The Chemistry of Polynuclear Compounds. Part 30.[1] Some Reactions of Dodecacarbonyltetrahydridotetraosmium: The Molecular and Crystal Structure of Trihydrido-μ_2-iodo-*cyclo*-tetrakis(tricarbonylosmium)-(4*Os–Os*)

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Dodecacarbonyltriosmium reacts with H_2 under pressure to produce $[Os_4(CO)_{12}H_4]$ almost quantitatively. Methanolic K[OH] converts this into $[Os_4(CO)_{12}H_3]^-$ which gives the title compound $[Os_4(CO)_{12}H_3I]$ with I_2. Crystals of $[Os_4(CO)_{12}H_3I]$ are monoclinic, with a = 17.307(8), b = 8.040(3), c = 17.760(9) Å, β = 119.80(2)°, space group $C2/c$, and Z = 4. The final residuals for 2 724 unique observed reflections are R 0.036 and R' 0.039. The four Os atoms are in a ' butterfly ' configuration: one edge has been extended and a bridging iodine inserted [Os–I 2.749(4) Å]. A crystallographic two-fold axis passes through the iodine atom and bisects the opposite Os–Os bond. The Os–Os distances are 2.876(1) (two), 2.927(3), and 3.052(1) Å (two): the crystallographic symmetry, ^1H n.m.r. spectrum, and geometrical arrangements of the carbonyls indicate that the three longest Os–Os bonds are hydride-bridged. Methanolic Na(OMe) converts $[Os_4(CO)_{12}H_4]$ into $[Os_4(CO)_{11}(CO_2Me)H_4]^-$, isolated as the $[N(PPh_3)_2]^+$ salt.

THE direct reaction of H_2 with $[Os_3(CO)_{12}]$ at elevated temperatures and atmospheric pressure[2] gives samples of $[Os_4(CO)_{12}H_4]$ contaminated with $[Os_3(CO)_{10}H_2]$, $[Os_4(CO)_{13}H_2]$, and $[Os_3(CO)_{12}]$, which are difficult to purify by standard techniques. We have developed an improved synthesis of $[Os_4(CO)_{12}H_4]$ from $[Os_3(CO)_{12}]$ which has enabled us to investigate some of the chemistry of this elusive hydride. All attempts to grow crystals suitable for *X*-ray diffraction have failed. The preparation and single-crystal *X*-ray study of $[Os_4(CO)_{12}H_3I]$ provide the first structure determination of an Os_4 cluster and indicate a possible structure for $[Os_3(CO)_{12}H_4]$.

RESULTS AND DISCUSSION

Treatment of $[Os_3(CO)_{12}]$ with hydrogen gas at 100 °C under pressure (120 atm) † leads almost quantitatively to $[Os_4(CO)_{12}H_4]$. This compound dissolves slightly in methanol to give a pale yellow solution. On stirring with K[OH] more $[Os_4(CO)_{12}H_4]$ dissolves to give a more intensely coloured solution, from which the anion $[Os_4(CO)_{12}H_3]^-$ can be precipitated as the $[NMe_4]^+$ or $[N(PPh_3)_2]^+$ salts; these were characterised by C and H analysis, conductivity measurements, and i.r. and n.m.r. spectroscopy. The ^1H n.m.r. spectrum of the anion over the range 0 to −70 °C showed three signals at τ 28.1, 28.7, and 30.8. At >0 °C coalescence occurs and at *ca.* 30 °C a single broad resonance is observed. This behaviour parallels that found for the ruthenium analogue,[3] and suggests the presence of two isomers (Figure 1) at low temperature, with fluxional behaviour and rapid interconversion at elevated temperatures. Unlike the ruthenium analogue, no ^1H–^1H coupling is observed for $[Os_4(CO)_{12}H_3]^-$. Low-temperature i.r. spectra of CH_2Cl_2 solutions were also consistent with the presence of two isomers, but because of limited solubility the spectra were of poor quality.

