(CO)_3F_3]$, prepared by the reaction of XeF_2 with $[Ir_4(CO)_{12}]$ in anhydrous HF.[10] Although carbonyl halide complexes of osmium have been extensively studied for the heavier halogens,[11] there is only one example of an osmium carbonyl fluoride complex, $[OsF(CO)_2(NNPh)(PPh_3)_2]$,[12] synthesised and characterised as part of an extensive study of azido-stabilised transition-metal species. Here, we report the controlled oxidative fluorination of $[Os_3(CO)_{12}]$ by XeF_2 in solution, and identify a range of osmium carbonyl fluoride complexes.

Experimental

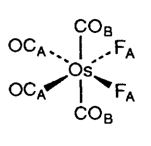
Proton, ^{13}C and ^{19}F NMR spectroscopies were carried out on a Bruker AM300 spectrometer at 300.13, 75.47 and 282.41 MHz respectively and on a Varian VXR600S at the University of Edinburgh SERC ultra-high field NMR service at 600.0, 150.87 and 564.29 MHz respectively. Spectra were recorded on samples 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 $[^2H_6]$acetone 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. Initial ^{19}F NMR spectra were recorded for *ca.* 400 scans between δ +200 and −600 using 125 000 Hz windows (*ca.* 7 Hz per point), acquisition times of 0.5 s without relaxation delays and pulse widths of 3 μs (28°). Higher-resolution spectra were recorded for narrower spectral widths dependent upon the experiment; typical data-point resolutions for 4000 scan acquisitions were *ca.* 1 Hz. Fourier transforms were carried out without exponential smoothing. Typical ^{13}C NMR spectra were recorded for *ca.* 10 000 scans using 20 000 Hz windows (*ca.* 1 Hz per point), acquisition times of 0.4 s with 0.8 s relaxation delays and pulse widths of 2 μs (30°). Fourier transforms were carried out with Lorentzian line broadening (1 Hz). X-Ray powder diffractions were carried out on a Philips 11.64 cm diameter camera using nickel-filtered Cu-Kα radiation and IR spectra were recorded for dry powders squashed between KBr discs on a Digilab FTS40 FTIR spectrometer.

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.[13] Hydrogen fluoride (Fluorochem) was purified by vacuum transfer, dried by repeated fluorination at room temperature and stored in Kel-F tubes over dry BiF_5.[14] Approximately 15% ^{13}CO-enriched $[Os_3(CO)_{12}]$ was prepared by stirring a solution of $[Os_3(CO)_{12}]$ (1 g, 1.1 mmol) (Aldrich) in toluene (50 cm^3) for approximately 2 weeks at 60 °C under 1 atm (101 325 Pa) of 99.5% ^{13}CO [MSD isotopes (Cambrian Gases)].[15] Weighed samples of $[Os_3(CO)_{12}]$ and XeF_2 were loaded, in a dry-box (< 10 ppm H_2O), into prefluorinated FEP reactors (4 mm outside diameter, 0.5 mm wall thickness) fitted with a poly(tetrafluoroethylene) valve (Production Techniques). After evacuation on the vacuum line, HF (*ca.* 0.3 cm^3) was condensed into the reaction tube at −196 °C. The HF was allowed to melt and, on warming, reaction ensued as evidenced by gas evolution. The reaction was controlled by judicious cooling in a solid CO_2–acetone bath and venting of the xenon gas generated. After the reaction was complete, the reaction mixture was warmed cautiously to room temperature and then the reactor was either heat-sealed as described previously[16] for NMR studies, or the HF solvent was removed *in vacuo* to leave solid samples which were manipulated in a dry-box for IR spectroscopy and X-ray powder diffraction.

Results and Discussion

Triosmium dodecacarbonyl was found to be insufficiently soluble and unreactive in simple halogenocarbons to allow an investigation of its fluorination by XeF_2 in these solvents. However, we have shown that $[Os_3(CO)_{12}]$ dissolves slowly in anhydrous HF at room temperature with protonation,[17] and that anhydrous HF acts as a catalyst for fluorination reactions with XeF_2 *via* the F–Xe–F·H–F adduct.[16] Therefore, reactions with molar ratios of 1 : 1 through to 5 : 1 XeF_2 : $[Os_3(CO)_{12}]$ in anhydrous HF were investigated; fluorination occurred at *ca.* −50 °C with the liberation of xenon gas and the generation of a number of HF-soluble osmium complexes. At ratios of > 3 : 1, unreacted XeF_2 was identified in the HF solution by ^{19}F NMR spectroscopy, while at ratios of < 3 : 1, ^1H NMR spectra showed the presence of unreacted $[OsH(CO)_5]^+$ and $[Os_3H(CO)_{12}]^+$[17,18] in solution. It is important to note that the fluorination reactions occur rapidly at −50 °C whilst the protonation of osmium carbonyl by HF only occurs slowly at room temperature,[17] *i.e.* it is unlikely that $[OsH(CO)_5]^+$ or $[Os_3H(CO)_{12}]^+$ play a significant role in these fluorination reactions.

