

The reaction of diphenyl ditelluride with triosmium clusters

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The reaction of Ph_2Te_2 with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ at room temperature gave the cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-TePh})_2$ **1**, in which one TePh bridges an “open” $\text{Os} \cdots \text{Os}$ edge and another bridges an $\text{Os}-\text{Os}$ bond. Thermolysis of **1** in refluxing cyclohexane led to isomerisation of **1** to **2**, in which both TePh moieties bridge the same “open” $\text{Os} \cdots \text{Os}$ edge; thermolysis of **2** in refluxing octane led to the cluster $\text{Os}_3(\text{CO})_9(\mu_3\text{-Te})_2$ **3**. The reaction of Ph_2Te_2 with $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$, on the other hand, resulted in a complex mixture of products among which were the clusters $\text{Os}_3\text{H}_2(\text{CO})_{10}(\mu\text{-TePh})_2$ **4** and $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-TePh})$ **5**; cluster **5** was also obtained in moderate yield from the reaction with $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-CO})]^-$. Cluster **4** comprises a four-membered Os_2Te_2 ring, with an $\text{H}(\text{CO})_4$ fragment attached to one of the osmium atoms; it decomposed on silica gel to afford the dinuclear compound $[\text{OsH}(\text{CO})_3(\text{TePh})]_2$ **6**. The clusters **1–6** have all been characterised by single crystal X-ray crystallography.

Introduction

One very important synthetic methodology in cluster chemistry is that of ligand-assisted synthesis. Within this genre, a very powerful method utilises the lone pair of a bridging or capping chalcogen to forge a linkage between the chalcogen-containing transition metal cluster and another metal fragment or cluster.¹ Although an extensive chemistry for osmium clusters containing sulfur ligands has been developed, that for the corresponding selenium- and, particularly, tellurium-containing clusters is scarce.² This is also to be contrasted with an extant chemistry that has been developed for iron–tellurium clusters.³

To date, only a handful of osmium–tellurium clusters are known. The earliest report was apparently that involving the reaction of $\text{Os}_3(\text{CO})_{12}$ with tellurium powder from which were isolated the clusters $\text{Os}_3(\text{CO})_9(\mu_3\text{-Te})_2$ and $\text{Os}_4(\mu\text{-H})_2(\text{CO})_{12}(\mu_4\text{-Te})_2$.⁴ Most of the reported syntheses involved the acetonitrile-substituted triosmium clusters $\text{Os}_3(\text{CO})_{12-n}(\text{CH}_3\text{CN})_n$ ($n = 1$ or 2). For example, $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ reacted with H_2Te to give $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-Te})$ and with $\text{Fe}_2\text{Te}_2(\text{CO})_6$ to afford $\text{Fe}_2\text{Os}_3(\text{CO})_{17}(\mu_4\text{-Te})(\mu_3\text{-Te})$,^{5,6} while reaction with benzo[*b*]tellurophene or tellurophene led to Te–C bond cleavage to give clusters containing an opened tellurophene bridge.⁷ An interesting reaction reported was that of $\text{Os}_3(\text{CO})_{11}(\text{CH}_3\text{CN})$ with $\text{Te}(\text{CF}_3)_2$ in cyclohexane, in which the CF_3 groups were replaced to give the cyclohexyl analogue $\text{Os}_3(\text{CO})_{11}(\text{TeCy}_2)$.⁸ Salt elimination has also been utilised, as in the reaction of the anionic cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-CO})]^-$ with $(p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2$ to give $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-TeC}_6\text{H}_4\text{OMe-}p)$; on thermolysis, this product gave the cluster $\text{Os}_3(\text{CO})_9(\mu_3\text{-Te})_2$.^{6b,9}

