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# THE SYNTHESIS OF NITROSYL-THIOCARBONYL COMPLEXES OF OSMIUM

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## Summary

Two procedures for the conversion of coordinated $CS_2$ into CS ligands are described involving the intermediacy of either $\eta^2$-carbonsulphide-telluride or hydridodithiomethoxycarbonyl complexes. The $CS_2$ ligand in $OsCl(NO)(CS_2)(PPh_3)_2$ is readily methylated to provide cationic dithiomethoxycarbonyl-containing complexes, which upon reduction with sodium hydrotelluride and sodium tetrahydroborate give $OsX(NO)(CS)(PPh_3)_2$ (X = Cl, I) and $OsH_2(CS_2Me)(NO)(PPh_3)_2$, respectively. The latter reacts with electrophilic reagents (HCl, HI, $I_2$) to give $OsX(NO)(CS)(PPh_3)_2$, the halide of which is labile and is easily extracted by silver salts, allowing coordination of neutral ligands and providing the cations $[Os(NO)(CS)(PPh_3)_2L]^+$ (L = CO, $PPh_3$). $OsH_2(CS_2Me)(NO)(PPh_3)_2$ and $OsI(NO)(CS)(PPh_3)_2$ react with an excess of $I_2$ to give the ionic product $[OsI_2(NO)(CS)(PPh_3)_2]^+ I_3^-$.

## Introduction

Complexes containing both NO and CS as strong acceptor ligands are interesting models for ligand–ligand interactions [1]. We have tried to prepare osmium complexes containing both of these ligands using $CS_2$, a common source for thiocarbonyl ligands. However, the desulphurisation of coordinated $CS_2$ by tertiary phosphines is not always as ready a process as the serendipitous discovery [2] of the first transition-metal thiocarbonyl, *trans*-$[RhCl(CS)(PPh_3)_2]$, might suggest. Attempts to introduce the thiocarbonyl ligand into a number of complexes using $CS_2$ as the "CS" source have proved unsuccessful [3]. Thus, the $CS_2$ complex $OsCl(NO)(CS_2)(PPh_3)_2$ (I) [4], is stable towards triphenylphosphine in refluxing xylene (ca. 140°C). We therefore report two alternative methods for achieving the desired ligand modification ($CS_2 \rightarrow CS$), one involving the presumed intermediacy of $\eta^2$-carbonsulphide-telluride complexes, and the other making use of hydridodithiomethoxycarbonyl complexes.

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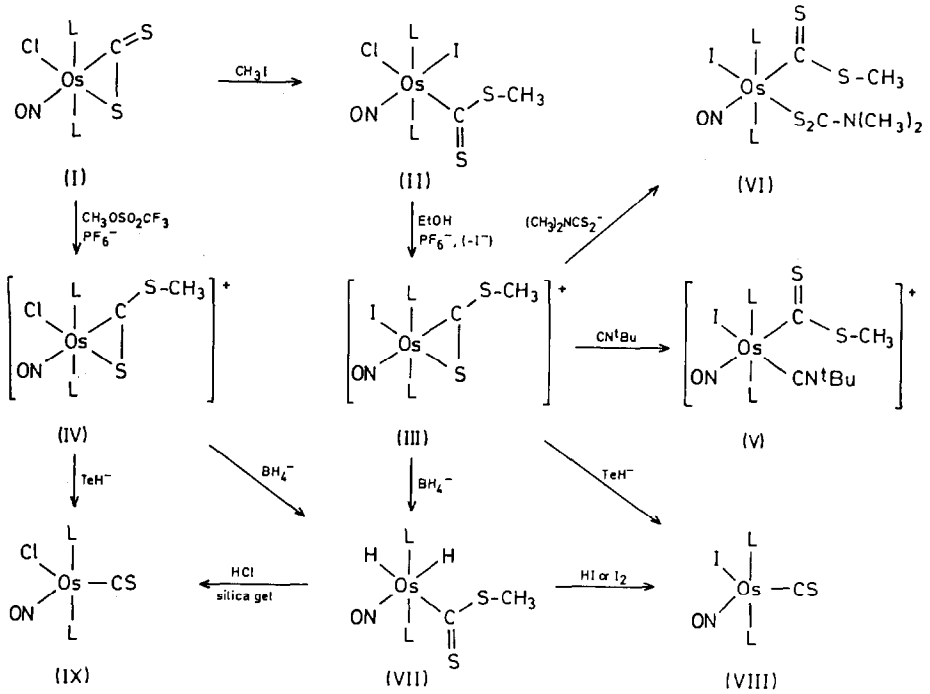
## Results and discussion

*Synthesis of dithiomethoxycarbonyl complexes*

An osmium analogue of Vaska's iridium complex ($IrCl(CO)(PPh_3)_2$ [5]), the nitrosyl compound "*trans*-$[OsCl(NO)(PPh_3)_2]$", can be conveniently generated in situ from the recently reported complex $OsCl(NO)(PPh_3)_3$ [6] because of the sterically induced lability of the three bulky phosphine ligands [7]. Thus, $OsCl(NO)(PPh_3)_3$ reacts with $CS_2$ to give $OsCl(NO)(CS_2)(PPh_3)_2$ (I) [4] (Scheme 1).

