Cluster Build-up using the $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ Cation; Synthesis and Structural Characterisation of Some Hexa- and Hepta-nuclear Arene-substituted Clusters†

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Reactions of the cluster dianion $[Os_5(CO)_{15}]^{2-}$ with $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ and $[Os(C_6H_5Me)(CF_3SO_3)_2]$ provided $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)]$ **1** and $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ **2**, respectively, in good yield ($\approx$45%). Reduction of the hexaosmium cluster $[Os_6(CO)_{18}]$ with K–Ph_2CO gave the cluster dianion $[Os_6(CO)_{17}]^{2-}$ **3** in quantitative yield. When this dianion was treated with $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ the heptanuclear cluster $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)]$ **4** was obtained in fair yield, while the corresponding reaction with $[Os(\eta^6\text{-}C_6H_5Me)(CF_3SO_3)_2]$ gave $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)]$ **5** in similar yield (*ca.* 25%). The four arene clusters have been characterised by spectroscopic techniques, and the molecular geometries of **1**, **2** and **4** established by single-crystal X-ray diffraction techniques. In both **1** and **2** the metal framework geometry is best described as a bicapped tetrahedron. In **1** the $\eta^6\text{-}C_6H_6$ ligand occupies a site on the central Os_4 tetrahedron while in **2** in the η^6-arene is co-ordinated to one of the capping Os atoms. The metal framework in **4** may be viewed as derived from a bicapped tetrahedron with the seventh metal capping one of the caps to give a chain of four fused tetrahedra. The $\eta^6\text{-}C_6H_6$ ligand in **4** occupies a similar site to that found in **1**.

The recent characterisation of transition-metal clusters containing $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-arene ligands, in which the arene caps a triangular face of the cluster, has led to an increase in interest in the area of cluster arene complexes[1] because of the use of these molecular species as potential models for the way that arenes co-ordinate to metal surfaces.[2] Over the last five years an extensive range of arene-substituted clusters of the cobalt[3] and iron[4] subgroups have been isolated, and the arene groups have been found to co-ordinate in either the terminal η^6 mode or in the face-capping $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ mode. For the clusters of the iron subgroup two main methods of synthesis have been developed. The first involves the addition of cyclohexa-1,3-diene to a weakly ligated cluster complex, such as $[Os_3(CO)_{10}(MeCN)_2]$, and its conversion into benzene *via* a cyclohexadienyl ligand.[5] The second method involves the addition of an $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ cation to a cluster anion.[5] Recent work within our group has focused on the synthesis and characterisation of higher-nuclearity arene-containing ruthenium and osmium carbonyl clusters.[6–14] The chemistry of arene-containing hexaruthenium carbido clusters $[Ru_6C(CO)_{14}(arene)]$[15] and $[Ru_6C(CO)_{11}(arene)_2]$[11] is well documented, and two different structural forms have been observed in the bis(arene) cluster. However, the synthesis of the analogous arenehexaosmium carbido clusters has not been attempted because of the low availability of the starting material, the pentaosmium carbido cluster.

Previously, using the dication $[Os(C_6H_6)(MeCN)_3]^{2+}$ as the arene-containing fragment, we have reported the synthesis and molecular structures of $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$[12] and $[Os_6H_2(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.[13] In the latter case the two benzene ligands adopt two different bonding modes as in $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.[11a] As part of our continuing effort in the studies of arene interaction with metal clusters, we report here the synthesis of the complexes $[Os_6(CO)_{15}(arene)]$ and $[Os_7(CO)_{17}(arene)]$ based on the reaction between a cationic 'Os(arene)' fragment and the dianions $[Os_5(CO)_{15}]^{2-}$ and $[Os_6(CO)_{17}]^{2-}$. Two structural forms have been found for the $[Os_6(CO)_{15}(arene)]$ complexes.

Results and Discussion

Our recent work shows that the dication $[Os(C_6H_6)(MeCN)_3]^{2+}$ can be employed in the synthesis of benzene-containing clusters. The pentaosmium cluster dianion $[Os_5(CO)_{15}]^{2-}$ was allowed to react with $[Os(C_6H_6)(MeCN)_3][BF_4]_2$ in dichloromethane at room temperature for 1 h. A neutral cluster $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)]$ **1** was obtained in *ca.* 45% yield after chromatographic separation on silica. It was first characterised by IR, ^1H NMR and mass spectroscopy (Table 1). A singlet at δ 6.03 is consistent with the presence of a η^6 terminally bonded benzene fragment. This chemical shift is comparable to the values observed for $[Os_5H_4(CO)_{11}(\eta^6\text{-}C_6H_6)]$ (δ 6.08) and $[Os_5H_4(CO)_{12}(\eta^6\text{-}C_6H_6)]$ (δ 6.05).[12] The ^1H NMR spectrum of **1** shows no change in the chemical shift of the co-ordinated benzene in the temperature range 215–320 K and there appears to be no evidence for benzene migration over the cluster surface on the NMR time-scale.

In order to study the electronic and steric factors which affect the bonding mode of the arene fragment in the clusters, the toluene-containing complex $[Os(C_6H_5Me)(CF_3SO_3)_2]$ has also been synthesised. Reaction of $[Os_5(CO)_{15}]^{2-}$ with $[Os(C_6H_5Me)(CF_3SO_3)_2]$ in dichloromethane gives $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ **2** in *ca.* 35% yield and trace amounts of $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)]$ **5** (*ca.* 5%) have been isolated. The ^1H NMR data for **2** show a multiplet at δ 5.8–6.5 which is diagnostic for η^6 co-ordination of the toluene ligand. However, the presence of two singlets at δ 2.66 and 2.53 for the methyl protons indicates that two isomers are present in solution. Variable-temperature NMR studies do not show

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Spectroscopic data for $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)]$ **1**, $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ **2**, the cluster dianion $[Os_6(CO)_{17}]^{2-}$ **3**, $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)]$ **4** and $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)]$ **5**