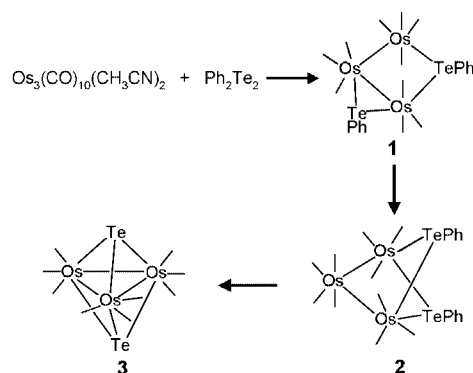
Given the paucity of information reported on the chemistry of tellurium-containing osmium clusters, and in line with our general interest in transition metal–main group element mixed-metal clusters, we have embarked on an exploration of the chemistry of this class of clusters. We have chosen Ph_2Te_2 as our tellurium precursor in this initial foray because diorganyl ditellurides are among the most readily available and easy to handle organotellurium compounds.¹⁰ In addition, some of the corresponding chemistry with the diselenide system is well established.¹¹ Thus, it has been found that $\text{Os}_3(\text{CO})_{12-n}(\text{CH}_3\text{CN})_n$ ($n = 1$ or 2) reacted with R_2Se_2 ($\text{R} = \text{Ph}$ or Me) to afford $\text{Os}_3(\text{CO})_{10}(\mu\text{-SeR})_2$ **1a**, in which one SeR moiety bridged an $\text{Os}-\text{Os}$ bond and the other an open $\text{Os} \cdots \text{Os}$ edge; it was believed that the reaction proceeded *via* an intermediate con-

taining a $\mu\text{-Se}_2\text{R}_2$ fragment. Thermolysis of **1a** was also reported to yield at least four products among which was an isomer of **1a** in which both the SeR moieties bridged the same $\text{Os} \cdots \text{Os}$ edge.

Results and discussion

Reaction with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$

The reaction of Ph_2Te_2 with $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ at room temperature was rapid, and gave the cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-TePh})_2$ **1** as the major product. Cluster **1** comprises a four-membered Os_3Te ring with the remaining TePh moiety bridging one of the $\text{Os}-\text{Os}$ edges. A second, minor product was also isolated, and it turned out to be an isomer of **1** in which both the TePh bridges are along the same open $\text{Os} \cdots \text{Os}$ edge, *i.e.* with a structure analogous to that of the corresponding bis(alkoxy) clusters $\text{Os}_3(\text{CO})_{10}(\text{OR})_2$.¹² On refluxing in cyclohexane, **1** isomerised to **2**, thus pointing to isomerisation of **1** as the source of **2** in the reaction. Thermolysis of cluster **2** in refluxing octane in turn gave the previously reported cluster $\text{Os}_3(\text{CO})_9(\mu_3\text{-Te})_2$ **3**. The sequence of reaction (Scheme 1) is thus quite similar to that for

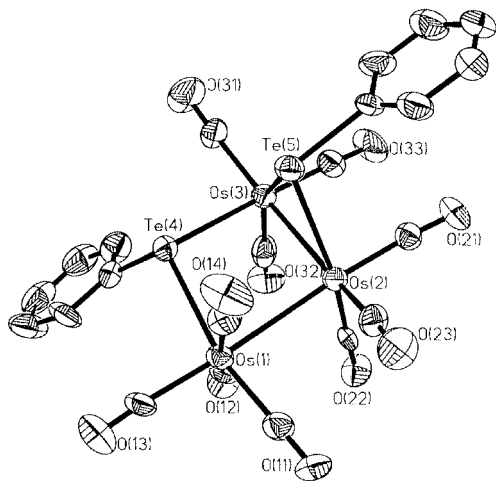


Scheme 1 Reaction of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ with Ph_2Te_2 .

the selenium system.¹¹ In contrast to the selenium system, however, we did not detect any evidence of an intermediate with an intact Te–Te bond in the formation of **1**. In addition, the thermolysis of **1** and **2** also proceeded more smoothly than with the selenium analogues; the isomerisation of **1** to **2** in

Table 1 Selected bond lengths (Å) and angles (°) for Os₃(CO)₁₀-(μ-SePh)₂ (E = Se or Te)

	1 (E = Te)	E = Se ^{11a}
Os(1)···Os(3)	4.143(1)	3.988(1)
Os(1)–Os(2)	2.9971(6)	2.947(1)
Os(2)–Os(3)	2.8816(6)	2.827(2)
Os(1)–E(4)	2.7190(9)	2.553(2)
Os(3)–E(4)	2.7274(9)	2.562(2)
Os(2)–E(5)	2.6976(9)	2.532(2)
Os(3)–E(5)	2.6886(10)	2.531(2)
Os(1)–Os(2)–Os(3)	85.59(2)	87.3(1)
E(4)–Os(1)–Os(2)	81.80(2)	81.8(1)
E(4)–Os(3)–Os(2)	83.82(2)	84.0(1)
Os(1)–E(4)–Os(3)	99.04(3)	102.5(1)
Os(2)–E(5)–Os(3)	64.69(2)	67.9(1)

