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Tetranuclear carbonyls of osmium

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Abstract

Osmium forms more neutral binary carbonyls than any other metal; before 1987, nine were known with one to eight osmium atoms. There were, however, no tetranuclear binary carbonyls of osmium known before this date. This review describes the synthesis of $Os_4(CO)_{14}$ (**1**), $Os_4(CO)_{15}$ (**2**) and $Os_4(CO)_{16}$ (**3**) along with various derivatives of these clusters. Addition of $Os(CO)_5$ to $Os_3(CO)_{10}(C_8H_{14})_2$ in hexane affords **2** in good yield. The crystal structure of **2** reveals it to have an unusual planar structure with short (2.775 Å) and long (2.998 Å) peripheral Os–Os bonds (the hinge Os–Os bond length of 2.948 Å is more typical of an Os–Os single bond). The unusual metal–metal bond lengths are rationalized in terms of three-center, two-electron metal–metal bonds so that the short bonds have a bond order of 1.5 and the long bonds an order of 0.5. In this way each osmium atom achieves an 18-electron configuration. Several clusters with essentially the same arrangement of metal atoms have also been synthesized (e.g., $Os_4(CO)_{14}(PMe_3)$ (**4**), $(\eta^5\text{-}C_5Me_5)IrOs_3(CO)_{12}$). The variable temperature ^{13}C NMR spectra of **2** and **4** indicate that rapid CO-exchange in the equatorial plane occurs in these compounds. Other 62-electron clusters prepared in this study were $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (**8**) and $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (**9**); whereas **8** has a planar metal skeleton, **9** adopts the more common butterfly arrangement. For these clusters, the planar configuration is adopted when at least one of the metal atoms in the hinge position has four terminal ligands. Refluxing **2** in hexane yields $Os_4(CO)_{14}$ (**1**), which as expected from polyhedral skeletal electron pair theory has a tetrahedral metal core. Evidence is presented which indicates that in solution the carbonyl ligands in **1** undergo exchange on the infrared time scale. Treatment of **2** in CH_2Cl_2 at 0 °C with CO (1 atm) gives $Os_4(CO)_{16}$ (**3**) in essentially quantitative yield. The crystal structure of **3** reveals it to have a cyclobutane-like Os_4 core; the Os–Os bonds are long and range in length from 2.979 to 3.000 Å. In solution at room temperature, **3** readily decomposes to give mainly $Os_3(CO)_{12}$. The much greater stability of the trinuclear cluster suggests that the metal–metal bonding in this cluster should be described in terms of a centrally directed molecular orbital plus edge-bridging molecular orbitals, rather than in terms of two-center, two-electron metal–metal bonds. The structures

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Table 1

The neutral binary carbonyls of osmium known before 1987

Formula	Structure	Ref.
$Os(CO)_5$	trigonal bipyramidal (D_{3h})	1
$Os_2(CO)_9$	single carbonyl bridge (C_{2v}) [a]	2
$Os_3(CO)_{12}$	triangular Os_3 (D_{3h})	3
$Os_5(CO)_{16}$	trigonal bipyramidal Os_5	4
$Os_5(CO)_{19}$	"bow-tie" Os_5	5
$Os_6(CO)_{18}$	capped trigonal bipyramidal Os_6	6
$Os_6(CO)_{21}$	planar, "raft-like" Os_6 [b]	7
$Os_7(CO)_{21}$	capped octahedral Os_7	9
$Os_8(CO)_{23}$	bicapped octahedral Os_8	[c]

[a] Probable structure. [b] Probable structure based on the structures of $Os_6(CO)_{21-x}[P(OMe)_3]_x$ ($x = 1$–4) [18,81]. [c] B.F.G. Johnson, personal communication.

of $Os_4(CO)_{15}(L)$ (L = PF_3, PMe_3, $P(OCH_2)_3CMe$, $CNBu^t$) have been determined. Only the PF_3 derivative has a puckered square arrangement of metal atoms (with long Os–Os bonds) like **3**; the other derivatives have a spiked triangular arrangement of metal atoms. The Os–Os bond lengths in the latter clusters range from 2.849 to 2.938 Å. From this study it is concluded that it is the electronic properties of L that dictate which structure a cluster of the type $Os_4(CO)_{15}(L)$ adopts. The nonrigid properties of **3** and the $Os_4(CO)_{15}(L)$ clusters are also briefly discussed.

Introduction

Osmium forms more neutral binary carbonyls than any other transition metal. Before 1987 the known binary carbonyls of osmium were $Os(CO)_5$ [1], $Os_2(CO)_9$ [2], $Os_3(CO)_{12}$ [3], $Os_5(CO)_{16}$ [4], $Os_5(CO)_{19}$ [5], $Os_6(CO)_{18}$ [6], $Os_6(CO)_{21}$ (previously thought to be $Os_6(CO)_{20}$) [7,8], $Os_7(CO)_{21}$ [9], and $Os_8(CO)_{23}$ [10]. The structures of these carbonyls are given in Table 1.

The first reported preparation of pentacarbonylosmium was that of Hieber and Stallmann in 1943 [11] *. Their best synthesis was the dry reaction of OsO_4 with carbon monoxide (300 atm) at 300 °C which gave quantitative yields of the carbonyl (eq. 1). With the exception of some notable work by Calderazzo and L'Eplattenier

$$OsO_4 + 9\ CO \rightarrow Os(CO)_5 + 4\ CO_2 \qquad (1)$$

in 1967–68 [13], the chemistry of $Os(CO)_5$ has received little attention until recently [14]. The structure of $Os(CO)_5$ is described below.

The first report of the genuine preparation of $Os_2(CO)_9$ was by Moss and Graham in 1970 [15]; they made the compound by the ultraviolet irradiation of pentacarbonylosmium in heptane at −40 °C (eq. 2). Unlike $Fe_2(CO)_9$, $Os_2(CO)_9$ is

$$Os(CO)_5 \xrightarrow[-40\,^\circ C]{h\nu} Os_2(CO)_9 \qquad (2)$$

soluble in hydrocarbon solvents. It readily decomposes in solution to give $Os_3(CO)_{12}$.

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* For a historical description of the discovery of the simple metal carbonyls see ref. 12.

The structure of $Os_2(CO)_9$ has not been determined but it is believed to contain a single bridging carbonyl ligand [2].

Dodecacarbonyltriosmium, $Os_3(CO)_{12}$, is the common carbonyl of osmium. It is a bright yellow, air-stable crystalline solid that is readily prepared, in near quantitative yield, by the treatment of OsO_4 in methanol with CO (100 atm) at 150 °C. When originally prepared by Hieber and Stallmann, it was believed to be $Os_2(CO)_9$ [11]. The correct formulation was provided by the crystal structure carried out by Corey and Dahl in 1961 [16]. The solid-state structure of $Os_3(CO)_{12}$ has approximate D_{3h} symmetry and consists of a triangular Os_3 unit with six axial and six equatorial CO ligands (i.e., no bridging carbonyls). The chemistry of $Os_3(CO)_{12}$ is extensive and has recently been reviewed by Deeming [17].

The synthesis and study of the higher-nuclearity carbonyl clusters of osmium is almost entirely due to the work of the group of Lewis and Johnson. In a landmark paper for cluster chemistry, published in 1975, they described the pyrolysis of $Os_3(CO)_{12}$ in vacuum at 210 °C or above to give a host of higher-nuclearity binary carbonyl (and carbido, carbonyl) clusters of osmium (eq. 3) [10].

$$Os_3(CO)_{12} \xrightarrow{\geqslant 210\,^\circ C}$$

$$Os_5(CO)_{16} + Os_6(CO)_{18} + Os_7(CO)_{21} + Os_8(CO)_{23} + Os_5C(CO)_{15} + Os_8C(CO)_{21} \qquad (3)$$

The other known binary carbonyls with five or more osmium atoms, $Os_5(CO)_{19}$ and $Os_6(CO)_{21}$, can be prepared by the careful carbonylation of $Os_6(CO)_{18}$ under different conditions [8]. An improved synthesis of $Os_6(CO)_{21}$ has subsequently been reported [7]. The synthesis and reactivity of the higher-nuclearity clusters of osmium (and other metals) has recently been reviewed by Vargas and Nicholls [18].

There were, however, no tetranuclear binary carbonyls of osmium known prior to 1987. It occurred to us many years ago that these compounds might be prepared by the addition of $Os(CO)_5$ to a suitably activated derivative of $Os_3(CO)_{12}$. The rest of this review is concerned with our studies in this area.

$Os(CO)_5$ and $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$

Heating $Os_3(CO)_{12}$ in hexane under 200 atm of CO at 280 °C results in an equilibrium mixture that contains ~ 60% $Os(CO)_5$ after 48 h [19]. We can confirm an earlier report [8] that there is no detectable conversion of $Os_3(CO)_{12}$ to $Os(CO)_5$ if a temperature of 220 °C or below is used. Our preparation of $Os(CO)_5$ is reminiscent of Hieber's original synthesis described above [11].

