Air-stable ruthenium(II) and osmium(II) fluoride complexes. Crystal structures of [*OC*-6-13][MF₂(CO)₂(PR₃)₂] [M = Ru, PR₃ = PEtPh₂; M = Os, PR₃ = PPh₃ or P(C₆H₁₁)₃]

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The reaction of Lewis bases L with [{MF₂(CO)₃}₄] (M = Ru or Os) in organic solvents provided a clean, high-yield, route to a series of air- and moisture-stable ruthenium(II) and osmium(II) fluoride co-ordination compounds of general formulae [MF₂(CO)₂L₂]. Characterisation by elemental analysis, FAB mass spectrometry, NMR and IR spectroscopy indicated a *cis,cis,trans* ligand arrangement. The crystal structures of [*OC*-6-13]-[MF₂(CO)₂(PR₃)₂] [M = Ru, PR₃ = PEtPh₂; M = Os, PR₃ = PPh₃ or P(C₆H₁₁)₃] have been determined by X-ray crystallography. The geometry about the central metal atoms for all three structures is distorted pseudo-octahedral with ligand environments consistent with the spectroscopic data. In all the structures the phosphine ligands are bent towards the fluoride ligands and show intramolecular H · · · F interactions.

Recently, there has been renewed interest in fluoride as a ligand in low-oxidation-state transition-metal co-ordination chemistry.[1–3] There have been only three previous reports of osmium(II) fluoride co-ordination compounds. In 1975, Heymore and Ibers[4] reported the first derivative in this class, [OsF(CO)₂(N=NPh)(PPh₃)₂], during a broad investigation of osmium aryldiazo complexes. More recently, we have described the application of xenon difluoride, as an oxidative source of fluorine, in the synthesis of [{OsF₂(CO)₃}₄][5] and [OsF(CO)-(COF)(PPh₃)₂] and [OsF₂(CO)₂(PPh₃)₂].[6] There have been more claims for ruthenium(II) fluoride co-ordination compounds.[7] However, for a number of these the reported characterisation data are limited. In addition to our reports of [{RuF₂(CO)₃}₄][8–10] and [RuF(CO)(COF)(PPh₃)₂] and [RuF₂-(CO)₂(PPh₃)₂],[6] substantiated ruthenium(II) fluoride complexes include [RuFCl₂(NO)(bipy)] (bipy = 2,2′-bipyridine),[2] the five-co-ordinate hydridofluoride complex *trans*-[RuF(H)(CO)-(PBuᵗ₂Me)₂] (and the products of the reaction of this complex with a variety of ligands),[11] and the cationic species [RuF(CO)-(dppe)₂]⁺ (dppe = Ph₂PCH₂CH₂PPh₂)[12] and [RuF(CO)₂(OH₂)-(PPh₃)₂]⁺.[13] These complexes have been prepared by diverse synthetic routes, several of which were not designed to produce low-oxidation-state fluorides. Here, we outline a general route to this class of co-ordination compound by the reaction of [{MF₂(CO)₃}₄] (M = Ru or Os) with a range of Lewis bases.

Experimental

Proton, ¹⁹F and ³¹P NMR spectra were recorded in CD₂Cl₂ (Os) and [²H₆]acetone (Ru) on a Bruker AM 300 spectrometer at 300.14, 282.36 and 121.50 MHz, referenced externally to SiMe₄, CFCl₃ and 85% H₃PO₄, respectively. Infrared spectra were recorded on Nujol mulls between KBr plates on a Digilab FTS40 spectrometer. Elemental analyses were performed by Butterworth Laboratories Ltd. and FAB mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

The complexes [{MF₂(CO)₃}₄] (M = Ru[9] or Os[5]) were prepared as described previously and stored in a dry-box. The ligands were commercial samples and used as supplied. Dichloromethane was dried by refluxing over calcium hydride, and acetone was dried over calcium sulfate.

Preparations

All of the complexes were prepared by the same general syn-

thetic procedure. A weighed amount of [{MF₂(CO)₃}₄] (M = Ru or Os) (*ca.* 0.10 g) was loaded into a Schlenk flask in a dry-box along with, for the solid reagents, a slight excess of the ligand (8 molar equivalents). After connecting the reaction vessel to a vacuum line, freshly distilled dichloromethane (M = Os) or acetone (M = Ru) (*ca.* 20 cm³) was transferred on-to the reagents. Reaction ensued immediately with vigorous gas evolution. The reaction mixture was then degassed and stirred under dinitrogen for 3 h, to ensure complete reaction, affording a yellow solution. The solvent was removed *in vacuo* and the pale yellow/white solid recrystallised from dichloromethane (Os) or benzene (Ru) and light petroleum (b.p. 40–60 °C) to give the products in *ca.* 90% yields.

In cases where the ligands are liquid the same procedures were followed except that the ligands were introduced directly into the reaction vessel after addition of the solvent.

