Reactions of *cis*-$[Os(CO)_4Me_2]$ and *cis*-$[Re(CO)_4(PPh_3)Me]$ with Anhydrous HF and $HOTeF_5$; Compatibility of Phosphine, Alkyl and $OTeF_5^-$ Ligands in Low-valent Transition-metal Complexes

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In the reactions of transition metal carbonyl methyls with HF or $HOTeF_5$ the elimination of methane has been shown to be a strong driving force in the formation of, for example, *cis*-$[OsF_2(CO)_4]$, *cis*-$[ReF(CO)_4(PPh_3)]$, *cis*-$[Os(OTeF_5)(CO)_4Me]$ and *cis*-$[Re(OTeF_5)(CO)_4(PPh_3)]$, which have been characterised by a combination of multinuclear NMR spectroscopic studies. These results also indicate that, with a suitable choice of metals and co-ligands, transition-metal teflate-phosphine and teflate-alkyl complexes can be prepared (teflate = $OTeF_5^-$).

We are currently investigating low-valent and organometallic transition metal fluoride complexes, an area which has received relatively little attention.[1] In particular, we have had considerable success using XeF_2 as an oxidising fluorinating agent for transition-metal carbonyls, *e.g.* $[Re_2(CO)_{10}]$,[2,3] $[Os_3(CO)_{12}]$,[4] $[Ru_3(CO)_{12}]$[5] and $[Ir_4(CO)_{12}]$,[6] and transition-metal phosphine carbonyls, *e.g.* $[Ru(CO)_3(PPh_3)_2]$,[7] $[Os(CO)_3(PPh_3)_2]$,[7] $[Ir(CO)_3(PEt_3)_2]^+$[8] and $[MX(CO)(PEt_3)_2]$ (M = Rh or Ir; X = F, Cl, Br or I).[9] The bulky, $OTeF_5^-$ (or teflate) ligand derived from pentafluorohydroxotellurium(VI), which is a pseudofluoride with an electronegativity comparable to that of fluoride,[10] is well established as a ligand in main-group and high-oxidation-state transition-metal chemistries.[11] However, investigations of its chemistry with low-valent transition metals have been limited; characterised complexes include $[Mn(OTeF_5)(CO)_5]$,[12] $[Pt(OTeF_5)_2(nbd)]$ {nbd = norbornadiene (= bicyclo[2.2.1]heptadiene)},[13] $[Pd(OTeF_5)_2(PhCN)_2]$,[13] $[Zn(OTeF_5)_2(PhNO_2)_n]$ ($n = 2$ or 3),[14] and $[Pt(OTeF_5)_2(PEt_3)_2]$.[15] We are investigating the teflate–fluoride analogy in low-valent and organometallic transition–metal complexes, and were interested in a synthetic route which could be applicable in both systems. Strauss and co-workers[12] have used a methyl–teflate metathesis route to prepare $[Mn(OTeF_5)(CO)_5]$ and $[Fe(C_5H_5)(OTeF_5)(CO)_2]$ whilst recently, Cotton and Wiesinger,[16] have exchanged fluoride for methyl using Olah's reagent (py·*x*HF) in the preparation of $[Mo_2F_4(PR_3)_4]$ ($R_3 = Me_3$ or Me_2Ph, py = pyridine). Here, we report the reactions of *cis*-$[Os(CO)_4Me_2]$ and *cis*-$[Re(CO)_4(PPh_3)Me]$ with anhydrous HF and $HOTeF_5$.

