Synthesis and Molecular Structure of the Novel Triosmium Bis(benzene) Cluster $[Os_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

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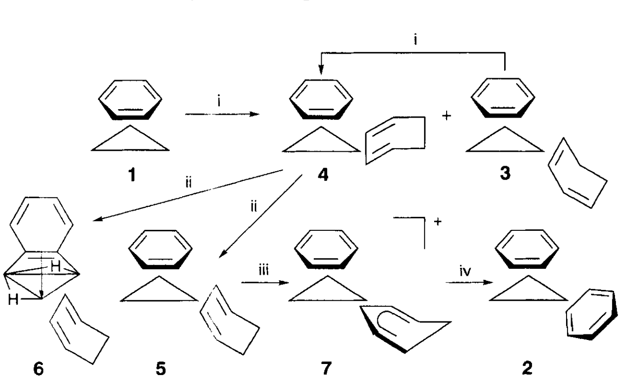
The novel bis(benzene) complex $[Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ is prepared and characterised by single-crystal X-ray analysis; the cluster exhibits two distinct coordination modes of benzene, one terminally bound in an η^6 manner, the other in a μ_3 face-capping coordination mode.

Over recent years a rich and diverse chemistry of carbocyclic cluster compounds has emerged[1] and systematic synthetic routes to a variety of benzene[2] and benzyne[3] cluster derivatives have been developed. Significantly, these compounds may be derived from benzene,[4] cyclohexa-1,3-diene[5] and cyclohexene.[6] A dominating feature of this chemistry is the ability of both ruthenium and osmium carbonyl clusters, containing from three to eight metal atoms, to both hydrogenate and dehydrogenate carbocyclic ring systems. In addition to this dehydrogenation we have observed the ring contraction of coordinated cyclohexene to form cyclopentadienyl complexes.[7] Furthermore, this reactivity is not restricted to six-membered ring systems, as similar chemistry is observed for related eight-membered cyclic compounds such as cyclooctene, cyclooctadiene, cyclooctatriene and cyclooctatetraene.[8] Using this methodology of C–H activation and subsequent dehydrogenation of a coordinated carbocyclic ligand, the prototypical benzene cluster $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **1** was first prepared in 1985 from cyclohexa-1,3-diene.[9] Compounds such as **1** are of special interest due to their potential as model compounds for the chemisorption of benzene on to metal surfaces.[10] In the formation of **1** initial dehydrogenation of cyclohexa-1,3-diene by the 'hydrogen-rich' cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ occurs to produce the dienyl derivative $[Os_3(\mu\text{-}H)(CO)_9(\mu_3:\eta^2:\eta^2:\eta^1\text{-}C_6H_7)]$, which may then be converted to the desired product **1** by hydride abstraction and deprotonation.

We now report that the novel bis(benzene) complex $[Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ **2** may be synthesised in a systematic stepwise manner from $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **1** (Scheme 1). Treatment of **1** with excess trimethylamine-*N*-oxide in the presence of cyclohexa-1,3-diene affords a mixture of two benzene–diene complexes $[Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_6H_8)]$ **3** and $[Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **4**. In compound **3** the cyclohexadiene replaces one carbonyl group and is coordinated to the cluster core as a monoene. In compound **4** elimination of two carbonyl ligands generates two vacant sites to which the cyclohexadiene ligates in an equatorial–equatorial fashion. On heating compound **4** two major products are observed in approximately equal quantities. The first, $[Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **5** is an isomeric form of compound **4**, in which a rearrangement has taken place and the diene moiety now occupies one axial and one equatorial site. The second product results from a double C–H activation of the face-capping benzene to produce the benzyne–diene complex $[Os_3H_2(CO)_7(\mu_3:\eta^2:\eta^1:\eta^1\text{-}C_6H_4)(\eta^4\text{-}C_6H_8)]$ **6**. Treatment of $[Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ **5** with trityl tetrafluoroborate results in hydride abstraction from the coordinated diene to yield the cationic benzene–dienyl cluster $[Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]^+$ **7**. Deprotonation of the latter compound **7** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) affords the bis(benzene) cluster $[Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$ **2** in moderate yield. Products **2**–**6** have been fully characterised by IR, NMR and mass spectrometry,‡ in addition **2**,† **4** and **6** have also been characterised by X-ray structural analyses, the results of these studies will be reported in depth elsewhere. In the ^1H NMR spectrum of **2** two singlet resonances are observed at δ 5.42 and 3.97 indicating that in solution the two benzene ligands adopt differing coordination modes, one being terminally bound to a single osmium atom, the other triply capping the triosmium face.

