Dynamic Behaviour of High-nuclearity Osmium–Mercury Clusters in Solution

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The dynamic behaviour of the Hg-capped decaosmium cluster anions $[Os_{10}C(CO)_{24}(HgY)]^-$ [Y = Cl, Br, I, CF_3 or $Mo(CO)_3(cp)$; cp = η^5-C_5H_5] **2a–2e** as well as the Hg-linked cluster $[\{Os_{10}C(CO)_{24}\}_2Hg]^{2-}$ **3** in solution has been investigated by variable-temperature ^{13}C NMR spectroscopy. The mercury fragment HgY has been found to be highly mobile on the surface of the Os_{10} cluster core and to undergo rapid exchange between the different μ-bridging and μ_3-capping sites of the parent cluster. Based on the spectroscopic results a unified model for the observed metal-core fluxionality is proposed.

Molecular structure plots obtained from the single-crystal X-ray structure analyses of transition-metal clusters may convey the impression of rigid metal cores embedded in their equally static ligand shells. While in many cases this appropriately reflects the situation of the molecules packed in a single crystal and thus restricted in their mobility, spectroscopic studies performed on their solutions have revealed the existence of dynamic processes effecting the permutation of nuclear positions in the molecules.

'Fluxionality', as it relates to organometallics in general and metal clusters in particular, refers to the reversible intramolecular site exchange of ligands bound to the surface or located in the inside of metal frameworks as well as the structural rearrangement of the metal core itself. It is the consequence of the existence of molecular configurations of a compound with energies similar to that of the ground state and which can therefore be thermally excited. The considerable interest that the study of the dynamic processes in carbonyl clusters has generated has been fuelled by the role that ligand migration on cluster surfaces might play in catalytic conversions involving these systems.[1,2] Their perceived importance as model systems for the chemisorption of substrates on metal surfaces has added a further dimension to the observed non-rigidity of many carbonyl clusters in solution.

Metal core fluxionality has been widely observed in mixed-metal clusters containing Group Ib or IIb metal fragments in their core.[3] The high mobility of μ-bridging mercury fragments in a number of transition metal–mercury clusters has led Rosenberg and co-workers[4] to liken the behaviour of the mercury units to that of the μ-H ligand in the corresponding hydrido clusters. In the light of these results and the observed exchange patterns in the room-temperature ^{13}C NMR spectra of derivatives of the decaosmium cluster dianion $[Os_{10}C(CO)_{24}]^{2-}$ **1**, a systematic investigation into their dynamic behaviour was carried out.

Results and Discussion

Mobility of the Hg-Y *Fragment in* $[Os_{10}C(CO)_{24}(HgY)]^-$ [Y = Cl, Br, I, CF_3 *or* $Mo(CO)_3(cp)$; (cp = η^5-C_5H_5) **2a**–**2e**.—X-Ray diffraction studies of $[Os_{10}C(CO)_{24}(HgBr)]^-$ **2b** and $[Os_{10}C(CO)_{24}(HgCF_3)]^-$ **2d** have established that the mercury fragment adopts a μ_3 co-ordination mode with respect to one of the triangular faces of a capping tetrahedral unit in the Os_{10} tetracapped octahedron.[5,6] Both clusters have idealised C_s symmetry and, if rigid on the NMR time-scale, would be expected to display 10 or 14 ^{13}CO resonances in their ^{13}C NMR spectra [depending on whether the frequently observed vertex-$Os(CO)_3$ 'rotation' is fast on the NMR time-scale or not].

