Products of the Reaction of $[H_2Os_3(CO)_{10}]$ with Cyclohexa-1,3-diene and Butadiene; *X*-Ray Structure of the Hexadienyl Complex $[HOs_3(CO)_9C_6H_7]$

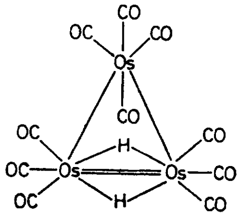
By ERIC G. BRYAN, BRIAN F. G. JOHNSON, JOHN W. KELLAND, and JACK LEWIS*
(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

and MARY MCPARTLIN
(*Department of Chemistry, The Polytechnic of North London, Holloway Road, London* N7 8DB)

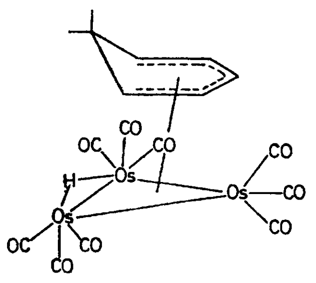
Summary $[H_2Os_3(CO)_{10}]$ reacts with cyclohexa-1,3-diene (C_6H_8) to give $[HOs_3(CO)_9C_6H_7]$ and $[Os_3(CO)_{10}C_6H_8]$ and the *X*-ray structure of $[HOs_3(CO)_9C_6H_7]$ is reported; butadiene (C_4H_6) reacts to give $[Os_3(CO)_{10}C_4H_6]$.

RECENTLY, structural and synthetic studies have shown the reactions of the *triangulo*-clusters $[Os_3(CO)_{12}]$ and $[H_2Os_3(CO)_{10}]$[1] (**1**) with simple alkenes and alkynes to be varied and interesting. Especially noteworthy is the variety of bonding modes these organometallic units adopt on combination with the triosmium unit which offer new models for the interaction of small organic molecules with metal surfaces. *X*-Ray studies, and spectroscopic and chemical evidence indicate that to date, attack on the Os_3 unit occurs with cleavage of C–H bonds and that oxidative-addition of C–H to three metal atoms occurs. We report here a new reaction of (**1**) with cyclohexa-1,3-diene in which, depending on the conditions, the major product is either a dienyl complex (**2**) corresponding to an oxidative-addition reaction, or a di-substituted triosmium carbonyl (**3**). We also report that on reaction with Ph_3CBF_4, complex (**2**) yields a benzene derivative (**4**) and complex (**3**) a dienyl derivative

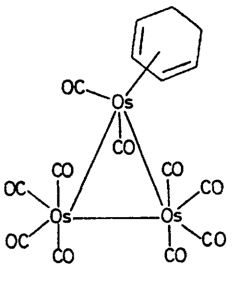
(**5**). Butadiene reacts with (**1**) under mild conditions to yield the butadiene analogue of (**3**).



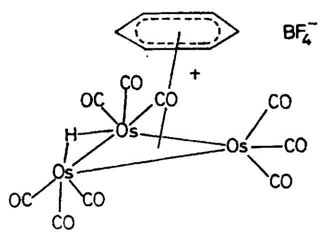
(1)



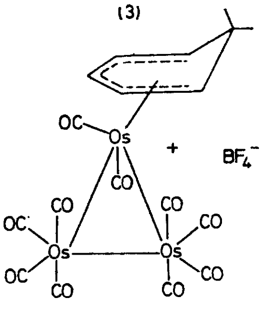
(2)



(3)



(4)



(5)

A solution of (**1**) and cyclohexa-1,3-diene in hexane at 25 °C yielded, after 40 h, a mixture of two products which were readily separated by t.l.c. on silica. The major product was identified as the di-substituted osmium carbonyl derivative $[Os_3(CO)_{10}C_6H_8]$ (**3**) on the basis of its spectroscopic properties [i.r. (C_6H_{12}) 2110m, 2061s, 2031s, 2021vs, 2007s, 1979m, 1970w, and 1934w cm^{-1}; *m/e* 936 (M^+), 856 $(M - C_6H_8^+)$, and peaks corresponding to $M - C_6H_8(CO)_n^+$ $(n = 1$—$10)$]. The ^1H n.m.r. spectrum (35 °C, 80 MHz, CFT 20 spectrometer, Me_4Si internal reference): τ 4·50 (2H, m), 6·25 (2H, m), and 7·53 (4H, s), is fully consistent with the assigned structure (**3**) and is similar to the ^1H n.m.r. spectrum of cyclohexa-1,3-dienetricarbonyliron.[2] A low-temperature ^{13}CO limiting spectrum (−80 °C) was obtained which displayed features corresponding to the static structure (**3**). Thus nine signals of relative intensity 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 2 were observed which, allowing for the accidental degeneracy of two single resonances, is compatible with structure (**3**). Other possible structures would possess higher symmetry and would require fewer than nine signals. The second product was a yellow, air-stable, solid whose spectroscopoic properties [i.r. (C_6H_{12}) 2080m, 2058s, 2034s, 2021s, 1992s, 1960m, and 1953m cm^{-1}; *m/e* 908 (M^+), and peaks corresponding to $M - (CO)_n^+$ $(n = 1$—$9)$] indicated that it was $[Os_3(CO)_9C_6H_8]$ (**2**). In the ^1H n.m.r. spectrum at 35 °C a high-field resonance (relative intensity 1) was observed at τ 29·3; in addition, signals at τ 4·12 (1H, t), 4·56 (1H, d), 5·23 (2H, dd), 7·06 (2H, d), and 7·30 (1H, d) may be assigned to a co-ordinated hexadienyl unit; spin decoupling experiments are consistent with this assignment. A structure corresponding to (**2**) was therefore indicated. This was confirmed by a single-crystal *X*-ray structure determination (see below).

