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Reaction of ruthenium(II) and osmium(II) hydrides with anhydrous HF

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The reactions of anhydrous HF with the ruthenium(II) and osmium(II) hydride complexes $[MH_2(CO)_x(PPh_3)_y]$ (M = Ru or Os; $x = y = 2$; $x = 1$, $y = 3$) have been studied. For $[OC\text{-}6\text{-}13][MH_2(CO)_2(PPh_3)_2]$, elimination of dihydrogen affords the previously described $[OC\text{-}6\text{-}13][MF_2(CO)_2(PPh_3)_2]$. For $[OC\text{-}6\text{-}13][MH_2(CO)(PPh_3)_3]$, elimination of dihydrogen is accompanied by loss of one phosphine ligand and aggregation to give the novel, triply fluoride-bridged, dinuclear, $[M_2(\mu\text{-}F)_3(CO)_2(PPh_3)_4][HF_2]$; anion exchange with $Na[BPh_4]$ afford air-stable products. These complexes have been characterised by mass spectrometry, NMR, IR and metal-edge extended X-ray absorption fine structure spectroscopies which confirm their dinuclear structures.

There has been a gradually increasing range of reagents used to introduce the fluoride ligand into organometallic and coordination compounds, however many of these are not generally applicable.[1] We have shown that XeF_2 can be used to introduce fluorine oxidatively into low-valent rhenium,[2] ruthenium,[3,4] osmium[3,4] and iridium[5] complexes and that the reaction of anhydrous HF with methyl metal derivatives, with the elimination of methane, offers a reasonable route to the related metal fluoride complexes,[6] but the number of suitable starting materials in these areas is limited. In marked contrast, there is a wide range of metal hydride complexes in the literature, and we are investigating whether an analogous reaction, with the elimination of H_2, could find wide application in this area. Six reports of the reaction of aqueous or ethanolic HF with metal hydride complexes have appeared,[7–12] but, apart from the crystallographically characterised $[WFH_2(H_2O)(PMe_3)_4]F$,[10,11] which has recently been reassigned as $[WFH_2(HF_2)(PMe_3)_4]$,[11,12] evidence for metal–fluorine bond formation in these systems is poor. Here, we illustrate the potential of this approach *via* the reactions of ruthenium(II) and osmium(II) hydrides with anhydrous HF.

Experimental

Proton, ^{19}F and ^{31}P NMR spectra were recorded in anhydrous HF [in 4 mm outside diameter FEP (perfluoroethylene–propylene copolymer) tubes as described previously],[4] C_4D_8O or $(CD_3)_2CO$ on a Bruker AM 300 spectrometer at 300.14, 282.36 and 121.50 MHz, referenced externally to $SiMe_4$, $CFCl_3$ and 85% H_3PO_4, respectively. Infrared spectra were recorded as Nujol mulls between KBr plates on a Digilab FTS40 spectrometer, electrospray (in tetrahydrofuran, thf) and FAB mass spectra on a Kratos Concept 1H spectrometer.

Ruthenium K-edge and osmium L_{III}-edge extended X-ray absorption fine structure (EXAFS) were collected at the Daresbury Synchrotron Radiation Source operating at 2 GeV (*ca.* 3.2×10^{-10} J) with an average current of 190 mA on stations 9:2 and 9:3 using order-sorting Si(220) monochromators, offset to 50% of the rocking curve for harmonic rejection. The EXAFS data were collected in transmission mode for solid samples, diluted by boron nitride and mounted between Sellotape strips in 1 mm aluminium spacers. The EXAFS data treatment utilised the programs EX[13] and EXCURV 92.[14] Several data sets were collected for each sample in k space (k = photoelectron wavevector/Å^{-1}), and averaged to improve the signal-to-noise ratio. The pre-edge background was removed by fitting the spectrum to a quadratic polynomial, and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using a fifth-order polynomial, and the optimum function judged by minimising the intensity of chemically insignificant shells at low r (r = radial distance from the primary absorbing atom) in the Fourier transform. The data were multiplied by k^3 to compensate for the decreased intensity at higher k. Curve fitting used multiple-scattering curved-wave theory with phase shifts and back-scattering factors calculated using the normal *ab initio* methods.[15]