**Fig. 1** An ORTEP diagram of cluster **1** (50% thermal ellipsoids, as in all figures).

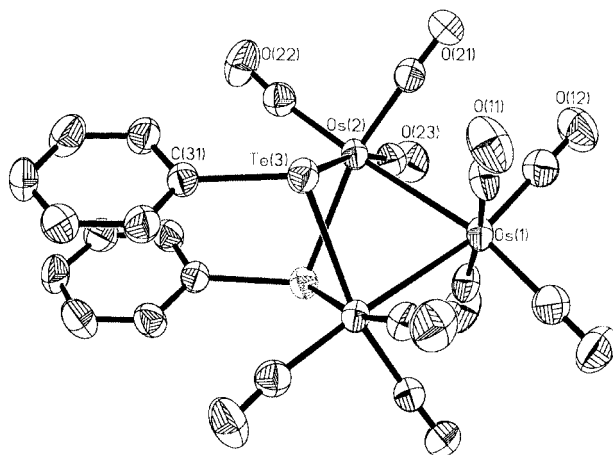
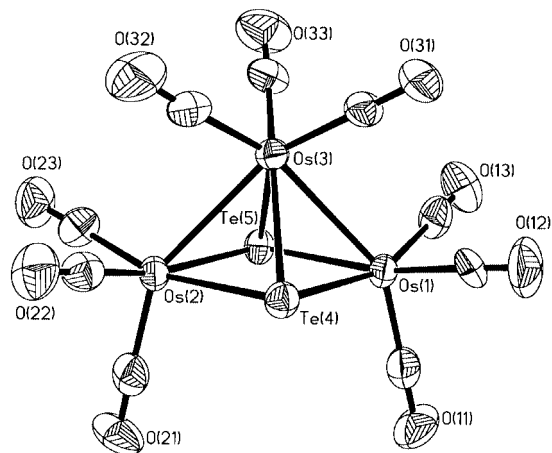
cyclohexane was essentially quantitative, as observed by IR spectroscopy.

An ORTEP¹³ plot of cluster **1** is given in Fig. 1, and selected molecular parameters, together with those for the selenium analogue, Os₃(CO)₁₀(μ-SePh)₂,^{11a} are listed in Table 1. Structurally, the two clusters are very similar; both possess two EPh (E = Se or Te) groups, one bridging an Os–Os bond and the other the open Os···Os edge, with the two phenyl groups directed away from the metal core. The two bridging EPh groups are tilted towards each other, but while the Te atom bridging the open edge is 0.800(1) Å above the plane of the Os₃ group, the EPh group bridging the closed Os–Os edge is oriented almost perpendicular to the Os₃ plane; the dihedral angle between the Os(1)Os(2)Os(3) and Os(2)Te(5)Os(3) planes is 98.0(1)°. The differences in bond parameters between the two clusters can largely be attributed to the difference in the covalent radii of the chalcogens (1.17 and 1.37 Å for Se and Te, respectively).¹⁴

The molecule of cluster **2** has crystallographic twofold symmetry. It is structurally similar to the OMe analogue in that both the TePh groups are bridging the open Os···Os edge (Fig. 2).¹² The most interesting feature here is that the two phenyl rings are arranged *syn* to each other and in an almost eclipsed stacking conformation; the angle between the centroid–centroid vector and the ring plane is about 4°. The phenyl ring centroids are 3.774 Å apart, compared to the Te···Te distance of 3.670 Å, and the dihedral angle between the ring planes is 6.3°. These parameters suggest that there should be some repulsive π–π interaction.¹⁵ The structure of **3** is also similar to that of the known selenium analogue (Fig. 3 and Table 2).¹⁶ It has a square pyramidal Os₃Te₂ core, with an

Table 2 Selected bond lengths (Å) and angles (°) for Os₃(CO)₉(μ-E)₂ (E = Se or Te)

