# Some Reactions of $[Os_3(CO)_{10}(NCMe)_2]$ with Arenes; the Molecular Structure of $[Os_3H_2(CO)_9(C_6H_4)]$ †

**Robert J. Goudsmit, Brian F. G. Johnson, Jack Lewis,* Paul R. Raithby, and Maria J. Rosales**
*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW*

The cluster $[Os_3H_2(CO)_9(C_6H_4)]$ was obtained in good yield by the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with benzene under reflux. This benzyne cluster crystallises in space group $P2_1/c$ with $a = 17.391(5)$, $b = 13.190(2)$, $c = 16.512(3)$ Å, $\beta = 92.39(2)°$, and $Z = 8$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least squares to $R = 0.079$ for 3 438 observed diffractometer data. In each of the two independent molecules the three Os atoms define an irregular triangle the longest edge [mean 3.034(4) Å] of which is bridged by the benzyne ligand which is co-ordinated to the third Os atom *via* a $\pi$ bond. This long edge is also bridged by a hydride and the other hydride bridges one of the other Os–Os edges [mean 2.858(3) Å]. The third Os–Os edge [mean 2.751(2) Å] is unbridged. When the reaction is carried out in toluene or chlorobenzene rather than benzene the complexes $[Os_3H_2(CO)_9(C_6H_3Me)]$ and $[Os_3H_2(CO)_9(C_6H_3Cl)]$ are obtained. In each case two isomers have been identified by $^1H$ n.m.r. spectroscopy. With *trans*-stilbene the only complex characterised has been formulated as $[Os_3H_2(CO)_9(C_6H_3CHCHC_6H_5)]$ in which one ring is co-ordinated to the cluster in a similar manner to that in $[Os_3H_2(CO)_9(C_6H_4)]$.

Although the chemistry of triosmium clusters with a wide variety of small molecules has been studied in detail [1] there have been problems caused by the relatively low reactivity of the parent complex, $[Os_3(CO)_{12}]$. In particular, products of the reactions between $[Os_3(CO)_{12}]$ and arenes have only been obtained in low yield,[2] despite the interest in the interactions between arenes and metal surfaces and the analogy with clusters.[3] Recently, the complex $[Os_3(CO)_{10}(NCMe)_2]$ has been exploited successfully as a much more reactive starting material,[4] the acetonitrile groups being replaced easily by other ligands. We now report the products of the reactions between $[Os_3(CO)_{10}(NCMe)_2]$ and a number of arenes. Related products have been obtained by other workers using other substituted triosmium clusters,[5-10] and the whole area has been the subject of a recent review.[11]

## Results and Discussion

Reasonable yields of complexes with the general formula $[Os_3H_2(CO)_9(C_6H_2R^1R^2)]$ [$R^1$ = H; $R^2$ = H (1), Me (2), $Pr^n$ (3), CHCHPh (4), Cl (5); $R^1$ = Me, $R^2$ = Me (6)] are obtained when a solution of $[Os_3(CO)_{10}(NCMe)_2]$ in the appropriate arene solvent is refluxed for *ca.* 30 min, the actual yield depending on the arene used. The complexes (3) ($R^1$ = H, $R^2$ = $Pr^n$) and (4) ($R^1$ = H, $R^2$ = CHCHPh) may also be obtained by adding an excess of the arene to a hot cyclohexane solution of $[Os_3(CO)_{10}(NCMe)_2]$. With *trans*-stilbene, PhCHCHPh, the other readily characterised products were $[Os_6(CO)_{18}]$, $[Os_3H(CO)_{10}Cl]$, $[Os_3(CO)_{12}]$, and $[Os_6H_2(CO)_{18}]$. In each case the triosmium-benzyne product was purified by t.l.c., being isolated as a yellow band. The benzyne complex, $[Os_3H_2(CO)_9(C_6H_4)]$ (1), was characterised by i.r., $^1H$ n.m.r. and mass spectroscopy and the values were in close agreement with those reported by Deeming *et al.*[2]

