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Syntheses and structures of the chalcocarbonyl complexes $OsCl_2(CO)(CE)(PPh_3)_2$ (E = S, Se, Te)

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Abstract

The Group VI nucleophiles HE^- (E = O, S, Se, Te) react with the electrophilic dichlorocarbene ligand in the complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ to form the corresponding chalcocarbonyl derivatives $OsCl_2(CO)(CE)(PPh_3)_2$. $OsCl_2(CO)(CTe)(PPh_3)_2$ is the first reported tellurocarbonyl complex, and the compounds $OsCl_2(CO)(CE)(PPh_3)_2$ constitute the first complete series of chalcocarbonyl complexes. H_2O, H_2S and H_2Se also react with the dichlorocarbene complex to yield the corresponding chalcocarbonyl derivatives $OsCl_2(CO)(CE)(PPh_3)_2$, although $OsCl_2(CO)(CTe)(PPh_3)_2$ cannot be formed this way. The thiocarbonyl, dichlorocarbene complex $OsCl_2(=CCl_2)(CS)(PPh_3)_2$ gives tractable products with H_2O, H_2S and H_2Se, and in this way the mixed chalcocarbonyl compounds $OsCl_2(CS)(CE)(PPh_3)_2$ can be isolated. X-ray crystal structure determinations have been carried out on the complexes $OsCl_2(CO)(CS)(PPh_3)_2$, $OsCl_2(CO)(CSe)(PPh_3)_2$ and $OsCl_2(CO)(CTe)(PPh_3)_2$. The CS and CSe complexes are isostructural and crystallise in space group $P\bar{1}$, with two molecules in unit cells of dimensions: CS *a* 12.837(1), *b* 14.302(1), *c* 10.452(1) Å, *α* 92.45(1), *β* 97.42(1), *γ* 99.86(1)°; CSe *a* 12.846(3), *b* 14.341(3), *c* 10.462(4) Å, *α* 92.26(2), *β* 97.67(2), *γ* 99.76(1)°. The CTe complex crystallises in space group $P2_1/n$, with four molecules in a cell of dimensions *a* 14.211(3), *b* 18.084(4), *c* 14.857(3) Å, *β* 113.29(2)°. The coordinated CTe ligand in $OsCl_2(CO)(CTe)(PPh_3)_2$ displays similar overall structural features to the other coordinated chalcocarbonyl ligands in that the Os–C–Te angle is ca. 180° and the Os–CTe and C–Te bonds are very short. For each of the complexes the Os–CE bond length is shorter than the Os–CO bond length in the same molecule, although only for the thiocarbonyl complex is the difference significant. The *trans*-influence of the chalcocarbonyl ligands increases in the order CO < CS $\leqslant$ CSe < CTe.

Introduction

In contrast to the vast number of transition metal carbonyl complexes that have been reported, relatively few thio- or seleno-carbonyl complexes are known, and before our initial communication in this area [1] no tellurocarbonyl complexes had been reported. Unlike CO, the free molecules CS and CSe are difficult to generate and handle [2,3] and the free molecule CTe is unknown. Consequently synthetic routes which do not rely on the direct coordination of these source molecules to appropriate metal substrates are desirable or essential. Most reported syntheses of thiocarbonyl and selenocarbonyl complexes have relied on the modification or elaboration of the source molecules CX_2 and $CXCl_2$ ($X = S, Se$) [2]. Tellurium analogues of these molecules are at present unknown and so syntheses of tellurocarbonyl complexes require different approaches yet again.

In a previous communication [1] we reported the synthesis of the dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ and its reaction with the hydrogen chalcogenides HE^- ($E = O, S, Se, Te$) to form the corresponding chalcocarbonyl complexes $OsCl_2(CO)(CE)(PPh_3)_2$. $OsCl_2(CO)(CTe)(PPh_3)_2$ was the first tellurocarbonyl complex to be isolated, and the complexes $OsCl_2(CO)(CE)(PPh_3)_2$ constitute the first complete series of chalcocarbonyl complexes to be reported. For these reasons we have carried out X-ray crystal structure determinations on the series of complexes $OsCl_2(CO)(CE)(PPh_3)_2$ ($E = S, Se, Te$) and now report here our results in full.

Results and discussion

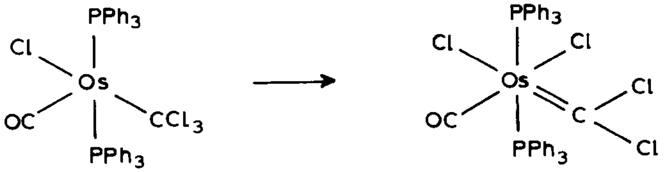
Synthesis of dichlorocarbene complexes of osmium

Our synthetic route to an osmium dichlorocarbene complex developed from earlier work [4,5] in which we had shown that $OsClH(CO)(PPh_3)_3$ reacts with diarylmercury compounds to yield coordinatively unsaturated σ-aryl-osmium(II) complexes thus:

$$OsClH(CO)(PPh_3)_3 + HgR_2 \rightarrow OsClR(CO)(PPh_3)_2 + RH + PPh_3 + Hg$$

($R = p$-tolyl, o-tolyl, phenyl)

We reasoned that if this reaction could be extended to include $R = CCl_3$, the resulting coordinatively unsaturated trichloromethyl intermediate might rearrange via α-chloride abstraction by the metal, thereby generating a dichlorocarbene complex.



We found, in fact, that reaction between $OsClH(CO)(PPh_3)_3$ and $Hg(CCl_3)_2$ gives directly the dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ in > 80% yield [1]. The dichlorocarbene ligand gives rise to bands at 880s, 780m and 770m cm^{-1} in the IR spectrum which are assigned to ν(C–Cl) (see Table 1 for IR data for all new compounds). The C(carbene) resonance in the ^{13}C NMR spectrum appears as a triplet (^2J(CP) 10 Hz) centred at 222.4 ppm (see Table 2). An X-ray crystal structure determination has confirmed the dichlorocarbene formulation, but reliable bond lengths and angles could not be obtained because of disorder between the carbene and carbonyl ligands.

Table 1

IR data (cm^{-1}) for osmium complexes [a]

Compound [b]	ν(CO) [c]	ν(CE) [c]	Other bands	Ref.
$OsCl_2(=CCl_2)(CO)(PPh_3)_2$	2012sh, 1990; [1994] [d]	–	880s, 780m, 770m [872s, 760m] [e] (CCl_2); 300w, 270w (OsCl)	f
$OsCl_2(=CCl_2)(CS)(PPh_3)_2$	–	1312	864s, 770m (CCl_2); 290w, 265w (OsCl)	6
$OsCl_2(CO)_2(PPh_3)_2$	2040, 1975	–	–	24
$OsCl_2(CO)(CS)(PPh_3)_2$	2040, 2030, 2022	1315	290w, 260w (OsCl)	26
$OsCl_2(CO)(CSe)(PPh_3)_2$	2036sh, 2018 [2030] [d]	1156	284w, 260w (OsCl)	f
$OsCl_2(CO)(CTe)(PPh_3)_2$	2040	1046	301w, 270w (OsCl)	f
$OsCl_2(CS)_2(PPh_3)_2$	–	1370, 1260	–	28
$OsCl_2(CS)(CSe)(PPh_3)_2$	–	1342, 1322 (ν(CS)) 1130 (ν(CSe))	271w, 253w (OsCl)	6
$[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]ClO_4$	2033	1048	2315w, 2288w ($NCCH_3$); 1090vs, 621m (ClO_4)	f

[a] Measured as Nujol mulls between KBr discs. [b] Satisfactory elemental analyses were obtained for all new compounds except $OsCl_2(=CCl_2)(CS)(PPh_3)_2$ (see discussion in text). [c] All bands very strong. [d] Solid state splitting; only one band observed in CH_2Cl_2 solution. [e] Solid state splitting; bands observed in CS_2 solution. [f] This work.