Satisfactory elemental analyses were obtained for representative products: [RuF₂(CO)₂(PPh₃)₂] (Found: C, 63.09; H, 4.07. C₃₈H₃₀F₂O₂P₂Ru requires C, 63.42; H, 4.20); [RuF₂(CO)₂-(PEtPh₂)₂] (Found: C, 57.90; H, 4.76. C₃₀H₃₀F₂O₂P₂Ru requires C, 57.78; H, 4.85%); [RuF₂(CO)₂{P(*p*-FC₆H₄)₃}₂] (Found: C, 54.84; H, 2.81. C₃₈H₂₄F₈O₂P₂Ru requires C, 55.15; H, 2.92); [RuF₂(CO)₂(AsPh₃)₂] (Found: C, 55.92; H, 3.72. C₃₈H₃₀As₂-F₂O₂Ru requires C, 56.52; H, 3.74); [OsF₂(CO)₂(PPh₃)₂] (Found: C, 56.36; H, 3.69. C₃₈H₃₀F₂O₂OsP₂ requires C, 56.43; H, 3.74); [OsF₂(CO)₂(PMe₃)₂] (Found: C, 22.07; H, 4.19. C₈H₁₈F₂O₂OsP₂ requires C, 22.02; H, 4.16); [OsF₂(CO)₂-{P(C₆H₁₁)₃}₂] (Found: C, 54.14; H, 7.93. C₃₈H₆₆F₂O₂OsP₂ requires C, 54.01; H, 7.87%).

Crystallography

Crystals of [OsF₂(CO)₂(PPh₃)₂], [OsF₂(CO)₂{P(C₆H₁₁)₃}₂] and [RuF₂(CO)₂(PEtPh₂)₂] suitable for diffraction were grown from dichloromethane (M = Os) or acetone (M = Ru) by slow evaporation of the solvent. The crystal data and experimental parameters are given in Table 4. Crystal stability was monitored by the observation of the intensities of three standard reflections and for none of the structures was there any significant loss of intensity. For each data set a semiempirical absorption correction was applied (based on ψ scans) and the data were corrected for Lorentz and polarisation effects. All structures were solved by Patterson methods using SHELXTL PC[14] and refined by full-matrix least squares on *F²* using the program package SHELXL 93.[15] All non-hydrogen atoms were

Table 1 Mass spectral, IR and NMR spectral data for [*OC*-6-13][OsF$_2$(CO)$_2$L$_2$]

L	m/z [a]	$\tilde{v}$(CO) [b]/cm^{-1}	NMR [c]
PPh$_3$	791 [$M - F$]$^+$ 763 [$M - F - CO$]$^+$	2017, 1937	^{1}H: 7.5 (m) ^{19}F: −303.3 [t, ^2J(PF) 30] ^{31}P: 1.0 (t)
PEtPh$_2$	695 [$M - F$]$^+$ 667 [$M - F - CO$]$^+$	2031, 1950	^{1}H: 1.1 (3 H, m), 2.0 (2 H, m), 7.3 (10 H, m) ^{19}F: −310.3 [t, ^2J(PF) 33] ^{31}P: 4.4 (t)
PMe$_3$	419 [$M - F$]$^+$ 391 [$M - F - CO$]$^+$	2024, 1939	^{1}H: 1.6 [vt, ^nJ(PH) 8] ^{19}F: −315.2 [t, ^2J(PF) 38] ^{31}P: −14.8 (t)
P(C$_6$H$_{11}$)$_3$	827 [$M - F$]$^+$ 799 [$M - F - CO$]$^+$	2005, 1925	^{1}H: 2.1 (m) ^{19}F: −309.6 [t, ^2J(PF) 29] ^{31}P: 15.5 (t)
PPh$_2$(C$_6$F$_5$)	971 [$M - F$]$^+$ 943 [$M - F - CO$]$^+$	2029, 1959	^{1}H: 7.6 (m) ^{19}F: −300.5 [2 F, t, ^2J(PF) 33, F$_{Os}$], −160.2 [4 F, F$_m$, m], −147.5 (2 F, F$_p$, m), −123.9 (4 F, F$_o$, m) ^{31}P: 2.8 (t)
P(p-MeC$_6$H$_4$)$_3$	827 [$M - 2F - CO$]$^+$	2021, 1942	^{1}H: 2.4 (3 H, s), 7.4 (4 H, m) ^{19}F: −302.7 [t, ^2J(PF) 32] ^{31}P: −3.0 (t)
P(p-FC$_6$H$_4$)$_3$	899 [$M - F$]$^+$ 871 [$M - F - CO$]$^+$	2035, 1962	^{1}H: 7.1 (m), 7.2 (m), 7.8 (m) ^{19}F: −308.8 [2 F, t, ^2J(PF) 32, F$_{Os}$], −108.8 (6 F, s, F$_p$) [d] ^{31}P: −4.0 (t)
PEt$_3$	503 [$M - F$]$^+$ 475 [$M - F - CO$]$^+$	2034, 1963	^{1}H: 1.3 (3 H, m), 2.0 (2 H, m) ^{19}F: −317.4 [t, ^2J(PF) 33] ^{31}P: 11.1 (t)
PMePh$_2$	667 [$M - F$]$^+$ 639 [$M - F - CO$]$^+$	2026, 1941	^{1}H: 2.0 (3 H, m), 7.3 (10 H, m) ^{19}F: −310.6 [t, ^2J(PF) 35] ^{31}P: −1.8 (t)
PMe$_2$Ph	543 [$M - F$]$^+$ 515 [$M - F - CO$]$^+$	2043, 1945	^{1}H: 1.7 (6 H, m), 7.3 (5 H, m) ^{19}F: −312.6 [t, ^2J(PF) 37] ^{31}P: −7.6 (t)
PEt$_2$Ph	599 [$M - F$]$^+$ 571 [$M - F - CO$]$^+$	2023, 1943	^{1}H: 1.0 (6 H, m), 2.1 (4 H, m), 7.3 (5 H, m) ^{19}F: −313.8 [t, ^2J(PF) 34] ^{31}P: 9.4 (t)
C$_5$H$_5$N	425 [$M - F$]$^+$	2010, 1943	^{1}H: 7.7 (m) ^{19}F: −286.8 (s)
AsPh$_3$	851 [$M - F - CO$]$^+$	2050, 2007	^{1}H: 7.5 (m) ^{19}F: −340.6 (s)