In the crystal of (1) there are two independent $[Os_3H_2(CO)_9(C_6H_4)]$ molecules per asymmetric unit which are separated by normal van der Waals distances. These two molecules are structurally equivalent and a view of one of them is shown in Figure 1. Selected bond parameters are presented in Table 1. The three atoms define a triangle in which the three Os–Os edges show significant variations in length. The benzyne ligand lies over one face of the triangle such that the dihedral angle between the plane of the ring and that of the triangle is 63.9° for molecule 1 (69.0° for molecule 2). The organic ring forms $\sigma$ bonds through C(111) and C(112) to two of the Os atoms, bridging the Os(1)–Os(2) edge, and the C(111)–C(112) bond interacts with the third Os atom, Os(3), in a $\pi$ fashion. The nine carbonyl ligands are all essentially linear [174(3)°] and three are terminally co-ordinated to each metal atom, two in pseudo-equatorial positions with respect to the $Os_3$ triangle and one in an axial position. The two hydrides in each molecule were not located directly but the distribution of the carbonyl groups indicates that they bridge the Os(1)–Os(2) and Os(1)–Os(3) edges. The *cis* Os–Os–C(carbonyl) angles for the carbonyl groups adjacent to these two edges are significantly wider (mean 106°) than for the carbonyls *cis*

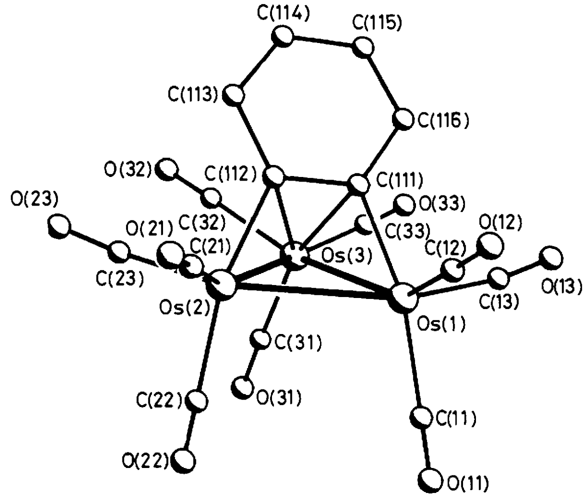


**Figure 1.** The molecular structure of $[Os_3H_2(CO)_9(C_6H_4)]$ (1) (the hydride ligands are omitted)

---

† $\mu_3$-Benzyne-di-$\mu$-hydrido-*cyclo*-tris(tricarbonylosmium)(3*Os*–*Os*).

*Supplementary data available* (No. SUP 23682, 31 pp.): structure factors, thermal parameters, least-squares planes, H-atom co-ordinates, full bond parameter data. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

to the Os(2)–Os(3) edge (mean 96°). This widening of carbonyl angles may be attributed to the steric influence of the bridging hydride ligands.

For the triosmium benzyne cluster to be considered a 'closed' 48-electron system the benzyne ligand must act as a four-electron donor. This is achieved by donating two electrons *via* the π bond to Os(3) and one electron each to Os(1) and Os(2) *via* σ bonds from C(111) and C(112), respectively. Despite the apparent donation from the C(111)–C(112) bond there are no significant variations in C–C bond distances [mean 1.43(7) Å], although the estimated standard deviations are rather high for an accurate assessment. In the related clusters $[Os_3H(CO)_9(SMe)(C_6H_4)]$ [6] and $[Os_3H(CO)_9(AsMe_2)(C_6H_4)]$ [7] the average C–C distances in the benzyne rings are 1.42(3) and 1.39(3) Å, and show little variation around the rings. In both these complexes the mode of coordination of the benzyne ligand is similar to that in $[Os_3H_2(CO)_9(C_6H_4)]$ (1), and the Os–C(benzyne) distances in this complex are similar to the σ Os–C bonds [mean 2.15(3) Å] and the π Os–C bonds [mean 2.36(2) Å] in $[Os_3H(CO)_9(SMe)(C_6H_4)]$.[6]