Our attempts to extend this reaction to other triphenylphosphine complexes of osmium have thus far met with very limited success. Only one other dichlorocarbene complex has been isolated, namely $OsCl_2(=CCl_2)(CS)(PPh_3)_2$. This complex can be prepared by reaction of $Hg(CCl_3)_2$ with either $OsClH(CS)(PPh_3)_3$ or $OsCl_2(CS)(PPh_3)_3$ [6]. For the reactions to be successful, however, it is essential that an excess of the mercurial and the triphenylphosphine are used. Unfortunately this leads to difficulties in purification of the product and consequently a satisfactory elemental analysis for $OsCl_2(=CCl_2)(CS)(PPh_3)_2$ has not been obtained. The complex has, however, been characterized on the basis of its IR spectrum (which is very similar to that of $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ – see Table 1) and its chemical reactivity (vide infra).

Reaction of $Hg(CCl_3)_2$ with $OsCl_2$ (CN-*p*-tolyl)$(PPh_3)_3$ or $OsCl_2(PPh_3)_3$ results in complex mixtures of products, none of which contains coordinated dichloro-

Table 2

^{13}C NMR data [a] for selected osmium complexes

Compound	Chemical shift (δ) and coupling constants (Hz)		Solvent
	CO	CE	
$OsCl_2(CO)_2(PPh_3)_2$	172.9 [b]	172.9 [b]	c
$OsCl_2(CO)(CS)(PPh_3)_2$	173.5 [b]	258.7 [b]	d
$OsCl_2(CO)(CSe)(PPh_3)_2$	173.0 (^2J(CP) 6.5)	278.8 (^2J(CP) 9.0)	d
$OsCl_2(CO)(CTe)(PPh_3)_2$	172.4 [b]	297.7 [b]	c
$OsCl_2(=CCl_2)(CO)(PPh_3)_2$	173.1 (^2J(CP) 6.5)	222.4 (^2J(CP) 10.0)	c

[a] δ in ppm; J in Hz. Reference TMS = 0, temperature 27 °C, ^1H decoupled. [b] Unresolved multiplet. [c] $CDCl_3$. [d] $CDCl_2CDCl_2$.

carbene, while reaction with $OsXH(CO)(PPh_3)_3$ (X = F, Br, SCN) produces only the previously described $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ [6].

Only two other dichlorocarbene complexes have been reported. $Fe(=CCl_2)(TPP)$ is formed on reaction of Fe(TPP) with CCl_4 in the presence of an excess of reducing agent such as iron powder [7] and $[CpFe(CO)_2(=CCl_2)]BCl_4$ is formed when $CpFe(CO)_2(CF_3)$ is treated with BCl_3 [8]. The porphyrin derivative has been reported to undergo reaction with primary amines to yield coordinated isocyanide [9] and the cyclopentadienyl complex hydrolyses rapidly to give $[CpFe(CO)_3]^+$ [8].

Synthesis of mixed chalcocarbonyl complexes

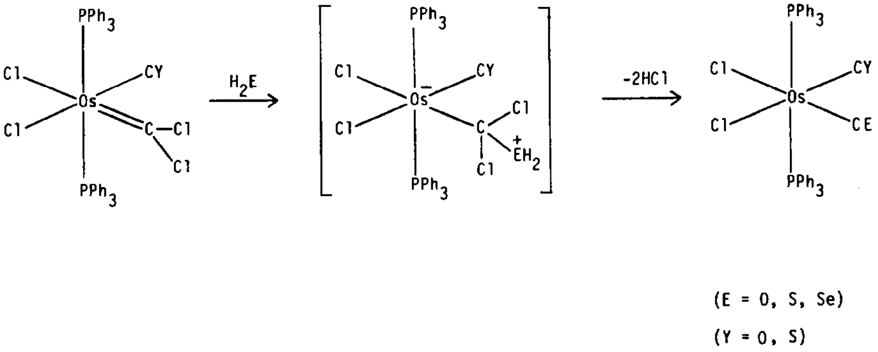
The complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ is a versatile synthetic intermediate. The dichlorocarbene ligand is readily attacked by nucleophiles and the chloro substituents are easily displaced. The reactivity of the thiocarbonyl analogue $OsCl_2(=CCl_2)(CS)(PPh_3)_2$ is very similar except that the thiocarbonyl ligand appears to compete successfully with the dichlorocarbene ligand for some nucleophiles.

Reactions with the dihydrogen chalcogenides H_2E (E = O, S, Se, Te). Heating toluene solutions of the dichlorocarbene complexes $OsCl_2(=CCl_2)(CY)(PPh_3)_2$ (Y = O, S) saturated with either water, dihydrogen sulfide or dihydrogen selenide forms the corresponding chalcocarbonyl complexes $OsCl_2(CE)(CY)(PPh_3)_2$ (E = O, S, Se). The reactions probably proceed via attack at C(carbene) by the chalcogen-containing nucleophile (Scheme 1).

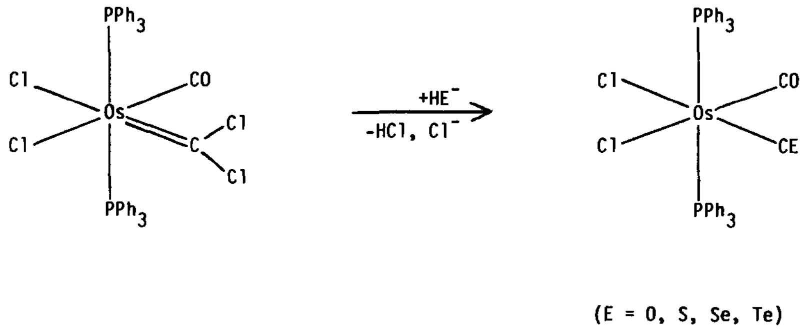
Compounds similar in nature to the proposed intermediate have been reported [10].

In contrast with these results, no detectable quantities of tellurocarbonyl products were formed on reaction with H_2Te. Decomposition of the thermodynamically unstable H_2Te to its constituent elements was a major problem, especially in the reactions that were investigated at higher temperatures.

