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Structural and bonding trends in osmium carbonyl cluster chemistry: metal–metal and metal–ligand bond lengths and calculated strengths, relative stabilities and enthalpies of formation of some binary osmium carbonyls, $[Os_x(CO)_y]$

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The metal–metal bond distances [d(M–M)] in the published structures of the osmium carbonyl clusters $[Os_3(CO)_{12}]$, $[Os_4(CO)_{14}]$, $[Os_4(CO)_{15}]$, $[Os_4(CO)_{16}]$, $[Os_5(CO)_{16}]$, $[Os_5(CO)_{18}]$, $[Os_5(CO)_{19}]$, $[Os_6(CO)_{18}]$ and $[Os_7(CO)_{21}]$ have been used to calculate bond-enthalpy terms E(M–M) using the relationship $E(\text{M–M}) = 1.928 \times 10^{13} [d(\text{M–M})]^{-4.6}$, itself derived from published structural and enthalpy data. Summation of the bond-enthalpy terms has revealed the varying efficiency with which these compounds use their skeletal bonding electrons and allowed estimates to be made of their enthalpies of disruption into gaseous metal atoms and carbon monoxide and of their enthalpies of formation, so providing insight into their relative stabilities. Correlations are noted between the metal : ligand ratios and metal–metal bond enthalpies, and with the metal–ligand bonding as reflected in metal–carbon and carbon–oxygen bond lengths.

The dramatic growth in metal–carbonyl cluster chemistry over the past two decades has seen the synthesis of an enormous number of metal clusters containing carbonyl ligands and the structural characterisation of many of them as indicated by reference to structural databases or to the recently published comprehensive surveys of organometallic compounds.[1] Although the vast majority of compounds studied contain carbonyl and other ligands, the number of simple binary carbonyls of known structure is growing steadily, and enough binary carbonyls $[M_x(CO)_y]$ of osmium in particular have now been prepared and structurally characterised (thanks largely to the work of Johnson, Lewis, McPartlin, Raithby, Einstein, Pomeroy and their co-workers)[2] to allow significant trends to be revealed. It is the purpose of this paper to explore and draw attention to the significance of these trends in this fascinating series of compounds.

The breaking and formation of metal–metal and metal–ligand bonds are fundamental to organometallic chemistry and a knowledge of the strengths of such bonds is necessary for an understanding of the thermodynamics underlying many important stoichiometric and catalytic organometallic reactions.[3] Bond-dissociation enthalpy and enthalpy of formation data have been measured by numerous experimental methods including microcalorimetry,[4] photoacoustic calorimetry[5] and laser pyrolysis.[6] Modern theoretical methods have the potential to provide accurate bond-enthalpy data,[7] although the correlation of theoretical and experimental data is not as good for organometallic compounds as it is for organic compounds.

The Method

Our approach to investigating the stabilities of the osmium carbonyl clusters discussed in the present paper is based on one first published in 1978,[8] which proved useful in correlating published thermochemical and structural data for some metal carbonyls of the iron and cobalt subgroups. That approach made some important assumptions in interpreting the energy of disruption, ΔH_{drpt}, of gaseous metal carbonyls $[M_x(CO)_y]$ into gaseous metal atoms and carbon monoxide molecules [equation (1)].

$$[M_x(CO)_y](g) \xrightarrow{\Delta H = \Delta H_{\text{drpt}}} x\text{M}(g) + y\text{CO}(g) \qquad (1)$$

First, it was assumed that the enthalpy of disruption could be partitioned between two terms [equation (2)] where ΣE(M–M)

$$\Delta H_{\text{drpt}} = \Sigma E(\text{M–M}) + \Sigma E(\text{M–CO}) \qquad (2)$$

represents the total enthalpy change associated with cleavage of all of the metal–metal bonds in the molecule in question and ΣE(M–CO) represents the enthalpy change associated with cleavage of all of the metal–ligand bonds.†

Secondly, it was assumed that the individual metal–metal bond-enthalpy terms, E(M–M), reflected the lengths, d(M–M), of the individual two-centre metal–metal bonds, to which they were related by the type of bond length–bond enthalpy relationship ($E \propto d^{-k}$) found generally useful in interpreting thermochemical and structural data and described below. It should be stressed that we are concerned here with pairwise-bonding interactions with neighbouring atoms, *not* two-centre two-electron (2c2e) bonds. Only rarely in metal-atom cluster chemistry does the number of electron pairs available for bonding, itself not always easily determined, equal the number of bonding contacts, so allowing a 2c2e localised-bond description. It is for this reason that we prefer to assume that, whatever the electron density associated with a particular metal–metal bond, whether an integral number of electron pairs or not, it will have a length and strength that reflect that electron density.

Thirdly, it was assumed that the metal–metal bonds in metal carbonyl clusters are similar to those in the bulk metals, and in particular that they show a common bond enthalpy–bond length relationship. A consideration of the metal–metal distances in metals that could crystallise in both body-centred cubic and hexagonal or face-centred cubic close-packed structures, and assignment of the metal–metal binding energy [as quantified by the enthalpy of atomisation, ΔH_f(M,g)]

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† We used the term D(M–CO) for the metal–ligand bond-enthalpy term in a previous paper,[8] but lest there be confusion with bond-dissociation enthalpies we prefer to use the term E(M–CO) here.

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exclusively to nearest-neighbour interactions for close-packed structures, but to nearest and next-nearest neighbour interactions for body-centred cubic structures, led to the conclusion that for transition metals the relationship (3)

$$E(\mathrm{M{-}M}) = A[d(\mathrm{M{-}M})]^{-4.6} \qquad (3)$$

provides a realistic means of assessing the strength E(M–M) of the metal–metal bonds in clusters, the value of A being calculated for a particular metal from its atomisation enthalpy and the atom–atom distances in the bulk metal.

For osmium, the bond enthalpy–bond length relationship found to be consistent with these assumptions, and with the known atomisation enthalpy (790 kJ mol^{-1})[9] and hexagonal-close-packed structure of the metal with nearest-neighbour distances of 268 pm,[10] was found to be equation (4) where

$$E(\mathrm{Os{-}Os}) = 1.928 \times 10^{13}\,[d(\mathrm{Os{-}Os})]^{-4.6} \qquad (4)$$

E(Os–Os) is in kJ mol^{-1} and d(Os–Os) is expressed in pm. In advocating the use of this relationship we are well aware that we are dealing with bonds for which the individual atomic orbital (s, p, d) contributions will vary with such factors as co-ordination number, oxidation state and the electron-withdrawing or -releasing nature of the ligands and that these and steric factors will affect the bond lengths and strengths. We nevertheless feel that, for the closely related series of compounds discussed here, our assumption that the metal–metal bonds are of the same consistent type is valid.