All preparative manipulations were carried out on a metal vacuum line with facilities to connect Kel-F and FEP reaction vessels. The complexes $[OC\text{-}6\text{-}13][MH_2(CO)_2(PPh_3)_2]$ (M = Ru[16] or Os[17]) and $[OC\text{-}6\text{-}13][MH_2(CO)(PPh_3)_3]$ (M = Ru or Os)[17] were prepared by the literature routes. Hydrogen fluoride (Fluorochem Ltd.) was purified by vacuum transfer, dried by repetitive fluorination at room temperature and stored in Kel-F tubes over dry BiF_5.[18] Weighed samples of the starting materials were loaded, in a dry-box (<10 ppm water), into prefluorinated FEP reactors (4 mm or 6 mm outside diameter, 0.5 mm wall thickness) fitted with poly(tetrafluoroethylene) valves (Production Techniques Ltd.). After evacuation on the vacuum line, HF (*ca.* 0.3 cm^3) was condensed into each reaction tube at −196 °C. The HF was allowed to warm to *ca.* −50 °C when 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 gas generated. After the reaction was complete, the mixture was warmed cautiously to room temperature, left to stand at room temperature overnight to ensure complete reaction and then either heat-sealed as described previously for NMR studies[5] or the HF solvent was removed *in vacuo* to leave a solid sample which was manipulated in a dry-box for IR spectroscopy, EXAFS and further NMR studies.

Results and Discussion

In the reactions of all the ruthenium(II) and osmium(II) hydride complexes with anhydrous HF an IR-inactive, non-condensable, gas is evolved at *ca.* −50 °C which is undoubtedly dihydrogen. Removal of the solvent from the solutions obtained from the reactions of $[OC\text{-}6\text{-}13][MH_2(CO)_2(PPh_3)_2]$ with anhydrous HF afforded off-white, air-stable, solids $[MF_2(CO)_2(PPh_3)_2]$ (M = Ru **1** or Os **2**). For both products the ^{19}F and ^{31}P NMR spectra, recorded in $(CD_3)_2CO$, each contain one resonance with mutual triplet coupling which corresponds