At the 3:1 molar ratio the reaction was judged to have reached completion, and the ^{19}F NMR spectrum (Table 1, Fig. 1) at room temperature was dominated by a large singlet at δ −342.5 (F_A), attributed to complex **I**, with 6 less intense resonances of similar integral intensity. A singlet at δ −433 (F_B) is assigned to complex **II**. Two doublets at δ −266 (F_C) and −340 (F_D) and a doublet of triplets at δ −412.5 (F_E), in the ratio of 2:1:1, showing related couplings of 86.4 and 117 Hz respectively, are ascribed to complex **III**. A doublet at δ −336 (F_F) and a triplet at δ −465 (F_G), with a ratio of 2:1, both showing coupling of 112 Hz, are attributed to complex **IV**. Hence, there are one major and three minor species in solution. These resonances, highly shielded from the usual ^{19}F NMR chemical-shift region, are characteristic of a fluoride ligand co-ordinated directly to a low-valent transition-metal centre.[10,19,20] Low-temperature ^{19}F NMR experiments had no significant effect on these signals, except that the peaks sharpened allowing easier identification of the multiplet structures. The ^{13}C NMR spectra, of the 3:1 molar ratio samples with *ca.* 15% ^{13}CO enrichment showed, both at room temperature and −60 °C, a large number of signals and assignment was only possible by recording selective ^{13}C-{^{19}F} NMR spectra (Table 2, Figs. 2–5) as employed previously in the characterisation of *mer*- and *fac*-$[Ir(CO)_3F_3]$.[10]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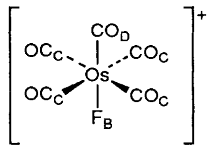
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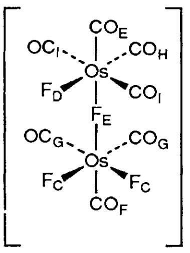
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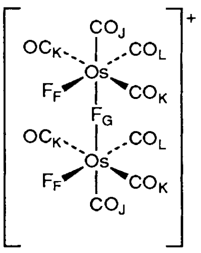
IV

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

Complex	δ(^{19}F)	$^2J_{FF}$/Hz	Assignment
I $[Os(CO)_4F_2]$	−342.5 (s)	—	F_A
II $[Os(CO)_5F]^+$	−433.0 (s)	—	F_B
III $[Os_2(CO)_7F_4]$	−266.0 (d)	86.4	F_C
	−340.0 (d)	117.0	F_D
	−412.5 (d of t)	86.4, 117.0	F_E
IV $[Os_2(CO)_8F_3]^+$	−336.0 (d)	112.0	F_F
	−465.0 (t)	112.0	F_G

* Recorded in anhydrous HF at room temperature at 282.41 MHz.

Irradiation at the sharp singlet in the ^{19}F NMR spectrum at δ −342.5 (F_A) (Fig. 2) sharpened the apparent singlet at δ 162.4 (CO_B) and collapsed most of the multiplet at δ 154.8 (CO_A), the main component of a broad resonance at *ca.* δ 155, to a singlet. (This broad resonance represents a number of ^{13}CO resonances from different osmium carbonyl fluorides, the major contribution of which is from the decoupled singlet at δ 154.8.) Sharpening of the singlet at δ 162.4 indicates removal of a very small fluorine–carbon coupling (typically < 2 Hz) which is characteristic of a *cis*-$^2J_{FC}$ coupling,[10] while the much larger coupling associated with the multiplet at δ 154.8 is typical of *trans*-$^2J_{FC}$ coupling. The ^{13}C chemical shifts support these coupling-constant interpretations where, in the majority of complexes, the ^{13}C resonances for carbonyls *trans* to a one-electron donor are at lower frequencies than carbonyls *trans* to a two-electron donor.[21] We therefore characterise the main product (*ca.* 70%) from the reaction of XeF_2 with $[Os_3(CO)_{12}]$ as the 18-electron *cis*-$[Os(CO)_4F_2]$ **I**, which was first postulated 16 years ago,[2] and which completes the series of complexes *cis*-$[Os(CO)_4X_2]$ (X = halide). For **I**, the ^{13}C NMR resonance for CO_A at δ 154.8, the major component of a number of overlapping resonances, will be a second-order AXX′ multiplet; the *trans*-$^2J_{FC}$ coupling constant of *ca.* 65 Hz (Table 2) can only, therefore, be estimated.