However, the ^{13}C NMR spectrum of compound **2d** in CD_2Cl_2 at 300 K consists of only two signals of roughly equal intensity at δ 174.4 and 184.1, *i.e.* the same signal pattern as that of the non-mercuriated dianion **1**, albeit shifted to higher field by *ca.* 5 ppm [Fig. 1(*a*)]. The effective symmetry of **2d** is thus the same (T_d) as that of **1** which implies a high degree of fluxionality of the mercury fragment attached to the osmium core. In principle, the dynamic process may involve rapid movement of the $HgCF_3$ group over the surface of the Os_{10} core, *i.e.* fast exchange between all possible μ and μ_3 positions on the cluster. Alternatively, a dissociative mechanism with intermolecular exchange would account for the observed spectrum. In order to assess whether the latter was the case, a solution of **1** was gradually titrated with $[Hg(CF_3)(O_2CCF_3)]$ and the conversion into **2d** monitored by successive recording of ^{13}C NMR spectra of the reaction mixture. In case of a fast intermolecular exchange of F_3CHg^+ a continuous shift of the two resonances from δ 178.2, 189.9 to δ 174.4, 184.1 would be observed. The sequence of spectra displayed in Fig. 1(*b*) clearly shows that exchange of F_3CHg^+ between **1** and **2d** is either a slow process relative to that responsible for the observed effective symmetry or does not take place at all. It may therefore be assumed that, on the time-scale of the experiment, the F_3CHg^+ fragment does not leave the solvent cage around **2d** and that an *intramolecular* exchange process must consequently be occurring.

In order to establish the nature of the dynamic behaviour of the F_3CHg group, a series of ^{13}C NMR spectra were recorded at variable temperature between 300 and 170 K (Fig. 2). Cooling of the sample first leads to exchange broadening and coalescence at 210 K of the low-field signal. Below 200 K three resonances with an intensity ratio of 1:1:2 appear in place of the original singlet. Similarly, the high-field signal at δ 174.1 is broadened and splits at 200 K into two broad resonances which are further split into a set of three relatively sharp signals below 180 K. At 170 K the spectrum consists of six singlets at δ 172.8, 174.1, 175.0, 181.3, 184.5 and 188.2 (CD_2Cl_2:$CFCl_3$ = 1:1) with an intensity ratio of 1:2:1:2:1:1. This signal pattern would be expected for an Os_{10} derivative with an effective C_{3v} symmetry in which the 'rotation' of the CO ligands b and c (Fig. 3) is frozen out. This implies that even at 170 K the spectrum does not reflect the molecular symmetry observed in the solid state.

The spectrum at 170 K can be explained by either invoking the rapid exchange of the mercury group between the three μ_3 positions of a single capping tetrahedron in the Os_{10} cluster or over a single Os_6 face of the core tetrahedron. However, closer examination of the solid-state structures of **2b** and **2d** indicates

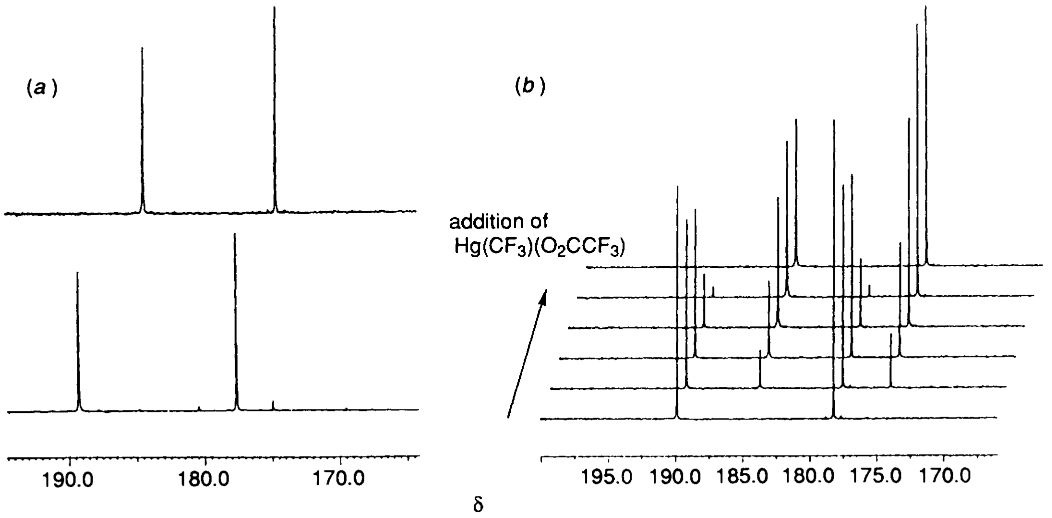

Fig. 1 (*a*) ^{13}C NMR spectra of compounds **1** (bottom) and **2d** (top) recorded in CD_2Cl_2 at 300 K. (*b*) Spectral sequence of the titration of **1** with $Hg(CF_3)(O_2CCF_3)$ in CD_2Cl_2

