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Reactions of coordinated tetrafluoroethylene with halogens. Synthesis of σ-bonded halotetrafluoroethyl complexes of ruthenium(II) and osmium(II) and the structure of $OsI(C_2F_4I)(CO)_2(PPh_3)_2$

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Abstract

The reactions of η^2-C_2F_4 complexes of ruthenium and osmium with halogens give rise to complexes containing a halotetrafluoroethyl ligand, *e.g.*, $M(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ (M = Ru or Os) with iodine or chlorine gives $MX(C_2F_4X)(CO)_2(PPh_3)_2$(M = Ru or Os; X = I or Cl). Similarly, $Os(\eta^2\text{-}C_2F_4)(CO)(CNR)(PPh_3)_2$ reacts with iodine to give $OsI(C_2F_4I)(CO)(CNR)(PPh_3)_2$, and $Os(\eta^2\text{-}C_2F_4)Cl(NO)(PPh_3)_2$ gives $OsCl_2(C_2F_4Cl)(NO)(PPh_3)_2$ upon treatment with chlorine. The ruthenium halotetrafluoroethyl compounds decompose readily to form $RuX_2(CO)_2(PPh_3)_2$, but the osmium halotetrafluoroethyl complexes proved to be quite unreactive, even towards abstraction of α-fluoride. The crystal structure of $OsI(C_2F_4I)(CO)_2(PPh_3)_2$ has been determined.

Key words: Ruthenium; Osmium; Tetrafluorethylene; Crystal structure

1. Introduction

Transition metal complexes with fluoroalkyl ligands [1], especially trifluoromethyl, exhibit a diverse chemistry. One of the most remarkable features of these compounds is the enhanced reactivity of the α-fluorines of the fluorocarbon ligand [1–4]. Many of the reactions that involve exchange and/or abstraction of the α-fluorines are thought to involve carbene complexes as intermediates [5,6]. In fact, in a number of reactions involving abstraction of the α-fluorines, stable halocarbene complexes have been isolated [7]. Previously, we have investigated the chemistry of trifluoromethyl complexes, in some detail [5,7–9]. More recently we have extended our study of fluorocarbon complexes to an examination of tetrafluoroethyl complexes [10]. These tetrafluoroethyl complexes are attractive in being accessible from easily prepared precursors. The conversion of η^2-C_2F_4 transition metal compounds into a tetrafluoroethyl complexes has been demonstrated in previous studies [10–18]. Several suitable η^2-tetrafluoroethylene complexes of ruthenium and osmium are available [19], and we describe here the reactions of these compounds with halogens, and a preliminary investigation of the chemistry of the resulting halotetrafluoroethyl complexes.

2. Results and discussion

2.1. Synthesis

Upon addition of I_2 to a solution of $Ru(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ there is a rapid loss of the iodine colour and formation of $RuI(C_2F_4I)(CO)_2(PPh_3)_2$. Similarly, a reaction of $Os(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ with I_2 gives $OsI(C_2F_4I)(CO)_2(PPh_3)_2$. The formation of the osmium and ruthenium iodotetrafluoroethyl complexes proceeds in relatively good (*ca.* 70%) yield (eqn. 1).

(1)

Unfortunately, similar reactions with the other halogens did not proceed so cleanly. Initially, reactions of

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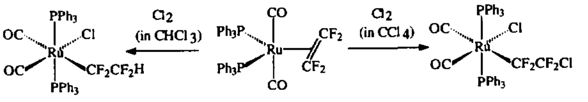
TABLE 1. IR data for the ruthenium and osmium compounds [a]

