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Chemical transformations on diols anchored to a triosmium cluster

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Clusters of the general formula $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-O–OH})$, **2**, have been synthesised from the reaction of $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OH})$ with the appropriate glycol. The free –OH function of the glycol derivative, $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2CH_2OH)$, **2a**, can be elaborated by esterification with benzoyl chloride to give $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2CH_2OC(O)Ph)$, **3**, and partially oxidised to give $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2CHO)$, **4a**. Cluster **4a** itself can undergo allylation to give $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2CH(OH)CH_2CH{=}CH_2)$, **5**, or react with PhMgBr to give $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2CH(OH)Ph)$, **2e**. Cluster **2a** can also be functionalised at the cluster metal core with PPh_3 as $Os_3(\mu\text{-H})(CO)_9(\mu\text{-OCH}_2CH_2OH)(PPh_3)$, **6**.

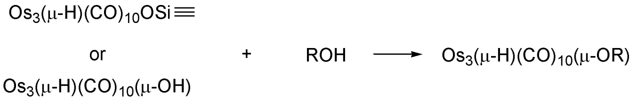
Introduction

Organometallic clusters offer the possibility of unique transformations as a result of synergistic interactions among the metal atoms. One of our long-term goals is to study the interaction between two ligands bound onto a cluster surface. In order to do so, it is useful to begin with a fairly robust cluster that is not likely to degrade or change in nuclearity in the course of the study and in that respect, the triosmium framework appears to be very well suited for the purpose. A second important requirement is the ability to anchor various organic molecules onto the cluster in a specific manner. This is not a trivial task since the reaction of clusters with even simple organic molecules can be notoriously complicated. For instance, the type of products obtained from the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with amines depend on the amines used.[1] For a sufficiently large molecule, the different functionalities lead to increased complexity and usually the most reactive functionality will dictate the major reaction product obtained, which may not be the desired one. For instance, the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with 2-furaldehyde gave a product in which the furaldehyde had undergone C–H cleavage at the aldehyde functionality, bonding to the cluster *via* the resultant acyl group; the acyl group could thermally decarbonylate to give a product in which the furan ring (without the aldehyde group) was now bound to the cluster. Hence it was not possible to obtain, say, a product in which the 2-furaldehyde was bound to the cluster *via* the furan ring with the aldehyde group still intact.[2]

One strategy to afford clusters in which an organic fragment is anchored in a specific manner is to begin with a cluster that already contains the anchored linkage and then elaborating on the remainder of the organic moiety through a series of transformations like those employed in a typical organic synthesis. A good example of this is the work of Rosenberg *et al.* on the employment of carbon-based nucleophiles to attack the carbocyclic ring of triosmium cluster-bound quinolines.[3] In order for this to work, however, the cluster core and the cluster-substrate linkage must be able to survive the conditions employed in the organic transformations; the challenge is therefore to seek out a set of organic transformations and reagents that will allow this. We would like to report here our initial investigations towards this challenge, employing as our starting point a triosmium cluster containing the alkoxy bridge as the substrate-cluster linkage.

Results and discussion

The high-yield synthesis of triosmium clusters containing bridging alkoxy groups has been reported recently, starting from either $Os_3(CO)_{12}$ anchored onto silica or the hydroxy-bridged cluster $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OH})$, **1** (Scheme 1).[4] We have used this methodology to prepare clusters of the type $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-O–OH})$, **2**, in which one of the hydroxyl functions has been anchored onto the trisomium cluster as an alkoxy group while the other is still free.



Scheme 1

The yields of the various cluster-bound diols are given in Table 1, and it is quite apparent that an increase in the steric bulk of the substituents about the hydroxyl groups leads to a decrease in overall yield. Furthermore, it also leads to a preference for attachment of the cluster at the primary alcohol group, for example, 1,2-propanediol gave **2b**, in which the 1-hydroxyl group is anchored, in 38% yield as opposed to 16% for **2c**, which has the 2-hydroxyl group anchored; likewise, 1-phenyl-1,2-ethanediol gave exclusively **2e** (in low yield), with the primary alcohol function anchored. These observations are in accord with increasing steric hindrance to attack by the cluster.