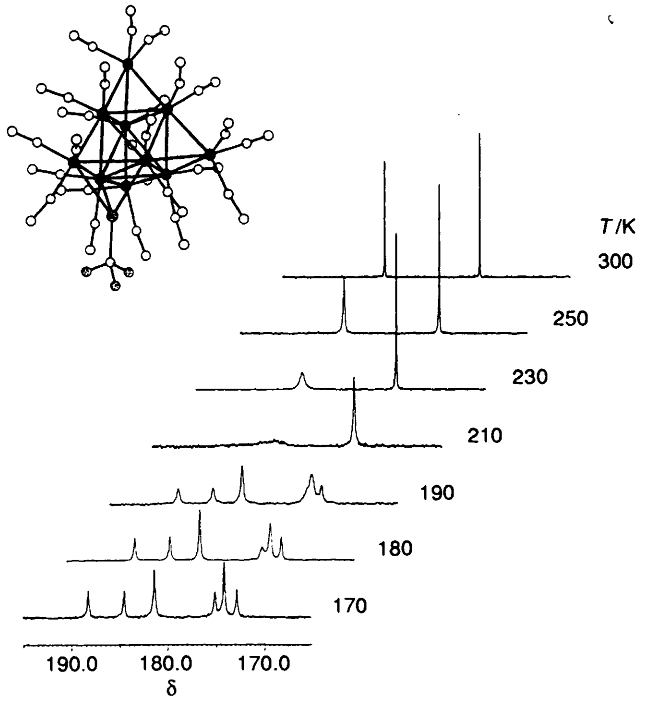

Fig. 2 Variable low-temperature 100.62 MHz ^{13}C NMR spectra of compound **2d**

that this second alternative is improbable. The steric requirements of the HgY fragment leads to a rotation of the vertex $Os(CO)_3$ group adjacent to it by *ca.* 60°, generating a tetragonal hole in the ligand shell of the cluster which is occupied by the mercury atom. The movement of the mercury over a single face of the Os_{10} tetrahedron would therefore be accompanied by 'rotation' of the $Os(CO)_3$ vertex on the same time-scale. This would rule out the spectral differentiation between the CO environments b and c and thus contradict the spectral pattern observed at 170 K.

Low-temperature spectral series were also recorded of the halogenomercury capped clusters **2a**–**2c**. They displayed essentially the same exchange patterns as that described in detail for **2d**. As a representative example, a stacked plot of the low-temperature series of $[Os_{10}C(CO)_{24}(HgI)]^-$ **2c** is shown in Fig. 4. From a quantitative point of view it should be noted that (given virtually identical chemical shifts of the two sets of signals) coalescence of the high-temperature spectral pattern is observed at a temperature which is 20 K higher than for **2d** (230 *vs.* 210 K) under the same experimental conditions (CD_2Cl_2, 100.6 MHz), while the transition to the frozen $Os(CO)_3$ rotation occurs in the same temperature range (190–180 K). Since the latter is thought to be due to the steric requirements of the Hg atom within the ligand shell of the cluster which is similar in both cases, this is not unexpected. On the other hand, the mobility of the HgY group itself is dependent on the nature of Y and seems to be slightly higher for F_3CHg in **2d** than XHg in **2a**–**2c** (X = Cl, Br or I). It appears that an increased positive charge on the mercury favours the fluxional process.