In the solid state the molecular structure of **2** consists of a regular triangular arrangement of osmium atoms with metal–metal bond lengths of 2.806(1), 2.841(1) and 2.843(1) Å (Fig. 1). To this metal framework there are two benzene ligands coordinated, one in a η^6 manner, the other in the so-called *face-capping* $\mu_3:\eta^2:\eta^2:\eta^2$ fashion. In the former instance where the arene is *terminally* coordinated, the C_6 ring makes interactions of lengths 2.19(2)–2.25(2) Å [mean Os(3)– C_{terminal} 2.22 Å]. In contrast a wider variation in Os–C bond lengths is observed for the facially coordinated ligand, where the range of distances is 2.14(2)–2.36(2) Å (mean Os–C_{facial} 2.28 Å). However it is noteworthy that the facially bound benzene forms significantly shorter interactions with Os(3) [mean Os(3)–C_{facial} 2.18 Å], than it does to the remaining two osmium atoms [mean Os(1,2)–C_{facial} 2.33 Å]. It seems likely that this asymmetry in the coordination of the facial arene is due to the π-acceptor capability of the remaining ligands to which the metal atoms coordinate. Both Os(1) and Os(2) have three terminally coordinated carbonyl ligands bound, whereas Os(3) is coordinated to the terminal benzene ligand. The latter ligand has a



Scheme 1 *Reagents and conditions*: i, Me_3NO, excess cyclohexa-1,3-diene; ii, heat; iii, $[Ph_3C]^+[BF_4]^-$; iv, DBU

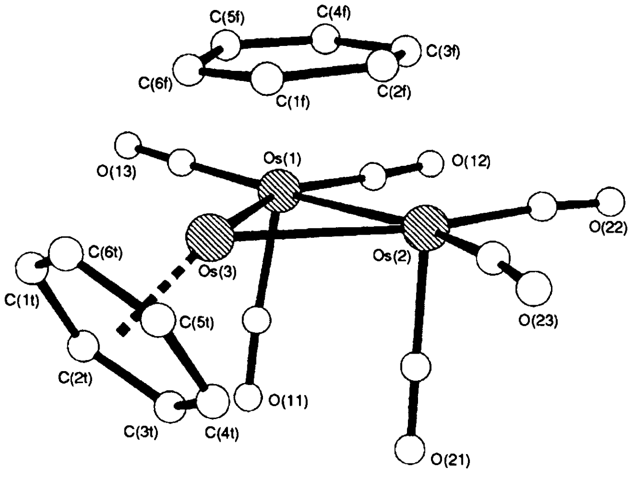


Fig. 1 Diagram depicting the molecular structure of **2**; relevant bond parameters are discussed in the text

greatly reduced π-acceptor capability as compared with that of the carbonyl groups and as a result there is more residual electron density available on Os(3) for back donation into the π* orbitals of the facially coordinated arene. Hence the average metal–C_{arene} distance of Os(3) (2.21 Å) is significantly shorter than that of Os(1) and Os(2) (2.33 Å).

The facially coordinated benzene is essentially planar (rms deviation from planarity = 0.028 Å), with the centroid of the ring lying 2.13 Å above the Os_3 plane and exhibiting an interplanar angle of 3.4°. In comparison the centroid of the terminally coordinated benzene is 1.72 Å from Os(3) and again the ring is essentially planar (rms deviation from planarity = 0.009 Å), making an angle of 55.8° to the plane in which the metal atoms lie. The relatively high esds associated with the C–C distances within the facially coordinated arene preclude an accurate assessment of the bonding within the ring. It is of some note that the mean coordinated and uncoordinated C–C bond lengths are 1.40 and 1.45 Å respectively, suggesting the possibility of a weak Kekulé-type distortion of the benzene ligand. However the range of C–C bond lengths within the terminally coordinated benzene [1.38(3)–1.49(3) Å] is greater than is observed for the facially bound ligand [1.30(3)–1.44(4) Å], demonstrating the difficulties associated with any comparison of C–C distances in the presence of metal clusters. The facially coordinated benzene is oriented in a manner similar to that observed for the three triosmium clusters which have been structurally characterised to date[9,11] {*i.e.* $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, $[Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and $[Os_3(CO)_8(PPh_3)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$}.