Compound	IR,[a] $\tilde{\nu}(CO)/cm^{-1}$	^1H NMR (δ)[b]	Mass spectrum, m/z[c]
1	2087w, 1956m, 1923s, 1885w	6.03 (s, 6 H)	1641 (1639)
2	2085w, 2054m, 2022s, 1983w	6.50–5.80 (m) 2.66 (s), 2.53 (s)	1654 (1653)
3	[d]2057w, 2019s, 1987s, 1951w, 1942w		
4	2088w, 2060vs, 2047s, 2024s, 1998w	6.08 (s, 6 H)	1886 (1885)
5	2087w, 2060vs, 2046s, 2024s, 1999w	6.30–5.80 (m, 5 H), 2.58 (s, 3 H)	1900 (1899)

[a] Spectra taken in CH_2Cl_2. [b] Spectra taken in $CDCl_3$. [c] Calculated values in parentheses. [d] Spectra taken in thf.

evidence of any change in the isomeric ratio of 1.7 : 1.0 over the temperature range 215–320 K. This suggests the presence of two non-interconverting isomeric forms. A similar type of isomerisation has also been suggested for the complex $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$.[14]

The hexanuclear cluster $[Os_6(CO)_{18}]$ was treated with an excess of potassium–benzophenone in tetrahydrofuran (thf) at −78 °C to give an air-sensitive dianionic cluster $[Os_6(CO)_{17}]^{2-}$ **3** which was not isolated but characterised by IR spectroscopy (Table 1). Treatment of **3** with an excess of the compounds $[Os(C_6H_6)(MeCN)_3][BF_4]_2$ and $[Os(C_6H_5Me)(CF_3SO_3)_2]$, in dichloromethane, gives $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)]$ **4** and $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)]$ **5**, respectively, in *ca.* 25% yield. The clusters can also be obtained in very low yield (< 5%) by treating $[Os_7(CO)_{21}]$ with 3.2 equivalents of Me_3NO in the presence of C_6H_7R (R = H **4** or Me **5**). Clusters **4** and **5** were characterised by IR, ^1H NMR and mass spectroscopy (Table 1). The ^1H NMR spectrum of **4** is very similar to that of **1**. A strong singlet at δ 6.08 implies the presence of a terminally η^6-co-ordinated benzene. For **5** a multiplet at δ 5.8–6.3 (5 H) and a singlet at δ 2.58 (3 H) also suggests a terminally bonded toluene ligand, and in this instance is consistent with the presence of only one isomer. The ^1H NMR spectra of **4** and **5** show no change in the chemical shift of the arene in the temperature range 215–320 K and there appears to be no evidence for arene migration or isomerisation over the cluster surface on the NMR time-scale.

Single crystals suitable for X-ray analysis were obtained for the clusters $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5R)]$ (R = H **1** or Me **2**). The molecular structure of **1** is shown in Fig. 1, while that of **2** is shown in Fig. 2. Selected bond parameters for the two molecules are presented in Tables 2 and 3, respectively. It is assumed that crystallisation of the thermodynamically preferred geometry occurred in both systems. In both **1** and **2** the metal framework is best described as a bicapped tetrahedron. Within this type of framework there are three different metal environments. The capping metals form three metal–metal contacts and have a formal electron count of 17e⁻, and the two different metal environments within the central tetrahedron have four and five metal–metal contacts, respectively, and are associated with formal electron counts of 18 and 19e⁻. The arenemetal fragment adopts the capping position (metal–metal connectivity of three) in the toluene derivative **2** but a tetrahedral position (metal–metal connectivity of four) in the benzene derivative **1**. The bicapped-tetrahedral geometry has been observed in the parent osmium binary cluster $[Os_6(CO)_{18}]$[16] and in a number of its derivatives.[17] A similar structure has also been observed for the mixed-metal cluster $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$[14] in which the benzene fragment is η^6 co-ordinated to the ruthenium atom in the capping position as in **2**.

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Os(1)–Os(2)	2.720(3)	Os(1)–Os(3)	2.810(3)
Os(1)–Os(4)	2.821(2)	Os(2)–Os(3)	2.788(3)
Os(2)–Os(4)	2.803(3)	Os(2)–Os(5)	2.706(2)
Os(3)–Os(4)	2.759(2)	Os(3)–Os(5)	2.767(2)
Os(3)–Os(6)	2.797(2)	Os(4)–Os(5)	2.757(3)
Os(4)–Os(6)	2.823(3)	Os(5)–Os(6)	2.802(3)
Os(2)–C(1)	2.26(3)	Os(2)–C(2)	2.22(3)
Os(2)–C(3)	2.19(3)	Os(2)–C(4)	2.19(3)
Os(2)–C(5)	2.23(3)	Os(2)–C(6)	2.26(3)
Os(2)–Os(1)–Os(3)	60.5(1)	Os(2)–Os(1)–Os(4)	60.7(1)
Os(3)–Os(1)–Os(4)	58.7(1)	Os(1)–Os(2)–Os(3)	61.3(1)
Os(1)–Os(2)–Os(4)	61.4(1)	Os(3)–Os(2)–Os(4)	59.1(1)
Os(1)–Os(2)–Os(5)	111.8(1)	Os(3)–Os(2)–Os(5)	60.5(1)
Os(4)–Os(2)–Os(5)	60.0(1)	Os(1)–Os(3)–Os(2)	58.1(1)
Os(1)–Os(3)–Os(4)	60.9(1)	Os(2)–Os(3)–Os(4)	60.7(1)
Os(1)–Os(3)–Os(5)	107.3(1)	Os(2)–Os(3)–Os(5)	58.3(1)
Os(4)–Os(3)–Os(5)	59.8(1)	Os(1)–Os(3)–Os(6)	116.1(1)
Os(2)–Os(3)–Os(6)	109.8(1)	Os(4)–Os(3)–Os(6)	61.1(1)
Os(5)–Os(3)–Os(6)	60.5(1)	Os(1)–Os(4)–Os(2)	57.8(1)
Os(1)–Os(4)–Os(3)	60.5(1)	Os(2)–Os(4)–Os(3)	60.2(1)
Os(1)–Os(4)–Os(5)	107.3(1)	Os(2)–Os(4)–Os(5)	58.2(1)
Os(3)–Os(4)–Os(5)	58.2(1)	Os(3)–Os(4)–Os(5)	60.2(1)
Os(1)–Os(4)–Os(6)	115.4(1)	Os(2)–Os(4)–Os(6)	108.6(1)
Os(3)–Os(4)–Os(6)	60.1(1)	Os(5)–Os(4)–Os(6)	60.3(1)
Os(2)–Os(5)–Os(3)	61.2(1)	Os(2)–Os(5)–Os(4)	61.7(1)
Os(3)–Os(5)–Os(4)	59.9(1)	Os(2)–Os(5)–Os(6)	112.1(1)
Os(3)–Os(5)–Os(6)	60.3(1)	Os(4)–Os(5)–Os(6)	61.0(1)
Os(3)–Os(6)–Os(4)	58.8(1)	Os(3)–Os(6)–Os(5)	59.2(1)
Os(4)–Os(6)–Os(5)	58.7(1)		