The molecular structures of compounds **2a**–**c** and **2e** have been confirmed by single crystal X-ray crystallographic studies; that for **2a** has already been reported.[5] The ORTEP plots for **2b**, **2c** and **2e** are shown below (Figs. 1, 2 and 3, respectively), and selected bond parameters for **2a**–**c** and **2e** are collected in Table 2. Both **2a** and **2c** crystallised in the triclinic system with two crystallographically distinct molecules in the asymmetric unit; the Os–Os bond lengths of the alkoxy-bridged edges in the two chemically equivalent molecules differ by as much as 20σ and 29σ (σ = estimated standard deviation) in **2a** and **2c**, respectively. This points to the large deviations in structural parameters that can occur under the influence of crystal packing forces. In all four clusters, there is a shortening of the dibridged $Os(\mu\text{-H})(\mu\text{-O})Os$ bond lengths (range of 2.7891(5) to 2.8040(7) Å) relative to the non-bridged Os–Os bonds (range of 2.8098(7) to 2.8333(6) Å). This net shortening of the dibridged $Os(\mu\text{-H})(\mu\text{-X})Os$ bond is characteristic for systems containing relatively

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Table 1 Yields of clusters **2**

Diol	Products	Yield (%)
1,2-Ethanediol	$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2OH)$, **2a**	60
1,2-Propanediol	$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)CH_3)$, **2b**	38
	$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH(CH_3)CH_2OH)$, **2c**	16
1,3-Propanediol	$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2CH_2OH)$, **2d**	15
1-Phenyl-1,2-ethanediol	$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)Ph)$, **2e**	8

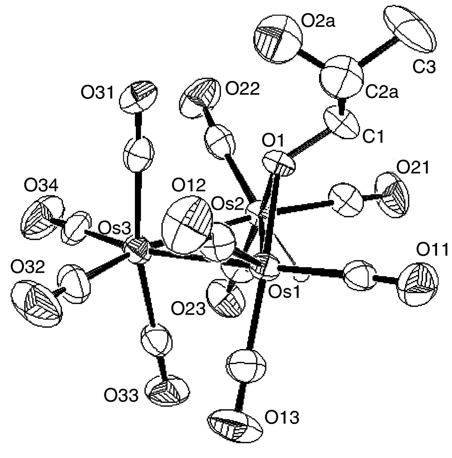

Fig. 1 ORTEP[21] diagram of **2b** (50% thermal ellipsoids).

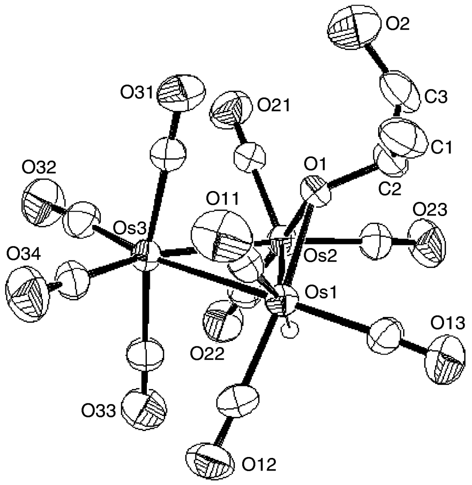

Fig. 2 ORTEP diagram of **2c** (50% thermal ellipsoids).

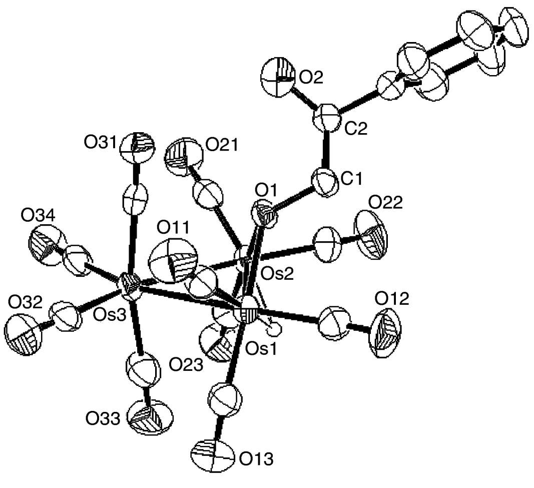

Fig. 3 ORTEP diagram of **2e** (50% thermal ellipsoids).

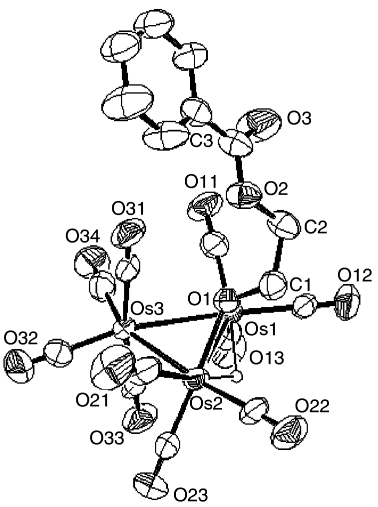

Fig. 4 ORTEP diagram of **3** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (°): Os(1)–Os(2) = 2.8016(5), Os(1)–Os(3) = 2.8237(5), Os(2)–Os(3) = 2.8286(6), Os(1)–O(1) = 2.117(6), Os(2)–O(1) = 2.102(7), O(1)–C(1) = 1.429(12), C(1)–C(2) = 1.528(16), O(2)–C(2) = 1.434(14), O(2)–C(3) = 1.336(14), O(3)–C(3) = 1.186(15); Os(2)–Os(1)–Os(3) = 60.373(14), Os(1)–Os(2)–Os(3) = 60.200(13), Os(1)–Os(3)–Os(2) = 59.428(13), Os(1)–O(1)–Os(2) = 83.2(2).

small X atoms.[6] The most noteworthy point, however, is probably that made earlier on **2a**, that the C–O single bond lengths for the free –OH and the alkoxy bridge in all four clusters are not significantly different, suggesting that the triosmium core has little structural effect on the organic fragments.