In the crystalline state, molecules of **2** pack in such a way that the terminal benzene ligand of one cluster lies above the facially bound arene of the adjacent molecule (Fig. 2). The ligands lie staggered with respect to each other, with an angle of 2.9° between the C_6 planes and the centroids of the rings are separated by 3.39 Å. This graphitic type interaction is extended in such a fashion that long 'snake-like' chains are formed, with adjacent layers of the chains separated by a thin layer of toluene molecules present as a solvate.

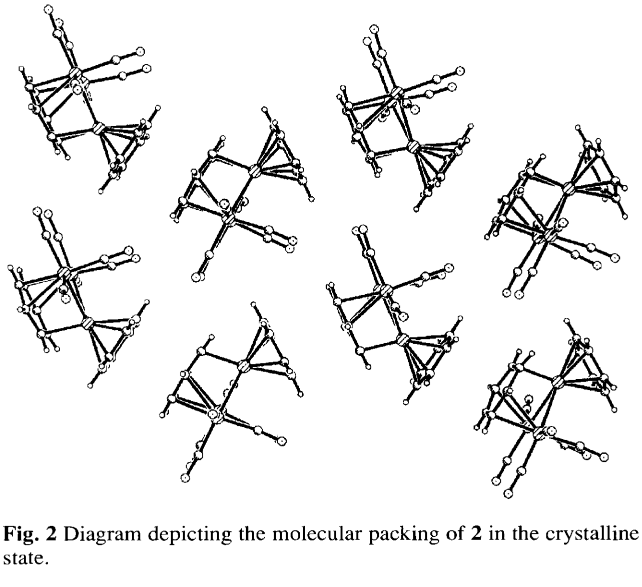


Fig. 2 Diagram depicting the molecular packing of **2** in the crystalline state.

A key feature of this work is the observation that on coordination to the central Os_3 core *either* C_6H_6 *or* C_6H_8 may undergo C–H bond cleavage according to the method of activation employed. In conclusion we have shown that the mono(benzene) cluster $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ may be smoothly converted to the bis(benzene) cluster $[Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)]$, the latter compound possessing an unusual geometry with one benzene terminally bound and the other triply bridging the cluster framework.

We wish to thank the EPSRC, The University of Edinburgh, The Royal Society and British Petroleum (J. G. M. N.) for financial support.

Received, 28th October 1994; Com. 4/06599I

Footnotes

† *Crystal data for* **2**: $C_{18}H_{12}O_6Os_3{\cdot}C_7H_8$, M = 987.01, orthorhombic, space group $P2_12_12_1$, a = 8.898(3), b = 14.409(5), c = 18.443(4) Å, U = 2364.7(13) Å^3, Z = 4, D_c = 2.772 g cm^{-3}, T = 200 K, $F(000)$ = 1784, R_1 = 0.0408 [1959 reflections with $F_o > 4\sigma(F_o)$], wR_2 = 0.0878 for 2363 independent reflections corrected for absorption [μ(Mo-Kα) = 16.119 mm^{-1}] and 153 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Spectroscopic data*: **3**, IR (CH_2Cl_2) ν(CO)/cm^{-1} 2063s, 2025vs, 1999s, 1984sh, 1957sh, FAB MS, *m/z* 952 (calc. 953, M^+); **4**, IR (CH_2Cl_2) ν(CO)/cm^{-1} 2057s, 2016vs, 1985s, 1973sh, 1944sh, FAB MS, *m/z* 927 (calc. 925, M^+); **5**, IR (CH_2Cl_2) ν(CO)/cm^{-1} 2048s, 2000vs, 1986s, 1958sh, 1938sh, FAB MS, *m/z* 927 (calc. 925, M^+); **6**, IR (CH_2Cl_2) ν(CO)/cm^{-1} 2092m, 2072vs, 2011vs br; FAB MS: *m/z* 926 (calc. 925, M^+); **2**, IR (CH_2Cl_2) ν(CO)/cm^{-1} 2038s, 2002vs, 1962sh, 1951sh, 1039sh; FAB MS, *m/z* 896 (calc. 895, M^+); ^{1}H NMR ($CDCl_3$) δ 5.42(s), 3.97(s).

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