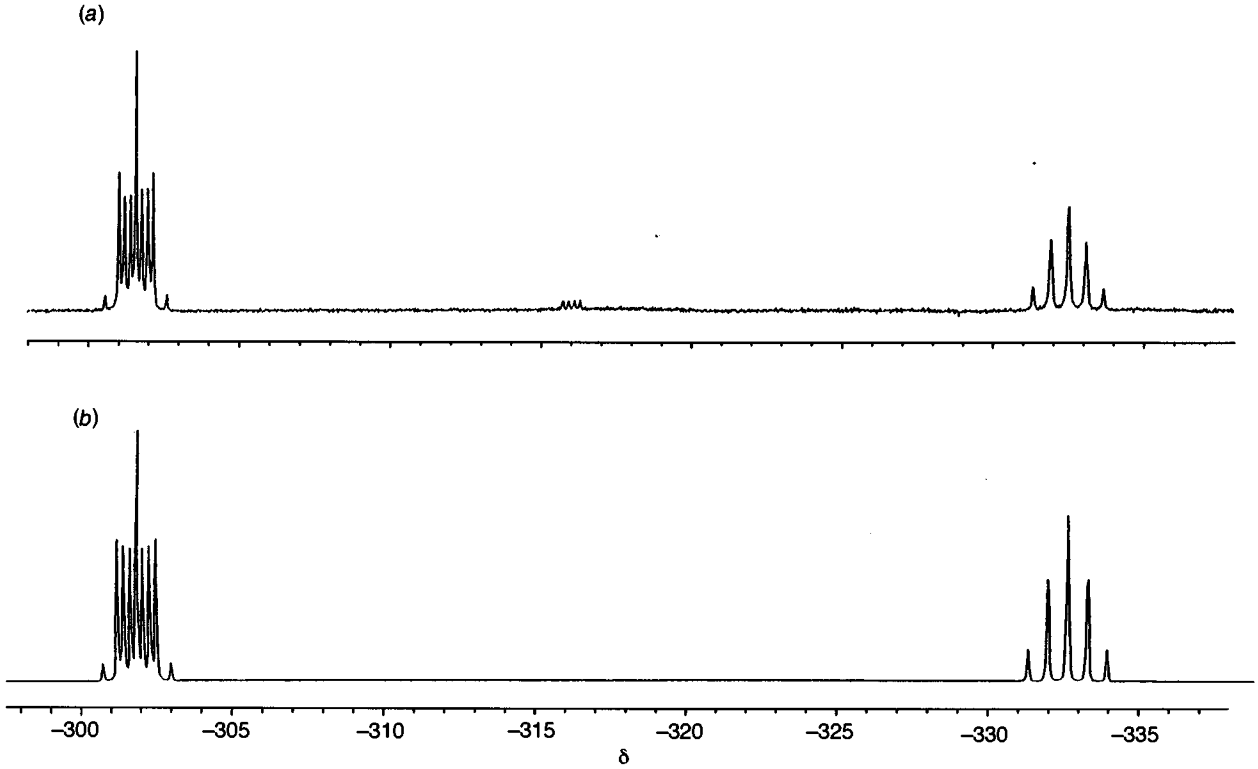


Fig. 1 The 282.41 MHz ^{19}F NMR spectra of $[Ru_2(\mu\text{-}F)_3(CO)_2(PPh_3)_4][BPh_4]$: (*a*) observed, (*b*) simulated using parameters listed in Table 1