In contrast to the labile $CS_2$ ligand in $IrCl(CO)(CS_2)(PPh_3)_2$, the analogous complex I shows no tendency towards $CS_2$ loss. When treated with methyl iodide in dichloromethane solution, I reacts smoothly to give $Os(Cl)I(CS_2Me)(NO)(PPh_3)_2$ (II); according to the IR spectrum ($\nu$(CS) 991 $cm^{-1}$ in Nujol), the dithiomethoxycarbonyl ligand binds in a monodentate fashion, allowing coordination of the iodide ion. Solutions of II in dichloromethane or benzene are bright orange. However, on addition of ethanol the colour rapidly fades to yellow, and a cationic complex containing a bidentate ligand, $[OsI(\eta^2\text{-}CS_2Me)(NO)(PPh_3)_2]^+$ (III), is formed which can be isolated as such by addition of a non-coordinating anion ($PF_6^-$ or $ClO_4^-$). The $\eta^1 \rightarrow \eta^2$ conversion of the dithiomethoxycarbonyl ligand is reversible; removal of the ethanol in the absence of $PF_6^-$ ions results in quantitative re-formation of the neutral complex II. The carbon–sulphur absorptions in the IR provide a useful diagnostic tool for determining the hapticity of the $CS_2Me$ group (ca. 1000 for $\eta^1$,




SCHEME 1. Synthesis and reactions of dithiomethoxycarbonyl complexes of osmium (L = triphenylphosphine).

ca. 1100 $cm^{-1}$ for $\eta^2$). It was not established whether the alkylation takes place at the *exo*-sulphur or at the metal-bound sulphur atom. It has been suggested that $Os(CO)_2(CS_2)(PPh_3)_2$ [8] and $Os(CO)(CS)(CS_2)(PPh_3)_2$ [9] undergo alkylation at the *exo*-sulphur atom, and an exocyclic methylthiolate group has been structurally verified for the cations $[Ru(CO)_2(CS_2Me)(PPh_3)_2]^+$ [10] and $[(\eta^5\text{-}C_5H_5)_2\text{-}V(CS_2Me)]^+$ [11]. Thus, by analogy the cation $[OsI(CS_2Me)(NO)(PPh_3)_2]^+$ (III) is assigned a structure with a methylated *exo*-sulphur (Scheme 1). The synthesis of the related chloro complex, $[OsCl(CS_2Me)(NO)(PPh_3)_2]^+$ (IV), was achieved by a similar procedure to that used for III, except that the alkylating agent used was methyl trifluoromethylsulphonate, MeOTf; the $OTf^-$ ion does not compete successfully with the chloride and, upon addition of an ethanolic solution of $NH_4PF_6$, the salt of cation IV is directly obtained.

The OsCS metallacycle is readily opened by two-electron donor ligands such as t-butyl isocyanide to give the cationic monodentate dithiomethoxycarbonyl complex $[OsI(CS_2Me)(NO)(CN^tBu)(PPh_3)_2]^+$ (V). Similarly the nucleophilic anion *N*,*N*-dimethyldithiocarbamate coordinates to III to provide the neutral complex $OsI(CS_2Me)(S_2CNMe_2)(NO)(PPh_3)_2$ (VI). The cationic III and the neutral II both react with ethanolic sodium tetrahydroborate, $NaBH_4$, to give the *cis*-dihydrido complex $OsH_2(CS_2Me)(NO)(PPh_3)_2$ (VII). The *cis*-stereochemistry follows from the infrared spectrum; two peaks assignable to the two $OsH_2$ stretching modes and one deformation mode are observed ($\nu_{as}(OsH_2)$ 2082, $\nu_s(OsH_2)$ 1954 and $\delta(OsH_2)$ 840 $cm^{-1}$). Confirmation is provided by the $^1H$ NMR data, the two hydrido ligands each give rise to two triplets, indicating coupling to one proton and two equivalent phosphorus nuclei ($^2J(H_a,H_b)$ 7.0, $^2J(H_a,P)$ 23.5 and $^2J(H_b,P)$ 19.8 Hz). In an all-*trans* configuration only one triplet would be expected for the chemically equivalent hydrido ligands. In contrast it should be noted that the topologically related cation $[IrI(CO)(CS_2Me)(PPh_3)_2]^+$ reacts under similar conditions to afford *trans*-$[IrH_2(CS_2Me)(CO)(PPh_3)_2]$ [12].