The forcing conditions necessary to break the metal–metal bonds in $Os_3(CO)_{12}$ may be compared with the corresponding reactions for $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$. The iron cluster is converted into $Fe(CO)_5$ under 1 atm of CO at room temperature [20], whereas for $Ru_3(CO)_{12}$ there is ~ 100% conversion to $Ru(CO)_5$ when it is treated with 200 atm of carbon monoxide at 150 °C [19,21]. Although the mechanisms of the reactions of CO with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are unknown, these reactions can probably be taken as a dramatic illustration of the increase in metal–metal bond strength on going to the transition metal in the chemical group that is lower in the periodic table [22].

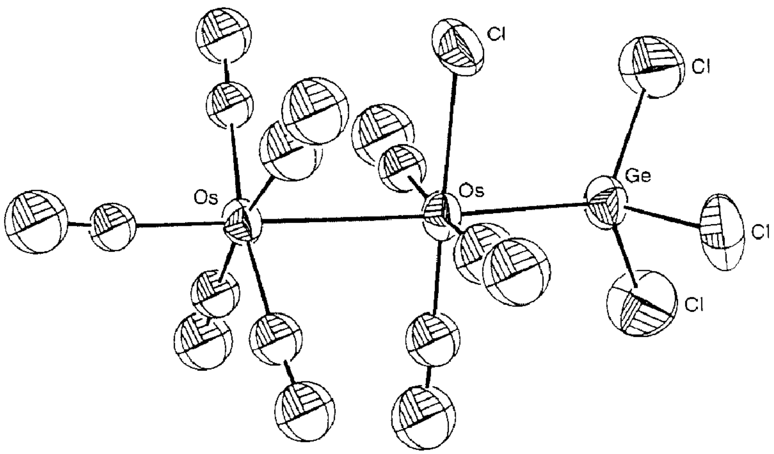


Fig. 1. Molecular structure of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$.

When pure, $Os(CO)_5$ melts at 2° C and is stable in solution under nitrogen at room temperature, but it slowly reverts back to $Os_3(CO)_{12}$ at 80 °C. This is in marked contrast to $Ru(CO)_5$ which decomposes to $Ru_3(CO)_{12}$ in solution at room temperature with a half life of about 2 h, in the dark [19]. It is often found that carbonyl complexes of second row transition metals are more labile than the corresponding complexes of the first and third row transition metals [23] ($Fe(CO)_5$ is, of course, stable in solution at room temperature).

Both the structures of $Os(CO)_5$ [1] and $Ru(CO)_5$ [24] have now been determined by electron diffraction. As indicated by infrared spectroscopy [13] both compounds have trigonal bipyramidal configurations. The metal–carbon bond lengths in both molecules are almost identical (Ru–C 1.952(3) Å, Os–C 1.955(4) Å) and, furthermore, there is little or no difference between the axial and equatorial metal–carbon distances. There is also no significant difference in the axial and equatorial Fe–C lengths in $Fe(CO)_5$ as revealed by the most recent low temperature X-ray diffraction study [25].

In the initial stages of our investigation of the chemistry of $Os(CO)_5$, we discovered that it was able to act as a two-electron donor ligand. Thus the reaction of $Os(CO)_5$ and $GeCl_4$ at 60 °C did not produce the expected $Os(CO)_4(GeCl_3)(Cl)$, in an analogous fashion to the reaction of $Fe(CO)_5$ with $GeCl_4$ [26], but rather $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ [27]. The crystal structure determination revealed that the 18-electron compound $Os(CO)_5$ acts as two-electron donor ligand to the 16-electron fragment $Os(CO)_3(GeCl_3)(Cl)$ via an unbridged, donor–acceptor metal–metal bond (Fig. 1). This is believed to be the first report where a neutral 18-electron complex had been shown to behave in this manner. The Os–Os bond lengths of the three independent molecules in the unit cell are 2.916(2), 2.927(2), and 2.931(1) Å.

We have subsequently shown that $Os(CO)_4(PMe_3)$, and related compounds, readily act as two-electron donor ligands to give complexes with unbridged, donor–acceptor bonds; some examples are $(Me_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W), $(Me_3P)(OC)_4OsRe(CO)_4(Br)$, and $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ [28]. Neutral complexes with unbridged, dative metal–metal bonds are still exceedingly rare [29] although there are numerous examples of compounds with formal dative metal–metal bonds bridged by ligands [30], or supported by other metal–metal bonds in clusters

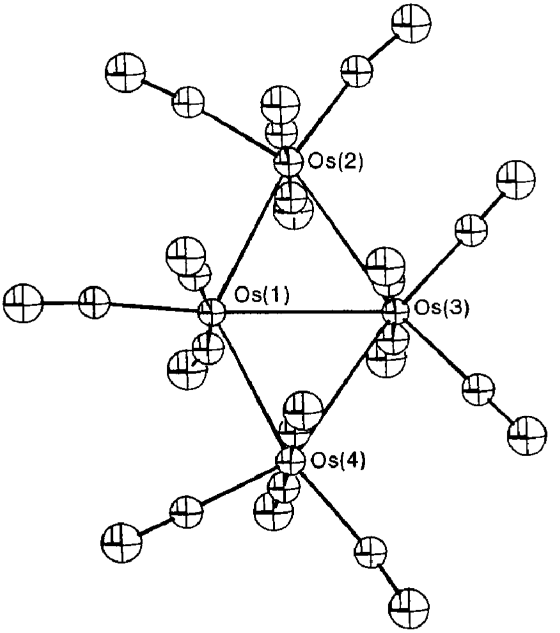


Fig. 2. Molecular structure of $Os_4(CO)_{15}$ (**2**).

[31]. That $Os(CO)_5$ and $Os(CO)_4(PMe_3)$ were able to act as ligands strongly suggested that this property could be used in cluster synthesis.

$Os_4(CO)_{15}$

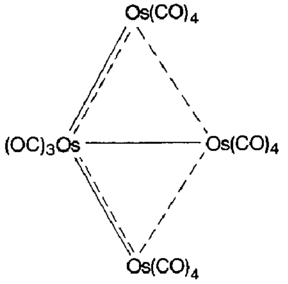
As described below, $Os(CO)_4(PMe_3)$ [32] readily displaces acetonitrile from $Os_3(CO)_{11}(CH_3CN)$ [33] to give $[(Me_3P)(OC)_4Os]Os_3(CO)_{11}$ [34]. Pentacarbonylosmium does not react with the acetonitrile derivative, but it does displace cyclooctene from $Os_3(CO)_{10}(\text{cyclooctene})_2$, a more lightly stabilized derivative of $Os_3(CO)_{12}$ first prepared by Tachikawa and Shapley [35]. The crystal structure of the product showed it to be $Os_4(CO)_{15}$ (**2**), the first tetranuclear, binary carbonyl of osmium (Fig. 2) [36]. The metal framework in **2** consists of a planar, "kite-like" Os_4 unit with adjacent short (2.775(1) Å) and long (2.998(1) Å) Os–Os bonds (Table 2). The hinge Os–Os bond length at 2.948(1) Å, although somewhat long, is more typical for an Os–Os single bond. (In $Os_3(CO)_{12}$, the average Os–Os bond length is 2.877(3) Å [3].) We had previously observed this unusual arrangement in $Os_4(CO)_{14}(PMe_3)$ and rationalized it in terms of three-center, two-electron metal–metal bonds [34,37]; this is shown for **2** in Scheme 1. In this way the short Os–Os bonds are assigned a bond order of 1.5 and the long Os–Os bonds an order of 0.5, and each osmium atom achieves an 18-electron configuration.

Table 2

Osmium–Osmium bond lengths (Å) in the tetranuclear clusters [a]

Compound	Os(1)–Os(2)	Os(1)–Os(3)	Os(1)–Os(4)	Os(2)–Os(3)	Os(2)–Os(4)	Os(3)–Os(4)
$Os_4(CO)_{14}$ **(1)** [b]	2.892(1)	2.834(1)	2.810(1)	2.810(1)	2.763(1)	2.892(1)
$Os_4(CO)_{13}(PMe_3)$ **(10)** [c]	2.842(1)	2.861(2)	2.831(1)	2.869(1)	2.765(1)	2.857(2)
$Os_4(CO)_{15}$ **(2)**	2.774(1)	2.948(1)	2.775(1)	2.998(1)		2.998(1)
$Os_4(CO)_{14}(PMe_3)$ **(4)** [d]	2.779(2)	2.935(2)	2.784(2)	3.013(2)	–	2.982(2)
$Os_4(CO)_{13}(PMe_3)[P(OMe)_3]$ **(5)** [e]	2.783(3)	2.937(2)	2.792(2)	2.978(2)	–	3.019(2)
$Os_4(CO)_{14}(CNBu^t)$ **(6)** [f]	2.793(2)	2.936(2)	2.775(2)	2.985(2)	–	2.983(2)
$(\eta^5\text{-}C_5Me_5)IrOs_3(CO)_{12}$ **(7)** [g]	2.794(2)	2.908(2)	2.703(2)	2.994(2)	–	2.939(2)
$Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ **(8)** [h]	2.807(1)	2.875(1)	2.810(1)	3.050(1)		2.851(1)
$Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ **(9)** [i]	2.868(1)	2.886(1)	2.939(1)	3.115(1)	–	2.850(1)
$Os_4(CO)_{16}$ **(3)**	2.997(1)	–	2.985(1)	2.979(1)	–	3.000(1)
$Os_4(CO)_{15}(PMe_3)$ **(11)** [j]	2.938(1)	–	–	2.852(1)	2.927(1)	2.894(1)
$Os_4(CO)_{15}[P(OCH_2)_3CMe]$ **(12)** [k]	2.926(1)	–	–	2.849(1)	2.936(1)	2.882(1)
$Os_4(CO)_{15}(CNBu^t)$ **(13)** [l]	2.918(2)	–	–	2.853(1)	2.929(1)	2.890(1)
$Os_4(CO)_{15}(PF_3)$ **(14)** [m]	3.005(2)	–	3.000(2)	2.977(2)	–	2.994(2)