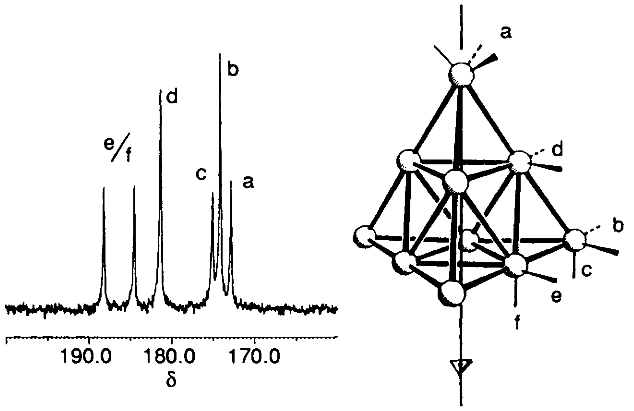

Fig. 3 100.62 MHz ^{13}C NMR spectrum of compound **2d** recorded at 170 K in CD_2Cl_2–$CFCl_3$ (1:1). The assignment is based on the assumption of an effective C_{3v} symmetry of the system

On substitution of the halide or F_3C ligand on the Hg atom by the heavier and bulkier organometallic fragment $(cp)(OC)_3$-Mo, the transition from the regime of fast HgY migration over the whole cluster core to that of restricted exchange around one of the capping tetrahedra occurs at *ca.* 310 K. Below this temperature it is therefore possible to observe the resonance pattern of an Os_{10} cluster with effective C_{3v} symmetry but rapid tripodal rotation of the vertex carbonyls leading to an overall five-signal pattern. The ^{13}C NMR spectrum of compound **2e** recorded at 244 K is shown in Fig. 5(*a*) and should be compared to that of $[Os_{10}C(CO)_{24}H]^-$ in Fig. 5(*b*).

In the light of these spectroscopic results it may be concluded that the mercury fragments in compounds **2a**–**2e** act as highly mobile 'ligands' on the cluster core. Their dynamic behaviour is explicable within the framework of a unified model. Three separate dynamic processes may be invoked for the explanation of the exchange phenomena observed in the spectra: (I) the

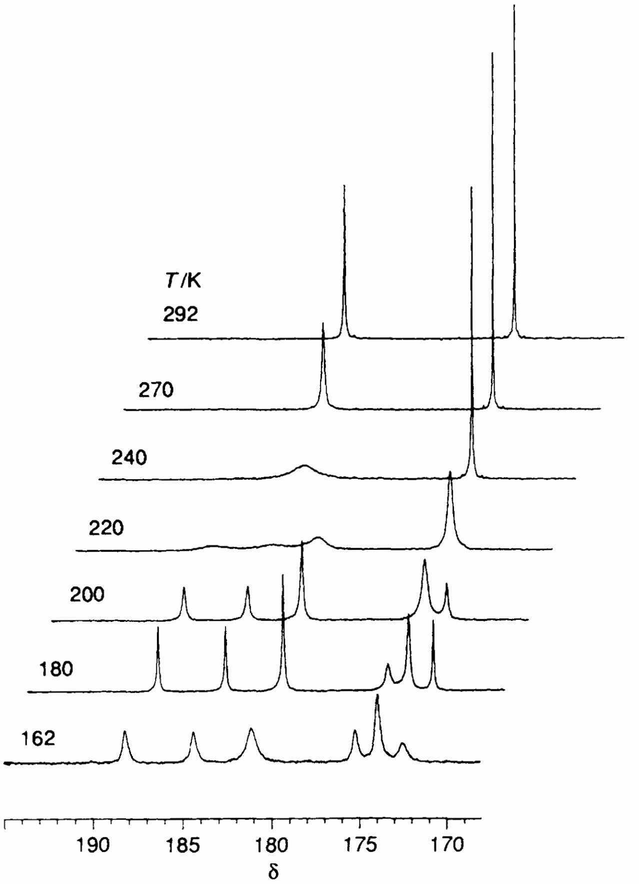

Fig. 4 Variable-temperature 100.62 MHz ^{13}C NMR spectra of $[N(PPh_3)_2][Os_{10}C(CO)_{24}(HgI)]$ **2c** recorded in CD_2Cl_2 and CD_2Cl_2–$CFCl_3$ (1:1)