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Os(1)–Os(2)	2.560(3)	Os(1)–Os(3)	2.757(3)
Os(1)–Os(4)	2.772(3)	Os(1)–Os(5)	2.716(3)
Os(1)–Os(6)	2.868(3)	Os(2)–Os(3)	2.990(3)
Os(2)–Os(6)	2.886(3)	Os(3)–Os(4)	2.842(3)
Os(3)–Os(5)	2.867(3)	Os(3)–Os(6)	2.757(3)
Os(4)–Os(5)	2.772(3)	Os(5)–Os(6)	2.796(3)
Os(2)–C(21)	2.20(7)	Os(2)–C(22)	2.17(5)
Os(2)–C(23)	2.16(5)	Os(2)–C(24)	2.24(5)
Os(2)–C(25)	2.23(5)	Os(2)–C(26)	2.21(6)
Os(2)–Os(1)–Os(3)	68.3(1)	Os(2)–Os(1)–Os(4)	121.9(1)
Os(3)–Os(1)–Os(4)	61.9(1)	Os(2)–Os(1)–Os(5)	118.8(1)
Os(3)–Os(1)–Os(5)	63.2(1)	Os(4)–Os(1)–Os(5)	60.7(1)
Os(2)–Os(1)–Os(6)	63.9(1)	Os(3)–Os(1)–Os(6)	58.7(1)
Os(4)–Os(1)–Os(6)	108.9(1)	Os(5)–Os(1)–Os(6)	60.0(1)
Os(1)–Os(2)–Os(3)	59.0(1)	Os(1)–Os(2)–Os(6)	63.2(1)
Os(3)–Os(2)–Os(6)	55.9(1)	Os(1)–Os(3)–Os(2)	52.7(1)
Os(1)–Os(3)–Os(4)	59.3(1)	Os(2)–Os(3)–Os(4)	106.1(1)
Os(1)–Os(3)–Os(5)	57.7(1)	Os(2)–Os(3)–Os(5)	101.7(1)
Os(4)–Os(3)–Os(5)	58.1(1)	Os(1)–Os(3)–Os(6)	62.7(1)
Os(2)–Os(3)–Os(6)	60.1(1)	Os(4)–Os(3)–Os(6)	110.0(1)
Os(5)–Os(3)–Os(6)	59.6(1)	Os(1)–Os(4)–Os(3)	58.8(1)
Os(1)–Os(4)–Os(5)	58.7(1)	Os(3)–Os(4)–Os(5)	61.4(1)
Os(1)–Os(5)–Os(3)	59.1(1)	Os(1)–Os(5)–Os(4)	60.7(1)
Os(3)–Os(5)–Os(4)	60.5(1)	Os(1)–Os(5)–Os(6)	62.7(1)
Os(3)–Os(5)–Os(6)	58.3(1)	Os(4)–Os(5)–Os(6)	111.0(1)
Os(1)–Os(6)–Os(2)	52.8(1)	Os(1)–Os(6)–Os(3)	58.7(1)
Os(2)–Os(6)–Os(3)	63.9(1)	Os(1)–Os(6)–Os(5)	57.3(1)
Os(2)–Os(6)–Os(5)	106.2(1)	Os(3)–Os(6)–Os(5)	62.2(1)

In the metal frameworks of the bicapped-tetrahedral clusters of osmium[14,16,17] it is observed that usually there is a metal–metal edge lengthening between metals with different electron counts and connectivities. In **1** the Os–Os bond distances are similar to those of the hexaosmium binary cluster except for Os(1)–Os(2) [2.720(3) Å] which is 0.09 Å shorter than the corresponding Os–Os bond in $[Os_6(CO)_{18}]$. This shortening results in an asymmetric capping mode for the Os(1) atom with the short distance to the arene-ligated metal, Os(2). This distortion may be caused by the variation in the bonding requirements of the benzene moiety compared to the tricarbonyl grouping.

The Os–Os bond distances in compound **2** are different from the corresponding metal–metal distances in the clusters $[Os_6(CO)_{18}]$ and **1**. The asymmetry for the capping atom Os(1) in **2** is enhanced with respect to the corresponding capping atom Os(1) in **1**. The Os(1)–Os(2) edge in **2**, which is bridged by a carbonyl ligand, is shortened by 0.24 and 0.26 Å with respect to the corresponding Os–Os bonds in $[Os_6(CO)_{18}]$ and **1**, respectively. This shorter edge, supported by the bridging carbonyl ligand, is as found in $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$,[14] but in $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ **2** the carbonyl is only slightly asymmetrically bonded with a C(O) ··· Os distance of 2.11(5) Å and a deviation from linearity for the Os–C–O angle [146(5)°] compared to the analogous parameters in $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$ which are 2.40(9) Å and 171(6)°, respectively.[14] The other two Os–Os edges in which Os(1) is involved in complex **2** are considerably longer (*ca.* 0.17 Å) with respect to the corresponding edges in $[Os_6(CO)_{18}]$ and **1**.