Attempts to induce thermal elimination of methyl thiol from VII failed to give the expected (and yet unknown) thiocarbonyl species $OsH(NO)(CS)(PPh_3)_2$. In contrast, $OsH(CS_2Me)(CO)_2(PPh_3)_2$ and $IrClH(CS_2Me)(CO)(PPh_3)_2$ lose MeSH on heating to give $Os(CO)_2(CS)(PPh_3)_2$ and $IrCl(CS)(PPh_3)_2$, respectively [13]. $OsH(NO)(CS)(PPh_3)_2$ is presumably unstable with respect to migratory insertion of hydrido and thiocarbonyl ligands under the conditions required for MeSH elimination from VII.

*Conversion of dithiomethoxycarbonyl to thiocarbonyl ligands*

*(a) Hydrotelluride reduction*

The extrusion of selenium from carbon sulphide-selenide complexes is more facile than that of sulphur from the corresponding carbon disulphide complex, e.g., while $CpCo(PMe_3)(CS_2)$ is inert to tertiary phosphines, $CpCo(PMe_3)(CSSe)$ readily affords the thiocarbonyl complex $CpCo(PMe_3)(CS)$ upon treatment with triphenylphosphine [14]. With this in mind we expected that the conversion of a $CS_2$ into a CSTe ligand might facilitate tellurium elimination and provide the desired thiocarbonyl ligand.

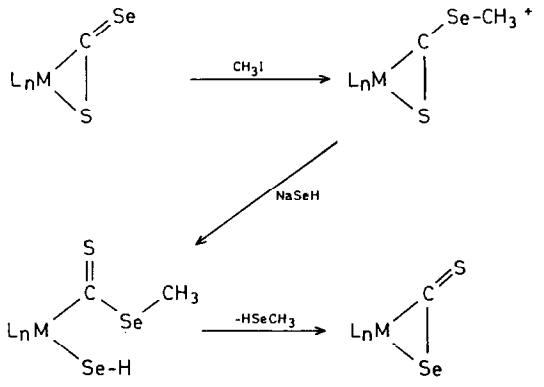
The construction or isomerisation of mixed carbondichalcogenide ligands can be achieved by the nucleophilic attack of a hydrochalcogenide anion at either a chalcocarbonyl [15] or a dichalcoalkoxycarbonyl [16] complex (e.g., see Scheme 2).

TABLE 1

CHARACTERISTIC DATA FOR DITHIOMETHOXYCARBONYL COMPLEXES OF OSMIUM [a]

| Complex | Colour | Infrared | | | $^1$H NMR ($^2J$(P,H)) [b] | |
|---|---|---|---|---|---|---|
| | | $\nu$(NO) | $\nu$(CS) | other | $\delta(CH_3)$ | other |
| $OsCl(I)(CS_2Me)(NO)(PPh_3)_2$ (II) | orange | 1843 | 991 | | | |
| $[OsI(CS_2Me)(NO)(PPh_3)_2]^+$ (III) | yellow | 1798 | 1122 | | 2.42 | |
| $[OsCl(CS_2Me)(NO)(PPh_3)_2]^+$ (IV) | yellow | 1792 | 1128 | | 2.43 | |
| $[OsI(CS_2Me)(NO)(CN^tBu)(PPh_3)_2]^+$ (V) | pink | 1891 | 1008 | 2234 $\nu$(CN) | 2.00 | 1.06 $C(CH_3)_3$ |
| $OsI(CS_2Me)(S_2CNMe_2)(NO)(PPh_3)_2$ (VI) | orange | 1837 | 985 | 1003, 1118, 1251, 1360 ($S_2CNMe_2$) | 1.92 | 3.24, 3.26 } $N(CH_3)_2$ |
| $OsH_2(CS_2Me)(NO)(PPh_3)_2$ (VII) | orange | 1748 | 975 | 2082, 1954 $\nu(OsH_2)$ 840 $\delta$ ($OsH_2$) | 1.68 | −2.14 (25.3), −6.88 (19.8) } $OsH_2$ |

[a] Infrared data ($cm^{-1}$) determined from Nujol mulls between KBr discs; $^1$H NMR data determined from saturated solutions in $CDCl_3$ at 25°C (90 MHz) and reported relative to internal $\delta(SiMe_4) = 0.00$. [b] Reported in Hz.




$L_nM$ = Os(CO)(CN-p-tolyl)$(PPh_3)_2$

SCHEME 2. Isomerization of an $\eta^2$-CSSe ligand [15].

It was hoped that this approach would provide a route to the previously unobserved carbontelluride-chalcogenide ligands, $\eta^2$-CTeE (E = S, Se, Te). A yellow solution of III in tetrahydrofuran reacts rapidly at −78°C with an ethanolic solution of sodium hydrotelluride, NaTeH, to give a deep red solution. On warming to −10°C, elemental tellurium rapidly separates out and a pale brown compound can be isolated following chromatographic purification. When the reaction is carried out in dichloromethane, tellurium deposition occurs instantly at −78°C. The product has the composition $OsI(NO)(CS)(PPh_3)_2$ (VIII); both thiocarbonyl (1258 $cm^{-1}$) and nitrosyl (1638 $cm^{-1}$) infrared activity (Table 2) indicate that VIII is formally an osmium(0) complex. The stereochemistry of VIII is presumably analogous to that of $RuI(NO)(CO)(PPh_3)_2$ for which a trigonal bipyramid (with *trans* phosphines) has been established crystallographically [17]. From the IR data of related $d^8$ thiocarbonyl and nitrosyl complexes (see e.g., [6,7]) it would appear that the nitrosyl in VIII is a better acceptor ligand than the thiocarbonyl group. Similarly $OsCl(NO)(CS)(PPh_3)_2$ (IX) can be prepared from IV and sodium hydrotelluride.