Irradiation at the second sharp singlet in the ^{19}F NMR spectrum at δ −433 (F_B) removes the small (*cis*) doublet coupling at δ 156.3 (CO_C) and the large (*trans*) doublet coupling at δ 149.2 (CO_D) in the ^{13}C NMR spectrum (Fig. 3) indicating that the complex responsible for these signals contains a single fluoride ligand and two types of carbonyl ligands, one *trans* to a one-electron donor and the other, higher frequency resonance, *trans* to a two-electron donor. These resonances are therefore assigned to the novel, cationic $[Os(CO)_5F]^+$ **II** (the counter ion is presumably HF_2^-), which is isoelectronic and isostructural with the well characterised $[W(CO)_5F]^-$[22] and $[Re(CO)_5F]$[7] species. In the fluorination of $[Os_3(CO)_{12}]$, the formation of $[Os(CO)_5F]^+$, with a higher CO to osmium ratio than the starting material, suggests that carbonyl scrambling must have occurred. The comparable hydride complex, $[OsH(CO)_5]^+$, has been observed in the protonation of $[Os_3(CO)_{12}]$,[16,17,23] where it has been suggested that metal–metal bond cleavage is associated with carbonyl scrambling around the cluster.[23] It is likely, therefore, that a similar process may be occurring during the fluorination of $[Os_3(CO)_{12}]$.

Analysis of the coupling constants for the multiplets observed in the ^{19}F NMR spectrum revealed that the doublets at δ −266

Table 2 Carbon-13 NMR data[a] for the osmium carbonyl fluorides

Complex	δ	$^2J(CO_{trans}$–F)/Hz[b]	$^2J(CO_{cis}$–F)/Hz[b,c]	Assignment
I $[Os(CO)_4F_2]$	162.4	—	< 2 (F_A)	CO_B
	154.8[d]	*ca.* 65 (F_A)	—	CO_A
II $[Os(CO)_5F]^+$	156.3	—	7 (F_B)	CO_C
	149.2	62 (F_B)	—	CO_D
III $[Os_2(CO)_7F_4]$[e]	159.7[f]	*ca.* 86 (F_C)[f]	n.r.	CO_G
	156.5	62 (F_C)	n.r.	CO_F[g]
	ca. 155	34 (F_D)	n.r.	CO_H
	152.2	83 (F_E)	n.r.	CO_E[g]
IV $[Os_2(CO)_8F_3]^+$	162.0	—	< 2 (F_G)	CO_K
	154.6	35 (F_G)	n.r.	CO_L
	151.4	87 (F_F)	n.r.	CO_J

[a] Recorded in anhydrous HF at room temperature at 150.87 MHz. [b] ^{19}F NMR resonance in parentheses. [c] n.r. = Not resolved. [d] A second-order AXX′ multiplet, $^2J_{FC}$ approximated. [e] CO_I not observed, see text. [f] A second-order AXX′Y multiplet, $^2J_{CX}$ approximated, $^2J_{CY}$ unresolved. [g] Provisional assignment, see text.

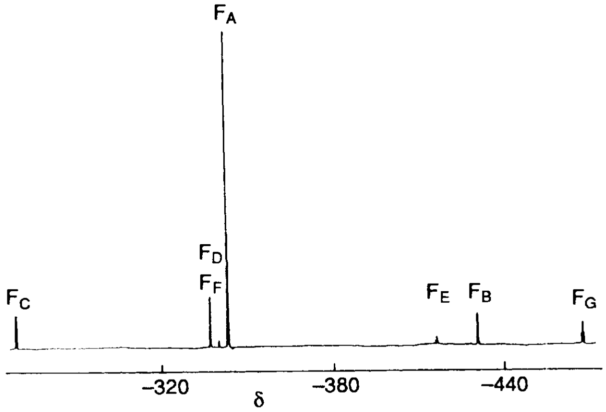

Fig. 1 282.41 MHz ^{19}F NMR spectrum of products from the reaction of [$Os_3(CO)_{12}$] with XeF_2 (1:3) in anhydrous HF