[a] See appropriate figure or that of the parent carbonyl for the labelling scheme. [b] Os(1B) = Os(3); Os(2B) = Os(4). [c] Os(1)–P 2.361(6) Å. [d] Os(2)–P 2.320 (6) Å. [e] Os(2)–P(PMe$_3$) 2.314(8) Å; Os(4)–P(P(OMe)$_3$) 2.22(1) Å. [f] Os(3)–C(CNBu$^t_{ax}$) 2.01(4) Å. [g] Ir = Os(4). [h] Os(2)–Sn 2.697(2) Å. [i] Os(2)–P 2.342(4) Å. [j] Os(1)–P 2.354(5) Å. [k] Os(1)–P 2.269(6) Å. [l] Os–C(CNBu^t) 2.04(4) Å. [m] Os(1)–P 2.192(2) Å.



Scheme 1

Many years ago Pauling proposed a simple equation for calculating the bond order of a bond given its length [38]; this is shown in eq. 4 where $d(n)$ is the

$$d(n) = d_1 - 0.60 \log(n) \tag{4}$$

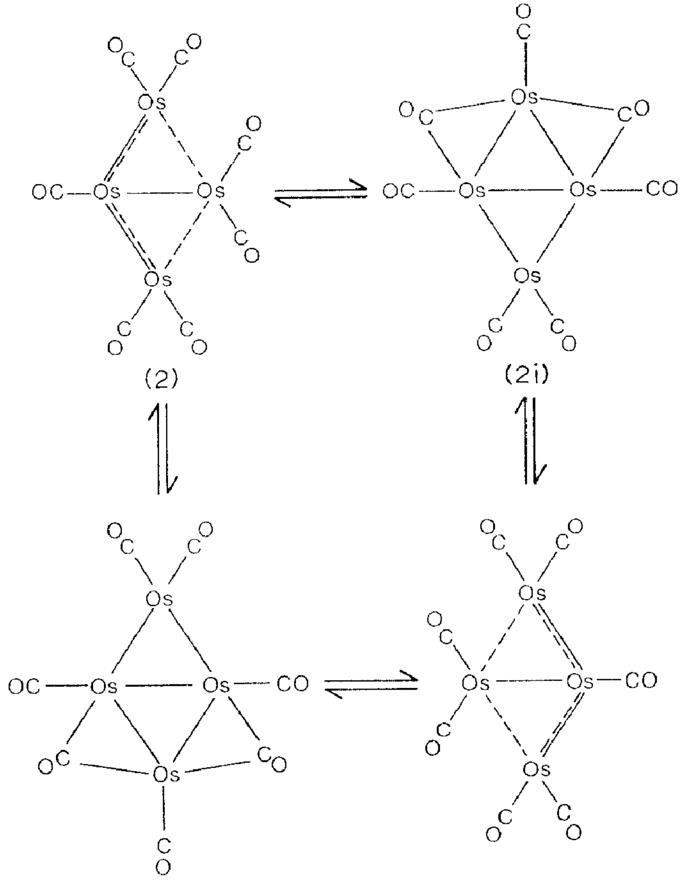
distance of the bond in question, d_1 is the length of a single bond of the same type, and n is the bond order. If one assumes a value of 2.88 Å for a single Os–Os bond (the value found in $Os_3(CO)_{12}$ [3]), then application of Pauling's relationship to **2** yields a bond order of 0.6 for the long Os–Os bonds and an order of 1.5 for the short Os–Os bonds. These bond orders are therefore consistent with the interpretation of the bonding in **2** shown in Scheme 1.

It is pointed out here that there have been recent reports in the literature of planar tetranuclear clusters in which there are long metal–metal bonds that are not adjacent (i.e., in $Os_4(CO)_{12}(\mu\text{-}O_2CCF_3)_2$ [39], $Ru_4(CO)_{13}(\mu\text{-}PPh_2)_2$ and $Ru_4(CO)_{10}(\mu\text{-}PPh_2)_4$ [40]). There are also a number of higher-nuclearity osmium clusters that contain short Os–Os bonds [4,6,41]. It is not, at present, apparent why the Os–Os bonds should have these unusual lengths, or if the bonding concepts used for **2** can be applied to these molecules.

Planar tetranuclear clusters were, until recently, quite rare (a number of planar clusters related to **2** are described below). The butterfly and tetrahedral arrangement of metal atoms are the common geometries observed for such clusters [42]. The butterfly configuration is the common structure found for 62-electron clusters; it is the structure that is the most consistent with polyhedral skeletal electron pair theory (PSEPT) [43] (cluster **2** is a 62-electron cluster). Prior to 1986 the only planar tetranuclear clusters without bridging ligands reported were $[Re_4(CO)_{16}]^{2-}$ [44] and $HOs_3Re(CO)_{15}$ [45]. The metal–metal bond lengths in these clusters do not, however, show the same variation as those in **2**. Planar tetranuclear osmium clusters with bridging ligands include $Os_4(\mu\text{-}S)(CO)_{13}$ [46] and $Cl_2SnOs_3(\mu\text{-}CH_2)(CO)_{11}$ [47] ($SnCl_2$ may be considered as isolobal with $Os(CO)_4$).

One of the fascinating properties of metal carbonyl clusters is their stereochemical nonrigidity [48,49] and the tetranuclear osmium carbonyls are no exception. Variable temperature ^{13}C NMR spectra of $Os_4(CO)_{15}$ in solution below 0 °C are shown in Fig. 3 [50]. Because of the unusual bonding in this cluster, care must be taken when assigning resonances in a specific region of the spectrum as due to carbonyls of a certain type (i.e., axial or equatorial). For example, some of the carbonyl signals in the ^{13}C NMR spectrum of $Os_4(CO)_{14}(PMe_3)$ have unusual chemical shifts [34]. However, by analogy to the spectra of most Os_3 clusters [51,52] and the spectrum of $Os_4(CO)_{14}(PMe_3)$, the two signals (each of intensity 4) downfield of δ 180 are assigned to axial carbonyls whereas the singlet (of intensity 7) to high field of δ 175 is assigned to the equatorial carbonyl ligands.

The spectrum at −56 °C is interpreted in terms of **2** with the same structure as found in the solid state, but with a rapid all-equatorial, merry-go-round CO-exchange taking place in the molecule, as shown in Scheme 2. This is consistent with the non-rigidity found in $Os_4(CO)_{14}(PMe_3)$ described below. The spectrum of **2** at −119 °C indicates that this exchange is beginning to slow down on the NMR time scale. The low activation barrier for the exchange may indicate that the intermediate with the bridging carbonyls (**2i**) is not much higher in energy than the ground state structure of **2**. Note that in **2i** all the Os–Os bonds are considered as two-center, two-electron metal–metal bonds. In the spectrum at −6 °C there is evidence for a further fluxional process since the signal at the lowest field, which is assigned to the axial carbonyls on the wingtip osmium atoms, is broadened along with the signal assigned to the equatorial carbonyls. A mechanism that accounts for this observation is a three-fold twist mechanism at the wingtip osmium atoms that exchanges an axial and the equatorial carbonyl ligands attached to these osmium atoms. We have proposed this type of rearrangement to account for some nonrigid processes that occur in the $Os_3(CO)_{12-x}[P(OMe)_3]_x$ ($x = 1$–5) clusters [52,53].



Scheme 2

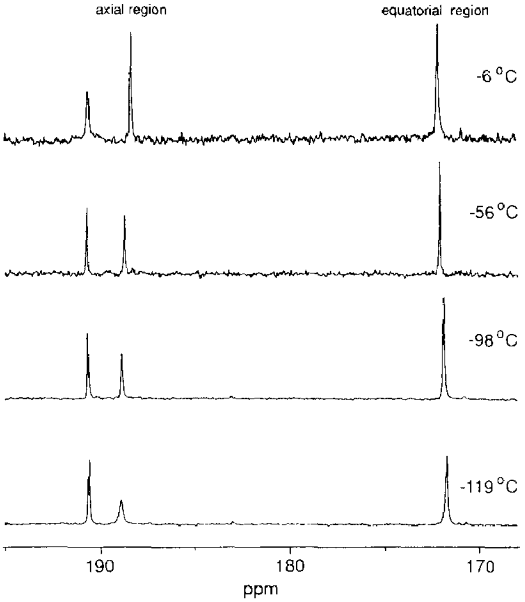


Fig. 3. Variable temperature ^{13}C NMR spectra of **2** (in $CHFCl_2/CD_2Cl_2$ except spectrum at −6 °C: CH_2Cl_2/CD_2Cl_2; ^{13}CO-enriched **2**; 100.6 MHz operating frequency).