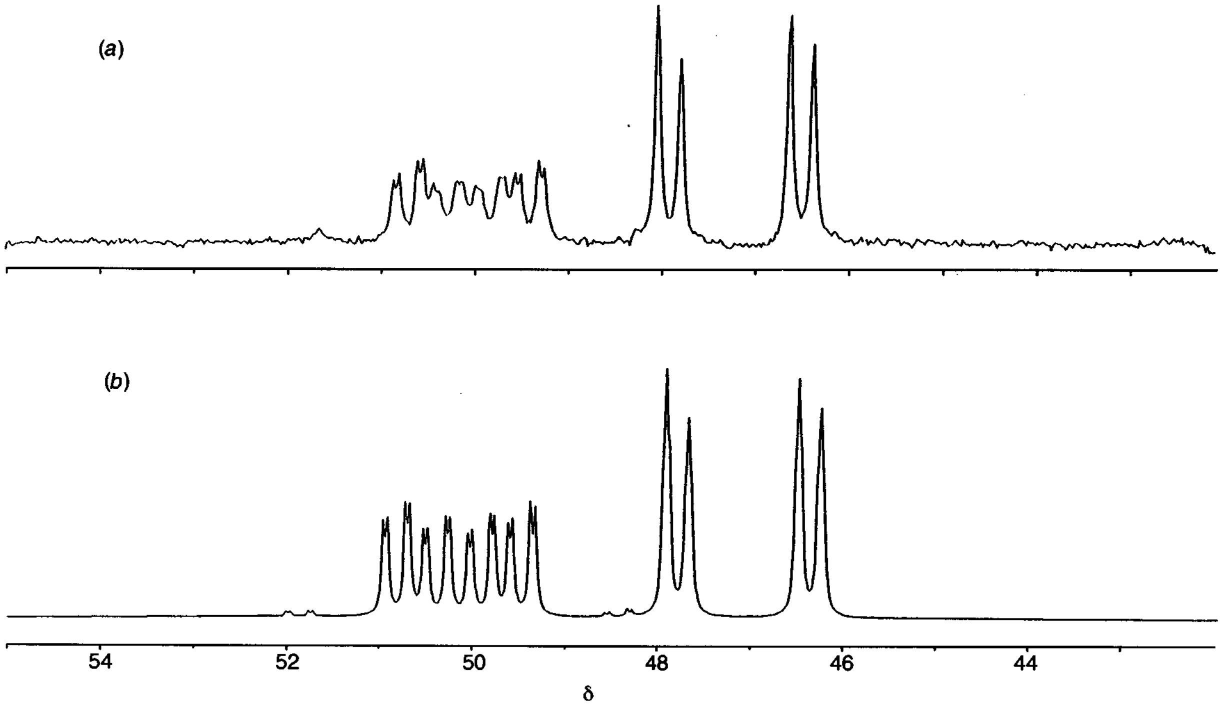


Fig. 2 The 121.50 MHz $^{31}P\text{-}\{^1H\}$ NMR spectra of $[Ru_2(\mu\text{-}F)_3(CO)_2(PPh_3)_4][BPh_4]$. Details as in Fig. 1

exactly with our previously characterised $[OC\text{-}6\text{-}13][MF_2(CO)_2(PPh_3)_2]$; IR spectroscopy and mass spectrometry confirm this assignment.[4,19]

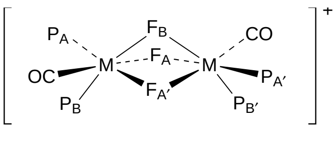
Likewise, removal of the solvent from the solutions obtained from the reactions of $[OC\text{-}6\text{-}13][MH_2(CO)(PPh_3)_3]$ with anhydrous HF also afforded off-white, air-stable, solids (M = Ru **3** or Os **4**). The ^{19}F NMR spectra (Fig. 1) of the products dissolved in C_4D_8O exhibit two multiplets in a 2:1 ratio (Table 1) in the region characteristic of a metal-bound fluoride together with resonances assignable to BF_4^- and SiF_6^{2-} (presumably arising from attack on the glass NMR tubes). The presence of these fluorine containing anions could be avoided by transferring the off-white solids isolated from the anhydrous HF reactions on to $Na[BPh_4]$ in dry thf in prefluorinated FEP reactors, indicating anion exchange and that the off-white products are ionic. The ^{19}F NMR resonances of the metal-bound F are second order and invariant with temperature. However, ^{19}F–^{19}F NMR correlation spectroscopy (COSY) experiments indicated that the two multiplets are mutually coupled. The $^{31}P\text{-}\{H\}$ NMR spectra (Fig. 2) of the two compounds (M = Ru or Os) are complicated but essentially identical, containing a complicated multiplet, an apparent doublet of doublets (Table 1) and a singlet assignable to unco-ordinated PPh_3, which could not be removed from the products despite repeated washings with boiling light petroleum (b.p. 40–60 °C).

These NMR data indicated that, in contrast to the reactions

Table 1 Spectroscopic data for complexes **3** and **4***

	3	**4**		**3**	**4**
m/z (M^+)	1363	1541	^2J(F$_{A'}$P$_B$)	4.0	2.0
$\tilde{\nu}$(CO)/cm^{-1}	1961	1976	^2J(F$_{A'}$P$_{A'}$)	4.0	2.0
δ(F$_A$)	−305.2	−280.2	^2J(F$_{A'}$P$_{B'}$)	4.0	2.0
δ(F$_B$)	−332.8	−299.8	^2J(F$_A$F$_B$)	160.0	180.0
δ(P$_A$)	51.0	2.2	^2J(F$_{A'}$F$_B$)	160.0	180.0
δ(P$_B$)	47.2	4.4	^2J(F$_B$P$_A$)	5.4	3.0
^2J(F$_A$F$_{A'}$)	180.0	190.0	^2J(F$_B$P$_B$)	173.5	180.0
^2J(F$_A$P$_A$)	4.0	2.0	^2J(F$_B$P$_{A'}$)	5.4	3.0
^2J(F$_A$P$_B$)	4.0	2.0	^2J(F$_B$P$_{B'}$)	173.5	180.0
^2J(F$_A$P$_{A'}$)	160.0	150.0	^2J(P$_A$P$_B$)	29.3	35.0
^2J(F$_A$P$_{B'}$)	4.0	2.0	^2J(P$_{A'}$P$_{B'}$)	29.3	35.0
^2J(F$_{A'}$P$_A$)	160.0	160.0			