This expression has been used in the present study to calculate the strengths of the two-centre metal–metal bonding interactions in a series of osmium carbonyl clusters of known structure. Since no thermochemical studies of carbonyl clusters appear to have been carried out since the original discussion of their disruption enthalpy, it has been necessary to make further assumptions regarding the strength of attachment of carbonyl ligands to osmium clusters in the present study, *e.g.*, that the metal–ligand bond-enthalpy terms, E(M–CO), vary little if at all with cluster nuclearity. The earlier study had shown evidence for a very slight increase in E(M–CO) with increasing cluster nuclearity for carbonyl complexes of iron {E(Fe–CO) = 117 kJ mol^{-1} [$Fe(CO)_5$], 123 [$Fe_2(CO)_9$] and 126 [$Fe_3(CO)_{12}$]}, cobalt {136 [$Co_2(CO)_8$] and 140 [$Co_4(CO)_{12}$]} and rhodium {178 [$Rh_4(CO)_{12}$] and 182 [$Rh_6(CO)_{16}$]} as the number of carbonyl ligands per metal atom decreased.

In principle, the strength of binding of a carbonyl ligand to a metal centre can be deduced from the lengths of the metal–carbon and carbon–oxygen bonds involved, d(M–C) and d(C–O), provided that bond length–bond energy relationships are available for these bonds. The familiar π-acid-ligand properties of carbon monoxide involve use of the lone pair of electrons on carbon to form a dative sigma bond, C⟶M, to the metal (which will not significantly affect the carbon–oxygen bond order), whilst the degenerate π* orbitals of the ligand take up spare electron density from metal d or pd hybrid orbitals, conferring multiple-bond character on the metal–carbon bond at the expense of the carbon–oxygen bond. The limiting possible modes of co-ordination of carbon monoxide to a single metal can be represented by the canonical forms $\overset{-}{\mathrm{M}}{-}\mathrm{C}{\equiv}\overset{+}{\mathrm{O}}$ (where there is no metal–carbon multiple bonding and only transfer of charge from ligand to metal) and M=C=O, where π-backbonding from metal to ligand offsets the dative σ-bond from ligand to metal. When co-ordinating to electron-rich transition metals, carbon monoxide indulges in the latter bonding mode, participating in significant metal–carbon π bonding, and the concomitant loss in carbon–oxygen bond order is reflected in the vibrational stretching frequency, ν(CO), which becomes typically lower than that of free gaseous carbon monoxide. It is also reflected in a reduction of d(C–O) relative to that of unco-ordinated carbon monoxide (112.82 pm),[10] though the increase in length is small (typically terminal carbonyls have C–O distances between 114 and 116 pm) and the structures of most metal carbonyl complexes have been determined to too little precision to determine d(C–O) with the accuracy needed if E(C–O) is to be calculated with confidence, since E(C–O) varies by some 40 kJ mol^{-1} pm^{-1} at the lengths under consideration. There is an urgent need for an accurate determination of d(M–C), and particularly d(C–O), in selected series of transition-metal complexes.

It should also be possible to correlate the vibrational stretching frequency, ν(CO), with the bond length, d(C–O), and indeed such correlations have been proposed,[11] although again the precision of available d(C–O) data limits the usefulness of such correlations.

The enthalpy gained by the formation of the M=C multiple bond should exceed the enthalpy lost by reduction in the C≡O bond order, which observation can in principle be tested by the development of bond length–bond enthalpy relationships for M–C and C–O bonds. In our previous discussion[12] of the thermodynamics of [$Fe_2(CO)_9$] we employed a bond length–bond enthalpy relationship for C–O bonds of $E(\mathrm{C{-}O}) = 1.955 \times 10^{13}[d(\mathrm{C{-}O})]^{-5}$. A greater body of experimental thermodynamic data, together with more precise crystallographic determinations of M–C and C–O distances, should allow us to derive a similar expression for E(M–C).

The energetics of metal–ligand bond cleavage for a metal carbonyl can be represented in a simplified form as follows. When a carbonyl ligand separates from a metal atom, M–CO ⟶ M + CO(g), the enthalpy change represents the difference between the total bond enthalpies before and after ligand cleavage according to equation (5), where $E(\mathrm{C{-}O})_{\mathrm{coord}}$

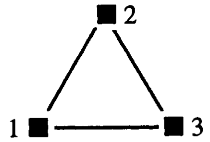
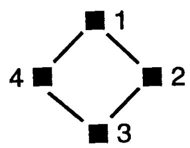
$$\Delta H = E(\mathrm{M{-}CO}) = E(\mathrm{M{-}C}) + E(\mathrm{C{-}O})_{\mathrm{coord}} - E(\mathrm{C{-}O})_{\mathrm{free}} \qquad (5)$$

represents the carbon–oxygen bond enthalpy for the co-ordinated ligand and $E(\mathrm{C{-}O})_{\mathrm{free}}$ represents the (greater) bond enthalpy of gaseous carbon monoxide.

