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The reaction of diphenyl ditelluride with triosmium clusters

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The reaction of Ph_2Te_2 with $Os_3(CO)_{10}(CH_3CN)_2$ at room temperature gave the cluster $Os_3(CO)_{10}(\mu\text{-}TePh)_2$ **1**, in which one TePh bridges an "open" Os · · · Os edge and another bridges an Os–Os bond. Thermolysis of **1** in refluxing cyclohexane led to isomerisation of **1** to **2**, in which both TePh moieties bridge the same "open" Os · · · Os edge; thermolysis of **2** in refluxing octane led to the cluster $Os_3(CO)_9(\mu_3\text{-}Te)_2$ **3**. The reaction of Ph_2Te_2 with $Os_3(\mu\text{-}H)_2(CO)_{10}$, on the other hand, resulted in a complex mixture of products among which were the clusters $Os_3H_2(CO)_{10}(\mu\text{-}TePh)_2$ **4** and $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}TePh)$ **5**; cluster **5** was also obtained in moderate yield from the reaction with $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CO)]^-$. Cluster **4** comprises a four-membered Os_2Te_2 ring, with an $HOs(CO)_4$ fragment attached to one of the osmium atoms; it decomposed on silica gel to afford the dinuclear compound $[OsH(CO)_3(TePh)]_2$ **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]

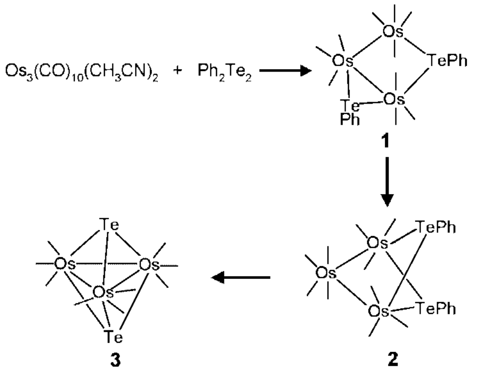
To date, only a handful of osmium–tellurium clusters are known. The earliest report was apparently that involving the reaction of $Os_3(CO)_{12}$ with tellurium powder from which were isolated the clusters $Os_3(CO)_9(\mu_3\text{-}Te)_2$ and $Os_4(\mu\text{-}H)_2(CO)_{12}(\mu_4\text{-}Te)_2$.[4] Most of the reported syntheses involved the acetonitrile-substituted triosmium clusters $Os_3(CO)_{12-n}(CH_3CN)_n$ ($n = 1$ or 2). For example, $Os_3(CO)_{10}(CH_3CN)_2$ reacted with H_2Te to give $Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}Te)$ and with $Fe_2Te_2(CO)_6$ to afford $Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$,[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 $Os_3(CO)_{11}(CH_3CN)$ with $Te(CF_3)_2$ in cyclohexane, in which the CF_3 groups were replaced to give the cyclohexyl analogue $Os_3(CO)_{11}(TeCy_2)$.[8] Salt elimination has also been utilised, as in the reaction of the anionic cluster $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CO)]^-$ with $(p\text{-}MeOC_6H_4)_2TeCl_2$ to give $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}TeC_6H_4OMe\text{-}p)$; on thermolysis, this product gave the cluster $Os_3(CO)_9(\mu_3\text{-}Te)_2$.[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 $Os_3(CO)_{12-n}(CH_3CN)_n$ ($n = 1$ or 2) reacted with R_2Se_2 (R = Ph or Me) to afford $Os_3(CO)_{10}(\mu\text{-}SeR)_2$ **1a**, in which one SeR moiety bridged an Os–Os bond and the other an open Os · · · Os edge; it was believed that the reaction proceeded *via* an intermediate containing a $\mu\text{-}Se_2R_2$ 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 Os · · · Os edge.

Results and discussion

Reaction with $Os_3(CO)_{10}(CH_3CN)_2$

The reaction of Ph_2Te_2 with $Os_3(CO)_{10}(CH_3CN)_2$ at room temperature was rapid, and gave the cluster $Os_3(CO)_{10}(\mu\text{-}TePh)_2$ **1** as the major product. Cluster **1** comprises a four-membered Os_3Te ring with the remaining TePh moiety bridging one of the Os–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 Os · · · Os edge, *i.e.* with a structure analogous to that of the corresponding bis(alkoxy) clusters $Os_3(CO)_{10}(OR)_2$.[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 $Os_3(CO)_9(\mu_3\text{-}Te)_2$ **3**. The sequence of reaction (Scheme 1) is thus quite similar to that for 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



Scheme 1 Reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with Ph_2Te_2.

