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Structural and bonding trends in osmium carbonyl cluster chemistry: metal–metal bond lengths and calculated strengths in the anions $[Os_x(CO)_y]^{2-}$, hydrides $[Os_x(CO)_yH_z]$ and hydride anions $[Os_x(CO)_yH_z]^{c-}$ *

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The metal–metal bond distances [d(M−M)] in the known structurally characterised osmium carbonyl anions, $[Os_x(CO)_y]^{2-}$, neutral carbonyl hydrides, $[Os_x(CO)_yH_z]$ and carbonyl hydride anions, $[Os_x(CO)_yH_z]^{c-}$, have been used to calculate bond enthalpy terms E(Os−Os) using the relationship $E(\text{Os−Os}) = 1.928 \times 10^{13} [d(\text{Os−Os})]^{-4.6}$, itself derived from published structural and enthalpy data. Summation of the metal–metal bond enthalpy terms, to give the total metal–metal bond enthalpy, ΣE(Os−Os), has revealed the varying efficiency with which these compounds use their electrons for metal–metal bonding. There is a strong correlation between the total metal–metal bond enthalpy per metal atom, ΣE(Os−Os)/x, and the number of ligand electrons per metal atom, the data falling on a curve which includes bulk osmium metal and $[Os(CO)_5]$ at the extremes. Correlations are also noted between ΣE(Os−Os) and the number of skeletal electron pairs (polyhedral skeletal electron pair theory) or number of formal two-centre two-electron (2c2e) bonds (18-electron rule). These correlations show that the electrons are used more efficiently for metal–metal bonding in larger clusters with fewer ligands. Thus, the metal–metal bond enthalpy per electron pair available (using the 18-electron rule) increases as the cluster becomes larger, indicating the error in models based on assigning fixed energies to notional 2c2e Os−Os bonds. Trends in ΣE(Os−Os) were explored as $Os(CO)_4$, $Os(CO)_3$ or $Os(CO)_2$ fragments are added to clusters in cluster build-up processes, as CO ligands are replaced by H^-, and on oxidative addition of H_2 to clusters, the latter leading to a prediction of limiting values of Os−H bond enthalpy terms. Trends in ΣE(Os−Os) were examined for series of closely related clusters, including those derivable from $[Os_4(CO)_{14}]$ by replacing CO by H^- or H_2, and a series of clusters derived from $[Os_6(CO)_{18}]$. The sum ΣE(Os−Os) is shown to be a single parameter which quantifies the overall effect of small changes in metal–metal distances in osmium carbonyl clusters.

In a recent paper[1] we showed how one could assess the relative stabilities of neutral osmium carbonyl clusters, $Os_x(CO)_y$, from their structures. Our approach assigned bond enthalpies, E(Os−Os), to the individual pairwise (though not necessarily *electron* pairwise) metal–metal bonding interactions they contained. These bond enthalpies were calculated from the respective bond lengths, d(Os−Os), using the relationship (1) where

$$E(\text{Os−Os}) = 1.928 \times 10^{13} [d(\text{Os−Os})]^{-4.6} \qquad (1)$$

E(Os−Os) is measured in kJ mol^{-1} when d(Os−Os) is measured in picometres. This relationship, and related ones of the same type ($E = Ad^{-4.6}$) for other metals, had been derived earlier[2] from published structural and thermochemical data on metals of the iron and cobalt sub-groups and had been shown to allow realistic estimates to be made of the strength of attachment, E(M−CO), of the carbonyl ligands to clusters $M_x(CO)_y$ of these elements. We found that E(M−CO) increased slightly, but consistently, as the cluster nuclearity x increased, and as the proportion of ligand molecules to metal atoms, y/x, decreased.

Here, we explore the value of using equation (1) to probe stability relationships within a wider series of osmium carbonyl clusters, including carbonyl anions, $[Os_x(CO)_y]^{c-}$, neutral osmium carbonyl hydrides, $[Os_x(CO)_yH_z]$, and osmium carbonyl hydride anions, $[Os_x(CO)_yH_z]^{c-}$. By focusing on the total metal–metal bond enthalpy, ΣE(Os−Os), we show how efficiently such clusters make use of the electrons that are in principle available for metal–metal bonding in these systems. They fall on a continuum extending from the mononuclear complex $[Os(CO)_5]$ at one extreme (no metal–metal bonding) to the bulk metal at the other extreme (only metal–metal bonding). We also show the relative efficiencies with which $Os(CO)_4$, $Os(CO)_3$ and $Os(CO)_2$ units use for metal–metal bonding purposes the electrons and orbitals available to them for cluster formation, estimate the strength of attachment to these clusters of hydride ligands, and note their influence on metal–metal bonding.

It should be stressed that the basis of our approach is that the metal–metal bonds in osmium carbonyl clusters resemble those in the bulk metal sufficiently to permit use of the same bond length–bond enthalpy relationship [equation (1)]. The metal–metal bonds in question are relatively weak, much weaker than the metal–ligand bonds, which is why adsorption of ligands such as carbon monoxide molecules on metal surfaces can cause drastic rearrangement of the metal surface atoms.[3] Being weak, the metal–metal bonds may be influenced by the bonding requirements of the ligands, and we illustrate that here. However, despite the relative softness of the metal–metal bonding potential-energy well, we consider the use of the bond length–bond enthalpy relationship (1) to be justified, particularly because we focus on the total bond enthalpy, ΣE(Os−Os), rather than attempt to interpret in detail the lengths and strengths of individual bonds. We are encouraged to use this approach because of the reliability of such relationships elsewhere in chemistry,†,[4] and in particular because of their evident superiority in cluster chemistry over energies assigned to notional single (two centre two electron, 2c2e), double (2c4e) or triple (2c6e)

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* *Supplementary data available* (No. SUP 57248, 12 pp.): Os−Os bond lengths and bond enthalpies. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

† We are aware of at least one case where longer bonds are associated with greater metal–ligand binding energies, although these energies were determined in a co-ordinating solvent.[5]

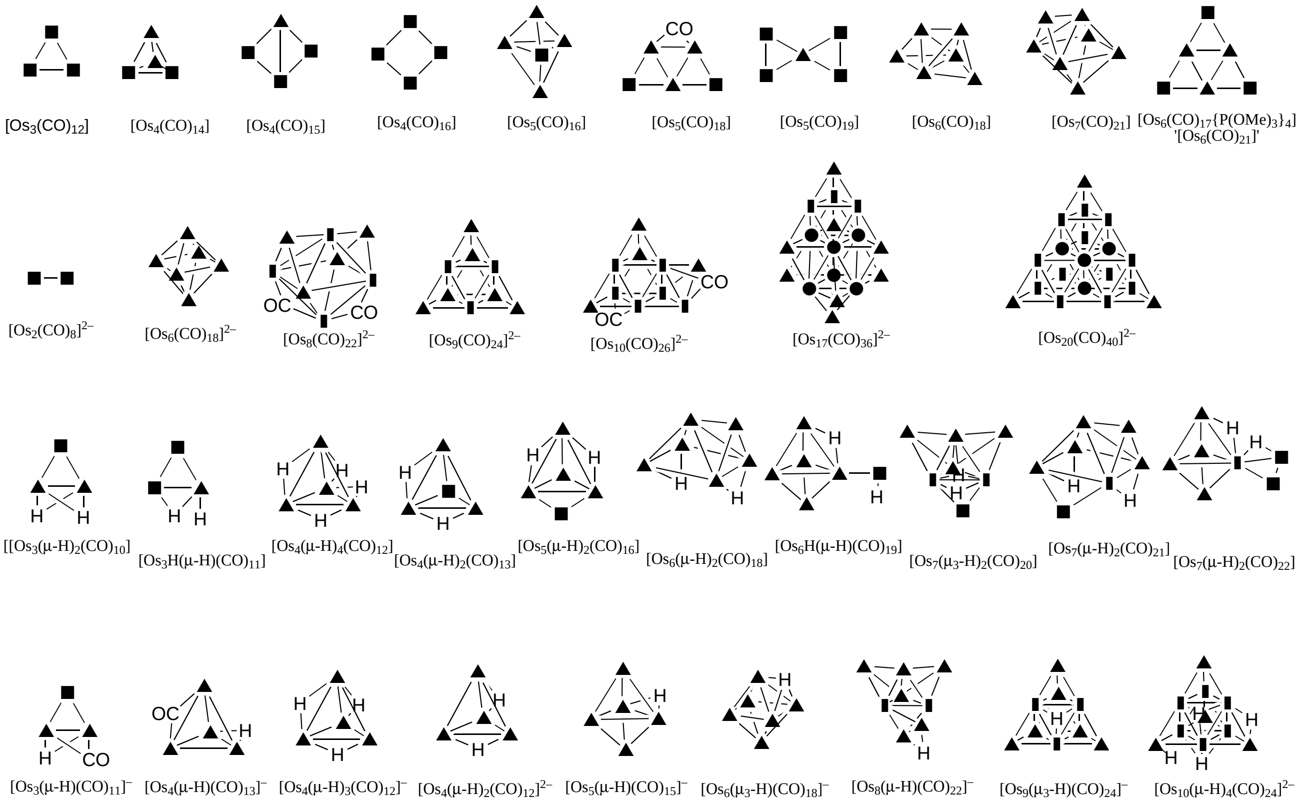

Fig. 1 Structures of the osmium carbonyl clusters discussed in this work. The following symbols are used: ■ = $Os(CO)_4$; ▲ = $Os(CO)_3$; ▮ = $Os(CO)_2$; ● = Os(CO). Hydride and bridging carbonyl ligands are drawn explicitly

