Triphenylphosphine-substituted selenido and sulfido clusters of osmium derived from $Ph_3P{=}Se$ or $Ph_3P{=}S$

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Abstract

Cleavage of P=Se bonds occurs readily in the room-temperature treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3P{=}Se$ to give three new compounds, $[Os_3(\mu_3\text{-}Se)_2(CO)_8(PPh_3)]$ (**2**), $[Os_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2]$ (**5**) and $[Os_3(\mu\text{-}OH)_2(CO)_8(PPh_3)_2]$ (**6**), respectively, and three known compounds, $[Os_3(\mu_3\text{-}Se)_2(CO)_9]$ (**1**), $[Os_3(\mu_3\text{-}Se)(\mu\text{-}CO)_2(CO)_7(PPh_3)]$ (**3**), and 1,2-$[Os_3(CO)_{10}(PPh_3)_2]$ (**4**). No evidence for any product containing a co-ordinated $Ph_3P{=}Se$ ligand was obtained. The analogous reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and $Ph_3P{=}S$ produces five new compounds $[Os_3(\mu_3\text{-}S)_2(CO)_8(PPh_3)]$ (**7**), $[Os_3(\mu_3\text{-}S)(\mu\text{-}CO)_2(CO)_7(PPh_3)]$ (**8**), $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2]$ (**9**), $[Os_3(\mu_3\text{-})_2(CO)_7(PPh_3)_2]$ (**11**) and compound **6** in addition to the known compound **4**. Treatment of **2** with Me_3NO at 50 °C gives the trinuclear cluster $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)(NMe_3)]$ (**13**) and the hexanuclear cluster $[Os_6(\mu_3\text{-}Se)_4(CO)_{14}(PPh_3)_2]$ (**12**). Treatment of compound **1** with PPh_3 and Me_3NO at room temperature gives $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ (**10**). Compound **2** reacts with PPh_3 similarly to give **10**. Compound **3** reacts with elemental selenium at 110 °C to give **2**. The new compounds **2**, **5**, **6** and **8** were characterized by single-crystal X-ray diffraction. The compounds **3**, **5**, **8** and **9** contain $Os_3(\mu_3\text{-}S)$ or $Os_3(\mu_3\text{-}Se)$cluster cores with three metal–metal bonds while **2**, **7**, **10**, **11** and **12** contain $Os_3(\mu_3\text{-}S)_2$or $Os_3(\mu_3\text{-}Se)_2$ cores two metal–metal bonds. The two hydroxy ligands in the triosmium cluster **6** bridging the open osmium-osmium edge and are probably derived from water. A study of the dynamic exchange of PPh_3 ligands in **5** is also reported.
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Keywords: Osmium carbonyl clusters; Triphenylphosphine selenide; Triphenylphosphine sulfide; Crystal structures

1. Introduction

Having a high affinity for later transition metals, chalcogen atoms are readily incorporated into transition-metal carbonyl clusters [1]. Many different coordination modes and geometries of the chalcogen atoms are adopted and the triply-bridging sulfido ligand in particular has been exploited for the purpose of cluster growth [2,3]. The larger tellurium atom stabilizes triangular and square arrays of metal atoms [4]. Selenido ligands should be similarly useful but have been studied rather less [5]. Lewis et al. [6] reported that $[Os_3(CO)_{12}]$ reacts with elemental chalcogens in refluxing octane to give $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}X)(CO)_9]$, $[Os_3(\mu_3\text{-}X)_2(CO)_9]$ and $[Os_4(\mu\text{-}H)_2(\mu_3\text{-}X)_2(CO)_{12}]$ (X = S, Se or Te), but a CO/H_2 pressure is required to prepare the ruthenium analogues $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}X)(CO)_9]$ and $[Ru_3(\mu_3\text{-}X)_2(CO)_9]$. It has recently been reported that the treatment of Fe and Ru

carbonyl complexes with R₃P=Se provides a simple, one-step synthesis of phosphine-substituted selenido clusters through oxidative transfer of the selenium to low-valent metal clusters [7]. For example, Cauzzi et al. [7a] reported the synthesis of tertiary phosphine-substituted selenido carbonyl Fe or Ru clusters in this way. For Ru, the reaction selectively gives the disubstituted trinuclear cluster [Ru₃(μ₃-Se)₂(CO)₇(PPh₃)₂] in high yield, together with only minor amounts of [Ru₃-(μ₃-Se)₂(CO)₈(PPh₃)] and [Ru₄(μ₄-Se)₂(μ-CO)₂-(CO)₇-(PPh₃)₂]. In contrast the reaction for Fe afforded a series of di- and tri-nuclear compounds. Although a range of PPh₃ derivatives of Ru and Fe compounds containing Se ligand from Ph₃P=Se has been described by Cauzzi and co-workers, relatively little is known of the corresponding Os chemistry. Adams et al. [8] recently reported some Mn and mixed Fe-Mn carbonyl clusters containing PPh₃ and μ₃-Se ligands from the reactions of Ph₃P=Se with [Mn₂(CO)₉(MeCN)] and [CpFeMn-(CO)₇] while Braunstein et al. [9] reported mixed metal tri- and tetra-nuclear clusters capped by Se ligands from treatment of [MCo₃(μ-H)(CO)₁₂] (M = Fe or Ru) with various phosphine selenides. Applying this approach we have synthesized compounds containing bridging dppm and capping Se ligands from the reactions of [Os₃-

(CO)₁₀(MeCN)₂] with dppmSe and dppmSe₂ and used these for the synthesis of higher nuclearity compounds [10]. We now report the synthesis of some PPh₃ substituted triosmium compounds containing capping Se and S ligands from room-temperature reactions of [Os₃ (CO)₁₀(MeCN)₂] with Ph₃P=Se and Ph₃P=S. During the progress of this work Leong et al. [11] reported some Os–Se compounds from the reactions of [Os₃(CO)₁₁-(MeCN)] and [Os₃(CO)₁₀(MeCN)₂] with Ph₃P=Se, but our results from similar investigations are significantly different from theirs and in particular we have repeatedly observed a wider range of products than they report.

2. Results and discussion

The lightly stabilized cluster [Os₃(CO)₁₀(MeCN)₂] reacts with Ph₃P=Se at room temperature to give three new compounds [Os₃(μ₃-Se)₂(CO)₈(PPh₃)] (**2**), [Os₃(μ₃-Se)(μ₃-CO)(CO)₇(PPh₃)₂] (**5**) and [Os₃(μ-H)₂(CO)₈-(PPh₃)₂] (**6**) in 10%, 16% and 7% yields, respectively, and three previously reported compounds [Os₃(μ₃-Se)-(μ-CO)₂(CO)₇(PPh₃)] (**3**), [Os₃(μ₃-Se)₂(CO)₉] (**1**) and 1,2-[Os₃(CO)₁₀(PPh₃)₂] (**4**) in 15%, 12% and 7% yields, respectively (Scheme 1). We obtained no evidence for

[Os₃(CO)₁₀(MeCN)₂] + Ph₃P=E (E = Se, S)

CH₂Cl₂ | 25 °C

Scheme 1.