Table 1 Selected bond lengths (Å) and angles (°) for $Os_3(CO)_{10}(\mu\text{-SePh})_2$ (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)

Table 2 Selected bond lengths (Å) and angles (°) for $Os_3(CO)_9(\mu\text{-E})_2$ (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)

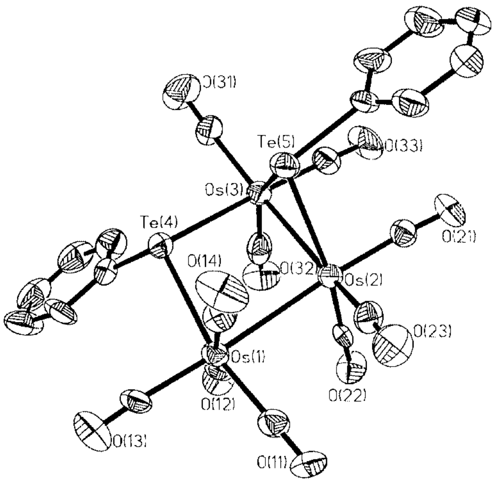


Fig. 1 An ORTEP diagram of cluster **1** (50% thermal ellipsoids, as in all figures).

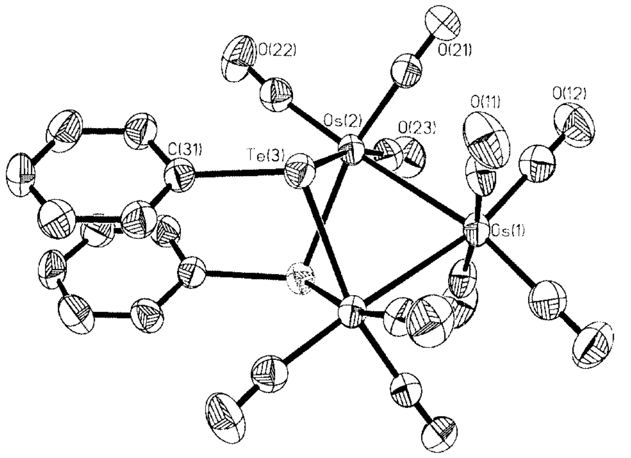


Fig. 2 An ORTEP diagram of cluster **2**. Os(1)–Os(2) 2.9618(4); Os(2)–Te(3) 2.7511(6); Os(2)–Te(3′) 2.7468(6); Os(2)···Os(2′) 3.610(1); Te(3)–C(31) 2.145(8) Å; Os(2)Os(1)Os(2′) 75.08(2); Os(1)Os(2)Te(3) 83.053(13); Os(2)Te(3)Os(2′) 82.07(2)°.

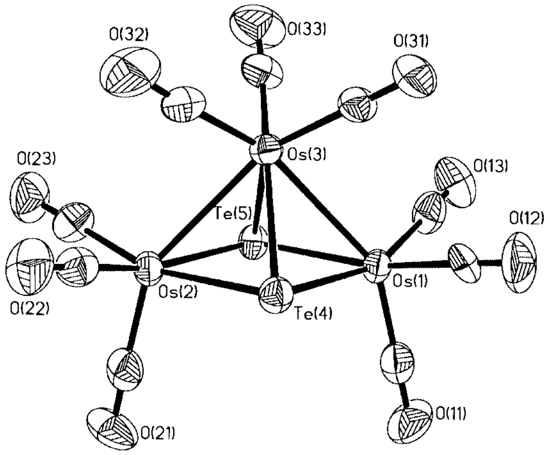


Fig. 3 An ORTEP diagram of cluster **3**.

cyclohexane was essentially quantitative, as observed by IR spectroscopy.

An ORTEP[13] plot of cluster **1** is given in Fig. 1, and selected molecular parameters, together with those for the selenium analogue, $Os_3(CO)_{10}(\mu\text{-SePh})_2$,[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 Os_3 group, the EPh group bridging the closed Os–Os edge is oriented almost perpendicular to the Os_3 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 Os_3Te_2 core, with an Os_2Te_2 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

