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The cluster/surface analogy: the binding of norbornene on a triangulated array of metals

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Reactions of $[Os_3(CO)_{10}(NCMe)_2]$ **1** with norbornene (bicyclo[2.2.1]hept-2-ene, nbe) led to two isomeric triosmium clusters $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **2** and **3** and also the dihydride species $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_7H_8)]$ **4**. The molecular structure of compound **4** established by single crystal X-ray analysis shows norbornene–metal interactions similar to the proposed adsorption mode of norbornene found on the Pt(111) surface. The two isomers **2** and **3** exhibit an intermediate bonding mode between the solely π bound ligand and the di-σ,π bonding mode exhibited by cluster **4**. These isomers differ in the orientation of the C_7H_8 moiety with respect to the triosmium triangle. Both **2** and **3** may exist in other isomeric forms which differ in the location of the hydride ligand. Compound **2** converts into **3** which on heating undergoes C–H bond cleavage to produce **4**.

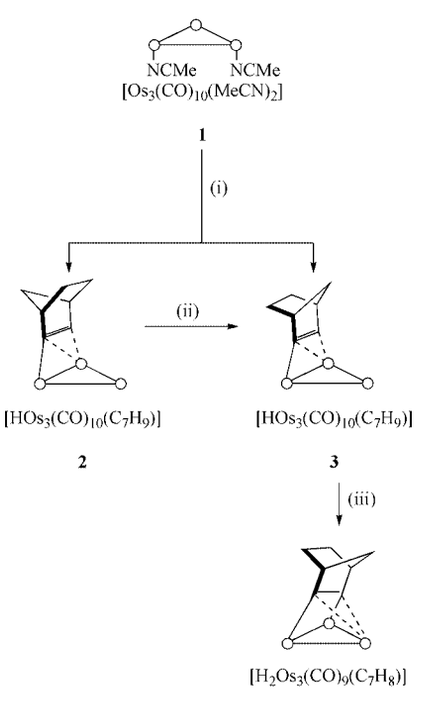
Introduction

The chemical and structural characterisation of molecular clusters bearing organic ligands has led to a clearer understanding of the bonding modes adopted by organic species chemisorbed on metal surfaces.[1] Surface chemists now frequently employ comparisons of the vibrational spectra of adsorbed species with those of fully characterised molecular metal clusters as a means of determining the structures of adsorbates on the surface.[2] A key example is the interaction of benzene with the Rh(111) surface,[3] and the trinuclear carbonyl clusters $[M_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_6H_6)]$.[4] It has been proposed that norbornene may bind to the Pt(111) surface *via* one double bond and an agostic interaction of the C–H bond on the bridging CH_2 unit.[5] We have recently been studying the interactions of norbornene (bicyclo[2.2.1]hept-2-ene) with transition metal carbonyl clusters with the intention of producing a cluster analogue for norbornene bound to a Pt(111) surface.[6] Until our work, cluster complexes containing norbornene have largely involved interaction of the ligand with one metal atom.[7] Here we report the synthesis and structural characterisation of three osmium clusters, the two isomers $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ and $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_7H_8)]$. The two isomers have been shown to be intermediates in the production of the dihydride species from a simple π-bound intermediate compound which has not been isolated. The dihydride **4** exhibits a bonding mode analogous to that proposed for norbornene adsorbed on the Pt(111) surface and, together with the triruthenium analogue,[6] may shed light on the reaction mechanism involved in the conversion of the C_7 moiety into benzene on the metal surface.

Results and discussion

The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ **1** with norbornene in dichloromethane under reflux for four hours affords two compounds, **2** and **3**, which, after separation by TLC and crystallisation, have been shown by single crystal X-ray diffraction to be the isomeric forms of the compound $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$. In a separate experiment we have further established that **2** undergoes complete isomerisation to **3** on heating in dichloromethane. On heating in hexane under reflux isomer **3** undergoes conversion by C–H bond cleavage to produce a third compound **4** which on the basis of a single crystal X-ray analysis has been shown to be $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_7H_8)]$ the analogue to the previously reported $[Ru_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_7H_8)]$.[6] Thus, the reaction sequence **1** ⟶ **2** ⟶ **3** ⟶ **4** (see Scheme 1) has been elucidated.

The molecular formula of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **2** was initially proposed from evidence provided by spectroscopic techniques and a single crystal analysis. The infrared spectrum contains peaks typical of terminally co-ordinated CO groups



Scheme 1 Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with norbornene. (i) Heat, dichloromethane–norbornene; (ii) heat, dichloromethane; (iii) heat, hexane.