[a] Fast-atom bombardment with m-nitrobenzyl alcohol matrix. [b] Recorded as Nujol mulls; ±2 cm^{-1}. [c] Recorded in CD$_2$Cl$_2$. Data given as: chemical shift (δ) (relative intensity, multiplicity, J in Hz, assignment); s = singlet, d = doublet, t = triplet, vt = virtual triplet, m = multiplet. [d] Only observed on broad-band proton decoupling.

refined as anisotropic with the exception of the solvent atoms in the [OsF$_2$(CO)$_2$(PPh$_3$)$_2$] structure. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with positional parameters riding on the attached atom and with a fixed isotropic thermal parameter ($U_{iso} = 0.08$ Å^2). The final Fourier-difference map of [OsF$_2$(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$] had +1.91 and −2.09 e Å^{-3} peaks approximately 1 Å from the osmium atom; in all other respects the final Fourier-difference maps were satisfactory.

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Results and Discussion

The complexes [{MF$_2$(CO)$_3$}$_4$] (M = Ru or Os) are highly moisture- and oxygen-sensitive and are insoluble in the common organic solvents. However, after addition of any one of a series of Lewis bases in dichloromethane (M = Os) or acetone (M = Ru) in an inert atmosphere, carbon monoxide gas is evolved and the metal complexes dissolve completely to give yellow solutions. Halogenated solvents are incompatible with the products when M = Ru since they appear to undergo halogen-exchange reactions; similar reactions have been observed for iridium(III) fluoride complexes in dichloromethane.[16] Removal of the solvent in vacuum yields the products as air-stable off-white or pale yellow solids. The NMR spectroscopic studies in solution (Tables 1 and 2), particularly for the products containing phosphine ligands, give a clear indication of the chemical composition. When L = PPh$_3$ the ^{19}F and ^{31}P NMR spectra show mutually-coupled triplet

resonances in excellent agreement with those of our previously characterised [*OC*-6-13][MF$_2$(CO)$_2$(PPh$_3$)$_2$] (M = Ru or Os).[6] For the other phosphine-containing products the NMR spectra exhibit similar mutually-coupled triplet resonances with comparable $^2J_{PF}$ coupling constants and ^{19}F NMR chemical shifts, indicative of F *trans* to CO, which confirm that this reaction offers a general route to [*OC*-6-13][MF$_2$(CO)$_2$L$_2$] (M = Ru or Os; L = two-electron donor ligand) co-ordination compounds.

For the range of phosphine ligands, δ(^{19}F) is virtually constant while δ(F$_{Ru}$) occurs to lower frequency than δ(F$_{Os}$) as observed throughout all of our studies of ruthenium and osmium carbonyl fluorides. When the ^{19}F NMR data for *cis*-[MF$_2$(CO)$_4$] (M = Ru, δ −349.0; M = Os, δ −342.5) are included, a general shift to higher frequency for δ(F$_{trans}$–CO) with increasing σ-donor strength of the axial ligand pyridine (py) > phosphine > CO > AsPh$_3$ is identified. Further work is underway to investigate whether this trend holds for all types of donor ligand. However, this observation is opposite to that previously reported for the co-ordination of CO or pyridine to five-co-ordinate [RuH(F)(CO)(PBu$^t_2$Me)$_2$], namely [RuH(F)-(CO)$_2$(PBu$^t_2$Me)$_2$] δ(F) −202 and [RuH(F)(CO)(py)(PBu$^t_2$-Me)$_2$] δ(F) −491.[11] We note that the chemical shift reported for this pyridine adduct is extremely low and, on the basis of our work, is not typical for δ(F) for fluoride *trans* to carbonyl, but is more typical of a bridging fluoride ligand or of fluoride *trans* to halide. This discrepancy between the observations from our work and that previously reported[11] indicates that more detailed study is necessary in this area.