The Os(1)–Os(2) distance in $[Os_3H_2(CO)_9(C_6H_4)]$ (1) is one of the longest reported in trinuclear Os clusters where a direct metal–metal interaction is presumed to be present, and more in keeping with the value of 3.078(2) Å for the di-bridged bond in $[Os_3(CO)_{10}(OMe)_2]$,[12] where the bond order is formally zero. However, it is probably better to consider the Os(1)(μ-H)C(111)C(112)Os(2) fragment as a delocalised bonding unit. It is well established that a bridging hydride is concomitant with a long metal–metal distance in the absence of other bridging groups.[13] When a second bridging group is added across the same metal–metal edge, with a single 'bridgehead' atom, there is normally a counter-balancing shortening effect.[14] When the second group has two 'bridgehead' atoms the counter-balancing effect is less marked as in the case of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}3\text{–}4\text{-}\eta\text{-}C_3H_3N_2)]$.[15] In the benzyne complex there appears to be no shortening effect, in fact an additional lengthening effect since the Os(1)–Os(2) distance is *ca.* 0.05 Å longer than the singly hydride-bridged Os–Os bond of 2.989(1) Å in $[Os_3H(\mu\text{-}H)(CO)_{11}]$.[16] Presumably electrons from the donor groups are entering symmetry orbitals which are antibonding with respect to the metal–metal interaction.

**Table 1.** Selected bond distances (Å) and angles (°) for $[Os_3H_2(CO)_9(C_6H_4)]$ (1)

| | Molecule 1 | Molecule 2 |
|---|---|---|
| Os(1)–Os(2) | 3.026(2) | 3.041(2) |
| Os(1)–Os(3) | 2.866(2) | 2.849(2) |
| Os(2)–Os(3) | 2.751(2) | 2.751(2) |
| Os(1)–C(111) | 2.11(3) | 2.09(4) |
| Os(2)–C(112) | 2.07(3) | 2.01(4) |
| Os(3)–C(111) | 2.31(3) | 2.33(4) |
| Os(3)–C(112) | 2.37(3) | 2.46(3) |
| C(111)–C(112) | 1.45(5) | 1.64(6) |

| | Molecule 1 | Molecule 2 |
|---|---|---|
| Os(2)–Os(1)–Os(3) | 55.6(1) | 55.6(1) |
| Os(3)–Os(2)–Os(1) | 59.3(1) | 58.7(1) |
| Os(1)–Os(2)–Os(3) | 65.2(1) | 65.8(1) |
| Os(2)–Os(1)–C(111) | 67.0(9) | 69.6(11) |
| Os(3)–Os(1)–C(111) | 52.6(8) | 53.8(10) |
| Os(1)–Os(2)–C(112) | 68.5(9) | 69.9(11) |
| Os(3)–Os(2)–C(112) | 56.7(8) | 59.8(10) |
| Os(1)–Os(3)–C(111) | 46.6(8) | 46.2(9) |
| Os(2)–Os(3)–C(111) | 70.4(8) | 72.6(10) |
| Os(1)–Os(3)–C(112) | 68.5(8) | 68.7(9) |
| Os(2)–Os(3)–C(112) | 47.0(8) | 45.0(9) |

It is of interest to contrast the Os(1)–Os(2) bridged distance in (1) with the non-bonded distance of 3.791(1) Å for the Os–Os vector which is bridged by both the benzyne and SMe ligands in $[Os_3H(CO)_9(SMe)(C_6H_4)]$.[6] This difference of *ca.* 0.76 Å between these two Os–Os distances illustrates the adaptability of the benzyne ligand to span various metal–metal edges in clusters. In these two cases it seems that the difference in the two metal–metal vectors is due to the nature of the other bridging group; the hydride in (1) is a one-electron donor while the thiol group in $[Os_3H(CO)_9(SMe)(C_6H_4)]$ [6] is a three-electron donor.

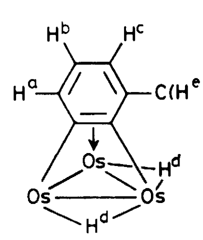
The Os(1)–Os(3) bond in $[Os_3H_2(CO)_9(C_6H_4)]$ (1) is also bridged by a hydride but this distance is slightly shorter than the Os–Os distance of 2.877(3) Å in the parent carbonyl $[Os_3(CO)_{12}]$.[16] This suggests that the π interaction between the benzyne ligand and Os(3) has a shortening influence on the Os(1)–Os(3) distance. A similar influence appears to be exerted on the unbridged Os(2)–Os(3) bond which is shortened by *ca.* 0.13 Å with respect to the Os–Os distance in $[Os_3(CO)_{12}]$.