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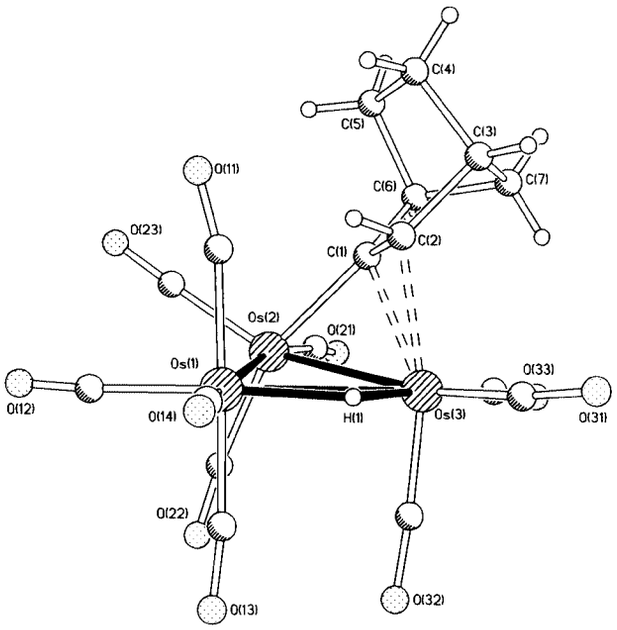


Fig. 1 The solid-state molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **2**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as that of the corresponding O atoms. Relevant bond lengths (Å) and angles (°) for **2** are: Os(1)–Os(2) 2.868(1), Os(1)–Os(3) 3.116(1), Os(2)–Os(3) 2.744(1), Os(2)–C(1) 2.13(2), Os(3)–C(1) 2.30(2), Os(3)–C(2) 2.27(2), C(1)–C(2) 1.37(3), C(1)–C(6) 1.54(3), C(2)–C(3) 1.61(4), C(3)–C(4) 1.58(4), C(3)–C(7) 1.52(3), C(4)–C(5) 1.49(4), C(5)–C(6) 1.59(4), C(6)–C(7) 1.52(4), mean $Os–C_{(CO)}$ 1.89(3), mean C–O 1.15(3), Os(1)–H 1.85 and Os(3)–H 1.85; Os(1)–H–Os(3) 114.8.

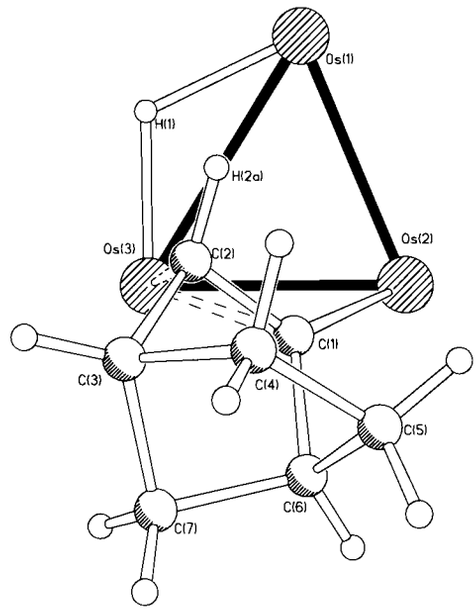


Fig. 2 The metallic and organic framework of compound **2** (CO ligands have been removed for clarity). The norbornene ligand has the appropriately labelled hydrogen atoms.

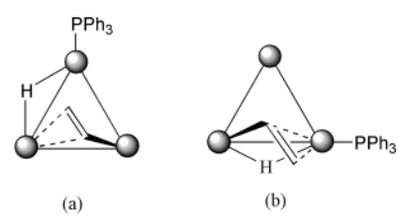


Fig. 3 Representation of the cluster–organic interaction in $[Os_3(\mu\text{-}H)(CO)_9(PPh_3)(\mu\text{-}\eta^1:\eta^2\text{-}CH{=}CH_2)]$; (a) minor isomer, (b) major isomer.

only. The mass spectrum exhibits a strong parent ion peak at *m/z* 946 (calc. 944) followed by peaks corresponding to the successive loss of several carbonyl ligands. The ^{1}H NMR spectrum is more complicated than expected and is discussed below. The molecular structure as determined by single crystal X-ray diffraction experiments on a crystal grown from a toluene solution at −25 °C is shown in Fig. 1 together with relevant structural parameters. Compound **2** consists of a triangular osmium core with a total of ten carbonyl ligands which are all essentially linear and terminal in nature. Two of the osmium atoms [Os(2) and Os(3)] carry three carbonyl moieties, two equatorially and one axially disposed, whilst the third [Os(1)], which has no bonding interactions with the norbornene ligand, has two equatorial and two axial carbonyl ligands. The organic moiety bridges the Os(2)–Os(3) edge and is bound to the cluster *via* one σ and one π interaction. The co-ordination sphere of the cluster is completed by a hydride located using XHYDEX,[18] which bridges the Os(1)–Os(3) edge. The metal bond lengths in **2** lie in the range 2.744(1)–3.116(1) Å. The Os(1)–Os(3) distance of 3.116(1) Å is significantly longer than the average metal–metal distance of 2.877 Å found in $[Os_3(CO)_{12}]$,[9] which is consistent with the observation that metal–metal bonds bridged by a hydride ligand are longer than unbridged bonds.[10]