One of the simplest and most common reactions that can be carried out on an alcohol group is ester formation. Thus we started with the esterification of **2a** with benzoyl chloride. This gave a compound which showed a similar profile for the CO absorption bands to **2a**, as well as a metal hydride signal in the ^1H NMR spectrum at −12.40 ppm, indicating that the metal core in **2a** was unaffected. An ester linkage was indicated by a weak 1733 cm^{-1} absorption band, and the ^1H resonances in the organic region were assignable to the presence of a $PhC(=O)OCH_2CH_2$ moiety. The product was thus identified as the new cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2OC(O)Ph)$, **3**. A single crystal X-ray crystallographic study was also carried out on **3**; an ORTEP plot together with selected bond parameters is given in Fig. 4. As may be expected from the above discussion, the bond parameters associated with the cluster core are similar to those in compounds **2**, and those associated with the organic moiety are within typical ranges.[7]

A key functional group in organic chemistry is the carbonyl group, as it is the starting point of a number of C–C bond formation reactions which may be used to build up molecules. Our main target was thus the transformation of the free alcohol group into the corresponding aldehyde. This was a particularly difficult transformation; we tried several oxidants that either gave low yields (PCC (pyridinium chlorochromate)[8] and Swern[9]) or failed completely (PDC (pyridinium dichromate),[10] MnO_2, $KMnO_4$ and Ag_2CO_3[11]). Eventually, we succeeded with the Dess–Martin reagent (triacetoxyperiodinane),[12] which gave the clusters $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CHO)$, **4a**, and $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2CHO)$ **4d**, from **2a** and **2d**, respectively, in moderate yields. These clusters exhibited a distinctive ^1H resonance in the *ca.* 9 ppm region for the aldehyde functionality.

From **4a**, we have carried out two representative C–C bond formation reactions, *viz.*, allylation and a Grignard reaction.

Table 2 Selected bond lengths (Å) and angles (°) for **2a**–**c** and **2e**

Bond parameter	**2a**^{a,b}	**2b**	**2c**^{b}	**2e**
Os(1)–Os(2)	2.7897(7) 2.8040(7)	2.8029(5)	2.7978(6) 2.7850(5)	2.7891(5)
Os(1)–Os(3)	2.8195(7) 2.8282(7)	2.8327(6)	2.8198(6) 2.8319(6)	2.8206(4)
Os(2)–Os(3)	2.8098(7) 2.8104(7)	2.8318(6)	2.8333(6) 2.8257(6)	2.8265(4)
Os(1)–O(1)	2.100(9) 2.108(9)	2.133(6)	2.126(7) 2.123(7)	2.113(5)
Os(2)–O(1)	2.109(9) 2.112(9)	2.114(6)	2.122(7) 2.117(7)	2.124(5)
O(1)–C(1)	1.462(17) 1.413(16)	1.436(12)	1.454(12) 1.435(11)	1.430(9)
O(2)–C(2)	1.418(18) 1.41(2)	1.372(19)^{c}	1.456(17) 1.426(17)	1.423(11)
Os(2)–Os(1)–Os(3)	60.120(18) 59.866(18)	60.327(14)	60.576(14) 60.401(15)	60.508(11)
Os(1)–Os(2)–Os(3)	60.466(18) 60.495(18)	60.358(14)	60.097(14) 60.622(15)	60.297(11)
Os(2)–Os(3)–Os(1)	59.415(18) 59.640(18)	59.316(14)	59.327(14) 58.977(14)	59.195(11)
Os(1)–O(1)–Os(2)	83.0(3) 83.3(3)	82.6(2)	82.4(2) 82.1(2)	82.321(18)

[a] From ref. 5. [b] Two molecules in the asymmetric unit. [c] Disordered.

For the allylation, we carried out an indium metal-mediated allylation with allyl bromide in an aqueous THF solution.[13] The new cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)CH_2CH{=}CH_2)$, **5**, was obtained as a yellow oil. This compound exhibited a carbonyl stretching profile in the infrared that is only slightly shifted in frequency as compared to **4a**, thus indicating the integrity of the cluster core. The presence of the allyl group was indicated by ^1H resonances at 5.74 and 5.13 ppm in the NMR spectrum, characteristic of a C=C double bond. The formulation for **5** was further supported by a FAB mass spectrum, which showed the highest mass fragment centred around *m*/*z* 953 (based on ^{192}Os). Reaction of **4a** with PhMgBr afforded **2e** in 44% yield (73% wrt consumed **4a**).