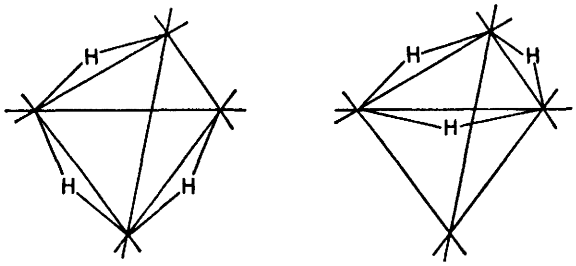

FIGURE 1 The two possible isomers of $[Os_4(CO)_{12}H_3]^-$

Treatment of $[Os_4(CO)_{12}H_3]^-$ with I_2 (1 mol) in

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† Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

[1] Part 29, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1977, 838.

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

[3] J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1975, **97**, 3947.

methanol gives $[Os_4(CO)_{12}H_3I]$. The composition after recrystallisation was confirmed by C and H analysis and mass, n.m.r., and i.r. [ν(CO)] spectroscopy. The ^1H Fourier-transform n.m.r. spectrum at 0 °C showed two sharp singlets (τ 27.75 and 27.35) in the intensity ratio 2 : 1. The spectrum was unchanged on cooling to −80 °C, but coalesced to a broad single resonance at room temperature, indicating fluxional behaviour.

Table 1

Bond lengths (Å) *

Os(1)–Os(2)	2.876(1)	Os(2)–C(22)	1.875(13)
Os(1)–Os(2′)	3.052(1)	Os(2)–C(23)	1.866(12)
Os(2)–Os(2′)	2.927(4)	C(11)–O(11)	1.125(14)
Os(1)–I(1)	2.749(4)	C(12)–O(12)	1.132(13)
Os(1)–C(11)	1.925(12)	C(13)–O(13)	1.123(15)
Os(1)–C(12)	1.915(12)	C(21)–O(21)	1.132(13)
Os(1)–C(13)	1.880(12)	C(22)–O(22)	1.167(15)
Os(2)–C(21)	1.942(11)	C(23)–O(23)	1.178(14)

* Primes indicate symmetry-related atoms.

Table 2

Bond angles (°)

Os(2)–Os(1)–I(1)	90.4(2)	I(1)–Os(1)–C(11)	89.2(4)
Os(1)–Os(2)–Os(2′)	63.5(2)	I(1)–Os(1)–C(12)	88.8(4)
Os(1)–Os(2)–C(21)	170.6(3)	I(1)–Os(1)–C(13)	177.0(3)
Os(1)–Os(2)–C(22)	91.6(4)	Os(2)–Os(1)–C(11)	171.7(3)
Os(1)–Os(2)–C(23)	89.8(4)	Os(2)–Os(1)–C(12)	93.3(4)
C(21)–Os(2)–C(22)	97.2(5)	Os(2)–Os(1)–C(13)	89.4(4)
C(21)–Os(2)–C(23)	93.1(5)	C(11)–Os(1)–C(12)	95.0(5)
C(22)–Os(2)–C(23)	91.4(6)	C(11)–Os(1)–C(13)	90.5(5)
Os(2)–C(21)–O(21)	175.0(10)	C(12)–Os(1)–C(13)	94.2(5)
Os(2)–C(22)–O(22)	178.6(11)	Os(1)–C(11)–O(11)	177.9(10)
Os(2)–C(23)–O(23)	175.1(10)	Os(1)–C(12)–O(12)	177.4(10)
Os(1)–I(1)–Os(1′)	87.9(2)	Os(1)–C(13)–O(13)	176.2(9)

* Primes indicate symmetry-related atoms.