The vast majority of compounds with analogous bonding configurations (*i.e.* $\mu\text{-}\sigma:\pi$) have a hydride moiety bridging the same edge as the olefinic ligand[11,12] and only two examples are known in which the hydride bridges a different edge. However, both these examples contain donor ligands other than CO.[13] Electron donation from the norbornene unit to the metal framework has little effect on the double bond length [C(1)–C(2) 1.37(3) Å *cf.* 1.348 Å for free norbornene[14]]. The Os–C σ bond formed by the carbon atom C(1) with the cluster [Os(2)–C(1) 2.13(2) Å] is shorter than the two π bonds formed with the second osmium atom [Os(3)–C(1) 2.30(2) and Os(3)–C(2) 2.27(2) Å]. The hydrogen atom H(2a) bound to C(2) sits over the cluster, the C(2)–H(2a) bond being directed towards Os(1) (see Fig. 2).

Studies on the related phosphorus containing compound $[Os_3(\mu\text{-}H)(CO)_9(PPh_3)(\mu\text{-}\eta^1:\eta^2\text{-}CH{=}CH_2)]$, showed an analogous olefinic bonding mode to that observed in **2**.[6] Single-crystal X-ray diffraction studies revealed the presence of two isomeric species in the solid state,[13a] the minor isomer having the structure shown in Fig. 3(a). The major isomer has the hydride bridging the same metal–metal edge as the organic moiety [see Fig. 3(b)]. This, together with two dithioformate phosphine triosmium compounds,[13b,c] are the only examples of three electron donor ligands on a triosmium cluster where the hydride does not bridge the same edge as the bridging ligand. Compound **2** is the only example which does not contain phosphine ligands as well as the three electron donor organic ligand. The ^{1}H NMR spectrum of **2** is more complex than expected for the given structure. This is thought to arise from the formation of an additional form in solution, **2a**. Thus the spectrum at room temperature exhibits twelve resonances which it is believed correspond to the two forms present, **2** and **2a**, in a ratio of approximately 4:1. From analysis of the spectrum, it is proposed that the major form corresponds to the product which has been characterised by X-ray crystallography, **2**. However, the structural identity of the minor form **2a** is less well established. Extensive NMR spectroscopy allows the full assignment of the ^{1}H and ^{13}C NMR spectra (see Experimental section). The spectra reveal an extensively fluxional system, whereby the dominant conformer (**2**) interconverts with the less populous form (**2a**) by virtue of a rapid reorientation of the norbornene ligand with respect to the osmium cluster core (see Scheme 2). The position of the signals corresponding to C(1) and C(2) in the ^{13}C NMR spectrum supports this conclusion. In conformer **2** C(2) is positioned above the Os_3 core of the cluster and has a chemical shift of δ 84, while C(1), which is orientated away from

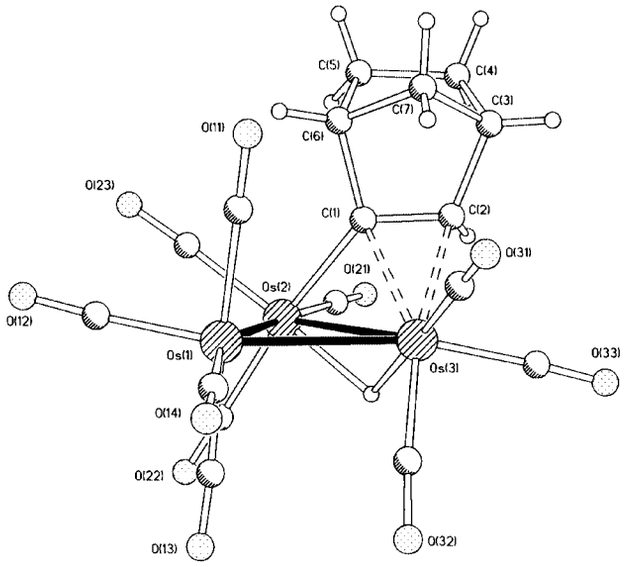
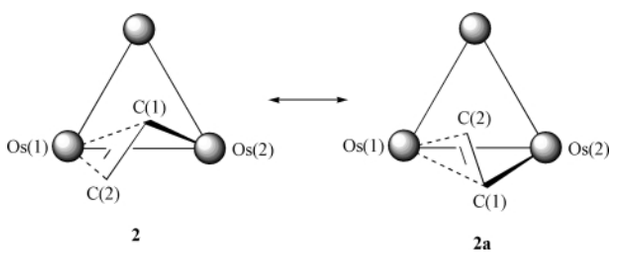


Fig. 4 The solid state molecular structure of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **3**, showing the atomic labelling scheme; the C atoms of the CO group bear the same numbering as that of the corresponding O atoms. Relevant bond lengths (Å) and angles (°) for **3** are: Os(1)–Os(2) 2.899(1), Os(1)–Os(3) 2.908(1), Os(2)–Os(3) 2.875(1), Os(2)–C(1) 2.10(1), Os(3)–C(1) 2.33(1), Os(3)–C(2) 2.40(2), C(1)–C(2) 1.36(2), C(1)–C(6) 1.57(2), C(2)–C(3) 1.53(2), C(3)–C(4) 1.55(2), C(3)–C(7) 1.55(2), C(4)–C(5) 1.55(2), C(5)–C(6) 1.57(2), C(6)–C(7) 1.56(2), mean $Os–C_{(CO)}$ 1.93(2), mean C–O 1.14(2), Os(2)–H(1) 1.85, Os(3)–H(1) 1.85 and Os(2)–H(1)–Os(3) 101.8.