Experimental

Proton, ^{13}C, ^{19}F and ^{31}P NMR spectroscopic studies were carried out on a Bruker AM300 NMR spectrometer at 300.14, 75.47, 282.41 and 121.50 MHz respectively in 5 mm selective and 10 mm broad-band probes. Spectra were recorded on samples in 4 mm outside diameter FEP (perfluoroethylene–propylene copolymer) tubes held coaxially in 5 or 10 mm precision glass NMR tubes containing D_2O as lock substance when necessary. Chemical shifts are reported as positive to high frequency of $SiMe_4$ (for ^1H and ^{13}C), 85% H_3PO_4 (for ^{31}P), and CCl_3F (for ^{19}F). 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). 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 acquistions were *ca.* 1 Hz. Fourier transforms were carried out without exponential smoothing. The ^{31}P-{^1H} spectra were recorded for *ca.* 1000 scans between δ +40 and −40 using 10 000 Hz windows (*ca.* 0.5 Hz per point), acquisition times of 1.5 s with 1 s relaxation delay, pulse widths of 6 μs (30°) and composite pulse decoupling. Fourier transformations were carried out with Lorentzian line broadening of 1 Hz. Infrared spectra were recorded for solid samples as Nujol mulls between KBr discs and for gaseous samples in a copper gas cell, pathlength 10 cm, fitted with AgCl windows on a Digilab FTS40 spectrometer.

cis-Tetracarbonyldimethylosmium,[17] and *cis*-tetracarbonyl(methyl)triphenylphosphinerhenium[18] were prepared by literature routes. Anhydrous HF (Fluorochem) was purified by vacuum transfer, dried by repeated fluorination at room temperature and stored in Kel-F tubes over dry BiF_5.[19] Prepared by the literature route,[20] $HOTeF_5$ was stored in a glass ampoule closed by a Young's greaseless valve. The solvent, CD_2Cl_2, was purified, dried, transferred under vacuum to a similar glass ampoule and degassed immediately prior to use.

Reaction of cis-$[Os(CO)_4Me_2]$ *with Anhydrous* HF.—The complex *cis*-$[Os(CO)_4Me_2]$ (0.04 g, 0.12 mmol) was sublimed under static vacuum into a pre-passivated 4 mm FEP tube fitted with a poly(tetrafluoroethylene) valve. Anhydrous HF (0.5 cm^3) was condensed onto this white crystalline material at −196 °C. On gradual warming to room temperature, vigorous gas evolution occurred at *ca.* −40 °C requiring recooling to −78 °C and venting. After the reaction had finished, as evidenced by no further gas evolution, the tube was sealed as described previously[21] and kept at low temperature for NMR studies (see below).

Reaction of cis-$[Os(CO)_4Me_2]$ *with* $HOTeF_5$.—The complex *cis*-$[Os(CO)_4Me_2]$ (0.05 g, 1.5 mmol) was sublimed under static vacuum into a pre-passivated 4 mm FEP tube. A four-fold molar excess of $HOTeF_5$ (1.4 g, 6 mmol) and CD_2Cl_2 (*ca.* 2

cm^3) were distilled onto the sample at -196 °C and the tube allowed to warm slowly to room temperature with gas evolution and venting. After the reaction had finished, the tube was sealed and kept at low temperature for NMR studies.

Reaction of cis-[Re(CO)$_4$(PPh$_3$)Me] *with Anhydrous* HF.—Solid *cis*-[Re(CO)$_4$(PPh$_3$)Me] (0.08 g, 1.4 mmol) was loaded in a dry-box into a prepared FEP tube and, after evacuation, dissolved in CD$_2$Cl$_2$ (*ca.* 2 cm^3). Aliquots of anhydrous HF (*ca.* 0.1 cm^3) were condensed onto the solution at -196 °C and the solution was allowed to warm to room temperature with gas evolution and venting until no more gas evolution was observed. The sample was then either sealed for NMR studies or the solvent removed under dynamic vacuum and the resulting solid transferred to the dry-box for IR studies.

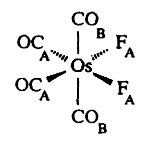
Reaction of cis-[Re(CO)$_4$(PPh$_3$)Me] *with* HOTeF$_5$.—This reaction was carried out in a similar fashion to the reaction of [Os(CO)$_4$Me$_2$] with HOTeF$_5$ except that the metal reagent (0.05 g) was loaded in the dry-box.