Although the estimated standard deviations associated with the Os–C(carbonyl) bonds make a detailed assessment of the bonding difficult the trends are similar to those observed in $[Os_3H(CO)_9(SMe)(C_6H_4)]$.[6] The Os–C(carbonyl) bonds *trans* to the σ Os–C(benzyne) bonds are longer [mean 2.00(3) Å] and the Os–C(carbonyl) *trans* to the π Os–C(benzyne)

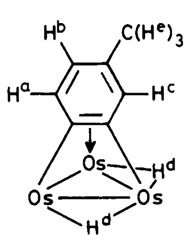
**Table 2.** Infrared and mass spectroscopic data for the complexes $[Os_3H_2(CO)_9(C_6H_2R^1R^2)]$

| Complex | ν(CO) [a]/cm$^{-1}$ | *m/e* [b] |
|---|---|---|
| (2) $[Os_2H_2(CO)_9(C_6H_3Me)]$ | 2 108m, 2 080s, 2 054s,<br>2 033s, 2 022m, 2 006s,<br>1 997m, 1 981m | 920<br>$M^+ - n$(CO) ($n$ = 1—9) |
| (3) $[Os_3H_2(CO)_9(C_6H_3Pr^n)]$ | 2 107m, 2 079s, 2 053s,<br>2 033s, 2 021s, 2 005s,<br>1 996m, 1 980m | |
| (4) $[Os_3H_2(CO)_9(C_6H_3CHCHPh)]$ | 2 107m, 2 080s, 2 054s,<br>2 033s, 2 022m, 2 007s,<br>1 996m, 1 981m | 1 008<br>$M^+ - n$(CO) ($n$ = 1—9) |
| (5) $[Os_3H_2(CO)_9(C_6H_3Cl)\}$ | 2 109s, 2 082s, 2 056s,<br>2 035s, 2 023m, 2 008s,<br>2 000m, 1 983m | 942 ($^{37}$Cl)<br>$M^+ - n$(CO) ($n$ = 1—9) |
| (6) $[Os_3H_2(CO)_9(C_6H_2Me_2)]$ | 2 106m, 2 078s, 2 053s,<br>2 031s, 2 019m, 2 003s,<br>1 996m, 1 979m | 934<br>$M^+ - n$(CO) ($n$ = 1—9) |

[a] Hexane solvent. [b] Parent peak ($^{192}$Os).



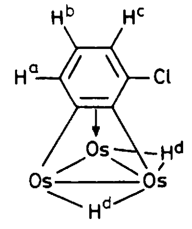
(2a)



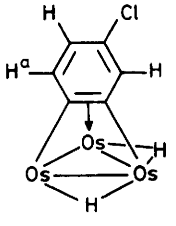
(2b)

| δ/p.p.m. | (2a) | (2b) |
|---|---|---|
| $H^a$ | 7·74 (d, $J$ = 8·3) | 7·84 (d, $J$ = 8·3) |
| $H^b$ | 6·73 (m) | 6·73 (dd, $J$ = 8·3) |
| $H^c$ | 7·08 (d, $J$ = 6·8) | 7·71 (s) |
| $H^d$ | −18·5 (s) | −18·9 (s) |
| $H^e$ | 2·45 (s) | 2·31 (s) |

Ratio 1 : 4 (approximate)



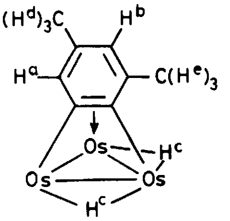
(5a)



(5b)

| δ/p.p.m. | (5a) | (5b) |
|---|---|---|
| $H^a$ | 7·83 (d, $J$ = 7·8) | 7·89 (d, $J$ = 8·4) |
| $H^b$ | 6·82 (t, $J$ = 7·5) | |
| $H^c$ | 7·30 (d, $J$ = 7·3) | |
| $H^d$ | −18·7 (s) | |

Ratio 3:1 (approximate)



(6)

| δ/p.p.m. | |
|---|---|
| $H^a$ | 7·52 (s) |
| $H^b$ | 6·89 (s) |
| $H^c$ | −18·53 (s) |
| $H^d$ | 2·28 (s) |
| $H^e$ | 2·42 (s) |

**Figure 2.** The $^1$H n.m.r. spectra assignments for $[Os_3H_2(CO)_9(C_6H_3Me)]$ (2), $[Os_3H_2(CO)_9(C_6H_3Cl)]$ (5), and $[Os_3H_2(CO)_9(C_6H_2Me_2)]$ (6) ($J$ values in Hz)

interaction are shorter [mean 1.88(3) Å] than the equatorial Os–C(carbonyl) bonds [1.94(3) Å].