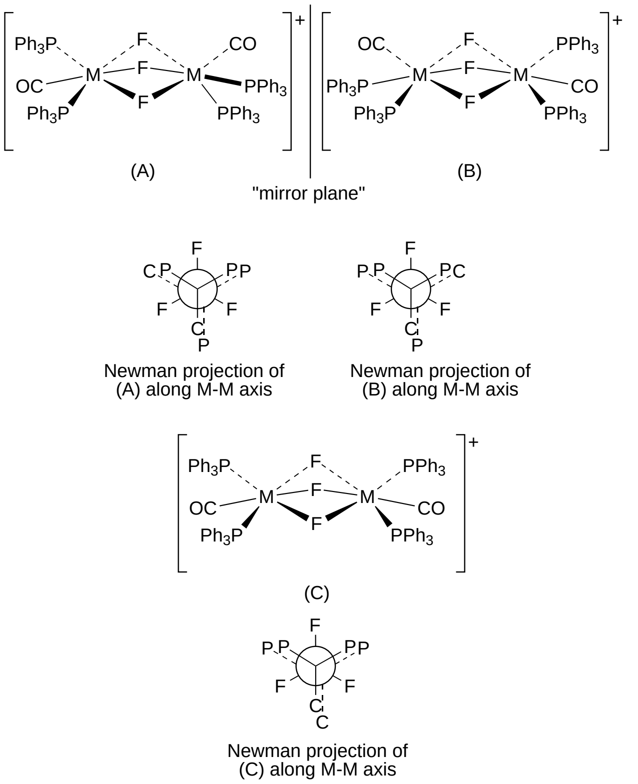
* Chemical shifts (δ) and coupling constants (Hz) established by modelling (see text).



M = Ru, Os; P = PPh$_3$

of [*OC*-6-13][MH$_2$(CO)$_2$(PPh$_3$)$_2$] with anhydrous HF, simple hydride–fluoride metathesis has not occurred. Infrared spectroscopy confirmed the presence of metal-bound carbonyls. Electrospray mass spectrometry using dry thf as solvent (M = Ru) and FAB mass spectrometry (M = Os) (Table 1) allowed assignment of the products to the unusual triply fluoride-bridged dinuclear cationic complexes [M$_2$(μ-F)$_3$(CO)$_2$(PPh$_3$)$_4$]$^+$; the counter ion from the anhydrous HF reaction is undoubtedly [HF$_2$]$^-$ which readily attacks borosilicate glass giving [BF$_4$]$^-$ and [SiF$_6$]$^{2-}$ and which can be exchanged with [BPh$_4$]$^-$. It is tempting to speculate that the mechanism of these reactions might be accounted for in terms of the high solution lability of the phosphines *trans* to hydride in the starting materials and the established solvation of some fluoride ligands in low-valent metal complexes by anhydrous HF[11,12,20] whereby the generation of vacant sites at the metal centres might be expected to lead to the formation of fluoride-bridged cations. However, in view of the range of fluoride derivatives obtained during other reactions in anhydrous HF[3,5,6] and, in particular, in this paper our observation of no fluoride-ligand solvation in the reactions of [*OC*-6-13][MH$_2$(CO)$_2$(PPh$_3$)$_2$] with anhydrous HF, it is surprising that such conditions would lead to a single product. We prefer, therefore, to reserve judgement about the mechanism until further evidence is available.

