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MIGRATORY-INSERTION REACTIONS INVOLVING THE THIOCARBONYL LIGAND. *dihapto*-THIOACYL COMPLEXES FROM THE REARRANGEMENT OF ARYLTHIOCARBONYL COMPLEXES OF OSMIUM(II). STRUCTURE OF $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$

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Summary

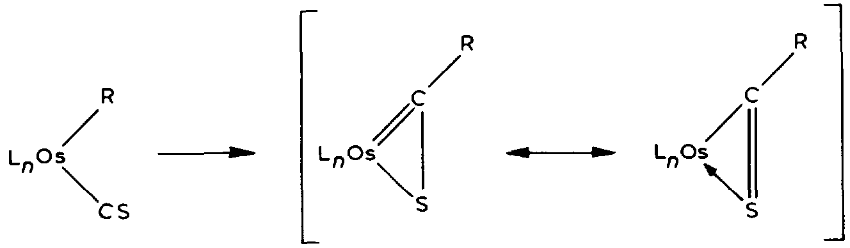
Reaction of HgR_2 with $OsHCl(CS)(PPh_3)_3$ yields red, five-coordinate, $OsRCl(CS)(PPh_3)_2$ ($R = p$-tolyl). From this have been derived the compounds $OsRX(CS)(PPh_3)_2$ with $X = Br$, I, S_2CNEt_2, O_2CMe, O_2CCF_3. These compounds add an additional ligand, MeCN, CO or CNR to form colourless, six coordinate arylthiocarbonyl complexes, which undergo migratory-insertion reactions to form red, *dihapto*-thioacyl complexes. The crystal structure of a representative example, $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$ has been determined. The red equant crystals are orthorhombic, space group $P2_12_12_1$, *a* 11.584(1), *b* 19.184(2), *c* 18.90(1) Å, *V* 4199 Å^3, $Z = 4$. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms except the carbon atoms of the triphenylphosphines. The final *R* factor is 0.057 for 2868 observed reflections.

The coordination geometry in the monomeric complex is that of an octahedron distorted by the constraints of the ligands. The triphenyl phosphine ligands are mutually *trans*; the equatorial plane contains carbonyl, *monohapto*-trifluoroacetate, and *dihapto*-thioacyl ligands. Bond distances and angles are Os–P 2.405, 2.407(4) Å; P–Os–P 173.9(1)°; Os–CO 1.83(2) Å; Os–O (trifluoroacetate) 2.206(11) Å; Os–C (thioacyl) 1.91(2); Os–S 2.513(6); C–S 1.72 Å. The C–S bond length implies a reduction in bond order from 2.0 to approx. 1.5 upon coordination to the metal.

The η^2-thioacyl ligand in $Os(\eta^2\text{-}CSR)Cl(CNR)(PPh_3)_2$ is methylated with methyl triflate and further reaction with LiCl produces the thiocarbene complex $OsCl_2(C[SMe]R)(CNR)(PPh_3)_2$.

Introduction

Hydride transfer to the thiocarbonyl ligand to form thioformyl ligands has been described [1]. The transfer of alkyl or aryl ligands to carbonyl or isocyanide ligands (migratory-insertion reaction) is one of the fundamental reactions of organotransition metal chemistry [2]. However, prior to this work, no alkyl- or aryl-thiocarbonyl complexes had been reported so that corresponding migratory-insertion reactions for thiocarbonyl ligands were unknown. We have previously studied aryl-carbonyl and aryl-isocyanide complexes of ruthenium and osmium and characterised the rearrangement products as *dihapto*-acyl and -iminoacyl compounds [3,4,5]. In this paper an extension of these studies to thiocarbonyl complexes is reported. Complexes of osmium(II) containing *cis*-aryl and thiocarbonyl ligands have been produced and rearrangement leads to *dihapto*-thioacyl complexes, i.e.

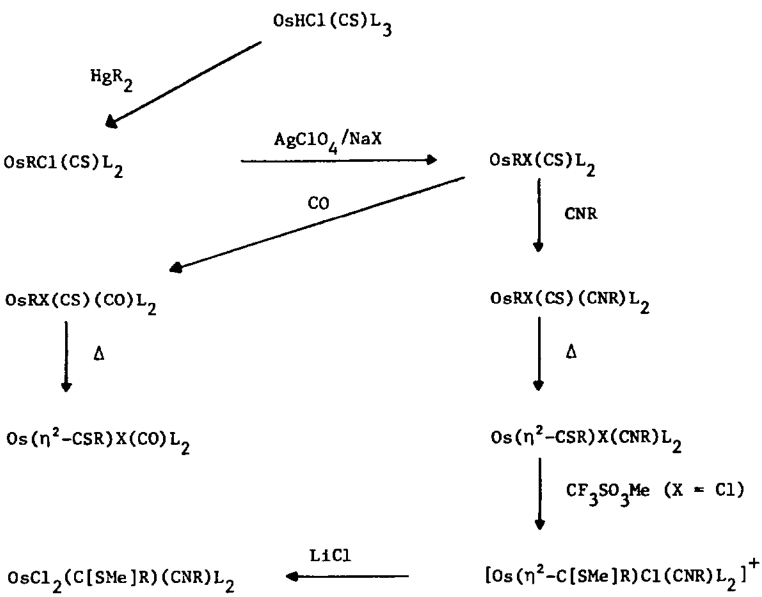


A preliminary report of this work has appeared [6].

Results and discussion

The reaction of $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) with diarylmercury compounds affords the strongly-coloured, coordinatively-unsaturated complexes $MR'Cl(CO)(PPh_3)_2$ (R′ = *p*-tolyl, *o*-tolyl) [3]. The high yield synthesis of $OsHCl(CS)(PPh_3)_3$ [1] has enabled an identical route to be employed to afford analogous thiocarbonyl complexes. Thus $OsHCl(CS)(PPh_3)_3$ reacts with HgR_2 (R = *p*-tolyl) in toluene under reflux to deposit Hg and afford a deep crimson solution from which crimson (near black) crystals of $OsRCl(CS)(PPh_3)_2$ can be isolated (ca. 90%). An X-ray crystal structure determination [3] has shown that, as for other five-coordinate complexes of ruthenium(II) and osmium(II) [7], $RuRCl(CO)(PPh_3)_2$ has a square pyramidal geometry. For this compound the phosphine ligands are mutually *trans* and the R group is apical. A similar geometry is also likely for $OsRCl(CS)(PPh_3)_2$, but in this complex the possibility also exists, in view of the pronounced *trans*-influence of the CS ligand, that CS could occupy the apical site.

Red solutions of $OsRCl(CS)(PPh_3)_2$ in dichloromethane lighten rapidly on addition of the potentially bidentate anions, diethyldithiocarbamate, acetate or trifluoroacetate to give the yellow six-coordinate complexes $OsR(\eta^2\text{-}Y)(CS)(PPh_3)_2$ (Y = S_2CNEt_2, O_2CCH_3, O_2CCF_3). If trifluoroacetic acid is used as a source of trifluoroacetate ion the R group is cleaved from the metal and the product obtained is $Os(\eta^1\text{-}O_2CCF_3)_2(EtOH)(CS)(PPh_3)_2$. An X-ray crystal structure analysis of the methanol-containing complex $Ru(\eta^1\text{-}O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2$ has shown that methanol is coordinated to the metal and hydrogen-bonded to one trifluoroacetato ligand [8]. Addition of silver perchlorate in ethanol to the red solution results in the rapid precipitation of silver chloride, but the solvated cation cannot be isolated from the yellow solution so formed and decomposes on attempted work-up. However, if NaX (X = Br, I) is added to this latter solution, rapid degeneration of the red colour



SCHEME 1. Synthesis of osmium(II) thioacyl complexes ($L = PPh_3$, $R = p$-tolyl, $X = Cl, Br, I, O_2CCF_3$).

is observed and $OsRX(CS)(PPh_3)_2$ can be obtained in high yields (see Scheme 1).

