

Stepwise Cluster Synthesis *via* Addition Reactions of $[\text{OsH}_2(\text{CO})_4]$ and $\text{Na}_2[\text{Os}(\text{CO})_4]$; the X-Ray Crystal Structure of $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$

Evert J. Ditzel, H. Diane Holden, Brian F. G. Johnson, Jack Lewis,* Arthur Saunders, and Michael J. Taylor

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

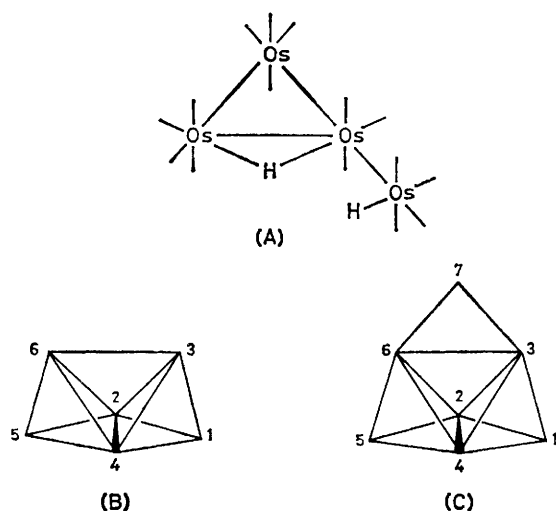
$[\text{OsH}_2(\text{CO})_4]$ and $\text{Na}_2[\text{Os}(\text{CO})_4]$ displace acetonitrile from Os_3 cluster species to afford $[\text{Os}_4\text{H}_2(\text{CO})_{15}]$, $[\text{Os}_4\text{H}_2(\text{CO})_{14}(\text{MeCN})]$, and $[\text{Os}_4\text{H}_2(\text{CO})_{13}]$ whilst Os_6 clusters afford $[\text{Os}_7\text{H}_2(\text{CO})_{21}]$ and $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$ in high yields, thereby allowing the stepwise conversion of Os_n into Os_{n+1} clusters; the structure of $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$ has been established by X-ray analysis.

Although osmium clusters of nuclearity $n = 3$ to $n = 10$ have recently been isolated and characterised,¹ their syntheses are not trivial. In general, pyrolysis methods have been employed, which usually result in a range of products.² In Scheme 1 the results of the reaction between $[\text{OsH}_2(\text{CO})_4]$ and acetonitrile complexes of osmium are reported and demonstrate for the first time a synthetic approach to the stepwise build-up of osmium clusters. The addition of $[\text{OsH}_2(\text{CO})_4]$ to Pt^0 and Fe^0 complexes has previously been reported.³

$[\text{OsH}_2(\text{CO})_4]$ readily displaces acetonitrile from $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ to afford $[\text{Os}_4\text{H}_2(\text{CO})_{15}]$ (1).[†] The ^1H n.m.r. spectrum exhibits one resonance at $\delta -9.6$ with a single $^{187}\text{Os}-\text{H}$ coupling⁴ and a second at $\delta -19.3$ exhibiting two $^{187}\text{Os}-\text{H}$

^1H n.m.r. spectrum exhibits one resonance at $\delta -9.6$ with a single $^{187}\text{Os}-\text{H}$ coupling⁴ and a second at $\delta -19.3$ exhibiting two $^{187}\text{Os}-\text{H}$

[†] (1) I.r. (hexane) 2106(m), 2075(s), 2054(s), 2040(w), 2028(w, sh), 2019(m), 2010(m), 2001(m), and 1991(w) cm^{-1} ; m/z 1188 corresponding to $[\text{Os}_4\text{H}_2(\text{CO})_{15}]^+$; ^1H n.m.r. $\delta -9.6$ (1H, s, J_{OsH} 37.4 Hz) and -19.3 (1H, s, J_{OsH} 25.5, 36.0 Hz); ^{13}C n.m.r. δ 194.5 (2C), 184.8 (2C), 182.2 (2C), 182.0 (1C), 177.4 (1C), 176.2 (2C), 172.5 (1C), 171.2 (1C), 168.2 (1C), 166.3 (1C), and 164.6 (1C) p.p.m.