Derivatives of $Os_4(CO)_{15}$ without bridging hydride ligands

A number of derivatives of **2** and a related heteronuclear cluster have been prepared. The methods of preparation of these clusters are summarized in eqs. 5–8 [34,36,50].

$$\left.\begin{array}{l}[(Me_3P)(OC)_4Os]Os_3(CO)_{11} + Me_3NO \searrow \\ Os(CO)_4(PMe_3) + Os_3(CO)_{10}(CH_3CN)_2 \nearrow\end{array}\right. \underset{\mathbf{(4)}}{Os_4(CO)_{14}(PMe_3)} \tag{5}$$

$$Os_4(CO)_{13}(PMe_3) + P(OMe)_3 \rightarrow \underset{\mathbf{(5)}}{Os_4(CO)_{13}(PMe_3)[P(OMe)_3]} \tag{6}$$

$$Os_4(CO)_{15}(CNBu^t) + Me_3NO \rightarrow \underset{\mathbf{(6)}}{Os_4(CO)_{14}(CNBu^t)} \tag{7}$$

$$Os_3(CO)_{10}(C_8H_{14})_2 + (\eta^5\text{-}C_5Me_5)Ir(CO)_2 \rightarrow \underset{\mathbf{(7)}}{(\eta^5\text{-}C_5Me_5)IrOs_3(CO)_{12}} \tag{8}$$

The structures of the clusters **4–7** all have similar planar Os_4 (or Os_3Ir) cores with long and short peripheral metal–metal bonds as found for **2** (Table 2). This indicates that the unusual bonding present in these compounds is an intrinsic property of the metal unit and cannot be attributed to the *trans* influences of the ligands or to packing effects.

Of these clusters, only for **4** have the dynamic properties of the molecule in solution been investigated (the clusters $Os_4(CO)_n(PMe_3)$ ($n = 13$, 14, 15) were prepared before their binary carbonyl analogues [34]). Variable temperature ^{13}C NMR spectra of **4** are shown in Fig. 4. As can be seen from the figure, the spectrum at −115 °C consists of four signals of intensity two (the signal at δ 202 is a doublet

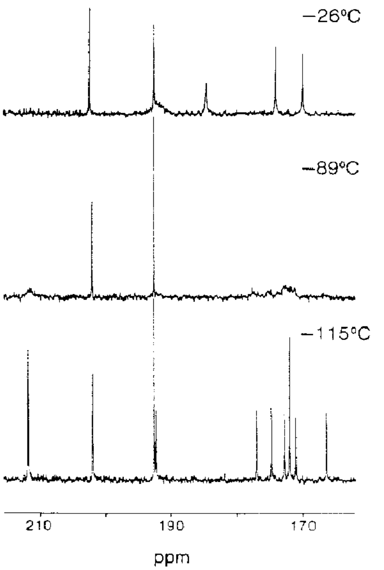
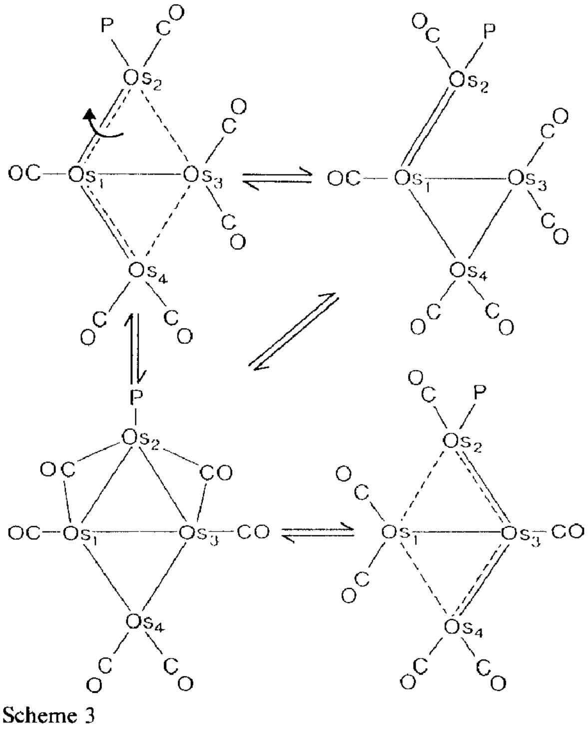
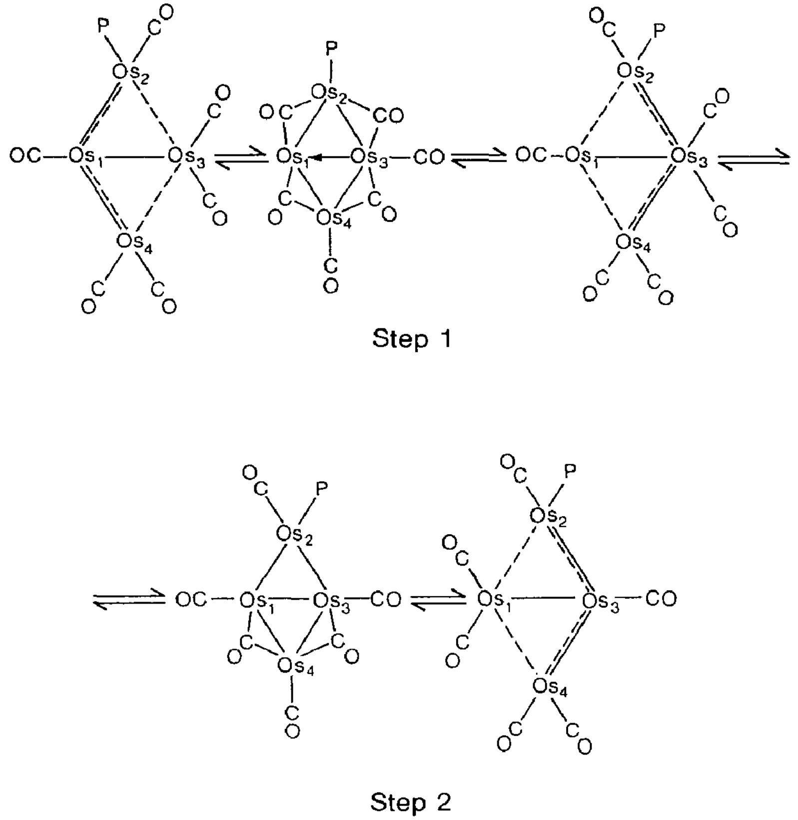


Fig. 4. Variable temperature ${}^{13}C$ NMR spectra of **4** (conditions as in Fig. 3). In the spectrum at −26 ° C there is a broad singlet at ~190 ppm and the signal at 191.6 ppm has lost intensity due to the onset of a second fluxional process.

due to phosphorus coupling) assigned to the axial carbonyls, and six signals of intensity one assigned to the equatorial carbonyls. The spectrum is consistent with the solid state structure (where the PMe_3 ligand occupies the equatorial site on



Scheme 3



Scheme 4

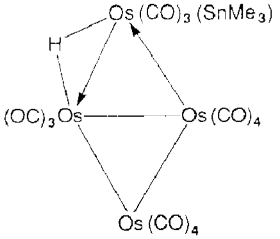
Os(2) that is adjacent to Os(1)) and indicates that, unlike **2**, the carbonyls in **4** are rigid at this temperature. Two of the signals attributed to axial carbonyls (namely those at δ 211.9 and 171.9) and one attributed to an equatorial carbonyl (at δ 192.2) come in unusual regions of the spectrum for resonances due to these types of carbonyl ligands in most osmium clusters [51,52]: this is probably indicative of the unusual bonding in these clusters.

On warming the solution of **4** to $-26\,^\circ\mathrm{C}$, eight of the signals coalesce in pairs to give four singlets. (One of the singlets, due to the coalescence of the two axial signals is, however, still broad at this temperature.) This behavior can be interpreted in terms of a mechanism that involves formation of a symmetric intermediate similar to that proposed for **2** (i.e., **2i**). Two possibilities of how the molecule can attain the intermediate form are shown in Schemes 3 and 4. We initially favored the mechanism in Scheme 3 since it involved essentially only one step. However, in view of the subsequent studies on the fluxionality exhibited by **2**, the two-step process in Scheme 4 now appears to be more likely. This latter mechanism also has the advantage that it does not require that any metal–metal bonds be broken. It is also pointed out that the carbonyl exchange is extremely rapid at $-26\,^\circ\mathrm{C}$: the rate constant necessary to cause coalescence of the two axial carbonyl signals (which are separated by about 4000 Hz) is $8.8 \times 10^3\ \mathrm{s}^{-1}$.