Scheme 2 The fluxional process proposed for $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-CH=CH}_2)]$ in which the hydride bridges the same edge as the acetylene unit.

the metal core, is relatively deshielded (δ 151). In conformer **2a** the relative positions of C(1) and C(2) are reversed. This would lead to the expectation that the resonance corresponding to C(1) would move downfield in the ^{13}C NMR spectrum while that for C(2) would move upfield by virtue of changes to the environment of each carbon centre with respect to the triosmium core. Indeed, this is borne out by experiment (for **2a** $\delta_{C(1)}$ 129 and $\delta_{C(2)}$ 119). This change in environment is also reflected in the ^1H NMR for H(2a). In conformer **2** it is observed at δ 3.39 whereas in **2a** it is significantly deshielded at δ 6.73.

The molecular formula of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **3** was initially proposed on spectroscopic and X-ray crystallographic evidence. The structure of compound **3** as determined by single crystal X-ray diffraction experiments on a crystal grown from toluene solution at −25 °C is shown, together with relevant structural parameters, in Fig. 4. Compound **3** consists of a triangular osmium core with a total of ten essentially linear and terminal carbonyls. Two of the osmium atoms [Os(2) and Os(3)] carry three carbonyl moieties (two equatorial and one axial) whilst the third osmium atom [Os(1)], which has no bonding interaction with the norbornene ligand, is bonded to two equatorial and to two axial carbonyl ligands. The organic moiety is bonded to the cluster *via* one σ and one π interaction bridging the Os(2)–Os(3) edge. The bonding mode is completed

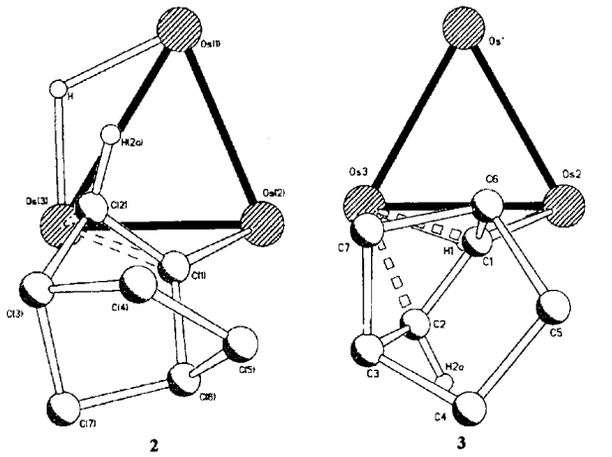


Fig. 5 The metallic and organic framework of compounds **2** and **3** (CO ligands have been removed for clarity).

by a hydride, located using XHYDEX,[18] which also bridges the Os(2)–Os(3) edge. The metal–metal bond lengths lie in the range 2.875(1)–2.908(1) Å. The edge bridged by the organic ligand and the hydride [Os(2)–Os(3)] is the shortest of the three [Os(2)–Os(3) 2.875(1) Å], whilst that between the $Os(CO)_4$ centre and the osmium atom π-co-ordinated by the organic moiety is the longest in the cluster [Os(1)–Os(3) 2.908(1) Å]. Both of these aspects are consistent with the results found in other crystallographically analysed hydrido $\mu\text{-}\eta^1:\eta^2$-allenyl clusters.[13a,15] Similarly, the edge bridged by the organic ligand in **2** [Os(2)–Os(3)] is also the shortest of the three in the cluster [Os(2)–Os(3) 2.744(1) Å], however it is considerably shorter than the corresponding distance [2.875(1) Å] in **3**. The difference in bond length is in accord with the absence of a hydride ligand bridging this edge. Again electron donation from the olefinic unit to the metal framework has little effect on the C=C double bond length [C(1)–C(2) 1.36(2) Å *cf.* 1.348 Å for free norbornene[14]]. The Os–C σ bond formed by carbon atom C(1) with the cluster [Os(2)–C(1) 2.102(14) Å] is shorter than the two π bonds formed with the second osmium atom [Os(3)–C(1) 2.327(13) and Os(3)–C(2) 2.40(2) Å]. All three of these bond lengths are very similar to those seen in **2** and the difference between the two isomers is a consequence of the positioning of the organic moiety with respect to the cluster. In **3** the ligand is positioned with the α-carbon of the olefinic unit C(1) positioned over the Os(2)–Os(3) edge, and with the β-carbon C(2) positioned away from the edge. In contrast, the olefinic unit of the norbornene ligand in **2** sits diagonally over the metal–metal edge with α-carbon C(1) in a very similar position to that in **3** but with the β-carbon C(2) positioned over the cluster. The hydrogen atom H(2a) on the β-carbon in **3** is directed away from the cluster and thus is not influenced greatly by a deshielding effect from the cluster. This explains the ^1H NMR chemical shift of δ 4.08 as compared with δ 2.76 for the analogous hydrogen centre in **2**, which is positioned over a metal–metal bond. The *exo* face of the norbornene in **3** is directed towards the π bound osmium atom Os(3) whilst the *endo* face is directed away from the triosmium core. The methylene CH_2 unit is positioned over the osmium atom Os(3) π-bonded to the ligand. In contrast the *endo* face of the ligand in **2** is oriented towards the triosmium core while the *exo* face is directed away from the cluster (see Fig. 5).