bonds, which still have some value elsewhere, *e.g.* for simple organic systems. Attempts have been made in the past to rationalise the bonding in metal clusters in terms of 2c2e metal–metal bonds of defined energy,[6] even though such electron-pair-based bond enthalpy terms are of negligible value for dealing with bulk metals (where bonding contacts greatly exceed the numbers of bond pairs available) and of very limited value for describing the bonding in metal clusters, as we shall show. Our approach allows us to show how variable is the metal–metal bond enthalpy per metal–metal bond pair [which in turn has to be calculated using the 18-electron rule or the polyhedral skeletal electron pair theory (PSEPT)], and so by implication how unreliable are bond-energy approaches that assume the enthalpy per bond pair to be constant.

Results and Discussion

Before embarking on a discussion of the likely strengths of the metal–metal bonds in these clusters, it is worthwhile noting the patterns to which their shapes conform. Although the shapes themselves have been documented in recent structural compilations,[7] and reviews of osmium[8] and cluster chemistry,[9] and the patterns defined by sets of osmium carbonyl clusters, *e.g.* those based on an octahedral Os_6 unit or fragment thereof, are now familiar figures in textbooks,[10] we are not aware of any recent surveys that explore all of the structural relationships that underpin the skeletal shapes in Fig. 1.

Three main ways of predicting or rationalising the shapes of metal clusters in general, and osmium carbonyl clusters in particular, have been explored. One, the treatment of metal clusters as fragments of the bulk metal,[11] has evident merit for several of the clusters illustrated in Fig. 1, *e.g.* most of the carbonyl anions, $[Os_x(CO)_y]^{2-}$, and several of the carbonyl hydrides, $[Os_x(CO)_yH_z]^{c-}$, can be seen as fragments of a close-packed metal lattice, although it is exceedingly difficult to estimate the ligand-bonding capacity of the metal atoms on the fragment surfaces. A second approach is to assume that each metal atom obeys the 18-electron rule, *i.e.* that it uses all nine valence-shell orbitals either to bond ligands, to accommodate lone-pair electrons, or to participate in two-centre two-electron metal–metal bonds. This approach works well for small clusters such as $[Os_2(CO)_8]^{2-}$, $[Os_3(CO)_{12}]$, $[Os_4(CO)_{14}]$, $[Os_4(CO)_{15}]$ and $[Os_4(CO)_{16}]$, indeed for rationalising the metal networks in most of the neutral carbonyls in Fig. 1, but has limited use for certain important species such as $[Os_6(CO)_{18}]^{2-}$, for which there is an electron pair too many to explain the 12 edges of the octahedron as 2c2e bonds. Drawing a localised bond structure in the case of even relatively simple clusters, such as $[Os_4(CO)_{14}]$, requires the use of dative bonds. Several resonance structures are possible and these dative bonds do not correlate well with the longer bond lengths in such clusters. The 18-electron rule approach to cluster-electron counting is not readily able to predict cluster geometries, in contrast to the third method described below. Nevertheless, we indicate the numbers of 2c2e Os–Os bonds required by the 18-electron rule approach in Tables 1–4 below. The third method of treating the bonding in osmium carbonyl and similar metal clusters, PSEPT,[12] exploits the analogy with borane clusters.[13] This too assumes that each metal atom uses all nine valence-shell atomic orbitals, six for bonding to carbonyl ligands or accommodating lone-pair electrons, the remaining three orbitals being available for metal–metal bonding use. This approach allows many structures to be rationalised or even predicted, including some important systems that appear anomalous in localised bond terms, like the octahedral $[Os_6(CO)_{18}]^{2-}$ (and related clusters) referred to above. However PSEPT classifies as skeletal electron pairs some electrons that contribute little or not at all to the actual metal–metal bonding, even though the presence of these (lone-pair) electrons does influence the molecular shape. In our discussion of metal–metal bond energies below we draw attention to some of these features, and analyse the effectiveness with which the available electrons, counted by each of these latter two schemes, are used for metal–metal bonding.

Since the important parameters we wish to consider in this discussion, apart from the metal–metal bond distances, are the polyhedral shapes of these metal carbonyl clusters, the numbers

Table 1 Neutral binary osmium carbonyls, $[Os_x(CO)_y]$, studied, with electron numbers, structural types and metal–metal bond energies[a]

Formula	$2y/x$	PSEPT type (S_p)	S_{1b}	ΣE(Os–Os)	ΣE(Os–Os)/x	ΣE(Os–Os)/S_{1b}	ΣE(Os–Os)/S_p
$[Os_4(CO)_{16}]$	8.0	*hypho* (8)	4	349	87	87	44
$[Os_3(CO)_{12}]$	8.0	*arachno* (6)	3	283	94	94	47
$[Os_5(CO)_{19}]$	7.6	*hypho* (9)	6	543	109	91	60
$[Os_4(CO)_{15}]$	7.5	*arachno* (7)	5	464	116	93	66
$[Os_5(CO)_{18}]$	7.2	*arachno* (8)	7	690	138	99	86
'$Os_6(CO)_{21}$'[b]	7.0	*arachno* (9)	9	860	143	96	96
$[Os_4(CO)_{14}]$	7.0	*nido* (6)	6	608	152	101	101
$[Os_5(CO)_{16}]$	6.4	*closo* (6)	9	955	191	106	159
$[Os_6(CO)_{18}]$	6.0	capped *closo* (6)	12	1290	215	108	215
$[Os_7(CO)_{21}]$	6.0	capped *closo* (7)	14[c]	1526	218	109	218

[a] All thermodynamic data in kJ mol^{-1}. [b] Structurally characterised as the phosphite-substituted cluster, $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$. [c] This compound has 15 polyhedron edges, but only 14 electron pairs in the localised-bond model.

Table 2 Osmium carbonyl anions $[Os_x(CO)_y]^{c-}$ studied, with electron numbers, structural types and metal–metal bond energies[a]

Formula	$(2y+c)/x$	PSEPT type (S_p)	S_{1b}	ΣE(Os–Os)	ΣE(Os–Os)/x	ΣE(Os–Os)/S_{1b}	ΣE(Os–Os)/S_p
$[Os_2(CO)_8]^{2-}$	9	*arachno* (5)	1	78	39.3	78	16
$[Os_6(CO)_{18}]^{2-}$	6.33	*closo* (7)	11	1205[b]	201	110	172
$[Os_8(CO)_{22}]^{2-}$	5.75	Bicapped *closo* (7)	17	1943	243	114	278
$[Os_9(CO)_{24}]^{2-}$	5.56	Tricapped *closo* (7)	20	2314	257	116	331
$[Os_{10}(CO)_{26}]^{2-}$	5.4	Capped tricapped *closo* (7)	23	2603	260	113	372
$[Os_{17}(CO)_{36}]^{2-}$	4.35	*c*	48	6011	354	125	
$[Os_{20}(CO)_{40}]^{2-}$	4.1	*c*	59	7108	355	120	

[a] All thermodynamic data in kJ mol^{-1}. [b] For the $2[Mo_4(\eta\text{-}C_5H_4Pr^i)_4S_4]^+$ salt form 1. For the $2[PMePh_3]^+$ salt, ΣE(Os–Os) = 1217 kJ mol^{-1}. For the $2[Mo_4(\eta\text{-}C_5H_4Pr^i)_4S_4]^+$ salt form 2, ΣE(Os–Os) = 1201 kJ mol^{-1}. [c] Contains some metal atoms that clearly use more than three AOs for skeletal bonding so are beyond the scope of simple PSEPT.