Derivatives of $Os_4(CO)_{15}$ with bridging hydride ligands

Treatment of $Os_4(CO)_{14}$ (described below) in solution with the Group IV hydrides EHR_3 ($E = Si$, Ge, Sn; $R = Me$, Ph) readily affords the clusters $Os_4(\mu\text{-}H)(CO)_{14}(ER_3)$ [54]. The structure of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (**8**) shows it too has a planar Os_4 skeleton (Fig. 5). Once again, there is a significant variation in the peripheral Os–Os bond lengths (Table 2). Surprisingly, calculations with the HYDEX program of Orpen [55] indicate that the hydride ligand bridges the short (2.807 Å) Os(1)–Os(2) bond rather than the long (3.050 Å) Os(2)–Os(3) bond. This location of the hydride ligand has been subsequently confirmed by ^1H and ^{13}C NMR studies.

The ^{13}C NMR spectra of **8** and its $SiMe_2Ph$ analogue indicate that the carbonyls in these clusters are rigid in solution even at 80 °C. The ^{13}C NMR spectrum of **8** also indicated that the long Os(2)–Os(3) bond should be regarded as a donor–acceptor bond (it is observed in other molecules that the ^{13}C chemical shifts of carbonyl ligands *trans* to dative metal–metal bonds appear at unusually high fields [27,28,56]). This in turn led to the formulation shown below as a description of the bonding in **8**.



The cluster $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (**9**) was one of the major products isolated

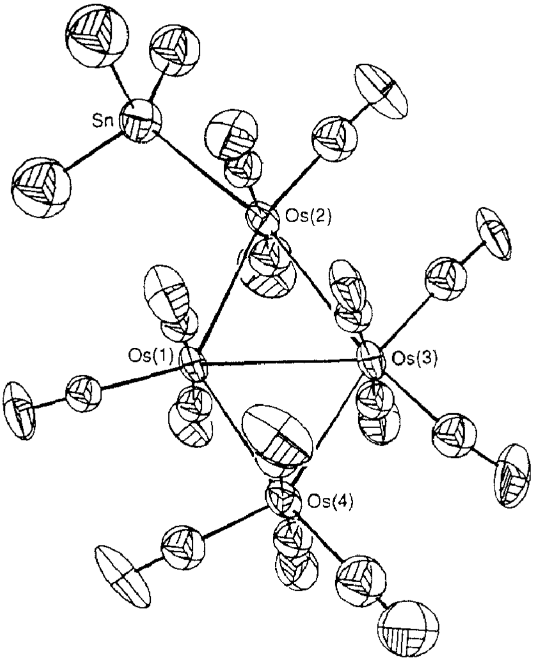


Fig. 5. Molecular structure of $Os_4(\mu\text{-}H)(CO)_{14}(SnMe_3)$ (**8**).

by the addition of Me_3NO to a solution of $Os_3(\mu\text{-}H)_2(CO)_{10}$ and $Os(CO)_4(PMe_3)$ (eq. 9) [57].

$$Os_3(\mu\text{-}H)_2(CO)_{10} + Os(CO)_4(PMe_3) \xrightarrow{Me_3NO} \underset{(\mathbf{9})}{Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)} + \text{other products} \qquad (9)$$

The X-ray structure of **9** revealed it to have a butterfly Os_4 framework (Fig. 6). It is believed that the hydride ligands bridge the Os(2)–Os(3) bond and the hinge, Os(1)–Os(3), bond. The ^{13}C NMR spectrum of **9** in solution at 0 °C indicates the carbonyls are rigid. The rigidity of the carbonyls in the hydride bridged clusters **8** and **9** is therefore in dramatic contrast to the non-rigidity exhibited by the carbonyls in the unbridged clusters **2** and **4**. The presence of the hydride ligands probably prevents the equatorial CO exchange from occurring with a low activation energy.

A survey of 62-electron Os_4 clusters with only terminal ligands, or with terminal ligands and bridging hydrides, discloses that clusters that adopt a planar arrangement have at least one metal atom in a hinge position with four terminal ligands. In the nonplanar, butterfly clusters both hinge atoms have only three terminal ligands. The hinge atoms in each case can be considered as having pseudo-octahedral coordination [57].

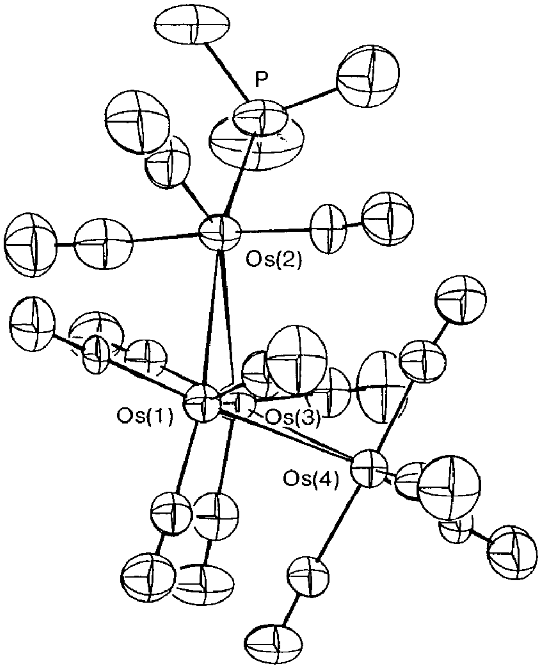


Fig. 6. Molecular structure of $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (**9**).

$Os_4(CO)_{14}$

Refluxing a hexane solution of $Os_4(CO)_{15}$ with a nitrogen purge readily affords $Os_4(CO)_{14}$ (**1**) in good yield (eq. 10) [58].

$$Os_4(CO)_{15} \xrightarrow[\text{hexane}]{\text{reflux in}} \underset{(\mathbf{1})}{Os_4(CO)_{14}} \qquad (10)$$

The structure of $Os_4(CO)_{14}$ is shown in Fig. 7. As can be seen from the figure, the Os_4 core in **1** is approximately tetrahedral as expected from PSEPT [44] although the Os–Os distances within the core do show significant variation (Table 2). There are four weak semibridging carbonyl interactions in the molecule that involve a carbonyl of an $Os(CO)_4$ unit interacting with an osmium atom of an $Os(CO)_3$ group.

Tetrahedral clusters with 14 carbonyl ligands are exceedingly rare and had been predicted to be unstable [59]. Shriver and co-workers have, however, reported the synthesis of $[Fe_3M(\mu\text{-}CO)_2(CO)_{12}]^{2-}$ (M = Cr, Mo, W) in 1984 [60]. To our knowledge, these are the only other tetrahedral clusters with 14 carbonyl substituents reported in the literature.

The ^{13}C NMR spectrum of **1** in $CHFCl_2/CD_2Cl_2$ consists of a sharp singlet even at −130 °C, that is, there is no detectable broadening due to exchange at this temperature. For two sites undergoing fast exchange, the rate constant required to observe a detectable broadening (of 0.5 Hz) due to exchange is given by $\pi(\Delta\nu)^2$, where $\Delta\nu$ is the chemical shift difference between the two signals when the molecule is rigid [61]. The chemical shift difference between signals due to axial and equatorial carbonyl groups in $Os(CO)_4$ units of rigid osmium clusters is usually at

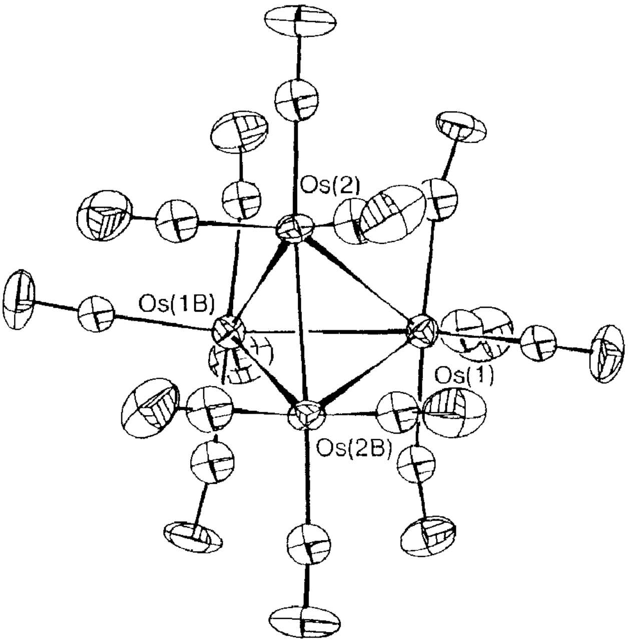


Fig. 7. Molecular structure of $Os_4(CO)_{14}$ (**1**). A crystallographic twofold axis passes through the center of the Os(1)–Os(1B) and Os(2)–Os(2B) bonds.