A number of clusters exhibiting a similar metal–organic interaction have been studied previously,[11,12] particularly those derivatives obtained from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with acetylene. By examining clusters of this type it has been noted that two isomers can be obtained from a σ,π-vinyl interchange process. While this was established for the parent acetylene compound $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-CH=CH}_2)]$[11,12] (see

Scheme 2), no evidence for such a process has been observed for compound **3**. This may be due to the preference of norbornene for bonding through the *exo* face. The mass spectrum of **3** exhibits a strong parent ion peak at 946 (calc. 944) followed by peaks corresponding to the successive loss of carbonyl ligands. The ^{1}H NMR spectrum in $CDCl_3$ has been assigned by comparison that of **2** (see Experimental section).

When compound **2** is left standing in solution at room temperature or is heated to reflux in dichloromethane for a short period of time it converts almost quantitatively into **3**. Heating **3** in hexane results in C–H bond activation and the formation of the di-σ,π product $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$ **4**.

The cluster $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$ **4** was originally characterised by comparison of its infrared spectrum [ν(CO)] with that $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$.[6] The molecular formula was supported by mass spectral and ^{1}H NMR evidence, and its structure confirmed by single crystal X-ray diffraction analysis. The mass spectrum of **4** contains a parent peak at *m/z* 948 (calc. 946) together with peaks corresponding to the sequential loss of several carbonyl groups. The ^{1}H NMR may be assigned in comparison with that of $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$. The bridgehead protons give rise to a signal at δ 3.16 while the aliphatic protons afford the signals at δ 1.90 and 1.21, the higher-field signal being due to the protons which point directly towards the cluster which are shielded to a greater extent. The two methylene hydrogen atoms afford signals at δ 1.48 and 0.67 with the proton directed towards the cluster again affording the higher-field chemical shift. The methylene hydrogen atoms in free norbornene exhibit a signal at δ 1.55 whereas upon co-ordination the signals appear at δ 1.48 and 0.67; this shift clearly indicates the shielding effect of the osmium cluster and suggests the presence of an agostic interaction. The two hydride atoms give rise to two broad signals at δ −18.0 and −22.0; these two distinct signals indicate that the hydrides are not fluxional at this temperature, in contrast to the compound $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$ in which the two hydrides give rise to only one signal only.[6]

The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$ **4** as determined by single crystal X-ray diffraction on a crystal grown from toluene solution at −25 °C is shown in Fig. 6 together with relevant structural parameters. The asymmetric unit contains two independent molecules. The metal cluster framework consists of a triangular core with Os–Os bond lengths ranging from 2.776(2) to 3.036(1) Å and from 2.773(1) to 3.089(1) Å. Two of the edges of the triangle are bridged by hydrides, and these are, accordingly, longer than the unbridged edge [Os(1)–Os(2) 3.036(1), Os(2)–Os(3) 2.932(2), Os(4)–Os(5) 3.089(1), Os(4)–Os(6) 2.888(1) Å *vs.* Os(1)–Os(3) 2.776(2), Os(5)–Os(6) 2.773(1) Å]. Space filling diagrams of the two hydrides are shown in Fig. 7. The organic moiety straddles one face of the cluster and each osmium atom has two equatorial and one axial carbonyl ligand, all of which are terminal and essentially linear.

The norbornene ligand is positioned over the face of the cluster with the alkene bond aligned parallel to the plane of the osmium triangle and in line with the Os(1)–Os(2), Os(4)–Os(5) edges. The moiety bonds to all three metal atoms and donates a total of four electrons *via* two σ and one π interaction in a typical alkyne fashion.[14] The two Os–C σ bonds formed by the carbon atoms C(2n), C(1n) and (C8n), C(9n) with the cluster [Os(1)–C(1n) 2.10(2), Os(2)–C(2n) 2.11(2) and Os(4)–C(9n) 2.08(2), Os(5)–C(8n) 2.10(2) Å] are shorter than the two π bonds formed with the third osmium atom [Os(3)–C(1n) 2.24(2), Os(3)–C(2n) 2.37(2) Å and Os(6)–C(8n) 2.32(2), Os(6)–C(9n) 2.28(2) Å]. Compound $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$ **4** is analogous to the ruthenium compound and may therefore be considered a cluster analogue of norbornene bound to a Pt(111) surface.