Reactions with the sodium hydrogen chalcogenides NaHE (E = O, S, Se, Te). The dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ was also found to react with the sodium hydrogen chalcogenides NaHE (E = O, S, Se, Te) to form the stable, crystalline, chalcocarbonyl complexes $OsCl_2(CO)(CE)(PPh_3)_2$. In addition to being a more convenient, high yield route to these complexes, the reaction with HTe^- was



Scheme 1. Possible mechanism for the reaction of $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ with the dihydrogen chalcogenides H_2E.



Scheme 2. Reaction of $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ with the sodium hydrogen chalcogenides NaHE.

successful in producing the first reported tellurocarbonyl complex, $OsCl_2(CO)(CTe)(PPh_3)_2$ (Scheme 2). The yield of this complex after chromatography was only 40–50% and this low yield may be associated with the difficulty in preparing pure NaHTe [11]. The complex (m.p. 221–223° C) is very stable and is not obviously affected by exposure to air, moisture or light.

ν(CTe) appears in the IR spectrum at 1046 cm^{-1} and the appearance of two ν(OsCl) absorptions in the far IR spectrum indicates *cis*-chloride ligands. The tellurocarbonyl formulation has been confirmed by an X-ray crystal structure determination (vide infra).

The chalcocarbonyl complexes $OsCl_2(CO)(CE)(PPh_3)_2$ (E = S, Se, Te) all display large downfield shifts for the ^{13}C resonances of the CE ligands (258.7 to 297.7 ppm, see Table 2). Low-field resonances have been reported for other terminal thiocarbonyl and selenocarbonyl complexes [12]. Examination of the data in Table 2 reveals that chalcocarbonyl carbon resonances shift to lower field in a regular manner as E changes from S to Se to Te but that the carbonyl resonances remain remarkably similar. Downfield shifts of CE on going from CO to CSe have been observed and commented upon previously [12].

One other complete series of homologous chalcocarbonyl complexes ($[Mo(CO)_2(CE)\{HB(3,5\text{-}Me_2-C_3HN_2)_3\}]^-$ (E = O, S, Se, Te) [13] has been reported since our initial communication. The heavier congeners of this series of anionic complexes were synthesised by reaction of the chloromethylidyne complex $Mo(CO)_2(\equiv CCl)\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}$ with the corresponding dilithium chalcogenides, Li_2E (E = S, Se, Te). No details of the structures of the complexes have, as yet, been reported.

In contrast to the carbonyl analogue, the thiocarbonyl dichlorocarbene complex, $OsCl_2(=CCl_2)(CS)(PPh_3)_2$, does not react with the nucleophiles HE^- (E = S, Se, Te) to form the corresponding chalcocarbonyl complexes. Instead, intractable products containing no thiocarbonyl ligands are formed, suggesting that the CS ligand may compete successfully with coordinated $=CCl_2$ for HE^- [6].

Formation of a cationic tellurocarbonyl complex

A solution of $OsCl_2(CO)(CTe)(PPh_3)_2$ and silver perchlorate in dichloromethane/acetonitrile, when heated under reflux, deposits AgCl over a period of ca. 15 min. The resulting soluble, cationic complex $[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]$-

ClO_4 can easily be removed from the precipitated silver chloride by filtration. The methyl group of acetonitrile ligand is observed in the ^1H NMR as a triplet centered at δ, 1.81 ppm ($^5J(HP)$ 1.1 Hz). $\nu(CO)$ in this cationic complex appears in the IR spectrum at 2033 cm^{-1} (7 cm^{-1} lower than in the original neutral complex) while $\nu(CTe)$ increases marginally from 1046 to 1048 cm^{-1}. If the value of $\nu(CO)$ can be taken as an indication of the electron richness of the metal centre, then little change occurs on replacement of Cl^- with $NCCH_3$. This may well indicate that the CTe ligand (like CS [2,14]) can display very different donor/acceptor ratios depending on the bonding environment.

The acetonitrile ligand in $[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]ClO_4$ is easily displaced by added chloride and $OsCl_2(CO)(CTe)(PPh_3)_2$ returned quantitatively. Thus, samples of crude $OsCl_2(CO)(CTe)(PPh_3)_2$ (which sometimes contain small amounts of $OsCl_2(CO)_2(PPh_3)_2$ as contaminant) can be successfully purified via conversion to $[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]ClO_4$. $OsCl_2(CO)_2(PPh_3)_2$, which does not react with $AgClO_4$, can be separated from the cationic tellurocarbonyl complex by fractional crystallization (see Ref. 1). Further reactions of $[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]ClO_4$ have been explored and preliminary results have been reported elsewhere [15].

Description and discussion of the crystal structures of $OsCl_2(CO)(CE)(PPh_3)_2$ (E = S, Se, Te)

Crystals of the three complexes each contain one monomer per asymmetric unit. In addition, the CS and CSe complexes crystallize with one half of a molecule of dichloromethane per complex molecule. In each case the osmium atoms are in octahedral coordination geometries with the two triphenylphosphine ligands mutually *trans* and the carbonyl and chalcocarbonyl ligands mutually *cis*. The overall structure of the thiocarbonyl complex is representative of the other two and is depicted in Fig. 1. A common atomic labelling scheme is used for all three complexes to facilitate comparisons. Important bond lengths and angles are given in Table 3. Some features of the individual structures and comparisons between them are now discussed.

$OsCl_2(CO)(CTe)(PPh_3)_2$

The CTe ligand is bonded to osmium through carbon and the Os–C–Te linkage is essentially linear. The C–Te distance of 1.923(12) Å appears to be the shortest C–Te distance so far reported and is consistent with there being considerable multiple character to the C–Te bond. Single C–Te bonds are usually close to 2.16 Å [16]. The Os–CTe distance of 1.813(12) Å is very short. It is shorter than the Os–CO distance (1.856(11) Å) in the same molecule and is only slighter longer than the Os≡C(carbyne) distance of 1.78(2) Å in Os(≡C-*p*-tolyl)Cl(CO)$(PPh_3)_2$ [17].

Inspection of the osmium-chlorine distances reveals that Os–Cl(2) is 0.060 Å larger than Os–Cl(1) indicating that the CTe ligand has a considerably larger *trans*-influence than CO in this molecule. Consistent with this observation is the fact that one chloride can be easily removed as AgCl by addition of Ag^+ (see earlier). The resulting cation most likely has coordinated acetonitrile *trans* to the CTe ligand.