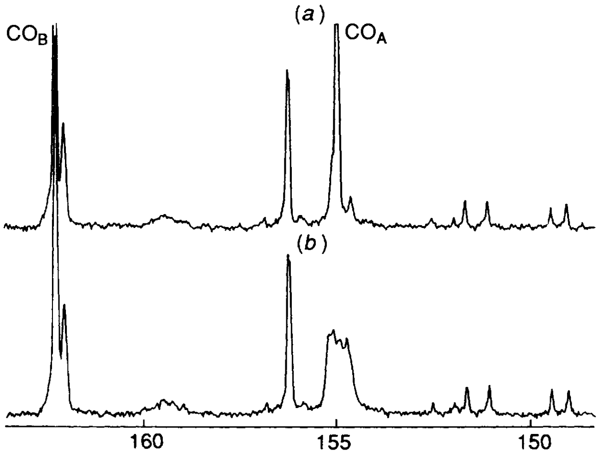

Fig. 2 150.87 MHz ^{13}C NMR spectra of products from the reaction of [$Os_3(CO)_{12}$] with XeF_2 (1:3) in anhydrous HF. (*a*) Selective ^{19}F decoupled at δ −342.5 and (*b*) fully coupled

(F_C) and δ −340 (F_D) are related to the doublet of triplets at δ −412.5 (F_E) in a ratio of intensities 2:1:1. The couplings of 86.4 and 117 Hz are typical of $^2J_{FF}$ couplings.[20] The absence of coupling between the doublets implies the presence of a mono-fluorine-bridged dimer. Complex **III**, [$Os(CO)_3F_2(\mu$-F)-$Os(CO)_4F$], accounts for this ^{19}F NMR data, an assignment which is confirmed by the selective ^{13}C-{^{19}F} NMR data (Fig. 4). Irradiation at the doublet of triplets at δ −412.5 (F_E) removes large doublet couplings on the ^{13}C NMR resonances at δ 152.2 and 156.5, which indicates that this fluorine resonance must be due to a bridging fluoride *trans* to two different carbonyl environments. However, since no *cis*-fluorine–carbon coupling could be resolved on either resonance, the firm assignment of resonances CO_E and CO_F cannot be made without additional evidence. Irradiation at the doublet at δ −266 (F_C) sharpens the broad structureless feature at δ 159.7 to a singlet. The resonance CO_G will be a second-order AXX′Y multiplet, and it is not surprising that coupling to the bridging F_E is unobserved for such a minor component in the solution. Irradiation at the second doublet at δ −340 (F_D) removes large coupling in the broad resonance at *ca.* δ 155 assigned to CO_H. Unfortunately, the ^{13}CO resonance labelled CO_I was not identified in the spectra, presumably because it has a very similar chemical environment to, and is obscured by the resonance for, CO_A. The only couplings to CO_I would be small *cis*-fluorine–carbon couplings and so, even on decoupling, the spectra are not likely to be significantly affected.

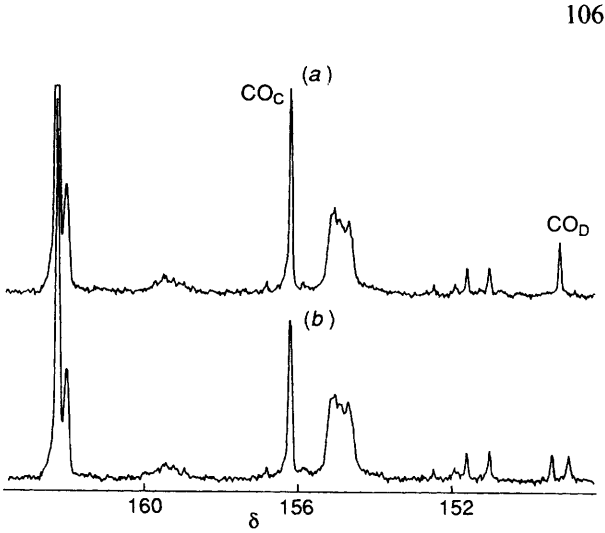

Fig. 3 150.87 MHz ^{13}C NMR spectra of products from the reaction of [$Os_3(CO)_{12}$] with XeF_2 (1:3) in anhydrous HF. (*a*) Selective ^{19}F decoupled at δ −433 and (*b*) fully coupled