TABLE 2

CHARACTERISTIC DATA FOR THIOCARBONYL COMPLEXES OF OSMIUM [a]

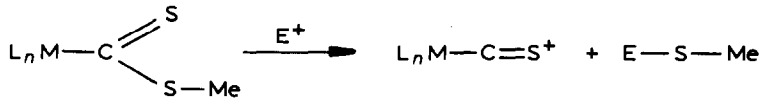
| Complex | Colour | Infrared | | |
|---|---|---|---|---|
| | | ν(NO) | ν(CS) | other |
| $OsI(NO)(CS)(PPh_3)_2$ (VIII) | brown | 1638 | 1258 | |
| $OsCl(NO)(CS)(PPh_3)_2$ (IX) | brown | 1610 | 1279 | |
| $[OsI_2(NO)(CS)(PPh_3)_2]^+$ (XI) | blood-red | 1868 | 1370 | |
| $[Os(NO)(CO)(CS)(PPh_3)_2]^+$ (XII) | yellow | 1705 | 1295 | ν(CO): 1990 |
| $[Os(NO)(CS)(PPh_3)_3]^+$ (XIII) | tan | 1702 | 1278 | |
| $Os(SeH)(NO)(CS)(PPh_3)_2$ [b] (XIV) | brown | 1608 | 1270 | |
| | | | 1260 | |

[a] Data determined as for Table 1. [b] Other bands observed in the ν(NO) region at 1592, 1581, 1571 and 1558 $cm^{-1}$. $^1H$ NMR: $\delta(SeH)$ −2.67 ppm, $^3J(P_2H)$ 8.5 Hz.

Also, the cations III and IV react with sodium hydroselenide to give VIII and IX, respectively. The instability of the presumed intermediates $OsX(NO)(CSSe)(PPh_3)_2$ (X = Cl, I) is surprising in view of the indefinitely stable isomeric complexes $\overline{Os(CSSe)}(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ and $\overline{Os(CSeS)}(CO)(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ [17]. The innocence of the nitrosyl ligand is therefore suspect. The red species which precedes the formation of VIII appears to be stable at −78°C and is presumably either $OsI(NO)(CTeS)(PPh_3)_2$ or $OsI(TeH)(CS_2Me)(NO)(PPh_3)_2$; however, attempts to characterize this labile intermediate have so far been unsuccessful.

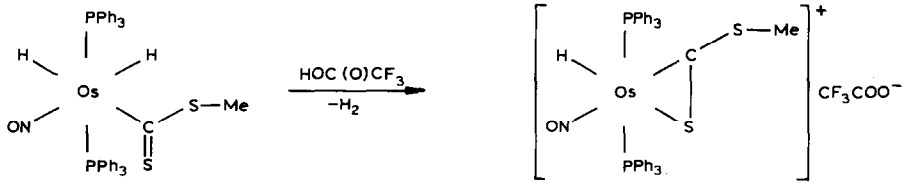
*(b) Acid-induced thiol elimination*

An alternative method of converting dithiomethoxycarbonyl ligands to thiocarbonyls involves electrophilic cleavage of the thiomethoxy group [8]:




$L_n$ = a generalized ligand set

This approach was therefore investigated. The *cis*-dihydrido species VII reacts with Lewis acids to give thiocarbonyl complexes. In contrast to the usually observed acid cleavage of dithiomethoxycarbonyl ligands the reactions of VII with acids were found to be ultimately reductive in nature. Treatment of VII with aqueous hydrochloric acid results in a modest (20–25%) yield of IX, while one equivalent of diiodine or hydriodic acid gives VIII in good yield. A number of mechanisms are plausible, but the reaction of VII with one equivalent of trifluoroacetic acid is informative:

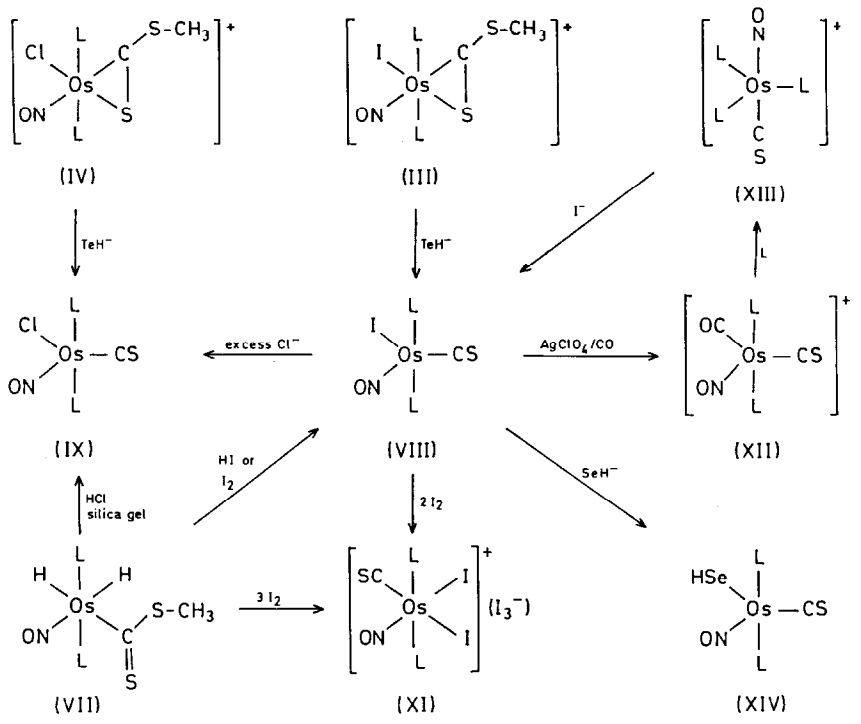



(VII) (X)

The yellow compound obtained retains the dithiomethoxycarbonyl group as well as one hydride. The IR spectrum indicates that the dithiomethoxycarbonyl group is bidentate and so the product is formulated as $[OsH(\eta^2\text{-}CS_2Me)(NO)(PPh_3)_2]^+ CF_3COO^-$ (X). Thus the site of attack at VII would appear to be the metal centre followed by elimination of dihydrogen. Subsequent reductive elimination of methyl thiol may therefore depend on the basicity or nucleophilicity of the counter anion. Neither of these qualities is pronounced in the trifluoroacetate anion.

*Reactions of $OsX(NO)(CS)(PPh_3)_2$ (X = Cl, I)*

Addition of two equivalents of iodine to a solution of VIII in toluene produces a blood-red precipitate of the oxidative-addition product $[OsI_2(NO)(CS)(PPh_3)_2]^+$ (XI) as the triiodide salt. Alternatively, XI may be obtained by the addition of three equivalents of iodine to $OsH_2(CS_2Me)(NO)(PPh_3)_2$ (VII) avoiding the isolation of VIII and thereby affording an improved yield (Scheme 3).




SCHEME 3. Synthesis and reactions of thiocarbonyl complexes of osmium (L = triphenylphosphine).

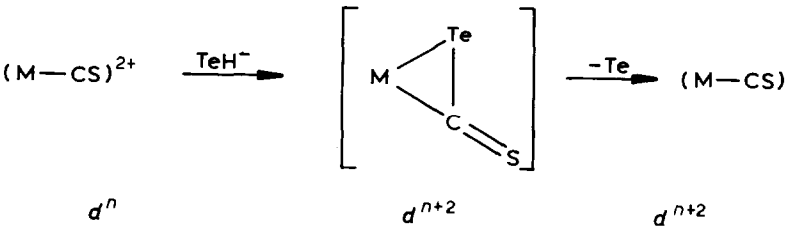
The iodide ligand in VIII is labile and may be abstracted with silver salts ($AgClO_4$, $AgBF_4$, $AgSbF_6$) in the presence of carbon monoxide providing the cationic complex $[Os(NO)(CO)(CS)(PPh_3)_2]^+$ (XII); salts containing the anions $ClO_4^-$, $BF_4^-$ and $SbF_6^-$ have been prepared. The carbonyl ligand in cation XII is labile and may be replaced by triphenylphosphine to give the cationic trisphosphine complex $[Os(NO)(CS)(PPh_3)_3]^+$ (XIII). As noted earlier, the triphosphine arrangement is sterically strained, and one phosphine is easily lost from the coordination sphere in solution. For example, treatment of XIII with an ethanolic solution of sodium iodide results in re-formation of VIII. The iodide VIII also reacts with ethanolic sodium hydroselenide (room temperature) and sodium chloride (reflux) to give $Os(SeH)(NO)(CS)(PPh_3)_2$ (XIV) and $OsCl(NO)(CS)(PPh_3)_2$ (IX), respectively.

The chemistry of these thiocarbonyl complexes parallels that observed for the analogous carbonyl compounds $OsX(NO)(CO)(PPh_3)_2$, $[Os(NO)(CO)_2(PPh_3)_2]^+$-$ClO_4^-$ and $[Os(NO)(CO)(PPh_3)_3]^+ClO_4^-$ [18] except that, in keeping with a reduced metal basicity, VIII and IX are more stable with respect to aerial oxidation and may be handled in solution in air for brief periods without significant decomposition.