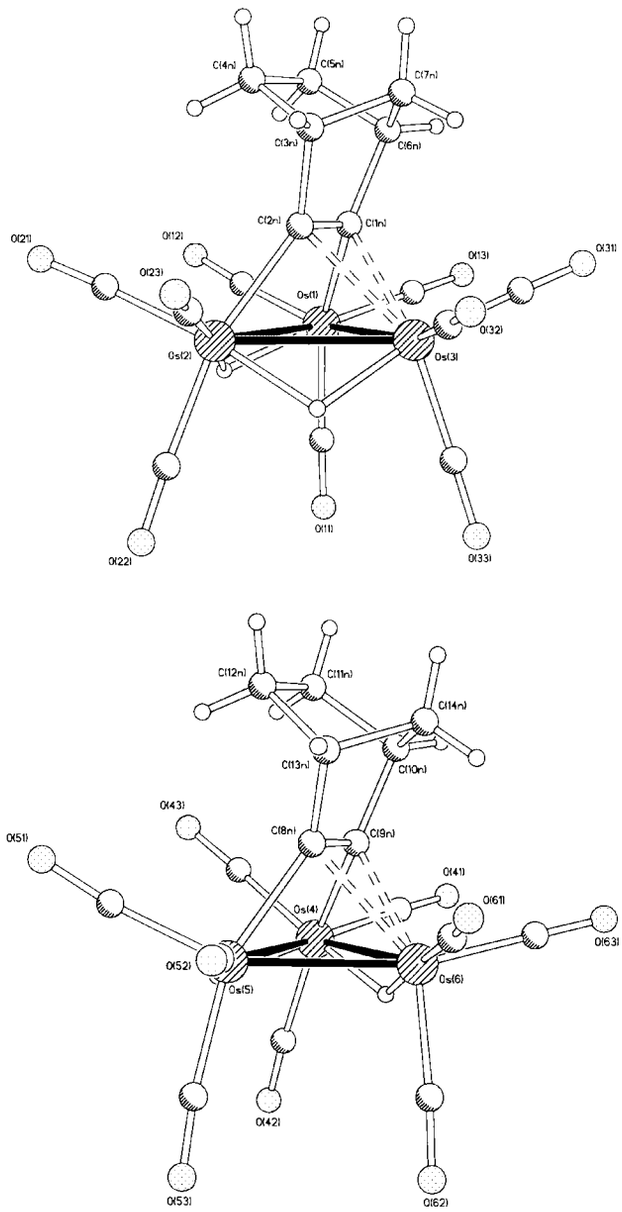


Fig. 6 The solid-state molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}\eta^1\!:\eta^2\!:\eta^1\text{-}C_7H_8)]$ **4**, showing both molecules of the asymmetric unit; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths (Å) and angles (°) for **4** are: Os(1)–Os(2) 3.036(1), Os(1)–Os(3) 2.776(2), Os(2)–Os(3) 2.932(2), Os(1)–C(1n) 2.10(2), Os(2)–C(2n) 2.11(2), Os(3)–C(1n) 2.24(2), Os(3)–C(2n) 2.37(2), C(1n)–C(2n) 1.30(3), C(1n)–C(6n) 1.57(3), C(2n)–C(3n) 1.55(3), C(3n)–C(4n) 1.46(3), C(3n)–C(7n) 1.50(3), C(4n)–C(5n) 1.62(4), C(5n)–C(6n) 1.50(3), C(6n)–C(7n) 1.50(3), mean Os–$C_{(CO)}$ 1.92 and mean C–O 1.14; Os(4)–Os(5) 3.089(1), Os(4)–Os(6) 2.888(1), Os(5)–Os(6) 2.773(1), Os(4)–C(9n) 2.08(2), Os(5)–C(8n) 2.10(2), Os(6)–C(8n) 2.32(2), Os(6)–C(9n) 2.28(2), C(8n)–C(9n) 1.44(2), C(8n)–C(13n) 1.48(3), C(9n)–C(10n) 1.55(2), C(10n)–C(11n) 1.57(3), C(10n)–C(14n) 1.56(2), C(11n)–C(12n) 1.55(3), C(12n)–C(13) 1.57(3), C(13n)–C(14n) 1.58(3), mean Os–$C_{(CO)}$ 1.92, mean C–O 1.15, Os(1)–H(1) 1.85, Os(2)–H(1) 1.87, Os(1)–H(1)–Os(2) 109.6, Os(2)–H(2) 1.86, Os(3)–H(2) 1.87, Os(2)–H(2)–Os(3) 103.8, Os(4)–H(3) 1.87, Os(5)–H(3) 1.85, Os(4)–H(3)–Os(5) 112.4, Os(4)–H(4) 1.84, Os(6)–H(4) 1.36 and Os(4)–H(4)–Os(6) 128.8.