Red solutions containing the five-coordinate complexes $OsRX(CS)(PPh_3)_2$ ($X =$ Cl, Br, I) are also decolourised rapidly upon reaction with acetonitrile, carbon monoxide or isocyanide to form the coordinatively saturated complexes $OsRX(CS)L(PPh_3)_2$. The reaction of $OsR(\eta^2\text{-}O_2CCF_3)(CS)(PPh_3)_2$ with p-chlorophenylisocyanide has also been investigated and these reactants in dichloromethane for 40 min afford the colourless compound $OsR(\eta^1\text{-}O_2CCF_3)(CN\text{-}p\text{-}C_6H_4Cl)(CS)(PPh_3)_2$.

Rearrangement reactions of arylthiocarbonyl complexes

When $OsRCl(MeCN)(CS)(PPh_3)_2$ is dissolved in dichloromethane a red colour begins to develop in the solution which intensifies rapidly on heating. Isolation of the red product shows this to be a mixture of $OsRCl(CS)(PPh_3)_2$ and $OsRCl(MeCN)(CS)(PPh_3)_2$. If excess acetonitrile is added to the red solution the colour is discharged, indicating that acetonitrile coordination to $OsRCl(CS)(PPh_3)_2$ is reversible, i.e.

$$OsRCl(CS)(PPh_3)_2 + MeCN \rightleftharpoons OsRCl(MeCN)(CS)(PPh_3)_2$$

However, solutions of $OsRCl(CS)(CO)(PPh_3)_2$ in dichloromethane, chloroform, benzene or toluene also rapidly turn red and the colour change is not reversed by excess carbon monoxide, even when forcing conditions are applied (100°C, 80 p.s.i., 3 h). This colour change is sufficiently rapid to prevent the isolation of pure $OsRCl(CO)(CS)(PPh_3)_2$ if the carbonylation of $OsRCl(CS)(PPh_3)_2$ is carried out at room temperature. The bromo and iodo analogues undergo this same reaction and a qualitative comparison of the rate of colour formation suggests that the reaction occurs most rapidly for the iodo complex and least rapidly for the chloro complex. In fact $OsRI(CO)(CS)(PPh_3)_2$ has not been isolated, but has only been observed as

TABLE 1

IR DATA[a] FOR OSMIUM THIOCARBONYL AND THIOACYL COMPLEXES

Compound[b]	ν(CS)	ν(CO)	ν(CN)	Other bands[c]
$OsRCl(CS)L_2$	1290			1190w, 1051wm (sh), 1012wm (sh), 800m (sh).
$OsR(\eta^2\text{-}S_2CNEt_2)(CS)L_2$	1270		1490	1048w (sh), 1015w (sh), 790w (sh); 1355w, 1216wm, 1146wm, 920w, 850w.
$OsR(\eta^2\text{-}O_2CMe)(CS)L_2$	1282			1520w, 1463m, 1052w, 1015w, 802m.
$OsR(\eta^2\text{-}O_2CCF_3)(CS)L_2$	1290			1603m, 1308m, 1205vs, 1162s, 870s (sh), 791w (sh), 737s.
$Os(\eta^1\text{-}O_2CCF_3)_2(EtOH)(CS)L_2$	1303			3560w (br), 1600w (br), 1665s (br), 1199vs, 1150s, 877w, 785w, 730wm.
$OsRBr(CS)L_2$	1285			1188w, 1050wm (sh), 1011w (sh), 799m (sh).
$OsRI(CS)L_2$	1281			1188w, 1052wm, 1010w (sh), 798m (sh).
$OsRCl(MeCN)(CS)L_2$	1282			1190w, 1058w, 1020w, 812wm (sh).
$OsRCl(CO)(CS)L_2$	1300	2055		1190w, 1015w, 805wm (sh).
$OsRBr(CO)(CS)L_2$	1292	2030		1175w, 1015w, 835w, 802m (sh).
$OsRCl(CS)(CNR)L_2$	1290		2142	1190w, 1018w (sh), 818m (sh), 802m (sh).
$OsR(\eta^1\text{-}O_2CCF_3)(CO)(CS)L_2$	1300	2035		1690 ($\eta^1\text{-}O_2CCF_3$).
$OsR(\eta^1\text{-}O_2CCF_3)\text{-}(CN\text{-}p\text{-}C_6H_4Cl)(CS)L_2$	1291		2130	1688vs, 1312w, 1195vs, 1141s, 790w, 727m (sh), 1017w (sh), 1410wm, 832m, 805m.
$Os(\eta^2\text{-}CSR)Cl(CO)L_2$		1902		1600m, 1315s, 1300s, 1293m, 1178m (sh), 975w, 830m, 818m, 789w (sh), 635w (sh).
$Os(\eta^2\text{-}CSR)Br(CO)L_2$		1897		1599m, 1310s, 1300s, 1287m, 1175s (sh), 972w, 830m, 815m, 789w (sh), 635w (sh).
$Os(\eta^2\text{-}CSR)I(CO)L_2$		1897		1599m, 1311s, 1300s, 1285m, 1175s (sh), 975w, 838m, 830m, 818m, 789w (sh), 633w (sh).
$Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)L_2$		1910		1691 ($\eta^1\text{-}O_2CCF_3$)
$Os(\eta^2\text{-}CSR)Cl(CNR)L_2$			1940[d] 1870[d]	1600m, 1308s, 1295s, 1172s (sh), 972m, 789w (sh), 635w (sh) 820vs.
$Os(\eta^1\text{-}O_2CCF_3)(\eta^2\text{-}CSR)\text{-}(CN\text{-}p\text{-}C_6H_4Cl)L_2$			1950s[d] 1890[d]	1705wm; 1684vs; 1599wm, 1310wm, 1302m (sh), 1293s, 1172s (sh), 1012w (sh), 980w, 790s (sh), 635w (sh); 1196vs, 1132s, 737s (sh), 1412s, 844s, 823s.
$Os(\eta^2\text{-}CSR)(\eta^2\text{-}S_2CNEt_2)(CO)L$		1893	1499	1599m, 1310s, 1302s, 1172s (sh), 975w, 832s, 821m, 788m, 635w (sh), 1360w, 1275s, 1211wm, 1147w, 911w.
$[\overline{Os(C[S}Me]R)Cl(CNR)L_2]ClO_4$			2100 2060[e]	1599m, 1327m, 1310w, 1298w, 1182w, 820wm, 1093vs, 625m (ClO_4).
$OsCl_2(C[SMe]R)(CNR)L_2$			2095 2060[e]	1603w, 1190w, 890w, 865m, 845w, 820m, 809s.

[a] cm^{-1}, measured as Nujol mulls; all bands strong unless indicated otherwise. [b] L = PPh_3; R = *p*-tolyl. [c] Absorptions due to coordinated PPh_3 are not given. [d] Very broad band. [e] Same two bands observed in spectrum obtained in CH_2Cl_2.

an intermediate by the loss of colour that occurs when $OsRI(CS)(PPh_3)_2$ is treated with CO. Recrystallisation of the complexes $OsRX(CO)(CS)(PPh_3)_2$ results in an increased quantity of the red product, which forms sufficiently rapidly at 40°C to prevent the observation of any signals in the ^1H NMR spectra, other than those attributable to the red products. The formation of the red colour also occurs rapidly if solid samples of $OsRCl(CO)(CS)(PPh_3)_2$ are heated to 60°C.