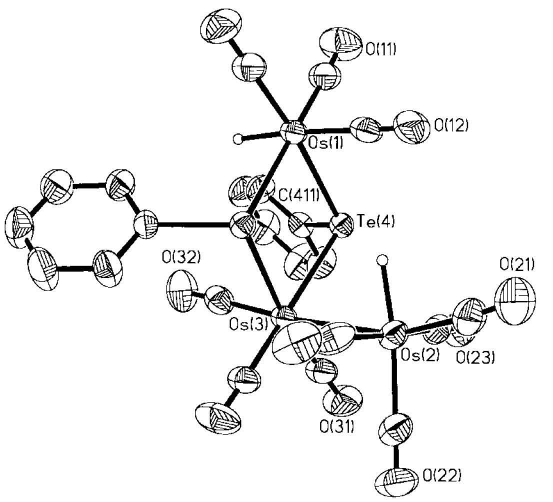


Fig. 4 An ORTEP diagram of cluster **4**. Os(2)–Os(3) 2.9489(5); Os(1)–Te(4) 2.7348(5); Os(3)–Te(4) 2.7493(4) Å; Os(1)···Os(3) 4.110(1); Te(4)···Te(4′) 3.619(1); Te(4)–C(41) 2.143(6) Å; Os(1)Te(4)Os(3) 97.095(13); Te(4)Os(1)Te(4′) 82.864(18); Te(4)Os(3)Te(4′) 82.331(18)°.

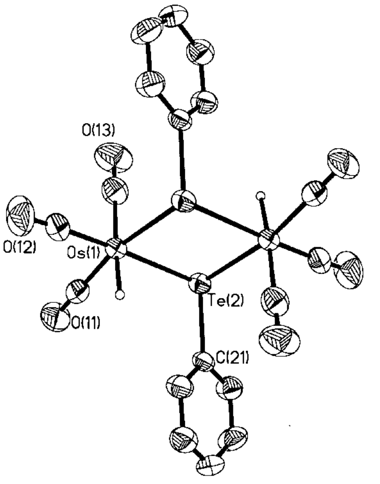


Fig. 5 An ORTEP diagram of cluster **6**. Os(1)–Te(2) 2.7372(5); Os(1)–Te(2′) 2.7318(5) Å; Os(1)···Os(1′) 4.057(1); Te(2)···Te(2′) 3.667(1); Te(2)–C(21) 2.144(6) Å; Os(1)Te(2)Os(1′) 95.774(14); Te(2)Os(1)Te(2′) 84.226(14)°.

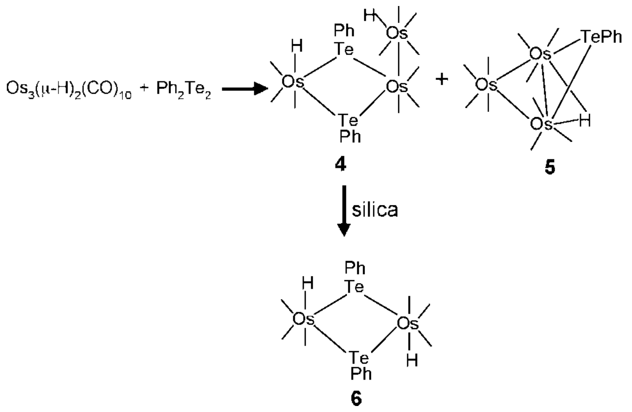
basal plane as a consequence of this expansion of the base, as suggested by the longer bond lengths to, but larger bond angles about, the apical Os(CO)$_3$ in **3**.

Reaction with Os$_3$(μ-H)$_2$(CO)$_{10}$

The reaction of Ph$_2$Te$_2$ with the unsaturated cluster Os$_3$(μ-H)$_2$(CO)$_{10}$, on the other hand, turned out to be very complicated; monitoring by ^{1}H 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.* Os$_3$H$_2$(CO)$_{10}$(μ-TePh)$_2$ **4**, Os$_3$(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 ^{1}H 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 ^{1}H resonance, at δ −3.903, while **5** showed a bridging metal hydride ^{1}H 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 Os$_2$Te$_2$ 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 Os$_2$Te$_2$ 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 Os$_2$Te$_2$ 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 ^{1}H NMR spectroscopies 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 Os$_3$(μ-H)$_2$(CO)$_{10}$ with Ph$_2$Te$_2$.