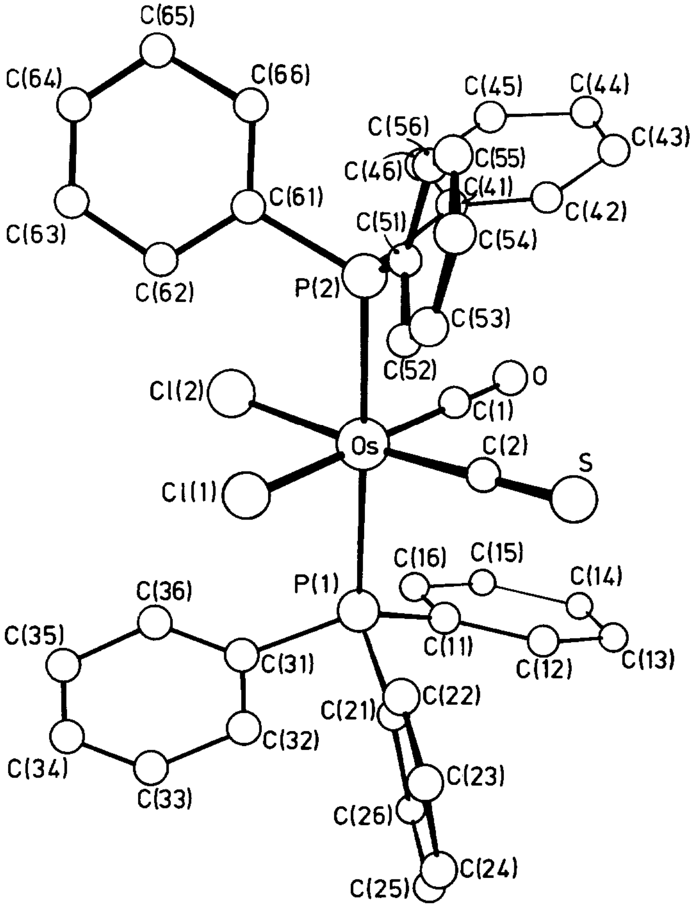


Fig. 1. The molecular geometry and atomic numbering for $OsCl_2(CO)(CS)(PPh_3)_2$.

$OsCl_2(CO)(CSe)(PPh_3)_2$

Structural studies of only three selenocarbonyl complexes have been previously reported [18]. Features of coordinated CSe common to all three examples are: linear M–C–Se linkages, short M–CSe distances and a lengthening of the M–X bonds *trans* to the CSe ligands. These same features are also observed in the structure of $OsCl_2(CO)(CSe)(PPh_3)_2$. The Os–CSe distance of 1.913(5) Å is short and practically the same as the Os–CO distance in the same molecule. The Os–Cl distances indicate that the *trans*-influence of the CSe ligand is large compared with CO, although the difference in bond lengths is not as pronounced as it is in the tellurocarbonyl analogue. As might be expected, the chloride *trans* to CSe is sufficiently labile that displacement from the osmium co-ordination sphere readily occurs; for example in acetonitrile containing perchloric acid the cation $[OsCl(NCCH_3)(CO)(CSe)(PPh_3)_2]^+$ is formed [19].

$OsCl_2(CO)(CS)(PPh_3)_2$

The Os–C–S linkage in this complex is linear and the Os–CS distance (1.883(11) Å) is shorter than the Os–CO distance (1.98(2) Å) in the same molecule. All other reported structures of mixed carbonyl-thiocarbonyl complexes also display this feature [20]. The C–S distance (1.481(12) Å is at the short end of the range of C–S distances (1.43–1.78 Å) so far reported for other terminal thiocarbonyl complexes. The length of the Os–Cl bond *trans* to the thiocarbonyl ligand is greater than that *trans* to the carbonyl ligand, illustrating the larger *trans*-influence of the thiocarbonyl ligand. The difference in Os–Cl bond lengths is similar to that observed for the selenocarbonyl complex.

Comparison of the three complexes indicates that the trend of increasing *trans*-influence follows the order CO < CS $\leqslant$ CSe < CTe. It is noteworthy that while the Os–Cl(2) distances increase as the chalcogen changes from S through Se to Te, the Os–Cl(1) distances decrease.

The Os–CE bond lengths are all numerically smaller than the Os–CO distances in the same molecules, although only in the thiocarbonyl complex is this difference statistically significant. The Os–CO distances follow a regular trend, decreasing in value as the chalcogen changes from S through Se to Te, with the distance in the tellurocarbonyl complex being significantly shorter than that in the thiocarbonyl analogue. The Os–CE distances do not follow a smooth trend, although the Os–CTe distance is significantly shorter than both the Os–CS and Os–CSe distances.

The Os–P distances in all three complexes do not vary significantly amongst themselves and are at the longer end of the range of Os–PPh_3 distances previously reported for other *trans*-triphenylphosphine complexes of osmium [21].

One unusual feature of the three structures is that in each case the carbonyl ligand is partially sandwiched between two triphenylphosphine phenyl rings

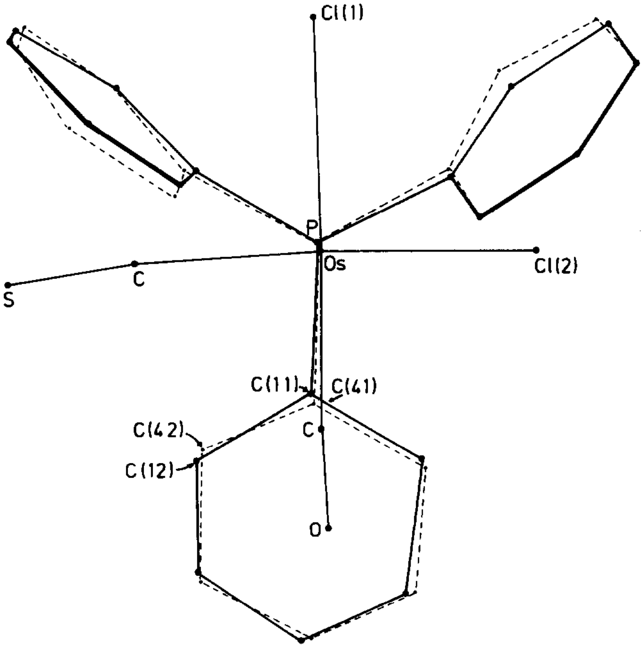


Fig. 2. View down the P(1)–Os–P(2) axis of $OsCl_2(CO)(CS)(PPh_3)_2$.

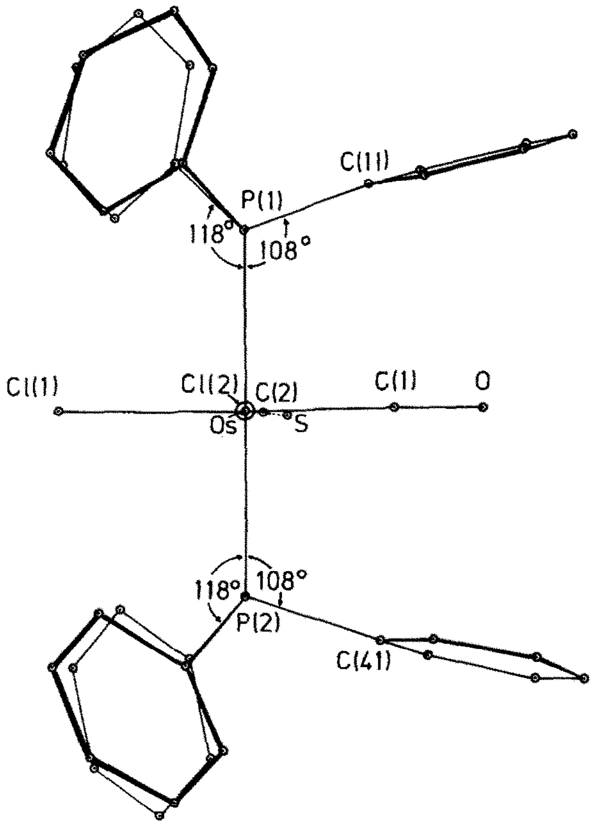


Fig. 3. View down the Cl(2)–Os–CS axis of $OsCl_2(CO)(CS)(PPh_3)_2$.