	3 (E = Te)	E = Se ¹⁶
Os(1)–Os(3)	2.8938(6)	2.836(1)
Os(2)–Os(3)	2.9073(6)	2.847(1)
Os(1)–E(4)	2.6872(8)	2.509(2)
Os(1)–E(5)	2.6795(8)	2.493(1)
Os(2)–E(4)	2.6870(8)	2.513(2)
Os(2)–E(5)	2.6781(8)	2.597(1)
Os(3)–E(4)	2.7351(8)	2.551(2)
Os(3)–E(5)	2.71714(9)	2.539(2)
Os(1)–Os(3)–Os(2)	88.042(16)	83.7(1)
E(4)–Os(1)–E(5)	82.58(2)	81.1(1)
E(4)–Os(2)–E(5)	82.61(2)	81.0(1)
E(4)–Os(3)–E(5)	81.00(2)	79.5(1)
Os(1)–E(4)–Os(2)	97.20(2)	98.0(1)
Os(1)–E(5)–Os(2)	97.6(2)	98.9(1)

**Fig. 2** An ORTEP diagram of cluster **2**. Os(1)–Os(2) 2.9618(4); Os(2)–Te(3) 2.7511(6); Os(2)–Te(3') 2.7468(6); Os(2)···Os(2') 3.610(1); Te(3)–C(31) 2.145(8) Å; Os(2)Os(1)Os(2') 75.08(2); Os(1)Os(2)Te(3) 83.053(13); Os(2)Te(3)Os(2') 82.07(2)°.**Fig. 3** An ORTEP diagram of cluster **3**.

Os₂Te₂ unit forming the base; there is no bonding interaction between the two tellurium atoms (Te···Te 3.541(1) Å) and between the two osmium atoms (Os···Os 4.031(1) Å) across the rhombic base. A comparison between **3** and its selenium analogue shows that the larger covalent radius of Te has distorted the base in such a way as to accommodate the Te···Te non-bonded interaction more than it does for the Os···Os interaction; the OsTeOs bond angles about the base are smaller than the OsSeOs angles, while the opposite is true of the EOSe angles. The apical Os(CO)₃ unit is also “sunk” deeper into the

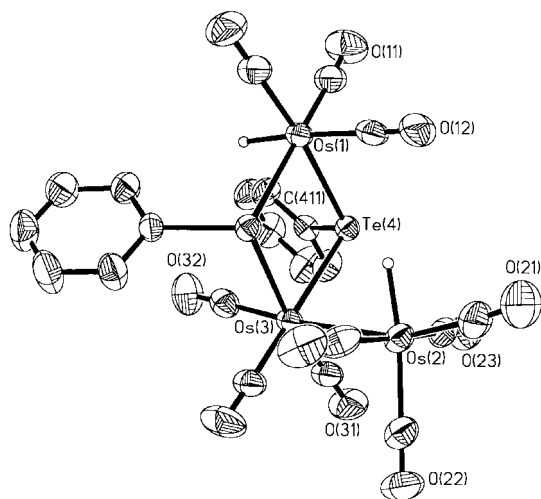


Fig. 4 An ORTEP diagram of cluster **4**. Os(2)–Os(3) 2.9489(5); Os(1)–Te(4) 2.7348(5); Os(3)–Te(4) 2.7493(4) Å; Os(1)⋯Os(3) 4.110(1); Te(4)⋯Te(4') 3.619(1); Te(4)–C(41) 2.143(6) Å; Os(1)Te(4)Os(3) 97.095(13); Te(4)Os(1)Te(4') 82.864(18); Te(4)Os(3)Te(4') 82.331(18)°.

basal plane as a consequence of this expansion of the base, as suggested by the longer bond lengths to, but larger bond angles about, the apical Os(CO)₃ in **3**.

Reaction with Os₃(μ-H)₂(CO)₁₀

The reaction of Ph₂Te₂ with the unsaturated cluster Os₃-(μ-H)₂(CO)₁₀, on the other hand, turned out to be very complicated; monitoring by ¹H NMR spectroscopy showed that a number of products were formed even in the early stages of the reaction. From the reaction mixture we were able to separate and identify three new clusters, viz. Os₃H₂(CO)₁₀(μ-TePh)₂ **4**, Os₃(μ-H)(CO)₁₀(μ-TePh) **5**, and [OsH(CO)₃(TePh)]₂ **6**. Cluster **4** was obtained as a pale yellow solid and exhibited two ¹H resonances corresponding to terminal metal hydrides at δ –3.463 and –9.763. Cluster **6** was also obtained as a pale yellow solid and showed a terminal metal hydride ¹H resonance, at δ –3.903, while **5** showed a bridging metal hydride ¹H resonance at δ –19.070. All three compounds were also characterised by single crystal X-ray crystallographic studies.