Table 1
Crystal data and structure refinement for **2**, **5**, **6** and **8**

Complex	2	5	6	8
Chemical formula	$C_{26}H_{15}O_8Os_3PSe_2$	$C_{44}H_{30}O_8Os_3P_2Se \cdot CH_2Cl_2$	$C_{44}H_{32}O_{10}Os_3P_2$	$C_{27}H_{15}O_9Os_3PS$
Formula weight	1214.87	1483.11	1353.24	1117.02
T (K)	293(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell parameters				
a (Å)	8.8222(6)	10.60210(10)	13.1197(6)	14.7118(9)
b (Å)	12.6657(9)	11.3496(2)	17.8055(8)	9.6925(6)
c (Å)	14.7417(10)	20.3179(3)	17.5309(18)	20.3593(12)
α (°)	69.4710(10)	89.7097(8)	90	90
β (°)	76.5650(10)	87.1785(8)	94.4190(10)	99.2290(10)
γ (°)	83.0960(10)	66.6625(6)	90	90
V (Å^3)	1499.05(18)	2241.83(6)	4081.4(3)	2865.5(3)
Z	2	2	4	4
D_{calc} (g/cm^3)	2.691	2.197	2.202	2.589
Absorption coefficient μ (mm^{-1})	15.209	9.359	9.455	13.450
$F(000)$	1092	1384	2536	2032
Crystal size (mm^3)	$0.44 \times 0.21 \times 0.14$	$0.24 \times 0.16 \times 0.16$	$0.23 \times 0.15 \times 0.08$	$0.38 \times 0.16 \times 0.12$
θ Range for data collection (°)	1.72–28.29	2.95–27.49	1.87–28.29	1.59–28.30
Index ranges	$-11 \leqslant h \leqslant 11$,	$-13 \leqslant h \leqslant 13$,	$-17 \leqslant h \leqslant 17$,	$-18 \leqslant h \leqslant 18$,
	$-16 \leqslant k \leqslant 16$,	$-23 \leqslant k \leqslant 23$,	$-14 \leqslant k \leqslant 14$,	$-12 \leqslant k \leqslant 12$,
	$-18 \leqslant l \leqslant 19$	$-26 \leqslant l \leqslant 26$	$-22 \leqslant l \leqslant 22$	$l -27 \leqslant l \leqslant 27$
Reflection collected	13 307	37 690	35 789	24 769
Independent reflections	6906	10 185	9715	6834
R_{int}	0.0388	0.0772	0.0283	0.0361
Reflections with $F^2 > 2\sigma$	5942	8989	8989	6419
Minimum and maximum transmission	0.0573 and 0.2333	0.3107 and 0.2081	0.2197 and 0.5184	0.0799 and 0.2952
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	6906/0/463	10185/0/550	9715/0/540	6834/0/371
R indices [$F^2 > 2\sigma$]	$R_1 = 0.0465$, $wR_2 = 0.1125$	$R_1 = 0.0387$, $wR_2 = 0.0919$	$R_1 = 0.0221$, $wR_2 = 0.0430$	$R_1 = 0.0274$, $wR_2 = 0.0560$
R indices (all data)	$R_1 = 0.0540$, $wR_2 = 0.1178$	$R_1 = 0.0498$, $wR_2 = 0.0978$	$R_1 = 0.0255$, $wR_2 = 0.0439$	$R_1 = 0.0304$, $wR_2 = 0.0572$
Goodness-of-fit on F^2	1.042	1.012	1.087	1.172
Largest and mean shift (su)	0.000 and 0.000	0.000 and 0.000	0.004 and 0.000	0.001 and 0.000
Largest difference in peak and hole (e Å^{-3})	2.189 and -3.071	2.776 and -2.489	0.876 and -0.767	2.515 and -0.945

any clusters with co-ordinated Ph$_3$P=Se ligands so the P=Se bond cleavage to give selenido clusters must occur rapidly following coordination. This observation is different from that of Ho and Wong [12] who reported [Os$_3$(CO)$_{10}${Ph$_2$(SH)NP(S)Ph$_2$-S,S}] and [(μ-H)Os$_3$-(CO)$_9${Ph$_2$P(S)NP(S)Ph$_2$-S,S}] containing undissociated bis(diphenylthiophosphinoyl)amine ligand from the reaction between [Os$_3$(CO)$_{10}$(MeCN)$_2$] and Ph$_2$P(S)-NHP(S)Ph$_2$. The new compounds **2**, **5** and **6** have been characterized spectroscopically and by single-crystal X-ray diffraction. The solid-state molecular structure of **2** (Fig. 1 and Table 2) consists of an open Os$_3$ cluster with two metal–metal bonds, eight terminal CO, a PPh$_3$ and two triply-bridging selenido ligands. The structure was refined with two equally populated disordered orientations of the phenyl groups as shown superimposed in Fig. 1. Both disordered arrangements have the same Os$_3$(μ$_3$-Se)$_2$(CO)$_8$P core structure and small variations within the core as a result of the disorder are believed to be insignificant.

The two Os–Os distances in **2** [Os(1)–Os(3) = 2.7741(5) and Os(2)–Os(3) = 2.8551(5) Å] are rather different, with that involving Os(2) bound to the PPh$_3$ ligand being longer. The Os(1)···Os(2) separation at 3.833 Å is similar to that observed in [Os$_3$(μ$_3$-Se)$_2$-(CO)$_6$(μ-dppm)(PPh$_3$)] [3.835 Å] [10] but is significantly longer than that in [Os$_3$(μ$_3$-S)$_2$(CO)$_9$] [3.662(1) Å] [13].

The Os$_3$Se$_2$ core is square pyramidal with two Os and two Se atoms alternating in base and the third Os atom at the vertex. The two Se atoms cap the Os triangle asymmetrically. The Os–Se distances to the central seven-coordinate metal atom Os(3) [Os(3)–Se(1) =

Table 2
Selected bond distances (Å) and angles (°) for [Os$_3$(μ$_3$-Se)$_2$(CO)$_8$(PPh$_3$)] (**2**)

Os(1)–Os(3)	2.7741(5)
Os(2)–Os(3)	2.8551(5)
Os(1)–Se(1)	2.5074(10)
Os(2)–Se(2)	2.4893(11)
Os(2)–Se(1)	2.5066(9)
Os(3)–Se(1)	2.5535(9)
Os(3)–Se(2)	2.5525(10)
Os(1)–Se(2)	2.5064(11)
Os(2)–P(1)	2.310(2)
P(1)–Os(2)–Se(2)	104.21(6)
P(1)–Os(2)–Se(1)	106.15(5)
Os(1)–Os(3)–Os(2)	85.810(13)
Se(1)–Os(1)–Os(3)	57.56(2)
Se(2)–Os(2)–Se(1)	80.10(3)
Se(1)–Os(3)–Os(1)	55.97(2)
Se(2)–Os(2)–Os(3)	56.56(2)
Se(2)–Os(3)–Os(2)	54.47(2)
Os(2)–Se(1)–Os(1)	99.71(3)
Os(2)–Se(1)–Os(3)	68.69(2)
Os(2)–Se(2)–Os(1)	100.21(3)
Os(1)–Se(2)–Os(3)	66.50(3)
Se(2)–Os(1)–Se(1)	79.76(3)
Se(2)–Os(1)–Os(3)	57.54(3)
P(1)–Os(2)–Os(3)	153.82(5)
Se(2)–Os(3)–Se(1)	78.04(3)
Se(2)–Os(3)–Os(1)	55.95(3)
Se(1)–Os(3)–Os(2)	54.88(2)
Os(1)–Se(1)–Os(3)	66.47(2)
Os(2)-Se(2)–Os(3)	68.97(3)
Se(1)–Os(2)–Os(3)	56.43(2)