Complex	ν(CO)	ν(CF)	other bands
$RuI(CF_2CF_2I)(CO)_2(PPh_3)_2$	2052, 1992	1190, 1126, 1109, 1041, 988	
$RuCl(CF_2CF_2Cl)(CO)_2(PPh_3)_2$	2059, 2004	1141, 1091, 1056, 1011, 969	294 ν(Ru–Cl)
$OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$	1977	1090, 1132, 1092, 1035, 1061	
$OsCl(CF_2CF_2Cl)(CO)_2(PPh_3)_2$	2004	1200m, 1160, 1101, 1090, 1084, 1040, 1021, 1003	
$OsI(CF_2CF_2I)(CO)(CN$-p-tolyl$)(PPh_3)_2$	1981	1144, 1091, 1028, 950	(2179, 2158) [b] (2164) [c] ν(CN)
$[Os(CH_3CN)(CF_2CF_2I)(CO)_2(PPh_3)_2]ClO_4$	2018	1038, 1000, 970	
$OsCl_2(CF_2CF_2Cl)(NO)(PPh_3)_2$		1191, 1153, 1092, 1070, 1034, 986	1851 ν(NO) 320 ν(Os–Cl)

[a] Spectra recorded as nujol mulls between KBr or CsI disks and calibrated with polystyrene, all bands strong unless indicated otherwise. [b] Solid state splitting. [c] Recorded in CH_2Cl_2 solution.

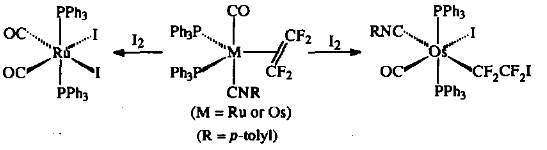
$Ru(\eta^2$-$C_2F_4)(CO)_2(PPh_3)_2$ with a solution of chlorine in chloroform gave $RuCl(C_2F_4H)(CO)_2(PPh_3)_2$ as the exclusive product [19,20]. This reaction appears to proceed via radical abstraction of the hydrogen from chloroform. In support of this hypothesis, when the same reaction was carried out with deuterated chloroform as the solvent, the product was $RuCl(C_2F_4D)(CO)_2$-$(PPh_3)_2$. The desired chlorotetrafluoroethyl complex, $RuCl(C_2F_4Cl)(CO)_2(PPh_3)_2$, is obtained if carbon tetrachloride is used as the solvent (eqn. 2).



(2)

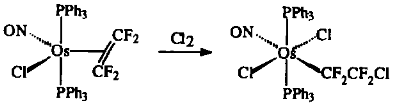
The corresponding osmium complex, $OsCl(C_2F_4Cl)$-$(CO)_2(PPh_3)_2$, can be obtained by a similar procedure, but in a low yield. Bromination of $Ru(\eta^2$-$C_2F_4)(CO)_2$-$(PPh_3)_2$ or $Os(\eta^2$-$C_2F_4)(CO)_2(PPh_3)_2$ also gave the halotetrafluoroethyl complexes $RuBr(C_2F_4Br)(CO)_2$-$(PPh_3)_2$ and $OsBr(C_2F_4Br)(CO)_2(PPh_3)_2$, respectively, but these reactions gave poor yields and the products were always contaminated with $MBr_2(CO)_2(PPh_3)_2$(M = Ru or Os).

Similar halogenation reactions were attempted with the related isocyanide complexes $Ru(\eta^2$-$C_2F_4)(CO)$ $(CNR)(PPh_3)_2$ and $Os(\eta^2$-$C_2F_4)(CO)(CNR)(PPh_3)_2$ (R = p-tolyl). While it was possible to isolate $OsI(C_2F_4I)$-$(CO)(CNR)(PPh_3)_2$, the only product that could be obtained from the reaction of $Ru(\eta^2$-$C_2F_4)(CO)$-$(CNR)(PPh_3)_2$ with I_2 was $RuI_2(CO)_2(PPh_3)_2$ (eqn. 3).



(3)

The reaction of $Os(\eta^2$-$C_2F_4)Cl(NO)(PPh_3)_2$ with halogens was also examined. This complex was surprisingly inert towards halogens. In fact, $Os(\eta^2$-$C_2F_4)Cl$-$(NO)(PPh_3)_2$ reacted only when treated with an excess of chlorine gas to give $OsCl_2(CF_2CF_2Cl)(NO)(PPh_3)_2$ (eqn. 4). No other reactions with halogens were observed.