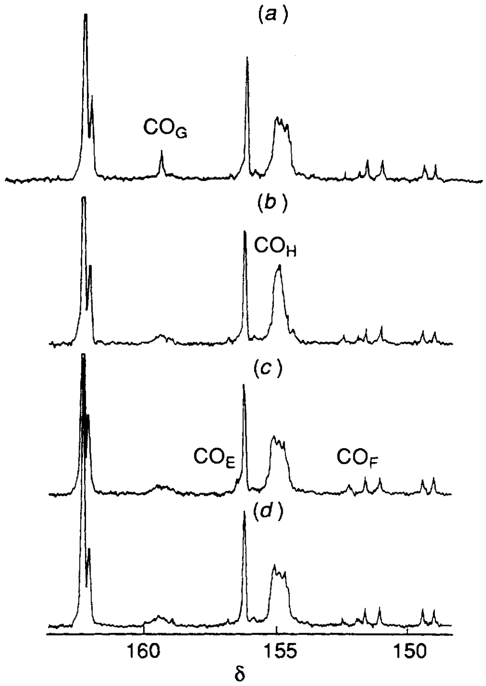

Fig. 4 150.87 MHz ^{13}C NMR spectra of products from the reaction of [$Os_3(CO)_{12}$] with XeF_2 (1:3) in anhydrous HF. Selective ^{19}F decoupled at (*a*) δ −266, (*b*) δ −340 and (*c*) δ −412.5, (*d*) fully coupled

The final two resonances in the ^{19}F NMR spectra are the doublet and triplet at δ −366 (F_F) and δ −465 (F_G), in a 1:2 ratio, which exhibit mutual coupling of 112 Hz (typical of $^2J_{FF}$). During the ^{13}C-{^{19}F} NMR experiment (Fig. 5), irradiation at F_G removes the large (*trans*) doublet coupling at δ 151.4 (CO_J) and causes minor variations in the singlet at δ 162.0 (CO_K) and the broad resonance at *ca.* δ 155 (CO_L). Irradiation at F_F sharpens CO_K, *i.e.* removes a small *cis* coupling, removes a large (*trans*) coupling in the broad resonance at *ca.* δ 155 but has little effect on CO_J. This species, therefore, contains three CO environments as well as two fluorine environments (in a 2:1 ratio) both of which must be *trans* CO. The fluorine-bridged cationic dimer [$Os_2(CO)_8F_3$]$^+$ **IV** (the counter ion is presumably HF_2^-) readily accounts for all of the NMR data, and is a further example of the well established class of fluorine-bridged transition-metal carbonyl fluorides.[6,9,24]

These NMR experiments indicate that there are four, HF-stable, osmium carbonyl fluorides formed in the reaction of [$Os_3(CO)_{12}$] with XeF_2. These are the first examples of osmium(II) complexes stabilized by only carbonyl and fluoride ligands. The experiments were found to be reproducible with

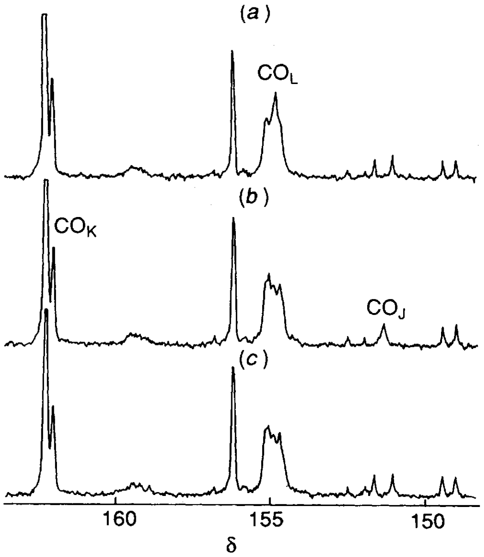

Fig. 5 150.87 MHz ^{13}C NMR spectra of products from the reaction of $[Os_3(CO)_{12}]$ with XeF_2 (1:3) in anhydrous HF. Selective ^{19}F decoupled at (*a*) δ −336 and (*b*) δ −465; (*c*) fully coupled

only minor variations in the product ratios, suggesting that the products are the thermodynamically favoured ones. Unfortunately the addition of Lewis acids (*e.g.* BF_3 or AsF_5) to the solutions of these osmium carbonyl fluorides did not stabilise the cationic complexes but, resulted in the total decomposition of the species, presumably by fluoride-ion abstraction, to afford an insoluble precipitate. In all of these complexes, there are no examples of F_{trans}–F which correlates with our work[10] on the fluorination of $[Ir_4(CO)_{12}]$, where *fac*-$[Ir(CO)_3F_3]$ is the thermodynamically preferred product. In contrast to the work on the fluorination of $[Ir_4(CO)_{12}]$, these osmium carbonyl fluorides are stable to oxidation by XeF_2 which may be accounted for by the stronger M–CO bond for osmium relative to iridium in the respective compounds.