Table 3 Neutral osmium carbonyl hydrides $[Os_x(CO)_yH_z]$ studied, with electron numbers, structural types and metal–metal bond energies[a]

Formula	$(2y+z)/x$	PSEPT type (S_p)	S_{1b}	ΣE(Os–Os)	ΣE(Os–Os)/x	ΣE(Os–Os)/S_{1b}	ΣE(Os–Os)/S_p
$[Os_3H(\mu\text{-}H)(CO)_{11}]$	8	*arachno* (6)	3	266	89	89	44
$[Os_3(\mu\text{-}H)_2(CO)_{10}]$	7.33	*nido* (5)	4	339[b]	113	85	68
$[Os_4(\mu\text{-}H)_4(CO)_{12}]$	7	*nido* (6)	6	536	134	89	89
$[Os_4(\mu\text{-}H)_2(CO)_{13}]$	7	*nido* (6)	6	596[c]	149	99	99
$[Os_5(\mu\text{-}H)_2(CO)_{16}]$	6.8	Edge-bridged tetrahedron (7)	8	763	153	95	109
$[Os_6H(\mu\text{-}H)(CO)_{19}]$	6.67	Spiked *TBPY* (8)[d]	10	1005	167.5	100.5	126
$[Os_7(\mu\text{-}H)_2(CO)_{22}]$	6.57	Spiked *TBPY* (9)	12	1179	168	98	131
$[Os_6(\mu\text{-}H)_2(CO)_{18}]$	6.33	Capped *nido* (7)	11	1114	186	101	159
$[Os_7(\mu\text{-}H)_2(CO)_{21}]$	6.29	Edge-bridged capped *nido* (8)	13	1300	186	100	162.5
$[Os_7(\mu_3\text{-}H)_2(CO)_{20}]$	6	Edge-bridged capped *closo* (7)	14	1430	204	102	204

[a] All thermodynamic data in kJ mol^{-1}. [b] For the structure of the pure cluster; ΣE(Os–Os) = 344 kJ mol^{-1} for 0.5 molecule of this cluster cocrystallised with $[Os_3Ni(CO)_9(\eta\text{-}C_5H_5)H_3]$. [c] For one molecule in the asymmetric unit; the other has ΣE(Os–Os) = 591 kJ mol^{-1}. [d] *TBPY* = Trigonal bipyramid.

of bonding contacts (polyhedron edge lengths) therein, and the numbers and distribution of the carbonyl ligands, it is helpful to illustrate their structures in a manner that shows where the ligands are. Fig. 1 shows the structures of the osmium carbonyl clusters discussed here in a way that draws attention to the polyhedral shape defined by the metal atoms, the number of terminal carbonyl ligands attached to each, and the locations of bridging carbonyl ligands and hydrides. The clusters are arranged within Fig. 1 according to cluster type (binary carbonyl, carbonyl anion, carbonyl hydride, carbonyl hydride anion) and by increasing cluster nuclearity. Although the neutral carbonyls were the subject of our previous paper,[1] for completeness, and to allow a wider range of comparisons to be made, we include them in the discussion in the current paper. Additionally, the parent binary carbonyl, $[Os(CO)_5]$, and the raft-cluster $[Os_6(CO)_{21}]$ are included in several aspects of the discussion in this paper, although the former has not been characterised by diffraction methods in the solid state,[14] and clearly contains no Os–Os bonding, and the Os_6 raft has only been structurally characterised as the phosphite derivative, $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$.[15] Details of the steric and electronic influence of phosphite, phosphine and other ligands on the metal–metal bond enthalpy will be discussed subsequently.[16] All of these clusters have been structurally characterised by diffraction techniques, the majority using X-ray diffraction, so that the hydrogen atoms have only rarely been located directly. Their positions have generally been determined by potential-energy calculations,[17,18] often using NMR evidence to confirm these positions. As an example, in the initial publication of the structure of $[Os_6H_2(CO)_{18}]$ it was suggested (mainly on the basis of NMR evidence) that there was one μ-H ligand and one μ_3- or μ_4-H ligand,[19,20] whilst potential-energy calculations[17] suggested that both ligands are in the μ-H sites shown in Fig. 1. The structural differences between $[Os_6(CO)_{18}]^{2-}$ and $[Os_6H_2(CO)_{18}]$, and the electronic origin of these differences, are discussed below.

We indicate in tabular form (Tables 1–4) the total metal–metal bond enthalpies, ΣE(Os–Os), calculated for these clusters using equation (1), including as before, all first-co-ordination-sphere contacts and cross-polyhedral distances $\leqslant$421 pm. The limit of 421 pm was chosen, as before,[1] in order to include cross-octahedron distances as in $[Os_6(CO)_{18}]^{2-}$, and equivalent distances in fragments of octahedra, *e.g.* across the square face of $[Os_6H_2(CO)_{18}]$, whilst excluding longer cross-polyhedra distances, such as the apex–apex distance in the trigonal bipyramid $[Os_5(CO)_{15}H]^-$. Cross-octahedron distances are included since these are equivalent to the next-nearest neighbour distances of

Table 4 Osmium carbonyl hydride anions, $[Os_x(CO)_yH_z]^{c-}$, studied, with electron numbers, structural types and metal–metal bond energies[a]

Formula	$(2y + z + c)/x$	PSEPT type (S_p)	S_{1b}	ΣE(Os–Os)	ΣE(Os–Os)/x	ΣE(Os–Os)/S_{1b}	ΣE(Os–Os)/S_p
$[Os_3(\mu\text{-}H)(CO)_{11}]^-$	8	*arachno* (6)	3	299	100	100	50
$[Os_4(\mu\text{-}H)_3(CO)_{12}]^-$	7	*nido* (6)	6	575[b]	144	96	96
$[Os_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$	7	*nido* (6)	6	600	150	100	100
$[Os_4(\mu\text{-}H)(CO)_{13}]^-$	7	*nido* (6)	6	614	153.5	102	102
$[Os_5(\mu\text{-}H)(CO)_{15}]^-$	6.4	*closo* (6)	9	935	187	104	156
$[Os_6(\mu_3\text{-}H)(CO)_{18}]^-$	6.33	*closo* (7)	11	1161[c]	193.5	105	166
$[Os_8(\mu\text{-}H)(CO)_{22}]^-$	5.75	(7)	17	1864[d]	233	110	266
$[Os_9(\mu_3\text{-}H)(CO)_{24}]^-$	5.56	Tricapped *closo* (7)	20	2178	242	109	311
$[Os_{10}(\mu\text{-}H)_4(CO)_{24}]^{2-}$	5.4	Tetracapped *closo* (7)	23	2513	251	109	359

[a] All thermodynamic data in kJ mol^{-1}. [b] For $[NMe_4]^+$ salt; ΣE(Os–Os) = 567 kJ mol^{-1} for $[Ph_2PNPPh_2]^+$ salt. [c] For $[Ph_2PNPPh_2]^+$ salt; ΣE(Os–Os) = 1158 kJ mol^{-1} for $[NBu_4]^+$ salt. [d] For $[PMePh_3]^+$ salt; ΣE(Os–Os) = 1871 kJ mol^{-1} for $[Ph_2PNPPh_2]^+$ salt. The structure consists of a tetrahedron sharing an edge of the monocapped *closo* six-vertex structure.

the body-centred cubic lattice, which were included in deriving equation (1). In order clearly to illustrate some of the trends which this paper explores, the clusters are listed in each table in order of increasing number of ligand electrons per metal atom {the fraction $(2y + z + c)/x$ for the general formula $[Os_x(CO)_yH_z]^{c-}$}; for clusters with the same number of ligand electrons per metal atom the total metal–metal bond enthalpy per metal atom is used to decide the order in which they are listed. The tables also show PSEPT structural type and number of skeletal electron pairs (S_p), and also the number of electron-pair bonds according to a localised [18-electron or effective atomic number (EAN)] bond model (S_{1b}), and show the total metal–metal bond enthalpy per osmium, per localised electron-pair bond and per PSEPT electron pair.

Tables 1–4 indicate, by footnotes, several cases where the same cluster has been crystallographically characterised more than once, either with differing cations or a second molecule such as a solvent cocrystallised. There are also clusters with more than one molecule in the asymmetric unit or the same molecular formula crystallises in more than one polymorph. The range of ΣE(Os–Os) values for the same cluster is a representation of the potential error in ΣE(Os–Os) and derived thermodynamic quantities.[21] The ΣE(Os–Os) data included in the tables as footnotes differ from the values in the main body of the tables by between 0.25 and 1.5% or 3 to 12 kJ mol^{-1}, suggesting that 2% can be taken as a likely crystallographic contribution to the error limit for the data in Tables 5–12. Tables 1–4 also contain cases where multiple structural determinations have been published of the same compound. These entries appear only once, the data being taken from the most recent or most accurate determination as referenced in the Experimental section.