Results and Discussion

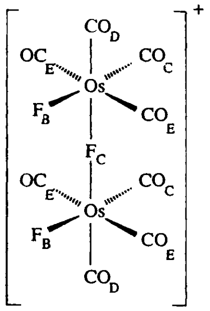
Methane, analysed by its characteristic gas-phase IR spectrum, was evolved in all of the reactions, indicating that the methodology was correct and that the reactions of metal–methyl reagents with HF or HOTeF$_5$ are convenient synthetic routes to metal fluorides or teflates.

In the reaction of tetracarbonyldimethylosmium with anhydrous HF, the ^{19}F NMR spectrum of the colourless solution at room temperature revealed two resonances typical of metal-bound fluoride at low frequency, δ -342.5 and -358.4. After leaving the sample at room temperature for several days, the resonance at δ -358.4 disappeared, the peak at δ -342.5 dominated the spectrum and two new weak features at δ -336.0 (doublet) and -465.0 (triplet) were evident. The features at δ -342.5, -336.0 and -465.0 are readily assigned to the *cis*-[OsF$_2$(CO)$_4$] **I** and [(OC)$_4$FOs(μ-F)OsF(CO)$_4$]$^+$ **II** respectively identified previously in the reaction of [Os$_3$(CO)$_{12}$] with XeF$_2$.[4] The fluorine-bridged dimer is formed by the dimerisation of **I** in anhydrous HF as we have already described.[4] Interestingly, we see no sign of the presence of [OsF(CO)$_5$]$^+$, identified in the reaction of [Os$_3$(CO)$_{12}$] with XeF$_2$, which contains a higher carbonyl to Os ratio than the starting material. This confirms our earlier suggestion that carbonyl scrambling around [Os$_3$(CO)$_{12}$] occurs during Os–Os bond cleavage, *i.e.* carbonyl scrambling does not occur in the reaction of *cis*-[Os(CO)$_4$Me$_2$] with anhydrous HF. We cannot isolate **I** since, on the removal of the solvent, CO evolution occurs and the tetrameric solid [{OsF$_2$(CO)$_3$}$_4$] is generated.[4] A ^{13}C NMR spectrum on the sample in solution (Table 1) confirmed our assignment by comparison with a literature spectrum.[4]

Further experiments have given additional information on the intermediates and mechanism of this reaction. After the initial gas evolution at -40 °C, the sample was frozen, the tube sealed and low-temperature (-50 °C) ^{1}H, ^{19}F and ^{13}C NMR spectra recorded. The ^{19}F NMR spectrum at this temperature was dominated by the resonance at δ -354.8 (temperature shifted from δ -358.4) which, under high resolution, resolved



I



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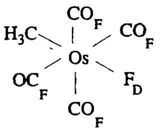

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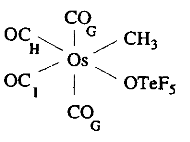
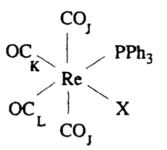


IV



V X = F

VI X = OTeF$_5$

Table 1 NMR data[a] for complexes I–VI

Complex	δ(^{19}F)	δ(^{13}C-{^{1}H})	$^2J_{FC}$/Hz
cis-[OsF$_2$(CO)$_4$] **I**	-342.5 (s) (F$_A$)	154.8[b] (CO$_A$)	*ca.* 65
		162.4 (s) (CO$_B$)	< 2
[Os$_2$F$_3$(CO)$_8$]$^+$ **II**	-336.0 (d) (F$_B$)	154.6 (d) (CO$_C$)	35
	-465.0 (t) (F$_C$)	151.4 (d) (CO$_D$)	87
		162.0 (s) (CO$_E$)	< 2
trans-[OsF(CO)$_4$Me] **III**	-358.4 (q) (F$_D$[c])	163.3 (s) (CO$_F$)	< 2
		-19.3 (d) (CH$_3$)	9
cis-[Os(OTeF$_5$)(CO)$_4$Me] **IV**	-34.4 (m) (F$_{ax}$[d])	172.2 (s) (CO$_G$)	—
	-47.8 (m) (F$_{eq}$[d])	168.9 (s) (CO$_{H/I}$)	—
		164.7 (s) (CO$_{H/I}$)	—
		-17.1 (q) (CH$_3$[e])	—
[ReF(CO)$_4$(PPh$_3$)] **V**	-374.9 (d) (F$_E$[f])	not observed	—
[Re(OTeF$_5$)(CO)$_4$(PPh$_3$)][g] **VI**	-33.3 (m) (F$_{ax}$[h])	186.3 (d) (CO$_J$[i])	—
	-47.9 (m) (F$_{eq}$[h])	184.7 (d) (CO$_K$[j])	—
		182.6 (d) (CO$_L$[k])	—