2.5535(9) Å and Os(3)–Se(2) = 2.5525(10) Å] are longer than those to Os(1) and Os(2), which are in the range 2.4893(11)–2.5074(10) Å. The PPh$_3$ ligand is coordinated

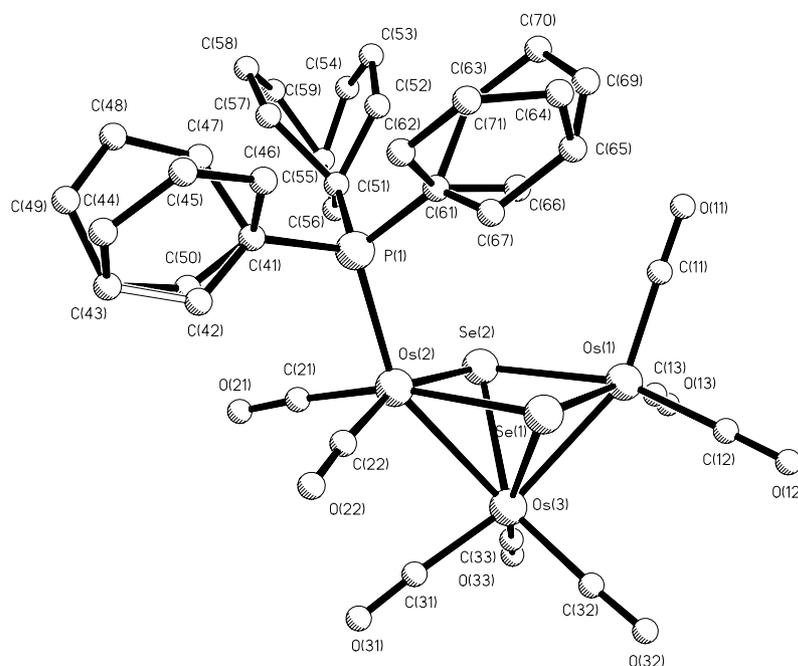Fig. 1. Solid-state molecular structure of [Os$_3$(μ$_3$-Se)$_2$(CO)$_8$(PPh$_3$)] (**2**) showing the two equally populated disordered arrangements of the phenyl groups of the PPh$_3$ ligand.

at Os(2), *trans* to an Os–Os bond. The Os–P bond distance of 2.310(2) Å is comparable to that in $[Os_3(\mu_3$-$S)_2(CO)_8(PMe_2Ph)]$ [2.298(3) Å] [12], and overall, the structure is similar to that of this sulfur analogue. Spectroscopic data for **2** indicate that it retains its solid-state structure in solution. As expected the $^{31}P\{^1H\}$ NMR spectrum of **2** is a singlet (δ 19.1) and the FAB mass spectrum contains the molecular ion peak at *m/z* 1216.

The solid-state molecular structure of $[Os_3(\mu_3$-$Se)$-$(\mu_3$-$CO)(CO)_7(PPh_3)_2]$ (**5**) (Fig. 2 and Table 3) consists of three mutually bonded Os atoms with a triply-bridging CO, seven terminal CO, a triply-bridging Se and two PPh_3 ligands. The Os–Os separations are only slightly different [Os(1)–Os(2) = 2.8418(3), Os(2)–Os(3) = 2.8752(3) and Os(1)–Os(3) = 2.8917(3) Å]. Each Os atom has a different co-ordination sphere and the phosphine ligands are co-ordinated inequivalently; P(1) is *trans* to Se(1) while P(2) is *cis* to Se(1). The tetrahedral Os_3Se core contains a symmetrically capped Se atom [Os(1)–Se(1) = 2.5140(6) Å, Os(2)–Se(1) = 2.5093(6) Å, Os(3)–Se(1) = 2.5101(6) Å]. In contrast, the μ_3-CO forms shorter bonds to the more electron-rich Os centers [Os(1)–C(8) = 2.193(6), Os(2)–C(8) = 2.154(6), Os(3)–C(8) = 2.141(6) Å].

The $^{31}P\{^1H\}$ NMR spectrum of **5** (CDCl$_3$ solution) at 223 K shows two equal intensity sharp singlets at δ 14.6 and -7.4, as expected for the molecular structure found in the crystal. However, at 323 K these signals have coalesced to a single resonance at δ 5.8 as a result of the interconversion of the two enantiomers **5a** and **5b** (Scheme 2). The calculated weighted-average signal would be at δ 3.6. Fig. 3 shows spectra over this temperature range with our best simulations using the program gNMR (Version 4.1, Cherwell Scientific, 1999) based on

Table 3
Selected bond distances (Å) and angles (°) for $[Os_3(\mu_3$-$Se)(\mu_3$-$CO)(CO)_7(PPh_3)_2]\cdot CH_2Cl_2$ (**5**)