The structure of cluster **4** comprises an Os₂Te₂ 4-membered ring with an HOs(CO)₄ “spike” (Fig. 4). The molecule has crystallographic mirror symmetry, with the mirror passing through the three osmium atoms. The Te(4)⋯Te(4') and Os(1)⋯Os(3) distances of 3.619(1) and 4.110(1) Å are clearly indicative of the absence of bonding interactions across the 4-membered ring, which is only slightly puckered; the dihedral angle between the Os(1)Te(4)Os(3) and Os(1)Te(4')Os(3) planes is 8.9°. The two phenyl rings are *syn* to each other with respect to the Os₂Te₂ ring, and *anti* to the HOs(CO)₄ “spike”. This would be expected to lead to some steric repulsion between the phenyls, which is apparent in the C(41)Te(4)Te(4') angle of 116.9°, as compared to the 112.6° for cluster **6**. There appears, on the other hand, to be less steric strain between the HOs(CO)₄ “spike” and the carbonyl on Os(1) that is *syn* to it; the Os(2)Os(3)Os(1) and Os(3)Os(1)C(12) angles are 91.2 and 93.3°, respectively.

The structure of cluster **6** is closely related to that of **4**, with the “spike” replaced with a hydride (Fig. 5); the Te⋯Te and Os⋯Os distances of 3.667(1) and 4.057(1) Å are again clearly indicative of the absence of bonding interactions across the 4-membered ring. Unlike **4**, however, **6** is centrosymmetric and hence the Os₂Te₂ ring is constrained to be planar. The most obvious difference, though, is that the two phenyl rings in **6** are *anti* to each other. Nevertheless, the gross similarity between the two structures suggested that the clusters were also chemically related. Indeed, monitoring by both IR and ¹H NMR spectro-

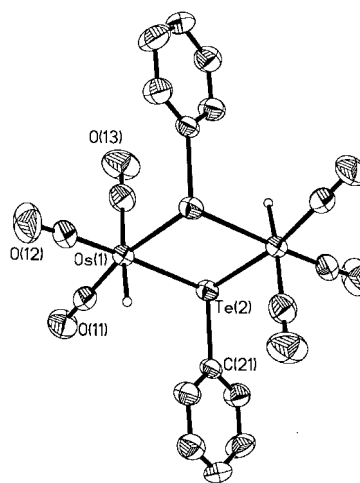
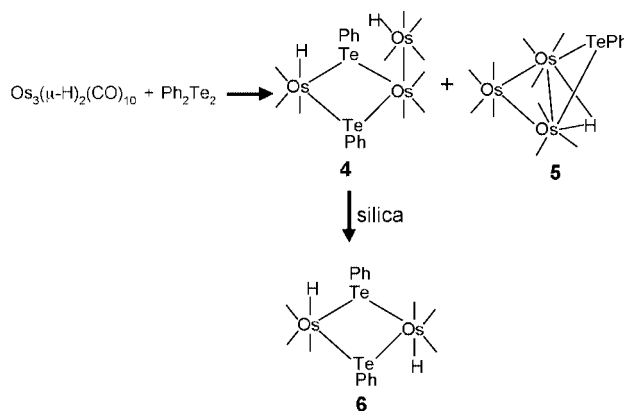


Fig. 5 An ORTEP diagram of cluster **6**. Os(1)–Te(2) 2.7372(5); Os(1)–Te(2') 2.7318(5) Å; Os(1)⋯Os(1') 4.057(1); Te(2)⋯Te(2') 3.667(1); Te(2)–C(21) 2.144(6) Å; Os(1)Te(2)Os(1') 95.774(14); Te(2)Os(1)Te(2') 84.226(14)°.

scopies showed that **6** was not formed directly in the reaction but resulted from the decomposition of **4** on the silica surface during chromatographic separation (Scheme 2).