The formation of a red complex also occurs for $OsRCl(CS)(CNR)(PPh_3)_2$, but this reaction proceeds much more slowly at room temperature than that for the carbonyl analogues and, consequently, this compound can be recrystallised and a ^{1}H NMR spectrum has been obtained. The reaction is rapid in boiling toluene and is complete, under these conditions, in less than 10 min. The formation of a red product occurs even more slowly for $OsR(\eta^1\text{-}O_2CCF_3)(CN\text{-}p\text{-}C_6H_4Cl)(CS)(PPh_3)_2$ where heating under reflux in boiling toluene for several hours is necessary for complete conversion. These red isocyanide-containing compounds exhibit very low (ca. 1900 cm^{-1}), very broad ν(CN) bands (see Table 1).

All the red products have elemental analysis figures which indicate that the compositions are identical to those of the starting materials, thus suggesting that a rearrangement reaction has occurred in each case. The ^{1}H NMR spectra indicate that the *p*-tolyl moiety is present in these rearranged products. However, the IR spectra contain some unusual features common to all the red products. The IR spectral changes that occur when the prototype, $OsRCl(CO)(CS)(PPh_3)_2$, undergoes this reaction will serve as an example. The ν(CO) band shifts from 2055 to 1902 cm^{-1} and the very strong ν(CS) band at 1300 cm^{-1} is replaced by a medium to strong structured band at 1310 cm^{-1}. Additional new bands occur at 1600 (m), 1178 cm^{-1} (m,sh). Changes also occur in the fingerprint region for the tolyl group. It seemed likely that the red products all contained *dihapto*-thioacyl ligands and to confirm this a single crystal X-ray structure determination of $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$ was undertaken.

Description and discussion of crystal structure

Geometry of the complex

The geometry of the monomeric complex is depicted in Fig. 1, whereas the packing of the complex molecules into the unit cell can be seen in the stereoview diagrams of Fig. 2. The osmium atom is bonded in an approximately octahedral arrangement of ligands consisting of two mutually *trans* triphenylphosphines, one carbonyl, a *monohapto*-trifluoroacetate, and a *dihapto*-thioacyl. The major distortion from ideal octahedral geometry is due to the bonding requirements of the thioacyl ligand, where the angle subtended at the osmium atom by the Os–C and Os–S bonds is 43.0°. Consequent upon this narrow angle is a widening of the opposite angle, C(1)–Os–O(2), to 112.3°. The carbon of the thioacyl ligand is approximately *trans* to the oxygen of the trifluoroacetate group, and the sulphur atom is approximately *trans* to the carbonyl ligand.

The triphenylphosphine ligands

The Os–P distances of 2.405 and 2.407(4) Å are equivalent, and compare with similar bonds in the majority of other octahedral or trigonal bipyramidal osmium complexes containing mutually *trans* triphenylphosphine ligands [9]. The P–Os–P angle is 173.9(1)°, the small deviation from linearity being most likely due to steric interactions associated with the bulky triphenylphosphine groups. Within the triphenylphosphine ligands themselves, the geometry is normal.

The P–C distances lie in the range 1.80–1.83(2) Å, the Os–P–C angles are in the range 112.8–117.3°, the benzene rings are all planar, and the average values for the C–C distances and C–C–C bond angles in the rings are 1.38 Å and 120° respectively. The P atoms are not displaced from the planes of the phenyl rings to any significant extent.

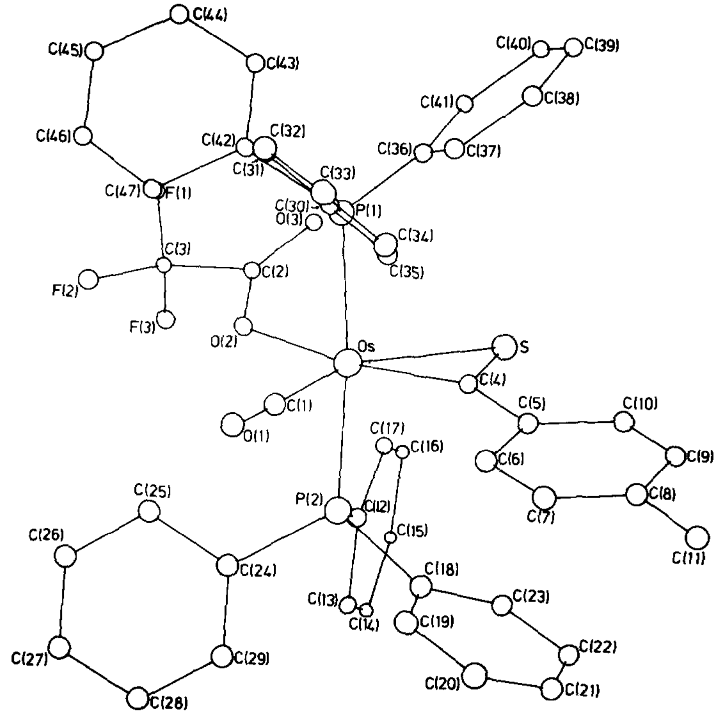


Fig. 1. The molecular geometry and atomic numbering scheme for $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$.

The carbonyl ligand

The bond distances and angles associated with the carbonyl ligand are Os–C(1) 1.82(1) Å, C(1)–O(1) 1.16(2) Å and Os–C(1)–O(1), 173(2)°. The Os–C(1) distance is at the very bottom end of the range found in non-cluster monomeric osmium carbonyl complexes [10]. The shortness would indicate that the CO has competed more successfully than the other ligands for π-electron density back-donated from the metal, and has not been subjected to any significant bond lengthening due to the sulphur atom in the *trans* position.

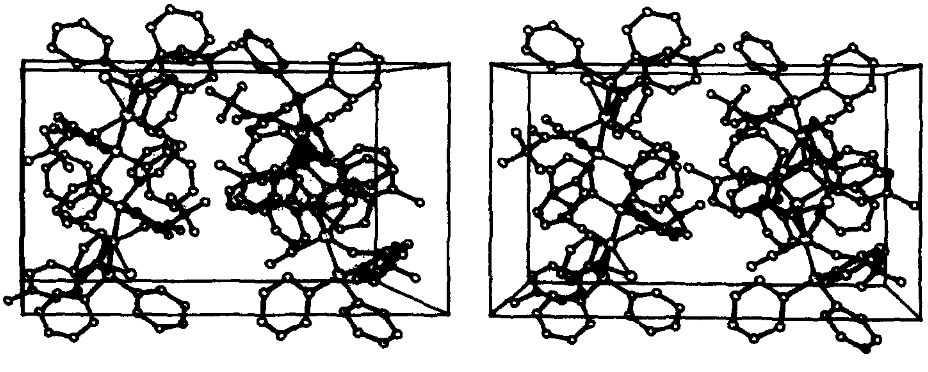


Fig. 2. Stereo-pair diagrams showing the molecular packing in $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$.

The trifluoroacetate ligand

The bond distances and angles in the *monodentate* trifluoroacetate ligand are comparable with those found in other complexes. For example, the C(2)–O(2) distance of 1.27(2) Å is similar to 1.282(7) Å in $Sb(O_2CCF_3)_3$ [11], and 1.287(7) Å in $[Cr_3(C_5H_5)_2(O_2CCF_3)_6]$ [12]. In contrast to these carbon–oxygen single bonds, the C(2)–O(3) bond length of 1.18(2) Å is characteristic of a double bond. It is similar in value to that of 1.192(7) Å in $Sb(O_2CCF_3)_3$ [11], and also compares well with values of 1.21 to 1.23 Å for C=O bonds in aldehydes and ketones [13].

The trifluoroacetate backbone (O(2), O(3), C(2), C(3)) is planar. Concomitant with the adoption of the monodentate bonding mode is a relaxation of any requirement that the ligand should adopt a particular orientation with respect to the equatorial coordination plane, and the plane of the backbone is in fact inclined at an angle of 30.3° to the plane defined by Os, S, C(4). This geometry is clearly seen in Fig. 1.

The fluorine atoms display the high degree of anisotropic thermal motion frequently observed in structures containing trihalomethyl groups [14]. The C–F distances calculated from the atom coordinates in Table 1 are 1.28 to 1.30 Å, but these become 1.34–1.38 Å when corrected for the effects of thermal motion [15].