Results and Discussion

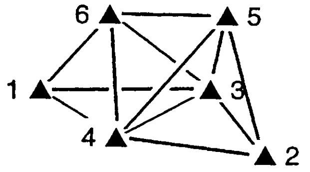
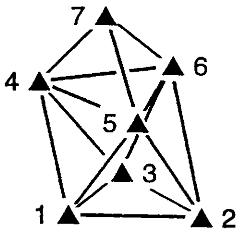
The compounds considered in the present work appear in Tables 1–3 together with diagrams of their structures, all metal–metal bond distances d(Os–Os) (pm) and calculated metal–metal bond enthalpies E(Os–Os) (to the nearest kJ mol^{-1}). Table 4 lists our preferred total metal–metal bond enthalpies ΣE(Os–Os) and estimated total metal–ligand bond enthalpies ΣE(Os–CO) for these compounds and also the enthalpies of disruption, ΔH_{drpt}, and of formation, ΔH_f(g) of gaseous [$Os_x(CO)_y$], implied by the listed values of ΣE(Os–Os) and ΣE(Os–CO). It is worth noting that Table 1 lists all of the metal–metal bond distances in these clusters, *i.e.*, all of the $3(x - 2)$ pairwise interactions in each molecule [$Os_x(CO)_y$] and their corresponding bond enthalpies (to the nearest kJ mol^{-1}). In Table 4, however, and in all our subsequent calculations, we list metal–metal bond-enthalpy totals, ΣE(Os–Os), compiled using $d(\mathrm{Os{-}Os}) \leqslant 421$ pm. Our reason for discarding longer interactions is that, in deriving the expression $E(\mathrm{M{-}M}) = A[d(\mathrm{M{-}M})]^{-4.6}$ linking bond enthalpies to distances, it was assumed that links to next-nearest neighbours should be assigned zero enthalpy for close-packed structures, but assigned enthalpies commensurate with their lengths in the case of body-centred structures, so allowing interactions between *trans* pairs of atoms in octahedral clusters to be included. In our previous consideration of the octahedral cluster [$Rh_6(CO)_{16}$] we chose to ignore the longer cross-cluster interactions[13] on the grounds that we had excluded interactions of *similar length* in bulk metals in deriving our bond enthalpy–bond length relationship. However, we now note that since the Os–Os distances in the [$Os_x(CO)_y$] clusters (Table 1) are consistently *ca.* 10–15% longer than the Os–Os distance in bulk metal, then such a strict

Table 1 The structures, all intermetallic distances and the strengths of the metal–metal bonds derived therefrom of the binary osmium tetracarbonyl clusters [Os(CO)$_4$]$_n$ (n = 3 or 4)

Formula	Structure[a]	Atom–atom pair	d(Os–Os)/pm	E(Os–Os)[b]/kJ mol^{-1}
[Os$_3$(CO)$_{12}$]		1–2	287.5	94
		1–3	288.2	93
		2–3	287.4	95
[Os$_4$(CO)$_{16}$]		1–2	299.7	78
		1–3	418.5	17
		1–4	298.5	79
		2–3	297.9	80
		2–4	420.1	17
		3–4	300.0	78

[a] ■ = Os(CO)$_4$ units. [b] Calculated to the nearest kJ mol^{-1} using equation (4).

Table 2 The structures, all intermetallic distances and the strengths of the metal–metal bonds derived therefrom of the binary osmium tricarbonyl clusters [Os(CO)$_3$]$_n$ (n = 5 or 6)

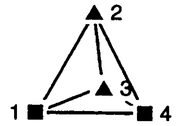
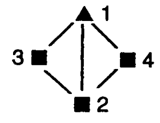
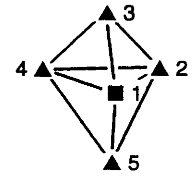
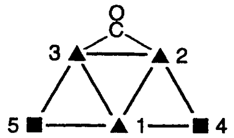
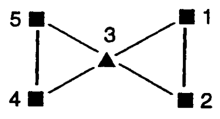
Formula	Structure[a]	Atom–atom pair	d(Os–Os)/pm	E(Os–Os)[b]/kJ mol^{-1}
[Os$_6$(CO)$_{18}$]		1–2	476.4	9[c]
		1–3	278.9	109
		1–4	283.1	101
		1–5	455.9	11[c]
		1–6	280.4	106
		2–3	282.5	102
		2–4	281.4	104
		2–5	278.3	110
		2–6	457.3	11[c]
		3–4	276.0	114
		3–5	278.8	109
		3–6	281.6	104
		4–5	280.5	106
		4–6	280.1	107
		5–6	273.9	118
[Os$_7$(CO)$_{21}$]		1–2	288.0	94
		1–3	293.5	86
		1–4	284.7	99
		1–5	284.8	99
		1–6	404.5	20
		1–7	490.5	8[c]
		2–3	289.4	92
		2–4	403.6	20
		2–5	287.6	94
		2–6	287.6	94
		2–7	493.9	8[c]
		3–4	285.5	98
		3–5	406.5	19
		3–6	283.9	100
		3–7	490.4	8[c]
		4–5	283.4	101
		4–6	282.6	102
		4–7	280.6	106
		5–6	284.8	99
		5–7	283.0	102
		6–7	282.1	103

[a] ▲ = Os(CO)$_3$ units. [b] Calculated to the nearest kJ mol^{-1} using equation (4). [c] Data not included in ΣE(Os–Os) in Table 4, see text.

criterion of bulk-metal interatomic distances is inappropriate. The Os–Os interactions within the clusters which are appropriate to consider for their contribution to ΣE(Os–Os) should be those which are equivalent to the nearest-neighbour interactions in close-packed structures and both nearest-neighbour and next-nearest-neighbour (*i.e.*, through a square face) interactions of a body-centred-cubic structure. In calculating ΣE(Os–Os), we have therefore included all three Os–Os links in the triangular cluster [Os$_3$(CO)$_{12}$], and all six Os–Os links in the tetrahedral cluster [Os$_4$(CO)$_{14}$], but ignored the long (494 pm) link between wing-tip metal atoms in the (flattened) butterfly-shaped cluster [Os$_4$(CO)$_{15}$]. The long-range interactions that it was felt appropriate to disregard in calculating ΣE(Os–Os) are indicated in Tables 2 and 3, and result in the differences between the values in the first column in Table 4 and the values in parentheses, from which it is apparent that they would have contributed between 1.2 and 4.6% of the total metal–metal bond enthalpy had they been included in the values of ΣE(Os–Os) listed in Table 4.