Concluding remarks

This work has expanded our knowledge of the interactions of norbornene with transition metal carbonyl clusters. C–H bond activation and dehydrogenation occurs upon co-ordination, giving a stepwise route to the osmium di-σ, π species which may be used as models of the chemisorption and reactivity on metal surfaces and which provides a further cluster

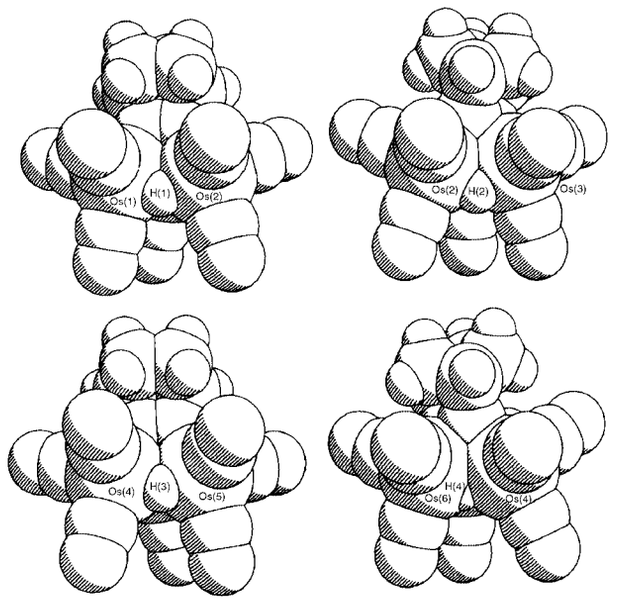


Fig. 7 Space filling diagrams showing the hydrides bridging the four osmium edges, Os(1)–Os(2), Os(2)–Os(3) and Os(4)–Os(5), Os(4)–Os(6), for compound **4**.

compound that can be viewed as an analogue of the norbornene ligand adsorbed onto a metal surface. A third isomer in the σ, π-flipping process has been observed wherein the π bond of the organic moiety no longer interacts with the cluster core.

Experimental

$[Os_3(CO)_{12}]$ was purchased from Oxkem. Trimethylamine *N*-oxide (Me_3NO), purchased from Aldrich Chemicals as the dihydrate, was dried initially by a Dean and Stark distillation in benzene followed by sublimation prior to reaction. All other chemicals were used as supplied without further purification. The reaction mixtures obtained were separated chromatographically on silica. Thin layer chromatography was carried out using glass plates (20 × 20 cm) supplied by Merck, coated with a 0.25 cm layer of silica gel 60 F_{254}. Infrared spectra were measured in dichloromethane (unless otherwise stated) in NaCl cells (0.5 mm path length) supplied by Specac Ltd on a Perkin-Elmer 1600 series Fourier Transform instrument, calibrated with carbon dioxide. Fast atom bombardment mass spectra were obtained on a Kratos MS890 spectrometer run in positive mode, using CsI as calibrant. Samples were dissolved in the minimum amount of acetone prior to addition of the matrix liquid. ^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker AC-250 and AM-400 Fourier transform instruments at 25 °C. An internal deuterium lock was used for all the accumulations. Crystallographic measurements were made on a RIGAKU AFC7R diffractometer equipped with a graphite-monochromator (Mo-Kα radiation, $\lambda = 0.71073$). An Oxford Cryosystems device was used for data collection at low temperature.[16] All calculations were performed using the program SHELXL 93[17] and the figures produced using SHELXTL PC.[18] When metal hydride ligands could not be located by direct experiment they were positioned using the program XHYDEX.[8]

Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ 1 with norbornene

The compound $[Os_3(CO)_{10}(NCMe)_2]$ **1** (300 mg) was dissolved in dichloromethane (50 ml) and norbornene (3 ml) and heated to reflux (39–40 °C) for four hours. IR spectroscopy indicated complete consumption of starting material. The solvent was removed *in vacuo* and two main bands were isolated by TLC, eluting with dichloromethane–hexane (1 : 4 v/v), and characterised as $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **2** (yellow, 32%) and $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **3** (yellow, 26%).