|	
Os(1)–Os(3)	2.8917(3)
Os(2)–Os(3)	2.8752(3)
Os(1)–Os(2)	2.8418(3)
Os(1)–Se(1)	2.5140(6)
Os(2)–Se(1)	2.5093(6)
Os(3)–Se(1)	2.5101(6)
Os(1)–C(8)	2.193(6)
Os(2)–C(8)	2.154(6)
Os(3)–C(8)	2.141(6)
Os(2)–P(1)	2.3528(15)
Os(2)–P(2)	2.3557(15)
Os(2)–Os(1)–Os(3)	60.188(8)
Os(1)–Os(2)–Os(3)	60.765(8)
Os(2)–Os(3)–Os(1)	68.905(16)
Se(1)–Os(3)–Os(2)	55.041(14)
Se(1)–Os(2)–Os(1)	55.625(15)
Se(1)–Os(2)–Os(3)	55.064(15)
Se(1)–Os(1)–Os(3)	54.797(15)
Se(1)–Os(1)–Os(2)	55.470(15)
Se(1)–Os(3)–Os(1)	54.925(15)
P(2)–Os(3)–Os(1)	99.32(4)
P(1)–Os(2)–Os(3)	122.67(4)
P(1)–Os(2)–Os(1)	111.89(4)
C(8)–Os(1)–Os(3)	47.40(15)
C(8)–Os(2)–Os(3)	47.80(15)
C(8)–Os(3)–P(2)	133.32(16)
C(8)–Os(3)–Se(1)	89.19(17)
C(8)–Os(3)–Os(2)	48.16(16)
C(8)–Os(1)–Se(1)	87.96(16)
C(8)–Os(1)–Os(2)	48.58(16)
P(2)–Os(3)–Se(1)	97.53(4)
C(8)–Os(2)–Se(1)	88.94(16)
P(2)–Os(3)–Os(2)	151.11(4)
C(8)–Os(3)–Os(1)	48.91(17)
Os(2)–Se(1)–Os(1)	68.905(16)
Os(2)–Se(1)–Os(3)	69.895(17)
Os(3)–Se(1)–Os(1)	70.278(17)
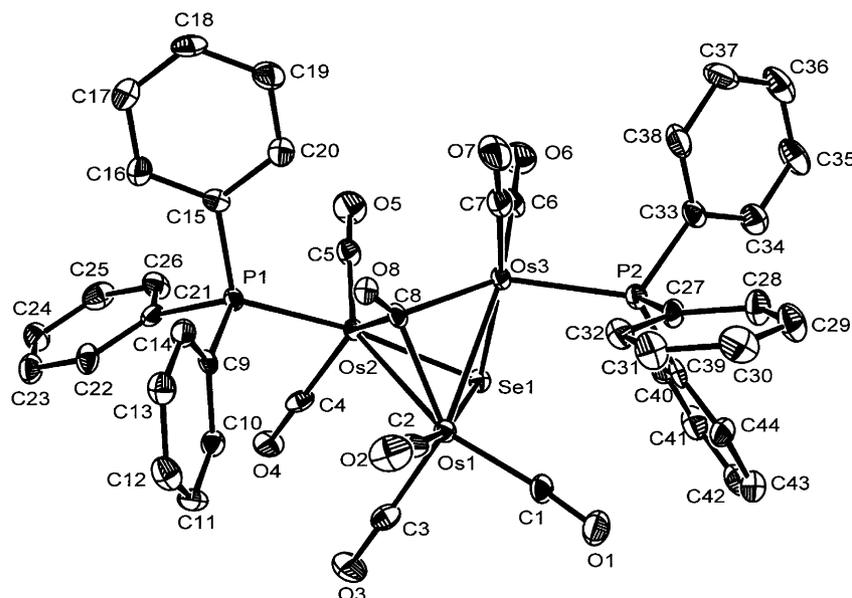
Fig. 2. Solid-state molecular structure of $[Os_3(\mu_3$-$Se)(\mu_3$-$CO)(CO)_7(PPh_3)_2]$ (**5**). Thermal ellipsoids are drawn at the 50% probability level.
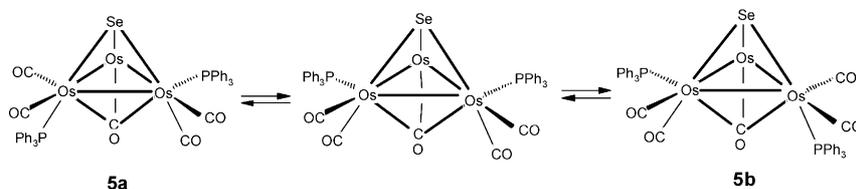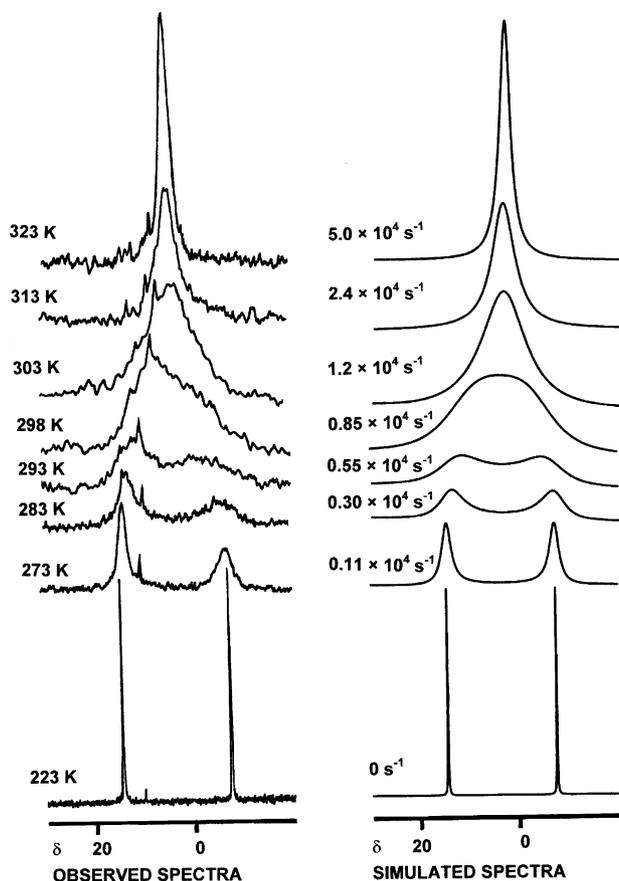
Scheme 2.

Fig. 3. Observed $^{31}P\{^1H\}$ NMR spectra (162 MHz) of cluster **5** in CDCl$_3$ solution and those simulated using the program gNMR. Spectra are annotated with temperatures and calculated rate coefficients.

site exchange between the two ^{31}P nuclei. Activation parameters were determined [$\Delta G^{\ddagger} = 50.4 \pm 0.8$ kJ mol^{-1} at 298 K; $\Delta H^{\ddagger} = 51.4 \pm 0.9$ kJ mol^{-1}; $\Delta S^{\ddagger} = 3.2 \pm 6.2$ J K^{-1} mol^{-1}] but these data should be considered with caution because of the unsymmetrical nature of the coalescing signals was not modelled. Although only one isomer is detected at 223 K, we believe that at higher temperatures there is a partial population of another isomer or isomers in equilibrium with the main isomer found in the crystal leading to distortion.

Scheme 2 is a possible mechanism. A symmetrical intermediate in the conversion of the enantiomers **5a** to **5b** such as that shown may be partially populated leading to the distortion of the coalescing signals. If this is correct, turnstile rotations of the two Os(CO)$_2$(PPh$_3$) groups would then not occur synchronously but as separate processes.

The molecular structure of **6** (Fig. 4 and Table 4) consists of an open triangular cluster of three Os atoms with eight terminal CO, two bridging OH and two PPh$_3$ ligands. The non-bonded Os(1)···Os(2) distance of 3.1197(2) Å is significantly longer than the Os(1)–Os(3) and Os(2)–Os(3) distances [2.8572(2) and 2.8585(2) Å]. The three metal atoms are electron-precise without the Os(1)–Os(2) bond. Both OH groups symmetrically span the open Os(1)···Os(2) edge and the Os-O distances [Os(1)–O(1) = 2.140(2), Os(1)–O(2) = 2.148(2), Os(2)–O(1) = 2.126(2) and Os(2)–O(2) = 2.141(2) Å] are comparable to the Os-O distances in other OH-bridged triosmium clusters: [Os$_3$(μ-H)(μ-OH)(CO)$_{10}$] [2.146(7), 2.136(7) Å] [14] [Os$_3$(μ-H)(μ-OH)(CO)$_9$(PMe$_2$Ph)] [2.135(5), 2.118(5) Å] [15] and [Os$_3$(μ-H)(μ-OH)(CO)$_8$(μ-dppm)] [2.157(8), 2.167(8) Å] [16]. We believe that the shortness of the non-bonded Os(1)···Os(2) edge is attributed to the presence of two light-atom bridges. A similar shortening of the open edges has been reported in [Ru$_3$-(μ-OH)$_2$(CO)$_8$(μ-BINAP)] [3.023(2) Å] [17] and [Ru$_3$(μ-OH)$_2$(CO)$_8$$\{\mu$-$\eta^2$-Fe(C$_5H_4PPh_2$)$_2\}$] [3.0358(8) Å] [18]. The good quality X-ray data allowed us to locate the hydroxy H-atoms. One is *exo* and the other *endo* with respect to the Os(CO)$_4$ group. Although this makes the OH bridges inequivalent there is no evidence for this in positions of the oxygen atoms. The origin of the hydroxy ligands in **6** may be dioxygen or more likely water and there are examples of the formation of OH ligands in triosmium and triruthenium clusters from water or dioxygen [19–21].