The π acidity of the arene will not be as great as for the tricarbonyl grouping and hence the metal atom bonded to the arene will be more electron rich than that associated with the metal tricarbonyl grouping. This is reflected in the variation in bonding of $[Os_6(CO)_{18}]$ and **2** with a bridging carbonyl group occurring in the latter compound, consistent with the higher π-bonding basicity of the metal group when co-ordinated to the arene. In terms of the potential electron-donor power of the metal it may be anticipated that the metal arene fragment would be in a tetrahedral position (metal–metal connectivity of four) as in **1**, as opposed to a capping position (metal–metal connectivity of three), as this enhances the possibility of a metal–metal donor bond. The difference in the structure of **1** and **2** may also reflect the more sterically demanding requirements of toluene compared to benzene on substitution of the three carbonyls in the initial $[Os_6(CO)_{18}]$ structure.

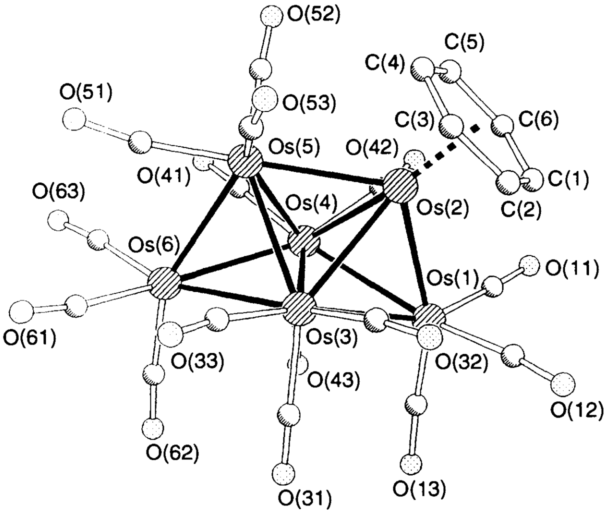

Fig. 1 Molecular structure of $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)]$ **1** showing the atom numbering

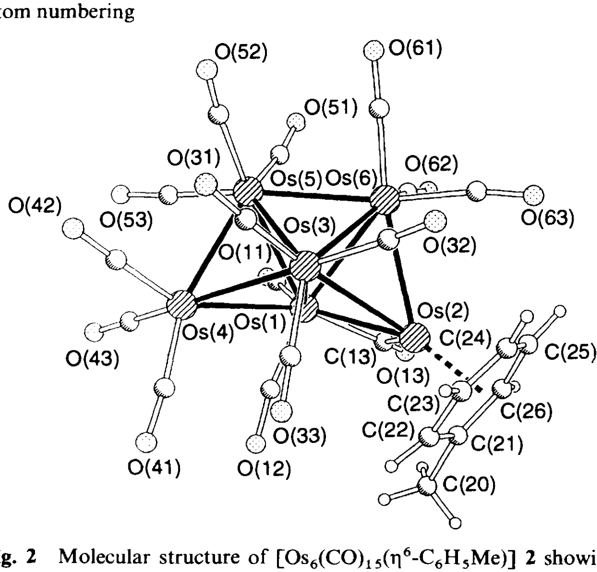

Fig. 2 Molecular structure of $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ **2** showing the atom numbering

In the cluster $[RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)]$ the ruthenium atom is electron deficient ($17e^-$) as is the osmium atom bonded to the arene in **2**, but the incipient character of the bridging carbonyl may be a reflection of the smaller electronegativity of ruthenium with respect to osmium.

In general terms, the position of substitution of the arene group is a balance between electronic and steric factors. Electronic factors, related to the enhanced donor power of the metal arene fragment, would favour substitution at the metal centres in order of their metal–metal connectivities five > four > three. On the basis of steric effects the order of substitution would be reversed in terms of the metal–metal connectivities, three > four > five. The observed substitution in the four connectivity position provides a compromise between the two opposing effects.

In order to investigate further steric factors associated with the structures of compounds **1** and **2** their crystal structures were analysed in terms of intermolecular packing. In both compounds the arene ligands form ribbons generated by the interlocking of two rows of arene fragments in a chevron-like fashion to give the 'herring-bone' pattern previously observed in other monoarene derivatives.[9] Thus the arene rings on adjacent molecules do not line up parallel with each other thereby generating graphitic packing, but the arene ring on one molecule interlocks with a tricarbonyl group on the next as shown in Figs. 3 and 4 for **1** and **2**, respectively. This packing pattern optimises the intermixing of the flat arene fragment and the carbonyl ligands protruding from the cluster surface, so that

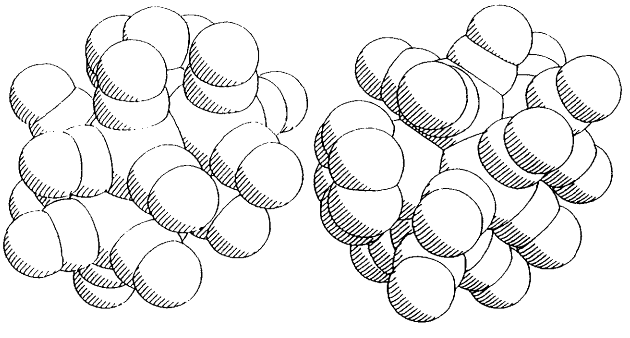

Fig. 3 Intermolecular interactions for complex **1**

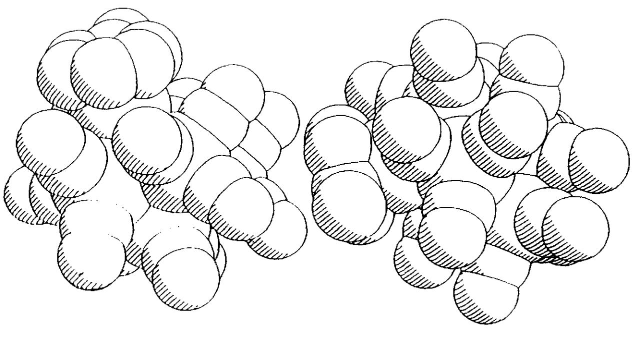

Fig. 4 Intermolecular interactions for complex **2**

although the positions of arene substitution are different in the two clusters and the steric requirements of the benzene and toluene ligands are different, the same localised packing interactions are similar in the two cases. The longer-range packing involving the arrangement and orientation of the arene ribbons is responsible for the difference in crystal system and space group for **1** and **2**; complex **1** crystallises in space group *Pbca* and **2** in $P2_1/n$.