(4)

2.2. Characterization

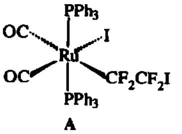
All the halotetrafluoroethyl complexes described above were characterized by IR spectroscopy, ^{31}P NMR spectroscopy, (Tables 1 and 2) and elemental analysis and in one case also by a single crystal X-ray diffraction study. Several differences are apparent between the spectra of the analogous ruthenium and osmium complexes. In particular, the IR spectra for the com-

TABLE 2. ^{31}P NMR data for the ruthenium and osmium compounds [a]

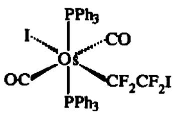
Complex	δ(ppm)	$^3J_{(PF)}$ (Hz)	$^4J_{(PF)}$ (Hz)
$RuI(CF_2CF_2I)(CO)_2(PPh_3)_2$	12.17 m		
$RuCl(CF_2CF_2Cl)(CO)_2(PPh_3)_2$	14.01 m		
$OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$	−13.76 tt	16.0	2.7
$OsCl(CF_2CF_2Cl)(CO)_2(PPh_3)_2$	−17.84 m		
$OsI(CF_2CF_2I)(CO)(CN$-p-tolyl$)$-$(PPh_3)_2$	−14.73 m		
$[Os(CH_3CN)(CF_2CF_2I)(CO)_2$-$(PPh_3)_2]ClO_4$	−4.8 m		
$OsCl_2(CF_2CF_2Cl)(NO)(PPh_3)_2$	−16.95 tt	12.5	2.1

[a] Recorded at room temperature in $CDCl_3$; t = triplet, m = multiplet.

plexes $MX(CF_2CF_2X)(CO)_2(PPh_3)_2$ (M = Ru or Os, X = I or Cl) show considerable variation. The most obvious differences occur in the ν(CO) region. The ruthenium halotetrafluoroethyl complexes show two strong ν(CO) bands. In contrast, the analogous osmium complexes display only a single, strong, ν(CO) band. Both the ^{31}P and ^{13}C NMR [20,21] spectra are consistent with a *trans* disposition of the triphenylphosphine ligands in all the complexes. The carbonyl ligands clearly have the *cis* configuration for the complexes $RuX(CF_2CF_2X)(CO)_2(PPh_3)_2$ (X = I or Cl), (A), whereas the analogous osmium complexes have *trans* carbonyl ligands, (B). The proposed geometry of $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$ was confirmed conclusively by a single crystal X-ray determination.



A



B

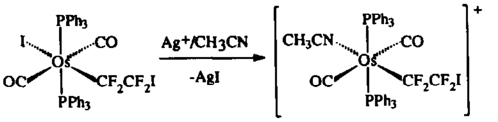
2.3. Structure of $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$

The structure, depicted in Fig. 1, is that of a distorted octahedron with *trans* triphenylphosphine groups and *trans* carbonyl ligands. The iodide ligand occupies the coordination site *trans* to the iodotetrafluoroethyl ligand. The iodotetrafluoroethyl ligand is orientated in such a way that the iodide has minimum steric interaction with any other parts of the molecule. Selected bond lengths and angles are presented in Table 3. It is be noteworthy that the α-carbon–fluorine distances are significantly greater than the β-carbon–fluorine distances.

2.4. Reactivity of halotetrafluoroethyl complexes

The stability of the halotetrafluoroethyl complexes of both ruthenium and osmium differs greatly from that of trifluoromethyl [7] and tetrafluoroethyl [20] analogues. This is most apparent with the ruthenium complexes. All of the complexes, $RuX(CF_2CF_2X)(CO)_2(PPh_3)_2$ (X = I, Br or Cl), decompose over time to give $RuX_2(CO)_2(PPh_3)_2$ (X = I, Br or Cl). This reaction is likely to proceed via a β-elimination. The decomposition of the halotetrafluoroethyl complexes occurs both in solution and in the solid state, although the transformation is much slower for the solid. This decomposition prevented further investigation of the ruthenium complexes as complete loss of the fluorocarbon moiety was observed in all attempted reactions.