In spite of their inequivalence in the solid-state structure, the OH protons in **6** give a single triplet at δ −0.18 (J_{PH} = 3.6 Hz) in the ^1H NMR spectrum. The high-field chemical shift and J_{PH} for the OH protons in **6** are in the range of values found for other structurally characterized OH-bridged trimetallic clusters: [Ru$_3$(μ-OH)$_2$(CO)$_8$-(μ-BINAP)] [δ −1.48, J_{PH} = 4.0 Hz] [17], [Ru$_3$(μ-OH)$_2$-(CO)$_8$$\{\mu$-$\eta^2$-Fe(C$_5H_4PPh_2$)$_2\}$] [$\delta$ −0.68, J_{PH} = 4.0 Hz] [18], [Os$_3$(μ-H)(μ-OH)(CO)$_8$(μ-dppm)] [δ 0.44, J_{PH} = 4.3 Hz] [16] and [Os$_3$(μ-OH)(μ-MeOCO)(CO)$_9$(PPh$_3$)] [δ −1.98, J_{PH} = 4.8 Hz] [22]. The $^{31}P\{^1H\}$ NMR singlet at δ 11.6 indicates that the ^{31}P nuclei are equivalent. The FAB MS shows the parent ion at m/z 1354 and IR spectrum contains a broad absorption at 3505 cm^{-1}, assignable to ν(OH).
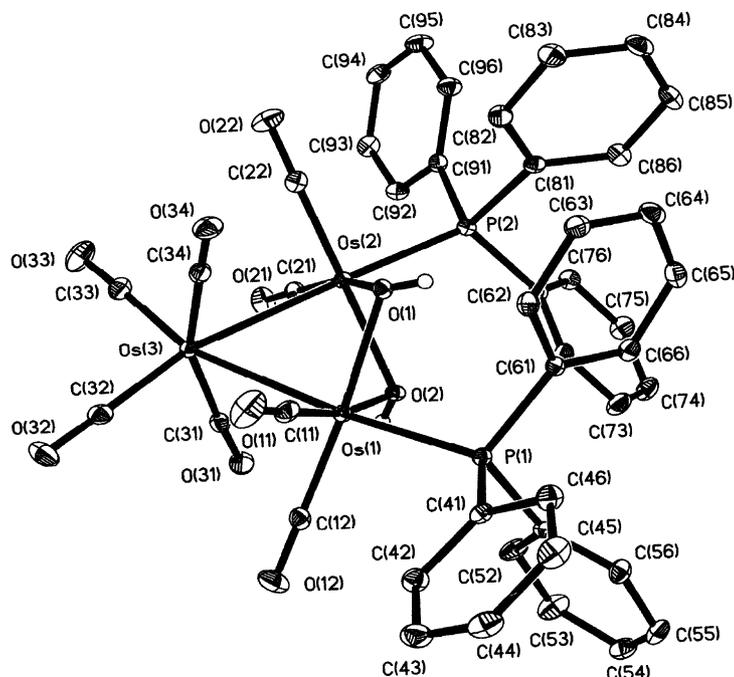
Fig. 4. Solid-state molecular structure of $[Os_3(\mu\text{-}OH)_2(CO)_8(PPh_3)_2]$ (**6**). Thermal ellipsoids are drawn at the 50% probability level.

The corresponding treatment of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3P{=}S$ at room temperature gives five new compounds $[Os_3(\mu_3\text{-}S)_2(CO)_8(PPh_3)]$ (**7**), $[Os_3(\mu_3\text{-}Se)(\mu\text{-}$

Table 4
Selected bond distances (Å) and angles (°) for $[Os_3(\mu\text{-}OH)_2(CO)_8(PPh_3)_2]$ (**6**)

Os(1)–Os(3)	2.8572(2)
Os(2)–Os(3)	2.8585(2)
Os(1)–Os(2)	3.1197(2)
Os(1)–O(1)	2.140(2)
Os(2)–O(1)	2.126(2)
Os(1)–O(2)	2.148(2)
Os(1)–P(1)	2.3682(8)
Os(2)–P(2)	2.3864(8)
Os(2)–O(2)	2.141(2)
Os(2)–O(2)–Os(1)	93.34(9)
Os(2)–O(1)–Os(1)	93.99(10)
Os(1)–Os(3)–Os(2)	66.160(5)
Os(3)–Os(2)–Os(1)	56.901(4)
C(12)–Os(1)–P(1)	94.05(11)
O(1)–Os(1)–Os(3)	81.64(7)
O(2)–Os(1)–P(1)	93.46(6)
O(1)–Os(2)–P(2)	98.28(7)
O(1)–Os(2)–O(2)	73.25(9)
O(1)–Os(1)–P(1)	92.67(7)
O(1)–Os(1)–O(2)	72.84(9)
C(11)–Os(1)–P(1)	91.95(11)
O(2)–Os(1)–Os(3)	84.92(6)
P(1)–Os(1)–Os(3)	118.53(2)
C(21)–Os(2)–P(2)	94.02(11)
C(22)–Os(2)–P(2)	90.70(11)
O(2)–Os(2)–Os(3)	85.02(6)
O(2)–Os(2)–Os(3)	85.02(6)
O(1)–Os(2)–Os(3)	81.83(7)
O(2)–Os(1)–Os(3)	84.92(6)
O(2)–Os(2)–P(2)	93.49(6)

$CO)_2(CO)_7(PPh_3)]$ (**8**), $[Os_3(\mu_3\text{-}S)(\mu\text{-}CO)(CO)_7(PPh_3)_2]$ (**9**), $[Os_3(\mu_3\text{-}S)_2(CO)_7(PPh_3)_2]$ (**11**) and **6** in 9%, 29%, 15%, 8% and 5% yields, respectively, in addition to the known compound **4** in 14% yield (Scheme 1).

The solid-state molecular structure of compound **8** (Fig. 5 and Table 5) consists of a closed Os_3 triangle with three CO ligands bonded to each Os atom, a $\mu_3\text{-}S$ ligand and a PPh_3 ligand. The Os(2)–Os(3) bond [2.7531(3) Å] is the shortest while the Os(1)–Os(2) bond *trans* to PPh_3 [2.8214(4) Å] is the longest. Two of the three CO ligands attached to Os(1) are semi-bridged to an adjacent Os centre with Os(2)···C(11) and Os(3)···C(13) distances of 2.682 and 2.581 Å, respectively, and O(13)–C(13)–Os(1) and O(11)–C(11)–Os(1) angles of 159.8(5)° and 163.7(4)°, respectively. The semibridging mode is due to the sterically congested and electron-rich nature of Os(1). The μ_3-sulfido ligand is bonded unsymmetrically [Os(2)–S(1) = 2.3911(11), Os(1)–S(1) = 2.4283(12) and Os(3)–S(1) = 2.4041(12) Å] but the average Os-S distance [2.411(2) Å] is comparable to those found for the μ_3-S ligands in $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_7(\mu\text{-}dppm)]$ [2.393(4) Å] [23], $[Os_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9]$ [2.378(3) Å] [24], $[Os_4(\mu_3\text{-}S)(CO)_{12}]$ [2.381(3) Å] [25] and $[Os_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7(\mu\text{-}dppm)]$ [2.5123(14)-2.5302(15) Å] [10]. The PPh_3 ligand is coordinated to Os(1) in an equatorial position. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ 8.0 and the MS shows the molecular ion at m/z 1118.