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 TeC$_6$H$_4$OMe-*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 [Os$_3$(μ-H)(CO)$_{10}$(μ-CO)]$^-$ with (*p*-MeOC$_6$H$_4$)$_2$TeCl$_2$.[6b,9] We found that **5** was obtainable in good yields from the reaction of Ph$_2$Te$_2$ with the cluster [Os$_3$(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 $I\bar{4}$) 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 ^{1}H 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 $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}TePh)$ **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)

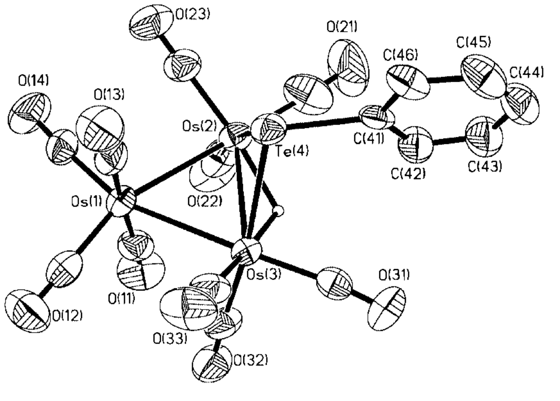


Fig. 6 An ORTEP diagram of cluster **5**.

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 Os_2Te ring. This is particularly cogent considering that the OsTeOs angle for the TePh bridging an Os–Os bond (≈65°) 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)° in **2** to 99.04(3)° in **1**).

It is clear from the reactions discussed above that Ph_2Te_2 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 $Os_3(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu\text{-}Se)_2(CO)_8$;[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 microanalytical laboratory at the National University of Singapore. The starting materials $Os_3(CO)_{10}(CH_3CN)_2$, $Os_3(\mu\text{-}H)_2(CO)_{10}$, $[Et_4N][Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CO)]$ and Ph_2Te_2 were prepared by published methods.[18–21]

Reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with Ph_2Te_2

The compound $Os_3(CO)_{10}(CH_3CN)_2$ (50 mg, 0.053 mmol) and Ph_2Te_2 (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 $C_{22}H_{10}O_{10}Os_3Te_2$: C, 20.96; H, 0.79%); $\tilde{\nu}_{max}/cm^{-1}$ (cyclohexane) 2106w, 2059s, 2042m, 2027s, 2011w, 1989w, 1972w, 1964w and 1956w (CO); ^1H NMR ($CDCl_3$) δ 7.59–7.17 (m, Ph). Compound **2** (Found: C, 20.85; H, 0.77. Calc. for $C_{22}H_{10}O_{10}Os_3Te_2$: C, 20.96; H, 0.79%); $\tilde{\nu}_{max}/cm^{-1}$ (cyclohexane) 2099m, 2074vw, 2057s, 2049w, 2013s, 1988vw, 1984m and 1977w (sh) (CO); ^1H NMR ($CDCl_3$) 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%). $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2069s, 2050m and 2010m (br) (CO).

Reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with Ph_2Te_2

The compound $Os_3(\mu\text{-}H)_2(CO)_{10}$ (50 mg, 0.059 mmol) and Ph_2Te_2 (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 CH_2Cl_2–hexane to give **4** (9.4 mg, 19%). Compound **4** (Found: C, 21.09; H, 0.75. Calc. for $C_{22}H_{12}O_{10}Os_3Te_2$: C, 20.94; H, 0.96%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 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 $C_{16}H_6O_{10}Os_3Te$: C, 18.19; H, 0.57%); $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 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 $C_9H_6O_3OsTe$: C, 22.52; H, 1.26%): $\tilde{\nu}_{max}/cm^{-1}$ (CH_2Cl_2) 2085s, 2037m and 2003s (CO); ^1H NMR (d_8-toluene) δ 7.85–6.71 (m, Ph) and −3.903 (s, OsH).

Reaction of $[Et_4N][Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CO)]$ with Ph_2Te_2

To $[Et_4N][Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CO)]$ (50 mg, 0.050 mmol) and Ph_2Te_2 (23.2 mg, 0.057 mmol) was added CH_2Cl_2 (8 ml). After stirring at RT for 1 h the solvent was removed and the residue recrystallised from CH_2Cl_2–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 $Å^2$ 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 ($2\theta \le 30°$) 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	$C_{22}H_{10}O_{10}Os_3Te_2$	$C_{22}H_{10}O_{10}Os_3Te_2$	$C_9O_9Os_3Te_2$	$C_{22}H_{12}O_{10}Os_3Te_2$	$C_{16}H_6O_{10}Os_3Te$	$C_{16}H_6O_{10}Os_3Te$	$C_{18}H_{12}O_6Os_2Te_2$
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 ($R_{int} = 0.0327$)	3302 ($R_{int} = 0.0388$)	4111 ($R_{int} = 0.0382$)	3763 ($R_{int} = 0.0411$)	5582 ($R_{int} = 0.0522$)	5141 ($R_{int} = 0.0334$)	2715 ($R_{int} = 0.0269$)
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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