The values of ΣE(Os–CO) listed in Table 4 were calculated using values of 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, whilst a value of 205 kJ mol^{-1} was used for the bridging CO of [Os$_5$(CO)$_{18}$]. These individual estimates of the metal–ligand bond enthalpies are believed to be realistic for the following reasons. First, the value of E(Os–CO) of 201 kJ mol^{-1} is that which was

Table 3 The structures, all intermetallic distances and the strengths of the metal–metal bonds derived therefrom of the binary osmium carbonyl clusters $[Os_x(CO)_y]$ containing both $Os(CO)_3$ and $Os(CO)_4$ units

Formula	Structure[a]	Atom–atom pair	d(Os–Os)/pm	E(Os–Os)[b]/kJ mol^{-1}
$[Os_4(CO)_{14}]$		1–4	283.4	101
		1–2	281.0	105
		1–3	289.2	92
		2–4	289.2	92
		2–3	276.3	113
		4–3	281.0	105
$[Os_4(CO)_{15}]$		1–2	294.8	84
		1–3	277.2	112
		1–4	277.2	112
		2–3	299.7	78
		2–4	299.7	78
		3–4	494.4	8[c]
$[Os_5(CO)_{16}]$		1–2	286.7	96
		1–3	288.9	92
		1–4	286.7	96
		1–5	289.1	92
		2–3	273.8	118
		2–4	274.8	116
		2–5	276.4	113
		3–4	276.5	113
		3–5	454.1	11[c]
		4–5	273.9	118
$[Os_5(CO)_{18}]$		1–2	284.7	99
		1–3	284.2	100
		1–4	284.2	100
		1–5	285.9	97
		2–3	283.9	100
		2–4	287.4	95
		2–5	493.2	8[c]
		3–4	493.6	8[c]
		3–5	283.9	100
		4–5	570.0	4[c]
$[Os_5(CO)_{19}]$		1–2	285.3	98
		1–3	291.8	88
		1–4	566.1	4[c]
		1–5	564.3	4[c]
		2–3	295.0	84
		2–4	434.9	14[c]
		2–5	566.7	4[c]
		3–4	294.1	85
		3–5	291.4	89
		4–5	284.8	99

[a] ▲ = $Os(CO)_3$ and ■ = $Os(CO)_4$ units; bridging carbonyl ligands are shown explicitly. [b] Calculated to the nearest kJ mol^{-1} using equation (4). [c] Data not included in ΣE(Os–Os) in Table 4, see text.

Table 4 Data for the binary osmium carbonyl clusters $[Os_x(CO)_y]$ studied

Cluster	ΣE(Os–Os)[a]/kJ mol^{-1}	ΣE(Os–CO)/kJ mol^{-1}	ΔH_{drpt}[b]/kJ mol^{-1}	ΔH_f {$[Os_x(CO)_y](g)$}/kJ mol^{-1}
$[Os_3(CO)_{12}]$	283	2412	2695	−1651
$[Os_4(CO)_{14}]$	608	2862	3470	−1857
$[Os_4(CO)_{15}]$	464 (472)	3039	3503	−2001
$[Os_4(CO)_{16}]$	349	3216	3565	−2173
$[Os_5(CO)_{16}]$	955 (966)	3312	4267	−2085
$[Os_5(CO)_{18}]$	690 (710)	3694	4384	−2423
$[Os_5(CO)_{19}]$	543 (569)	3843	4386	−2536
$[Os_6(CO)_{18}]$	1290 (1322)	3762	5052	−2301
$[Os_7(CO)_{21}]$	1526 (1550)	4389	5915	−2706

[a] Derived using only those Os–Os distances ⩽421 pm. The value in parentheses is that derived from all the Os–Os distances (when it differs from the first value). [b] $[Os_x(CO)_y](g) \longrightarrow x\,Os(g) + y\,CO\,(g)$.

calculated[8] for $[Os_3(CO)_{12}]$ using its published[14] experimental value of ΔH_f and the metal–metal bond enthalpies listed in Table 4. In the absence of further experimental thermochemical studies on osmium carbonyl clusters, we have assumed this same value to be appropriate for other clusters containing $Os(CO)_4$ units. Secondly, since earlier studies on $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ had shown small (*ca.* 4%), but apparently significant, increases in E(M–CO) as the ratio of ligand to metal decreased from 5 to 4, or 4 to 3, a similar percentage increase appeared reasonable as the ratio of ligand to metal decreased from 4 to 3 in the present series of compounds. A value of E(Os–CO) = 201 kJ mol^{-1} per CO was therefore used in the cases of $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{16}]$ in the present work, whilst a value of 209 kJ mol^{-1} per CO was assumed for E(Os–CO) in the cases of $[Os_6(CO)_{18}]$ and

$[Os_7(CO)_{21}]$. The remaining compounds, $[Os_4(CO)_{14}]$, $[Os_4(CO)_{15}]$, $[Os_5(CO)_{16}]$, $[Os_5(CO)_{18}]$ and $[Os_5(CO)_{19}]$ were assigned E(Os–CO) values reflecting the proportions of $Os(CO)_4$ and $Os(CO)_3$ units they contained, *e.g.*, $[Os_4(CO)_{14}]$ was treated as $[Os(CO)_4]_2[Os(CO)_3]_2$, for which $\Sigma E(\text{Os–CO}) = 2 \times 4 \times 201 + 2 \times 3 \times 209 = 2862\ \text{kJ mol}^{-1}$. The enthalpy of adsorption of CO to bulk osmium metal is expected to be slightly greater than 209 kJ mol^{-1}, since formation of a monolayer is expected to give an average surface stoichiometry less than $Os(CO)_3$. This value is well below that (300 kJ mol^{-1}) at which CO adsorption is expected to be dissociative.[15]

The enthalpy of formation of gaseous $[Os_x(CO)_y]$, ΔH_f, is derived from the enthalpy of disruption, ΔH_{drpt}, and other thermodynamic parameters according to equation (6), where

$$\Delta H_f\{[Os_x(CO)_y], g\} = x\,\Delta H_f(Os, g) + y\,\Delta H_f(CO, g) - \Delta H_{drpt}[Os_x(CO)_y] \qquad (6)$$

the values of $\Delta H_f(CO, g) = -110.5\ \text{kJ mol}^{-1}$ and $\Delta H_f(Os, g) = 790\ \text{kJ mol}^{-1}$ have been taken.[9]

The calculated values of ΔH_{drpt} listed in Table 4 for the osmium carbonyl clusters $[Os_x(CO)_y]$ show the expected increases with x and y, as do the calculated values of ΔH_f. The stabilities of these compounds with respect to gaseous metal atoms and carbon monoxide, or with respect to osmium, carbon and oxygen are of less interest, however, than their relative stabilities with respect to each other. We have chosen to investigate the relationship of the enthalpies of formation, ΔH_f, of the gaseous osmium carbonyl clusters $[Os_x(CO)_y]$ to their thermodynamic stabilities, and further to relate these to the known solid-state reactions of these clusters. The enthalpies of sublimation are unknown but assumed to be small and varying little with nuclearity.[14] Examination of the data for $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{16}]$ which represent the differing ways in which three or four $Os(CO)_4$ units can bond to each other, show that the more stable aggregate of $Os(CO)_4$ units is $[Os_3(CO)_{12}]$. This is evident if one explores the enthalpy change (-85 kJ mol^{-1}) associated with the reaction $3[Os_4(CO)_{16}](g) \longrightarrow 4[Os_3(CO)_{12}](g)$. Alternatively, it is possible to express the enthalpy of formation per $Os(CO)_4$ unit, *i.e.*, -550 for $[Os_3(CO)_{12}]$ and -543 kJ mol^{-1} for $[Os_4(CO)_{16}]$.