In our previous publication we used our calculations of the metal–metal bond enthalpies for neutral binary osmium carbonyl clusters, together with the experimentally determined enthalpy of formation of $[Os_3(CO)_{12}]$, to determine the Os–CO bond enthalpy of these neutral clusters, and hence the enthalpies of disruption [to Os(g) and CO(g)] and gas-phase standard enthalpies of formation (from the elements in their standard states) of all the known crystallographically characterised binary osmium carbonyls, $Os_x(CO)_y$. Such data are clearly of relevance to cluster-interconversion reactions, and we have previously explored some examples. The calculation of enthalpies of disruption and formation of the wider range of osmium clusters discussed in this work would require knowledge of bond enthalpy terms for terminal, μ- and μ_3-Os–H bonds, as well as the electron affinities of osmium carbonyl clusters. Reliable data are not available for these terms, and so we have chosen to investigate the usefulness of the total metal–metal bond enthalpy, ΣE(Os–Os), in exploring trends within these osmium carbonyl clusters, the thermodynamics of cluster interconversion reactions, and the implication of ΣE(Os–Os) for possible values of Os–H bond enthalpy terms. The thermodynamics of reactions involving CO and H_2 at metal clusters and on metal surfaces are of fundamental importance in catalysis,[22] and there is a need for consistent values for bond enthalpies and bond-dissociation enthalpies of M–CO and M–H bonds,[23] as well as for other important moieties including surface and core carbide (MC), methylene ($M{=}CH_2$) and formyl [M–C(O)H] for a range of metals.

Trends in ΣE(Os–Os) as a function of the number of metal atoms and ligand electrons

In our earlier publication on the neutral binary osmium carbonyls, $[Os_x(CO)_y]$, we demonstrated that there is a relationship between the metal–metal bond enthalpy per metal atom, ΣE(Os–Os)/x, and the number of carbonyl ligands per metal atom, y/x. In considering the wider range of clusters in Fig. 1 we similarly examine the relationship (Fig. 2) between the total metal–metal bond enthalpy per metal atom, ΣE(Os–Os)/x, and the number of ligand electrons per metal atom, counting two electrons for each CO ligand and one electron for each H ligand or anionic charge. Fig. 2 shows the same overall trend as was observed for the smaller range of data available for the neutral binary carbonyls, namely an upward trend in the curve towards larger cluster species (with fewer ligands per metal atom). The figure shows that there are a number of isoelectronic series of clusters, and the trends in metal–metal bond enthalpy as CO ligands are replaced by H^- or H_2 are discussed below. As before, the data fit a second-order polynomial (see Experimental section for details) which, given the wider range of data made possible by considering the large cluster anions, predicts a value of the metal–metal bond enthalpy for zero ligand electrons per metal of 785 kJ mol^{-1}, satisfyingly close to the value for bulk osmium metal (790 kJ mol^{-1}).

Given that the total number of electrons which can be accommodated per metal atom is limited by the 18-electron rule, we can expect that as the number of electrons involved in metal–ligand bonding decreases the number of electrons available for metal–metal bonding will increase. The observation that the data plotted in Fig. 2 follow a curve, rather than a straight line, indicates that as more electrons become available for metal–metal bonding so these electrons are used more efficiently in metal–metal bonding. The metal–metal distances in small clusters are typically 10–15% longer than those in bulk metal; those in the larger clusters are nearer to those in the bulk metal.

Trends in ΣE(Os–Os) as a function of the number of PSEPT skeletal electron pairs, S_p

Metal carbonyl clusters can be viewed as analogues of borane clusters, and their bonding considered in terms of the number of skeletal electron pairs, S_p, formally available for cluster bonding.[13] One way of viewing the trends in metal–metal bond enthalpy is to chart the metal–metal bond enthalpy per skeletal electron pair, ΣE(Os–Os)/S_p, against the number of skeletal

Table 5 The efficiency, $\Sigma E(\text{Os–Os})/S_p$ (kJ mol^{-1}), with which the S_p skeletal electron pairs are used in metal–metal bonding in the osmium carbonyl clusters, classified by their cluster type. Clusters marked with an asterisk have structures which are more open than required on the basis of their electron counts

	Skeletal electron pairs									
Cluster type	5		6		7		8		9	
Tetracapped *closo*					$[Os_{10}(CO)_{26}]^{2-}$*	372				
					$[Os_{10}H_4(CO)_{24}]^{2-}$	359				
Tricapped *closo*					$[Os_9(CO)_{24}]^{2-}$	331				
					$[Os_9H(CO)_{24}]^{-}$	311				
Bicapped *closo*					$[Os_8(CO)_{22}]^{2-}$	278				
					$[Os_8H(CO)_{22}]^{-}$*	266				
Monocapped *closo*			$[Os_6(CO)_{18}]$	215	$[Os_7(CO)_{21}]$	218				
					$[Os_7H_2(CO)_{20}]$*	204				
closo			$[Os_5(CO)_{16}]$	159	$[Os_6(CO)_{18}]^{2-}$	172	$[Os_7H_2(CO)_{21}]$*	162		
			$[Os_5H(CO)_{15}]^{-}$	156	$[Os_6H(CO)_{18}]^{-}$	166				
					$[Os_6H_2(CO)_{18}]$*	159				
nido	$[Os_3H_2(CO)_{10}]$	68	$[Os_4H(CO)_{13}]^{-}$	102	$[Os_5H_2(CO)_{16}]$*	109	$[Os_6H_2(CO)_{19}]$*	126	$[Os_7H_2(CO)_{22}]$*	131
			$[Os_4(CO)_{14}]$	101						
			$[Os_4H_2(CO)_{12}]^{2-}$	100						
			$[Os_4H_2(CO)_{13}]$	99						
			$[Os_4H_3(CO)_{12}]^{-}$	96						
			$[Os_4H_4(CO)_{12}]$	89						
arachno	$[Os_2(CO)_8]^{2-}$	16	$[Os_3H(CO)_{11}]^{-}$	50	$[Os_4(CO)_{15}]$	66	$[Os_5(CO)_{18}]$	86	$[Os_6(CO)_{17}\text{-}\{P(OMe)_3\}_4]$*	96
			$[Os_3(CO)_{12}]$	47						
			$[Os_3H_2(CO)_{11}]$	44						
hypho			$[Os_2(CO)_{10}]$	0			$[Os_4(CO)_{16}]$	44	$[Os_5(CO)_{19}]$*	60

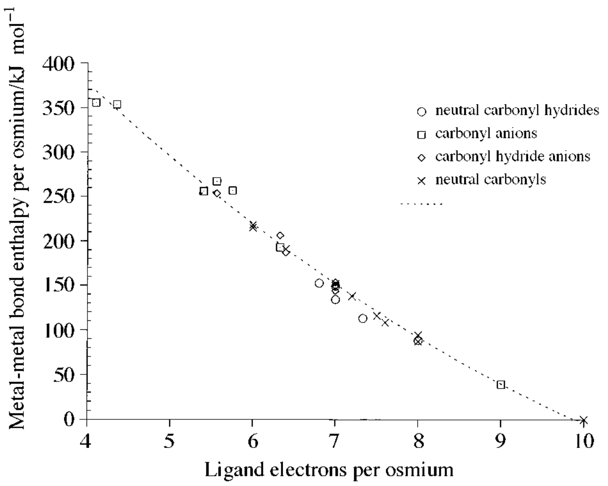

Fig. 2 Plot of metal–metal bond enthalpy per osmium as a function of the number of ligand electrons per osmium

electron pairs and the resulting predicted cluster geometry, as shown in Table 5. It should be noted that some clusters[24,25] show isomeric geometries less symmetrical than the simplest corresponding to the electron count, *e.g.* capped-*nido* instead of *closo*, *etc.* Such clusters are classified in Table 5 according to the simplest formal type, and are indicated by an asterisk. The reasons for their less symmetrical actual shapes are not always clear, and may arise from both steric and electronic factors, thus $[Os_6H_2(CO)_{18}]$ needs to accommodate 20 ligands rather than the 18 of $[Os_6(CO)_{18}]^{2-}$, equally a comparison of $[Os_6(CO)_{18}]^{2-}$ (*closo*, octahedral) with $[Os_6H_2(CO)_{18}]$ (capped-*nido*) may suggest that the need by bridging hydride ligands for regions of relatively high electron density may favour the less spherically symmetrical skeleton of the latter, as indicated by calculations on $[B_6H_6]^{2-}$, $[B_6H_7]^{-}$ and B_6H_8 as models.[26] Indeed most of the 'anomalous' systems marked by an asterisk in Table 5 contain bridging hydride ligands. It may also be worth noting that where less symmetrical, more open, capped-*nido* or similar structures are found, these generally have the numbers of metal–metal contacts (polyhedron edges) that are compatible with the 18-electron rule and 2c2e metal–metal bonds.[27,28] These perturbations in the overall structural pattern do not appear to affect very greatly the efficiency with which the skeletal electron pairs are used.