Table 2 Mass spectral, IR and NMR spectral data for [OC-6-13][$RuF_2(CO)_2L_2$]

L	m/z [a]	$\nu(CO)$ [b]/cm^{-1}	NMR [c]
PPh$_3$	701 [$M - F$]$^+$ 673 [$M - F - CO$]$^+$	2045, 1973	^{1}H: 7.6 (m) ^{19}F: −324.3 [t, ^2J(PF) 20] ^{31}P: 21.6 (t)
PEtPh$_2$	577 [$M - F - CO$]$^+$	2046, 1961	^{1}H: 1.1 (3 H, m), 2.3 (2 H, m), 7.4 (10 H, m) ^{19}F: −327.1 [t, ^2J(PF) 22] ^{31}P: 24.8 (t)
PMe$_3$	301 [$M - F - CO$]$^+$	2047, 1974	^{1}H: 1.6 [vt, ^nJ(PH) 7] ^{19}F: −328.7 [t, ^2J(PF) 28] ^{31}P: 3.3 (t)
P(C$_6$H$_{11}$)$_3$	737 [$M - F$]$^+$	2017, 1936	^{1}H: 1.8 (m) ^{19}F: −324.3 [t, ^2J(PF) 20] ^{31}P: 36.6 (t)
PPh$_2$(C$_6$F$_5$)	881 [$M - F$]$^+$ 853 [$M - F - CO$]$^+$	2055, 1986	^{1}H: 7.5 (m) ^{19}F: −321.2 [2 F, t, ^2J(PF) 25, F$_{Ru}$], −162.0 (4 F, F$_m$, m), −149.7 (2 F, F$_p$, m), −123.9 (4 F, F$_o$, m) ^{31}P: 21.7 (t)
P(p-MeC$_6$H$_4$)$_3$	757 [$M - F - CO$]$^+$	2045, 1975	^{1}H: 2.1 (3 H, s), 7.2 (4 H, m) ^{19}F: −327.5 [t, ^2J(PF) 22] ^{31}P: 15.7 (t)
P(p-FC$_6$H$_4$)$_3$	809 [$M - F$]$^+$ 781 [$M - F - CO$]$^+$	2047, 1974	^{1}H: 7.5 (m), 8.2 (m) ^{19}F: −333.1 [2 F, t, ^2J(PF) 23, F$_{Ru}$], −108.9 (6 F, s, F$_p$) [d] ^{31}P: 14.9 (t)
PEt$_3$	413 [$M - F$]$^+$ 385 [$M - F - CO$]$^+$	2036, 1963	^{1}H: 1.2 (3 H, m), 2.1 (2 H, m) ^{19}F: −330.2 [t, ^2J(PF) 23] ^{31}P: 28.8 (t)
PMePh$_2$	549 [$M - F - CO$]$^+$	2046, 1977	^{1}H: 1.9 (3 H, m), 7.5 (10 H, m) ^{19}F: −324.5 [t, ^2J(PF) 25] ^{31}P: 16.9 (t)
PMe$_2$Ph	453 [$M - F$]$^+$ 425 [$M - F - CO$]$^+$	2043, 1964	^{1}H: 1.8 (6 H, m), 7.5 (5 H, m) ^{19}F: −325.1 [t, ^2J(PF) 25] ^{31}P: 7.8 (t)
PEt$_2$Ph	481 [$M - F - CO$]$^+$	2047, 1978	^{1}H: 1.1 (6 H, m), 2.0 (4 H, m), 7.6 (5 H, m) ^{19}F: −327.0 [t, ^2J(PF) 21] ^{31}P: 24.3 (t)
C$_5$H$_5$N	335 [$M - F$]$^+$	2042, 1959	^{1}H: 7.8 (m) ^{19}F: −269.7
AsPh$_3$	789 [$M - F$]$^+$ 761 [$M - F - CO$]$^+$	2031, 1958	^{1}H: 7.5 (m) ^{19}F: −349.0

[a] Fast-atom bombardment with m-nitrobenzyl alcohol matrix. [b] Recorded as Nujol mulls; ±2 cm^{-1}. [c] Recorded in [^{2}H$_6$]acetone. [d] Only observed on broad-band proton decoupling.

The co-ordination chemical shift Δ^{31}P($\delta_{complex} - \delta_{free\ ligand}$) [17] and the $^2J_{PF}$ coupling constants show a decrease and increase, respectively, with increasing cone angle of the phosphine ligand. Similar trends have been identified for [OC-6-33]-[$RuCl_2(CO)_2L_2$] [18] and [OC-6-13][$IrF(COF)(CO)_2L_2$][BF$_4$], [19] although the origin of this influence is not clear. A better indication of ligand effects arises from the observed variation in $\delta(^{31}$P) in a series of complexes [$MX_2(CO)_2L_2$] where only the anionic ligand X is varied for constant L. The first derivatives in this class were reported in the early 1960s and so ^{31}P NMR data are not available for all ligand combinations. From the limited data available it appears that the ^{31}P chemical shifts decrease in the order F > SCN > Cl > Br > I in line with the nephelauxetic effect [$i.e.$ L = PPh$_3$, M = Ru; X = SCN δ(P) = 20.9, X = Cl δ(P) = 17.1, X = Br δ(P) = 13.3, X = I δ(P) = 7.8]. [20]