These relative stabilities for $[Os(CO)_4]_x$ aggregates are consistent with the known chemistry of these clusters.[2] A similar comparison can be made of the relative stabilities of two compounds that can be regarded as aggregates of $Os(CO)_3$ units, *i.e.*, $[Os_6(CO)_{18}]$ and $[Os_7(CO)_{21}]$, for which the calculated enthalpies of formation per $Os(CO)_3$ unit are -384 and -387 kJ mol^{-1}, respectively, suggesting that $[Os_7(CO)_{21}]$ is marginally the more stable aggregate of $Os(CO)_3$ units, although the difference, 3 kJ mol^{-1}, is too small to be regarded as significant. In this case the experimental evidence is that $[Os_6(CO)_{18}]$ is the thermodynamic sink.

Since we have assumed the same values of E(Os–CO) for $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{16}]$, an alternative way of assessing their relative stabilities is to compare the metal–metal bond enthalpies of these compounds, expressed per $Os(CO)_4$ unit, *i.e.* 94.33, $[Os_3(CO)_{12}]$; 87.25, $[Os_4(CO)_{16}]$; 215, $[Os_6(CO)_{18}]$; and 218 kJ mol^{-1} $[Os_7(CO)_{21}]$. Again these figures clearly support the stability sequences $[Os_3(CO)_{12}] > [Os_4(CO)_{16}]$ and $[Os_7(CO)_{21}] \approx [Os_6(CO)_{18}]$ for these compounds.

If one examines the metal–metal bonding in these $Os(CO)_4$ aggregates, one can regard their $Os(CO)_4$ units as sources of one empty orbital {fragments of $[Os(CO)_5]$ from which one carbonyl ligand has been removed}, as sources of two orbitals and two electrons, or as sources of three orbitals and four electrons. Viewed as sources of two orbitals and two electrons (isolobal with methylene units, CH_2) they are capable of forming Os_x ring systems formally held together by single metal–metal bonds, and this is the simplest way of treating the bonding in $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{16}]$. The greater stability of the trinuclear species can then be understood in terms of lesser non-bonded repulsions between carbonyl ligands on adjacent metal atoms in the trimer and tolerance of the more acute Os–Os–Os bond angles. The Os_4 ring in $[Os_4(CO)_{16}]$ does show slight folding (dihedral angle 14.9°) which is less than the ring puckering shown by cyclobutane, C_4H_8, with which $[Os_4(CO)_{16}]$ is formally analogous (isolobal). The puckering can be interpreted in terms of non-bonded repulsions between ligands, though an alternative interpretation is to treat both systems, C_4H_8 and $[Os_4(CO)_{16}]$, as four skeletal atom–eight skeletal electron-pair *hypho* clusters of the borane-type cluster family, in which the four skeletal atoms occupy the two axial positions and two non-adjacent equatorial positions of a pentagonal bipyramid that has three vacant (equatorial) vertices.[16]

The remaining clusters in Tables 1–4, $[Os_4(CO)_{14}]$, $[Os_4(CO)_{15}]$, $[Os_5(CO)_{16}]$, $[Os_5(CO)_{18}]$ and $[Os_5(CO)_{19}]$, are not simple aggregates of either $Os(CO)_4$ or $Os(CO)_3$ units, but contain varying proportions of both such units and therefore pose more subtle relative stability problems in that their interconversions involve gain or loss of carbonyl ligands, and hence significant entropy terms. There are no experimental data available for the entropy changes associated with the interconversion of osmium carbonyl clusters, although we note that Bor and co-workers[17–19] have carried out some elegant studies on cobalt, rhodium and ruthenium carbonyl complexes in hexane solution.

We have chosen to investigate the free-energy change associated with the solid-state cluster-interconversion reaction $2[Os_3(CO)_{12}](s) \longrightarrow [Os_6(CO)_{18}](s) + 6\ CO(g)$. This reaction proceeds in up to 80% yield at 210 °C, the other products being other higher nuclearity clusters, the yields of which increase at the expense of $[Os_6(CO)_{18}]$ at temperatures above 210 °C.[20] For the species involved, Table 4 lists values of gas-phase enthalpies of formation, ΔH_f, although as we do not have any knowledge of the enthalpies of sublimation of the two clusters we shall assume that these are small and cancel. The entropy of CO(g) is 198 J K^{-1} mol^{-1}.[9] We have chosen to estimate the entropies of the solid carbonyl clusters using a method first proposed by Latimer,[21a] such that the entropy of a solid can be represented as the sum of constants characteristic of the elements present. We have taken the values of 63 for Os and 48 J K^{-1} mol^{-1} for CO.[21] The thermodynamic data may be summarised as below.

	$2[Os_3(CO)_{12}](s) \longrightarrow$	$[Os_6(CO)_{18}](s)$	$+\ 6\ CO(g)$
ΔH_f	2 × -1651	-2301	6 × -110.5 (kJ mol^{-1}, for the gaseous species)
S°	2 × 765	1242	6 × 198 (J K^{-1} mol^{-1}, for solid, solid, gas)

These data give $\Delta H = +338$ kJ mol^{-1} and $\Delta S = +900$ J K^{-1} mol^{-1}. Defining a thermodynamic decomposition temperature (T_{decomp}) as the temperature at which $\Delta G = 0$ gives $T_{decomp} = 376$ K (103 °C). The reaction is thermodynamically feasible above this temperature, with no account being taken of activation energy. Given the approximations involved, we feel that this result is in good accord with the experimental data. The above discussion illustrates that, using reasonable approximations, it is possible to perform thermodynamic calculations on carbonyl clusters, but that the reliability of these calculations needs to be improved by the determination of further experimental thermochemical data.