Table 5 illustrates the same trends in cluster stability as we noted when discussing the binary carbonyls. The data illustrate that the available skeletal electrons are used more efficiently for metal–metal bonding as the clusters become less open, or as the number of metal atoms increases. In the open series of clusters (*arachno* and *hypho*) some of the skeletal electrons are not involved in metal–metal bonding but are effectively lone pairs (and thus are important in determining the cluster geometry). The most extensive trend of data is within the series of clusters with seven skeletal electron pairs, whose structures are based on the octahedron, either with vertices removed, or with up to four of the eight faces capped; these clusters show a steady, and regular, progression in the value of $\Sigma E(\text{Os–Os})/S_p$, the difference between successive rows in the table being around 50 kJ mol^{-1}. The trends in total metal–metal bond enthalpy within the series of clusters isoelectronic with $[Os_4(CO)_{14}]$ will be discussed below.

The Os_{17} and Os_{20} cluster anions cannot be accounted for simply in terms of the PSEPT rules, because they contain metal atoms that evidently use more than three atomic orbitals (AOs) for cluster bonding. They have structures closely related to the bulk metal, a fact which is also borne out by the multiple redox behaviour of these clusters.

Trends in $\Sigma E(\text{Os–Os})$ as a function of the number of polyhedron edges and metal–metal bonds

As indicated above, the bonding in many of the clusters in Fig. 1 can be accounted for in terms of a localised 18-electron bonding model. The number of metal–metal bonds in a structure can be determined by application of the 18-electron rule, and a localised bonding model can be appropriate when the number of metal–metal bonds equals the number of cluster edges. In clusters such as $[Os_6(CO)_{18}]^{2-}$, which has only 11 metal–metal bonding electron pairs for the 12 edges of the octahedron, it is either necessary to invoke resonance of the 11 bonds around the polyhedron, or to accept that delocalised bonding models such as PSEPT are preferable for such clusters. Tables 1–4 list for each cluster the number (S_{1b}) of localised Os–Os bonds

Table 6 Pairs of osmium carbonyl clusters related by the addition or removal of $Os(CO)_2$ fragments, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in ΣE(Os–Os). Clusters labelled with an asterisk have structures which are more open than required for their electron counts

Cluster pair	ΣE(Os–Os)	$\Delta[\Sigma E$(Os–Os)]
With six skeletal electron pairs		
$[Os_3(CO)_{12}] \longrightarrow [Os_4(CO)_{14}]$	$283 \longrightarrow 608$	+325
$[Os_4(CO)_{14}] \longrightarrow [Os_5(CO)_{16}]$	$608 \longrightarrow 955$	+347
$[Os_5(CO)_{16}] \longrightarrow [Os_6(CO)_{18}]$	$955 \longrightarrow 1290$	+335
$[Os_3H_2(CO)_{11}] \longrightarrow [Os_4H_2(CO)_{13}]$	$266 \longrightarrow 596$	+330
$[Os_3H(CO)_{11}]^- \longrightarrow [Os_4H(CO)_{13}]^-$	$299 \longrightarrow 614$	+315
$[Os_4H(CO)_{13}]^- \longrightarrow [Os_5H(CO)_{15}]^-$	$614 \longrightarrow 935$	+321
With seven skeletal electron pairs		
$[Os_4(CO)_{15}] \longrightarrow [Os_7(CO)_{21}]$	$464 \longrightarrow 1526$	+1062 (÷3 = 354)
$[Os_5H_2(CO)_{16}]^* \longrightarrow [Os_6H_2(CO)_{18}]^*$	$763 \longrightarrow 1114$	+351
$[Os_6H_2(CO)_{18}]^* \longrightarrow [Os_7H_2(CO)_{20}]^*$	$1114 \longrightarrow 1430$	+316
$[Os_6(CO)_{18}]^{2-} \longrightarrow [Os_8(CO)_{22}]^{2-}$	$1205 \longrightarrow 1943$	+738 (÷2 = 369)
$[Os_8(CO)_{22}]^{2-} \longrightarrow [Os_9(CO)_{24}]^{2-}$	$1943 \longrightarrow 2314$	+371
$[Os_9(CO)_{24}]^{2-} \longrightarrow [Os_{10}(CO)_{26}]^{2-}$	$2314 \longrightarrow 2603$	+289
$[Os_8H(CO)_{22}]^{-}* \longrightarrow [Os_9H(CO)_{24}]^-$	$1864 \longrightarrow 2178$	+314
With eight skeletal electron pairs		
$[Os_4(CO)_{16}] \longrightarrow [Os_5(CO)_{18}]$	$349 \longrightarrow 690$	+341
$[Os_6H_2(CO)_{19}]^* \longrightarrow [Os_7H_2(CO)_{21}]^*$	$1005 \longrightarrow 1300$	+295

Table 7 Pairs of osmium carbonyl clusters related by the addition or removal of $Os(CO)_3$ fragments, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in ΣE(Os–Os). Clusters labelled with an asterisk have structures which are more open than required for their electron counts

Cluster pair	ΣE(Os–Os)	$\Delta[\Sigma E$(Os–Os)]
Capped-*closo*		
$[Os_6(CO)_{18}] \longrightarrow [Os_7(CO)_{21}]$	$1290 \longrightarrow 1526$	+236
closo		
$[Os_6H_2(CO)_{18}]^* \longrightarrow [Os_7H_2(CO)_{21}]^*$	$1114 \longrightarrow 1300$	+186
$[Os_5H(CO)_{15}]^- \longrightarrow [Os_6H(CO)_{18}]^-$	$935 \longrightarrow 1161$	+226
nido		
$[Os_3H_2(CO)_{10}] \longrightarrow [Os_4H_2(CO)_{13}]$	$339 \longrightarrow 596$	+257
$[Os_4H_2(CO)_{13}] \longrightarrow [Os_5H_2(CO)_{16}]$	$596 \longrightarrow 763$	+167
$[Os_5H_2(CO)_{16}]^* \longrightarrow [Os_6H_2(CO)_{19}]^*$	$763 \longrightarrow 1005$	+242
$[Os_6H_2(CO)_{19}]^* \longrightarrow [Os_7H_2(CO)_{22}]^*$	$1005 \longrightarrow 1179$	+174
arachno		
$[Os_3(CO)_{12}] \longrightarrow [Os_4(CO)_{15}]$	$283 \longrightarrow 464$	+181
$[Os_4(CO)_{15}] \longrightarrow [Os_5(CO)_{18}]$	$464 \longrightarrow 690$	+226
$[Os_3(CO)_{12}] \longrightarrow [Os_5(CO)_{18}]$	$283 \longrightarrow 690$	+407 (÷2 = 203)
hypho		
$[Os_4(CO)_{16}] \longrightarrow [Os_5(CO)_{19}]^*$	$349 \longrightarrow 543$	+194

Table 8 Pairs of osmium carbonyl clusters related by the addition or removal of $Os(CO)_4$ fragments, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in ΣE(Os–Os). Clusters labelled with an asterisk have structures which are more open than required for their electron counts

Cluster pair	ΣE(Os–Os)	$\Delta[\Sigma E$(Os–Os)]
$[Os_3(CO)_{12}] \longrightarrow [Os_4(CO)_{16}]$	$283 \longrightarrow 349$	+66
$[Os_4(CO)_{14}] \longrightarrow [Os_5(CO)_{18}]$	$608 \longrightarrow 690$	+82
$[Os_4(CO)_{15}] \longrightarrow [Os_5(CO)_{19}]^*$	$464 \longrightarrow 543$	+79
$[Os_6H_2(CO)_{18}] \longrightarrow [Os_7H_2(CO)_{22}]$	$1114 \longrightarrow 1179$	+65

required to satisfy the EAN rule, and the total metal–metal bond enthalpy per localised bond, ΣE(Os–Os)/S_{1b}. In the majority of cases the number of Os–Os bonds equals the number of polyhedron edges, and it is possible to draw electron-precise structures, with a metal–metal bond along each polyhedron edge, using dative bonds and resonance structures where necessary. We have included the number of localised bonds for all the clusters, including those with fewer metal–metal bond pairs than polyhedron edges. The data in each of Tables 1–4 show a trend to increasing ΣE(Os–Os)/S_{1b} as the cluster nuclearity increases, again indicating that metal–metal bonding electron pairs are used more efficiently in bonding in larger clusters, but also showing the error of any approach to cluster thermodynamics which assumes that all 2c2e Os–Os bonds have the same strength.