The molecular structure of compound **4** is shown in Fig. 5. Selected bond parameters are presented in Table 4. The metal core of $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)]$ provides an interesting stereochemical variation, and may be described as consisting of four tetrahedra fused together to form a face-sharing chain of tetrahedra. It represents the basic structural unit of a winding helix.[18] The Os–Os distances range from 2.611(1) to 2.922(1) Å, comparable to those found in other high-nuclearity osmium carbonyl clusters. If the synthetic pathway is considered first, it is reasonable to think that the benzene should be co-ordinated to the capped Os(2) atom, however, as in **1**, a migration of the benzene from 17-electron Os(2) to 18-electron Os(4) has been observed. Attempts have been made to obtain crystals for **5** but the clusters decomposed upon prolonged standing. According to the structures of **1** and **2**, the toluene could be either bound to Os(2) or Os(4), but the close similarities in the IR spectra of complexes **4** and **5** would indicate that **5** has a similar bonding pattern to that of **4**.

Experimental

All the reactions were performed under an atmosphere of dry, oxygen-free nitrogen. Technical grade solvents were purified by standard procedures. The complexes $[Os_5(CO)_{15}]^{2-}$ (ref. 19), $[Os(C_6H_6)(MeCN)_3][BF_4]_2$[20] and $[\{Os(C_6H_5Me)Cl_2\}_2]$[21] were prepared by literature procedures. Mass spectra were recorded using a Kratos model MS 902 spectrometer, IR spectra on a Perkin-Elmer 1710 FT-IR spectrometer and ^1H NMR spectra on a Bruker WH 250 MHz spectrometer.

Preparations.—$[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5R)]$. *Method* 1 (R = H). To a solution of $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ (50 mg) in dichloromethane (10 cm^3) was added $[Os(C_6H_6)(MeCN)_3][BF_4]_2$ (25 mg) and the solution stirred for *ca.* 0.5 h. After removal of solvent the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (50:50) as eluent. The dark brown cluster $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)]$ **1** was isolated as the major product, R_f 0.7, *ca.* 45% yield.

Method 2 (R = H *or* Me). To a solution of $[Os_6(CO)_{18}]$ (50 mg) and an excess of C_6H_7R (R = Me or H) in CH_2Cl_2 (10 cm^3) was added dropwise Me_3NO (3.2 equivalents) in dichloromethane (10 cm^3) and the solution was stirred for 1 h. After removal of solvent the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (50:50) as eluent. The dark brown cluster $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5R)]$ was isolated as the major product, R_f 0.7, *ca.* 5% yield.

$[Os(C_6H_5Me)(CF_3SO_3)_2]$. The compound $[\{Os(C_6H_5Me)Cl_2\}_2]$ (20 mg) was suspended in CH_2Cl_2 and $Ag(CF_3SO_3)$ (40 mg) was added with stirring until a white precipitate of AgCl was formed. The solution was filtered and after removal of solvent the yellow oil was dissolved in CH_2Cl_2 and used without further purification.

$[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ *and* $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)]$. To a solution of $[Os(C_6H_5Me)(CF_3SO_3)_2]$ (25 mg) in dichloromethane (10 cm^3) was added $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ (50 mg) and the solution stirred for *ca.* 0.5 h. After removal of solvent the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (50:50) as eluent. The first black band was characterised as $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)]$ **5**, R_f 0.8, *ca.* 5% yield. The second brown band was identified as $[Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)]$ **2**, R_f 0.7, *ca.* 35% yield.

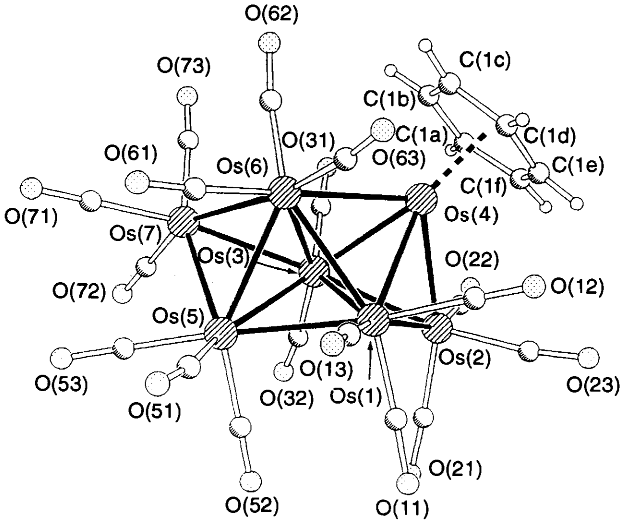

Fig. 5 Molecular structure of $[Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)]$ **4** showing the atom numbering