The Os–O(2) distance of 2.206(11) Å is longer than expected for an Os–O single bond, which is usually in the range 2.00–2.13 Å [16]. The sum of the covalent radii is 2.099 Å [17]. The lengthening of the Os–O bond in the present complex is presumably due to a strong *trans* influence of the Os–C(4) σ bond.

The thioacyl ligand

The thioacyl ligand is coordinated to the osmium centre through both the carbon and sulphur atoms. The Os–C(4) bond (1.91(2) Å) exhibits a pronounced degree of multiple bond character, as can be seen from a comparison with M–C σ bond lengths found in third row transition metal complexes (2.06–2.16 Å [18]). This Os–C distance is more typical of Os–C carbonyl bonds, suggesting a degree of π-acidity for the thioacyl ligand similar to that of a carbonyl ligand, although not as great as that of the carbonyl ligand in this same complex. Relatively short metal–carbon bonds have been observed in other *dihapto*-acyl and -thioacyl complexes. For example, in $Ru(\eta^2\text{-}COR)I(CO)(PPh_3)_2$ the Ru–C distances were 1.92(1) and 1.88(3) Å for R = *p*-tolyl and Me respectively [4], in $RhCl(\eta^2\text{-}S_2CNMe_2)(\eta^2\text{-}SCNMe_2)(PPh_3)\cdot CCl_3H$ Rh–C was 1.90(2) Å [19], and in $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ BF_4^-$ Ir–C were 2.005(9) and 1.96(2) Å [20].

The Os–C distance of 2.513(6) Å is longer than that observed in $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot 0.5C_6H_6$ [21] where the Os–S bonds were 2.426 and 2.442(4) Å for the methylated and unmethylated S respectively. In the ruthenium η^2-acyl complexes, quoted above [4], the Ru–O distances (av. 2.41 Å) were also quite long by comparison with other Ru–O bonds. The explanation proposed for this observation was that the *trans*-carbonyl groups exerted strong *trans* influences on the Ru–O bonds. In the present case, the S atom of the thioacyl ligand is also *trans* to a carbonyl ligand and hence the strong π-acidity of this CO ligand is also likely to result in a weakening of the *trans* Os–S bond in the present complex. In addition to this, there is the competition for metal π-electrons by the adjacent carbon atom (not present in the case of $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]^+$) [21] which would also lead to a weakening of the Os–S bond.

TABLE 2

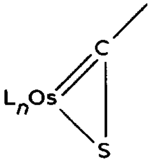
C–S BOND LENGTHS, (Å) AND C–M–S ANGLES (°) IN η^2-CS(R) COMPLEXES

Compound	C–S	C–M–S	Ref.
$Fe(\eta^2\text{-}CSNMe_2)(S_2CNMe_2)(CO)_2$	1.653(7)	43.6(2)	27
$Fe(\eta^2\text{-}CS_2)(CO)_2(PMe_3)(PPh_3)$	1.676(7)	44.8(2)	28
$[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ BF_4^-$	1.681	42.6	
	1.688(11)	42.9(4)	20
$Pt(\eta^2\text{-}CS_2)(PPh_3)_2$	1.72(5)	46(2)	29
$Mn(\eta^2\text{-}CSNMe_2)(CO)_3(PPh_3)$	1.682(6)	44.0(2)	30
$[Mn(C[SMe]NMe_2)(CO)_3(PPh_3)]^+$	1.78(2)	48.3(5)	
$Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$	1.72(2)	43.0(5)	This work

The C–S bond length (1.72(2) Å) lies between the values observed for C–S single bonds (1.79–1.86 Å) in $Fe_2(CO)_6(SC_2H_5)_2$ [22] and $[CH_2SFe_2(CO)_6]_2S$ [23] and C=S double bonds of 1.55–1.56 Å in CS_2 [24], COS [25], and CSTe [26]. Thus there is a reduction of the C–S bond order from 2.0 to ~ 1.5 upon coordination to the metal. Analogous observations have been made with other η^2-CS coordinated species (Table 2).

The angles within the Os-η^2-C(S)-*p*-tolyl moiety are all normal. The 'bite' angle C(4)–Os–S of 43.0(5)° is comparable with those of similar compounds (Table 2). The Os–C(4)–S plane is tilted at an angle of 6.80° to the plane containing Os, C(1), O(2), and the tolyl plane is tilted at an angle of 4.8° to the plane containing Os, S, C(4), C(1), O(2).

From the established bond lengths and angles it is possible to explain the bonding of the thioacyl complex. The carbon of the thioacyl group is trigonally hybridized and the unhybridized p_z orbital is in a position to interact with orbitals of appropriate energy and symmetry on the Os, C(5) and S atoms to form delocalized π-orbitals potentially involving all four atoms. The observed bond distances clearly indicate that the p_z orbital of the ligand carbon has sufficient Lewis acidity to interact significantly with all three adjacent atoms. The bonding is perhaps best represented by the structure below.



It is interesting that the same compounds are accessible by addition of sulphur to the osmium–carbon triple bond in $Os(CR)Cl(CO)(PPh_3)_2$ [31].

Other reactions of the η^2-CSR compounds

No conditions have been found for reversing the thioacyl formation reaction. Nor has it been possible to convert the η^2-CSR arrangement to a η^1-C[S]R arrangement. In an experiment to test this $Os(\eta^2\text{-}CSR)Cl(CO)(PPh_3)_2$ with sodium diethyldithiocarbamate was heated under reflux in $CHCl_3$ for 4 h. No reaction occurred.

However, prolonged heating (15 h) in the high-boiling solvents xylene and 2-methoxyethanol yields, by displacement of chloride and triphenylphosphine, the η^2-CSR complex, $\mathrm{Os}(\eta^2\text{-CSR})(\eta^2\text{-}\mathrm{S_2CNEt_2})(\mathrm{CO})(\mathrm{PPh_3})$. This result suggests that the thioacyl ligand has a very strong tendency to remain *dihapto*.

The *dihapto*-iminoacyl complexes, $\mathrm{Ru}(\eta^2\text{-C[NR]R})\mathrm{X(CO)(PPh_3)_2}$ [5] are protonated by acids but are inert towards alkylation by methyl triflate. The *dihapto*-thioacyl complexes obtained in this work are not attacked by acids but do react very slowly with methyl triflate. In dry benzene this reaction affords a red oily product with $\mathrm{Os}(\eta^2\text{-CSR})\mathrm{Cl(CO)(PPh_3)_2}$ which is difficult to handle and has eluded characterisation. However, for $\mathrm{Os}(\eta^2\text{-CSR})\mathrm{Cl(CNR)(PPh_3)_2}$ two products are obtained. The minor product is again a red oily compound which, because of handling difficulties, has eluded satisfactory characterisation. The major product is a green crystalline solid which the IR spectrum shows contains a trifluoromethanesulphonate ion. This ion can be exchanged for perchlorate ion to afford a perchlorate salt, but reaction with chloride ion affords a red neutral complex. The green solid is formulated as the cationic bidentate carbene complex $[\overline{\mathrm{Os}(\eta^2\text{-C[S}}\mathrm{Me]R})\mathrm{Cl(CNR)(PPh_3)_2}]^+$, which on reaction with chloride ion leads to the neutral monodentate carbene complex $\mathrm{OsCl_2[C(SMe)R](CNR)(PPh_3)_2}$. The former compound exhibits a medium intense band in the IR spectrum at 1327 $\mathrm{cm^{-1}}$, but the latter has no activity between 1200 and 1400 $\mathrm{cm^{-1}}$. Both compounds exhibit a split $\nu(\mathrm{CN})$ band for the isocyanide ligand in the spectra obtained in Nujol mulls and the splitting remains in the spectra obtained in dichloromethane (Table 1) suggesting that geometrical isomers are present.