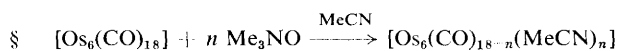
couplings, characteristic of terminal and bridging hydrides, respectively. The ^{13}C n.m.r. spectrum exhibits four resonances of intensity two, and seven of intensity one. These data are consistent with a 'spiked-triangle' geometry (A). Complex (1) is a 64-electron cluster and the formation of four metal-metal bonds is consistent with each metal atom obeying the 18-electron rule.

$[\text{OsH}_2(\text{CO})_4]$ also displaces acetonitrile from $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ to produce $[\text{Os}_4\text{H}_2(\text{CO})_{14}(\text{MeCN})]$ (2).[‡] Complex (2) is also a 64-electron cluster and the n.m.r. data are consistent with structure (A) for the arrangement of metal atoms. Complexes (1) and (2) are closely related to $[\text{Os}_3\text{ReH}(\text{CO})_{16}]^5$ and $[\text{Os}_3\text{ReH}(\text{CO})_{15}(\text{MeCN})]^6$ in which an $\text{Re}(\text{CO})_5$ group has been replaced by the isoelectronic $\text{OsH}(\text{CO})_4$ group.

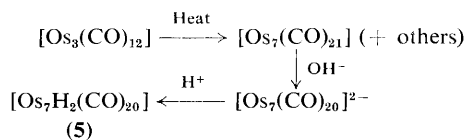
The cluster $[\text{Os}_4\text{H}_2(\text{CO})_{13}]$ has previously only been available in small quantities as a by-product of the reaction between $\text{Na}[\text{BH}_4]$ and $[\text{Os}_3(\text{CO})_{12}]$,⁷ which has impeded attempts to investigate its chemistry. The reaction of $\text{Na}_2[\text{Os}(\text{CO})_4]$ with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ at elevated temperature (Scheme 1), however, produces a mixture of cluster anions, which on protonation gives high yields of $[\text{Os}_4\text{H}_2(\text{CO})_{13}]$.

$[\text{OsH}_2(\text{CO})_4]$ will also displace acetonitrile from the hexanuclear clusters $[\text{Os}_6(\text{CO})_{17}(\text{MeCN})]$ and $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$,[§] to afford $[\text{Os}_7\text{H}_2(\text{CO})_{21}]$ (3)[¶] and $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$ (4)[¶] respec-

[‡] (2) I.r. (tetrahydrofuran) 2113(w), 2085(s), 2059(s), 2039(w), 2027(m, sh), 2017(m, br), 2001(m, br), and 1971(w, br) cm^{-1} ; ^1H n.m.r. δ 2.5 (3H, s), -9.7(1H, s), and -17.2 (1H, s).

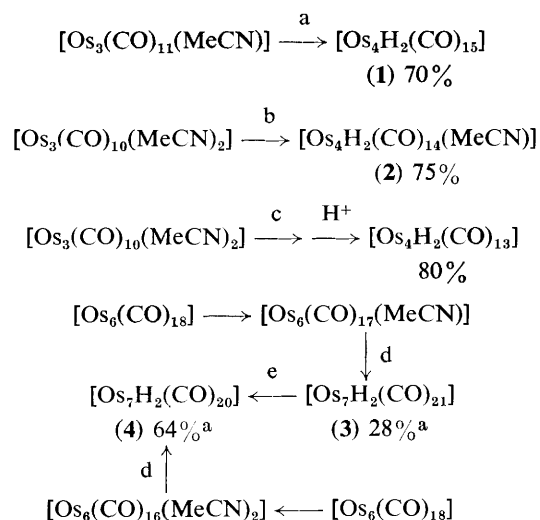


B. F. G. Johnson, J. Lewis, and M. Suss-Fink, unpublished results.



(5) i.r. 2072(vs), 2062(m), 2042(w), and 2027(m) cm^{-1} . B. F. G. Johnson, J. Lewis, and M. Vargas, unpublished results.