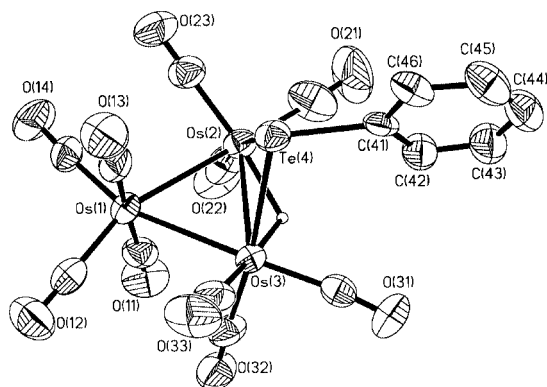
Scheme 2 Reaction of Os₃(μ-H)₂(CO)₁₀ with Ph₂Te₂.

Cluster **5** is of a well known structural type; the other EPh (E = O, S or Se) analogues are known, although apparently no structural studies have appeared yet.¹⁷ As mentioned above, the TeC₆H₄OMe-*p* analogue has also been reported, although there is again no structural study, and it was obtained only in very low yield (7%) from the reaction of the cluster anion [Os₃(μ-H)(CO)₁₀(μ-CO)][–] with (*p*-MeOC₆H₄)₂TeCl₂.^{6b,9} We found that **5** was obtainable in good yields from the reaction of Ph₂Te₂ with the cluster [Os₃(μ-H)(CO)₁₀(μ-CO)][–]; presumably, half the ditelluride was lost as the PhTe[–] anion in the reaction. Cluster **5** crystallised out in two forms; an orange, triclinic form and a yellow, tetragonal (space group *I*4̄) form. Although the crystallographic data on the triclinic crystal are of a significantly poorer quality, it is apparent that the main bond parameters are mostly similar (Fig. 6 and Table 3). The molecule has a TePh moiety bridging an Os–Os edge, with the phenyl ring pointing away from the triosmium framework. Although the metal hydrides in both studies were located directly from low angle difference maps and refined to adopt what appeared to be (or nearly) terminal positions, the ¹H NMR signal at δ –19.07 indicated that, in solution at least, the hydrides were actually bridging an Os–Os edge.

In comparing the bond parameters across the seven structures reported here, an interesting point that arises is that the Os–Te bond distances are longer for a TePh bridging an open Os⋯Os edge than for one bridging an Os–Os bond; the

Table 3 Selected bond lengths (Å) and angles (°) for Os₃(μ-H)(CO)₁₀-(μ-TePh) **5**

	Tetragonal form	Triclinic form
Os(1)–Os(2)	2.8879(7)	2.8702(12)
Os(1)–Os(3)	2.8764(6)	2.8642(11)
Os(2)–Os(3)	2.8992(6)	2.8980(10)
Os(2)–Te(4)	2.6936(9)	2.6971(12)
Os(3)–Te(4)	2.6959(8)	2.6973(11)
Te(4)–C(41)	2.134(11)	2.127(11)
Os(1)–Os(2)–Os(3)	59.608(14)	59.54(3)
Os(1)–Os(3)–Os(2)	60.001(15)	59.75(3)
Os(2)–Os(1)–Os(3)	60.390(15)	60.71(2)
Os(2)–Te(4)–Os(3)	65.09(2)	64.99(2)
Te(4)–Os(2)–Os(3)	57.50(2)	57.51(3)
Te(4)–Os(3)–Os(2)	57.42(2)	57.50(3)

**Fig. 6** An ORTEP diagram of cluster **5**.

range of values are 2.7190(9) to 2.7511(6) and 2.6886(10) to 2.6976(9) Å, respectively. This therefore suggests that there is little strain associated with an Os₂Te ring. This is particularly cogent considering that the OsTeOs angle for the TePh bridging an Os–Os bond ($\approx 65^\circ$) is very acute for a formally sp^3 hybridised tellurium. Indeed, even for an open bridge, the angles are fairly acute (from $82.07(2)^\circ$ in **2** to $99.04(3)^\circ$ in **1**).

It is clear from the reactions discussed above that Ph₂Te₂ is a very reactive agent towards osmium clusters; the reactions were all carried out at ambient temperatures, and often lead to metal–metal bond cleavage. Loss of the phenyl ring is also facile, as illustrated in the conversion of **2** into **3**. In the selenium analogue of this reaction it was found that the loss of the phenyl ring could be accounted for by formation of the cluster Os₃(μ-Ph)(μ-PhCO)(μ-Se)₂(CO)₈,¹¹ we have tried but failed to identify an analogous product in our system. The fate of the phenyl ring in our case thus remains unknown. We are now actively exploring the chemistry of some of the species reported here, such as **2** and **5**.