[a] Recorded at room temperature in anhydrous HF, HOTeF$_5$ or CD$_2$Cl$_2$ as appropriate, see text. [b] A second-order AXX′ multiplet.[4] [c] Proton NMR resonance observed at δ 0.2; $^2J_{HF}$ = 13 Hz. [d] $^2J_{F_{ax}F_{eq}}$ = 181 Hz. [e] Proton NMR resonance observed at δ 0.81; $^1J_{CH}$ = 132 Hz. [f] Phosphorus-31 NMR resonance at δ 10.8; $^2J_{PF}$ = 34 Hz. [g] Phosphorus-31 NMR resonance at δ 13.5. [h] $^2J_{F_{ax}F_{eq}}$ = 180 Hz. [i] $^2J_{PC}$ = 9 Hz. [j] $^2J_{PC}$ = 7 Hz. [k] $^2J_{PC}$ = 52 Hz.

as a quartet ($^2J_{HF}$ = 13 Hz) exhibiting coupling to three equivalent protons (in the ^{19}F-{^{1}H} NMR spectrum this resonance is a singlet), indicating a single fluorine-containing product. The ^{1}H NMR spectrum revealed a related doublet resonance at δ 0.2 showing that the intermediate contains a metal-bound methyl group coupled to a single fluorine atom. A second resonance, a singlet at δ 0.1 in a 2 : 1 ratio relative to the resonance at δ 0.2, was also present in this spectrum (see below). The low-temperature ^{13}C-{^{1}H} NMR spectrum revealed five resonances, three singlets assignable to metal-bound carbonyl ligands at δ 170.5, 167.2 and 163.3, and two C_{methyl} resonances at δ −23.0 (singlet) and δ −19.3 (doublet, $^2J_{FC}$ = 9 Hz). The C_{methyl} doublet resonance confirms that the intermediate is a metal methyl monofluoride species, the other C_{methyl} resonance can be assigned to unreacted starting material (see below). The two high-frequency carbonyl resonances are also assigned to unreacted starting material (see below) and the absence of a large (typically 80 Hz) fluorine–carbon coupling for CO_{trans}–F suggests that the final resonance (δ 163.3) must correspond to CO_{cis}–F in the unusual monofluorinated, monomethylated osmium intermediate *trans*-[OsF(CO)$_4$Me] **III**. The observation of all-*trans* carbonyl groups in **III** strongly suggests that this is the kinetic product of this reaction and correlates with our work on the fluorination of [Ir$_4$(CO)$_{12}$].[6] The remaining ^{13}C and ^{1}H NMR resonances can be assigned to unreacted starting material; solvent and temperature shifts make a direct comparison difficult, but in C_6D_6 at 30 °C, ^{13}C resonances at δ 177.7 and 170.6 and a ^{1}H resonance at δ 0.15 are observed for *cis*-[Os(CO)$_4$Me$_2$]. It is clear, therefore, that the reaction of *cis*-[Os(CO)$_4$Me$_2$] with anhydrous HF proceeds in two stages. Initially *trans*-[OsF(CO)$_4$Me] **III** is formed which reacts, more slowly, to form *cis*-[OsF$_2$(CO)$_4$] **I** which undergoes partial dimerisation in solution to **II**. This stability of the Os–CH$_3$ bond to electrophilic attack has been demonstrated previously in the reaction of bromine with *cis*-[Os(CO)$_4$Me$_2$] where in the initial product, *cis*-[OsBr(CO)$_4$Me], the second Os–CH$_3$ bond is unreactive to Br$_2$.[22] Here, at elevated temperatures, the thermodynamically favourable *cis*-carbonyl arrangement is observed.