Table 4 Selected bond lengths (Å) and angles (°) for compound **4**

Os(1)–Os(2)	2.913(1)	Os(1)–Os(3)	2.779(1)
Os(1)–Os(4)	2.816(1)	Os(1)–Os(5)	2.841(1)
Os(1)–Os(6)	2.816(1)	Os(2)–Os(3)	2.657(1)
Os(2)–Os(4)	2.744(1)	Os(3)–Os(4)	2.611(1)
Os(3)–Os(5)	2.708(1)	Os(3)–Os(6)	2.716(1)
Os(3)–Os(7)	2.670(1)	Os(4)–Os(6)	2.859(1)
Os(5)–Os(6)	2.847(1)	Os(5)–Os(7)	2.794(2)
Os(6)–Os(7)	2.922(1)	Os(4)–C(1a)	2.19(3)
Os(4)–C(1b)	2.21(3)	Os(4)–C(1c)	2.26(4)
Os(4)–C(1d)	2.29(3)	Os(4)–C(1e)	2.25(3)
Os(4)–C(1f)	2.26(4)		
Os(2)–Os(1)–Os(3)	55.61(3)	Os(2)–Os(1)–Os(4)	57.21(4)
Os(2)–Os(1)–Os(5)	104.05(4)	Os(2)–Os(1)–Os(6)	106.17(4)
Os(3)–Os(1)–Os(4)	55.62(3)	Os(3)–Os(1)–Os(5)	57.60(3)
Os(3)–Os(1)–Os(6)	58.07(3)	Os(4)–Os(1)–Os(5)	106.57(4)
Os(4)–Os(1)–Os(6)	61.01(4)	Os(5)–Os(1)–Os(6)	60.40(4)
Os(1)–Os(2)–Os(3)	59.64(3)	Os(1)–Os(2)–Os(4)	59.62(4)
Os(3)–Os(2)–Os(4)	57.77(4)	Os(1)–Os(3)–Os(2)	64.76(4)
Os(1)–Os(3)–Os(4)	62.91(4)	Os(1)–Os(3)–Os(5)	62.36(4)
Os(1)–Os(3)–Os(6)	61.65(4)	Os(1)–Os(3)–Os(7)	115.69(4)
Os(2)–Os(3)–Os(4)	62.79(4)	Os(2)–Os(3)–Os(5)	115.45(5)
Os(2)–Os(3)–Os(6)	117.00(5)	Os(2)–Os(3)–Os(7)	175.98(5)
Os(4)–Os(3)–Os(5)	117.01(5)	Os(4)–Os(3)–Os(6)	64.90(4)
Os(4)–Os(3)–Os(7)	121.16(5)	Os(5)–Os(3)–Os(6)	63.31(4)
Os(5)–Os(3)–Os(7)	62.57(4)	Os(6)–Os(3)–Os(7)	65.70(4)
Os(1)–Os(4)–Os(2)	63.17(4)	Os(1)–Os(4)–Os(3)	61.46(4)
Os(1)–Os(4)–Os(6)	59.50(3)	Os(2)–Os(4)–Os(3)	59.45(4)
Os(2)–Os(4)–Os(6)	109.67(4)	Os(3)–Os(4)–Os(6)	59.33(3)
Os(1)–Os(5)–Os(3)	60.05(4)	Os(1)–Os(5)–Os(6)	59.36(3)
Os(1)–Os(5)–Os(7)	109.95(4)	Os(3)–Os(5)–Os(6)	58.50(3)
Os(3)–Os(5)–Os(7)	58.06(4)	Os(6)–Os(5)–Os(7)	62.42(4)
Os(1)–Os(6)–Os(3)	60.27(4)	Os(1)–Os(6)–Os(4)	59.49(3)
Os(1)–Os(6)–Os(5)	60.23(4)	Os(1)–Os(6)–Os(7)	107.02(4)
Os(3)–Os(6)–Os(4)	55.78(3)	Os(3)–Os(6)–Os(5)	58.20(3)
Os(3)–Os(6)–Os(7)	56.40(4)	Os(4)–Os(6)–Os(5)	105.29(4)
Os(4)–Os(6)–Os(7)	105.43(4)	Os(5)–Os(6)–Os(7)	57.90(4)
Os(3)–Os(7)–Os(5)	59.36(4)	Os(3)–Os(7)–Os(6)	57.90(4)
Os(5)–Os(7)–Os(6)	59.68(4)		

$[Os_6(CO)_{17}]^{2-}$ **3**. The compound $[Os_6(CO)_{18}]$ (50 mg) was suspended in thf (10 cm^3) and a solution of K–Ph_2CO (1.1 equivalents) in thf (10 cm^3) was added dropwise with stirring until all the $[Os_6(CO)_{18}]$ had dissolved and a clear brown solution resulted. After removal of solvent the remaining orange-brown oil was dissolved in dichloromethane and used without further purification.

$[Os_7(CO)_{17}(\eta^6\text{-}C_6H_5R)]$ (R = Me *or* H). *Method* 1. To a solution of the dianion $[Os_6(CO)_{17}]^{2-}$ (50 mg) in dichloromethane (10 cm^3) was added $[Os(C_6H_6)(MeCN)_3][BF_4]_2$

Table 5 Crystal data and data-collection parameters* for the structures of [$Os_6(CO)_{15}(\eta^6\text{-}C_6H_6)$] **1**, [$Os_6(CO)_{15}(\eta^6\text{-}C_6H_5Me)$] **2** and [$Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)$] **4**

	1	**2**	**4**
Formula	$C_{21}H_6O_{15}Os_6$	$C_{22}H_8O_{15}Os_6$	$C_{23}H_6O_{17}Os_7$
M	1639.5	1653.5	1885.7
Crystal colour, habit	Dark red irregular prism	Black block	Black block
Crystal size/mm	0.25 × 0.32 × 0.35	0.42 × 0.46 × 0.56	0.30 × 0.34 × 0.40
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbca*	$P2_1/n$	*Pbca*
a/Å	16.819(6)	9.651(3)	18.279(9)
b/Å	17.732(6)	18.666(4)	18.377(7)
c/Å	18.160(6)	15.688(5)	18.497(5)
β/°		90.58(2)	
U/Å^3	5416(3)	2826(1)	6213(4)
T/K	150(2)	290(2)	290(2)
Z	8	4	8
D_c/g cm^{-3}	4.021	3.886	4.030
F(000)	5664	2864	6496
μ(Mo-Kα)/cm^{-1}	281.14	269.41	286.35
2θ Range/°	7.0–45.0	5.0–45.0	4.0–45.0
Scan mode	ω–θ	ω–2θ	ω–2θ
Scan speed/° min^{-1}	0.25–1.00	3.0–19.53	1.03–8.24
Scan range (ω)/°	0.90 plus Kα separation	1.50 plus Kα separation	0.55 + 0.34 tanθ
Reflections measured	3520	4145	4509
Unique reflections	3520	3712	4509
Observed reflections (criterion)	2685 [$F > 5\sigma(F)$]	2620 [$F > 5\sigma(F)$]	3139 [$F > 3\sigma(F)$]
Transmission factors	0.0523, 0.0943	0.0424, 0.0783	0.0495, 0.0881
Weighting scheme	$[\sigma^2(F) + 0.002(F)^2]^{-1}$	$[\sigma^2(F) + 0.003(F)^2]^{-1}$	$4F^2[\sigma^2(F)^2 + (0.04F^2)^2]$
R	0.087	0.089	0.052
R'	0.105	0.113	0.061