By analogy with the formation of $[Os_6(\mu_3\text{-}Se)_4(CO)_{12}(\mu\text{-}dppm)_2]$ [10] by treatment of $[Os_3(\mu_3\text{-}Se)_2(CO)_7(\mu\text{-}dppm)]$ with Me_3NO, and $[Ru_6(\mu_3\text{-}Se)_4(CO)_{12}(\mu\text{-}dppm)_2]$ [5b] by treatment of $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(\mu\text{-}dppm)]$ with Me_3NO, it was considered that the reaction of **2** with
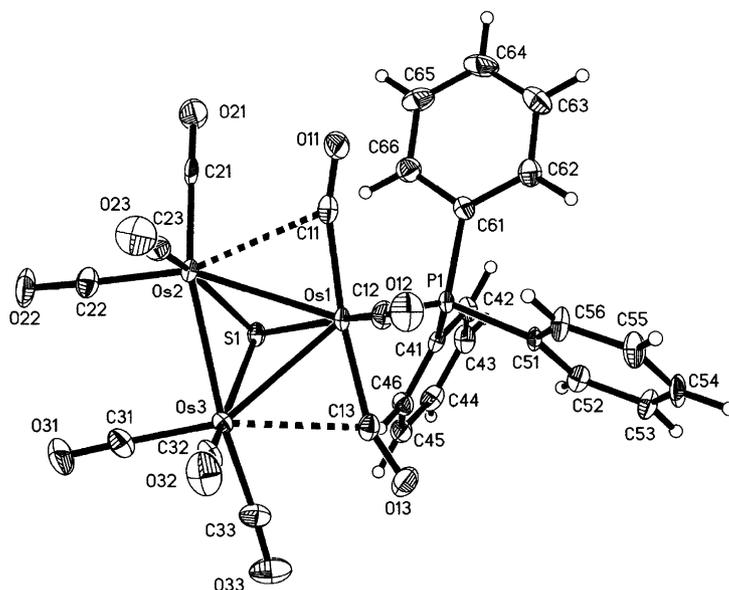
Fig. 5. Solid-state molecular structure of $[Os_3(\mu_3\text{-}S)(\mu\text{-}CO)_2(CO)_7(PPh_3)]$ (**8**). Thermal ellipsoids are drawn at the 50% probability level.

Table 5
Selected bond distances (Å) and angles (°) for $[Os_3(\mu_3\text{-}S)(\mu\text{-}CO)_2(CO)_7(PPh_3)]$ (**8**)

|	
Os(1)–Os(3)	2,.7948(3)
Os(2)–Os(3)	2.7531(3)
Os(1)–Os(2)	2.8214(4)
Os(1)–S(1)	2.4283(12)
Os(2)–S(1)	2.3911(11)
Os(3)–S(1)	2.4041(12)
Os(1)–P(1)	2.3727(12)
Os(1)–C(11)	1.958(5)
Os(2)–C(11)	2.682
Os(1)–C(13)	1.968(5)
Os(3)–C(13)	2.5816(5)
Os(3)–Os(1)–Os(2)	58.707(7)
Os(3)–Os(2)–Os(1)	60.164(7)
Os(2)–Os(3)–Os(1)	61.129 (7)
S (1)–Os(1)–Os(3)	54.26(3)
S (1)–Os(2)–Os(3)	55.18(3)
S (1)–Os(2)–Os(1)	54.78(3)
S(1)–Os(1)–Os(2)	53.56(3)
S(1)–Os(3)–Os(1)	55.07(3)
S (1)–Os(3)–Os(2)	54.74(3)
P(1)–Os(1)–Os(3)	133.03(3)
P(1)–Os(1)–Os(2)	136.22(3)
P(1)–Os(1)-S (1)	96.27(4)
Os(2)–S(1)–Os(3)	70.08(3)
Os(3)-S (1)–Os(1)	70.66(3)
Os(2)-S (1)–Os(1)	71.66(3)
O(11)–C(11)–Os(1)	163.7(4)
O(13)–C(13)–Os(1)	159.8(5)

Me_3NO might give the corresponding hexanuclear compound $[Os_6(\mu_3\text{-}Se)_4(CO)_{14}(PPh_3)_2]$ (**12**). Indeed, treatment of $[Os_3(\mu_3\text{-}Se)_2(CO)_8(PPh_3)]$ (**2**) with Me_3NO in toluene at 50 °C gave a dark green hexanuclear cluster $[Os_6(\mu_3\text{-}Se)_4(CO)_{14}(PPh_3)_2]$ (**12**) and a trinuclear cluster $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)(NMe_3)]$ (**13**) in 46% and 32%

yields, respectively (Scheme 3). Cluster **12** has been characterized by elemental analysis, infrared, ^{1}H NMR, ^{31}P NMR and mass spectra. The singlet at δ 5.9 in the ^{31}P NMR spectrum indicates equivalent ^{31}P nuclei. The FAB MS shows a molecular ion peak at m/z 2374 corresponding to $[Os_6(\mu_3\text{-}Se)_4(CO)_{14}(PPh_3)_2]$. We propose the structure for **12** as shown in Scheme 3.

Compound **13** is formed by oxidation of CO by Me_3NO to give the corresponding NMe_3 derivative. This reaction is similar to the reported formation of $[FeCo_3(\mu\text{-}H)(CO)_{11}(NMe_3)]$ and $[FeCo_3(\mu\text{-}H)(CO)_{10}(PPh_2H)(NMe_3)]$ from the reaction of Me_3NO with $[FeCo_3(\mu\text{-}H)(CO)_{12}]$ and $[FeCo_3(\mu\text{-}H)(CO)_{11}(PPh_2H)]$, respectively. We grew X-ray quality crystals of **13** but were unable to collect diffraction data because these are unstable. In addition to the usual Ph resonances in the ^{1}H NMR spectrum, a singlet at δ 2.80 is assigned to the NMe_3 ligand. The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 13.77. The FAB MS shows a molecular ion peak at m/z 1247 corresponding to $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)(NMe_3)]$.