The osmium complexes were somewhat more stable, enabling a preliminary investigation of their reactivity. For example, the strong *trans* effect of the fluorocarbon ligand imparts a significant lability to the iodide ligand. Treatment of an acetonitrile solution of $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$ with Ag^+ in acetonitrile produces $[Os(CH_3CN)(CF_2CF_2I)(CO)_2(PPh_3)_2]^+$ (eqn. 5).



(5)

In general, σ-bonded fluorocarbon ligands exhibit an enhanced reactivity for the α-fluorines [1–7]. This propensity for exchange or abstraction of the α-fluorine has been explored with a number of complexes that closely resemble the halotetrafluoroethyl complexes described here. It was surprising, therefore, that $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$ demonstrated no reactivity associated with the α-fluorines. Thus, while $OsCl(CF_2H)(CO)_2(PPh_3)_2$ reacts with BCl_3 at −78°C to give products resulting from α-fluorine abstraction [22], the complex, $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$, was so inert towards Lewis acids that it remained unchanged even when heated to reflux in toluene solutions containing an excess of BCl_3.

The only osmium halotetrafluoroethyl complex to demonstrate any reactivity towards electrophiles was

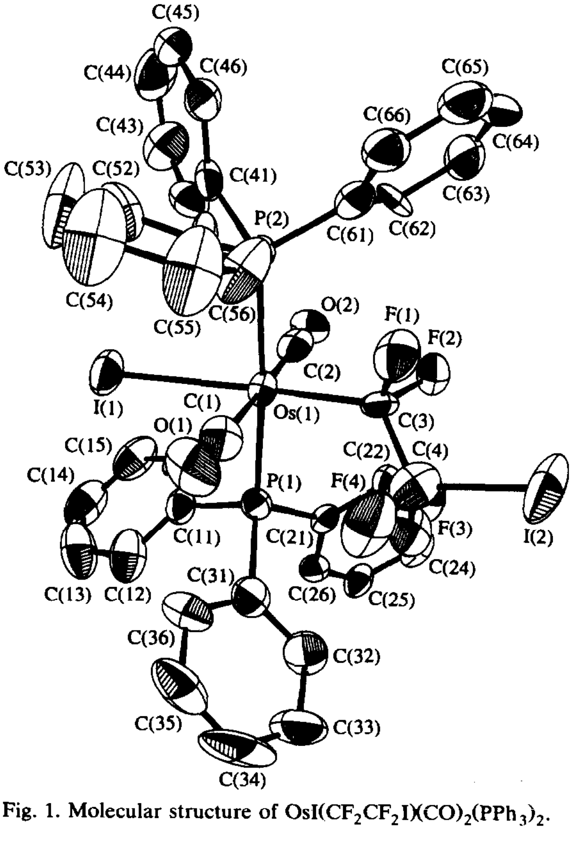


Fig. 1. Molecular structure of $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$.

TABLE 3. Selected bond lengths [Å] and angles [deg] for $OsI(C_2F_4I)(CO)_2(PPh_3)_2$.

Os(1)–C(2)	1.956(14)
Os(1)–C(1)	1.989(14)
Os(1)–C(3)	2.144(11)
Os(1)–P(2)	2.423(3)
Os(1)–P(1)	2.427(3)
Os(1)–I(1)	2.8001(9)
I(2)–C(4)	2.164(14)
C(3)–F(2)	1.384(11)
C(3)–F(1)	1.457(12)
C(3)–C(4)	1.48(2)
C(4)–F(4)	1.349(14)
C(4)–F(3)	1.348(13)
C(2)–Os(1)–C(1)	178.2(5)
C(2)–Os(1)–C(3)	94.6(4)
C(1)–Os(1)–C(3)	86.6(4)
C(2)–Os(1)–P(2)	88.1(3)
C(1)–Os(1)–P(2)	90.6(4)
C(3)–Os(1)–P(2)	89.2(3)
C(2)–Os(1)–P(1)	86.4(3)
C(1)–Os(1)–P(1)	94.8(4)
C(3)–Os(1)–P(1)	97.9(3)
P(2)–Os(1)–P(1)	171.40(9)
C(2)–Os(1)–I(1)	99.3(3)
C(1)–Os(1)–I(1)	79.4(3)
C(3)–Os(1)–I(1)	165.1(3)
P(2)–Os(1)–I(1)	85.89(8)
P(1)–Os(1)–I(1)	88.44(8)
F(2)–C(3)–F(1)	101.5(8)
F(2)–C(3)–C(4)	105.0(9)
F(1)–C(3)–C(4)	99.7(9)
C(4)–C(3)–Os(1)	123.2(8)
F(4)–C(4)–F(3)	108.0(11)
F(4)–C(4)–C(3)	110.2(11)
F(3)–C(4)–C(3)	108.1(11)
F(4)–C(4)–I(2)	106.9(8)
F(3)–C(4)–I(2)	107.3(8)
C(3)–C(4)–I(2)	115.9(9)