(C(11)–C(16) and C(41)–C(46)). To illustrate this, views down the P(1)–Os–P(2) and the Cl(2)–Os–CS axes of the CS complex are depicted in Figs. 2 and 3.

The angle between the two planes containing these sandwiching phenyl rings is 40° for the CTe complex and only 26° for the CS and CSe complexes. This compares with an expected angle of ca. 50° for a linear P–Os–P arrangement and Os–P–C angles set at the normally observed value of ca. 115°. These smaller than expected angles are the result of reduced Os–P–C(11) and Os–P–C(41) angles (see Table 3) and also a tilting of the planes of the sandwiching phenyl groups by ca. 6° towards the carbonyl groups. These distortions are in the direction that one would expect if there were an attractive interaction between the sandwiching phenyl rings and the carbonyl ligands. At the moment, any explanation of the origins of these distortions must remain speculative.

Experimental

General

Solvents were degassed either by the freeze-thaw method using nitrogen (< 6 ppm oxygen) or by passing a stream of nitrogen through the boiling solvent for 10 min prior to use. Reactions involving heating under reflux were performed under

Table 3

Bond lengths (Å) and angles (°)

Atom	CS	CSe	CTe
Os–Cl(1)	2.441(3)	2.438(3)	2.413(3)
Os–Cl(2)	2.465(4)	2.466(4)	2.473(3)
Os–P(1)	2.432(3)	2.427(4)	2.429(3)
Os–P(2)	2.431(3)	2.443(3)	2.422(3)
Os–C(1)	1.98(2)	1.920(20)	1.856(11)
Os–C(2)	1.883(11)	1.913(15)	1.813(12)
X–C(2)	1.481(12)	1.609(15)	1.923(12)
O–C(1)	1.18(2)	1.23(2)	1.19(2)
P(1)–C(11)	1.791(11)	1.819(13)	1.819(11)
P(1)–C(21)	1.824(11)	1.834(14)	1.835(11)
P(1)–C(31)	1.834(11)	1.823(14)	1.825(11)
P(2)–C(41)	1.829(11)	1.801(14)	1.829(10)
P(2)–C(51)	1.833(11)	1.835(14)	1.835(11)
P(2)–C(61)	1.817(11)	1.833(13)	1.842(11)
Cl(1)–Os–Cl(2)	91.5(1)	91.0(1)	89.8(1)
Cl(1)–Os–P(1)	88.9(1)	89.1(1)	87.0(1)
Cl(1)–Os–P(2)	90.5(1)	90.8(1)	91.2(1)
Cl(1)–Os–C(1)	176.4(4)	175.3(5)	171.1(4)
Cl(1)–Os–C(2)	96.9(3)	96.8(4)	99.1(4)
Cl(2)–Os–P(1)	89.2(1)	89.6(1)	90.5(1)
Cl(2)–Os–P(2)	87.8(1)	87.9(1)	88.0(1)
Cl(2)–Os–C(1)	85.1(4)	84.4(5)	81.4(4)
Cl(2)–Os–C(2)	171.6(3)	172.1(4)	171.0(4)
P(1)–Os–P(2)	176.9(1)	177.5(1)	177.6(1)
P(1)–Os–C(1)	89.7(4)	89.9(4)	91.7(4)
P(1)–Os–C(2)	91.0(3)	91.7(4)	91.5(4)
P(2)–Os–C(1)	90.7(4)	90.0(4)	89.9(4)
P(2)–Os–C(2)	92.1(3)	90.8(4)	90.3(4)
C(1)–Os–C(2)	86.5(2)	87.8(6)	89.7(6)
Os–P(1)–C(11)	108.3(4)	108.3(4)	111.0(4)
Os–P(1)–C(21)	117.6(4)	117.3(5)	114.2(4)
Os–P(1)–C(31)	118.8(4)	119.6(5)	117.8(4)
Os–P(2)–C(41)	108.0(4)	108.0(4)	108.6(4)
Os–P(2)–C(51)	116.1(4)	116.3(4)	117.1(4)
Os–P(2)–C(61)	118.9(4)	118.5(4)	119.8(4)
Os–C(1)–O	178.4(12)	179.1(13)	179.1(1)
Os–C(2)–X	176.3(8)	175.3(9)	175.3(7)

nitrogen. Characterisation of new compounds was achieved by means of elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy. Analytical data were obtained from the Microanalytical Laboratory, University of Otago, and the services of Professor A.D. Campbell are gratefully acknowledged. IR spectra (4000–200 cm^{-1}) were measured on a Perkin–Elmer 597 spectrometer as nujol mulls or as dichloromethane solutions between KBr plates. ^{1}H NMR spectra were recorded on a Varian Associates T60 spectrometer and ^{13}C NMR spectra were recorded on a JEOL JNM-FX60 Fourier transform spectrometer using tetramethylsilane (δ 0 ppm) as internal calibrant in both cases. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. OsClH(CO)(PPh$_3$)$_3$ [22], OsCl$_2$(CS)(PPh$_3$)$_3$ [23] and OsCl$_2$(=CCl$_2$)(CO)(PPh$_3$)$_2$ [1] were prepared by published methods.

$OsCl_2(CO)_2(PPh_3)_2$

Method (a). $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.500 g) was added to a solution comprised of benzene (300 ml), methanol (50 ml) and aqueous sodium hydroxide solution (4 mol l^{-1}, 20 ml) and stirred for 6 h at room temperature. The solvent volume was then reduced on a rotary evaporator to effect crystallization of the product. The product was collected, washed well with water and ethanol, and recrystallized from dichlormethane/ethanol to yield $OsCl_2(CO)_2(PPh_3)_2$ (0.405 g, 88%). The product was identified by comparison of its spectral properties with those of an authentic sample [24].

Method (b). $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.500 g) was heated under reflux for 5 min in xylene (200 ml) to which water (2 ml) had been added. Most of the xylene was removed under reduced pressure, and ethanol was added to complete the crystallization of the product. This was filtered off, and recrystallized from dichloromethane/ethanol to yield $OsCl_2(CO)_2(PPh_3)_2$ (0.424 g, 92%). The product was identified as above.

$OsCl_2(CO)(CS)(PPh_3)_2$

Method (a). To $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.500 g) in a deoxygenated solution of methanol (25 ml) and benzene (175 ml) was added a solution of NaHS in ethanol [25] (2.2 ml). The solution was stirred for 6 h at 25 ° C. The solvent volume was lowered under reduced pressure and crystallization effected by the addition of ethanol. The product was recrystallized from dichloromethane/ethanol to give $OsCl_2(CO)(CS)(PPh_3)_2$ (0.411 g, 86%). The product was identified by comparison of its spectral properties with those of an authentic sample [26].