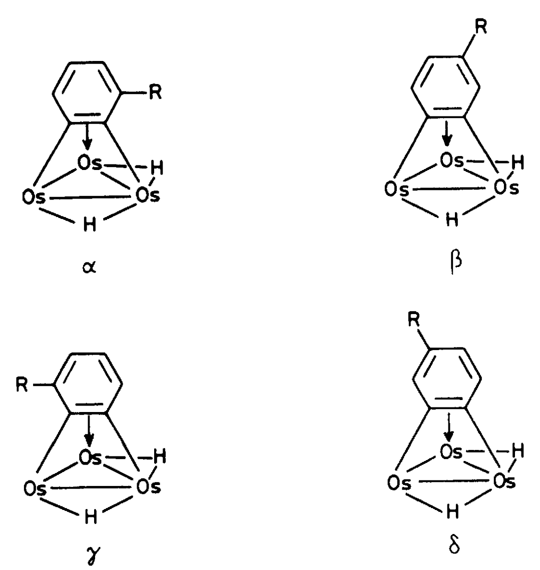


**Figure 3.** Possible isomers for $[Os_3H_2(CO)_9(C_6H_3R)]$

The remaining complexes $[Os_3H_2(CO)_9(C_6H_2R^1R^2)]$ [$R^1$ = H; $R^2$ = Me (2), Pr$^n$ (3), CHCHPh (4), Cl (5); $R^1$ = Me, $R^2$ = Me (6)] were characterised by spectroscopic techniques (Table 2). The $^1$H n.m.r. spectra of complexes $[Os_3H_2(CO)_9(C_6H_3Me)]$ (2) and $[Os_3H_2(CO)_9(C_6H_3Cl)]$ (5) show the existence of isomers, which cannot be separated on the t.l.c. plate. It has been possible to analyse the room-temperature proton spectra, and assign the isomers as shown in Figure 2. These assignments represent only some of the possible isomers. Figure 3 illustrates four possible isomers which would result from a ring-flipping mechanism which is presumably occurring rapidly at room temperature on the n.m.r. time-scale. The observed $^1$H n.m.r. spectra for (2), (5), and (6) are also consistent with a time-averaging mechanism involving the hydride ligands, which results in the single hydride resonance. In the case of complex (2a), for example, this process could involve exchange between the two isomeric forms, denoted α and γ in Figure 3, or, alternatively, by an exchange process which leaves the substituted benzyne ligand unmoved and exchanges the hydrides directly. With either mechanism the process is rapid on the n.m.r. time-scale.

It is interesting to compare these results with those obtained by Arce and Deeming[7] for the related species $[Os_3H(CO)_9(AsMe_2)(C_6H_3Me)]$ and $[Os_3H(CO)_9(AsMe_2)(C_6H_3OMe)]$. In the former complex only a pair of isomers (β and δ in Figure 3) corresponding to (2b) in Figure 2 was observed, while for the latter only a pair of isomers (α and γ in Figure 3) corresponding to (2a) was observed at the slow exchange limit. In these systems the observed isomers are likely to be the result of a rapidly equilibrating mixture and this is true for all the systems discussed in this work. In the present study, the methyl substituent isomers corresponding to both (2a) and (2b) (Figure 2) are observed in a 1 : 4 ratio favouring the assignment found for $[Os_3H(CO)_9(AsMe_2)(C_6H_3Me)]$. Also, the major isomer observed for (5) corresponds to the only pair of isomers observed for $[Os_3H(CO)_9(AsMe_2)(C_6H_3OMe)]$. There is apparently no adverse steric interaction in any of these complexes which would favour the existence of any particular isomer over another. Arce and Deeming[7] proposed that electronic influences are important in determining which isomer predominates. It is probable that in $[Os_3H(CO)_9(AsMe_2)(C_6H_3OMe)]$ there is a conjugative interaction of OMe with the aromatic ring favouring the α and γ type structures (Figure 3); there being an unfavourable competition between the OMe group, in the β and δ type structures, and the metal for the benzyne lowest unoccupied molecular orbital (l.u.m.o.) that would be involved in π bonding between the Os atom and the benzyne ligand. A similar argument would apply to the chlorine derivative (5), although to perhaps a lesser extent since the three-electron donor $AsMe_2$ group has been replaced by the one-electron hydride ligand. A complete type (5b) $^1$H n.m.r. spectrum was not obtained because of the low concentration of this isomer in solution.