We have also explored the stability of **2e** with respect to cleavage of the triosmium framework from the organic moiety; we were of the view that **2e** may be regarded as a "partially protected" 1-phenyl-1,2-ethanediol. Cluster **2e** was stirred with concentrated hydrochloric acid at ambient temperature. An IR spectrum of the orange residue obtained suggested generation of the cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}Cl)$, which was also corroborated by a singlet at −14.36 ppm in the ^1H NMR spectrum.[14] ^1H resonances assignable to that of free 1-phenyl-1,2-ethanediol were also observed, indicating cleavage of the ligand from the cluster. We were likewise able to "deprotect" **2a** similarly to afford $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}Cl)$ and the free 1,2-ethanediol.

The ability to transform the cluster core without detriment to the organic moiety was also of interest to us. We have thus also carried out a simple amine-*N*-oxide activated ligand substitution with PPh_3 on **2a**, which afforded the expected derivative $Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}OCH_2CH_2OH)(PPh_3)$, **6**. Cluster **6** has been fully characterised spectroscopically, including a single crystal X-ray crystallographic study (Fig. 5). This substitution with a phosphine ligand has a very significant effect on the cluster core; the Os–Os and Os–O bonds are all lengthened with respect to the parent cluster **2a**.

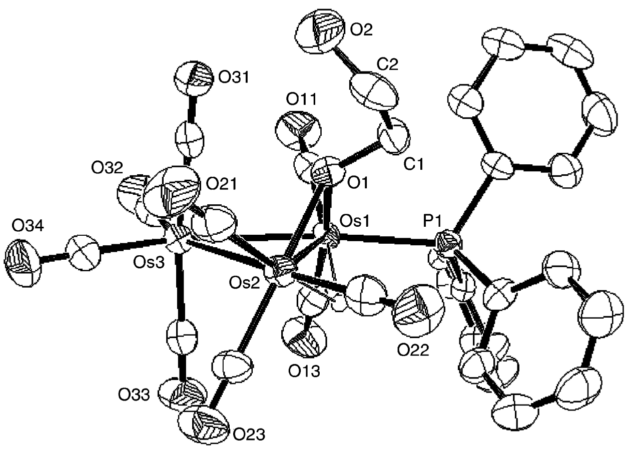

Fig. 5 ORTEP diagram of **6** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (°): Os(1)–Os(2) = 2.8364(4), Os(1)–Os(3) = 2.8528(4), Os(2)–Os(3) = 2.8682(4), Os(1)–O(1) = 2.150(5), Os(2)–O(1) = 2.168(5), O(1)–C(1) = 1.468(9), C(1)–C(2) = 1.514(11), O(2)–C(2) = 1.423(11), Os(2)–Os(1)–Os(3) = 60.550(10), Os(1)–Os(2)–Os(3) = 60.007(10), Os(1)–Os(3)–Os(2) = 59.443(10), Os(1)–O(1)–Os(2) = 82.12(16).

Although the crystal structure indicates that the phosphine ligand is in an equatorial position, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **6** indicated that there were two isomers in solution. There are three possible positions for substitution at one of the alkoxy bridged osmium atoms (Fig. 6); position **A** corresponds to that in the crystal structure. In an earlier work on similar phosphite-substituted alkoxy-bridged triosmium clusters, Lewis *et al.* used the magnitude of $^2J_{PH}$ between the phosphite and the metal hydride to determine that the two isomers present in solution were of structures **A** and **B**; the latter showed a large $^2J_{PH}$ of ≈50–60 Hz.[15] In **6**, both isomers have small $^2J_{PH}$, indicating

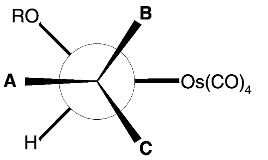

Fig. 6 Possible substitution positions at an alkoxy bridged osmium; Newman projection along the bridged Os–Os bond.