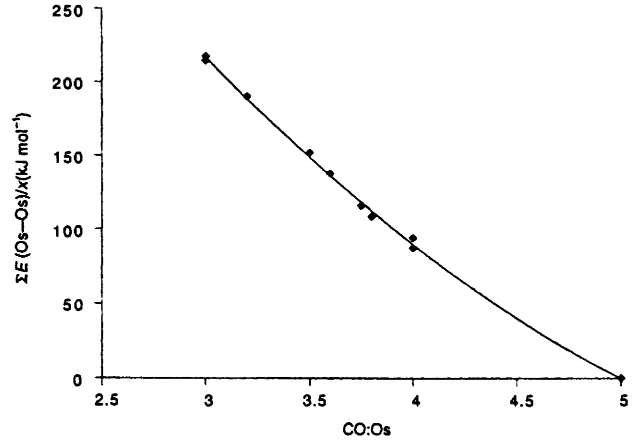


Fig. 1 Relationship between Os–Os bond enthalpy per metal atom and the number of CO ligands per metal atom in neutral binary [$Os_x(CO)_y$] clusters. The curve is a second-order polynomial fit to the data (see text)

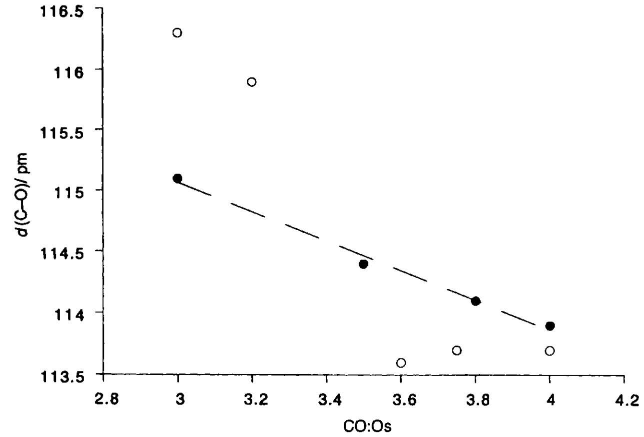


Fig. 3 Plot of mean C–O distance (pm) as a function of the number of CO ligands per Os in [$Os_x(CO)_y$] clusters. Data shown as open and closed circles have been refined differently (see text)

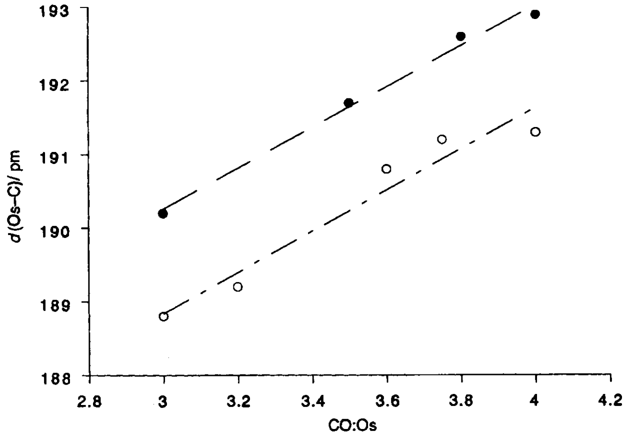


Fig. 2 Plot of mean Os–C distance (pm) as a function of the number of CO ligands per Os in [$Os_x(CO)_y$] clusters. Data shown as open and closed circles have been refined differently (see text)

Table 5 Mean values of Os–C and C–O distances of the binary osmium carbonyl clusters [$Os_x(CO)_y$]

Cluster	$\bar{d}$(Os–C)/pm	$\bar{d}$(C–O)/pm
[$Os_3(CO)_{12}$]	192.9	113.9
[$Os_4(CO)_{14}$]	191.7	114.4
[$Os_4(CO)_{15}$]	191.2	113.7
[$Os_4(CO)_{16}$]	191.3	113.7
[$Os_5(CO)_{16}$]	189.2	115.9
[$Os_5(CO)_{18}$]	190.8	113.6
[$Os_5(CO)_{19}$]	192.6	114.1
[$Os_6(CO)_{18}$]	190.2	115.1
[$Os_7(CO)_{21}$]	188.8	116.3

Our assumptions that the entropies of solid carbonyl clusters can be approximated by the method of Latimer inevitably leads to the conclusion that the entropy change involved in the conversion of any solid carbonyl cluster into another solid cluster and CO gas is always + 150 J K^{-1} mol^{-1} per mole of CO evolved. The values experimentally determined in hexane solution by Bor and co-workers,[17–19] where the entropy of solution must also be taken into account, are not totally at odds with our assumptions.

We note that the data predict that the conversion of small clusters into higher nuclearity clusters, with the concomitant loss of CO, is in general an *endothermic* process, involving an increase in metal–metal bonding but a greater loss of metal–ligand bonding, the thermodynamic driving force for these reactions being the entropy change associated with the formation of a gaseous product, CO. In this context it is relevant that at sufficiently high temperatures all [$Os_x(CO)_y$] clusters which are the subject of this study are thermodynamically unstable (ΔG is negative) with respect to osmium metal and CO. The exotherm associated with this reaction was studied by microcalorimetry in order to establish the known experimental thermodynamic data for metal carbonyl clusters.[14]

It is instructive to consider the relationship between the total metal–metal bond enthalpy per metal atom and the number of carbonyl ligands per metal atom in the cluster and this is displayed in Fig. 1, which also includes the value of zero for the metal–metal bond-enthalpy term for [$Os(CO)_5$]. Fig. 1 demonstrates that the metal–metal bond-enthalpy per metal atom increases as the number of carbonyl ligands present decreases allowing the metal atoms to undertake more effectively metal–metal bonding. Considering the data in the CO : Os range 4.0 to 3.0 it is possible to obtain a reasonable linear fit to the data, however for the full range of data, including [$Os(CO)_5$], a curve appears to be a better fit, and Fig. 1 includes a second-order polynomial fit. There does not appear to be a good theoretical reason why either a linear or non-linear relationship should be predicted, but the observation of a curve in Fig. 1 indicates that as the number of carbonyl ligands per metal reduces, the metal–metal bonding becomes increasingly more efficient. At CO : Os ratios below 3.0 it is possible that the data do not continue to follow the same relationship as depicted in Fig. 1. In particular, extrapolation to a CO : Os ratio of zero is considered too far to give a good estimate of the atomisation enthalpy of osmium metal.