Spectroscopic data for compound 2. IR (hexane): ν(CO)/cm^{-1} 2116w, 2100w, 2069m, 2032s, 2018m sh, 1993m and 1952w. ^{1}H NMR ($CDCl_3$): (major conformer) **2**, δ 3.39 (s, 1 H, H2a), 3.38 (sh, 1 H, H6a), 2.76 (s, 1 H, H3a), 1.76 (m, 1 H, H5a/H5b), 1.62 (m, 1 H, H4a/H4b), 1.26 (m, 1 H, H4a/H4b), 1.17 (m, 1 H, H5a/H5b), 0.93 (d, 1 H, H7a/H7b), 0.76 (d, 1 H, H7a/H7b) and −18.51 (s, 1 H, H); (minor conformer) **2a**, δ 6.73(s, 1 H, H2a), 2.96 (s, 1 H, H6a), 2.69 (s, 1 H, H3a), 1.84 (m, 1 H, H5a/H5b), 1.62 (masked by **2**, H4a/H4b), 1.26 (masked by **2**, H4a/H4b), 1.17 (masked by **2**, H5a/H5b), 1.07 (br, s, 1 H, H7a/H7b), 0.93 (masked by **2**, H7a/H7b) and −16.5(s, 1 H). ^{13}C NMR ($CDCl_3$): (major conformer) **2**, δ 151.3 (C1), 84.1 (C2), 62.8 (C6), 42.2 (C3), 41.9 (C7), 26.1 (C4) and 25.5 (C5); (minor conformer) **2a**, δ 129.8 (C1), 119.5 (C2), 62.8 (C6), 43.0 (C7), 41.0 (C3), 25.0 (C4) and 23.2 (C4). Positive FAB mass spectrum: M^+ at *m*/*z* 946 (calc. 944).

Crystal data and measurement details for compound 2. Formula $C_{17}H_{10}O_{10}Os_3$, $M = 944.85$, $T = 293(2)$ K, orthorhombic, space group *Pbca*, $a = 15.458(4)$, $b = 18.686(5)$, $c = 14.223$ Å, $V = 4108(2)$ Å^3, $Z = 8$, μ(Mo-Kα) = 18.563 mm^{-1}, yellow column, 5273 unique data collected, 2703 reflections with $F \geq 4\sigma(F)$ used in all calculations, $R = 0.0681$, $R' = 0.1969$, for 136 parameters.

Spectroscopic data for compound 3. IR (CH_2Cl_2). ν(CO)/cm^{-1} 2099w, 2074m, 2066s, 2056m, 2024s and 2013s; ^{1}H NMR ($CDCl_3$): δ 4.08 (s, 1 H, H2a), 3.49 (s, 1 H, H6a), 2.71 (s, 1 H), 1.93 (m, 1 H, H5a/H5b), 1.71 (m, 1 H, H4a/H4b), 1.18 (m, 1 H, H4a/H4b), 1.13 (m, 1 H, H5a/H5b), 1.06 (d, 1 H, H7a/H7b) 0.55 (d, 1 H, H7a/H7b) and −18.78 (s, 1 H, H1). Positive FAB mass spectrum: M^+ at *m*/*z* 946 (calc. 944).

Crystal data and measurement details for compound 3. Formula $C_{17}H_{10}O_{10}Os_3$, $M = 944.85$, $T = 293(2)$ K, triclinic, space group $P\bar{1}$, $a = 9.696(2)$, $b = 13.847(3)$, $c = 8.991(2)$ Å, $\alpha = 93.48(3)$, $\beta = 117.55(3)$, $\gamma = 80.14(3)°$, $V = 1054.2(4)$ Å^3, $Z = 2$, μ(Mo-Kα) = 18.085 mm^{-1}, yellow block, 5115 unique data collected, 3966 reflections with $F \geq 4\sigma(F)$ used in all calculations, $R = 0.0424$, $R' = 0.2047$, for 271 parameters.

Conversion of compound 2 into 3

A suspension of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **2** (5 mg) in hexane (20 ml) was heated to reflux for 3 hours. During this time the reaction was monitored by IR spectroscopy indicating the production of **3** in quantitative yield.

Reaction of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ 3

The compound $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}\eta^1:\eta^2\text{-}C_7H_9)]$ **3** (20 mg) dissolved in hexane (50 ml) and was heated to reflux for 6 hours. During this time the reaction was monitored by IR spectroscopy, indicating the complete consumption of starting material. The solvent was removed *in vacuo* and one main band was isolated by TLC, eluting with dichloromethane–hexane (1 : 4, v/v), and characterised as $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_7H_8)]$ **4**.

Spectroscopic data for compound 4. IR (CH_2Cl_2): ν(CO)/cm^{-1} 2106w, 2076s, 2050m and 2025s. ^{1}H NMR ($CDCl_3$): δ 3.16 (s, 2 H), 1.90 (m, 2 H), 1.48 (d, 1 H), 1.21 (m, 2 H), 0.67 (d, 1 H), −18.0 (br, s, 1 H) and −22.0 (br, s, 1 H). Positive FAB mass spectrum: M^+ at *m*/*z* 948 (calc. 946).

Crystal data and measurement details for compound 4. Formula $C_{16}H_{10}O_9Os_3$, $M = 916.84$, $T = 293(2)$ K, triclinic,

space group $P\bar{1}$, $a = 14.499(5)$, $b = 16.061(5)$, $c = 10.192(3)$ Å, $\alpha = 104.51$, $\beta = 93.90(3)$, $\gamma = 116.48(3)°$, $V = 2011.9(11)$ Å^3, $Z = 4$, μ(Mo-Kα) = 18.944 mm^{-1}, 7383 unique data collected, 7062 reflections with $F \geq 4\sigma(F)$ used in all calculations, $R = 0.0465$, $R' = 0.2091$, 506 parameters.

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