*Conclusions*

Two novel approaches to the reduction of transition-metal bound $CS_2$ have been developed. The exceptional reactivity of the thiocarbonyl ligand towards nucleophiles

renders many common reducing reagents inappropriate for the reductive activitation of thiocarbonyl-containing complexes. Conversion of a thiocarbonyl ligand to a carbon sulphide-telluride ligand, as described here, is reductive, and the apparent metastability of the CSTe group provides the basis of a new method of regenerating the thiocarbonyl ligand in a reduced oxidation state:




## Experimental

*General*

Solvents were purified by distillation from the appropriate drying agents (tetrahydrofuran, benzene, toluene, ether, hexane and pentane from sodium/potassium alloy, halogenated solvents from $P_4O_{10}$ and alcohols from the corresponding alkoxide). All reactions and solvent distillations were carried out under prepurified nitrogen (4 Å molecular sieves (Merck) and BTS catalyst (Fluka)) using conventional Schlenk techniques [19]. Characterization of new compounds was by elemental analysis (Prof. A.D. Campbell, Microanalytical Laboratory, University of Otago, and Pascher, Mikroanalytisches Laboratorium, Bonn), and $^1H$ NMR (JEOL NMR-PMX 60 and FX 90Q and Varian Associates T60), and IR (Perkin–Elmer 297, 597 and Beckman 4240) spectroscopy. The melting points (uncorrected) were measured in open capillaries with a Büchi 510 apparatus.

Some of the compounds described herein were prepared in several different ways, but only the preferred method of synthesis is described in detail.

*$OsCl(NO)(CS_2)(PPh_3)_2$ (I)*

The method described here is a variation of a previous preparation [4], being different only in that the reactive intermediate $OsCl(NO)(PPh_3)_3$ was not isolated but generated and then used in situ.

To a suspension of $OsCl(O_2CO)(NO)(PPh_3)_2$ [20] (1.00 g, 1.19 mmol) and triphenylphosphine (0.60 g, 2.3 mmol) in rigorously deoxygenated toluene (20 ml) is added carbon disulphide (3 ml, 50 mmol). The mixture is refluxed for 5 min then allowed to cool slowly to room temperature. Orange needles form on cooling, and crystallization is completed by addition of ethanol (150 ml) followed by stirring at room temperature for 1 h. The product is isolated by filtration, washed with ethanol (2 × 20 ml) and hexane (2 × 20 ml) and dried in vacuo. M.p. 165°C. Yield 0.99–1.00 g (97–99%). Crystals of I are air-stable, as are its solutions, but surface darkening of the crystalline compound occurs over a period of days owing to slight light-sensitivity. The identity of the product was confirmed by comparison of its spectral properties with those of an authentic sample [4].

*$OsCl(I)(CS_2Me)(NO)(PPh_3)_2$ (II)*

$OsCl(NO)(CS_2)(PPh_3)_2$ (I) (0.50 g, 0.58 mmol) is suspended in dichloromethane (50 ml) and treated with an excess of methyl iodide (5 ml). The orange suspension is stirred for 30 min to give a red solution. Hexane (30 ml) is added and some solvent taken off (rotary evaporator), with subsequent additions of hexane (2 × 15 ml) to maintain the volume in the range 30–50 ml. The orange microcrystalline solid is filtered off and washed with hexane (2 × 20 ml). The complex may be recrystallized from $CH_2Cl_2$/hexane. M.p. 134–136°C (decomp.). Yield 0.50–0.52 g (86–90%).

*$[OsI(\eta^2\text{-}CS_2Me)(NO)(PPh_3)_2]PF_6$ (III · $PF_6$)*

The dichloromethane solution of II prepared above is treated with a solution of excess ammonium hexafluorophosphate (0.20 g) in water (5 ml) and ethanol (30 ml); the resulting yellow solution is stirred for 5 min and, if necessary, more ethanol is added to give a homogeneous solution. Some solvent volume is evaporated off (rotary evaporator) with intermittent addition of ethanol to maintain the solvent volume in the range 30–50 ml and to bring about azeotropic removal of $CH_2Cl_2$. The yellow needles are filtered off, washed with ethanol (2 × 10 ml) and hexane (2 × 10 ml) and dried in air. M.p. 223–225°C (decomp.). Yield 0.56–0.59 g (86–90%). Anal. Found: C, 45.52; H, 3.90; N, 1.28. $C_{38}H_{33}ClINO_5OsP_2S_2$ (III · $ClO_4$) calcd.: C, 45.64; H, 3.13; N, 1.32%.

*$[OsCl(\eta^2\text{-}CS_2Me)(NO)(PPh_3)_2]PF_6$ (IV · $PF_6$)*

$OsCl(NO)(CS_2)(PPh_3)_2$ (I) (0.30 g, 0.35 mmol) is dissolved in dichloromethane (20 ml), treated with a solution of methyl trifluoromethylsulphonate in dichloromethane (4.0 ml, 0.10 mol/l, 1.1 equivalents) and the mixture stirred for 30 min. A solution of $NH_4PF_6$ (0.20 g) in water (3 ml) and ethanol (30 ml) is then added. The mixture is further diluted with ethanol until a homogeneous solution is obtained. The solvent volume is then reduced with a rotary evaporator and further ethanol added to effect crystallization of the product as yellow needles. Yield 0.33–0.34 g (94–96%). M.p. 219°C. $^1H$ NMR indicates that IV · $PF_6$ crystallizes from $CH_2Cl_2$/EtOH as a dichloromethane monosolvate. Crystallization from chloroform provides the solvate-free complex.