Trends in ΣE(Os–Os) for cluster interconversions

The total metal–metal bond enthalpy, ΣE(Os–Os), provides a parameter which can be used to explore the influence of adding osmium carbonyl fragments to clusters leading to larger clusters. We note that ΣE(Os–Os) data, when presented in the format of Table 5, illustrate trends in the total metal–metal bond enthalpy per skeletal electron pair, ΣE(Os–Os)/S_p, both vertically and horizontally, and an investigation of these data illustrates important trends in cluster geometry and bonding. Columns in Table 5 contain clusters which are formally related by the addition or removal of an $Os(CO)_2$ fragment. Rows in Table 5 contain clusters related by addition or removal of $Os(CO)_3$ units. We have chosen to investigate changes in ΣE(Os–Os) accompanying the formal reactions of adding $Os(CO)_2$, $Os(CO)_3$ and $Os(CO)_4$ fragments to clusters and also the more practical reactions of oxidative addition of H_2, and addition or removal of H^+ or H^- to osmium carbonyl clusters.

Table 6 lists all the pairs of osmium carbonyl clusters described in this work which are related by the addition of an $Os(CO)_2$ fragment to the smaller cluster. The $Os(CO)_2$ fragment provides three orbitals but no electrons to the cluster, and so addition of an $Os(CO)_2$ fragment will convert a cluster into the next example along the sequence: *hypho*, *arachno*, *nido*, *closo*, capped-*closo*, retaining the same number of skeletal electron pairs as the cluster becomes less ‘open’. Table 6 shows that the increase in ΣE(Os–Os) on addition of an $Os(CO)_2$ fragment is remarkably insensitive both to the number of skeletal electron pairs and to the presence of hydride ligands or negative charges.

An $Os(CO)_3$ fragment provides three orbitals and two electrons to the cluster and so its addition will convert a cluster into another of the same class (*hypho*, *arachno*, *nido*, *closo* or capped-*closo*) with an additional vertex, and hence an additional pair of skeletal electrons. Table 7 shows that the increase in metal–metal bonding, as quantified by ΣE(Os–Os), is remarkably similar for the addition of $Os(CO)_3$ to a wide range of clusters, of different classes and with differing numbers of skeletal electron pairs. An $Os(CO)_4$ unit can be considered as providing three AOs and four electrons or two AOs and two electrons to a cluster {as if derived from $[Os(CO)_4Cl_2]$ by removal of two Cl atoms}. Addition of an $Os(CO)_4$ unit to a cluster will therefore generate a more ‘open’ cluster, with two additional pairs of skeletal electrons. Alternatively $Os(CO)_4$ can offer one vacant orbital to a cluster, when viewed as derived from $Os(CO)_5$ by removal of a CO ligand. As Table 8 shows, there are fewer examples of this formal addition of an $Os(CO)_4$ unit, but again the additional metal–metal bonding when an $Os(CO)_4$ fragment is added to a cluster is remarkably similar for these examples.

The addition of an $Os(CO)_2$ unit increases the value of ΣE(Os–Os) by an average of 326 kJ mol^{-1} for each of the single $Os(CO)_2$ additions listed. Similarly, the addition of $Os(CO)_3$

Table 9 Pairs of osmium carbonyl clusters related by addition of CO, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in ΣE(Os–Os). Clusters labelled with an asterisk have structures which are more open than required for their electron counts

Cluster pair	ΣE(Os–Os)	$\Delta[\Sigma E$(Os–Os)]
$[Os_4(CO)_{14}] \longrightarrow [Os_4(CO)_{15}]$	$608 \longrightarrow 464$	−144
$[Os_4(CO)_{15}] \longrightarrow [Os_4(CO)_{16}]$	$464 \longrightarrow 349$	−115
$[Os_5(CO)_{16}] \longrightarrow [Os_5(CO)_{18}]$	$955 \longrightarrow 690$	−265 (÷2 = −133)
$[Os_5(CO)_{18}] \longrightarrow [Os_5(CO)_{19}]^*$	$690 \longrightarrow 543$	−147
$[Os_6H_2(CO)_{18}]^* \longrightarrow [Os_6H_2(CO)_{19}]^*$	$1114 \longrightarrow 1005$	−109
$[Os_7H_2(CO)_{21}]^* \longrightarrow [Os_7H_2(CO)_{22}]^*$	$1300 \longrightarrow 1179$	−121

Table 10 Pairs of osmium carbonyl clusters related by the oxidative addition of H_2, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in [ΣE(Os–Os) + $E(H_2)$]. All the hydride clusters have structures which are more open than required for their electron counts and are labelled with an asterisk

Cluster pair	ΣE(Os–Os)	$\Delta\{[\Sigma E$(Os–Os)] + $E(H_2)\}$
$[Os_5(CO)_{16}] \longrightarrow [Os_5H_2(CO)_{16}]^*$	$955 \longrightarrow 763$	$-176 - 436 = -612$
$[Os_6(CO)_{18}] \longrightarrow [Os_6H_2(CO)_{18}]^*$	$1290 \longrightarrow 1114$	$-192 - 436 = -628$
$[Os_7(CO)_{21}] \longrightarrow [Os_7H_2(CO)_{21}]^*$	$1526 \longrightarrow 1300$	$-228 - 436 = -664$

units increases the total metal–metal bond enthalpy by an average of 209 kJ mol^{-1}, and the addition of an $Os(CO)_4$ unit increases the metal–metal bonding by an average of 73 kJ mol^{-1}.

Many experimentally accessible cluster-interconversion reactions involve either spontaneous loss, or gain under pressure, of CO ligands. Table 9 illustrates the change in metal–metal bond enthalpy, ΣE(Os–Os), associated with the addition of a CO ligand for a number of examples. Increasing the number of CO ligands will increase the ratio of y/x in $Os_x(CO)_y$, or in the more general case of $[Os_x(CO)_yH_z]^{c-}$ will increase the number of ligand electrons per metal atom, and will have an influence on ΣE(Os–Os) which can be predicted from the fit to the data in Fig. 2. The ligand addition will also have a small influence on the osmium–carbon monoxide bond enthalpy, E(Os–CO), for the ligands already present, since we have previously argued that E(Os–CO) is a function of the ratio y/x. The reactions shown in Table 9 will be exothermic left to right (addition of CO) provided that the gain in osmium–carbon monoxide bond enthalpy, E(Os–CO), exceeds significantly the losses in metal–metal bond enthalpy, ΣE(Os–Os), which will be the case since E(Os–CO) is *ca.* 200 kJ mol^{-1}. The exact thermodynamic viability of the CO addition reactions will be influenced by entropic factors, since one of the reactants, CO, is a gas.

Table 10 lists three pairs of clusters which are related by the formal oxidative addition of H_2 to one of the clusters. The total metal–metal bond enthalpies, ΣE(Os–Os), are also listed, along with the change in ΣE(Os–Os) plus the H_2 bond enthalpy term. The significance of [$\Delta\Sigma E$(Os–Os) + $E(H_2)$] is that the oxidative-addition reactions listed in Table 10 would be thermoneutral ($\Delta H = 0$) if the total Os–H bond enthalpy were equal to [$\Delta\Sigma E$(Os–Os) + $E(H_2)$]. It seems reasonable to suppose that the enthalpy difference between $[Os_5(CO)_{16}] + H_2$ and $[Os_5H_2(CO)_{16}]$ does not exceed say 50 kJ mol^{-1}. There must also be an entropy difference, which we have neglected, which can be estimated[29] at about 14 J K^{-1} mol^{-1}, giving a $T\Delta S$ term less than 5 kJ mol^{-1}. We can predict a mean value for the Os–H bond enthalpy in $[Os_5H_2(CO)_{16}]$ of (612 ± 50)/2 = 306 ± 25 kJ mol^{-1}. Similar arguments provide estimates of mean Os–H bond enthalpy terms for $[Os_6H_2(CO)_{18}]$ (314 ± 25 kJ mol^{-1}) and $[Os_7H_2(CO)_{21}]$ (332 ± 25 kJ mol^{-1}), although $[Os_7H_2(CO)_{21}]$ does contain a slightly different distribution of carbonyl ligands from the parent binary carbonyl cluster. In all three of these dihydride clusters the two hydride ligands have been placed by potential-energy calculations in doubly bridging sites, and it seems reasonable to suggest that the bond enthalpy terms for terminal Os–H or triply bridging, μ_3-H, hydride ligands will differ from these estimates.