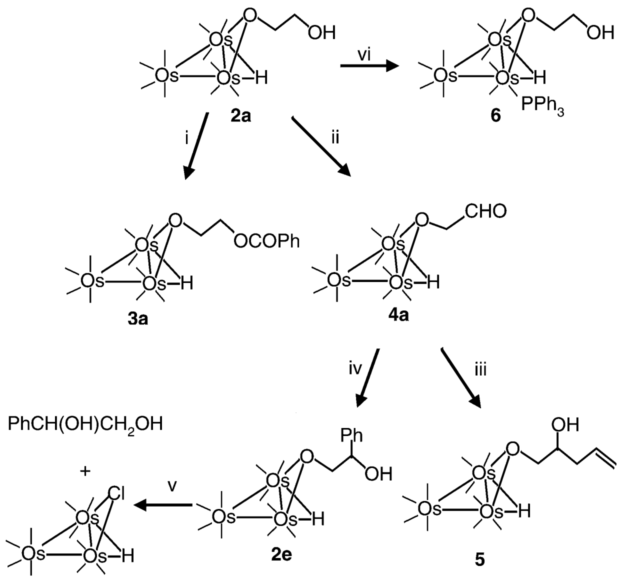

Fig. 7 Reagents and conditions: (i) PhCOCl, Et_3N, THF, 2 h. (ii) Dess–Martin reagent, CH_2Cl_2, 6 h, followed by saturated aq. $NaHCO_3 + Na_2S_2O_3$. (iii) $CH_2{=}CHCH_2Br$, indium metal, THF–H_2O (1 : 1), 1 d. (iv) PhMgBr, anhydrous THF, −20 °C, 2.5 h, followed by aq. HCl. (v) Conc. HCl, CH_2Cl_2. (vi) $Me_3NO{\cdot}2H_2O$, followed by PPh_3.

that the second isomer probably corresponds to substitution at position **C**; this is the less sterically hindered of the two pseudo-axial positions.

In conclusion, we have shown that it is possible to transform a glycol that has been anchored onto a triosmium cluster with judicious choice of the synthetic methods in the organic synthesis arsenal. The transformations that we have studied, together with investigations into the chemical stability of the organic-cluster linkage, and of the metal core, are summarised below starting from cluster **2a** (Fig. 7).

Experimental

General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. NMR spectra were recorded at ambient temperature on a Bruker ACF-300 FT-NMR spectrometer in $CDCl_3$ unless otherwise stated. IR spectra were recorded as hexane solutions, unless otherwise stated, in solution cells with NaCl windows and 0.1 mm path-lengths, at 1 cm^{-1} resolution. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. All reagents were from commercial sources and used as supplied. The cluster $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OH)$, **1**, was prepared according to the literature method.[4]

Syntheses

Preparation of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2OH)$, 2a. A 240 mL toluene solution of the cluster **1**, prepared from $Os_3(CO)_{12}$ (420 mg, 464 mmol), was refluxed under N_2 with ethylene glycol (5 mL) for 5 h. Removal of the solvent followed by column chromatographic separation of the residue on silica gel using dichloromethane–hexane (70 : 30, v/v) as eluant gave unreacted **1** (164 mg, 39%) and **2a** (252 mg, 60%) as yellow bands. **2a**: ν_{CO}/cm^{-1}: 2110w, 2071vs, 2058m, 2022vs, 2000m, 1987m (literature:[16] 2111w, 2071vs, 2059s, 2023vs, 1999s, 1989m, 1982m). ^1H NMR δ 3.72 (t, 2H, μ-OCH_2CH$_2$OH, $^3J_{HH} = 4.9$ Hz), 3.64 (dt, 2H, OCH$_2$CH_2OH, $^3J_{HH} = 5.4$ Hz, 4.9 Hz), 1.63 (t, 2H, CH$_2$OH), −12.44 (s, 1H, OsHOs) (literature:[16] 3.67(t), 3.48(dt), 1.59(t), −12.51(s)). Analysis (Found): C, 15.81; H, 0.76. Calc. for $C_{12}H_6O_{12}Os_3$: C, 15.78; H, 0.66%.

Preparation of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)CH_3)$ 2b and $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH(CH_3)CH_2OH)$, 2c. A similar reaction starting from **1** (63.9 mg, 73.6 μmol) and 1,2-propanediol (2.5 mL) yielded unreacted **1** (25.6 mg, 40%), $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)CH_3)$, **2b** (25.8 mg, 38%) and $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH(CH_3)CH_2OH)$, **2c** (11.1 mg, 16%).

2b: ν_{CO}/cm^{-1}: 2110w, 2070vs, 2059m, 2023vs, 2016sh, 2007w, 1999s, 1989m. ^1H NMR δ 3.83 (m, 1H, CH), 3.69 (dd, 1H, CH$_2$, $^2J_{HH} = 10.2$ Hz, $^3J_{HH} = 8.8$ Hz), 3.31 (dd, 1H, CH_2, $^3J_{HH} = 2.9$ Hz), 1.97 (d, 1H, OH), 1.06 (d, 3H, CH_3, $^3J_{HH} = 5.9$ Hz), −12.39 (s, 1H, OsHOs). Analysis (Found): C, 16.91; H, 0.97. Calc. for $C_{13}H_8O_{12}Os_3$: C, 16.84; H, 0.86%.