Method (b). $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.500 g) was dissolved in toluene (150 ml) and H_2S slowly bubbled through the solution while it was heated under reflux for 15 min. The solution was cooled and the toluene removed under reduced pressure. The product was recrystallized from dichloromethane/ethanol to give $OsCl_2(CO)(CS)(PPh_3)_2$ (0.393 g, 82%). The product was identified as above.

$OsCl_2(CO)(CSe)(PPh_3)_2$

Method (a). To $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.75 g) in a rigorously deoxygenated solution of methanol (150 ml) and dichloromethane (75 ml), was added NaSeH solution in ethanol [25] (3.2 ml). The suspension was stirred for 3 h, most of the dichloromethane removed under reduced pressure, and the product collected. It was then dissolved in dichloromethane, and the solution filtered through a Celite pad and then purified by chromatography on silica gel (25 × 3 cm column) with dichloromethane as eluant. The pale yellow band was collected, ethanol (ca. 30 ml) was added, and the dichloromethane removed under reduced pressure. The resulting pale yellow crystals of the dichloromethane solvate $OsCl_2(CO)(CSe)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.5}$ (0.72 g, 91%) were collected and washed with ethanol and n-hexane. M.p. 271–274 ° C. Anal. Found: C, 48.36; H, 3.46. $C_{38}H_{30}Cl_2OOsP_2Se \cdot (CH_2Cl_2)_{0.5}$ calc: C, 48.82; H, 3.30%.

Method (b). $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.50 g) was heated under reflux in toluene (100 ml) for 15 min while H_2Se was bubbled through the solution. After cooling, the mixture was filtered through Celite to remove traces of elemental selenium and the toluene was removed under reduced pressure. The product was recrystallized twice from dichloromethane/ethanol to yield $OsCl_2(CO)(CSe)(PPh_3)_2$

(0.47 g, 89%). The product was identified by comparison of its spectral properties with those of an authentic sample.

$OsCl_2(CO)(CTe)(PPh_3)_2$

A slightly modified version [11] of the method we previously reported [1,27] has been found to give higher yields of product.

An ethanolic solution of NaTeH was prepared as follows. Te (0.20 g) and $NaBH_4$ (0.27 g) were dried in vacuo and ethanol (20 ml) added under nitrogen. The mixture was heated under reflux until all the tellurium had dissolved and the solution was a pale mauve colour (about 45 min). The solution was cooled to −78 °C and then allowed to warm slowly to room temperature. The flask was sealed and after standing for ca. 16 h a clear solution with a small amount of black sediment was obtained. The concentration of NaTeH was ca. 7.87×10^{-2} mol l^{-1}. Freshly distilled, deoxygenated dichloromethane (5 ml) was placed in a Schlenk tube and frozen using liquid nitrogen. Dry $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (0.75 g) was then added, and after warming to room temperature the resulting solution was cooled to −78 °C.

The NaTeH solution (−78 °C, 11 ml, 1.05 eq.) was transferred to the reaction vessel by means of a cannula. The vessel was sealed, allowed to warm to −30 °C, and then stirred at this temperature for 12 h. n-Hexane (50 ml) was added and then the solvents were removed in vacuo. The dark brown residue was taken up in a minimum of dichloromethane and the solution was passed through a silica-gel column (3 × 1.5 cm) to remove insoluble salts and the tellurium. The eluate yielded an orange solid, which was recrystallised from dichloromethane/ethanol. The product was chromatographed on a silica-gel column (3 × 5 cm) using dichloromethane as the eluant. The orange band was collected and crystallised as above to give orange crystals (0.41 g, 51%). (This yield was the best obtained, but yields of 40–50% were routinely recorded). M.p. 221–223 °C. Anal. Found: C, 47.61; H, 3.39. $C_{38}H_{30}Cl_2OOsP_2Te$ calc: C, 47.88; H, 3.17%.

$[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]ClO_4$

$OsCl_2(CO)(CTe)(PPh_3)_2$ (0.300 g) and $AgClO_4$ (0.070 g) were heated under reflux in a solution of dichloromethane (20 ml) and acetonitrile (20 ml) for 15 min. The solution was allowed to cool and then filtered through a Celite pad. Ethanol (ca. 30 ml) was added and the solvent volume slowly lowered under reduced pressure to effect crystallization. The product was collected and recrystallized twice from dichloromethane/ethanol to give pale orange needles (0.250 g, 76%). M.p. 239–241 °C. Anal. Found: C, 45.51; H, 3.50. $C_{40}H_{33}Cl_2NO_5OsP_2Te$ calc: C, 45.40; H, 3.14%.

$OsCl_2(=CCl_2)(CS)(PPh_3)_2$

$OsCl_2(CS)(PPh_3)_3$ (2.00 g), $Hg(CCl_3)_2$ (4.00 g) and PPh_3 (1.00 g) were heated under reflux in toluene (500 ml) for 15 min. The mixture was cooled in an ice-bath for 1 h then filtered. The solvent was removed from the filtrate under reduced pressure. The resulting red oil was dissolved in a minimum of benzene. Portions of ethanol were added successively as the solvent was removed under reduced pressure. The initially formed white crystals were discarded after filtration, and further reduction of solvent volume yielded crystals of the above product. Three successive recrystallizations of the product from dichloromethane/ethanol produced red crystals of $OsCl_2(=CCl_2)(CS)(PPh_3)_2$ (1.20 g, 72%). M.p. 262–265 °C. Anal. Found: C, 47.79; H, 3.02. $C_{38}H_{30}Cl_4SP_2Os$ calc: C, 50.01; H, 3.31%. (See text for discussion of analytical figures.)

$OsCl_2(CS)_2(PPh_3)_2$

$OsCl_2(=CCl_2)(CS)(PPh_3)_2$ (0.200 g) was dissolved in toluene (20 ml) and the mixture was heated under reflux for 10 min while H_2S was bubbled through the solution. After cooling the solvent was removed under reduced pressure. The resulting oil was dissolved in dichloromethane and ethanol added. Solvent removal under reduced pressure yielded yellow crystals of the product (0.140 g, 73%). The product was identified by comparison of its spectral properties with those of an authentic sample [28].