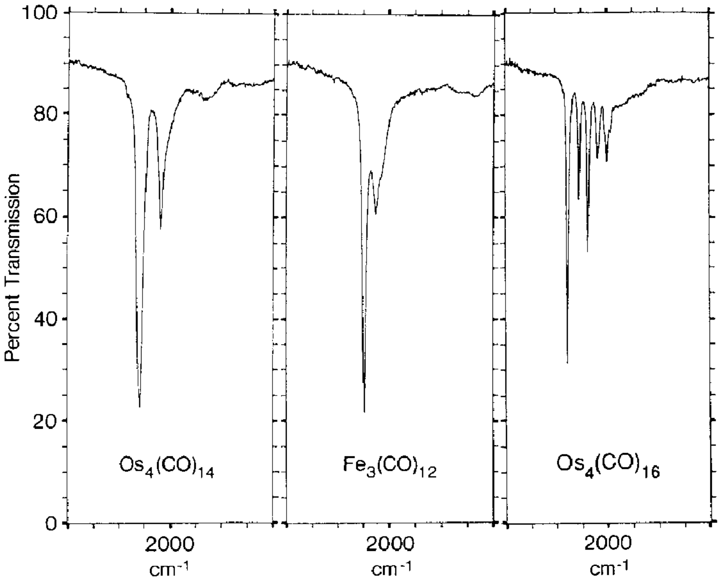


Fig. 8. Carbonyl stretching region of the infrared spectra of **1**, $Fe_3(CO)_{12}$, and **3** (all samples in hexane).

least 10 ppm, or ~ 1000 Hz at an operating frequency of 100.6 MHz [51,52]. For example, this shift separation is 11.9 ppm in $Os_3(CO)_{12}$ [62] (consider also the ^{13}C NMR spectrum of **2** shown in Fig. 3). If the chemical shift range of the carbonyl resonances in **1** in the absence of exchange is also at least 1000 Hz then the sharp singlet observed in the spectrum at $-130\,°C$ suggests the carbonyls are undergoing exchange with a rate constant of at least 3×10^6 s^{-1} at this temperature. If it is further assumed that the rate constant doubles with every ten degree rise in temperature, then a minimum rate constant of ~ 2×10^{11} s^{-1} is estimated for the exchange at 30 °C. This is a rate constant approaching that necessary to cause detectable broadening of infrared absorptions [63]. From the uncertainty principle [64], a rate constant necessary to cause a broadening of 5 cm^{-1} and thus coalesce two infrared peaks separated by this frequency is approximately 9.4×10^{11} s^{-1}.

There is evidence in the infrared spectrum of **1** in hexane for broadening due to exchange. The spectrum in the carbonyl stretching region consists of two broad absorptions plus a third even broader absorption that is barely detectable above the base line (Fig. 8). This is far fewer CO stretches than is predicted by group theory for **1**: twelve infrared-active carbonyl stretches are predicted for **1** with C_{2v} symmetry (all CO ligands terminal) whereas for the more symmetric form with a carbonyl bridging two opposite edges of a regular tetrahedron (i.e., D_{2d} $Os_4(\mu\text{-}CO)_2(CO)_{12}$) five infrared-active CO absorptions are predicted. The half-width of the two intense CO-stretches in the spectrum of **1** is 14.5 cm^{-1} whereas for the corresponding absorptions of $Os_4(CO)_{16}$ under the same conditions it is 5 cm^{-1} (see Fig. 8). Furthermore, preliminary studies show that as a methylcyclohexane solution of **1** is cooled to $-90\,°C$ the major bands in the infrared spectrum split and other bands appear from the base line. This is consistent with a CO exchange that is slowed on the infrared time scale. Further studies are, however, needed to substantiate this proposal.

The infrared spectrum of **1** in the CO stretching region shows remarkable similarity to that of $Fe_3(CO)_{12}$ (Fig. 8). The structure of $Fe_3(CO)_{12}$ in solution has been a subject of debate for many years [65]. Cotton and Hunter have proposed that $Fe_3(CO)_{12}$ adopts a continuum of structures in solution and that this is responsible for the broadness of the infrared absorptions [66]. This interpretation has, however, been recently questioned [67]. It may be that in solution the carbonyls in $Fe_3(CO)_{12}$ also exchange on the infrared time scale. Consistent with this view is that the ^{13}C NMR spectrum of $Fe_3(CO)_{12}$ in solution consists of a sharp singlet at −150 °C [66]. In iron complexes that contain both bridging and terminal carbonyl ligands and that are also rigid in solution, the ^{13}C NMR signals due to the bridging carbonyls are typically 50 ppm downfield from the signals due to the terminal carbonyls [68]. Furthermore, in the ^{13}C NMR spectrum of $Fe_3(CO)_{12}$ in the solid state at −93 °C (where CO exchange is slow) the signals span the range 198.3 to 238.8 ppm (i.e., 40.5 ppm) [69]. This suggests that if in solution $Fe_3(CO)_{12}$ has bridging carbonyls that exchange with terminal carbonyls then they do so with a rate of at least $3 \times 10^6\ s^{-1}$ at −150 °C! * Dynamic rearrangement observable on the infrared time scale has also been recently reported for some (η^4-diene)$Fe(CO)_3$ complexes [70]. It may be that this phenomenon can be observed in other types of organometallic complexes and studies with this purpose in mind are planned.

$Os_4(CO)_{13}(PMe_3)$

The only derivative of $Os_4(CO)_{14}$ we have prepared so far is $Os_4(CO)_{13}(PMe_3)$ (**10**). This cluster was synthesized by the pyrolysis or the ultraviolet irradiation of $Os_4(CO)_{14}(PMe_3)$ in hexane [34]. The structure of **10** also has a pseudo-tetrahedral core with metal–metal bond lengths similar to those in **1** (Table 2); the phosphine ligand is bound to an osmium atom that has three carbonyl ligands.

The ^{13}C NMR spectrum of **10** in $CHFCl_2/CD_2Cl_2$ consists of a sharp singlet at 0 °C that broadens almost to the base line in the spectrum at −125 °C. This indicates that, in contrast to **1**, the CO-exchange is becoming slow on the NMR time scale at −125 °C. The infrared spectrum in the CO-stretching region of **10** in hexane (at room temperature) consists of five, relatively sharp absorptions [34].

$Os_4(CO)_{16}$

Treatment of $Os_4(CO)_{15}$ in CH_2Cl_2 at 0 °C with an atmosphere of carbon monoxide causes essentially quantitative conversion to $Os_4(CO)_{16}$ (**3**) [71]. The structure of **3** shows it to be a metal carbonyl analogue of cyclobutane (Fig. 9); the CH_2 and $Os(CO)_4$ fragments are, of course, isolobal [72]. The dihedral angle between the Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) planes in **3** is 158.9° (in cyclobutane the angle is ~ 145° [73]). The metal–metal bonds in **3** are remarkably long for Os–Os single bonds: Os(1)–Os(2) 2.997(1) Å, Os(1)–Os(4) 2.985(1) Å, Os(2)–Os(3) 2.979(1) Å, Os(3)–Os(4) 3.000(1) Å. Once again, these bond lengths should be compared with the average Os–Os bond length of 2.877(3) Å in $Os_3(CO)_{12}$ [3].

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* Calculation based on an operating frequency of 25 MHz.

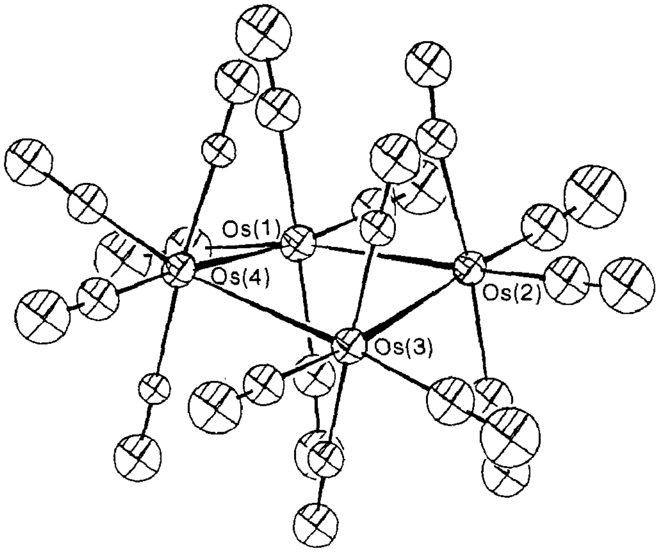


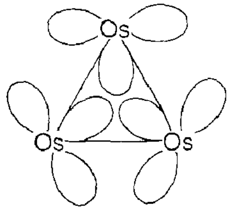
Fig. 9. Molecular structure of $Os_4(CO)_{16}$ (3).

The long Os–Os bonds in **3** indicate they are weak. Use of the bond order relationship of Pauling (described above) yields a bond order of 0.6 for an Os–Os bond of length 2.997 Å. In agreement with the view that the metal–metal bonds are weak, **3** decomposes when stirred in hexane (under nitrogen) at room temperature to give mainly $Os_3(CO)_{12}$ plus traces of $Os_4(CO)_{15}$ after 30 h (eq. 11). (It is probable

$$Os_4(CO)_{16} \xrightarrow[\text{hexane}]{25\,°C} Os_3(CO)_{12} + \underset{\text{(trace)}}{Os_4(CO)_{15}} \tag{11}$$

that **3** was the unidentified intermediate Moss and Graham observed in the decomposition of $Os_2(CO)_9$ in heptane [2].)