This unusual cationic structure can be used to rationalise the complicated ^{19}F and ^{31}P NMR spectra. The triply bridged cations have seven magnetically inequivalent 100% spin $\frac{1}{2}$ nuclei: two distinct sets of fluoride ligands [(F$_A$, F$_{A'}$) and F$_B$] and two sets of phosphine ligands [(P$_A$, P$_{A'}$) and (P$_B$, P$_{B'}$)]. The two fluoride ligands F$_A$ and F$_{A'}$ are chemically equivalent as they are both *trans* to one carbonyl group and one phosphine ligand. However, they are magnetically inequivalent due to their different coupling to P$_A$ (F$_A$ is *cis* to P$_A$ whereas F$_{A'}$ is *trans* to P$_A$; *trans*-$^2J_{PF}$ couplings are typically much larger than *cis*-$^2J_{PF}$ couplings). The third fluoride ligand (F$_B$) is chemically unique as it is *trans* to two phosphine ligands. Hence, two distinct mutually-coupled multiplets are observed in a 2 : 1 ratio in the ^{19}F NMR spectra. Similarly, the two pairs of phosphine ligands are chemically inequivalent (P$_B$, P$_{B'}$ *trans* to F$_B$ and P$_A$, P$_{A'}$ *cis* to F$_B$) resulting in two distinct multiplets in the ^{31}P-{H} NMR spectra in a 1 : 1 ratio. However, P$_B$ and P$_{B'}$ are magnetically inequivalent due to their different coupling to P$_A$ (^2J and ^4J couplings respectively) and P$_A$ and P$_{A'}$ are magnetically inequivalent due to their different coupling to P$_B$ (also ^2J and ^4J couplings respectively). The second-order NMR spectra could be simulated using this model (Figs. 1 and 2 and Table 1).



Scheme 1 Possible isomers of the [M$_2$(μ-F)$_3$(CO)$_2$(PPh$_3$)$_4$]$^+$ cations (M = Ru or Os; P = PPh$_3$, C = CO)

The combination of two metal fragments can result in two geometrical isomers, one with the two carbonyls *syn* is achiral (**C**), and the other where the carbonyls are in an *anti* arrangement is chiral (**A** and **B**) (Scheme 1). The NMR evidence suggests that, in solution, only the chiral *anti* isomer (presumably a racemic mixture) is present; in **C** the phosphine ligands are chemically equivalent and would produce a single resonance in the ^{31}P-{^{1}H} NMR spectrum. A similar *anti* configuration of a terminal chloride and a CS ligand, and of the terminal chloride ligands has been observed in the crystallographically characterised, neutral [Ru$_2$Cl(μ-Cl)$_3$(CS)(PPh$_3$)$_4$][21] and [Ru$_2$Cl$_2$(μ-Cl)$_3$(PPh$_3$)$_4$][22] respectively. However, the *syn* arrangements (**C**) cannot be disallowed on steric grounds since the crystallographically characterised [Ru$_2$Cl$_2$(μ-Cl)$_3$(CO)(PPh$_3$)$_3$] adopts the *syn* configuration.[23] Molecular modelling on this chloride complex and on the fluoride complexes (using structural data from EXAFS analysis, see below) suggests that in complexes with this M$_2$(μ-X)$_3$ fragment the triphenylphosphine ligands on adjacent metal centres are not subject to steric interactions. Rotation of one of the octahedra by 120° about the M···M axis to the *syn* isomer from either of the *anti* isomers results in no significant van der Waals clashes of the phenyl rings on the phosphine ligands from adjacent metal centres which cannot be overcome by small rotation about the P–C bonds.

Unfortunately, these triply bridged complexes are unstable in solution over extended periods of time, and we have been unable to obtain crystals suitable for X-ray crystallography. However, we have previously shown[24] that EXAFS spectroscopy, in combination with spectroscopic studies, is a valuable structural probe in the absence of crystallographic data. Since our spectroscopic investigations indicate triply fluoride-bridged dimeric structures, we initially obtained the ruthenium K-edge EXAFS data for the structurally characterised [RuF$_2$(CO)$_2$(PPh$_3$)$_2$] **1**,[4] [Ru$_2$(μ-Cl)$_3$(PMe$_2$Ph)$_6$][BPh$_4$][25] and the osmium L$_{III}$-edge data for [OsF$_2$(CO)$_2$(PPh$_3$)$_2$] **2**[19] as model systems to test the reliability of our data collection and treatment.