2c: ν_{CO}/cm^{-1}: 2110w, 2070vs, 2059m, 2023vs, 2016sh, 2007w, 1999s, 1989m. ^1H NMR δ 4.75 (m, 1H, CH), 3.76 (dd, 1H, CH_2, $^2J_{HH} = 10.7$ Hz, $^3J_{HH} = 2.6$ Hz), 3.47 (dd, 1H, CH_2, $^3J_{HH} = 9.4$ Hz), 2.36 (d, 1H, CH_3, $^3J_{HH} = 1.8$ Hz), 2.00 (br s, 1H, OH), −12.35 (s, 1H, OsHOs). Analysis (Found): C, 16.88; H, 1.06. Calc. for $C_{13}H_8O_{12}Os_3$: C, 16.84; H, 0.86%.

Preparation of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2CH_2OH)$, 2d. A similar reaction of **1** (73.6 mg, 84.8 μmol) and 1,3-propanediol (1.5 mL) afforded unreacted **1** (50.6 mg, 69%) and $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2CH_2OH)$, **2d** (11.6 mg, 15%). ν_{CO}/cm^{-1}: 2110m, 2071vs, 2059m, 2024vs, 1999m, 1987m. ^1H NMR δ 3.69 (t, 2H, OCH_2CH$_2$, $^3J_{HH} = 6.6$ Hz), 3.66 (q, 2H, CH$_2$CH_2OH, $^3J_{HH} = 5.9$ Hz), 1.72 (q, 2H, CH$_2$CH_2), 1.29 (t, 1H, CH$_2$OH), −12.46 (s, 1H, OsHOs). MS (FAB): *m*/*z* 926 (Calculated for M$^+$, 927).

Preparation of $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)Ph)$, 2e. A similar reaction of **1** (75.3 mg, 86.7 μmol) and 1-phenyl-1,2-ethanediol (104.5 mg, 75.7 mmol) afforded unreacted **1** (67.0 mg, 89%) and $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH(OH)Ph)$, **2e** (7.0 mg, 8%). ν_{CO}/cm^{-1}: 2110w, 2071vs, 2059s, 2022vs, 2016s, 2007m, 1999s, 1987m. ^1H NMR δ 7.31 (m, 5H, Ph), 4.75 (m, 1H, CH(OH)), 3.76 (dd, 1H, CH_2, $^2J_{HH} = 11.0$ Hz, $^3J_{HH} = 9.5$ Hz), 3.47 (dd, 1H, CH_2, $^3J_{HH} = 2.9$ Hz), 2.37 (d, 1H, OH, $^3J_{HH} = 1.5$ Hz), −12.39 (s, 1H, OsHOs). Analysis (Found): C, 22.01; H, 1.06. Calc. for $C_{18}H_{10}O_{12}Os_3$: C, 21.85; H, 1.01%.

Esterification reactions of 2a with benzoyl chloride

To a solution of **2a** (74.7 mg, 85.6 μmol) in anhydrous THF (16 mL) kept at 0 °C was added Et_3N (15 mL), followed by the dropwise addition of benzoyl chloride (5 mL) in anhydrous THF (14 mL). The reaction mixture was stirred for 2 h, the solvent and volatiles removed under vacuum, and the residue chromatographed to yield $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CH_2OC(O)Ph)$, **3**, as a yellow band (22.8 mg, 31%). ν_{max}/cm^{-1} (hexane) 2111w, 2071s, 2060s, 2024vs, 2001s, 1990w (CO), 1733w (C=O). ^1H NMR δ 7.40–8.10 (m, 5H, Ph), 4.26 (t, 2H, 2H, OCH$_2$CH$_2$OCOPh, $^3J_{HH} = 4.4$ Hz), 3.93 (t, 2H, OCH$_2$CH_2OCOPh), −12.40 (s, 1H, OsHOs). Analysis (Found): C, 22.46; H, 0.95. Calc. for $C_{19}H_{10}O_{13}Os_3$: C, 22.44; H, 0.99%.

Partial oxidation of 2a to $Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OCH_2CHO)$, 4a

A solution of **2a** (75.2 mg, 82.4 μmol) in dichloromethane (5 mL) was added to a stirred solution of triacetoxyperiodinane (146.2 mg, 344.9 μmol) in dichloromethane (5 mL) over 1 min. The reaction mixture was stirred for 6 h and then quenched by pouring onto a solution of saturated aqueous

