Synthesis and Characterisation of Osmium Carbonyl Fluorides

Stuart A. Brewer, John H. Holloway and Eric G. Hope*
Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

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
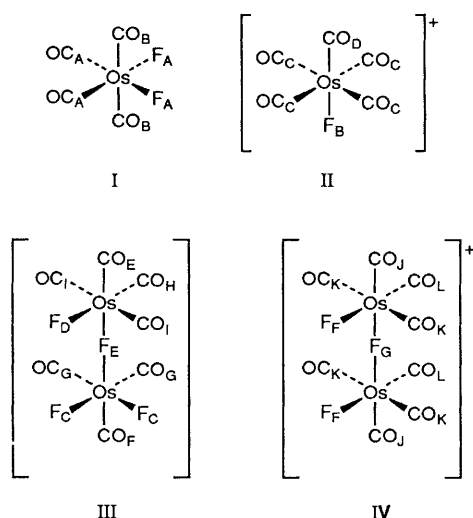
samples with ca. 15% ^{13}CO enrichment showed, both at room temperature and $-60\,^{\circ}$C, a large number of signals and assignment was only possible by recording selective ^{13}C-$\{^{19}$F$\}$ NMR spectra (Table 2, Figs. 2–5) as employed previously in the characterisation of mer- and fac-[Ir(CO)$_3$F$_3$].[10]

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 ca. δ 155, 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)$_4$F$_2$] I, which was first postulated 16 years ago,[2] and which completes the series of complexes cis-[Os(CO)$_4$X$_2$] (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)$_5$F]$^+$ II (the counter ion is presumably HF$_2^-$), which is isoelectronic and isostructural with the well characterised [W(CO)$_5$F]$^-$ [22] and [Re(CO)$_5$F]^7 species. In the fluorination of [Os$_3$(CO)$_{12}$], the formation of [Os(CO)$_5$F]$^+$, 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
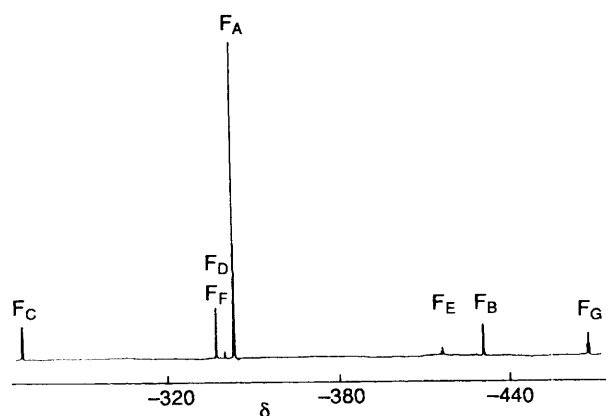

Table 1 Fluorine-19 NMR data * for the osmium carbonyl fluorides

Complex	$\delta(^{19}F)$	$^2J_{FF}/Hz$	Assignment
I [Os(CO)$_4$F$_2$]	-342.5 (s)	—	F_A
II [Os(CO)$_5$F]$^+$	-433.0 (s)	—	F_B
III [Os$_2$(CO)$_7$F$_4$]	-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)$_8$F$_3$]$^+$	-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.

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)$_4$F$_2$]	162.4	—	< 2 (F_A)	CO_B
	154.8^d	ca. 65 (F_A)	—	CO_A
II [Os(CO)$_5$F]$^+$	156.3	—	7 (F_B)	CO_C
	149.2	62 (F_B)	—	CO_D
III [Os$_2$(CO)$_7$F$_4$]^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)$_8$F$_3$]$^+$	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
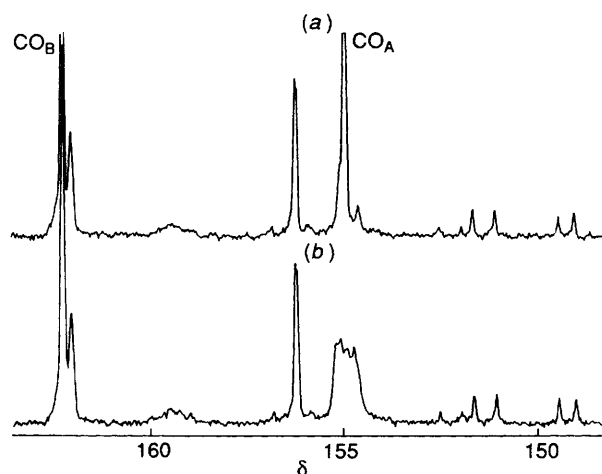

Fig. 2   150.87 MHz ^{13}C NMR spectra of products from the reaction of [Os$_3$(CO)$_{12}$] with XeF$_2$ (1:3) in anhydrous HF. (a) Selective ^{19}F decoupled at δ −342.5 and (b) fully coupled

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

(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)$_3$F$_2$(μ-F)-Os(CO)$_4$F], 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.