As expected, these derivatives show two carbonyl stretching vibrations in their IR spectra, which are insensitive to the nature of L (Tables 1 and 2). Comparison of these data with those for the analogous chloride, bromide and iodide complexes (Table 3), indicates that ν(CO) is lower for fluoride than chloride ≈ bromide ≈ iodide. This trend is contrary to that expected from electronegativity arguments. However, theoretical studies on the 18-electron [$RuF(H)(CO)(PBu^t_2Me)_2L$] (L = py or CO) [11] indicate that the CO π^* orbitals can interact to stabilise Ru–X π^* orbitals, thus allowing some degree of net Ru–X π bonding. Hence, these data offer further experimental evidence to support the view that fluoride can behave as a significant π-electron donor to low-valent transition-metal derivatives when π-acidic ligands are present. Similar trends in CO and NO stretching frequencies have been described for $trans$-[$MX(CO)(PPh_3)_2$]

Table 3 Comparison of the CO stretching frequencies for the complexes $cis,cis,trans$-[$MX_2(CO)_2(PPh_3)_2$] as a function of X

X	M = Os	M = Ru
H	2020, 1990 [a]	2011, 1974 [a]
F	2017, 1937 [b]	2045, 1973 [b]
Cl	2041, 1970 [c]	2061, 1998 [d]
Br	2042, 1970 [c]	2058, 1994 [d]
I	2040, 1975 [c]	2050, 1990 [d]

[a] Recorded in heptane. [21] [b] Recorded in Nujol, this work. [c] Recorded in C$_2$Cl$_4$. [22] [d] Recorded in Nujol. [19]

(M = Rh or Ir), [23] [ReX(NO)(PR$_3$)(η^5-C$_5$H$_5$)], [24] [ReCl$_2$F(NO)-(bipy)], [3] [RuX(H)(CO)(py)(PBu$^t_2$Me)$_2$] and [RuX(H)(CO)-(PBu$^t_2$Me)$_2$] [11] (X = halide).

There are five possible isomers for [$MX_2(CO)_2L_2$] complexes. For the heavier halides (X = Cl, Br or I), four isomers (M = Os) and all five isomers (M = Ru) have been prepared, although the $cis,cis,trans$ and $trans,cis,cis$ isomers have been shown to be more stable than the other isomers and have been described more frequently. [25] The $cis,cis,trans$ isomer is usually formed at high temperatures and is recognised as the thermodynamic product; the $trans,cis,cis$ isomer, the kinetic product, is usually found at lower temperatures. When X = F, we have only observed the $cis,cis,trans$ isomer, even when the reaction mixture is held at low temperatures, indicating the strong thermodynamic driving force for this configuration and the strong preference for the fluoride $trans$ to carbonyl arrangement. We have noted a similar thermodynamic preference for a fluoride

Table 4 X-Ray crystal data collection, solution and refinement details for $[OC\text{-}6\text{-}13][RuF_2(CO)_2(PEtPh_2)_2]$, $[OC\text{-}6\text{-}13][OsF_2(CO)_2\{P(C_6H_{11})_3\}_2]\cdot$
CH_2Cl_2 and $[OC\text{-}6\text{-}13][OsF_2(CO)_2(PPh_3)_2]\cdot CH_2Cl_2$*