* Details in common: Mo-Kα radiation (λ = 0.710 69 Å), background measurement, stationary crystal–stationary counter at beginning and end of scan, each for 25% of total scan time.

Table 6 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	2 359(1)	8 367(1)	233(1)	O(32)	655(19)	9 616(18)	−411(15)
Os(2)	959(1)	8 091(1)	932(1)	C(33)	1 072(28)	10 436(26)	1 298(22)
Os(3)	1 607(1)	9 535(1)	1 013(1)	O(33)	746(20)	11 001(18)	1 367(16)
Os(4)	2 315(1)	8 376(1)	1 786(1)	C(41)	2 414(29)	8 162(27)	2 807(23)
Os(5)	832(1)	8 887(1)	2 198(1)	O(41)	2 574(20)	8 005(19)	3 415(16)
Os(6)	2 157(1)	9 812(1)	2 441(1)	C(42)	2 275(26)	7 291(26)	1 603(22)
C(1)	771(18)	7 339(17)	−56(12)	O(42)	2 337(20)	6 666(18)	1 585(16)
C(2)	236	7 940	−83	C(43)	3 386(31)	8 594(28)	1 635(23)
C(3)	−262	8 083	515	O(43)	4 116(19)	8 677(17)	1 531(15)
C(4)	−227	7 626	1 139	C(51)	704(30)	9 427(28)	3 045(25)
C(5)	308	7 025	1 166	O(51)	584(24)	9 683(22)	3 646(20)
C(6)	806	6 881	568	C(52)	604(27)	7 984(26)	2 727(22)
C(11)	2 660(24)	7 379(24)	70(21)	O(52)	415(23)	7 465(22)	2 996(19)
O(11)	2 853(19)	6 740(18)	−13(16)	C(53)	−148(27)	9 192(24)	1 922(21)
C(12)	1 973(29)	8 450(26)	−745(23)	O(53)	−795(19)	9 302(17)	1 710(15)
O(12)	1 746(18)	8 575(17)	−1 344(14)	C(61)	1 746(24)	10 799(22)	2 699(18)
C(13)	3 340(22)	8 726(21)	26(17)	O(61)	1 460(22)	11 314(20)	2 890(17)
O(13)	4 013(21)	8 974(19)	−169(17)	C(62)	3 195(24)	10 230(21)	2 248(18)
C(31)	2 579(29)	10 059(25)	685(22)	O(62)	3 806(20)	10 456(18)	2 076(15)
O(31)	3 134(21)	10 346(18)	496(16)	C(63)	2 429(26)	9 657(24)	3 455(21)
C(32)	960(24)	9 576(22)	156(19)	O(63)	2 644(21)	9 608(19)	4 066(16)

(25 mg) or [$Os(C_6H_5Me)(CF_3SO_3)_2$] and the solution stirred for *ca.* 0.5 h. After removal of solvent the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (60:40) as eluent. The brown clusters [$Os_7(CO)_{17}(\eta^6\text{-}C_6H_6)$] **4** and [$Os_7(CO)_{17}(\eta^6\text{-}C_6H_5Me)$] **5** were isolated respectively as the major products, R_f 0.8, *ca.* 25% yield.

Method 2. To a solution of [$Os_7(CO)_{21}$] (50 mg) and an excess of C_6H_7R (R = Me or H) in CH_2Cl_2 (10 cm^3) was added dropwise Me_3NO (3.2 equivalents) in dichloromethane (10 cm^3) and the solution was stirred for 1 h. After removal of solvent the solid residue was chromatographed by TLC using CH_2Cl_2–hexane (60:40) as eluent. The dark brown cluster [$Os_7(CO)_{17}(\eta^6\text{-}C_6H_5R)$] was isolated as the major product, R_f 0.8, *ca.* 3% yield.

X-Ray Analysis of Compounds **1, 2** *and* **4**.—For compound **1** intensity data were collected on a Stoe four-circle diffractometer equipped with an Oxford Cryostream cooling device, for **2** on a Nicolet R3m/V diffractometer and for **4** on an Enraf–Nonius CAD4 diffractometer. In each case the data were corrected for Lorentz polarisation effects and for absorption by the ψ-scan method. The crystals of **1** and **2** were irregular in shape and it was not possible to apply a particularly accurate absorption correction; this resulted in relatively high final residuals. The relevant data for the crystal structure analyses are summarised in Table 5. The structures were solved by a combination of direct methods and Fourier-difference techniques and refined on *F* by full-matrix least-squares analysis (using the SHELXTL PLUS program[22] for **1** and **2**, SDP program[23] for **4**) until