In contrast, the reaction of tetracarbonyldimethylosmium with HOTeF$_5$ in CD$_2$Cl$_2$ afforded a single product which also could not be isolated. After gas evolution had ceased, removal of the solvent and excess of HOTeF$_5$ resulted in decomposition and the generation of an insoluble black precipitate. However, the product was stable in solution in the presence of excess of HOTeF$_5$ and could be identified by a combination of NMR spectroscopic studies. The ^{19}F NMR was dominated by the characteristic AB$_4$ pattern due to the excess of HOTeF$_5$, but, a second AB$_4$ pattern was clearly visible which could be simulated by δ(F$_{ax}$) −34.4, δ(F$_{eq}$) −47.8, $^2J_{F_{ax}F_{eq}}$ = 181 Hz, *R* = 0.048† ($^1J_{TeF_{eq}}$ = 3610 Hz, ^{125}Te satellites on F$_{ax}$ unresolved). The large shift of the F$_{ax}$ resonance from that for HOTeF$_5$ the low value for *R*[23] and the highly first-order appearance of the spectrum confirm the co-ordination of the teflate ligand to the metal centre. Indeed *R* is very similar to that reported for the other metal carbonyl teflate complexes; [Mn(OTeF$_5$)(CO)$_5$], *R* = 0.046; [Re(OTeF$_5$)(CO)$_5$], *R* = 0.040; [Fe(C$_5$H$_5$)(OTeF$_5$)(CO)$_2$], *R* = 0.040,[12] suggesting also that the osmium–teflate bond is highly ionic. The ^{1}H NMR spectrum shows a single resonance at δ 0.81, typical of a metal-bound methyl group. The ^{13}C NMR spectrum revealed four resonances; three typical of metal-bound carbonyl ligands at δ 172.2, 168.9 and 164.7, and a quartet at δ −17.1 ($^1J_{CH}$ = 132 Hz), characteristic of a metal-bound methyl group which collapses to a singlet on proton decoupling. These data allow characterisation of the single product from the reaction of *cis*-[Os(CO)$_4$Me$_2$] with HOTeF$_5$ as *cis*-[Os(OTeF$_5$)(CO)$_4$Me] **IV**. Carbon-13 NMR data have not been reported previously for transition-metal carbonyl teflate complexes, but these data compare reasonably with our data for osmium carbonyl fluorides.[4] This represents the first example of a transition-metal alkyl teflate complex (metal alkyl teflate complexes are well established for main-group metals) and contrasts with our observations of decomposition in the reaction of *cis*-[PtMe$_2$(PEt$_3$)$_2$] with HOTeF$_5$.[15] In an attempt to induce *cis*-[Os(OTeF$_5$)(CO)$_4$Me] to react with a second equivalent of HOTeF$_5$, the reaction mixture was heated to 60 °C for several hours. However, the NMR spectra were unchanged after this time indicating that reaction would not proceed beyond the monosubstituted derivative. The failure of HOTeF$_5$ to react beyond monosubstituted derivatives has been noted previously.[24] This result also compares with the single dealkylation observed in the reaction of *cis*-[Os(CO)$_4$Me$_2$] with Br$_2$,[22] but contrasts with our observation of complete dealkylation in the reaction with HF *via* the *trans*-[OsF(CO)$_4$Me] **III** intermediate, which suggests that the metal–teflate and metal–fluoride interactions are significantly different in low-valent metal complexes.