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
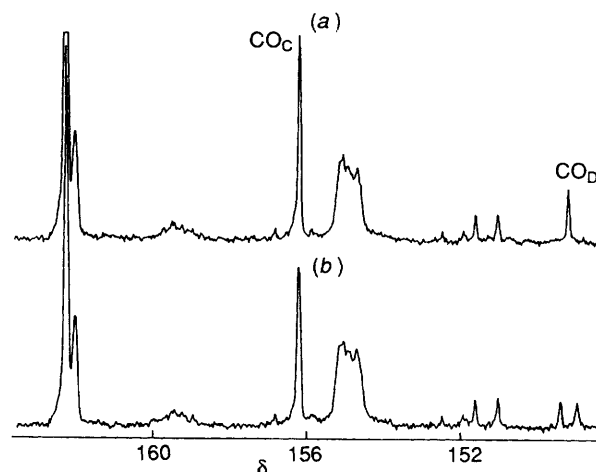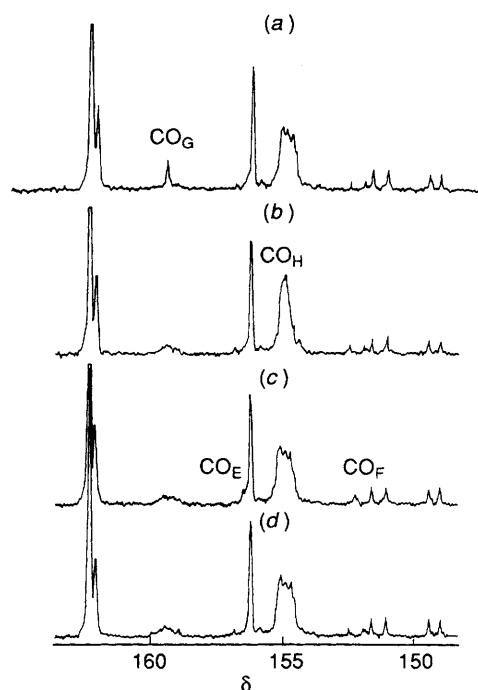
ratio, which exhibit mutual coupling of 112 Hz (typical of $^2J_{FF}$). During the ^{13}C-{^{19}F} NMR experiment (Fig. 5), irradiation at F$_G$ removes the large (*trans*) doublet coupling at δ 151.4 (CO$_J$) and causes minor variations in the singlet at δ 162.0 (CO$_K$) and the broad resonance at *ca.* 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)$_8$F$_3$]$^+$ **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
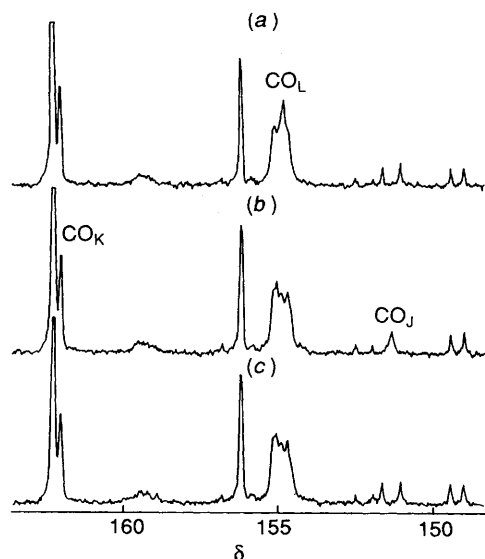
Fig. 5 150.87 MHz ^{13}C NMR spectra of products from the reaction of [Os$_3$(CO)$_{12}$] with XeF$_2$ (1:3) in anhydrous HF. Selective ^{19}F decoupled at (a) δ −336 and (b) δ −465; (c) fully coupled