[¶] (3) I.r. (CH_2Cl_2) 2111(w), 2084(s), 2073(s), 2060(vs), 2024(vs), 2005(m, sh), and 1973(w, br) cm^{-1} ; ^1H n.m.r. δ -19.9 (1H, d) and -22.1 (1H, d, J_{HH} 2 Hz). (4) I.r. (CH_2Cl_2) 2116(w), 2086(s), 2065(vs), 2053(s), 2022(m), 2004(m), and 1936(w, br) cm^{-1} ; m/z corresponding to $[\text{Os}_7\text{H}_2(\text{CO})_{20}]^+$; ^1H n.m.r. δ -14.3 (s).



Scheme 1. (a) $[\text{OsH}_2(\text{CO})_4]$, CH_2Cl_2 , room temp. for 15 min.; (b) $[\text{OsH}_2(\text{CO})_4]$, THF, room temp. for 15 min; (c) $\text{Na}_2[\text{Os}(\text{CO})_4]$, THF, reflux for 1 h; (d) $[\text{OsH}_2(\text{CO})_4]$, CH_2Cl_2 , room temp. for 24 h; (e) cyclohexane, reflux for 1 h. ^a Yields from $[\text{Os}_6(\text{CO})_{18}]$.

tively. A second isomer of $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$ (5) is produced by the protonation of $[\text{Os}_7(\text{CO})_{20}]^{2-}$.[§] The i.r. spectra of (4) and (5) are dissimilar and their mass spectra both reveal ions corresponding to $[\text{Os}_7\text{H}_2(\text{CO})_{20}]^+$, but with dissimilar breakdown patterns. The i.r. spectrum of (3) is different from that of both (4) and (5), but the mass spectrum of (3) is identical to that of (4). It is therefore likely that (3) is being converted into (4) in the mass spectrometer, in accord with our observation that (3) is transformed to (4) on heating in cyclohexane (Scheme 1).

Crystals of (4) suitable for X-ray analysis have been obtained by slow evaporation of a CH_2Cl_2 -hexane solution and the structure is shown in Figure 1 together with some important bond parameters.** The molecule as a whole exhibits approximate C_{2v} symmetry, with the 2-fold axis passing through Os(7) and bisecting the Os(3), Os(6) and the Os(2), Os(4) bonds.

The heavy metal atom framework is probably best considered as being derived from $[\text{Os}_6(\text{CO})_{18}]$ (B) by the addition of one extra atom [Os(7)], to give a triangle linked to the original Os_6 core through a common edge [Os(3)-Os(6)] (C). The three fused tetrahedra of $[\text{Os}_6(\text{CO})_{18}]$ have been considerably distorted in (4) with osmium-osmium bond lengths varying between 2.663(3) and 2.993(3) Å. Potential energy calculations suggest that the hydrides asymmetrically cap the faces Os(2)Os(3)Os(6) and Os(3)Os(4)Os(6), lying closer to the Os(3) and Os(6) atoms, although they were not located directly in the X-ray analysis. The shortest osmium-osmium

** *Crystal data:* $\text{C}_{20}\text{H}_2\text{O}_{20}\text{Os}_7$ $M = 1893.62$, monoclinic, space group $P2_1/c$, $a = 12.239(2)$, $b = 12.405(2)$, $c = 20.935(4)$ Å, $\beta = 93.33(2)^\circ$, $U = 3137.1(10)$ Å³, $Z = 4$, $D_c = 4.01$ g cm^{-3} , $F(000) = 3255$, graphite monochromated Mo- $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K\alpha) = 279.99$ cm^{-1} . The diffracted intensities were measured to $2\theta_{\text{max}} = 45.0^\circ$ on a Stoe four-circle diffractometer and were corrected for absorption. 2525 reflections [$F > 5\sigma(F)$] were used to solve the structure (utilising direct methods and Fourier difference techniques). Refinement was by blocked-cascade least-squares (Os anisotropic; C, O isotropic) to $R = 0.070$ and $R_w = 0.072$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by a full literature citation for this communication.