Experimental

General experimental conditions and instrumentation were as described previously [1]. The ^{1}H NMR spectral data are listed in Table 3.

Arylthiocarbonyl complexes

$\mathrm{OsRCl(CS)(PPh_3)_2}$

$\mathrm{OsHCl(CS)(PPh_3)_3 \cdot (CH_2Cl_2)_{0.5}}$ [1] (1.0 g) and di-*p*-tolylmercury(II) (0.5 g) were heated under reflux in degassed toluene (40 ml) for 40 min. The red solution was passed through a celite pad and the solvent volume was reduced to 10 ml. Addition of ethanol and further reduction of the solvent volume gave crimson (near black) crystals which were collected and washed with boiling ethanol. Recrystallisation from dichloromethane/ethanol gave crimson-black crystals (0.78 g, 93.9%) containing 0.33 mol dichloromethane of solvation. ^{1}H NMR ($\mathrm{CDCl_3}$) shows τ, 4.73 [s, 0.67H, $\mathrm{CH_2Cl_2}$]. M.p. 215–217°C. Anal. Found: C, 58.37; H, 4.25; P, 6.90. $\mathrm{C_{44}H_{37}ClOsP_2S \cdot (CH_2Cl_2)_{0.33}}$ calcd.: C, 58.27; H, 4.16; P, 6.78%.

$\mathrm{OsR}(\eta^2\text{-}\mathrm{S_2CNEt_2})\mathrm{(CS)(PPh_3)_2}$

$\mathrm{OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}}$ (0.15 g) was stirred in dichloromethane (40 ml) and sodium diethyldithiocarbamate (0.2 g) in ethanol (10 ml) was added. After 20 min stirring the yellow solution was passed through a celite pad and upon reduction of the solvent volume yellow crystals deposited which were recrystallised from dichloromethane/ethanol (0.155 g, 94.6%). M.p. 221–224°C. Anal. Found: C, 59.21; H, 5.06; N, 1.22. $\mathrm{C_{49}H_{47}NOsP_2S_3}$ calcd.: C, 58.95; H, 4.75; N, 1.40%.

TABLE 3. ^{1}H NMR DATA [a] FOR OSMIUM COMPLEXES

Compound [b]	Chemical shift (τ) and coupling constants (Hz)
$\mathrm{OsRCl(CS)L_2}$	7.83, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.72, s, 4H, $\mathrm{C_6H_4}$
	2.58, m, 30H, Ph
$\mathrm{OsR(\eta^2\text{-}S_2CNEt_2)(CS)L_2}$	9.36, t, 3H, $\mathrm{NCH_2}CH_3$, J(HH) 7.2
	9.15, t, 3H, $\mathrm{NCH_2}CH_3$, J(HH) 7.2
	7.90, s, 3H, $\mathrm{C_6H_4}CH_3$
	7.26, q, 2H, $\mathrm{N}CH_2\mathrm{CH_3}$, J(HH) 7.2
	6.88, q, 2H, $\mathrm{N}CH_2\mathrm{CH_3}$, J(HH) 7.2
	3.43, q, 4H, $\mathrm{C_6H_4}$
	2.62, m, 30H, Ph
$\mathrm{OsR(\eta^2\text{-}O_2CMe)(CS)L_2}$	9.40, s, 3H, $\mathrm{O_2CCH_3}$
	7.94, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.43, q, 4H, $\mathrm{C_6H_4}$
	2.62, m, 30H, Ph
$\mathrm{OsRBr(CS)L_2}$	7.83, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.80, q, 4H, $\mathrm{C_6H_4}$
	2.55, m, 30H, Ph
$\mathrm{OsRCl(MeCN)(CS)L_2}$	8.37, s, 3H, $\mathrm{NCCH_3}$
	7.78, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.36, q, 4H, $\mathrm{C_6H_4}$
	2.60, m, 30H, Ph
$\mathrm{OsRCl(CS)(CNR)L_2}$	7.77, s, 3H 7.70, s, 3H $\mathrm{C_6H_4}CH_3$
	3.49, m, 8H, $\mathrm{C_6H_4}$
	2.65, m, 30H, Ph
$\mathrm{OsR(\eta^1\text{-}O_2CCF_3)(CN\text{-}}p\mathrm{\text{-}C_6H_4Cl)(CS)L_2}$	7.80, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.00, 38H, $\mathrm{C_6H_4}$ + Ph
$\mathrm{Os(\eta^2\text{-}CSR)Cl(CO)L_2}$	7.90, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.17, q, 4H, $\mathrm{C_6H_4}$
	2.60, m, 31H, Ph
$\mathrm{Os(\eta^2\text{-}CSR)Br(CO)L_2}$	7.87, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.14, q, 4H, $\mathrm{C_6H_4}$
	2.57, m, 30H, Ph
$\mathrm{Os(\eta^2\text{-}CSR)I(CO)L_2}$	7.90, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.08, q, 4H, $\mathrm{C_6H_4}$
	2.60, m, 30H, Ph
$\mathrm{Os(\eta^2\text{-}CSR)Cl(CNR)L_2}$	$\left.\begin{array}{l}\text{7.95, s, 3H}\\\text{7.72, s, 3H}\end{array}\right\}\mathrm{C_6H_4}CH_3$
	3.02, m, 39H, $\mathrm{C_6H_4}$ + Ph
$\mathrm{Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CN\text{-}}p\mathrm{\text{-}C_6H_4Cl)L_2}$	7.85, s, 3H, $\mathrm{C_6H_4}CH_3$
	3.10, m, 40H, $\mathrm{C_6H_4}$ + Ph
$\mathrm{Os(\eta^2\text{-}CSR)(\eta^2\text{-}S_2CNEt_2)(CO)L}$	8.76, t, 3H, $\mathrm{NCH_2}CH_3$, J(HH) 7.3
	8.67, t, 3H, $\mathrm{NCH_2}CH_3$, J(HH) 7.3
	7.73, s, 3H, $\mathrm{C_6H_4}CH_3$
	6.33, m, 4H, $\mathrm{N}CH_2\mathrm{CH_3}$
	2.55, m, 18H, Ph
$\mathrm{[\overline{Os(C[S}Me]R)Cl(CNR)L_2]ClO_4}$	8.20, s, 3H, $\mathrm{SCH_3}$
	$\left.\begin{array}{l}\text{7.88, s, 3H}\\\text{7.64, s, 3H}\end{array}\right\}\mathrm{C_6H_4}CH_3$
	3.15, m, 39H, $\mathrm{C_6H_4}$ + Ph
$\mathrm{OsCl_2(C[SMe]R)(CNR)L_2}$	8.64, s, 3H, $\mathrm{SCH_3}$
	7.67, s, 6H, $\mathrm{C_6H_4}CH_3$
	3.84, m, 8H, $\mathrm{C_6H_4}$
	2.52, m, 32H, Ph

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[a] $\mathrm{CDCl_3}$ used as solvent. All phenyl resonances quoted as mid-point of multiplet. [b] L = $\mathrm{PPh_3}$, R = p-tolyl.

$OsR(\eta^2\text{-}O_2CCH_3)(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.15 g) and sodium acetate (0.2 g) were treated as above to give yellow crystals of the hemidichloromethane solvate (0.15 g, 96%). ^1H NMR ($CDCl_3$) shows τ, 4.73 [s, 1H, CH_2Cl_2]. M.p. 212–214°C. Anal. Found: C, 58.54; H, 4.44; P, 6.41. $C_{46}H_{40}O_2OsP_2S \cdot (CH_2Cl_2)_{0.5}$ calcd.: C, 58.70; H, 4.34; P, 6.51%.