Table 2 The EXAFS data for complexes **1**–**4**[a]

	1		**2**		$[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6][BPh_4]$			
	X-Ray	EXAFS	X-Ray	EXAFS	X-Ray	EXAFS	**3**	**4**
d(M–C)/Å	1.841(7)	1.827(7)	1.844(9)	1.888(2)	—	—	1.818(3)	1.824(3)
$2\sigma^2$/Å[b]	—	0.019(2)	—	0.005(1)	—	—	0.001(1)	0.001(1)
d(M–P)/Å	2.406(1)	2.413(5)	2.418(2)	2.401(2)	2.29[c]	2.275(2)	2.292(4)	2.420(3)
$2\sigma^2$/Å[b]	—	0.017(1)	—	0.015(1)	—	0.008(1)	0.004(1)	0.010(1)
d(M–X)/Å	2.011(4)	2.028(5)	2.023(5)	2.017(2)	2.49[c]	2.468(2)	2.043(6)	2.042(3)
$2\sigma^2$/Å[b]	—	0.013(1)	—	0.006(1)	—	0.011(1)	0.019(2)	0.015(1)
d(M···O)/Å	2.976	2.974(4)	3.010	2.980(2)	—	—	2.893(5)	2.947(4)
$2\sigma^2$/Å[b]	—	0.012(1)	—	0.016(1)	—	—	0.023(3)	0.009(1)
d(M···M)/Å	—	—	—	—	3.39(1)	3.408(5)	2.970(3)	3.093(6)
$2\sigma^2$/Å[b]	—	—	—	—	—	0.015(1)	0.009(1)	0.017(1)
Fit index[d]	—	0.39	—	0.20	—	0.35	0.11	0.24
R[e]	—	22.9	—	20.3	—	22.7	15.6	23.0

[a] Standard deviation in parentheses. Note that the systematic errors in bond distances arising from the EXAFS data collection and analysis procedures are *ca.* ±0.02 Å for the first co-ordination shells and *ca.* ±0.04 Å for subsequent shells. [b] Debye–Waller factor. [c] Average value. [d] Fit index $= \Sigma_i[(\chi^T - \chi^E)k_i^3]^2$. [e] $R = [\int(\chi^T - \chi^E)k^3dk/\int\chi^E k^3dk] \times 100\%$.

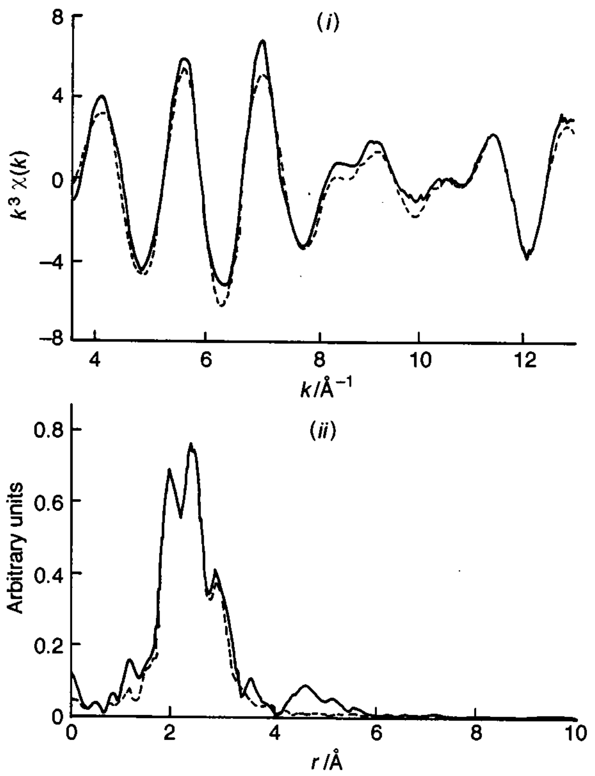


Fig. 3 Background-subtracted EXAFS (*i*) (——, experimental × k^3; – – –, curved-wave theory × k^3) and the Fourier transform (*ii*) (——, experimental; – – – theoretical) for $[Os_2(\mu\text{-}F)_3(CO)_2(PPh_3)_4][BPh_4]$