There are experimental data which also allow an estimation of the Os–H bond enthalpy terms in osmium carbonyl hydride clusters. From a study of the kinetics of the interconversion of $[Os_3(CO)_{12}]$, $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Os_3H(\mu\text{-}H)(CO)_{11}]$ Poë *et al.*[30] were able to determine that the enthalpy of formation of $[Os_3H(\mu\text{-}H)(CO)_{11}]$ was 35 kcal mol^{-1} (146 kJ mol^{-1}) more positive than that of $[Os_3(CO)_{12}]$, whilst that of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ was 72 kcal mol^{-1} more positive than that of $[Os_3(CO)_{12}]$. However, ref. 30 appears to contain an error for the enthalpy of formation, ΔH_f, of $[Os_3(CO)_{12}]$(g), which is given as 637 kcal mol^{-1}, quoting a review by Connor,[31] which in fact contains the value −1644 ± 28 kJ mol^{-1}. The enthalpy of formation of gaseous $[Os_3(CO)_{12}]$ is quoted as −393 kcal mol^{-1} (−1644 kJ mol^{-1}) in the *original publication* by Connor *et al.*[32] Close examination of the data in ref. 30 indicates to us that Poë *et al.* have correctly calculated the difference in the enthalpies of formation of the three Os_3 clusters, but have used an incorrect value (in sign and magnitude) for the enthalpy of formation of $[Os_3(CO)_{12}]$ as their base point. Using the correct value, we suggest that the experimentally determined enthalpy of formation is −393 + 35 = −358 kcal mol^{-1} (−1498 ± 28 kJ mol^{-1}) for gaseous $[Os_3H(\mu\text{-}H)(CO)_{11}]$ and −393 + 72 = −321 kcal mol^{-1} (−1343 ± 28 kJ mol^{-1}) for gaseous $[Os_3(\mu\text{-}H)_2(CO)_{10}]$.

Using the ΣE(Os–Os) bond enthalpy terms for the Os_3 hydride clusters, $[Os_3H(\mu\text{-}H)(CO)_{11}]$ and $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, together with the ΣE(Os–CO) enthalpy terms [calculated using E(Os–CO) of 201 kJ mol^{-1} for each CO in $Os(CO)_4$ units and 209 kJ mol^{-1} in $Os(CO)_3$ units, as described in ref. 1] and the experimental enthalpies of formation of these two clusters, the only unknown terms are the Os–H and Os(μ-H)Os bond enthalpy terms which are derived as in equations (2) and (3) for

$$\Delta H_{\text{disrupt}} = \Sigma E(\text{Os–Os}) + \Sigma E(\text{Os–CO}) + 2E(\text{Os–H–Os}) = 338.7 + (4 \times 201 + 6 \times 209) + 2x = 2396.7 + 2x \qquad (2)$$

$$\Delta H_f = -1343 \text{ kJ mol}^{-1} = 3\Delta H_f[\text{Os(g)}] + 10\Delta H_f[\text{CO(g)}] + 2\Delta H_f[\text{H(g)}] - \Delta H_{\text{disrupt}} \qquad (3)$$

$[Os_3(\mu\text{-}H)_2(CO)_{10}]$. Hence E(Os–H–Os) = 324 kJ mol^{-1}. The largest contribution to the error bar on this number is the 2.5 kJ mol^{-1} per CO ligand error which we estimate for the Os–CO bond enthalpy term. From equations (4) and (5) for $[Os_3H(\mu\text{-}H)(CO)_{11}]$, E(Os–H) = 264 kJ mol^{-1}.

$$\Delta H_{\text{disrupt}} = \Sigma E(\text{Os–Os}) + \Sigma E(\text{Os–CO}) + E(\text{Os–H–Os}) + E(\text{Os–H}) = 265.6 + (8 \times 201 + 3 \times 209) + 324 + y = 2824.6 + y \qquad (4)$$

$$\Delta H_f = -1498 \text{ kJ mol}^{-1} = 3\Delta H_f[\text{Os(g)}] + 11\Delta H_f[\text{CO(g)}] + 2\Delta H_f[\text{H(g)}] - \Delta H_{\text{disrupt}} \qquad (5)$$

These calculations suggest experimentally derived Os–H bond enthalpies of 264 (Os–H) and 324 kJ mol^{-1} (Os_2–μ-H). We note that the enthalpy required to convert the bridging hydride in $[Os_3H(\mu\text{-}H)(CO)_{11}]$ into the terminal form has been estimated[33] at 46 kJ mol^{-1}, the values which we have derived are consistent and would suggest a value of 60 kJ mol^{-1}. Our values are also consistent with other data for M–H bond strengths for third-row transition metals.[23]

The replacement of a CO ligand by H^- leads to no net change in cluster electron count, and Table 11 lists the four examples, together with the ΣE(Os–Os) change accompanying

Table 11 Pairs of osmium carbonyl clusters related by the isoelectronic replacement of a CO ligand by H^-, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in ΣE(Os–Os)

Cluster pair	ΣE(Os–Os)	$\Delta[\Sigma E$(Os–Os)]
$[Os_3(CO)_{12}] \longrightarrow [Os_3H(CO)_{11}]^-$	$283 \longrightarrow 299$	+16
$[Os_4(CO)_{14}] \longrightarrow [Os_4H(CO)_{13}]^-$	$608 \longrightarrow 614$	+6
$[Os_4H(CO)_{13}]^- \longrightarrow [Os_4H_2(CO)_{12}]^{2-}$	$614 \longrightarrow 598$	−16
$[Os_5(CO)_{16}] \longrightarrow [Os_5H(CO)_{15}]^-$	$955 \longrightarrow 935$	−20

this substitution. These data do not cover a wide range, but there are clearly two cases where this substitution leads to an increase in metal–metal bonding, ΣE(Os–Os), and two cases where the metal–metal bonding is reduced. Conversion of $[Os_3(CO)_{12}]$ (all COs terminal) into $[Os_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ gives a cluster where one Os–Os bond is bridged by both a hydride ligand and a carbonyl ligand. There are a number of possible rationalisations for this structural change. Replacement of a π-acceptor ligand (CO) by a strong σ donor (H) and an anionic charge results in an increased 'π-electron density' within the Os_3 core, which can be accommodated by the introduction of a μ-CO ligand, which is a better π acceptor than a terminal CO ligand. Alternatively, the bond enthalpy term for a bridging hydride, μ-H, is larger than for a terminal hydride ligand, so there is a thermodynamic preference for H to occupy a bridging site. Equally the bond enthalpy term which we have associated[1] with a bridging CO ligand (205 kJ mol^{-1}) is slightly greater than that for a CO ligand in an $Os(CO)_4$ group (201 kJ mol^{-1}), so that there is a small enthalpic preference for a CO group in $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ to occupy a bridging position. The shorter Os–Os bond needed to accommodate both the bridging hydride and carbonyl ligands will also make enhance ΣE(Os–Os). Similarly, replacement of one CO ligand in $[Os_4(CO)_{14}]$ by μ-H^- gives a cluster, $[Os_4(\mu\text{-}H)(CO)_{13}]^-$, which in the, hypothetical, all terminal-CO form contains one $Os(CO)_4$ vertex, whilst the observed structure is $[Os_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{12}]^-$. The observed cluster has a thermodynamically preferred μ-CO ligand rather than an $Os(CO)_4$ vertex, and $[Os_4(\mu\text{-}H)(\mu\text{-}CO)(CO)_{12}]^-$again has stronger metal–metal bonding, ΣE(Os–Os), than in neutral $[Os_4(CO)_{14}]$, although here it appears likely that the μ-H and μ-CO functions do not bridge the same Os–Os bond, but are on opposite edges of the tetrahedron. In contrast, replacement of one CO ligand in $[Os_5(CO)_{16}]$ by $(\mu\text{-}H)^-$ gives $[Os_5(\mu\text{-}H)(CO)_{15}]^-$, which contains only $Os(CO)_3$ fragments, and there is no thermodynamic driving force for a CO ligand to occupy a bridging site. Similarly there are no $Os(CO)_4$ fragments in the product when $[Os_4H_2(CO)_{13}]$ is converted into $[Os_4H_3(CO)_{12}]^-$, and both of these conversions are accompanied by a reduction in ΣE(Os–Os).