$OsCl_2(CS)(CSe)(PPh_3)_2$

$OsCl_2(=CCl_2)(CS)(PPh_3)_2$ (0.200 g) was dissolved in toluene (20 ml) and the mixture heated under reflux for 15 min while H_2Se was bubbled through the

Table 4

Summary of crystal data and intensity data collections for $OsCl_2(CO)(CS)(PPh_3)_2 \cdot 0.5\ CH_2Cl_2$, $OsCl_2(CO)(CSe)(PPh_3)_2 \cdot 0.5\ CH_2Cl_2$ and $OsCl_2(CO)(CTe)(PPh_3)_2$

	CS	CSe	CTe
Molecular weight	900.3	947.2	953.3
Colour and habit	yellow needles	yellow needles	orange tablets
a (Å)	12.837(1)	12.846(3)	14.211(3)
b (Å)	14.302(1)	14.341(3)	18.084(4)
c (Å)	10.452(1)	10.462(4)	14.857(3)
α (°)	92.45(1)	92.26(2)	
β (°)	97.42(1)	97.67(2)	113.29(2)
γ (°)	99.86(1)	99.76(1)	
V (Å^3)	1871.5	1878.5	3507.0
ρ_c (g cm^{-3})	1.60	1.67	1.81
ρ_o (aq. $KI/ZnBr_2$)	1.58		1.81
Z	2	2	4
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Crystal size (mm × 10^2)	6×5×20	18×12×6	9×20×20
Diffractometer	Hilger Watts	Nonius	Nonius
X-radiation	Cu	Mo	Mo
Filter	Ni	Zr	Zr
μ (cm^{-1})	93.39	49.06	49.85
Mosaic spread (degrees)	0.19	0.23	0.15
T (K)	291	292	291
θ_{max} (°)	57	22	25
Maximum and minimum	0.661	0.746	0.644
transmission coefficients	0.461	0.529	0.347
Observed data, $I > 3\sigma(I)$	3883	3596	3106
Final R and R_w	0.063	0.051	0.044
	0.071	0.054	0.054

solution. After cooling the mixture was filtered through Celite to remove traces of elemental selenium. The solvent was removed under reduced pressure and the resulting oil dissolved in dichloromethane. Three successive recrystallizations from

Table 5

Atom positions for $OsCl_2(CO)(CS)(PPh_3)_2 \cdot 0.5\ CH_2Cl_2$

Atom	*x*	*y*	*z*
Os	0.35391(5)	0.24394(4)	0.35732(6)
S	0.4352(4)	0.4768(3)	0.3238(6)
Cl(1)	0.2618(3)	0.1990(3)	0.1385(3)
Cl(2)	0.3109(3)	0.0792(3)	0.4206(4)
P(1)	0.1864(3)	0.2738(2)	0.4212(3)
P(2)	0.5179(3)	0.2050(2)	0.2941(3)
O	0.4665(8)	0.2916(8)	0.6455(11)
C(1)	0.4234(11)	0.2730(10)	0.5378(23)
C(2)	0.3973(10)	0.3742(11)	0.3343(13)
Cl(S1)	0.0178(6)	0.7563(6)	0.0901(9)
Cl(S2)	0.1326(6)	0.9385(6)	0.0403(10)
C(S)	0.0338	0.8417	−0.0214
C(11)	0.2107(10)	0.3185(9)	0.5874(13)
C(12)	0.2472(11)	0.4153(10)	0.6230(15)
C(13)	0.2765(12)	0.4489(11)	0.7569(17)
C(14)	0.2718(12)	0.3820(11)	0.8469(16)
C(15)	0.2385(12)	0.2880(11)	0.8154(16)
C(16)	0.2089(12)	0.2456(11)	0.6853(17)
C(21)	0.1230(10)	0.3633(9)	0.3376(14)
C(22)	0.1540(12)	0.3949(11)	0.2206(16)
C(23)	0.1013(13)	0.4622(12)	0.1518(17)
C(24)	0.0169(13)	0.4934(12)	0.2050(17)
C(25)	−0.0136(13)	0.4620(11)	0.3161(18)
C(26)	0.0400(13)	0.3972(11)	0.3848(16)
C(31)	0.0738(10)	0.1743(9)	0.4122(13)
C(32)	−0.0036(11)	0.1778(10)	0.4935(15)
C(33)	−0.0959(12)	0.1035(11)	0.4759(17)
C(34)	−0.1066(12)	0.0336(11)	0.3872(16)
C(35)	−0.0310(12)	0.0286(11)	0.3074(16)
C(36)	0.0630(11)	0.1004(10)	0.3220(14)
C(41)	0.6220(10)	0.2328(9)	0.4341(13)
C(42)	0.6836(12)	0.3213(11)	0.4540(16)
C(43)	0.7550(13)	0.3426(12)	0.5705(18)
C(44)	0.7618(11)	0.2796(11)	0.6599(15)
C(45)	0.7014(12)	0.1922(11)	0.6388(16)
C(46)	0.6308(11)	0.1659(10)	0.5274(15)
C(51)	0.5737(10)	0.2747(9)	0.1678(13)
C(52)	0.5100(10)	0.3202(10)	0.0834(14)
C(53)	0.5523(12)	0.3673(11)	−0.0176(16)
C(54)	0.6554(13)	0.3654(11)	−0.0358(17)
C(55)	0.7205(12)	0.3209(11)	0.0432(16)
C(56)	0.6805(12)	0.2730(10)	0.1487(15)
C(61)	0.5197(10)	0.0832(9)	0.2391(13)
C(62)	0.4264(11)	0.0302(10)	0.1658(15)
C(63)	0.4320(13)	−0.0633(11)	0.1188(16)
C(64)	0.5232(13)	−0.0978(12)	0.1402(17)
C(65)	0.6150(15)	−0.0476(14)	0.2070(20)
C(66)	0.6152(13)	0.0474(12)	0.2567(17)

dichloromethane/ethanol yielded golden-brown crystals of the product (0.125 g, 62%). M.p. 267–270 ° C. Anal. Found: C, 49.25; H, 3.60. $C_{38}H_{30}Cl_2SSeP_2Os$ calc: C, 49.58; H, 3.29%.