The room temperature $^1$H n.m.r. spectrum of the dimethyl substituted complex, $[Os_3H_2(CO)_9(C_6H_2Me_2)]$ (6), shows only one isomer. The assignments are consistent with the methyl groups occupying the 3 and 5 positions on the ring (Figure 2). However, it should again be emphasised that the observed product is the result of a rapidly equilibrating mixture of isomers.

It is interesting to note that in the reaction with *trans*-stilbene to give the complex $[Os_3H_2(CO)_9(C_6H_3CHCHC_6H_5)]$ (4), where one arene ring is co-ordinated to the cluster as in (1), there is no evidence for the formation of a complex in which two triosmium units are bound to one stilbene molecule. The structure of (4) contrasts with that of $[Os_3H(CO)_{10}(CHCHPh)]$ obtained by the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with styrene.[17] In this derivative the styrene bonds to the cluster through the C=C double bond and not *via* the phenyl ring.

## Experimental

Infrared spectra were recorded as hexane solutions in 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer with CO calibrant. Mass spectra were obtained using an A.E.I. M.S. 12 instrument at 70 eV ionizing potential. Proton n.m.r. spectra were recorded on a Varian Associates CFT (80 MHz) spectrometer using an internal deuterium lock. Thin layer chromatography (t.l.c.) was carried out on commercial Merck plates coated with a 0.25-mm layer of silica. Solvents were dried and distilled before use; $[Os_3(CO)_{10}(NCMe)_2]$ was prepared by literature methods.[4]

*Preparation of* $[Os_3H_2(CO)_9(C_6H_2R^1R^2)]$ [$R^1$ = H; $R^2$ = H (1), Me (2), $Pr^n$ (3), CHCHPh (4), Cl (5); $R^1$ = Me; $R^2$ = Me (6)].—In a typical reaction, a solution of $[Os_3(CO)_{10}(NCMe)_2]$ in the appropriate arene was refluxed for 30 min. Alternatively an excess of the arene ($R^1$ = H; $R^2$ = $Pr^n$, or CHCHPh) was added to a hot solution of $[Os_3(CO)_{10}(NCMe)_2]$ in cyclohexane. The solvent was removed under vacuum and the dichloromethane-soluble residue chromatographed in hexane to yield several bands. The yellow band ($R_f$ 0.60) was characterised on the basis of i.r. and mass spectra as $[Os_3H_2(CO)_9(C_6H_2R^1R^2)]$. The yield was dependent on the arene used: $R^1$ = H; $R^2$ = H (37%), $R^2$ = Me (32%), $R^2$ = $Pr^n$ (30%), $R^2$ = CHCHPh (23%), $R^2$ = Cl (29%); $R^1$ = Me, $R^2$ = Me (27%).

*Molecular Structure Determination of* $[Os_3H_2(CO)_9(C_6H_4)]$ (1).—A single crystal of the complex (1) was mounted on a glass fibre with epoxy-resin adhesive, and unit-cell dimensions and space group determined *via* Weissenberg (Cu) *X*-ray photography. 7 223 Intensity data were recorded in the range $5 < 2\theta \leqslant 50°$ on a Stoe four-circle diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation and a 24-step $\omega/\theta$ scan technique. The step size was fixed at 0.05° and the time for each step varied between 0.5 and 3.0 s depending on the intensity obtained from a 0.5 s per step prescan. Three check reflections were monitored every 100 reflections throughout the data collection and showed no significant variations. Accurate cell dimensions were obtained from the centring of 54 reflections in the range $15 < 2\theta < 25°$.