In addition to $[Os_4H(CO)_{13}]^-$, there are four further Os_4 clusters which are formally derived from $[Os_4(CO)_{14}]$; in order of decreasing ΣE(Os–Os) these are $[Os_4(\mu\text{-}H)_2(CO)_{12}]^{2-}$, $[Os_4(\mu\text{-}H)_2(CO)_{13}]$, $[Os_4(\mu\text{-}H)_3(CO)_{12}]^-$ and $[Os_4(\mu\text{-}H)_4(CO)_{12}]$, all containing tetrahedral Os_4 cores. The trend within this series is for the Os–Os bonds to become longer, and hence for ΣE(Os–Os) to become smaller, as the number of hydride ligands increases. With one exception, these four clusters all contain only $Os(CO)_3$ fragments, and effectively the hydride ligands {which can be thought of as protonating a hypothetical tetrahedral anion $[Os_4(CO)_{12}]^{4-}$, which formally contains six skeletal electron pairs, *i.e.* a 2c2e bond along each edge} convert into metal–hydrogen–metal (3c2e) bonding electrons which would otherwise be exclusively metal–metal bonding. Protonation of a cluster does not affect the number of skeletal electron pairs available for bonding, but since it does require electrons which were previously involved in metal–metal bonding to adopt a metal–hydrogen–metal bonding role it reduces ΣE(Os–Os) as observed for these Os_4 clusters, and illustrated in Table 12 for all the pairs of clusters which are related by protonation. The data suggest that the absolute loss of metal–metal bonding is greater for the larger clusters, although the reduction in metal–metal bonding is comparable in percentage terms. However, the large reduction in metal–metal bonding energy on protonation of $[Os_9(CO)_{24}]^{2-}$ implies that this cluster is a weak base, or that $[Os_9H_2(CO)_{24}]$ and $[Os_9H(CO)_{24}]^-$ are strong acids, as borne out by the chemistry exhibited by these three clusters.[34] The delocalisation of charge in metal carbonyl cluster anions also means that (de)protonation reactions are accompanied by changes in bond length *throughout* the cluster, and the reorganisation associated with this results in carbonyl clusters, in common with many organometallic acids, having low kinetic acidities.[35]

Table 12 Pairs of osmium carbonyl clusters related by protonation, with total metal–metal bond enthalpies, ΣE(Os–Os)/kJ mol^{-1}, and the change in ΣE(Os–Os). Hydride clusters labelled with an asterisk have structures which are more open than required for their electron counts

Cluster pair	ΣE(Os–Os)	$\Delta[\Sigma E$(Os–Os)]
$[Os_3H(CO)_{11}]^- \longrightarrow [Os_3H_2(CO)_{11}]$	$299 \longrightarrow 266$	−33
$[Os_4H(CO)_{13}]^- \longrightarrow [Os_4H_2(CO)_{13}]$	$614 \longrightarrow 593$	−21
$[Os_4H_2(CO)_{12}]^{2-} \longrightarrow [Os_4H_3(CO)_{12}]^-$	$598 \longrightarrow 570$	−28
$[Os_4H_3(CO)_{12}]^- \longrightarrow [Os_4H_4(CO)_{12}]$	$570 \longrightarrow 536$	−34
$[Os_6(CO)_{18}]^{2-} \longrightarrow [Os_6H(CO)_{18}]^-$	$1205 \longrightarrow 1161$	−44
$[Os_6H(CO)_{18}]^- \longrightarrow [Os_6H_2(CO)_{18}]$*	$1161 \longrightarrow 1114$	−47
$[Os_8(CO)_{22}]^{2-} \longrightarrow [Os_8H(CO)_{22}]^-$*	$1943 \longrightarrow 1871$	−72
$[Os_9(CO)_{24}]^{2-} \longrightarrow [Os_9H(CO)_{24}]^-$	$2314 \longrightarrow 2178$	−136

The series of hexaosmium clusters also displays an interesting trend in total metal–metal bond enthalpy. The most efficiently bonded Os_6 cluster is $[Os_6(CO)_{18}]$, which has 12 metal–metal bonding electron pairs in a localised bond treatment, and has ΣE(Os–Os) = 1290 kJ mol^{-1}. This cluster can be converted into $[Os_6(CO)_{18}]^{2-}$ by the addition of two electrons, considered as metal–metal antibonding in a localised bond description, resulting in a reduced total metal–metal bond enthalpy, ΣE(Os–Os) = 1209 kJ mol^{-1}. Addition of protons to the dianionic cluster requires electrons which are involved in 2c2e Os–Os bonds to be used for 3c2e Os–H–Os bonds, and so the total metal–metal bond enthalpies for $[Os_6H(CO)_{18}]^-$ and $[Os_6H_2(CO)_{18}]$ are 1158 and 1114 kJ mol^{-1} respectively.

Conclusion

We have shown that the use of a bond length–bond enthalpy relationship for the Os–Os contacts in osmium carbonyl clusters leads to a single parameter, the total metal–metal bond enthalpy, ΣE(Os–Os), which reflects and quantifies energetically the structural changes which occur in series of such clusters. Use of this parameter has allowed us to investigate the electronic factors which determine such structural changes, using either localised-bond (18-electron rule) or delocalised (PSEPT) electron-counting methods. Knowledge of the changes in metal–metal bond enthalpy which accompany cluster interconversion reactions has allowed estimates to be made of limiting values of the Os–H and Os–H–Os bond enthalpies, and it is expected that extension of these ideas could lead to estimates of other metal–ligand bond enthalpies, and of the electron affinities of metal carbonyl clusters.

Experimental

Fractional atomic coordinates for the osmium carbonyl clusters $[Os_2(CO)_8]^{2-}$,[36] $[Mo(\eta\text{-}C_5H_4Pr^i)_4S_4]_2[Os_6(CO)_{18}]$ (two forms),[37] $[Os_8(CO)_{22}]^{2-}$,[38] $[Os_9(CO)_{24}]^{2-}$,[34] $[Os_{10}(CO)_{26}]^{2-}$,[39] $[Os_{17}(CO)_{36}]^{2-}$,[40] $[Os_{20}(CO)_{40}]^{2-}$,[41] $[Os_3H_2(CO)_{10}]$,[42] $[Os_3H_2(CO)_{11}]$,[43] $[Os_4H_4(CO)_{12}]$,[44] $[Os_4H_2(CO)_{13}]$,[45] $[Os_5H_2(CO)_{16}]$,[46] $[Os_7H_2(CO)_{22}]$,[47] $[Os_3H(CO)_{11}]^-$,[45] $[Os_4H(CO)_{13}]^-$,[48] $[Os_4H_3(CO)_{12}]^-$,[49]

$[Os_5H(CO)_{15}]^-$,[50] $[NBu_4][Os_6H(CO)_{18}]$,[51] $[PMePh_3][Os_8H(CO)_{22}]$,[28] $[Ph_2PNPPh_2][Os_8H(CO)_{22}]$,[28] $[Os_9H(CO)_{24}]^-$ [34] and $[Os_{10}H_4(CO)_{24}]^{2-}$ [52] were retrieved from the Cambridge Structural Database (CSD April 1996 release, version 5.11 on the University of Durham UNIX network)[53] using QUEST and Os–Os distances were evaluated using BABEL.[54] Fractional atomic coordinates for the clusters $[Os_6H_2(CO)_{19}]$ [55] and $[Os_7H_2(CO)_{21}]$ [47] have not been deposited in the CSD and were retrieved from the Inorganic Crystal Structure Datafile (ICSD) at Daresbury Laboratory; the resulting CSSR files were analysed with BABEL or directly with the Daresbury program CRAD. Fractional atomic coordinates for $[PMePh_3]_2[Os_6(CO)_{18}]$,[20] $[Os_7H_2(CO)_{20}]$,[27] $[Os_4H_2(CO)_{12}]^{2-}$ [56] and $[Ph_2PNPPh_2][Os_6H(CO)_{18}]$ [20] are not available in either of the databases or in the original publications, and metal–metal distances were retrieved directly from figures or tables in the publications, in some of these cases it was necessary to estimate next-nearest neighbour distances. Tables of Os–Os distances from BABEL or CRAD were pasted directly into a spreadsheet for bond enthalpy calculations. Given the large number of clusters discussed in this work, and the number of Os–Os interatomic distances in some of the larger clusters, tables listing all of the Os–Os interatomic distances, d(Os–Os), used in deriving the E(Os–Os) and ΣE(Os–Os) data in this paper are available separately as SUP 57248.

The data in Fig. 2 relate Os–Os bond enthalpy per metal atom, $\Sigma E(\text{Os–Os})/x$, to ligand electron : Os ratio in $[Os_x(CO)_yH_z]^{c-}$. Given the trends in ΣE(Os–Os) as CO is replaced by H^- or H_2, the curve is fitted only for the neutral binary carbonyls, $Os_x(CO)_y$, and the carbonyl anions, $[Os_x(CO)_y]^{c-}$. It is described by $\Sigma E(\text{Os–Os})/x = 785.5 - 117.4e_c + 3.84(e_c)^2$ [where e_c = number of ligand electrons per osmium = $(2y + z + c)/x$] with a correlation coefficient of 0.9968. A Kaleidagraph running on a Mac LCII computer was used to draw Fig. 2 and to fit the data.

The Os–Os distances used in this work are without estimated standard deviations (e.s.d.s) since they were derived from fractional atomic coordinate data available from the Cambridge Structural Database which does not contain e.s.d.s, and in many cases complete lists of Os–Os distances (especially next-nearest neighbour) are not available in the original publication, so we are unable to extract e.s.d.s from that source; as indicated previously,[1] we feel that the crystallographic contribution to the errors in ΣE(Os–Os) is less than 1 kJ mol^{-1}. In contrast the e.s.d.s on M–C and C–O distances are typically larger, reflecting the lighter atomic masses of these elements and libration of carbonyl ligands,[57] and mean that any attempt to estimate Os–C and C–O bond enthalpies from current crystallographic data will result in large estimated errors.

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