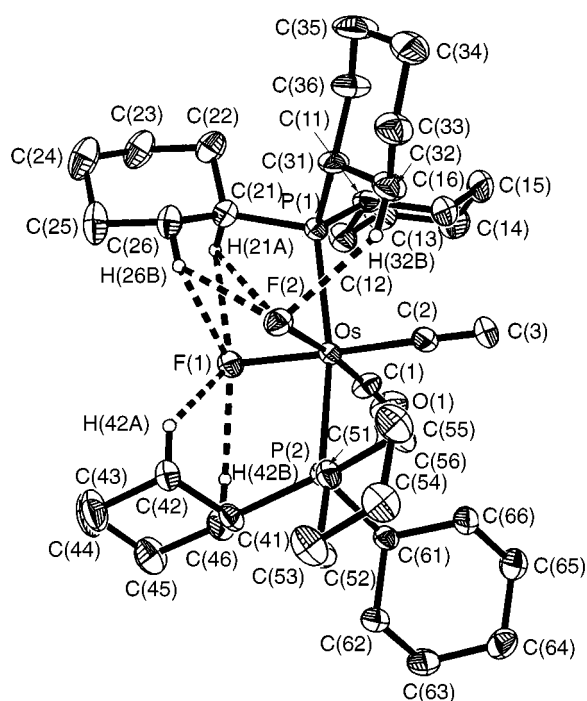|	$[OsF_2(CO)_2(PPh_3)_2]$	$[OsF_2(CO)_2\{P(C_6H_{11})_3\}_2]$	$[RuF_2(CO)_2(PEtPh_2)_2]$
Formula	$C_{39}H_{32}Cl_2F_2O_2OsP_2$	$C_{39}H_{36}Cl_2F_2O_2OsP_2$	$C_{30}H_{30}F_2O_2P_2Ru$
M	893.69	929.97	623.55
T/K	293	190	193
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$
$a/\text{Å}$	17.197(2)	10.732(2)	9.751(1)
$b/\text{Å}$	10.791(2)	12.519(2)	13.022(1)
$c/\text{Å}$	20.034(3)	17.228(4)	22.415(2)
$\alpha/°$		81.14(1)	
$\beta/°$	102.94(1)	76.12(2)	100.93(1)
$\gamma/°$		71.13(2)	
$U/\text{Å}^3$	3623.4(10)	2118.9(7)	2794.6(4)
Cell measurement reflections used, θ range/°	53, 4.2–12.5	22, 5.2–12.5	29, 3.8–12.5
Z	4	2	4
$D_c/\text{Mg m}^{-3}$	1.638	1.458	1.482
μ/mm^{-1}	3.799	3.250	0.714
Maximum, minimum transmission	0.94, 0.78	0.86, 0.67	0.80, 0.78
$F(000)$	1760	952	1272
Crystal size/mm	$0.38 \times 0.18 \times 0.11$	$0.60 \times 0.56 \times 0.55$	$0.70 \times 0.40 \times 0.28$
Index ranges	$-1 \leq h \leq 20, -1 \leq k \leq 12,$ $-23 \leq l \leq 23$	$-1 \leq h \leq 12, -14 \leq k \leq 14,$ $-20 \leq l \leq 20$	$-1 \leq h \leq 12, -1 \leq k \leq 16,$ $-28 \leq l \leq 28$
θ Range/°	2.5–25	2.5–25	2.5–27
Reflections collected	4071	8688	7820
Independent reflections (R_{int})	3184 (0.0294)	7406 (0.0301)	6100 (0.0245)
Data, restraints, parameters	3184, 0, 210	7405, 0, 442	6100, 0, 334
Goodness of fit on F^2	0.963	1.045	1.041
Final $R1$, $wR2$ indices	0.0485, 0.1170	0.0447, 0.1083	0.0359, 0.0840
(all data)	0.0682, 0.1236	0.0576, 0.1165	0.0513, 0.0921
Largest difference peak and hole/e Å^{-3}	0.924, −1.03	1.910, −2.093 (*ca.* 1 Å from Os)	0.536, 0.391

* Details in common: Siemens P4 diffractometer, λ(Mo-Kα) = 0.7107 Å, ω-scan type; $R1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.
Goodness of fit, $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where n = number of reflections and p is the total number of parameters refined.
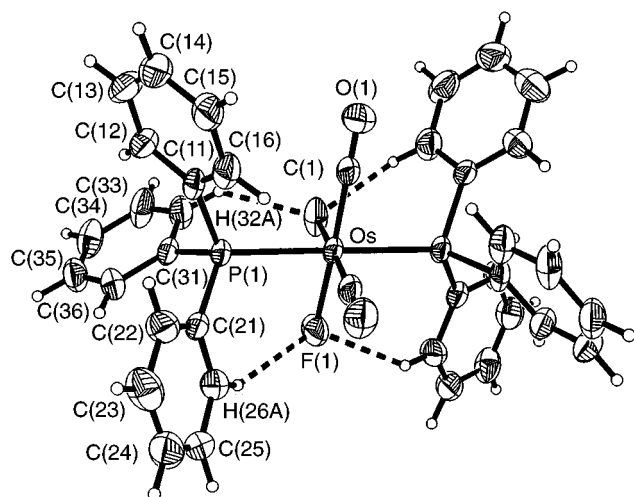
Fig. 1 Molecular structure of $[OC\text{-}6\text{-}13][OsF_2(CO)_2(PPh_3)_2]\cdot CH_2Cl_2$; displacement ellipsoids are shown at the 30% level

Fig. 2 Molecular structure of $[OC\text{-}6\text{-}13][OsF_2(CO)_2\{P(C_6H_{11})_3\}_2]\cdot$ CH_2Cl_2; displacement ellipsoids are shown at the 30% level. The hydrogen atoms other than those involved in hydrogen bonding are omitted for clarity

trans to carbonyl arrangement in the isomerisation of *mer-* and *fac*-$[IrF_3(CO)_3]$ even at very low temperatures.[1]

The complexes $[OC\text{-}6\text{-}13][MF_2(CO)_2L_2]$ [M = Os, L = PPh$_3$ or P(C$_6$H$_{11}$)$_3$; M = Ru, L = PPh$_2$Et] have been further characterised by X-ray crystallography; these structure determinations include the first examples of crystallographic analyses of osmium(II) fluoride complexes. The structures are shown in Figs. 1–3 and selected bond lengths and angles, together with data for the isostructural $[OC\text{-}6\text{-}13][RuF_2(CO)_2(PPh_3)_2]$,[6] are given in Table 5. The complexes are pseudo-octahedral with the two phosphine ligands *trans* to each other and the fluoride ligands *trans* to the carbonyl groups, as indicated by NMR spectroscopy, for these same complexes in solution. The metal–

fluorine bond lengths are very similar to each other and to those of the only other crystallographically characterised carbonyl fluoride complexes of d^6-transition metals: $[ReF(CO)_3$-$(Me_2NCH_2CH_2NMe_2)]$, Re–F 2.039(4) Å,[26] $[\{RuF_2(CO)_3\}_4]$,