Table 7 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	220(2)	7 210(1)	5 973(1)	O(12)	−2 393(42)	7 447(24)	4 900(27)
Os(2)	−813(2)	6 224(1)	6 906(1)	O(13)	125(42)	5 736(22)	5 173(27)
Os(3)	−148(2)	7 669(1)	7 626(1)	O(31)	277(47)	9 002(26)	8 741(31)
Os(4)	−353(2)	8 647(1)	6 243(1)	O(32)	−151(36)	6 829(20)	9 287(24)
Os(5)	2 219(2)	8 071(1)	6 646(1)	O(33)	−3 287(43)	7 876(24)	7 559(25)
Os(6)	1 952(2)	6 699(1)	7 339(1)	O(41)	−3 387(53)	8 913(30)	6 107(37)
C(11)	1 442(45)	7 315(25)	5 127(30)	O(42)	210(46)	10 003(21)	7 211(28)
C(12)	−1 351(49)	7 407(27)	5 320(32)	O(43)	46(50)	9 269(27)	4 436(33)
C(13)	−66(50)	6 160(28)	5 651(33)	O(51)	4 790(49)	7 363(27)	6 008(30)
C(31)	57(49)	8 495(27)	8 330(32)	O(52)	3 488(73)	8 904(31)	8 097(37)
C(32)	−111(47)	7 087(27)	8 612(31)	O(53)	2 848(57)	9 227(27)	5 288(30)
C(33)	−2 141(47)	7 807(25)	7 595(28)	O(61)	4 461(50)	7 159(29)	8 363(25)
C(41)	−2 214(50)	8 773(26)	6 182(31)	O(62)	3 531(48)	5 759(22)	6 128(34)
C(42)	−54(50)	9 490(28)	6 877(32)	O(63)	1 572(55)	5 424(31)	8 506(37)
C(43)	−73(58)	8 995(32)	5 123(39)	C(20)	−3 250(64)	5 623(35)	5 524(41)
C(51)	3 723(72)	7 599(38)	6 159(43)	C(21)	−2 559(71)	5 577(39)	6 427(48)
C(52)	3 032(67)	8 642(39)	7 555(45)	C(22)	−3 043(51)	6 109(28)	6 983(33)
C(53)	2 484(71)	8 799(40)	5 904(46)	C(23)	−2 491(48)	6 032(28)	7 775(32)
C(61)	3 460(54)	6 978(29)	7 990(35)	C(24)	−1 595(50)	5 607(28)	8 029(33)
C(62)	2 976(61)	6 170(34)	6 563(40)	C(25)	−993(52)	5 125(29)	7 455(33)
C(63)	1 811(54)	5 921(30)	8 108(36)	C(26)	−1 500(57)	5 114(31)	6 640(37)
O(11)	2 100(37)	7 247(26)	4 414(25)				

Table 8 Atomic coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.191 01(5)	0.232 49(5)	0.167 08(5)	C(1d)	0.090(2)	0.113(2)	0.338(2)
Os(2)	0.035 25(5)	0.243 40(6)	0.135 56(6)	C(1e)	0.033(2)	0.159(2)	0.319(2)
Os(3)	0.115 21(5)	0.138 23(6)	0.076 58(5)	C(1c)	0.092(2)	0.044(2)	0.303(2)
Os(4)	0.088 40(5)	0.128 81(5)	0.214 89(5)	C(1b)	0.040(2)	0.025(2)	0.249(2)
Os(5)	0.252 56(5)	0.176 78(6)	0.037 35(5)	C(1f)	−0.020(2)	0.141(2)	0.272(2)
Os(6)	0.226 37(5)	0.083 64(6)	0.157 53(5)	C(1a)	−0.016(1)	0.074(1)	0.233(1)
Os(7)	0.196 36(6)	0.038 35(6)	0.009 02(6)	C(11)	0.178(1)	0.326(2)	0.135(1)
O(11)	0.172(1)	0.386(1)	0.113(1)	C(12)	0.165(2)	0.260(2)	0.264(2)
O(12)	0.156(1)	0.278(2)	0.322(1)	C(13)	0.287(2)	0.252(2)	0.197(2)
O(13)	0.347(1)	0.264(1)	0.217(1)	C(21)	0.028(2)	0.318(2)	0.069(2)
O(21)	0.023(1)	0.364(2)	0.022(2)	C(22)	−0.062(2)	0.216(2)	0.117(2)
O(22)	−0.119(1)	0.194(1)	0.107(1)	C(23)	0.011(2)	0.310(2)	0.209(2)
O(23)	−0.005(1)	0.344(1)	0.259(2)	C(31)	0.048(1)	0.063(1)	0.075(1)
O(31)	0.004(1)	0.015(1)	0.076(1)	C(32)	0.072(1)	0.180(2)	−0.008(1)
O(32)	0.050(1)	0.200(1)	−0.061(1)	C(51)	0.347(2)	0.212(2)	0.060(2)
O(51)	0.408(1)	0.225(2)	0.070(1)	C(52)	0.225(2)	0.262(2)	−0.009(2)
O(52)	0.206(1)	0.312(1)	−0.039(1)	C(53)	0.292(2)	0.146(2)	−0.050(2)
O(53)	0.320(1)	0.127(1)	−0.105(1)	C(61)	0.324(1)	0.062(1)	0.133(1)
O(61)	0.382(1)	0.046(1)	0.121(1)	C(62)	0.200(2)	−0.014(2)	0.171(2)
O(62)	0.179(1)	−0.073(1)	0.185(1)	C(63)	0.253(2)	0.099(2)	0.253(1)
O(63)	0.271(1)	0.102(1)	0.313(1)	C(71)	0.286(2)	−0.006(2)	−0.018(2)
O(71)	0.343(1)	−0.031(1)	−0.032(1)	C(72)	0.162(2)	0.044(2)	−0.087(2)
O(72)	0.144(1)	0.048(2)	−0.147(1)	C(73)	0.147(2)	−0.053(2)	0.022(2)
O(73)	0.123(2)	−0.105(1)	0.028(2)				

convergence was reached. The hydrogen atoms of the coordinated arene molecules were generated in their ideal positions (C–H 0.96 Å) for compounds **2** and **4**, and these atoms were allowed to ride on the relevant carbons. For complex **1** the arene ring was constrained to be a regular hexagon with a C–C distance fixed at 1.395 Å. Final atomic coordinates for the three structures are presented in Tables 6–8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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