$OsI(CF_2CF_2I)(CO)(CNR)(PPh_3)_2$. Treatment of $OsI(CF_2CF_2I)(CO)(CNR)(PPh_3)_2$ with HCl quickly gave solutions containing mixtures of $OsX_2(CO)_2(PPh_3)_2$. This reaction is clearly related to that of $Ru(\eta^2\text{-}C_2F_4)(CO)(CNR)(PPh_3)_2$ and I_2. It is reasonable to assume that both the reaction of $OsI(CF_2CF_2I)(CO)(CNR)(PPh_3)_2$ with HCl forming $OsX_2(CO)_2(PPh_3)_2$ and the formation of $RuI_2(CO)_2(PPh_3)_2$ from $Ru(\eta^2\text{-}C_2F_4)(CO)(CNR)(PPh_3)_2$ and I_2, proceed via similar mechanisms. Thus, it is likely that $RuI(CF_2CF_2I)(CO)(CNR)(PPh_3)_2$ is formed as the initial product from the reaction of $Ru(\eta^2\text{-}C_2F_4)(CO)(CNR)(PPh_3)_2$ and I_2. However, trace amounts of water must react with $RuI(CF_2CF_2I)$-$(CO)(CNR)(PPh_3)_2$ to give an intermediate acyl complex, which after reverse migration and further undetermined steps gives $RuI_2(CO)_2(PPh_3)_2$.

3. Conclusions

Complexes in which the η^2-C_2F_4 ligand is coordinated to either ruthenium or osmium have proved to be excellent precursors for σ-bonded halotetrafluoroethyl complexes. In most cases the reactions proceed cleanly and in reasonable yield. It must be noted, however, that several of these new fluorocarbon complexes show an unexpected lack of reactivity towards Lewis acids. This can probably be attributed mainly to the steric protection provided by the β-halogen towards the α-fluorines. However, the very large changes in reactivity accompanying changes in the ancillary ligands in these complexes suggests that electronic factors are also of great importance. It is expected that a systematic investigation of possible support ligands will provide a ligand system capable of both activating the α-fluorines and of stabilizing any subsequent carbene-containing products.

4. Experimental details

Standard Schlenk techniques were used for all manipulations involving oxygen- or moisture-sensitive compounds. Solvents used were freshly distilled over appropriate drying agents prior to use. When procedures involved materials that were not air sensitive, solvents were purified by chromatography on alumina (Spence type H, 100-200 mesh) or filtered prior to use. In these cases, solvent removal under reduced pressure was achieved using a rotary evaporator. Routine recrystallizations were achieved by the following method: the sample was dissolved in a low boiling point solvent and a higher boiling point solvent, in which the compound was insoluble, was added. Evaporation at reduced pressure effected gradual crystallization.