Experimental

General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use. NMR spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer. Microanalyses were carried out by the micro-analytical laboratory at the National University of Singapore. The starting materials Os₃(CO)₁₀(CH₃CN)₂, Os₃(μ-H)₂(CO)₁₀, [Et₄N][Os₃(μ-H)(CO)₁₀(μ-CO)] and Ph₂Te₂ were prepared by published methods.^{18–21}

Reaction of Os₃(CO)₁₀(CH₃CN)₂ with Ph₂Te₂

The compound Os₃(CO)₁₀(CH₃CN)₂ (50 mg, 0.053 mmol) and

Ph₂Te₂ (219 mg, 0.0533 mmol) were stirred in dichloromethane (8 ml) at RT for 1 h. Column chromatographic separation on silica gel (hexane as eluent) gave two bands; compounds **2** (9.5 mg, 19%) and **1** (20 mg, 45%) were eluted in that order. Compound **1** (Found: C, 21.38; H, 0.82. Calc. for C₂₂H₁₀O₁₀Os₃Te₂: C, 20.96; H, 0.79%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (cyclohexane) 2106w, 2059s, 2042m, 2027s, 2011w, 1989w, 1972w, 1964w and 1956w (CO); ¹H NMR (CDCl₃) δ 7.59–7.17 (m, Ph). Compound **2** (Found: C, 20.85; H, 0.77. Calc. for C₂₂H₁₀O₁₀Os₃Te₂: C, 20.96; H, 0.79%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (cyclohexane) 2099m, 2074vw, 2057s, 2049w, 2013s, 1988vw, 1984m and 1977w (sh) (CO); ¹H NMR (CDCl₃) δ 7.79–7.17 (m, Ph).

Thermolysis of compound **1** in cyclohexane

Cluster **1** (50 mg, 0.039 mmol) was refluxed in cyclohexane (10 ml) for 4 h. Recrystallisation from hexane of the residue after solvent removal gave **2** (45 mg, 90%).

Thermolysis of compound **2** in octane

Cluster **2** (50 mg, 0.039 mmol) was refluxed in octane (10 ml) for 15 h. Recrystallisation from hexane of the residue after solvent removal gave **3** (23 mg, 47%). $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CH₂Cl₂) 2069s, 2050m and 2010m (br) (CO).

Reaction of Os₃(μ-H)₂(CO)₁₀ with Ph₂Te₂

The compound Os₃(μ-H)₂(CO)₁₀ (50 mg, 0.059 mmol) and Ph₂Te₂ (24.6 mg, 0.059 mmol) were stirred in hexane (8 ml) at RT for 1 h. TLC separation of the reaction mixture (hexane as eluent) gave two major bands. Recrystallisation of band 1 from hexane gave **6** (3.9 mg, 7.8%), and further concentration of the supernatant gave **5** (20 mg, 40%). Band 2 was recrystallised from CH₂Cl₂–hexane to give **4** (9.4 mg, 19%). Compound **4** (Found: C, 21.09; H, 0.75. Calc. for C₂₂H₁₂O₁₀Os₃Te₂: C, 20.94; H, 0.96%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CH₂Cl₂) 2113w, 2091m, 2054s, 2041m (sh), 2022s, 2004m (sh) and 1987w (CO); ¹H NMR (*d*₈-toluene) δ 7.26–6.98 (m, Ph), –3.463 (s, OsH) and –9.763 (s, OsH). Compound **5** (Found: C, 18.28; H, 0.79. Calc. for C₁₆H₆O₁₀Os₃Te: C, 18.19; H, 0.57%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CH₂Cl₂) 2105w, 2065vs, 2055m, 2025s, 2009s, 2000ms and 1986w (CO); ¹H NMR (*d*₈-toluene) δ 7.09–6.97 (m, Ph) and –19.070 (s, OsHOs). Compound **6** (Found: C, 22.31; H, 1.40. Calc. for C₉H₆O₃OsTe: C, 22.52; H, 1.26%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (CH₂Cl₂) 2085s, 2037m and 2003s (CO); ¹H NMR (*d*₈-toluene) δ 7.85–6.71 (m, Ph) and –3.903 (s, OsH).