The data were profile fitted on line,[18] and a semi-empirical absorption correction based on a pseudo-ellipsoid model and 300 azimuthal scan data from eight independent reflections were applied. Transmission factors ranged from 0.018 to 0.001 for the full data set. Lorentz polarisation corrections were also applied and equivalent reflections averaged to give 3 438 unique observed data [$F > 5\sigma(F)$].

*Crystal data.* $C_{15}H_6O_9Os_3$, $M$ = 900.80, Monoclinic, $a$ = 17.391(5), $b$ = 13.190(2), $c$ = 16.512(3) Å, $\beta$ = 92.39(2)°, $U$ = 3 784.3 Å$^3$, $D_m$ not measured, $Z$ = 8, $D_c$ = 3.16 g cm$^{-3}$, $F(000)$ = 3 168, Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 213.23 cm$^{-1}$, space group $P2_1/c$ from systematic absences.

**Table 3.** Atom co-ordinates (× $10^4$) for $[Os_3H_2(CO)_9(C_6H_4)]$ (1)

| Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|
| Os(1) | 10 029(1) | 2 600(1) | 4 226(1) |
| Os(2) | 8 324(1) | 2 753(1) | 4 509(1) |
| Os(3) | 8 836(1) | 2 050(1) | 3 058(1) |
| Os(4) | 5 035(1) | 2 896(1) | 1 661(1) |
| Os(5) | 3 341(1) | 2 544(1) | 1 951(1) |
| Os(6) | 3 805(1) | 3 506(1) | 576(1) |
| C(11) | 10 359(20) | 1 534(23) | 5 048(21) |
| O(11) | 10 525(17) | 892(21) | 5 395(19) |
| C(12) | 10 468(25) | 3 676(27) | 4 872(25) |
| O(12) | 10 767(18) | 4 343(19) | 5 175(15) |
| C(13) | 10 914(20) | 2 464(22) | 3 541(21) |
| O(13) | 11 417(19) | 2 523(23) | 3 119(19) |
| C(21) | 8 186(29) | 3 754(32) | 5 365(29) |
| O(21) | 8 088(22) | 4 301(23) | 5 833(17) |
| C(22) | 8 225(23) | 1 458(26) | 5 121(23) |
| O(22) | 8 165(19) | 765(23) | 5 415(21) |
| C(23) | 7 262(27) | 2 759(28) | 4 145(26) |
| O(23) | 6 623(17) | 2 895(24) | 3 958(20) |
| C(31) | 8 553(26) | 696(29) | 3 200(26) |
| O(31) | 8 397(21) | −161(19) | 3 248(22) |
| C(32) | 7 854(26) | 2 331(27) | 2 439(25) |
| O(32) | 7 316(17) | 2 436(26) | 2 086(21) |
| C(33) | 9 456(20) | 1 911(22) | 2 130(20) |
| O(33) | 9 824(21) | 1 857(26) | 1 570(16) |
| C(41) | 5 451(23) | 3 826(25) | 2 505(23) |
| O(41) | 5 685(25) | 4 401(24) | 2 980(21) |
| C(42) | 5 912(28) | 3 224(29) | 1 002(27) |
| O(42) | 6 354(17) | 3 346(31) | 604(23) |
| C(43) | 5 619(27) | 1 663(29) | 2 150(25) |
| O(43) | 5 810(24) | 977(20) | 2 317(23) |
| C(51) | 3 124(29) | 3 772(31) | 2 632(29) |
| O(51) | 2 962(20) | 4 408(25) | 3 012(19) |
| C(52) | 3 228(24) | 1 442(26) | 2 648(25) |
| O(52) | 3 265(21) | 768(22) | 3 141(20) |
| C(53) | 2 275(27) | 2 413(27) | 1 584(25) |
| O(53) | 1 695(15) | 2 368(22) | 1 310(13) |
| C(61) | 3 360(22) | 4 754(25) | 868(22) |
| O(61) | 3 194(17) | 5 507(20) | 1 055(19) |
| C(62) | 2 946(36) | 3 194(38) | −68(33) |
| O(62) | 2 379(25) | 3 039(27) | −432(21) |
| C(63) | 4 374(25) | 3 938(28) | −343(26) |
| O(63) | 4 771(22) | 4 087(24) | −859(17) |
| C(111) | 9 441(20) | 3 561(20) | 3 388(19) |
| C(112) | 8 641(20) | 3 698(21) | 3 579(20) |
| C(113) | 8 146(27) | 4 479(29) | 3 100(26) |
| C(114) | 8 504(29) | 4 980(31) | 2 458(28) |
| C(115) | 9 285(24) | 4 844(25) | 2 320(24) |
| C(116) | 9 776(22) | 4 144(23) | 2 760(21) |
| C(211) | 4 529(24) | 2 024(24) | 727(23) |
| C(212) | 3 661(23) | 1 727(26) | 993(23) |
| C(213) | 3 300(28) | 998(29) | 401(26) |
| C(214) | 3 642(32) | 509(35) | −168(31) |
| C(215) | 4 343(27) | 805(29) | −373(27) |
| C(216) | 4 762(22) | 1 579(24) | 37(22) |