Table 6

Atom positions for $OsCl_2(CO)(CSe)(PPh_3)_2 \cdot 0.5\ CH_2Cl_2$

Atom	*x*	*y*	*z*
Os	0.35018(3)	0.24217(3)	0.35603(5)
Se	0.4373(1)	0.4851(1)	0.3236(1)
Cl(1)	0.2586(2)	0.1983(2)	0.1371(3)
Cl(2)	0.3061(2)	0.772(2)	0.4167(3)
P(1)	0.1836(2)	0.2732(2)	0.4192(3)
P(2)	0.5156(2)	0.2038(2)	0.2946(3)
O	0.4603(7)	0.2836(6)	0.6452(10)
C(1)	0.4170(12)	0.2666(11)	0.5323(18)
C(2)	0.3965(10)	0.3734(10)	0.3316(12)
Cl(S1)	0.0210(14)	0.7589(13)	0.0809(17)
Cl(S2)	0.1283(15)	0.9334(13)	0.0493(18)
C(S)	0.036(4)	0.836(4)	0.006(5)
C(11)	0.2088(9)	0.3177(8)	0.5877(11)
C(12)	0.2472(11)	0.4104(9)	0.6232(13)
C(13)	0.2738(13)	0.4467(12)	0.7501(16)
C(14)	0.2698(13)	0.3834(12)	0.8436(16)
C(15)	0.2355(13)	0.2870(12)	0.8125(16)
C(16)	0.2064(12)	0.2565(10)	0.6836(14)
C(21)	0.1210(10)	0.3636(9)	0.3347(12)
C(22)	0.1527(12)	0.3955(10)	0.2203(14)
C(23)	0.0955(15)	0.4623(13)	0.1545(18)
C(24)	0.0172(14)	0.4976(12)	0.2039(17)
C(25)	−0.0115(14)	0.4639(13)	0.3145(17)
C(26)	0.0373(12)	0.3973(11)	0.3826(15)
C(31)	0.0700(10)	0.1765(9)	0.4097(13)
C(32)	−0.0065(13)	0.1768(12)	0.4920(16)
C(33)	−0.0965(15)	0.1058(13)	0.4813(18)
C(34)	−0.1103(15)	0.0357(13)	0.3869(18)
C(35)	−0.0321(13)	0.0298(12)	0.3053(17)
C(36)	0.0560(12)	0.1026(11)	0.3162(15)
C(41)	0.6175(10)	0.2307(9)	0.4333(12)
C(42)	0.6823(11)	0.3192(10)	0.4549(13)
C(43)	0.7530(13)	0.3435(12)	0.5684(16)
C(44)	0.7606(12)	0.2778(11)	0.6608(15)
C(45)	0.6979(12)	0.1911(11)	0.6416(15)
C(46)	0.6263(12)	0.1655(11)	0.5304(14)
C(51)	0.5718(10)	0.2725(9)	0.1678(12)
C(52)	0.6748(12)	0.2705(11)	0.1517(15)
C(53)	0.7175(14)	0.3201(12)	0.0512(17)
C(54)	0.6556(13)	0.3659(12)	−0.0333(16)
C(55)	0.5514(12)	0.3671(10)	−0.0136(14)
C(56)	0.5091(11)	0.3204(10)	0.0833(14)
C(61)	0.5176(10)	0.0813(9)	0.2394(12)
C(62)	0.4272(12)	0.0303(10)	0.1624(14)
C(63)	0.4315(13)	−0.0603(12)	0.1147(16)
C(64)	0.5203(14)	−0.0990(12)	0.1384(17)
C(65)	0.6082(17)	−0.0506(15)	0.2114(21)
C(66)	0.6075(15)	0.0449(13)	0.2628(18)

X-Ray Experimental

Suitable crystals of the three compounds were mounted on fine glass fibres and subjected to initial photography to establish crystal systems, space groups and approximate cell dimensions. They were then transferred to either a Hilger Watts

Table 7

Atom positions for $OsCl_2(CO)(CTe)(PPh_3)_2$

Atom	*x*	*y*	*z*
Os	0.12640(3)	0.30518(3)	0.30742(3)
Te	0.27892(8)	0.14289(7)	0.44349(8)
Cl(1)	0.0019(2)	0.2466(2)	0.1638(2)
Cl(2)	0.0465(3)	0.4266(2)	0.2467(3)
P(1)	0.2336(2)	0.3180(2)	0.2152(2)
P(2)	0.0134(2)	0.2935(2)	0.3932(2)
O	0.2689(7)	0.4018(7)	0.4729(7)
C(1)	0.2140(9)	0.3640(7)	0.4081(8)
C(2)	0.1965(9)	0.2238(7)	0.3698(8)
C(11)	0.3443(9)	0.3760(7)	0.2803(9)
C(12)	0.4157(10)	0.3494(8)	0.3693(10)
C(13)	0.4994(11)	0.3937(9)	0.4239(11)
C(14)	0.5097(11)	0.4598(9)	0.3943(12)
C(15)	0.4458(11)	0.4869(9)	0.3112(11)
C(16)	0.3624(10)	0.4447(8)	0.2527(10)
C(21)	0.2909(9)	0.2311(7)	0.1978(9)
C(22)	0.2312(9)	0.1679(8)	0.1773(9)
C(23)	0.2727(10)	0.0998(8)	0.1541(10)
C(24)	0.3668(10)	0.1023(8)	0.1528(10)
C(25)	0.4256(10)	0.1619(8)	0.1761(11)
C(26)	0.3873(10)	0.2343(8)	0.1990(10)
C(31)	0.1747(9)	0.3545(7)	0.0908(9)
C(32)	0.1795(10)	0.3102(9)	0.0166(10)
C(33)	0.1355(12)	0.3407(10)	−0.0856(12)
C(34)	0.1004(11)	0.4085(9)	−0.0992(11)
C(35)	0.0961(10)	0.4555(9)	−0.0224(11)
C(36)	0.1366(9)	0.4254(8)	0.0719(9)
C(41)	0.0764(8)	0.3345(6)	0.5150(8)
C(42)	0.1525(9)	0.2945(7)	0.5925(9)
C(43)	0.2065(10)	0.3291(8)	0.6772(10)
C(44)	0.1920(10)	0.4020(8)	0.6964(10)
C(45)	0.1187(10)	0.4417(8)	0.6212(10)
C(46)	0.0605(10)	0.4083(8)	0.5276(10)
C(51)	−0.0194(8)	0.1995(7)	0.4173(8)
C(52)	−0.0234(9)	0.1419(7)	0.3518(9)
C(53)	−0.0622(11)	0.0752(9)	0.3671(11)
C(54)	−0.0883(10)	0.0603(9)	0.4414(11)
C(55)	−0.0828(11)	0.1199(10)	0.5094(12)
C(56)	−0.0461(11)	0.1863(9)	0.4972(11)
C(61)	−0.1153(8)	0.3351(7)	0.3408(8)
C(62)	−0.1632(9)	0.3534(7)	0.2426(9)
C(63)	−0.2662(10)	0.3782(8)	0.2040(10)
C(64)	−0.3157(11)	0.3872(9)	0.2659(11)
C(65)	−0.2667(11)	0.3704(9)	0.3647(11)
C(66)	−0.1672(10)	0.3462(8)	0.4022(10)

Y290 or a Nonius CAD-4 automatic diffractometer, depending on availability. Accurate unit cell dimensions were determined by least-squares fits to the setting angles of twenty-five high-theta reflections widely dispersed throughout reciprocal space. All relevant crystal information is summarised in Table 4.

Intensity data collections employed the $2\theta/\omega$ scan technique. Crystal alignment and possible decomposition were monitored throughout the data collection by remeasuring three selected standard reflections after every 100 measurements, however no significant variations were recorded. The data were corrected for Lorentz, polarization and absorption effects, and equivalent reflections were averaged together.

Structure determinations and refinements

All structures were solved independently (including the isostructural CS and CSe complexes) using conventional Patterson and heavy-atom electron density maps, and refined by full-matrix least-squares procedures. Atomic scattering factors and dispersion corrections were from standard listings [29]. The function minimised was $\Sigma w(|F_o|-|F_c|)^2$. Residuals quoted in Table 4 are $R=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$ and $R_w=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma|F_o|^2\}^{1/2}$. After initial isotropic refinement, the non-phenyl atoms were assigned anisotropic thermal parameters, and hydrogen atoms were placed in geometrically derived positions.

Final atomic positions are listed in Tables 5, 6 and 7 for the CS, CSe and CTe complexes respectively. Atomic thermal parameters, and tables of observed and calculated structure factor amplitudes are available from the authors.

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