Reaction of [Et₄N][Os₃(μ-H)(CO)₁₀(μ-CO)] with Ph₂Te₂

To [Et₄N][Os₃(μ-H)(CO)₁₀(μ-CO)] (50 mg, 0.050 mmol) and Ph₂Te₂ (23.2 mg, 0.057 mmol) was added CH₂Cl₂ (8 ml). After stirring at RT for 1 h the solvent was removed and the residue recrystallised from CH₂Cl₂–hexane to give compound **5** (30.3 mg, 60%).

Crystal structure determinations

Phenyl H atoms were placed in calculated positions and given isotropic thermal parameters at 1.2 times those of the C atoms to which they are attached. The metal hydrides in compound **4** were placed at 1.60 Å from the attached Os atoms and *trans* to a carbonyl; the Os–H distances were restrained at 1.600(1) Å during refinement, and a fixed isotropic thermal parameter of 0.05 Å² was assigned. For **5** the hydrides were placed by potential energy minimisation with the program XHYDEX,²² they were refined with isotropic thermal parameters and riding on one of the osmium atoms which they bridged. The metal hydride in **6** was located by a low angle ($2\theta \leq 30^\circ$) difference map and refined. All non-hydrogen atoms were given anisotropic thermal parameters in the final model. A summary of the crystal data is given in Table 4.

CCDC reference number 186/1874.

Table 4 Crystal data for clusters 1–6 collected at 295(2) K

	1	2	3	4	5	5	6
Empirical formula	C ₂₂ H ₁₀ O ₁₀ Os ₃ Te ₂	C ₂₂ H ₁₀ O ₁₀ Os ₃ Te ₂	C ₉ O ₉ Os ₃ Te ₂	C ₂₂ H ₁₂ O ₁₀ Os ₃ Te ₂	C ₁₆ H ₆ O ₁₀ Os ₃ Te	C ₁₆ H ₆ O ₁₀ Os ₃ Te	C ₁₈ H ₁₂ O ₆ Os ₂ Te ₂
Formula weight	1260.10	1260.10	1077.89	1262.12	1056.41	1056.41	959.88
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Tetragonal	Triclinic	Monoclinic
Space group	P2 ₁	C2/c	P $\bar{1}$	Pnma	I $\bar{4}$	P $\bar{1}$	P2 ₁ /n
a/Å	7.9677(1)	15.7411(1)	7.1681(2)	20.6376(5)	18.8844(1)	9.202(4)	9.3686(4)
b/Å	16.8612(1)	12.7360(1)	9.8835(2)	15.3639(4)	18.8844(1)	9.205(4)	6.2656(3)
c/Å	10.8686(1)	14.6953(2)	13.4332(2)	9.0517(2)	12.5297(2)	13.707(5)	19.0147(8)
α /°			96.014(1)			97.331(13)	
β /°	117.07(1)	113.71(1)	96.142(1)			108.240(12)	90.448(1)
γ /°			109.986(1)			98.024(11)	
V/Å ³	1362.49(2)	2697.29(4)	879.01(3)	2870.06(12)	4468.35(8)	1073.7(8)	1116.13(9)
Z	2	4	2	4	8	2	2
μ /mm ⁻¹	16.103	16.269	24.918	15.290	18.346	19.088	13.964
Reflections collected	17638	18176	6555	18514	28082	8192	7115
Independent reflections	5992	3302	4111	3763	5582	5141	2715
	($R_{\text{int}} = 0.0327$)	($R_{\text{int}} = 0.0388$)	($R_{\text{int}} = 0.0382$)	($R_{\text{int}} = 0.0411$)	($R_{\text{int}} = 0.0522$)	($R_{\text{int}} = 0.0334$)	($R_{\text{int}} = 0.0269$)
Final R [$I > 2\sigma(I)$]	0.0409	0.0350	0.0493	0.0332	0.0359	0.0440	0.0301
$wR2$ (all data)	0.1103	0.0952	0.1366	0.0807	0.0777	0.1183	0.0719

See <http://www.rsc.org/suppdata/dt/a9/a909628k/> for crystallographic files in .cif format.

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