Table 5 Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [OC-6-13][RuF$_2$(CO)$_2$(PPh$_3$)$_2$]·CD$_2$Cl$_2$,[6] [OC-6-13][RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$], [OC-6-13][OsF$_2$(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$]·CH$_2$Cl$_2$ and [OC-6-13][OsF$_2$(CO)$_2$(PPh$_3$)$_2$]·CH$_2$Cl$_2$

	[RuF$_2$(CO)$_2$(PPh$_3$)$_2$]·CD$_2$Cl$_2$	[RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$]	[OsF$_2$(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$]·CH$_2$Cl$_2$	[OsF$_2$(CO)$_2$(PPh$_3$)$_2$]·CH$_2$Cl$_2$
M–F	2.011(4)	2.017(2) / 2.028(2)	2.023(4) / 2.022(4)	2.023(5)
M–P	2.406(1)	2.3921(7) / 2.3872(7)	2.438(2) / 2.423(2)	2.418(2)
M–C	1.841(7)	1.855(3) / 1.853(3)	1.841(8) / 1.854(7)	1.832(9)
C–O	1.135(9)	1.146(4) / 1.132(4)	1.158(9) / 1.154(8)	1.178(9)
P–M–P	178.2(1)	171.82(2)	166.41(5)	177.59(10)
F–M–F	84.4(2)	86.40(7)	83.5(2)	81.3(3)
C–M–C	92.2(4)	91.9(2)	86.6(3)	90.5(5)
M–C–O	178.7(8)	179.3(3)	177.5(6)	178.8(7)
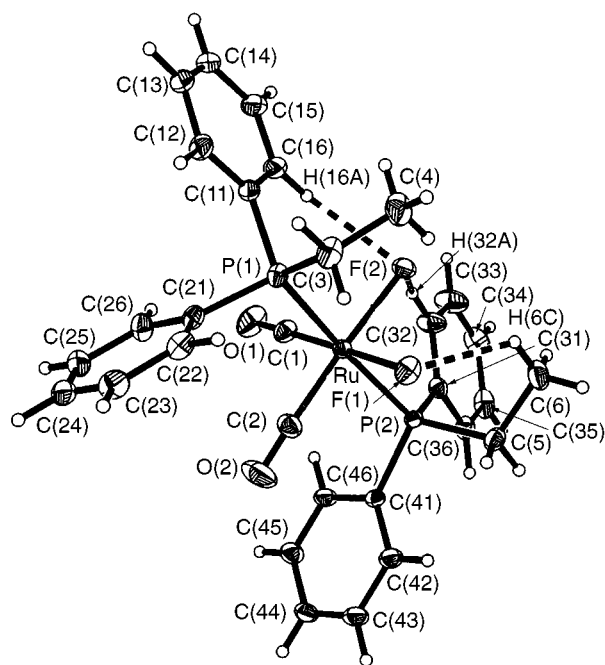
Fig. 3 Molecular structure of [OC-6-13][RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$]; displacement ellipsoids are shown at the 30% level

Ru–F$_{terminal}$ 1.99(7), Ru–F$_{bridging}$ 2.04(7) Å,[8] [IrF(COF)(CO)$_2$-(PEt$_3$)$_2$][BF$_4$], Ir–F 1.998(3) Å,[27] [IrF(Cl)(NSF$_2$)(CO)(PPh$_3$)$_2$], Ir–F 2.089(4) Å.[28] In [OC-6-13][RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$] only there is a discernible difference between the two M–F bond lengths. The metal–phosphorus bond lengths are slightly longer than those in other neutral d^6-transition-metal complexes,[29] but are not unreasonable when compared to those in the other d^6 metal fluoride complexes.[26,28] The phosphine ligands with the smaller cone angle have the shorter M–P distance [2.3896(7) Å (mean) for PEtPh$_2$, 2.413(2) Å (mean) for PPh$_3$ and 2.430(2) Å (mean) for P(C$_6$H$_{11}$)$_3$] which may be linked to the variation in $\Delta(^{31}P)$. The metal–carbon distances are very similar to, although slightly shorter than, those observed for other osmium(II) and ruthenium(II) compounds (1.873–1.880 Å).[29] There is a similar variation in the C–O bond length which correlates with the variation in ν(CO).