tripodal 'rotation' of the $Os(CO)_3$ vertices; (II) the exchange of the mercury group between the μ and μ_3 positions on one of the capping tetrahedra of the Os_{10} core; and (III) the exchange between the four tetrahedral 'caps' of the cluster which effectively amounts to the migration of HgY over the entire surface of the metal core. By combining these processes the spectral patterns observed may be classified in five regimes: (1) processes I–III are rapid on the NMR time-scale [effective symmetry T_d, two CO resonances; *e.g.* **2d** at 300 K, see Fig. 1(*a*)]; (2) processes I and II are rapid while III is slow on the NMR time-scale [effective symmetry C_{3v}, five CO resonances, *e.g.* **2e** at 244 K, see Fig. 5(*a*)]; (3) process II is rapid, I and III are slow on the NMR time-scale (effective symmetry C_{3v}, six CO resonances, *e.g.* **2d** at 170 K, see Fig. 3); (4) process I is rapid, II and III are slow on the NMR time-scale [effective symmetry C_s or C_1, $\geqslant$ 10 CO resonances, see Fig. 7(*b*), discussed in the following section]; (5) processes I–III are slow on the NMR time-scale [effective symmetry C_s or C_1, $\geqslant$14 resonances (see below)]. Regimes (1)–(3) have been encountered in the spectral series of **2a**–**2e**. For none of these clusters was it possible to freeze out the mercury migration and thus observe the signal patterns of regimes (4) and (5). This proved to be possible to a certain extent in the ^{13}C NMR investigation of the mercury-linked cluster $[\{Os_{10}C(CO)_{24}\}_2Hg]^{2-}$ **3**. The complicated nature of the spectral series of this compound merits its discussion in a separate section.

Dynamic Behaviour of $[\{Os_{10}C(CO)_{24}\}_2Hg]^{2-}$ **3** *in Solution.*—The structure of compound **3** has been described in the previous paper[5] as consisting of two Os_{10} subclusters linked by a mercury atom in a μ_4 co-ordination mode. Both osmium subunits are symmetry-related by a C_2 axis through the Hg atom but due to the twist angle between the two bridged Os–Os vectors there is no further local symmetry in the structure. In the limit of total structural rigidity, all of the 24 CO carbon atoms on an Os_{10} fragment would therefore be chemically inequivalent. To facilitate the interpretation of the ^{13}C NMR spectra the CO ligands on an $Hg[Os_{10}C(CO)_{24}]$ unit have been numbered as shown in Fig. 6, with $c_1{}^{1-3}$–$c_3{}^{1-3}$, $c_{3'}{}^{1-3}$ representing the 12 carbonyls co-ordinated to the vertices and