Table 3 Crystal and refinement data for **2b**, **2c**, **2e**, **3** and **6**

Compound	**2b**	**2c**	**2e**	**3**	**6**
Empirical Formula	$C_{13}H_8O_{12}Os_3$	$C_{13}H_8O_{12}Os_3$	$C_{18}H_{10}O_{12}Os_3$	$C_{19}H_{10}O_{13}Os_3$	$C_{29}H_{21}O_{11}Os_3P$
Formula weight	926.79	926.79	988.86	1016.87	1147.03
No. of reflections for final cell	7862	8192	8192	5467	6398
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a/Å	7.5248(2)	8.9663(1)	32.5756(4)	7.5496(1)	9.8090(1)
b/Å	16.6875(4)	13.9410(1)	9.8496(2)	11.5398(1)	10.8456(1)
c/Å	16.1098(3)	16.6032(2)	14.1537(2)	14.3430(1)	16.4270(1)
α/°		105.225(1)		90.910(1)	104.859(1)
β/°	95.111(1)	90.345(1)	92.198(1)	93.875(1)	102.320(1)
γ/°		98.629(1)		93.197(1)	93.160(1)
V/Å^3	2014.87(8)	1977.65(3)	4537.97(13)	1244.54(2)	1639.04(2)
Z	4	4	8	2	2
ρ_c/Mg m^{-3}	3.055	3.113	2.895	2.714	2.324
μ/mm^{-1}	18.928	19.284	16.819	15.339	11.704
F(000)	1640	1640	3536	912	1052
Crystal size/mm^3	0.36 × 0.36 × 0.18	0.36 × 0.28 × 0.26	0.44 × 0.31 × 0.24	0.465 × 0.263 × 0.150	0.180 × 0.180 × 0.036
Reflections collected	13123	15111	23031	8636	10753
Independent reflections	4945 [R(int) = 0.0507]	9413 [R(int) = 0.0287]	3264 [R(int) = 0.0332]	5942 [R(int) = 0.0346]	7404 [R(int) = 0.0261]
Max. and min. transmission	0.106451–0.044451	0.060868–0.010223	0.068504–0.030565	0.139959–0.050690	0.404929–0.263592
Data/restraints/parameters	4945/2/250	9413/6/511	3264/0/311	5942/2/319	7404/0/402
Goodness-of-fit on F^2	1.038	1.052	1.148	0.996	1.024
Final R [$I > 2\sigma(I)$]	0.0466	0.0405	0.0252	0.0484	0.0373
$wR2$ (all data)	0.1220	0.1092	0.0685	0.1254	0.0863
Largest diff. peak and hole e/Å^{-3}	1.816 and −4.380	2.227 and −1.967	0.824 and −1.043	2.201 and −2.977	1.137 and −1.065

$NaHCO_3$ containing $Na_2S_2O_3$ (8 mL). The aqueous layer was decanted off, brine solution (≈8 mL) was added, and the dichloromethane layer separated and dried over $MgSO_4$. Removal of the solvent followed by TLC of the residue gave one major yellow band which yielded unreacted **1** (38.0 mg, 50%) and $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2\text{CHO})$, **4a** (37.2 mg, 50%). ν_{max}/cm^{-1}: 2112w, 2073vs, 2061s, 2026vs, 2022vs, 2011m, 2000s, 1988m. ^{1}H NMR δ 9.34 (s, 1H, CHO), 4.31 (s, 2H, OCH_2), −12.35 (s, 1H, OsHOs). Analysis (Found): C, 16.19; H, 0.73. Calc. for $C_{12}H_4O_{12}Os_3$: C, 15.81; H, 0.44%.

A similar reaction between **2d** (15.0 mg, 16.2 µmol) and triacetoxyperiodinane (18.7 mg, 45.4 µmol) afforded unreacted **2d** (6.3 mg, 42%) and $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2\text{CH}_2\text{CHO})$, **4d** (8.5 mg, 57%). ν_{CO}/cm^{-1}: 2112w, 2073vs, 2061s, 2026vs, 2022vs, 2011m, 2000s, 1988m. ^{1}H NMR δ 9.70 (s, broad, 1H, CHO), 3.94 (t, 2H, OCH_2CH$_2$CHO, J = 5.9 Hz), 2.56 (t, 2H, CH$_2$CH_2CHO), −12.44 (s, 1H, OsHOs). MS (FAB): m/z 928 (calculated for M$^+$, 925).

Reaction of 4a with PhMgBr

A solution of PhMgBr in anhydrous ether (1.25 mL) was added dropwise to a solution of **4a** (86.2 mg, 94.6 µmol) in anhydrous THF (0.5 mL) maintained at −20 °C, and then stirred for 2.5 h. The reaction was then quenched with aq. HCl, extracted with ether, and the combined ether extracts dried over $MgSO_4$. Removal of the ether followed by chromatographic separation of the residue gave unreacted **4a** (34.5 mg, 40%) and **2e** (41.0 mg, 44%) as yellow bands.