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer Model 597 double-beam spectrophotometer calibrated with polystyrene film. All spectra were recorded as Nujol mulls between KBr plates or as a dichloromethane solution in KBr cells. Far-infrared spectra (400–200 cm^{-1}) were recorded as concentrated Nujol mulls between CsI plates. ^1H NMR were recorded on a Bruker AM-400 spectrometer operating at 400 MHz and are quoted in ppm down field from TMS. $^{31}P\{^1H\}$ NMR were recorded on a Bruker AM-400 at 162 MHz and are quoted relative to 85% phosphoric acid solution (external). Melting points were determined on a Reichert microscope hot stage and are uncorrected. All ruthenium and osmium η^2-C_2F_4 complexes were obtained following procedures described in reference 19.

4.1. $RuI(CF_2CF_2I)(CO)_2(PPh_3)_2$

$Ru(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ (300 mg, 0.38 mmol) was dissolved in dichloromethane (20 ml) and a solution of iodine (0.4 mmol) in dichloromethane (10 ml) was added at such a rate that the iodine colour was discharged before the next portion was added. Ethanol (30 ml) was added to the solution and the dichloromethane was removed under reduced pressure to give the product as cream coloured crystals (282 mg, 71%), m.p. 217–220°C. Anal. Calcd. for $C_{40}H_{30}I_2F_4O_2P_2Ru$: C, 46.40; H, 2.92. Found: C, 46.41; H, 3.57%.

4.2. $RuCl(CF_2CF_2Cl)(CO)_2(PPh_3)_2$

$Ru(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ (300 mg, 0.38 mmol) was dissolved in carbon tetrachloride (20 ml) and a solution of chlorine (0.4 mmol) in carbon tetrachloride was added rapidly. The solvent was removed *in vacuo* and the residue taken up in dichloromethane (20 ml). Ethanol (30 ml) was added to the solution and the dichloromethane was removed under reduced pressure to give the product as cream coloured crystals (222 mg, 68%), m.p. 208–211°C. Anal. Calcd. for $C_{40}H_{30}Cl_2F_4O_2P_2Ru \cdot 0.5CH_2Cl_2$: C, 53.80; H, 4.46. Found: C, 53.90; H, 3.85%.

4.3. $OsCl_2(CF_2CF_2Cl)(NO)(PPh_3)_2$

$Os(\eta^2\text{-}C_2F_4)Cl(NO)(PPh_3)_2$ (200 mg, 0.23 mmol) was dissolved in dichloromethane (30 ml) and chlorine gas was bubbled through the solution for 20 s. This mixture then stirred for 5 min and ethanol (30 ml) was then added. The dichloromethane was removed under reduced pressure to give the product as orange crystals (132 mg, 63%), m.p. 210–215°C. Anal. Calcd. for $C_{38}H_{30}Cl_3F_4NOOsP_2$: C, 47.99; H, 3.18; N, 1.47. Found: C, 48.05; H, 3.90, N 1.48%.

4.4. $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$

$Os(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ (200 mg, 0.23 mmol) was dissolved in dichloromethane (20 ml) and a solution of iodine (58 mg, 0.24 mmol) in dichloromethane (10 ml) was added at such a rate that the iodine colour was discharged before the next portion was added. Ethanol (30 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as cream coloured crystals (199 mg, 71%), m.p. 132°C dec. Anal. Calcd. for $C_{40}H_{30}I_2F_4O_2OsP_2$: C, 42.72; H, 2.69; F, 6.76. Found: C, 43.22; H, 3.31; F, 6.27%.

4.5. $OsCl(CF_2CF_2Cl)(CO)_2(PPh_3)_2$

$Os(\eta^2\text{-}C_2F_4)(CO)_2(PPh_3)_2$ (100 mg, 0.11 mmol) was dissolved in carbon tetrachloride (20 ml) and a solution of chlorine (0.12 mmol) in carbon tetrachloride (10 ml) was added rapidly. The solvent was removed *in vacuo* and the residue taken up in dichloromethane (20 ml). Ethanol (30 ml) was added and the dichloromethane was removed under reduced pressure to give the product as cream coloured crystals (43 mg, 45%), m.p. 167°C dec. Anal. Calcd. for $C_{40}H_{30}Cl_2F_4O_2OsP_2$: C, 51.02; H, 3.21, F, 8.07. Found: C, 49.90; H, 3.32; F 7.64%.