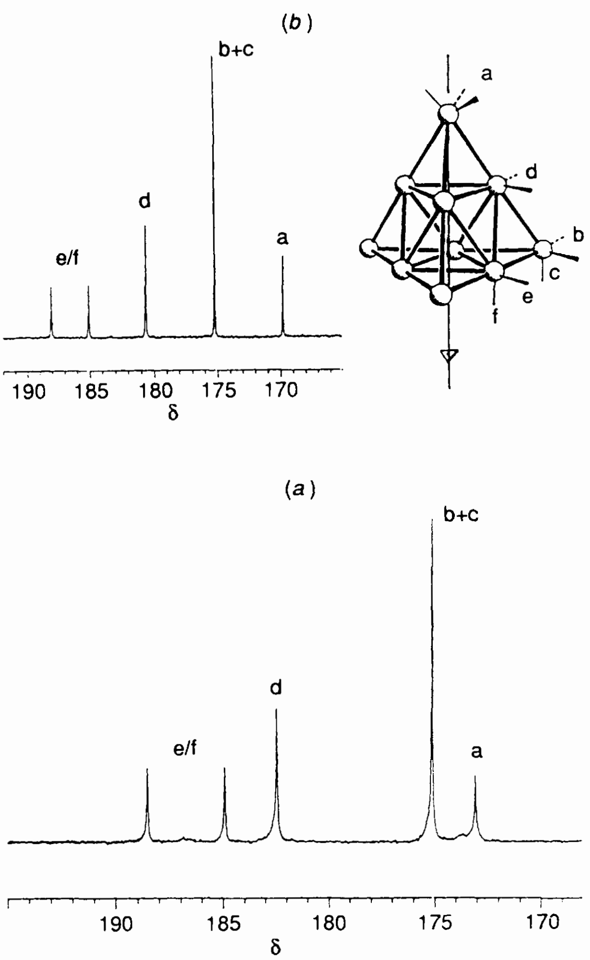

Fig. 5 (*a*) 100.62 MHz ^{13}C NMR spectrum of $[N(PPh_3)_2][Os_{10}C(CO)_{24}\{Mo(CO)_3(cp)\}]$ **2e** recorded at 244 K in CD_2Cl_2. (*b*) 100.62 MHz ^{13}C NMR spectrum of $[N(PPh_3)_2][Os_{10}C(CO)_{24}H]$ recorded at 300 K in CD_2Cl_2 (from ref. 7). The assignment is based on the assumption of an effective C_{3v} symmetry of the system

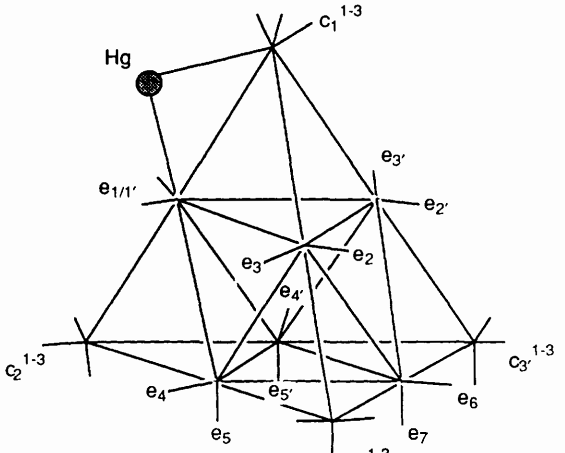

Fig. 6 Labelling of the CO ligands in one of the two symmetry-related Os_{10} fragments in $[N(PPh_3)_2]_2[\{Os_{10}C(CO)_{24}\}_2Hg]$ **3**