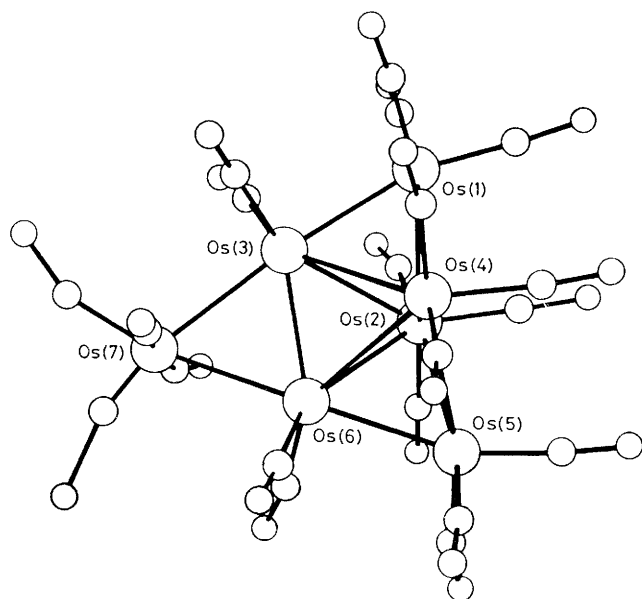


Figure 1. The molecular structure of $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$. Bond lengths: Os(1)–Os(2), 2.830(3); Os(1)–Os(3), 2.715(4); Os(1)–Os(4), 2.885(4); Os(2)–Os(3), 2.981(3); Os(2)–Os(4), 2.793(3); Os(2)–Os(5), 2.829(4); Os(2)–Os(6), 2.993(4); Os(3)–Os(4), 2.912(4); Os(3)–Os(6), 2.665(4); Os(3)–Os(7), 2.810(4); Os(4)–Os(5), 2.925(3); Os(4)–Os(6), 2.879(4); Os(5)–Os(6), 2.697(4); Os(6)–Os(7), 2.787(4) Å. Bond angle: Os(3)–Os(7)–Os(6), 56.9(1)°.

bond length is that which is bridged by the seventh osmium as an $\text{Os}(\text{CO})_4$ unit, and represents a contraction of *ca.* 0.05 Å compared to the analogous distance in $[\text{Os}_6(\text{CO})_{18}]$.

In terms of electron counting, this complex is a 98-electron system, which is consistent with the existence of the 14 observed metal–metal bonds. It does not, however, adopt a regular polyhedral framework.

It is noteworthy that the two isomers of $[\text{Os}_7\text{H}_2(\text{CO})_{20}]$, (4) and (5), were obtained by different synthetic routes; (4) by an addition reaction under mild conditions and (5) by (in the first

step) a pyrolysis reaction. We are currently attempting to obtain crystals of (5) suitable for X-ray analysis but, in view of its method of synthesis, it is likely that the metal framework is 'closed' with a more even carbonyl distribution than that found in (4).

The addition of $[\text{OsH}_2(\text{CO})_4]$ to osmium clusters containing labile ligands allows a controlled step-wise synthesis of clusters under very mild conditions. This has resulted in the isolation of clusters with novel open geometries and promises to provide a useful synthetic route to numerous interesting and potentially reactive molecules.

We thank the 'Tunku Abdul Raman' Foundation for a Fellowship (to M.J.T.) and the Royal Commission for the Exhibition of 1851 and the New Zealand University Grants Committee for a studentship (to E.J.D.).

Received, 15th September 1982; Com. 1097

References

- 1 B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 225.
- 2 C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1975, 2606.
- 3 (a) J. R. Moss and W. A. G. Graham, *J. Organomet. Chem.*, 1970, **23**, C23; (b) M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1971, 1288; (c) L. J. Farrugia, J. A. K. Howard, P. Mitraprachachon, J. L. Spencer, F. G. A. Stone, and P. Woodward, *ibid.*, 1978, 260.
- 4 E. C. Constable, B. F. G. Johnson, J. Lewis, G. Pain, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 754.
- 5 J. R. Shapley, G. A. Pearson, M. Tachikawa, G. E. Schmidt, M. R. Churchill, and F. J. Hollander, *J. Am. Chem. Soc.*, 1977, **99**, 8064.
- 6 (a) M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1981, **20**, 4124; (b) M. R. Churchill, F. J. Hollander, R. A. Lashewycz, G. A. Pearson, and J. R. Shapley, *J. Am. Chem. Soc.*, 1981, **103**, 2430.
- 7 B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc. A*, 1968, 2859.
- 8 R. Mason, K. M. Thomas, and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1973, **95**, 3802.