The metal–metal bonds in $Os_3(CO)_{12}$ are usually regarded as two-center two-electron bonds [74]. If this were the case it would be expected that **3** would be more stable than $Os_3(CO)_{12}$ since in **3** the angles about each osmium atom approach the 90° required for octahedral coordination. But **3** is thermodynamically unstable with respect to $Os_3(CO)_{12}$. This suggests that the most important component of the metal–metal bonding in the trinuclear cluster is the occupancy of a molecular orbital located in the center of the metal triangle. Such a molecular orbital can be considered the result of an overlap of an atomic orbital on each osmium atom directed to the middle of the cluster as shown below. There are several theoretical



studies that indicate that the bonding in trinuclear, metal carbonyl clusters should be described in terms of a central molecular orbital, plus edge-bridging molecular orbitals [75]. The longer distance from the osmium atoms to the center of the cluster in **3** compared to that in $Os_3(CO)_{12}$ (~ 2.11 Å vs. ~ 1.66 Å, respectively) does not allow for the good overlap of the centrally-directed atomic orbitals in **3**. The bonding would therefore be mainly through the edge-bridging molecular orbitals.

In hexane, **3** exhibits six infrared active CO stretches which indicate it has a puckered (D_{2d}) rather than planar (D_{4h}) configuration in solution as well as in the solid state (Fig. 8). The ^{13}C NMR spectrum of **3** (^{13}CO enriched) in CH_2Cl_2/CD_2Cl_2 consists of two signals of equal intensity at δ 168.6 (assigned to the equatorial carbonyls) and δ 176.6 (assigned to the axial carbonyls). These signals remain sharp in the spectrum at −95°C which probably indicates there is rapid exchange between the various puckered configurations of **3** such that the inner and outer axial carbonyls are rendered equivalent on the NMR time scale [71].

When the reaction of **2** with ^{13}CO in CD_2Cl_2 was monitored by ^{13}C NMR spectroscopy, the spectrum after 4 h showed that the labelled carbon monoxide was equally distributed between the axial and equatorial sites in the product. This suggests that either the initial addition of CO to **2** is non-stereospecific or the addition is stereospecific but there is axial–equatorial carbonyl exchange that although slow on the NMR time scale, is fast on the time scale of the experiment.

Derivatives of the type $Os_4(CO)_{15}(L)$

We have prepared and structurally characterized the following clusters of this type: $Os_4(CO)_{15}(PMe_3)$ (**11**) [34], $Os_4(CO)_{15}[P(OCH_2)_3CMe]$ (**12**) [76], $Os_4(CO)_{15}(CNBu^t)$ (**13**) [77], and $Os_4(CO)_{15}(PF_3)$ (**14**) [76]. The first cluster was prepared by the addition of $Os(CO)_4(PMe_3)$ to either $Os_3(CO)_{11}(CH_3CN)$ or $Os_3(\mu\text{-}H)_2(CO)_{10}$ [34]. The other three clusters were prepared by the reaction of the appropriate noncarbonyl ligand with $Os_4(CO)_{15}$ in solution at or below 0°C.

Whereas the PF_3 derivative has the cyclobutane-like geometry found for **3** the other derivatives have the so-called spiked triangular configuration in which the spike metal–metal bond is a dative metal–metal bond. Interestingly, the phosphorus ligand is *trans* to this bond in **11** and **12**, whereas in **13** the $CNBu^t$ group is *cis* to the dative metal–metal bond. The structures of **12**, **13**, and **14** are shown in Fig. 10

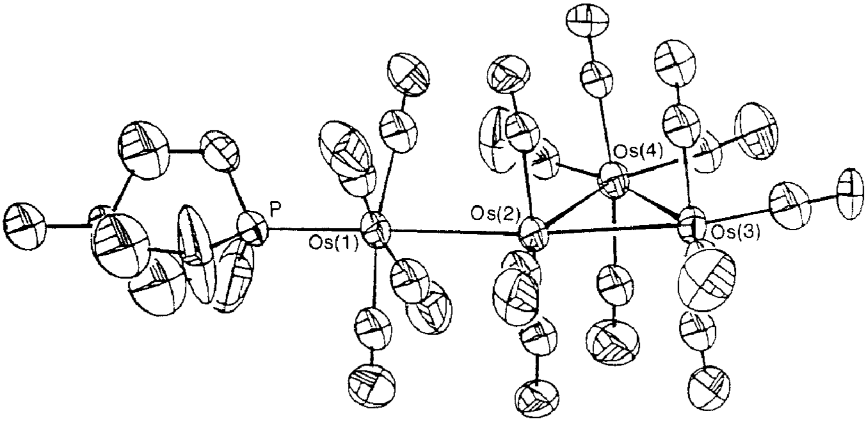


Fig. 10. Molecular structure of $Os_4(CO)_{15}[P(OCH_2)_3CMe]$ (**12**).

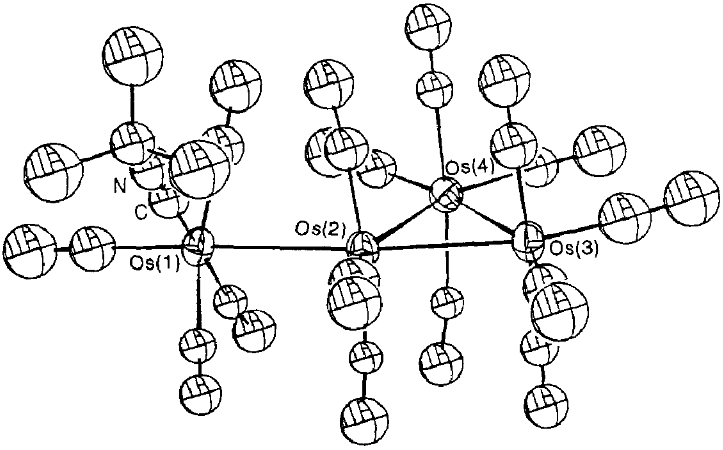


Fig. 11. Molecular structure of $Os_4(CO)_{15}(CNBu^t)$ (**13**).

to 12, respectively. The cone angles [78] of $P(OCH_2)_3CMe$ (θ 101°) and PMe_3 (θ 118°) span that of PF_3 (θ 104°) so that it is doubtful that the difference in the structure of **14** compared to that of **12** and **13** can be attributed to steric reasons. It is well known that the electronic properties of PF_3 are similar to those of carbon monoxide [79]. It is therefore concluded that it is the electronic properties of L that dictate which geometry, puckered square or spiked triangle, clusters of the type $Os_4(CO)_{15}(L)$ adopt.

Cluster **14** is a fragile molecule that rapidly decomposes in solution above 0 °C. Once again the metal–metal bonds in the molecule are long for Os–Os single bonds; the lengths range from 2.977(2) Å to 3.005(2) Å (Table 2). The dihedral angle between the Os(1)–Os(2)–Os(3) and Os(1)–Os(3)–Os(4) planes is 151.7°. The ^{13}C NMR spectrum of **14** in $CHFCl_2/CD_2Cl_2$ indicates it is rigid in solution between

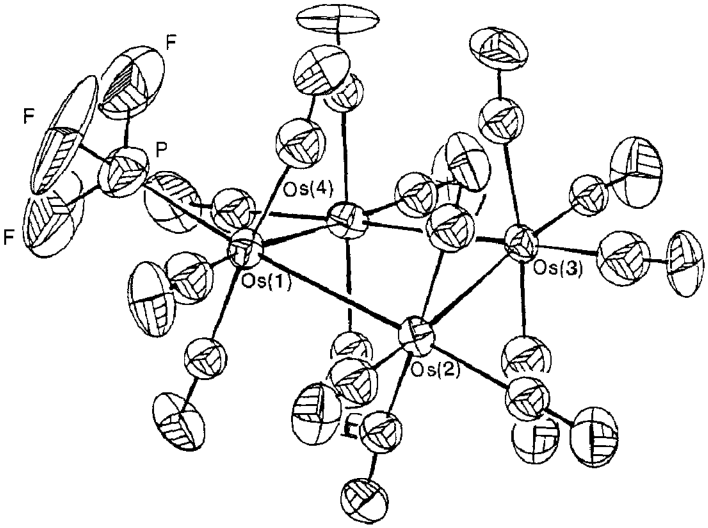
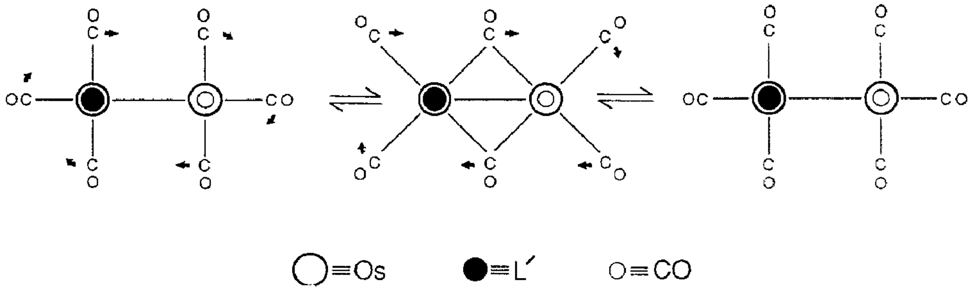


Fig. 12. Molecular structure of $Os_4(CO)_{15}(PF_3)$ (**14**).