Following these results, we considered the monomethylated *cis*-[Re(CO)$_4$(PPh$_3$)Me] complex. A ^{19}F and ^{31}P NMR spectroscopic examination of the yellow solution obtained in the reaction of *cis*-[Re(CO)$_4$(PPh$_3$)Me] with anhydrous HF indicated a single product. Related doublets at δ(^{19}F) −374.9 and δ(^{31}P) 10.8, $^2J_{PF}$ = 34 Hz, are consistent with a *cis*-[ReF(CO)$_4$(PPh$_3$)] **V** formulation. Solid-state IR spectroscopy [ν(CO) 2107s, 1995s, 1933 (br) cm^{-1}] confirms this assignment. This complex completes the series, [ReF(CO)$_{5-x}$(PPh$_3$)$_x$] (*x* = 0, 1 or 2), and confirms that substitution of CO by the more basic phosphine ligand confers additional stability on these transition-metal fluoro complexes, *i.e.* whilst the phosphine-substituted derivatives are stable in the solid state and in solution, [ReF(CO)$_5$] undergoes room temperature decarbonylation in solution with the formation of the fluoride-bridged tetramer, [{ReF(CO)$_3$}$_4$].[25]

The analogous teflate species, the first transition-metal triphenylphosphine teflate complex, is readily prepared in the reaction of *cis*-[Re(CO)$_4$(PPh$_3$)Me] with HOTeF$_5$. As we have shown for *cis*-[Os(OTeF$_5$)(CO)$_4$Me], *cis*-[Re(OTeF$_5$)(CO)$_4$(PPh$_3$)] **VI** has limited stability as a solid, and hence, has been characterised by NMR spectroscopies in solution in the presence of excess of TeF$_5$OH. The ^{31}P NMR spectra obtained for the green solution obtained from the reaction of *cis*-[Re(CO)$_4$(PPh$_3$)Me] with TeF$_5$OH show a singlet at δ 13.5 due to co-ordinated triphenylphosphine. The ^{13}C NMR spectrum consists of three doublets at δ 186.3 ($^2J_{PC}$ = 9 Hz), 184.7 ($^2J_{PC}$ = 7 Hz) and 182.6 ($^2J_{PC}$ = 52 Hz) typical of metal-bound carbonyl ligands; assignment of the three carbonyl environments is simplified by the ^{31}P–^{13}C couplings, *i.e.* in [Re(CO)$_4$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)][26] (*trans*-$^2J_{PC}$ = 41 Hz while *cis*-$^2J_{PC}$ = 8 Hz). The ^{19}F NMR spectrum revealed the expected AB$_4$ pattern for a co-ordinated teflate ligand; δ(F$_{ax}$) = −33.3, δ(F$_{eq}$) = −47.9, $^2J_{F_{ax}F_{eq}}$ = 180 Hz, *R* = 0.044, $^1J_{TeF_{eq}}$ = 3590 Hz (^{125}Te satellites on F$_{ax}$ unresolved). These data indicate a highly ionic metal–teflate interaction and are very similar to those obtained for the other transition-metal carbonyl teflate complexes, *cis*-[Os(OTeF$_5$)(CO)$_4$Me] (above), [Mn(OTeF$_5$)(CO)$_5$], [Re(OTeF$_5$)(CO)$_5$] and [Fe(C$_5$H$_5$)(OTeF$_5$)(CO)$_2$].[12] The preparation of *cis*-[Re(OTeF$_5$)(CO)$_4$(PPh$_3$)] is further evidence that the phosphine and teflate ligands are not mutually incompatible when co-ordinated to transition-metal centres as had been claimed previously,[13] but supports our assertion that, with a suitable choice of metal and phosphine ligands, stable transition-metal phosphine teflate complexes are obtainable.[15]

Conclusion

The reactions of HF or HOTeF$_5$ with transition-metal methyl complexes is a convenient route to low-valent transition metal

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† *R* = *J*(AB)/δ(AB) where *J*(AB) is the coupling constant between axial and equatorial fluorines and δ(AB) their chemical shift difference (both parameters in Hz).

fluoride and teflate complexes. Previously characterised fluoro complexes have been prepared by this method. The novel *cis*-$[Os(OTeF_5)(CO)_4Me]$ and *cis*-$[Re(OTeF_5)(CO)_4(PPh_3)]$ have been prepared and characterised, which illustrate that the $OTeF_5^-$ ligand and metal-bound methyl and triphenylphosphine ligands are mutually compatible.

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