It is noteworthy that there is a considerable difference in the P–M–P angles [177.59(10)–166.41(5)°] as the phosphine ligand is changed. The orientation of the substituents on these ligands also varies; for [OC-6-13][MF$_2$(CO)$_2$(PPh$_3$)$_2$] (M = Ru or Os) the aryl rings are staggered whilst for [OC-6-13][OsF$_2$-(CO)$_2${P(C$_6$H$_{11}$)$_3$}$_2$] and [OC-6-13][RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$] the alkyl groups are eclipsed. All of the complexes contain short intramolecular interactions between hydrogen atoms on the ligands and the fluorides. For [OC-6-13][OsF$_2$(CO)$_2$(PPh$_3$)$_2$] a
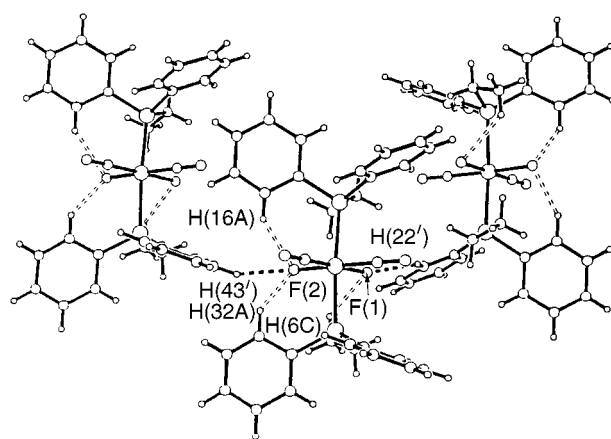
Fig. 4 Extended structure of [OC-6-13][RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$] showing intermolecular interactions; displacement ellipsoids are shown at the 30% level

number of short H···F distances are observed [H(26B)··· F(1) 2.253, H(32B)···F(1) 2.238, H(26A)···F(1A) 2.252 and H(32A)···F(1A) 2.238 Å], all of which are shorter than the sum of the van der Waals radii of hydrogen and fluorine [r_{vdw}(H) = 1.20, r_{vdw}(F) = 1.47 Å].[30] In the absence of stronger interactions, it is now recognised that weak F···H–C interactions, like these, are important in aligning molecules.[31] Indeed, an early example of intramolecular C–F bond activation was believed to occur *via* HF elimination arising from incipient H···F hydrogen bonding,[32] but the number of examples of F···H–C interactions involving metal-bound fluoride ligands is limited.[33] In [OC-6-13][OsF$_2$(CO)$_2$-{P(C$_6$H$_{11}$)$_3$}$_2$], the P(C$_6$H$_{11}$)$_3$ ligands are bent towards the fluoride ligands [P–Os–P 166.41(5)°] resulting in more non-bonding, short intramolecular H···F distances [H(21A)···F(1) 2.470, H(26B)···F(1) 2.373, H(42A)···F(1) 2.279, H(46B)···F(1) 2.304, H(26B)···F(2) 2.454 and H(32B)···F(2) 2.356 Å]. Similarly, in [OC-6-13][RuF$_2$(CO)$_2$(PEtPh$_2$)$_2$], the phosphines are bent towards the fluorine atoms [P–Ru–P 171.82(2)°] with short non-bonding, intramolecular H···F interactions [H(6C)···F(1) 2.476, H(32A)···F(2) 2.298 and H(16A)··· F(2) 2.421 Å]. The eclipsed ligand orientation results in the ethyl groups lying coplanar with the Ru–F(1) axis which may account for the variation in the Ru–F bond lengths in this complex. For all three complexes the intramolecular H···F interactions do not significantly influence the angles at phosphorus. The ruthenium complex is unique among these structures since, in addition to these short intramolecular interactions, an extended view of the structure indicates short intermolecular interactions between the fluoride ligands and hydrogen atoms on the phenyl rings of two adjacent molecules in the unit cell [H(22A′)···F(1) 2.235 and H(43A″)···F(2)

2.378 Å]. These hydrogen-bonding interactions also appear to influence the C–O bond lengths. For [*OC*-6-13][RuF$_2$(CO)$_2$-(PEtPh$_2$)$_2$], in particular, C(1)–O(1) [*i.e. trans* to F(1)] is shorter than C(2)–O(2) which may be rationalised by a reduction of the F→Ru π bonding which offers further support to the conclusion that fluoride can act as a significant π-electron donor in these systems.

One molecule of dichloromethane cocrystallises with one molecule of the metal complexes in the crystal structures of [*OC*-6-13][OsF$_2$(CO)$_2$(PPh$_3$)$_2$] and [*OC*-6-13][OsF$_2$(CO)$_2${P(C$_6$-H$_{11}$)$_3$}$_2$]. In both cases the solvent molecule is very close to the equatorial plane containing the metal, carbonyl and fluoride ligands and is held by further, short intramolecular H $\cdots$ F interactions.

Conclusion

The reaction of [{MF$_2$(CO)$_3$}$_4$] (M = Ru or Os) with Lewis bases represents a convenient route to some air- and moisture-stable ruthenium(II) and osmium(II) fluoride co-ordination complexes of general formulae [MF$_2$(CO)$_2$L$_2$], which preferentially adopt *cis,cis,trans* ligand arrangements.

Acknowledgements

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