$OsR(\eta^2\text{-}O_2CCF_3)(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.15 g) and triethylammonium trifluoroacetate (ca. 0.2 g) were treated as above to give yellow crystals which were too insoluble for ^1H NMR measurements but which analysis indicates contain 0.33 mol dichloromethane of solvation (0.16 g, 98.3%). M.p. 210–215°C. Anal. Found: C, 56.01; H, 4.06; P, 6.49. $C_{46}H_{37}F_3O_2OsP_2S \cdot (CH_2Cl_2)_{0.33}$ calcd.: C, 56.14; H, 3.83; P, 6.25%.

$Os(\eta^1\text{-}O_2CCF_3)_2(EtOH)(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.15 g) and trifluoroacetic acid (0.2 ml) were stirred in dichloromethane (30 ml) for 5 min. Ethanol was added and reduction of the solvent volume gave yellow crystals which were collected and recrystallised from dichloromethane/ethanol (0.16 g, 94.5%). M.p. 180–183°C. Anal. Found: C, 50.43; H, 3.92; P, 6.72%. $C_{43}H_{36}F_6O_5OsP_2S$ calcd.: C, 50.09; H, 3.52; P, 6.01%.

$OsRBr(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.15 g) was dissolved in dichloromethane (30 ml) and silver perchlorate (0.04 g, 1.18 eq) in ethanol (10 ml) was added. The yellow solution was passed through a pad of celite and sodium bromide (0.2 g) in ethanol/water (5 ml, 1/1) was rapidly added. The solvent volume was reduced to give crimson-black crystals which were redissolved in dichloromethane and passed down a florisil column using dichloromethane as eluent. The crimson band was collected, ethanol was added and reduction of the solvent volume gave crimson-black crystals (0.13 g, 85.2%). M.p. 210–214°C. Anal. Found: C, 56.69; H, 4.33; P, 6.43. $C_{44}H_{37}BrOsP_2S$ calcd.: C, 56.83; H, 4.01; P, 6.66%.

$OsRI(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$, silver perchlorate (0.04 g, 1.18 eq) and sodium iodide (0.2 g) were treated as above to give crimson-black crystals (0.135 g, 84.2%). M.p. 217–219°C. Anal. Found: C, 54.15; H, 4.06; P, 5.97. $C_{44}H_{37}IOsP_2S$ calcd.: C, 54.10; H, 3.82; P, 6.34%.

$OsRCl(MeCN)(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.1 g) was dissolved in dichloromethane (20 ml) and acetonitrile (1 ml) was added. The solvent volume was reduced to 5 ml and ethanol was added to give white crystals containing 0.25 mol dichloromethane of solvation (0.014 g, 100%). ^1H NMR ($CDCl_3$) shows τ, 4.70 [s, 0.5H, CH_2Cl_2]. M.p. 161–163°C. Anal. Found: C, 58.73; H, 4.50; P, 7.43. $C_{46}H_{40}ClNOsP_2S \cdot (CH_2Cl_2)_{0.25}$ calcd.: C, 58.61; H, 4.31; P, 6.54%.

$OsRCl(CS)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.15 g) was stirred in the minimum quantity of dichloromethane to effect complete dissolution and the solution was cooled to 0°C. Carbon monoxide was passed through the solution for 10 s and hexane at 0°C was added. The solvent volume was reduced, without application of heat, to afford white crystals (0.15 g, 100%). M.p. 220–222°C (turns red 145–150°C). Anal. Found: C, 59.26; H, 4.38; P, 6.77. $C_{45}H_{37}ClOOsP_2S$ calcd.: C, 59.16; H, 4.08; P, 6.78%.

$OsRBr(CO)(CS)(PPh_3)_2$

$OsRBr(CS)(PPh_3)_2$ (0.15 g) was treated with carbon monoxide as above to afford white crystals (0.15 g, 97.1%). M.p. 139–144°C (turns red 135–140°C). Anal. Found: C, 56.78; H, 4.40; P, 6.65. $C_{45}H_{37}BrOOsP_2S$ calcd.: C, 56.42; H, 3.89; P, 6.47%.

$OsR(\eta^1\text{-}O_2CCF_3)(CO)(CS)(PPh_3)_2$

$OsR(\eta^2\text{-}O_2CCF_3)(CS)(PPh_3)_2(CH_2Cl_2)_{0.33}$ (0.15 g) was dissolved in CH_2Cl_2 (40 ml). Carbon monoxide was passed through the solution until it became colourless. Addition of hexane (30 ml) and reduction of the solvent volume afforded white crystals (0.15 g, 100%). M.p. 218–222°C (turns red 160°C). Anal. Found: C, 57.62; H, 4.02. $C_{47}H_{37}F_3O_3OsP_2S$ calcd.: C, 56.96; H, 3.76%.

$OsRCl(CS)(CNR)(PPh_3)_2$

$OsRCl(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (0.3 g) was dissolved in dichloromethane (40 ml) and the solution was cooled to 10°C. A dichloromethane solution (10 ml) of *p*-tolylisocyanide (0.05 g, 1.3 eq) was added followed by hexane (40 ml). Upon reduction of the solvent volume white crystals were deposited (0.33 g, 100%). Recrystallisation from dichloromethane/ethanol, without application of heat, gave white crystals. M.p. 170–172°C (turns red above 140°C). Anal. Found: C, 62.61; H, 4.77; N, 1.19. $C_{52}H_{44}ClNOsP_2S$ calcd.: C, 62.29; H, 4.42; N, 1.40%.

$OsR(\eta^1\text{-}O_2CCF_3)(CN\text{-}p\text{-}C_6H_4Cl)(CS)(PPh_3)_2$

$OsR(\eta^2\text{-}O_2CCF_3)(CS)(PPh_3)_2$ (0.15 g) and *p*-chlorophenylisocyanide were stirred in dichloromethane (30 ml) for 40 min. The solvent volume was reduced to 5 ml and ethanol was added to give a cream, floccular solid (0.17 g, 99.2%). Recrystallisation from dichloromethane/ethanol gave large, colourless crystals containing 0.25 mol dichloromethane of solvation. ^1H NMR ($CDCl_3$) shows τ, 4.72 [s, 0.5H, CH_2Cl_2]. M.p. 117–179°C (turns red above 160°C). Anal. Found: C, 57.16; H, 4.28; N, 1.36. $C_{33}H_{41}ClF_3NO_2OsP_2S \cdot (CH_2Cl_2)_{0.25}$ calcd.: C, 57.01; H, 3.73; N, 1.25%.

Bidentate thioacyl complexes

$Os(\eta^2\text{-}CSR)Cl(CO)(PPh_3)_2$

$OsRCl(CO)(CS)(PPh_3)_2$ (0.15 g) was dissolved in dichloromethane (30 ml) and the solution was heated under reflux for 5 min. Ethanol was added and reduction of the solvent volume gave scarlet crystals (0.15 g, 100%). M.p. 251–254°C. Anal. Found: C, 59.42; H, 4.72; P, 6.62. $C_{45}H_{37}ClOOsP_2S$ calcd.: C, 59.17; H, 4.08; P, 6.78%.

$Os(\eta^2\text{-}CSR)Br(CO)(PPh_3)_2$

$OsRBr(CO)(PPh_3)_2$ (0.15 g) was treated as above to give crimson crystals containing 0.125 mol dichloromethane of solvation (0.15 g, 98.9%). ^1H NMR

($CDCl_3$) shows τ, 4.72 [s, 0.25H, CH_2Cl_2]. M.p. 260–263°C. Anal. Found: C, 55.66; H, 4.33; P, 6.12. $C_{45}H_{37}BrOOsP_2S \cdot (CH_2Cl_2)_{0.125}$ calcd.: C, 55.96; H, 3.88; P, 6.40%.

$Os(\eta^2\text{-}CSR)I(CO)(PPh_3)_2$

$OsRI(CS)(PPh_3)_2$ (0.15 g) was treated as above to give sienna crystals which were recrystallised from chloroform/ethanol to give a mixture of sienna platelets and burnt umber crystals (0.15 g, 100%). M.p. 253–255°C. Anal. Found: C, 53.81; H, 4.13; P, 5.99. $C_{45}H_{37}IOOsP_2S$ calcd.: C, 53.78; H, 3.71; P, 6.16%.

$Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$

$OsR(\eta^1\text{-}O_2CCF_3)(CO)(CS)(PPh_3)_2$ (0.15 g) was heated under reflux in benzene (30 ml) for 15 min. Ethanol was added and reduction of the solvent volume gave red crystals which were recrystallised from dichloromethane/ethanol (0.15 g, 100%). M.p. 128–131°C. Anal. Found: C, 57.02; H, 3.89; P, 6.46. $C_{47}H_{37}F_3O_3OsP_2S$ calcd.: C, 56.96; H, 3.76; P, 6.25%.

$Os(\eta^2\text{-}CSR)Cl(CNR)(PPh_3)_2$

$OsRCl(CS)(CNR)PPh_3)_2$ (0.3 g) was heated under reflux in toluene (30 ml) for 20 min. Ethanol was added and reduction of the solvent volume gave red crystals which were recrystallised from dichloromethane/ethanol (0.3 g, 100%). M.p. 225°C. Anal. Found: C, 62.54; H, 4.77; N, 1.29. $C_{52}H_{44}ClNOsP_2S$ calcd.: C, 62.29; H, 4.42; N, 1.40%.

$Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CN\text{-}p\text{-}C_6H_4Cl)(PPh_3)_2$

$OsR(\eta^1\text{-}O_2CCF_3)(CN\text{-}p\text{-}C_6H_4Cl)(CS)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ (0.15 g) was heated under reflux in toluene (25 ml) for 3 h. Ethanol was added and reduction of the solvent volume gave maroon crystals which were recrystallised from dichloromethane/ethanol to give large maroon crystals (0.147 g, 100%). M.p. 208–212°C. Anal. Found: C, 58.40; H, 4.35; N, 1.50. $C_{53}H_{41}ClF_3NO_2OsP_2S$ calcd.: C, 57.84; H, 3.76; N, 1.27%.

$Os(\eta^2\text{-}CSR)(\eta^2\text{-}S_2CNEt_2)(CO)(PPh_3)$

$Os(\eta^2\text{-}CSR)Cl(CO)(PPh_3)_2$ (0.15 g) and sodium diethyldithiocarbamate (0.1 g) were heated under reflux in xylene (20 ml) and 2-methoxyethanol (20 ml) for 15 h. Upon reduction of the solvent volume crimson crystals deposited which were recrystallised from dichloromethane/ethanol to give burgundy platelets (0.115 g, 91.7%). M.p. 235–240°C. Anal. Found: C, 50.81; H, 4.94; N, 1.69. $C_{32}H_{32}NOOsPS_3$ calcd.: C, 50.31; H, 4.22; N, 1.83%.

$[\overline{Os(C[S}Me]R)Cl(CNR)(PPh_3)_2]ClO_4$

$Os(\eta^2\text{-}CSR)Cl(CNR)(PPh_3)_2$ (0.3 g) was stirred in dry benzene with methyl triflate (0.2 ml) for 3 h. The lime green needles were collected and recrystallised from dichloromethane (20 ml) and ethanol (20 ml) containing sodium perchlorate (0.2 g) to give lime green crystals (0.17 g, 50.9%). M.p. 134–136°C. Anal. Found: C, 56.60; H, 4.47; N, 1.12. $C_{53}H_{47}Cl_2NO_4OsP_2S$ calcd.: C, 56.98; H, 4.24; N, 1.25%.

$OsCl_2[C(SMe)R](CNR)(PPh_3)_2$

$[\overline{Os(C[S}Me]R)Cl(CNR)(PPh_3)_2]ClO_4$ (0.1 g) and lithium chloride (0.1 g) were heated under reflux in ethanol (10 ml) for 10 min. The red crystals were recrystallised from dichloromethane/ethanol to give red crystals (0.9 g, 95.5%). M.p. 158–161°C. Anal. Found: C, 60.41; H, 5.31; N, 1.20. $C_{53}H_{47}Cl_2NOsP_2S$ calcd.: C, 60.45; H, 4.50; N, 1.33%.

X-ray data

Preliminary X-ray photography showed the red equant crystals of $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$ to belong in the orthorhombic class with space group $P2_12_12_1$ (systematic absenses $h\ 0\ 0\ h = 2n+1$, $0\ k\ 0\ k = 2n+1$, $0\ 0\ l\ l = 2n+1$). Accurate unit cell constants were determined from a least-squares refinement of the setting angles of twelve high-theta reflections using a Hilger & Watts four-circle diffractometer [32].

Crystal data

$C_{47}H_{37}F_3O_3OsP_2S$, $M = 991.0$, orthorhombic, a 11.584(1), b 19.184(2), c 18.90(1) Å, V 4199 Å^3, space group $P2_12_12_1$, $Z = 4$, d_m 1.56 (aqueous KBr/KI), d_c 1.57, $F(000)$ 1968, Cu-K_α radiation of λ 1.5418 Å, Ni filter, μ(Cu-K_α) 74.52 cm^{-1}, crystal size 0.28 × 0.24 × 0.24 mm, mosaic spread 0.23°, temperature 291 K, boundary faces $\{0\ 0\ 1\}$, $\{1\ 0\ 1\}$, $(0\ 1\ 1)$, $(0\ \bar{1}\ \bar{1})$.

Intensity data to a Bragg limit of 57° ($\sin\theta/\lambda = 0.544$) were collected using a symmetrical 2θ-ω scan of 1.60° at a scan rate of 0.02° s^{-1}. Each background was counted for 15 s. After averaging zonal reflections the data set comprised 2868 observed independent reflections with $I > 3\sigma(I)$ $\{\sigma(I) = [T + t^2B + (pI)^2]^{1/2}$, $T =$ integrated peak count, $B =$ average background count, $t =$ ratio of scan to background times, p was assigned an initial value of 0.04 [33] but this did not require changing as $\langle\omega(|F_0| - |F_c|)^2\rangle$ remained satisfactorily constant throughout the refinement process$\}$. The data were corrected for Lorentz and polarisation factors and for absorption (maximum and minimum transmission coefficients were 0.334 and 0.193 respectively) [34].

Structure determination and refinement

The position of the osmium atom was deduced from a three-dimensional Patterson synthesis as (0.21 0.25 0.25). The adventitious occurrence of coordinates of 0.25 meant that for one half of all data F_c was zero, but nevertheless it was possible to identify a consistent set of phosphorus and sulphur atoms in an electron density map. Subsequent 'difference' maps enabled the site of all remaining non-hydrogen atoms to be found. Full-matrix least-squares refinement was then commenced [35]. Atomic scattering factors and dispersion corrections were from standard listings [36]. The function minimised was $\Sigma\omega(|F_0| - |F_c|)^2$, with weights $\omega = 4|F_0|^2/(\sigma^2(F_0)^2)$. After two cycles the residual R was 0.073. The temperature factors for the four heaviest atoms were then relaxed to allow for possible thermal or vibrational anisotropy and two further cycles computed. A difference Fourier synthesis was generally featureless (maximum residual electron density ~ 1.0 e Å^{-3}) consistent with there being no evidence in the NMR spectrum for the presence of any solvent molecules. Positions were then calculated for all hydrogen atoms except the methyl (C–H 1.0 Å) and they were incorporated into subsequent structure factor calculations but were not refined. Their isotropic temperature factors were set according to $B_H = B_C + 1.0$ where B_C is the isotropic temperature factor of the atom to which the