*$[OsI(CS_2Me)(NO)(CN^tBu)(PPh_3)_2]PF_6$ (V · $PF_6$)*

A solution of III (0.30 g, 0.27 mmol) in tetrahydrofuran (30 ml) is treated with a solution of t-butylisonitrile in tetrahydrofuran (3.0 ml, 0.10 mol/l, 1.1 equiv.) and the mixture is stirred for 15 min. The solvent is then removed under reduced pressure and the residue triturated with hexane to remove excess isonitrile. The oil is then crystallized from dichloromethane/toluene to give pink needles. Yield 0.29 g (90%). M.p. 147°C (decomp. to III · $PF_6$).

*$OsI(CS_2Me)(S_2CNMe_2)(NO)(PPh_3)_2$ (VI)*

A solution of III · $PF_6$ (0.30 g, 0.27 mmol) in dichloromethane (20 ml) is treated with a solution of sodium dimethyldithiocarbamate dihydrate (0.20 g, 1.0 mmol) in water (3.0 ml) and ethanol (30 ml). The mixture is stirred for 30 min during which the product separates as orange crystals which were filtered off, washed with water (10 ml), ethanol (2 × 10 ml), and finally hexane (2 × 10 ml), then dried in vacuo. Yield 0.28 g (96%). M.p. 128°C (decomp.).

*$OsH_2(CS_2Me)(NO)(PPh_3)_2$ (VII)*

A suspension of II, III or IV (ca. 0.50 g) in ethanol (10 ml) is treated with a filtered solution of sodium tetrahydroborate (0.20 g, 5.4 mmol) in ethanol (30 ml) at 0°C. The suspension is stirred for 15 min at room temperature and then water (30 ml) added to decompose the excess of $NaBH_4$ and complete the precipitation of the product. The mixture is stirred for a further 5 min and the orange solid is then filtered off, washed with water (10 ml), ethanol (2 × 5 ml) and finally hexane (2 × 10 ml) and dried in vacuo. The yield is quantitative. Anal. Found: C, 54.04; H, 4.71. $C_{38}H_{35}NOOsP_2S_2$ calcd.: C, 54.48; H, 4.21%. As a solid VII is stable in air, but the compound is slowly attacked by aerated or halogenated solvents. The microcrystalline solid isolated as above is spectroscopically pure (IR, $^1H$ NMR and $^{31}P$ NMR). Better crystals can be obtained by recrystallization form dichloromethane/ethanol.

*Ethanolic sodium hydrotelluride solution for preparations of VIII and IX*

Sodium tetrahydroborate (1.00 g, 27 mmol) and elemental tellurium powder (1.30 g, 10.0 mmol) are added to ethanol (100 ml) and the resulting suspension refluxed until gas evolution ceases (monitored by a mercury no-return, over-pressure valve) and a colourless solution is obtained. This solution (0.10 mol $l^{-1}$ in $Te^{-II}$ (i.e., $TeH^-$, $Te^{2-}$)) is exceedingly air-sensitive and is best used immediately after cooling to room temperature.

*$OsI(NO)(CS)(PPh_3)_2$ (VIII)*

A solution of II or III (0.50 mmol) in rigorously degassed tetrahydrofuran (60 ml) is cooled to −10°C in an ice/ethanol bath. An ethanolic solution of sodium hydrotelluride (5.0 ml, 0.10 mol $l^{-1}$, 1.0 equiv., vide infra) is added dropwise and the mixture stirred for 15 min before being allowed to warm up to room temperature. The resulting brown-black suspension is stirred for 20 min and then exposed to air with rapid stirring for 5 min to ensure that any unreacted hydrotelluride is converted into insoluble elemental tellurium. The suspension is then diluted with dichloromethane (100 ml) and filtered through Celite to remove the bulk of the tellurium formed. The solvent is removed under reduced pressure, the residue extracted with a minimum of dichloromethane, and chromatographed on silica gel with dichloromethane as eluent. The first, pale brown band is collected, the solvent removed and the residue crystallized from dichloromethane/ethanol to give brown plates which are filtered off, washed with ethanol (2 × 10 ml) and hexane (2 × 10 ml) and dried in vacuo. Yield 0.32–0.35 g (70–75%). M.p. 203°C (decomp.). Anal. Found: C, 48.47; H, 3.89; N, 1.51. $C_{37}H_{30}INOOsP_2S$ calcd.: C, 48.56; H, 3.31; N, 1.53%.