It is also instructive to investigate the variation of bond distances to and within the carbonyl ligands. Table 5 lists mean values of Os–C and C–O distances in the osmium carbonyl clusters. Figs. 2 and 3 show that the mean Os–C and C–O distances are related to the ligand-to-metal ratio {y/x in [$Os_x(CO)_y$]}. We note that the typical precision of crystallographic structure determinations of metal carbonyls results in estimated standard deviations (e.s.d.s) on M–C distances of approximately 1 pm, and on C–O distances rather more than 1 pm, and so discussion of the data in Figs. 2 and 3 needs to be made with these error bars in mind, although the averaging of many M–C or C–O distances is likely to result in smaller e.s.d.s for the mean values. (For a discussion of the estimated error in averaged Os–C and C–O distances see ref. 22). The refinement method used in a structural determination of a carbonyl cluster is known to influence M–C and C–O distances, with the C atom 'sliding' along the M ⋯ O vector as the refinement method is changed.[23] Thus, isotropic refinement of all relevant C and O atoms leads to shorter M–C and longer C–O distances than are observed when both C and O are refined anisotropically. The data in Fig. 2 appear to fall on two parallel straight lines, the upper line, with data points shown as closed circles, represents $[Os_3(CO)_{12}]$ (all atoms anisotropic) together with $[Os_5(CO)_{19}]$, $[Os_4(CO)_{14}]$ and $[Os_6(CO)_{18}]$ for all of which the Os and O atoms were refined anisotropically and only the C atoms isotropically. The lower line, shown as open circles, represents structures where only the Os atom was refined anisotropically, with both O and C refined isotropically, this is usually due to insufficient reflections being available; additionally the structure of $[Os_4(CO)_{15}]$ is very poorly parameterised, with all atoms treated isotropically. The fact that the points in Fig. 2 fall into two classes appears to be due to the refinement procedure used in each case, however, the data in Figs. 2 and 3 do show that as the number of CO ligands per metal atom is reduced in higher nuclearity clusters, and the available π-electron density per CO ligand increases, so the average Os–C distance becomes shorter, the mean Os–C distances in the $[Os(CO)_3]_n$ species being approximately 4 pm shorter than the mean Os–C distances in the $[Os(CO)_4]_n$ species. The data for the C–O distances in Fig. 3 are drawn with open and closed circles as in Fig. 2. Whilst the data points representing the C–O distances in the clusters $[Os_3(CO)_{12}]$, $[Os_5(CO)_{19}]$, $[Os_4(CO)_{14}]$ and $[Os_6(CO)_{18}]$, all of which have the oxygen atom refined anisotropically, do fall on a straight line, the data points for the remaining clusters are more scattered. In the series from $[Os(CO)_3]_n$ to $[Os(CO)_4]_n$ the mean C–O distance becomes longer by between 1.5 and 2.5 pm, although there is more scatter in Fig. 3. Shorter Os–C distances imply higher Os–C bond enthalpies and the associated longer C–O bonds imply lower C–O bond enthalpy terms. The relationship between these two terms and the metal–ligand bond-enthalpy term was discussed earlier in this paper. Overall, these changes are consistent with the tighter binding of CO that we have assumed as the number of carbonyl ligands per metal atom decreases. In principle, it is possible to correlate M–C and C–O distances with M–CO bond enthalpy, but the large scatter in Figs. 2 and 3 indicate that there is a need to perform structural determinations of these, and other carbonyl complexes, with higher precision, utilising appropriate refinement procedures.

We referred earlier, in our discussion of $[Os_3(CO)_{12}]$ and $[Os_4(CO)_{16}]$, to the way that these clusters, treated as members of the borane cluster family, could be regarded as *arachno* and *hypho* clusters respectively, formally containing six and eight skeletal electron pairs respectively. We also noted, in our comparisons of $[Os_6(CO)_{18}]$ and $[Os_7(CO)_{21}]$, that these aggregates of $Os(CO)_3$ units had the capped-*closo* structures appropriate for *n* atom clusters held together by *n* skeletal bond pairs. Pursuing the borane analogy, we show in Table 6 how all of the osmium clusters considered in the present work can be classified according to their number of skeletal (metal) atoms and the number of skeletal bond pairs, *n*, formally available to hold their metal atoms together. The efficiency with which the skeletal electron pairs are used for metal–metal bonding can be expressed simply as $\Sigma E(Os–Os)/n$ (*i.e.*, the total metal–metal bond enthalpy per skeletal electron pair), values of which are listed in Table 6. The data illustrate dramatically how the efficiency with which the skeletal electron pairs are used increases as the structure becomes progressively less open, or alternatively as the number of metal atoms increases, whether within a family of clusters containing the same number of skeletal bond pairs (columns in Table 6), or within a particular category of cluster (*e.g.*, capped-*closo*, *arachno* or *hypho*; rows in Table 6). Table 6 also provides light on some interesting trends in bond enthalpy, thus for each step down the $n = 6$ pairs column the bond enthalpy per electron pair changes by approximately 50 kJ mol^{-1}, whilst across the *arachno* and *hypho* series of clusters the metal–metal bond enthalpy per electron pair increases by approximately 20 kJ mol^{-1} for each additional electron pair.