Allylation reaction of 4a

Allyl bromide (0.04 mL, 747.7 µmol) and indium metal (19.5 mg, 170 µmol) were stirred in a water–tetrahydrofuran mixture (0.5 mL, 1 : 1, v/v) while a solution of **4a** (147 mg, 161 µmol) in water–tetrahydrofuran (1.5 mL, 1 : 2, v/v) was added. The reaction was allowed to stir overnight before extracting with ether. One major yellow band was obtained upon TLC separations of the ether extract, which afforded $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-OCH}_2\text{CH(OH)CH}_2\text{CH=CH}_2)$, **5**, as a yellow oil (18.1 mg, 12%). ν_{CO}/cm^{-1}: 2109w, 2071vs, 2058s, 2022vs, 2017sh, 2000s, 1986m. ^{1}H NMR δ 5.74 (m, 1H, CH=CH$_2$), 5.13 (m, 2H, CH=CH_2), 3.67 (m, 2H, OCH_2), 3.49 (m, 1H, CHOH), 2.11 (m, 2H, CH_2CH), 2.03 (d, 1H, OH, $^3J_{HH}$ = 2.3 Hz), −12.40 (s, 1H, OsHOs). MS (FAB): m/z 953 (calculated for M$^+$, 954).

Cleavage reaction of 2e

A solution of **2e** (10.7 mg, 10.9 µmol) in dichloromethane (seven drops) was placed inside a Schlenk tube, followed by addition of seven drops of concentrated hydrochloric acid. Removal of dichloromethane and excess hydrochloric acid on a vacuum line followed by spectroscopic analysis of the residue showed it to contain 1-phenyl-1,2-ethanediol and $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-Cl})$. ^{1}H NMR δ 7.36 (m, 5H, Ph), 4.84 (dd, 1H, CH(OH)Ph, $^3J_{HH}$ = 3.5 Hz and 8.0 Hz), 3.78 (dd, 1H, CH_2OH, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 3.5 Hz), 3.67 (dd, 1H, CH_2OH, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 8.0 Hz), 2.50 (br s, 1H, –OH), 2.00 (br s, 1H, –OH) and –12.78 (s, 1H, OsHOs). ν_{CO}/cm^{-1}: 2116w, 2077vs, 2068s, 2028vs, 2016s, 1991m, 1988m.

Reaction of 2a with PPh$_3$

To a solution of **2a** (55.5 mg, 63.6 µmol) in CH_3CN (21 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (7.8 mg, 70 µmol) in CH_3CN (16 mL) over 10 min. After stirring for an additional 50 min, the mixture was filtered through a short column of silica gel. A solution of PPh_3 (22.4 mg, 85.4 µmol) in CH_3CN (2 mL) was then added and the mixture stirred at room temperature for 20 min before removal of solvent and volatiles on a vacuum line, followed by chromatographic separation on a silica gel column to give $Os_3(\mu\text{-H})(CO)_9(\mu\text{-OCH}_2\text{CH}_2\text{OH})(PPh_3)$, **6**, as the major product. ν_{CO}/cm^{-1}: 2092m, 2053s, 2012vs, 1992w, 1975w, 1951w. ^{1}H NMR δ 7.30–7.62 (m, aromatic), 3.74 (m, 2H, µ-OCH_2), 3.22 (m, 2H, CH_2OH), 2.40 (t, OH, $^3J_{HH}$ = 3.0 Hz), 2.36 (t, OH, $^3J_{HH}$ = 3.0 Hz), −10.19 (d, OsHOs, $^2J_{PH}$ = 6.9 Hz), −10.96 (d, OsHOs, $^2J_{PH}$ = 6.9 Hz). ^{31}P{^{1}H} NMR δ 26.8 (s), 14.5 (s). Analysis (Found): C, 30.40; H, 1.83. Calc. for $C_{29}H_{21}O_{11}Os_3P$: C, 30.37; H, 1.85%.

Crystal structure determinations

Crystals were grown by slow cooling of dichloromethane–hexane solutions, and the selected crystals were mounted on quartz fibres. X-Ray data were collected on a Siemens SMART CCD system, using Mo-Kα radiation, at ambient temperatures

(293(2) K). Data were corrected for Lorentz and polarisation effects with the SMART suite of programs,[17] and for absorption effects with SADABS.[18] The final unit cell parameters were obtained by least-squares on a number of strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs.[19]

The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic hydrogen atoms were placed in calculated positions and given isotropic thermal parameters at 1.5 times that of the C atoms to which they are attached, except for the alkyl hydrogens in **2e**, which were located by a low angle difference map. The metal hydride positions were located by low angle ($2\theta \leq 30°$) difference maps, except for **3** in which the hydride was placed with the program XHYDEX.[20] All non-hydrogen atoms were given anisotropic thermal parameters in the final model. Cluster **2b** has disorder of the OH with the CH_3 group, which were modelled with two sites of equal occupancy together with appropriate restraints on bond and atomic parameters. Crystal and refinement data are tabulated in Table 3.

CCDC reference numbers 163860–163864.

See http://www.rsc.org/suppdata/dt/b1/b103800c/ for crystallographic data in CIF or other electronic format.

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