Scheme 5

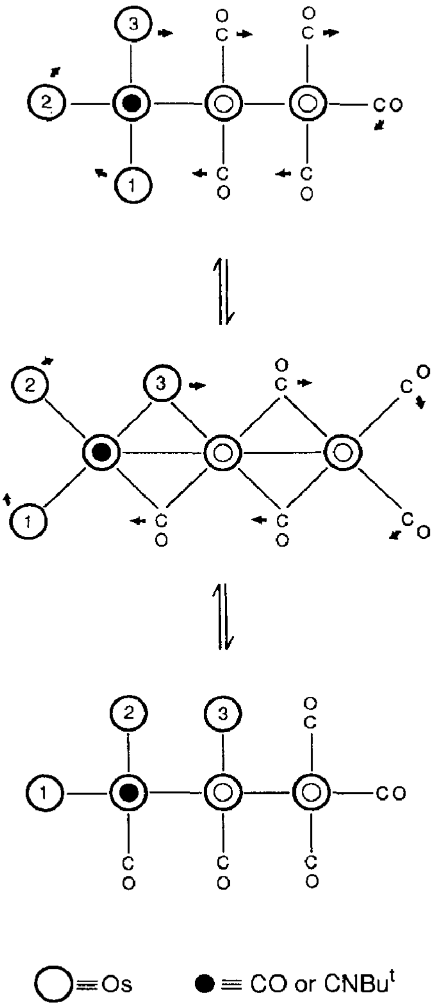
-122 and $-55\,^\circ$C except that, as in **3**, an axial carbonyl is equivalent to its *trans* partner, presumably due to rapid ring inversion.

The ^{13}C NMR spectrum of **13** in $CHFCl_2/CD_2Cl_2$ at $-108\,^\circ$C exhibits 15 carbonyl resonances consistent with the solid-state structure with the CNBu^t ligand locked to one side of the Os_4 plane, that is, the rotation about the Os–Os dative bond is restricted. It is believed that this is due to steric interactions between both the isocyanide ligand and the carbonyl *trans* to this ligand, and the vicinal carbonyl on Os(4). As the temperature of the sample is raised to $-48\,^\circ$C eight of the signals coalesce in pairs in agreement with the rapid oscillation of the CNBu^t ligand about the metal plane. Models show that the interaction of the isocyanide ligand and the vicinal carbonyl on Os(4) is so severe that it is doubtful that there is completely free rotation about the Os(1)–Os(2) bond at ordinary temperatures.

The solution ^{13}C NMR spectra of the spiked triangular clusters **11** [34] and **13** [77] between $-60\,^\circ$C and room temperature undergo changes that are similar to those in the spectra of $Os_3(CO)_{11}(PR_3)$ (R = organic group) clusters [52,80]: sets of signals associated with the $Os_3(CO)_{11}$ unit collapse to the base line at different rates. The mode of the first collapse is consistent with a terminal-bridge, merry-go-round CO exchange in the axial plane that passes through Os(2) and Os(4) and is *cis* perpendicular to $Os(CO)_4(L)$ or PR_3; this is illustrated in Scheme 5 ($L' = Os(CO)_4(L)$ or PR_3).

At higher temperatures than those at which the first process occurs, further signals collapse to the base line consistent with merry-go-round CO exchanges occurring in the two other planes in the tetranuclear clusters, that is, in those planes passing through Os(3) and Os(4), and Os(2) and Os(3). In the $Os_3(CO)_{11}(PR_3)$ derivatives the exchange in the latter plane apparently does not occur presumably because the bulky PR_3 group is prevented from entering an axial site for steric reasons [52]. In **11** and **13** some of the carbonyls of the $Os(CO)_4(L)$ moiety also take part in the exchange in the Os(2)–Os(3) axial plane as shown in Scheme 6 (for **11**, position 2 is occupied by PMe_3; the other positions labelled 1–3 in both **11** and **13** are occupied by CO).

When this process occurs in **11** it results in isomerization since the PMe_3 is in a site *cis* to the Os–Os dative bond upon completion of the exchange. Weak peaks are present in the spectrum of **11** at low temperatures which may indicate the presence of small amounts of a second isomer. From Scheme 6, it can be seen that for **13** the carbonyl *trans* to the isocyanide substituent does not take part in the exchange. Consistent with this mechanism is that one signal remains sharp in the spectrum



Scheme 6

even at room temperature, whereas all the other signals have completely collapsed to the base line.

Conclusions

The clusters $Os_4(CO)_{14}$ (**1**), $Os_4(CO)_{15}$ (**2**), and $Os_4(CO)_{16}$ (**3**) are the missing links between $Os_3(CO)_{12}$ and the higher nuclearity clusters of osmium. Furthermore, the clusters **1**–**3**, and $Os_4(CO)_n(PMe_3)$ ($n = 13$, 14, 15) represent the first report of conversion of a 62-electron cluster to a 64-, and also to a 60-electron cluster (Fig. 13) [42]. Although the number of metal–metal bonds in these tetranuclear clusters is as predicted from PSEPT [43], the variation in the metal–metal bond lengths in the individual clusters cannot be explained by the theory in its present state. The theory also cannot rationalize the different structures of $Os_4(CO)_{15}(PF_3)$ and $Os_4(CO)_{15}[P(OCH_2)_3CMe]$, or of $Os_4(CO)_{14}(PMe_3)$ and $Os_4(\mu\text{-}H)_2(CO)_{13}(PMe_3)$ (Fig. 13).

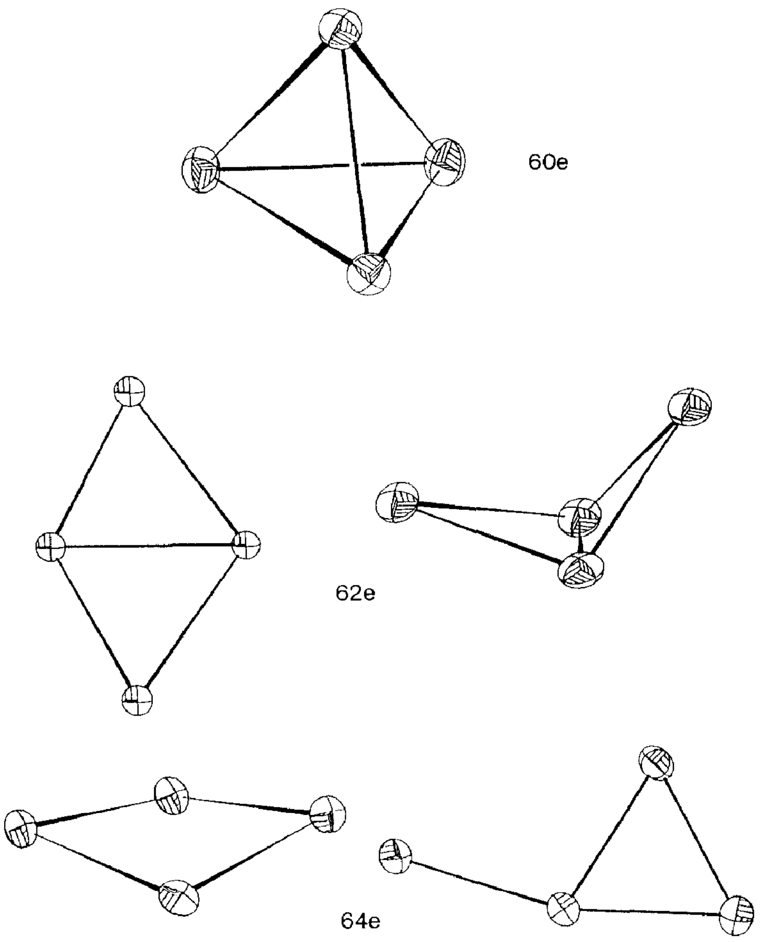


Fig. 13. The metal skeletons in **1**, **2**, **9**, **3** and **11**.

Extended Hückel molecular orbital calculations that take into account relativistic effects are in progress in an attempt to provide further insight into the bonding in these molecules. We are also actively investigating the chemistry of these remarkable compounds.

Acknowledgements

I dedicate this article to my first chemistry teacher, Mr. George Spinoza. I would like to thank the members of my research group both past and present for their enthusiastic support. In particular, I thank Dr. Victor Johnston and Dr. Lillian Martin who did most of the work described in this review. I also wish to acknowledge the invaluable contribution of Professor Fred Einstein to all aspects of the X-ray crystallography described above.

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