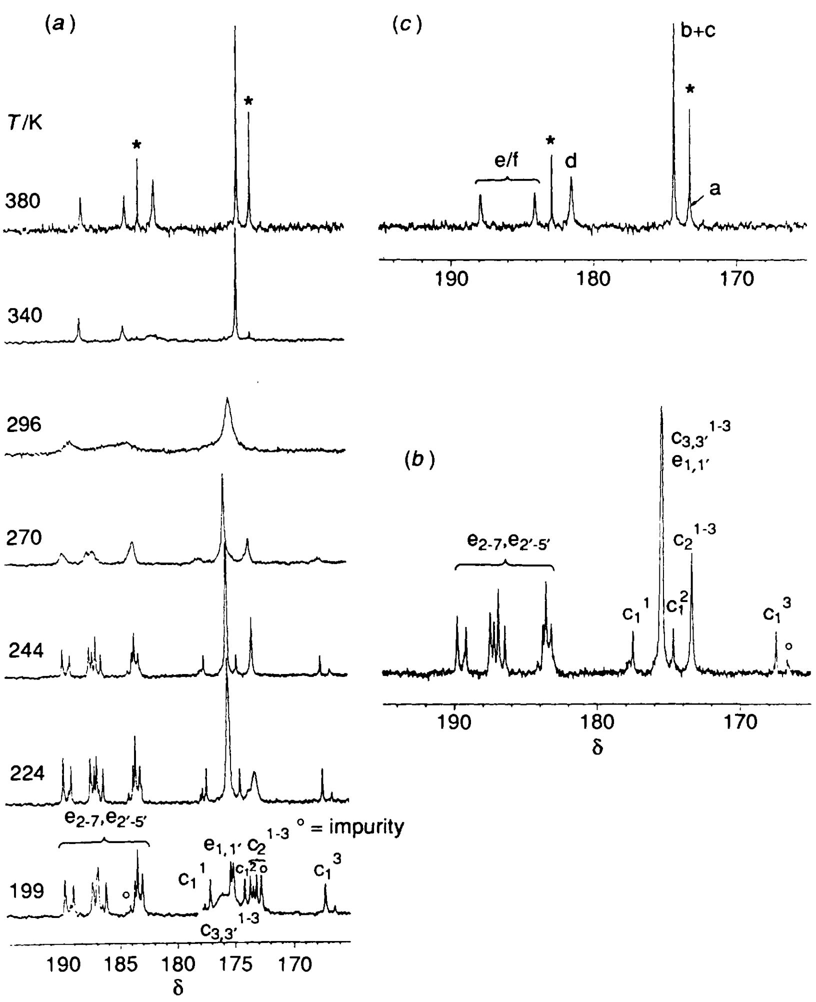

Fig. 7 (*a*) Variable-temperature series of ^{13}C NMR spectra of compound **3** between 199 and 380 K recorded in CD_2Cl_2 (< 300 K) and $C_2D_2Cl_4$ (> 300 K). (*b*) Spectrum recorded at 244 K with a tentative assignment of the signals. (*c*) Spectrum recorded at 380 K (the unidentified decomposition product is marked with an asterisk, impurity with a circle)

e_1–e_7 and $e_{1'}$–$e_{5'}$ the remaining 12 CO attached to the Os atoms on the edges of the Os_{10} tetrahedron.

As in the case of the HgY-capped species, an unambiguous assignment of the spectra is not feasible; however, based on known chemical shift tendencies, relative intensities of the signals, stereochemical arguments as well as the exchange pattern itself, a self-consistent explanation of the spectroscopic results is possible. A series of ^{13}C NMR spectra covering a temperature range of 199–380 K is shown in Fig. 7(*a*). The spectrum recorded at 296 K displays broad exchange features which are indicative of fluxional behaviour of the cluster on the NMR time-scale. On cooling the sample to 244 K, a set of sharp singlets emerge which may be divided into three groups: (*i*) the nine sharp signals between δ 183 and 190 with an overall relative intensity corresponding to approximately 10 CO; (*ii*) the three sharp resonances at δ 177.3, 174.4 and 167.3 and (*iii*) the intense and broadened signals at *ca.* δ 175.5 and 173.4 [Fig. 7(*b*)].

(*i*) The chemical shifts of the signals between δ 183 and 190 lie in the typical region for $Os(CO)_2$-edge CO ligands in derivatives of **1** and may be assigned to the CO positions e_2–e_7 and $e_{2'}$–$e_{5'}$. The carbonyls e_1 and $e_{1'}$ are co-ordinated to an Os atom adjacent to the linking mercury bridge and are therefore expected to have an anomalous chemical shift (see below). A precedent for this is set in $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ in which the signal attributed to the CO group co-ordinated to the Os atoms adjacent to the central Hg_3 triangle are shifted to higher field (δ 177.7) than those in the $Os(CO)_2$ groups of the basal Os_6 triangles of the cluster (δ 184.9, 185.7).[6]

(*ii*) The signals in the second group have a relative intensity of 1:1:1 and are assigned to the three vertex CO c_1^{1-3} in the $Os(CO)_3$ group adjacent to the Hg atom. The steric requirements of the mercury atom as well as the interaction with the CO ligands of the second Os_{10} subcluster inhibit the exchange of the ligands on this vertex. On heating the sample the three resonances coalesce and re-emerge as a singlet at δ 173.2 (380 K), the weighted mean of the chemical shifts of the three chemically distinct CO environments at 244 K.

(*iii*) The slightly broadened signal at δ 173.4 has a relative intensity corresponding to three CO groups and may be assigned to the rapidly exchanging three vertex carbonyls c_2^{1-3} while the broad (and split) signal at δ 175.5 with a relative intensity of approximately eight arises from the overlap of the $Os(CO)_3$ resonances c_3^{1-3} and $c_{3'}^{1-3}$ as well as the two 'hidden' signals e_1 and $e_{1'}$. The latter is substantiated by their emergence near the coalescence point of c_3^{1-3} and $c_{3'}^{1-3}$ at 199 K.