4.6. $OsI(CF_2CF_2I)(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$

$Os(\eta^2\text{-}C_2F_4)(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (200 mg, 0.23 mmol) was dissolved in dichloromethane (20 ml) and a solution of iodine (58 mg, 0.24 mmol) in dichloromethane (10 ml) was added at such a rate that the iodine colour was discharged before the next portion was added. Ethanol (30 ml) was then added and the dichloromethane was removed under reduced pressure to give the product as cream coloured crystals (94 mg, 46%), m.p. > 200°C. Anal. Calcd. for $C_{47}H_{37}I_2F_4NOOsP_2$: C, 46.51; H, 3.11; N, 1.15. Found: C, 47.67; H, 3.57; N, 1.34%.

TABLE 4. Crystal data for $OsI(C_2F_4I)(CO)_2(PPh_3)_2$

Formula	$C_{40}H_{30}F_4I_2P_2Os$
Molecular weight	1124.58
Crystal system	Orthorhombic
Space group	*Pbca*
a	17.542(3) Å
b	18.141(2) Å
c	24.864(3) Å
V	7913(2) $Å^3$
Z	8
d(calc)	1.888 g cm^{-3}
$F(000)$	4272
μ	49.2 cm^{-1}
Radiation Mo Kα (Monochromatic) λ	0.71069 Å
Temperature	293 K
Diffractometer	Nonius CAD4
Scan technique	$\omega/2\theta$
2θ (min-max)	2°–46°
h,k,l, range	$-19 \leq k \leq 0$, $-19 \leq k \leq 0$, $-27 \leq l \leq 0$
No. of unique reflections	5481
No. of observed reflections	2521 $I > 2\sigma(I)$
Crystal size	0.08 × 0.14 × 0.22 mm
A (min-max)	1.00 0.94
Least squares weights	$1.0/[\sigma^2(F_o^2) + \{0.0203(F_o^2 + 2F_c^2)/3\}^2]$
Number of variables in LS	460
Goodness of fit on F^2	0.756
Function minimized	$\Sigma w[F_o^2 - F_c^2]^2$
R and wR^2	0.037 0.074
Max. min peak heights in final electron density map.	0.62 −0.65 e $Å^{-3}$
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	$wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

4.7. $[Os(CH_3CN)(CF_2CF_2I)(CO)_2(PPh_3)_2]ClO_4$

$OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$ (100 mg, 0.09 mmol) was dissolved in a mixture of dichloromethane (40 ml) and acetonitrile (5 ml), $AgClO_4$ (20 mg, 0.1 mmol) was added, and the solution stirred for a further 30 min. The solution was filtered through Celite to remove the silver salts, and toluene (40 ml) was added to the filtrate. The solvent volume was reduced to give the product as cream crystals (74 mg, 73%), m.p. 145–148°C. Anal. Calcd. for $C_{42}H_{33}ClIF_4NO_6OsP_2$: C, 44.32; H, 2.92; N, 1.23. Found: C, 44.70; H, 3.65; N, 0.91%.