The regions of the ^{19}F NMR spectrum associated with a terminal fluoride *trans* to either a carbonyl or a halide have been established for rhodium and iridium organometallic complexes;[19] typically $^{19}F_{trans}$–CO occurs between δ −270 and −350 and $^{19}F_{trans}$–halide occurs below δ −400. This work extends the ^{19}F NMR data available for low-valent metal fluoride complexes, and although during this study F_{trans}–F environments are not observed, the ^{19}F chemical shift range for F_{trans}–CO is δ −266 to −465. The lowest frequency resonances are readily assigned to bridging-fluoride ligands, but, nevertheless extreme care must be taken in the assignment of a particular resonance in a complicated ^{19}F NMR spectrum of transition-metal fluoride complexes purely on the basis of chemical-shift data. It is interesting to note that F_A, F_D and F_F have very similar ^{19}F NMR chemical shifts and have very similar chemical environments in **I**, **III** and **IV**, *i.e.* they are bound to octahedral osmium(II) metal centres with *cis*-'$(CO)_4F_2$' ligand arrangements. Decreasing the number of fluorines bound to the metal centre causes a low frequency shift (*ca.* 90 ppm for F_B) while increasing the number of fluorines causes a high frequency shift (*ca.* 70 ppm for F_C). We have observed comparable shifts in transition-metal carbonyl fluoride phosphine complexes,[25] and a similar though less pronounced effect is observed for the bridging fluorides F_E and F_G. It may, therefore, be postulated that the electron density at the metal centre determines the ^{19}F NMR chemical shifts in these systems. This is controlled by both the number and configuration of the carbonyl ligands. Comparable, though less pronounced, effects are observed for the ^{13}CO chemical shifts; for a *cis*-'$(CO)_4F_2$' octahedral osmium(II) metal centre, $^{13}CO_{trans}$–CO is at *ca.* δ 162 (CO_B, CO_I, CO_K) and $^{13}CO_{trans}$–F is at *ca.* δ 155 (CO_A, CO_H, CO_L). Decreasing the number of fluorines bound to the metal centre causes a low frequency shift (*ca.* 4–6 ppm, CO_C, CO_D) while increasing the number of fluorines causes a high frequency shift (*ca.* 4–6 ppm, CO_G). This offers a provisional assignment of the two unassignable resonances at δ 156.5 and 152.2 in the ^{13}C NMR spectrum of **III**. Both CO_E and CO_F are *trans* to the bridging fluoride, the former at a *cis*-'$(CO)_4F_2$' metal centre, the latter at a *cis*-'$(CO)_3F_3$', *i.e.* δ 156.5 is the resonance for CO_F while that for CO_E is at δ 152.2.

Removal of the solvent from these 3:1 molar ratio reaction mixtures affords a buff, moisture-sensitive solid. This poorly crystalline material gave an X-ray powder diffraction pattern very similar to that reported for the X-ray crytallographically characterised $[\{Ru(CO)_3F_2\}_4]$[9] suggesting that the solution-stable osmium carbonyl fluorides readily lose CO *in vacuo* and polymerise to afford the analogous fluorine-bridged $[\{Os(CO)_3F_2\}_4]$. A dry-powder IR spectrum recorded for this solid exhibited two carbonyl stretches in the region characteristic of transition-metal carbonyl fluorides[6,7,9,10] as expected for the approximate C_{3v} '$Os(CO)_3$' fragment in the tetramer. Polymerisation of the major species, *cis*-$[Os(CO)_4F_2]$, on removal of the solvent is anomalous when compared to the heavier halide congeners which can all be isolated in the solid state.[11,26] For these complexes, polymerisation to the halide-bridged dimers, $[Os(CO)_3X_2]$, only occurs at elevated temperatures,[26,27] suggesting that the fluoro complex has a greater carbonyl lability. This greater lability is identical to that observed for the related rhenium complexes, $[Re(CO)_5X]$ and $[Re(CO)_3(PPh_3)_2X]$ (X = F, Cl, Br or I).[24,28,29]

Acknowledgements

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