The spectrum at 244 K thus represents a situation in which the $(Os_{10})_2Hg$ metal core is virtually rigid while exchange through $Os(CO)_3$ 'rotation' is still rapid on the NMR time-scale, as was defined for regime (4) in the previous section. The transition from regime (4) to (5) is indicated in the spectrum recorded at 199 K in which the exchange of c_2^{1-3} is frozen out (δ 173.6, 173.1, 172.7) and c_3^{1-3} and $c_{3'}^{1-3}$ approach their coalescence point. Unfortunately, spectra recorded at lower temperatures were obscured by rapid precipitation of the cluster so that the limiting spectrum could not be obtained.

For the ^{13}C NMR spectra recorded above 300 K the high-boiling solvent $C_2D_2Cl_4$ was used. Unfortunately, on raising the temperature above 340 K partial decomposition of compound

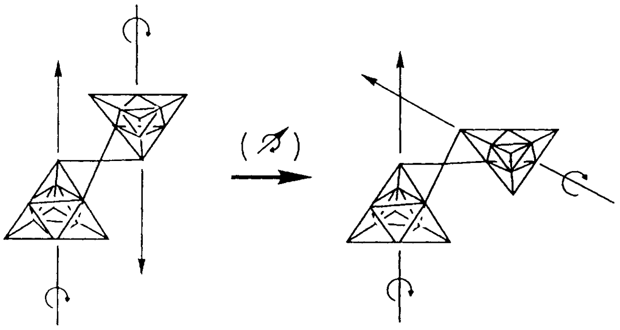

Fig. 8 Proposed intramolecular motion of the Os_{10} fragments relative to the mercury bridge to account for the ^{13}C NMR spectral patterns observed for compound **3** at 380 K

3 occurs generating a species which has two very sharp ^{13}C resonances at δ 182.9 and 173.3 of which the latter accidentally coincides with a (broader) signal of **3** at this temperature. If these two signals are disregarded, the spectrum at 380 K [Fig. 7(*c*)] displays the familiar five-signal pattern associated with regime (2) as defined in the previous section, similar to the spectrum of **2e** at 244 K [Fig. 5(*a*)]. For the linked cluster **3** this implies a fast migration of the mercury 'linker' around one tetrahedral cap in both Os_{10} subclusters, a motion which would necessitate a rapid rotation of the two halves relative to each other at this temperature (Fig. 8). The conclusion is that an $Os_{10}Hg$ unit acts very much like the HgY fragments in **2a**–**2e** towards the respective second Os_{10} subcluster in the linked species, a characteristic which is reflected in its dynamic behaviour on the NMR time-scale.

Experimental

The $[N(PPh_3)_2]^+$ salts of the ^{13}C-enriched compounds **2a**–**2e** and **3** were prepared as described in the previous paper[5] from *ca.* 50% ^{13}C-enriched $[Os_3(CO)_{12}]$.[8] The solutions used typically contained *ca.* 20 mg of **2a**–**2e** and *ca.* 6–8 mg **3** in CD_2Cl_2 (0.5 cm^3).

The ^{13}C NMR spectra were recorded using a Bruker AM400 spectrometer with an ASPECT 3000 computer and equipped with a B-VT-1000 variable-temperature unit. The temperature measurements in the high- and low-temperatures series were made with the internal thermocouple of the spectrometer VT unit. Spectra at temperatures < 180 K were recorded by addition of $CFCl_3$ (as freezing-point depressant) to the CD_2Cl_2 sample solution. Chromium(III) acetylacetonate was routinely added as a shiftless relaxation agent which enabled the reduction of the delay between consecutive pulses (*i.e.* the sum of the aquisition time AQ and the relaxation delay RD) to *ca.* 1.4 s. Typical aquisition parameters were as follows: number of pulses (NS), 200–2000; spectrometer frequency (SF), 100.62 MHz; number of data points (SI), 64 K; sweep width (SW), 45 000–45 000 Hz; offset frequency (O1), 16 000 Hz; relaxation delay (RD), 0.7–0.8 s. The accumulated free induction decay was treated with an exponential filter (LB = 1.0–1.2) before Fourier transformation.

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