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)$_3$F$_3$] 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 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)$_4$F$_2$' 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)$_4$F$_2$' 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)$_4$F$_2$' metal centre, the latter at a cis-'(CO)$_3$F$_3$', 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)$_3$F$_2$}$_4$][9] suggesting that the solution-stable osmium carbonyl fluorides readily lose CO in vacuo and polymerise to afford the analogous fluorine-bridged [{Os(CO)$_3$F$_2$}$_4$]. 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)$_4$F$_2$], 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)$_3$X$_2$], 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)$_5$X] and [Re(CO)$_3$(PPh$_3$)$_2$X] (X = F, Cl, Br or I).[24,28,29]

References

1 E. Horn, M. R. Snow and P. C. Zeleny, Aust. J. Chem., 1980, 33, 1659.
2 D. M. Bruce and J. H. Holloway, Transition Met. Chem., 1978, 3, 317.
3 J. H. Holloway, J. B. Senior and A. C. Szary, J. Chem. Soc., Dalton Trans., 1987, 741.
4 A. J. Hewitt, J. H. Holloway, R. D. Peacock, J. B. Raynor and I. L. Wilson, J. Chem. Soc., Dalton Trans., 1976, 579.
5 R. D. W. Kemmitt, R. D. Peacock and I. L. Wilson, Chem. Commun., 1968, 772.
6 D. M. Bruce, J. H. Holloway and D. R. Russell, J. Chem. Soc., Chem. Commun., 1973, 321.
7 D. M. Bruce, J. H. Holloway and D. R. Russell, J. Chem. Soc., Dalton Trans., 1978, 1627.
8 A. J. Blake, R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, Chem. Commun., 1988, 529.
9 C. J. Marshall, R. D. Peacock, D. R. Russell and I. L. Wilson, Chem. Commun., 1970, 1643.
10 S. A. Brewer, J. H. Holloway, E. G. Hope and P. G. Watson, J. Chem. Soc., Chem. Commun., 1992, 1577.
11 S. C. Tripathi, S. C. Srivastava, R. P. Mani and A. K. Shrimal, Inorg. Chim. Acta, 1975, 15, 249.
12 B. L. Haymore and J. A. Ibers, Inorg. Chem., 1975, 14, 2784.
13 J. H. Holloway, Chem. Commun., 1966, 22.
14 K. O. Christe, W. W. Wilson and C. J. Schack, J. Fluorine Chem., 1978, 11, 71.
15 J. W. Gleeson and R. W. Vaughan, J. Chem. Phys., 1983, 78, 5384.
16 W. W. Dukat, J. H. Holloway, E. G. Hope, P. J. Townson and R. L. Powell, J. Fluorine Chem., 1993, 62, 293.
17 S. A. Brewer, J. H. Holloway and E. G. Hope, J. Fluorine Chem., in the press.
18 J. Knight and M. J. Mays, J. Chem. Soc. A, 1970, 711.
19 R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, J. Am. Chem. Soc., 1987, 109, 2194.

20 R. W. Cockman, E. A. V. Ebsworth, J. H. Holloway, M. Murdoch, N. Robertson and P. G. Watson, *ACS Symp. Ser.*, in the press.
21 L. Vancea and W. A. G. Graham, *J. Organomet. Chem.*, 1977, **134**, 219.
22 J. L. Clhonski and R. A. Levenson, *Inorg. Chem.*, 1975, **14**, 1717; W. Douglas and J. K. Ruff, *J. Organomet. Chem.*, 1974, **65**, 65.
23 A. J. Deeming, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. A*, 1970, 2967.
24 E. Horn and M. R. Snow, *Aust. J. Chem.*, 1981, **34**, 737.
25 S. A. Brewer, J. H. Holloway and E. G. Hope, unpublished work.
26 R. D. Adams and J. P. Selegue, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, p. 973, and refs. therein.
27 P. Rushman, G. N. Van Buuren, M. Shiralian and R. K. Pomeroy, *Organometallics*, 1983, **2**, 693.
28 R. Colton and J. E. Garrard, *Aust. J. Chem.*, 1973, **26**, 1781.
29 N. W. Hoffman, N. Prokopuk, M. J. Robbins, C. M. Jones and N. M. Doherty, *Inorg. Chem.*, 1991, **30**, 4177.