TABLE 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $OsI(C_2F_4I)(CO)_2(PPh_3)_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Os(1)	2264(1)	1098(1)	902(1)	33(1)
I(1)	684(1)	1319(1)	923(1)	61(1)
I(2)	4836(1)	−317(1)	852(1)	94(1)
P(1)	2194(2)	1059(2)	−73(1)	34(1)
P(2)	2220(2)	1304(2)	1864(1)	39(1)
C(1)	1900(7)	68(7)	1003(5)	49(3)
O(1)	1672(5)	−493(5)	1070(3)	71(3)
C(2)	2597(7)	2120(8)	819(4)	49(3)
O(2)	2766(5)	2677(4)	752(3)	44(2)
C(3)	3395(6)	666(6)	989(4)	39(3)
C(4)	3704(8)	66(8)	648(5)	64(4)
F(1)	3492(4)	333(4)	1518(3)	63(2)
F(2)	3958(3)	1201(3)	995(3)	52(2)
F(3)	3729(4)	310(4)	136(3)	64(2)
F(4)	3240(5)	−526(4)	664(4)	93(3)
C(11)	1352(6)	1523(7)	−364(5)	44(3)
C(12)	786(7)	1177(8)	−646(5)	68(4)
C(13)	171(8)	1577(10)	−846(7)	87(5)
C(14)	158(9)	2299(11)	−787(6)	81(5)
C(15)	716(9)	2705(8)	−530(6)	76(5)
C(16)	1321(7)	2280(7)	−310(4)	56(4)
C(21)	2940(6)	1522(6)	−463(4)	32(3)
C(22)	3624(6)	1787(6)	−248(5)	42(3)
C(23)	4170(8)	2089(7)	−577(6)	55(4)
C(24)	4072(8)	2165(7)	−1113(6)	56(4)
C(25)	3380(7)	1923(6)	−1328(5)	45(3)
C(26)	2845(6)	1603(6)	−1006(4)	37(3)
C(31)	2155(8)	125(6)	−367(5)	53(3)
C(32)	2712(8)	−101(6)	−733(5)	63(4)
C(33)	2641(9)	−844(8)	−897(7)	89(5)
C(34)	2066(13)	−1310(8)	−739(8)	112(8)
C(35)	1523(9)	−1021(9)	−401(7)	88(5)
C(36)	1560(8)	−331(7)	−212(5)	56(4)
C(41)	1714(6)	2127(6)	2132(5)	41(3)
C(42)	1465(7)	2692(7)	1798(5)	53(3)
C(43)	1188(8)	3323(8)	2026(7)	78(5)
C(44)	1105(9)	3416(9)	2563(8)	86(5)
C(45)	1347(7)	2848(10)	2892(6)	75(5)
C(46)	1674(6)	2232(8)	2678(5)	61(4)
C(51)	1757(7)	531(7)	2220(5)	55(4)
C(52)	1026(7)	606(7)	2393(5)	60(4)
C(53)	654(8)	5(9)	2631(6)	87(5)
C(54)	1001(10)	−667(9)	2666(7)	102(6)
C(55)	1754(9)	−731(8)	2496(7)	88(5)
C(56)	2126(8)	−124(7)	2276(5)	65(4)
C(61)	3126(7)	1479(7)	2199(5)	51(3)
C(62)	3560(7)	2056(9)	2016(5)	63(4)
C(63)	4245(8)	2236(8)	2280(6)	73(5)
C(64)	4469(9)	1867(10)	2723(6)	83(6)
C(65)	4065(9)	1308(9)	2915(6)	78(5)
C(66)	3366(7)	1112(8)	2657(5)	61(4)

4.8. X-ray diffraction study of $OsI(CF_2CF_2I)(CO)_2(PPh_3)_2$

Crystal data. Unit cell parameters were obtained from least-squares fits to the four circle coordinates of 25 reflections determined on a Nonius CAD-4 diffractometer. Intensity data collection used graphite monochromated Mo Kα radiation and $\omega/2\theta$ scans with a peak to background time of 2 : 1. The scan width was $0.80 + 0.347 \tan \theta$ and reflections were counted until $\sigma(I)/I$ was 0.02 or for a maximum of 60 s. Three reflections were monitored every 100 measurements as a check on crystal movement or decomposition, no systematic trend being evident. The data were corrected for Lorentz, polarisation and absorption effects using locally written programs [23]. Data collection parameters are given in Table 4.

The structures were solved by conventional Patterson and Fourier techniques [24] and refined by full-matrix least squares [25]. Atomic scattering factors were for neutral atoms [26]. Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached with thermal parameter 20% greater than the bonded atom. All non-hydrogen atoms were allowed to assume anisotropic motion. Refinement converged to conventional $R = 0.037$ for the observed data. Final refinement details are given in Table 4. Selected interatomic distances and angles are given in Table 3 and atomic coordinates in Table 5. An ORTEP diagram is given in Fig. 1 which shows the atom numbering scheme. Complete lists of bond lengths and angles and tables of anisotropic displacement parameters and hydrogen coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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