The results are in satisfactory agreement with the single-crystal X-ray data (Table 2). For **1** and **2** the Fourier transform of the EXAFS shows four distinct shells which model for the bonded M–C, M–F and M–P interactions and the non-bonded, multiply scattered, M···O distance. For $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6][BPh_4]$, in addition to the terminal Ru–P distance 2.275 Å [as compared to 2.29 Å (mean) from the X-ray single-crystal study] and the bridging Ru–Cl distance 2.468 Å [as compared to 2.49 Å (mean)], the Fourier transform of the EXAFS clearly shows a longer, non-bonded, Ru···Ru interaction at 3.408 Å (as compared to 3.39 Å), which confirms that this approach can validate the dimeric nature of the complexes.

Transmission ruthenium K-edge and osmium L_{III}-edge EXAFS were then collected for complexes **3** and **4** out to k = 15 Å^{-1} beyond the edge but, due to the poor signal-to noise ratio at high k, the data were truncated at 13 Å^{-1}. Three data sets were averaged for each compound and the data multiplied by k^3 to compensate for a decrease in intensity at higher k. No smoothing or Fourier filtering was applied, and the fits discussed below were all compared with the average raw (background-subtracted) EXAFS data. The data were modelled to a five-shell fit (1C, 2P, 3F, 1O, 1M), with the M–C–O bond angle fixed at 180° for multiple scattering, using the AFAC and VPI values taken from the analyses for **1** and **2** (Fig. 3 and Table 2). Each shell was added stepwise, iterated in the usual way, and the best fits tested for statistical significance. The M–P, M–C and C–O bond lengths are all consistent with the values obtained from the single crystal X-ray diffraction studies of mononuclear ruthenium and osmium fluoride complexes.[4,19] There have been no verified reports of dinuclear, fluoride-bridged, ruthenium or osmium complexes, but the M–F distances are entirely reasonable, *i.e.* significantly longer, as expected, than terminal M–F distances in low-valent ruthenium and osmium fluoride complexes, and, for the ruthenium complex, slightly longer than the bridging Ru–F distance [2.04(7) Å] in the tetrameric $[\{RuF_2(CO)_3\}_4]$.[26] Furthermore, the data clearly indicate long-range metal–metal scattering where the M···M distances are consistent with other non-bonded M···M interactions established by X-ray crystallography.[27–29] Trigonometry allows an estimate of the M–F–M bridging angle, 93 ± 3 (Ru), 98 ± 3° (Os), indicating that the metal centres are further apart than expected in a regular cofacial bioctahedron (70.5°); the analogous angle for $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6][BPh_4]$ is also larger than 70.5°. Although the ligand donor sets are not identical, a series of halide-bridged dimers $[Ru_2(\mu\text{-}X)_3L_6]^+$ (X = F, Cl or Br)[23,30] have been structurally investigated and, as expected on the basis of the size of the halide, the Ru···Ru distance decreases in the order Br > Cl > F.

These complexes represent the first, verified, examples of late transition-metal dinuclear triply fluoride-bridged complexes; an early claim[7] for $[Ru_2(\mu\text{-}F)_3(PMe_2Ph)_6]^+$ includes no supporting spectroscopic data. However, there have been a growing number of early transition-metal dinuclear triply fluoride-bridged complexes, including the crystallographically characterised, triply bridged $[Mo_2H_4(\mu\text{-}F)_3(PMePh_2)_6][BF_4]$,[27] $[Mo_2(\mu\text{-}F)_3(CO)_4(PPh_3)_4][BF_4]$[28] and $[W_2(\mu\text{-}F)_3(CO)_4(PMe_2Ph)_4][BF_4]$[29] for which the M–F–M bridging angles (97.7, 97.1 and 98.6° respectively) also indicate distortion of the cofacial bioctahedra. Further work on the protonation of other metal hydride complexes with anhydrous HF is underway.

Acknowledgements

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