The reaction of **2** with PPh_3 and Me_3NO at room temperature results in substitution of one CO ligand to produce $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ (**10**) (Scheme 4) in 44% yield. Compound **10** can also be obtained from the reaction of **1** with PPh_3 and Me_3NO. Single crystals of **10** for X-ray diffraction were unavailable. The IR spectrum of **10** in CH_2Cl_2 is similar to that of $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$, obtained from the reaction of $[Ru_3(CO)_{12}]$ and $PPh_3{=}Se$ and characterized by X-ray diffraction [7a]. The two phosphorus atoms in **10** are inequivalent, since the ^{31}P{^{1}H} NMR spectrum shows singlets at δ 25.7 and 13.5. The formation of **10** is also confirmed by its FAB mass spectrum (m/z 1450).
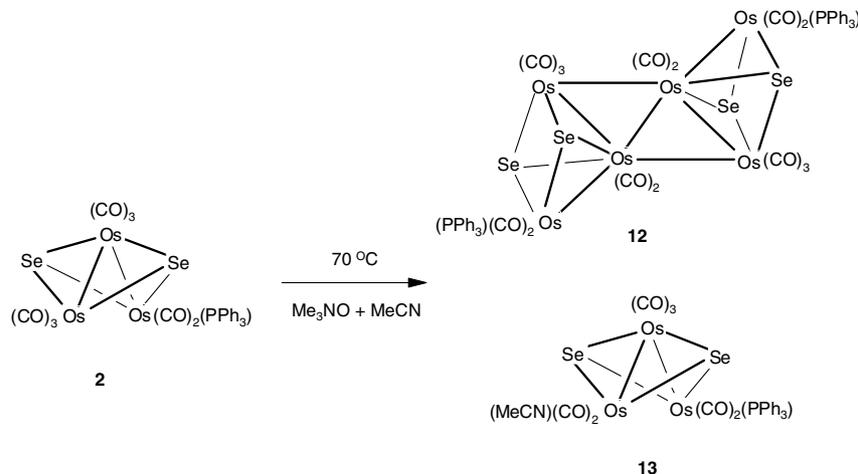
Scheme 3.
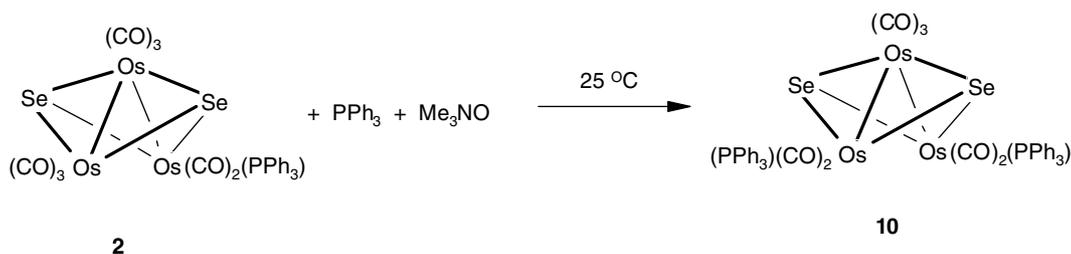
Scheme 4.

Finally, the treatment of **3** with Se in refluxing toluene gives compound **2** in 38% yield.

In summary, in contrast to the reaction between PPh₃=Se and [Ru₃(CO)₁₂], the reaction of [Os₃(CO)₁₀(MeCN)₂] with PPh₃=Se gives six products: three (**2**, **3** and **5**) are monosubstituted phosphine derivatives containing capping Se ligands, two are phosphine-only derivatives (**4** and **6**) and the unsubstituted capped Se compound **1** is also formed. Notably [Os₃(μ₃-Se)₂(CO)₇(PPh₃)₂], the osmium analogue of the open triangular Ru₃Se₂ *nido* cluster [Ru₃(μ₃-Se)₂(CO)₇(PPh₃)₂] which was formed in 92% yield, was not detected from the room temperature reaction between PPh₃=Se and [Os₃(CO)₁₀(MeCN)₂]. This might be due to the relatively high substitutional lability of the ruthenium carbonyl clusters compared with that of osmium. As shown in Scheme 1 the reaction of Ph₃P=S with [Os₃(CO)₁₀(MeCN)₂] takes a different course in terms of the formation of capping sulfido compounds. The details of the initial reaction are still unresolved but it is likely that Os-S or Os–Se bonds are formed initially to give [Os₃(CO)₁₀(MeCN)(Ph₃PE)] which looses MeCN to give [Os₃(μ-EPPh₃)(CO)₁₀]. Cleavage of the P=E bond would lead to free PPh₃ and further reaction with PPh₃=E would lead to the disulfido and diselenido products. Note that other authors reported the formation of only **3** and [Os₃(CO)₁₁(PPh₃)] with

Ph₃P=Se [11]. They used identical reaction conditions and we are unable to account for their different observations.

3. Experimental

3.1. Reaction of [Os₃(CO)₁₀(MeCN)₂] with Ph₃P=Se

A dichloromethane solution (50 mL) of [Os₃(CO)₁₀(MeCN)₂] (0.225 g, 0.241 mmol) and Ph₃P=Se (0.165

g, 0.482 mmol) was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2 and separated by TLC on silica. Elution with hexane/CH_2Cl_2 (10:3 by volume) produced six bands. The first and fourth bands gave the known compounds $[Os_3(\mu_3\text{-}Se)_2(CO)_9]$ (**1**) (0.028 g, 12%) and 1,2-$[Os_3(CO)_{10}(PPh_3)_2]$ (**4**) (0.023 g, 7%). The third band gave the recently reported cluster $[Os_3(\mu_3\text{-}Se)(\mu\text{-}CO)_2(CO)_7(PPh_3)]$ (**3**) (0.042 g, 15%) [11] as orange crystals from hexane/CH_2Cl_2 at -4 °C (Calc. for $C_{27}H_{15}O_9Os_3PSe$: C, 27.86; H, 1.30. Found: C, 27.99; H, 1.42%). IR (v(CO), CH_2Cl_2): 2079s, 2039vs, 2019m, 1990s(br) and 1900br (KBr) cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 8.1 (s); mass spectrum: m/z 1164. The second band gave $[Os_3(\mu_3\text{-}Se)_2(CO)_8(PPh_3)]$ (**2**) (0.033 g, 10%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at -4 °C (Calc. for $C_{26}H_{15}O_8Os_3PSe_2$: C, 25.70; H, 1.25. Found: C, 25.95; H, 1.35%). IR (v(CO), CH_2Cl_2): 2079s, 2046vs, 2015s, 2000s, 1956w cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 19.1(s); mass spectrum: m/z 1216. The fifth band gave $[Os_3(\mu_3\text{-}Se)(CO)_7(\mu_3\text{-}CO)(PPh_3)_2]\cdot CH_2Cl_2$ (**5**) (0.057 g, 16%) as yellow crystals from hexane/CH_2Cl_2 at -4 °C (Calc. for $C_{45}Cl_2H_{32}O_8Os_3P_2Se$: C, 36.44; H, 2.18. Found: C, 36.65; H, 2.29%). IR (v(CO), CH_2Cl_2): 2064s, 2019s, 2002vs, 1959w, 1942w cm^{-1} plus 1610m (KBr) cm^{-1}; ^1H NMR (CDCl$_3$): δ 7.38 (m, 30H), 5.32 (s, 2H, CH_2Cl_2); $^{31}P\{^1H\}$ NMR (-50 °C, CDCl$_3$): δ 14.6(s), 7.4(s); mass spectrum: m/z 1398. The slowest moving band gave $[Os_3(\mu\text{-}OH)_2(CO)_8(PPh_3)_2]$ (**6**) (0.024 g, 7%,) as pale yellow crystals after recrystallization from hexane/CH_2Cl_2 at -4 °C (Calc. for $C_{44}H_{32}O_{10}Os_3P_2$: C, 39.05; H, 2.39. Found C, 39.14; H, 2.48%). IR (v(CO), CH_2Cl_2): 2062s, 2002vs, 1983s, 1961w, 1923m plus 3505br (KBr) cm^{-1}; ^1H NMR (CDCl$_3$): δ 7.25 (m, 30H), -0.18 (t, 2H, $J = 3.6$ Hz); $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 11.6 (s); mass spectrum: m/z 1354.