The six unique Os atom positions were located by multi-solution sign-expansion techniques and all the remaining non-hydrogen atoms from subsequent electron-density difference syntheses. The aromatic H atoms were placed in idealised positions (C–H 1.08 Å) and constrained to ride on the relevant C atom; these atoms were assigned a common isotropic thermal parameter. The hydride ligands were not located. The structure was refined by blocked-cascade least squares with the Os and O atoms assigned anisotropic thermal parameters, and the C atoms assigned isotropic thermal parameters. In the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F) + 0.003|F|^2]^{-1}$ was applied and the refinement continued until convergence was reached. The final residuals were $R = 0.079$ and $R' = [\Sigma_w{}^{\frac{1}{2}}\Delta/\Sigma_w{}^{\frac{1}{2}}|F|] = 0.079$. The atomic fractional co-ordinates for the non-hydrogen atoms are listed in Table 3.

Complex neutral-atom scattering factors [19] were employed throughout. Computations were performed on the University of Cambridge IBM 370/165 computer using programs written by Professor G. M. Sheldrick. The molecular plot was drawn using the PLUTO program written by Dr. W. D. S. Motherwell.

## Acknowledgements

We thank the S.E.R.C. for financial support.

## References

1 A. J. Deeming, 'Transition Metal Clusters,' ed. B. F. G. Johnson, John Wiley and Sons, Chichester, 1980.

2 A. J. Deeming, R. E. Kimber, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1973, 2589; A. J. Deeming and M. Underhill, *ibid.*, 1974, 1415.

3 E. L. Muetterties, *Pure Appl. Chem.*, 1982, **54**, 83.

4 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407; B. F. G. Johnson, J. Lewis, T. I. Odiaka, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **216**, C56; A. J. Arce and A. J. Deeming, *J. Chem. Soc., Chem. Commun.*, 1982, 364; A. J. Deeming, I. Ghatak, D. W. Owen, and R. Peters, *ibid.*, p. 392.

5 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1981, 1879.

6 R. D. Adams, D. A. Katahira, and L.-W. Yang, *Organometallics*, 1982, **1**, 235.

7 A. J. Arce and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1982, 1155.

8 S. C. Brown, J. Evans, and L. E. Smart, *J. Chem. Soc., Chem. Commun.*, 1980, 1021.

9 C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 1972, 87.

10 G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organomet. Chem.*, 1972, **40**, C70.

11 E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, and T. A. Albright, *Chem. Rev.*, 1982, **82**, 499.

12 V. F. Allen, R. Mason, and P. B. Hitchcock, *J. Organomet. Chem.*, 1977, **140**, 297.

13 M. R. Churchill, B. G. DeBoer, and F. J. Rotella, *Inorg. Chem.*, 1976, **15**, 1843.

14 P. R. Raithby, 'Transition Metal Clusters,' ed. B. F. G. Johnson, John Wiley and Sons, Chichester, 1980.

15 J. R. Shapley, D. E. Samkoff, C. Bueno, and M. R. Churchill, *Inorg. Chem.*, 1982, **21**, 634.

16 M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.

17 R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby, and W. Clegg, *Acta Crystallogr., Sect. B*, 1982, **38**, 2689.

18 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

19 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

*Received* 11*th February* 1983; *Paper* 3/221