TABLE 4

ATOMIC POSITIONS FOR Os(η^2-CSR)(η^1-O_2CCF_3)(CO)(PPh_3)$_2$

Atom	x/a	y/b	z/c
Os	0.21097(6)	0.25779(3)	0.25521(3)
P(1)	0.0712(4)	0.1663(2)	0.2709(2)
P(2)	0.3633(4)	0.3402(2)	0.2333(2)
S	0.0543(5)	0.3335(3)	0.2047(3)
C(1)	0.284(2)	0.2244(9)	0.334(1)
O(1)	0.334(1)	0.2099(8)	0.3848(7)
O(2)	0.286(1)	0.1871(5)	0.1754(6)
C(2)	0.295(2)	0.200(1)	0.1095(9)
O(3)	0.268(1)	0.2492(7)	0.0759(6)
C(3)	0.350(2)	0.137(1)	0.072(1)
F(1)	0.400(2)	0.1554(9)	0.0135(9)
F(2)	0.424(2)	0.1011(8)	0.1084(8)
F(3)	0.274(1)	0.0940(8)	0.050(1)
C(4)	0.105(1)	0.326(1)	0.2896(7)
C(5)	0.053(1)	0.3616(8)	0.352(1)
C(6)	0.098(2)	0.345(1)	0.418(1)
C(7)	0.048(2)	0.380(1)	0.478(1)
C(8)	−0.035(2)	0.430(1)	0.470(1)
C(9)	−0.074(2)	0.446(1)	0.403(1)
C(10)	−0.033(2)	0.414(1)	0.345(1)
C(11)	−0.090(2)	0.465(1)	0.536(1)
C(12)	−0.009(2)	0.1391(9)	0.1941(9)
C(13)	−0.087(2)	0.083(1)	0.199(1)
C(14)	−0.153(2)	0.063(1)	0.141(1)
C(15)	−0.137(2)	0.095(1)	0.079(1)
C(16)	−0.062(2)	0.151(1)	0.069(1)
C(17)	0.002(2)	0.172(1)	0.130(1)
C(22)	−0.041(2)	0.1917(8)	0.3327(9)
C(23)	−0.017(2)	0.193(1)	0.406(1)
C(24)	−0.102(2)	0.218(1)	0.453(1)
C(25)	−0.201(2)	0.242(1)	0.427(1)
C(26)	−0.226(2)	0.242(1)	0.358(1)
C(27)	−0.148(2)	0.2150(9)	0.3087(9)
C(32)	0.129(2)	0.0841(8)	0.3040(8)
C(33)	0.238(2)	0.0621(9)	0.2789(9)
C(34)	0.276(2)	−0.004(1)	0.298(1)
C(35)	0.214(2)	−0.046(1)	0.342(1)
C(36)	0.108(2)	−0.023(1)	0.368(1)
C(37)	0.068(2)	0.0423(9)	0.3498(9)
C(42)	0.434(2)	0.3717(9)	0.3116(9)
C(43)	0.554(2)	0.375(1)	0.320(1)
C(44)	0.601(2)	0.402(1)	0.382(1)
C(45)	0.538(2)	0.429(1)	0.433(1)
C(46)	0.423(2)	0.428(1)	0.427(1)
C(47)	0.368(2)	0.398(1)	0.368(1)
C(52)	0.325(1)	0.4207(9)	0.1870(8)
C(53)	0.259(2)	0.4147(9)	0.1266(9)
C(54)	0.223(2)	0.475(1)	0.090(1)
C(55)	0.258(2)	0.539(1)	0.115(1)
C(56)	0.323(2)	0.547(1)	0.174(1)
C(57)	0.359(2)	0.486(1)	0.213(1)
C(62)	0.481(2)	0.3035(9)	0.1820(9)
C(63)	0.523(2)	0.3362(9)	0.1246(9)
C(64)	0.614(2)	0.307(1)	0.085(1)
C(65)	0.661(2)	0.246(1)	0.107(1)
C(66)	0.623(2)	0.213(1)	0.166(1)
C(67)	0.528(2)	0.239(1)	0.2057(9)

TABLE 5

BOND LENGTHS (Å) AND ANGLES (°) FOR $Os(\eta^2\text{-}CSR)(\eta^1\text{-}O_2CCF_3)(CO)(PPh_3)_2$

Os–S	2.513(6)	O(2)–C(2)	1.27(2)
Os–P(1)	2.407(4)	O(3)–C(2)	1.18(2)
Os–P(2)	2.405(4)	C(2)–C(3)	1.54(3)
Os–O(2)	2.206(11)	C(4)–C(5)	1.49(2)
Os–C(1)	1.83(2)	C(5)–C(6)	1.39(3)
Os–C(4)	1.91(2)	C(5)–C(10)	1.42(3)
S–C(4)	1.72(2)	C(6)–C(7)	1.44(3)
F(1)–C(3)	1.30(3)	C(7)–C(8)	1.37(3)
F(2)–C(3)	1.30(3)	C(8)–C(9)	1.38(3)
F(3)–C(3)	1.28(3)	C(8)–C(11)	1.55(3)
O(1)–C(1)	1.16(2)	C(9)–C(10)	1.34(3)
S–Os–P(1)	89.0(2)	Os–C(1)–O(1)	173(2)
S–Os–P(2)	94.9(2)	O(2)–C(2)–O(3)	131(2)
S–Os–O(2)	112.3(3)	O(2)–C(2)–C(3)	109(2)
S–Os–C(1)	147.8(6)	O(3)–C(2)–C(3)	119(2)
S–Os–C(4)	43.0(5)	F(1)–C(3)–F(2)	108(2)
P(1)–Os–P(2)	173.9(1)	F(1)–C(3)–F(3)	102(2)
P(1)–Os–O(2)	84.3(3)	F(1)–C(3)–C(2)	111(2)
P(1)–Os–C(1)	87.4(6)	F(2)–C(3)–F(3)	107(2)
P(1)–Os–C(4)	91.4(5)	F(2)–C(3)–C(2)	117(2)
P(2)–Os–O(2)	89.9(3)	F(3)–C(3)–C(2)	112(2)
P(2)–Os–C(1)	91.8(6)	Os–C(4)–S	87.7(7)
P(2)–Os–C(4)	94.6(5)	Os–C(4)–C(5)	147.6(12)
O(2)–Os–C(1)	99.2(7)	S–C(4)–C(5)	124.3(11)
O(2)–Os–C(4)	155.2(5)	C(4)–C(5)–C(6)	117(1)
C(1)–Os–C(4)	105.1(8)	C(4)–C(5)–C(10)	122(1)
Os–S–C(4)	49.4(5)	C(6)–C(5)–C(10)	121(2)
Os–P(1)–C(12)	117.3(6)	C(5)–C(6)–C(7)	117(2)
Os–P(1)–C(22)	111.4(6)	C(6)–C(7)–C(8)	122(2)
Os–P(1)–C(32)	115.2(6)	C(7)–C(8)–C(9)	119(2)
Os–P(2)–C(42)	114.5(6)	C(7)–C(8)–C(11)	120(2)
Os–P(2)–C(52)	117.3(5)	C(9)–C(8)–C(11)	120(2)
Os–P(2)–C(62)	112.8(6)	C(8)–C(9)–C(10)	122(2)
Os–O(2)–C(2)	125.5(11)	C(5)–C(10)–C(9)	120(2)

hydrogen is bonded. All remaining non-hydrogen atoms (except for the carbon atoms of the triphenylphosphines) were assigned anisotropic thermal parameters and an extinction coefficient was included in the refinement [37]. Four final cycles returned R and R_w $(\{\Sigma w(|F_0|-|F_c|)^2/\Sigma wF_0^2\}^{1/2})$ as 0.057 and 0.071 respectively.

The final atomic positions are listed in Table 4. The molecular geometry and atomic numbering scheme are shown in Fig. 1. Important bond lengths and angles are listed in Table 5. Lists of thermal parameters, bond lengths and angles in the phenyl rings of the triphenyl phosphine ligands, calculated hydrogen atom positions, and tables of observed and calculated structure factors are available on request from the authors (G.R.C.).

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