3.2. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $Ph_3P=S$

A similar reaction to that above of $[Os_3(CO)_{10}(MeCN)_2]$ (0.225 g, 0.241 mmol) and $Ph_3P=S$ (0.142 g, 0.483 mmol) in CH_2Cl_2 (50 mL) for 48 h at room temperature followed by similar TLC separation produced six bands which gave the following compounds in order of elution: $[Os_3(\mu_3\text{-}S)_2(CO)_8(PPh_3)]$ (**7**) (0.024 g, 9%) (Calc. for $C_{26}H_{15}O_8Os_3PS_2$: C, 27.85; H, 1.35. Found: C, 28.05; H, 1.42%). IR (v(CO), CH_2Cl_2): 2079s, 2045vs, 2015s, 2000s, 1956m cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 19.15(s); mass spectrum: m/z 1122. $[Os_3(\mu_3\text{-}S)(\mu\text{-}CO)_2(CO)_7(PPh_3)]$ (**8**) (0.078 g, 29%) as (Calcd. for $C_{27}H_{15}O_9Os_3PS$: C, 29.03; H, 1.35. Found: C, 30.15; H, 1.52%). IR (v(CO), CH_2Cl_2): 2079s, 2040vs, 2023m, 1990s(br), 1902w, 1886w cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 8.02 (s); mass spectrum: m/z 1118. $[Os_3(CO)_{10}(PPh_3)_2]$ (**4**) (14%). $[Os_3(CO)_7(\mu_3\text{-}CO)(\mu_3\text{-}$

S)(PPh$_3$)$_2$] (**9**) (0.049 g, 15%) (Calc. for $C_{44}H_{30}O_8Os_3P_2S$: C, 39.10; H, 2.24. Found: C, 39.25; H, 2.34%). IR (v(CO), CH_2Cl_2): 2062s, 2019s, 2001vs, 1958w, 1942w cm^{-1}; IR (v(CO), KBr): 1610m cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 9.25 (s); mass spectrum: m/z 1352. $[Os_3(\mu_3\text{-}S)_2(CO)_7(PPh_3)_2]$ (**11**) (0.025 g, 8%). (Calc. for $C_{43}H_{30}O_7Os_3P_2S_2$: C, 38.1; H, 2.23. Found: C, 38.26; H, 2.38%). IR (v(CO), CH_2Cl_2): 2046vs, 2014vs, 2004vs, 1965vs, 1934s cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 25.62(s), 12.95(s); mass spectrum: m/z 1356. $[Os_3(\mu\text{-}OH)_2(CO)_8(PPh_3)_2]$ (**6**) (0.019 g, 5%).

3.3. Thermolysis of compound **2** in the presence of trimethylamine-N-oxide

On heating solution of **2** (0.015 g, 0.012 mmol) and $Me_3NO\cdot 2H_2O$ (0.003 g, 0.039 mmol) in toluene (20 mL) at 50 °C for 1 h, the color changed from yellow to green. The solvent was pumped off and the residue chromatographed by TLC on silica. Elution with hexane/CH_2Cl_2 (2:1 by volume) gave three bands. The faster moving band ($R_f = 0.82$) gave the unreacted starting material **2** (0.002 g). Second band ($R_f = 0.61$) afforded $[Os_6(\mu_3\text{-}Se)_4(CO)_{14}(PPh_3)_2]$ (**12**) (0.007 g, 46%) (Calc. for $C_{50}H_{30}O_{14}Os_6P_2Se_4$: C, 25.30; H, 1.27. Found: C, 26.12; H, 1.45%). IR (v(CO), CH_2Cl_2): 2066vs, 2023s, 2008s, 1961m, 1923w, 1907w cm^{-1}; ^1H NMR (CD$_2$Cl$_2$): δ 7.64(m), $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 25.9 (s); mass spectrum: m/z 2374. The slower moving band ($R_f = 0.46$) gave $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)(NMe_3)]$ (**13**) (0.005 g, 32%) (Calc. for $C_{28}H_{24}O_7Os_3PSe_2N$: C, 26.99; H, 1.94; N, 1.13. Found: C, 27.25; H, 2.15; N, 1.34%). IR (v(CO), CH_2Cl_2): 2044s, 1996vs, 1976sh, 1954m, 1886vw cm^{-1}; ^1H NMR (CD$_2$Cl$_2$): 7.58(m), 7.45(m), 2.80(s); δ $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): δ 13.77 (s); mass spectrum: m/z 1247.

3.4. Reaction of cluster **2** with PPh_3

$Me_3NO\cdot 2H_2O$ (0.003 g, 0.040 mmol) was added to a CH_2Cl_2 solution (25 mL) of **2** (0.023 g, 0.019 mmol) and PPh_3 (0.010 g, 0.038 mmol) and the reaction mixture was stirred at room temperature for 2 h. The solution was filtered through a short silica column (4 cm) to remove the excess of Me_3NO. The solvent was removed at reduced pressure and the residue chromatographed by TLC on silica. Elution with hexane/CH_2Cl_2(3:2 by volume) gave two bands. The first gave unconsumed **2** (0.003 g) while the second band gave $[Os_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ (**10**) (0.012 g, 44%) as orange crystals after recrystallyzation from hexane/CH_2Cl_2 (Calc. for $C_{43}H_{30}O_7Os_3P_2Se_2$: C, 35.64; H, 2.09. Found: C, 35.78; H, 2.24%). IR (v(CO), CH_2Cl_2): 2046vs, 2014s, 2000m, 1965m, 1934s cm^{-1}; $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 25.7 (s), 13.5 (s); mass spectrum: m/z 1450.

3.5. Reaction of cluster 1 with PPh₃

Me₃NO · 2H₂O (0.005 g, 0.067 mmol) was added to a dichloromethane solution (25 mL) of **1** (0.027 g, 0.028 mmol) and PPh₃ (0.015 g, 0.057 mmol) (0.005 g, 0.067 mmol). The solution was stirred at room temperature for 3 h, filtered through a short silica column and the solvent was removed under reduced pressure. Chromatography of the residue by TLC on silica gel, eluting with hexane/CH_2Cl_2 gave a single band which afforded compound **2** (0.010 g, 30%).

3.6. Reaction of 3 with elemental selenium

A mixture of **3** (0.020 g, 0.018 mmol) and black selenium (0.040 g, 0.037 mmol) in toluene (25 mL) was heated to reflux for 2 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica. Elution with hexane/CH_2Cl_2 (10:3 by volume) gave a single band which afforded **2** (0.008 g, 38%).

3.7. X-ray crystallography for compounds 2, 5, 6 and 8

Intensity data for **5** were obtained using a Bruker Nonius Kappa CCD diffractometer using Mo Kα radiation. Data collection and processing were carried out by using the programs COLLECT [27] and DENZO [28]. Data were corrected for absorption effects using SORTAV [29]. Data for complexes **2**, **6** and **8** were obtained on a Bruker SMART APEX CCD diffractometer using Mo Kα radiation. Data reduction and integration were carried out with SAINT+ and absorption corrections using SADABS [30].

The structures were solved by direct methods and refined on F^2 by full-matrix least-squares (SHELXTL PLUS V6.10) [30] using all unique data. For all structures, the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions (riding model) except for the OH hydrogens in **6** which were located and their positions refined. The three phenyl rings in **2** were disordered over two sets of orientations, each 50% populated.

Acknowledgements

Appendix A. Supplementary material

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