Fig. 1 and Table 6 show that there are relationships between metal–metal bond enthalpy and cluster empirical formula or geometry which can be potentially used in a predictive fashion for hypothetical osmium carbonyl clusters and those whose structure has not been determined. First, the trends within Table 6 indicate a metal–metal bond enthalpy per electron pair of zero for the hypothetical *hypho* six electron-pair cluster $[Os_2(CO)_{10}]$, which is better known as the monomer $[Os(CO)_5]$ and clearly has no metal–metal bond. Secondly, following the trend across the *arachno* series of clusters, we might predict a bond enthalpy for the *arachno* five electron-pair species, $[Os_2(CO)_9]$,[24] of approximately 27 ± 2 kJ mol^{-1} per electron pair or an Os–Os bond enthalpy of 135 ± 10 kJ mol^{-1}. This value does, however, seem rather high in the light of the data in Tables 1–3. If, however, we use the data of Fig. 1, for a CO:Os ratio of 4.5 we predict a metal–metal bond enthalpy of 40.375 kJ mol^{-1} per metal atom, giving a more reasonable value for the Os–Os bond enthalpy of 80.75 kJ mol^{-1}. Finally, the most significant cluster missing from Table 6 is $[Os_5(CO)_{17}]$, for which electron-counting rules predict a square-based pyramidal structure consistent with a *nido* seven electron-pair formulation. The data in Table 6 would predict an Os–Os bond enthalpy of $\leqslant 120$ kJ mol^{-1} per skeletal electron pair giving a total of $\leqslant 840$ kJ mol^{-1}, alternatively the fit to the data in Fig. 1 predicts an Os–Os bond enthalpy of 162.1 kJ mol^{-1} per metal atom giving a $\Sigma E(Os–Os)$ of 810.5 kJ mol^{-1}. A likely structure of $[Os_5(CO)_{17}]$ is a square-based pyramid with an apical $Os(CO)_3$ group, and the base containing two further $Os(CO)_3$ groups and two $Os(CO)_4$ groups or alternatively an $Os(CO)_3$ group at each vertex with CO ligands bridging two of the basal Os–Os bonds. The bond-length distortions necessary to accommodate either two $Os(CO)_4$ groups or two carbonyl-bridged Os–Os bonds might account for the apparent low stability of this molecule; it has not yet been isolated. For a structure containing two $Os(CO)_4$ fragments and three $Os(CO)_3$ fragments we predict $\Delta H_{drpt} = 3489 + 810.5 = 4299.5$ kJ mol^{-1} and $\Delta H_f = -2228$ kJ mol^{-1}. We note that the formally isoelectronic clusters $[Os_5(\mu_5\text{-}C)(CO)_{15}]$ (square-based pyramid)[25] and $[Os_5(\mu\text{-}H)_2(CO)_{16}]$ (edge-bridged tetrahedron)[26] are known. The relationship between the thermodynamics and the structures of these clusters will be discussed in a future paper.

Conclusion

The application of a bond length–bond enthalpy relationship to the Os–Os distances in the structurally characterised examples of neutral osmium carbonyl clusters has allowed us to calculate metal–metal bond-enthalpy terms for these clusters, using the well established enthalpy of atomisation of osmium metal as our foundation. The values of the individual metal–metal bond-enthalpy terms and their totals, $\Sigma E(Os–Os)$, demonstrate a trend to increasingly effective use of electrons in metal–metal bonding as the number of carbonyl ligands per metal is reduced. Using our calculated metal–metal bond enthalpies, together with Connor's experimentally determined enthalpy of formation of $[Os_3(CO)_{12}]$,[14] we have calculated enthalpies of formation of the known neutral osmium carbonyls. The enthalpy of formation data are consistent with the known relative stabilities of $[Os(CO)_3]_n$ and $[Os(CO)_4]_n$ oligomers. We have also explored the trends in metal–carbon and carbon–oxygen distances within these clusters and suggested that these two parameters are related to each other and also to the metal–carbonyl bond enthalpy.

In future papers we will investigate the consequences of bond length–bond enthalpy relationships for other metal carbonyl clusters, including ligand-substituted carbonyl clusters, hydrido carbonyl clusters and cluster anions for osmium and other transition metals.

Table 6 Classification of [$Os_x(CO)_y$] clusters according to the number of skeletal electron pairs (n) and the efficiency with which these electron pairs are used for metal–metal bonding [ΣE(Os–Os)/n, kJ mol^{-1}]

	n			
	6	7	8	9
capped-*closo*	[$Os_6(CO)_{18}$] 215	[$Os_7(CO)_{21}$] 218		
closo	[$Os_5(CO)_{16}$] 159			
nido	[$Os_4(CO)_{14}$] 101	'[$Os_5(CO)_{17}$]' $\leqslant 120$ (see text)		
arachno	[$Os_3(CO)_{12}$] 47	[$Os_4(CO)_{15}$] 66	[$Os_5(CO)_{18}$] 86	
hypho	'[$Os_2(CO)_{10}$]' 0 (see text)		[$Os_4(CO)_{16}$] 44	[$Os_5(CO)_{19}$] 60

Experimental

Fractional atomic coordinates for the osmium carbonyl clusters [$Os_3(CO)_{12}$],[22] [$Os_4(CO)_{14}$],[27] [$Os_4(CO)_{16}$],[28] [$Os_5(CO)_{16}$],[29] [$Os_5(CO)_{18}$],[30] [$Os_5(CO)_{19}$],[31] [$Os_6(CO)_{18}$][32] and [$Os_7(CO)_{21}$][33] were retrieved from the Cambridge Structural Database (CSD, April 1996 release)[34] using QUEST and Os–Os distances were evaluated using XPluto. Mean Os–C and C–O distances were evaluated using either the 3D Constraints menu of QUEST or by manual calculation of individual distances measured with XPluto. The cluster [$Os_4(CO)_{15}$] has a disordered structure[35] and the data are excluded from the CSD, fractional atomic coordinates were instead retrieved from the Inorganic Crystal Structure Datafile (ICSD) at the Daresbury Laboratory; given the disorder present in [$Os_4(CO)_{15}$] the coordinates for [$Os_4(CO)_{14}(PMe_3)$][36] were retrieved from CSD; the Os–Os distances in the two clusters were found to be similar, suggesting that the [$Os_4(CO)_{15}$] data are sufficiently accurate for the current work. Kaleidagraph running on a Mac LCII was used to draw Figs. 1–3 and to fit the data. The data in Fig. 1 relating Os–Os bond enthalpy per metal atom to CO:Os ratio are described by $E = 824.5 - 258.4\,y/x + 18.7\,(y/x)^2$ {where E = Os–Os bond enthalpy per metal atom and y/x is the CO:Os ratio in [$Os_x(CO)_y$]} with a correlation coefficient of 0.999.

The Os–Os distances in Tables 1–3 are listed 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. For the most simple example of [$Os_3(CO)_{12}$], Table 1 uses the Os–Os distances of 287.5, 288.2 and 287.4 pm, whilst ref. 26 lists these distances as 287.52(5), 288.24(5) and 287.37(5) pm, which correspond to Os–Os bond enthalpy terms of 94.45(8), 93.37(8) and 94.68(8) kJ mol^{-1} respectively. We thus feel that the crystallographic contribution to the errors in derived thermodynamic quantities 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 and mean that any attempt to estimate Os–C and C–O bond enthalpies from current crystallographic data will result in large estimated errors. Ref. 14 indicates that the estimated error bar in the calorimetric enthalpy of formation of [$Os_3(CO)_{12}$], ΔH_f(g), is 29 kJ mol^{-1}, which would indicate an error bar for the Os–CO bond enthalpy terms in this paper of *ca.* 2.5 kJ mol^{-1} per CO ligand.

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