*$OsCl(NO)(CS)(PPh_3)_2$ (IX)*

Use of IV in the procedure outlined for the preparation of VIII afforded IX in 50–60% yield as brown platelets. M.p. 198–200°C. Anal. Found: C, 52.67; H, 3.63; N, 1.59. $C_{37}H_{30}ClNOOsP_2S$ calcd.: C, 53.23; H, 3.42; N, 1.70%.

*$[OsI_2(NO)(CS)(PPh_3)_2]I_3$ ($XI \cdot I_3$)*

A suspension of VII (0.15 g, 0.18 mmol) in toluene (5 ml) at 0°C is treated dropwise with a cooled (0°C) solution of iodine in toluene (17.5 ml, 0.033 mol $l^{-1}$, 3.2 equiv.) during ca. 5 min. The mixture is stirred for a further hour and cooled to

−30°C overnight. The blood-red product is filtered off and washed with toluene (0°C, 10 ml), then with hexane (3 × 10 ml). The yield is quantitative (0.34 g). M.p. 160–162°C. Anal. Found: C, 31.75; H, 2.71; N, 0.96. $C_{37}H_{30}I_4NOOsP_2S$ calcd.: C, 31.22; H, 2.12; N, 0.98%.

*$[Os(NO)(CO)(CS)(PPh_3)_2]ClO_4$ (XII · $ClO_4$)*

Both VIII and IX may be easily converted to the cations XII and XIII, the best yields being obtained from IX. A solution of IX (0.30 g, 0.36 mmol) in tetrahydrofuran (30 ml) is saturated with carbon monoxide and then treated with a solution of $AgClO_4 \cdot H_2O$ (0.085 g, 0.38 mmol, 1.03 equivalents) in ethanol (30 ml). The resulting suspension is stirred for 10 min and placed under two atmospheres of carbon monoxide. The vessel is vented and the solution diluted with dichloromethane (50 ml) and filtered through Celite to remove AgCl. The volume of the filtrate is reduced with subsequent addition of hexane to effect crystallization of the yellow product. The solid is filtered off, washed with hexane (2 × 10 ml), then dried in vacuo. Yield 0.31 g (94%). M.p. 140–143°C. Anal. Found: C, 49.90; H, 3.89; N, 1.67. $C_{38}H_{30}ClNO_6OsP_2S$ calcd.: C, 49.81; H, 3.30; N, 1.53%.

*$[Os(NO)(CS)(PPh_3)_3]ClO_4$ (XIII · $ClO_4$)*

Whilst the perchlorate salt of XIII may be prepared from isolated XII · $ClO_4$, the synthesis of the latter is sufficiently clean that in the preparation of XIII · $ClO_4$ a solution of XII · $ClO_4$ prepared in situ can be used without isolation, thereby improving the overall yield.

A solution of IX (0.10 g, 0.12 mmol) in tetrahydrofuran (30 ml) is saturated with carbon monoxide and then treated with a solution of $AgClO_4 \cdot H_2O$ (0.028 g, 1.1 equivalents) in ethanol (30 ml). The resulting suspension is filtered through Celite to remove the AgCl precipitate and the filtrate treated with a solution of triphenylphosphine (0.30 g, 1.15 mmol, ca. 10 equivalents) in hexane (30 ml). The mixture is placed in a Schlenk tube equipped with a gas inlet. Nitrogen is passed slowly through the solution for 2 h. The solvent volume is then reduced on a rotary evaporator with subsequent addition of hexane to effect the formation of chunky tan crystals. Yield 0.13 g (90%). M.p. 131°C (decomp.). Consistent elemental microanalytical data were not obtained, but spectroscopic data and subsequent conversion to VIII confirm the assigned formulation.

*$Os(SeH)(NO)(CS)(PPh_3)_2$ (XIV)*

The best procedure for the preparation of XIV involves the reaction of III with an excess of sodium hydroselenide, a procedure involving intermediate VIII but not its isolation. Ethanolic sodium hydroselenide is prepared in a completely analogous way to that described for sodium hydrotelluride except that the initial mixing of reactants has to be carried out at 0°C owing to the vigorous nature of the reaction.

A solution of VIII (0.30 g, 0.34 mmol) in tetrahydrofuran (20 ml) is treated with a solution of ethanolic sodium hydroselenide (13.6 ml, 0.10 *M*, 4.0 equivalents) and the mixture stirred for 24 h. The solvent is then removed in vacuo and the residue extracted with a minimum of dichloromethane and chromatographed on silica gel with dichloromethane as eluent. The first pale-brown band is collected, freed from solvent under reduced pressure, and crystallized from dichloromethane/ethanol. Yield 0.20 g (68%). $^1H$ NMR indicates that XIV crystallizes from $CH_2Cl_2$/EtOH as

a dichloromethane monosolvate. Anal. for XIV · $CH_2Cl_2$. Found: C, 48.18; H, 3.93; N, 1.65. $C_{38}H_{33}Cl_2NOOsP_2SSe$ calcd.: C, 47.85; H, 3.49; N, 1.47%.

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