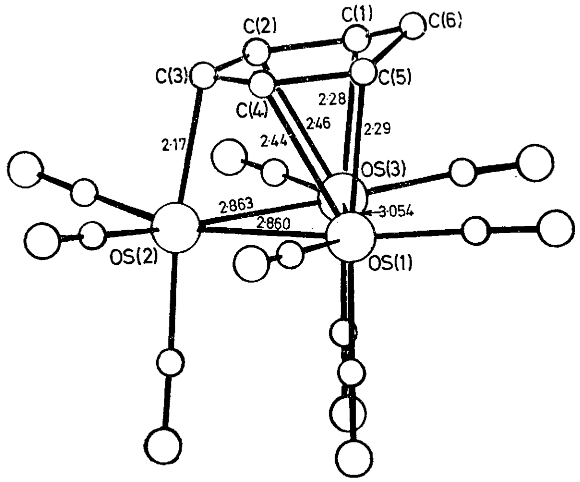


FIGURE. The structure of $[HOs_3(CO)_9C_6H_7]$ (**2**). The e.s.d.s of the bond lengths (Å) are: Os–Os 0·002 and Os–C 0·03 Å. Relevant non-bonding contacts are: Os(2)–C(2), Os(2)–C(4) 2·83 Å; Os(1)–C(6), Os(3)–C(6) 3·22 Å.

When the reaction between (**1**) and cyclohexa-1,3-diene was carried out in refluxing octane it was observed that after 5 min all the $[H_2Os_3(CO)_{10}]$ had reacted to give (**2**) and only a small amount of (**3**). We were able to show that (**3**) was not an intermediate in the formation of (**2**) since on heating a pure sample of (**3**) in refluxing octane for 5 min complex (**2**) was not obtained, although in refluxing toluene for 5 h complex (**2**) was obtained in 20% yield. Treatment of (**2**) with Ph_3CBF_4 in CH_2Cl_2 led to H^- abstraction and the formation of an unstable cationic complex (**4**). The ^1H n.m.r. spectrum of this complex was simple, exhibiting one singlet resonance in the aromatic region (τ 4·17) and one singlet resonance at τ 27·2. The i.r. spectrum (Nujol; 2177m, 2090s, 2048br,vs, 2028s, 2006m, 1982 m, and 1972m cm^{-1}) indicates low symmetry and is somewhat similar to that of (**2**). These data are consistent with more than one structure but, in view of the method of preparation, structure (**4**) is the more likely.

Butadiene reacts with (**1**) in hexane at 25 °C, after 12 h, to give the butadiene analogue of (**3**). The i.r. spectrum of this yellow complex was very similar to that of (**3**), $(C_6H_{12}$: 2112m, 2062s, 2031s, 2026s, 2023s, 2009s, 1982m, 1943w, 1932vw cm$^{-1})$; however, the mass spectrum showed the parent peak, followed by loss of CO, followed by loss of C_4H_6. The ^1H n.m.r. spectrum at 35 °C [τ 4·63 (2H, 2 overlapping t), 7·58 (2H, m), and (2H, dd) resembles that of butadiene tricarbonyliron[3] and shows the same variation with temperature as (**3**).

Single-crystal *X*-ray analysis has shown that the complex (**2**) has the structure shown in the Figure; this is consistent with hydrogen bridging between Os(1) and Os(3). The crystals of (**2**), $M = 902·8$, are monoclinic, space-group

$P2_1$; $a = 8{\cdot}477(2)$, $b = 12{\cdot}056(4)$, $c = 9{\cdot}013(3)$ Å, $\beta = 92{\cdot}88(2)°$; $Z = 2$. Full matrix least-squares refinement of the atomic parameters (Os anisotropic) using 2044 independent reflections (Philips PW1100 diffractometer, Mo-K_α radiation) has given an R-value of 0·044. The principal bond lengths are shown in the Figure.

The triangle of osmium atoms is nearly isosceles, with a non-crystallographic plane of symmetry perpendicular to it and through Os(2), C(6), and C(3). In the cyclohexadienyl ligand the five carbon atoms which form the pentadienyl fragment are planar to within 0·01 Å, and C(6) is 0·32 Å above this plane. The pentadienyl plane slopes away from the osmium triangle at an angle of 3·3° so that the Os(2)–C(3) bond (2·17 Å) is significantly shorter than the other Os–C bonds (2·28, 2·45 Å) and similar in length to Os–C σ-bonds observed in other cluster compounds.[4] The angles around C(3), C(4)–C(3)–C(2) = 114(2)°, Os(2)–C(3)–C(2) = 99(2)°, and Os(2)–C(3)–C(4) = 99(2)°, are also consistent with considerable σ-character in the Os(2)–C(3) bond. It seems the bonding requirements of a *triangulo*-trimetal cluster favour more hexa-1,4-diene character in the cyclohexadienyl ligand than is observed in its mononuclear complexes.[5]

We thank the S.R.C. for financial support and Johnson, Matthey and Company Limited for the loan of OsO_4.

(*Received, 8th December* 1975; *Com.* 1362.)

---

[1] S. A. R. Knox, J. W. Koepke, M. A. Andrews, and K. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3942.

[2] A. J. Birch, P. E. Cross, D. A. White, J. Lewis, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

[3] D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1969, **91**, 6968.

[4] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J.C.S. Chem. Comm.*, 1972, **87**; G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1974, 1813.

[5] M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950.