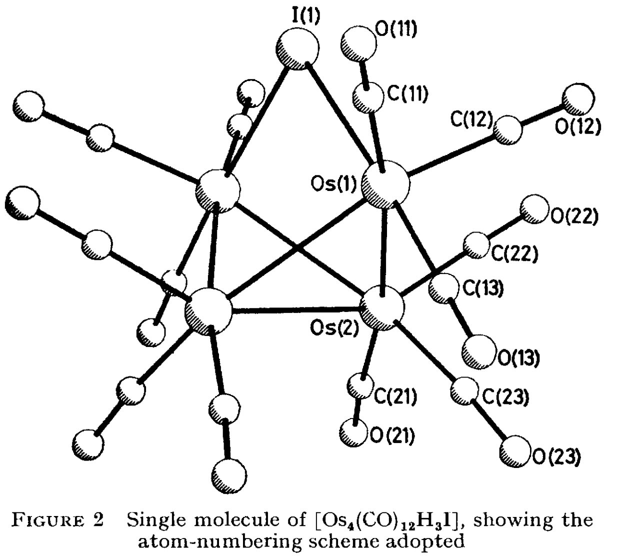
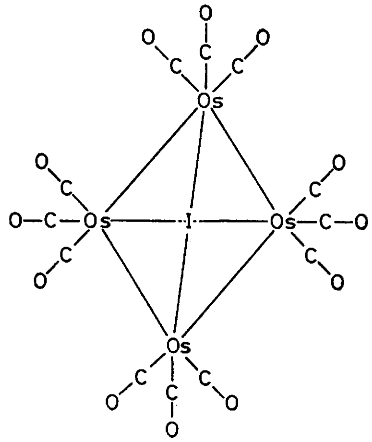


Figure 2 Single molecule of $[Os_4(CO)_{12}H_3I]$, showing the atom-numbering scheme adopted

The compound $[Os_4(CO)_{12}H_3I]$ exists in the solid state as discrete neutral molecules. Interatomic distances and interbond angles appear in Tables 1 and 2, respectively. Figure 2 shows a perspective plot of a single molecule, while (I) is a diagrammatic representation of the structure.



(I)

The four osmium atoms define a ' butterfly ' configuration in which two triangles share a common edge (the ' hinge ') but are not coplanar. There is no direct metal–metal bond across the ' wing tips ' [Os(1) · · · Os(1′) 3.817 Å], but the tips are symmetrically bridged by an iodine atom. Each osmium atom is bonded to three terminal carbonyl ligands, so including metal–metal bonding, but neglecting the hydrido-ligands (which were not located in the structure determination), all the four osmium atoms are six-co-ordinate, having slightly distorted octahedral geometries. The bond angles subtended at Os fall in the range 88.8(4)—97.2(5)°. The molecule has a two-fold crystallographic axis passing through the iodine atom and bisecting the Os(2)–Os(2′) ' hinge '.

The two shortest Os–Os bonds [2.876(1) Å] are in agreement with the mean Os–Os distance [2.877(3) Å] in $[Os_3(CO)_{12}]$, where there are no bridging ligands. The remaining Os–Os bonds [3.052(1) twice, and 2.927(3) Å bisected by the molecular two-fold axis] are more typical of values assigned to bonds with hydrido- or other bridges.[4-6] The crystallographic symmetry and 2 : 1 ^1H n.m.r. intensity ratio require one hydride to lie on the two-fold axis, presumably bridging the Os–Os bond. If the two remaining hydrides bridge the longest pair of Os–Os bonds, then all three hydrides occupy suitable holes in the carbonyl foliage of the molecule.

If the two Os–I bonds are replaced by a hydride-bridged Os–Os bond (bringing the two osmium atoms closer together) we generate the parent hydride $[Os_4(CO)_{12}H_4]$. The resulting molecular symmetry would then be close to or exactly D_{2d} ($\bar{4}2m$) with the inverse

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

[5] 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.

[6] G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organometallic Chem.*, 1972, **40**, C70.

tetrad axis perpendicular to the Os–Os bonds not bridged by hydrides. The simple i.r. and single-line ^{1}H n.m.r. spectrum are consistent with such a highly symmetric structure. The Os–I distance is not significantly different from the value [2.740(4) Å] in $[Os_5(CO)_{15}I]^-$,[7] where the terminal iodine is attached to an eight-co-ordinate osmium atom.

The carbonyls are approximately linear, and the angles at the carbon atoms do not vary from 180.0° by more than 5.0°. Mean Os–C and C–O bond lengths (1.901 and 1.145 Å respectively) are similar to those found in a number of Os_3 and Os_5 carbonyl clusters.[8-11] Figure 3 shows the molecular packing viewed along the *b* axis. The molecules are separated by typical van der Waals distances. There is only one intermolecular contact shorter than the sum of the van der Waals radii [O(12)–O(13′) 3.00 Å, where O(13′) is generated from O(13) by the transformation $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$].

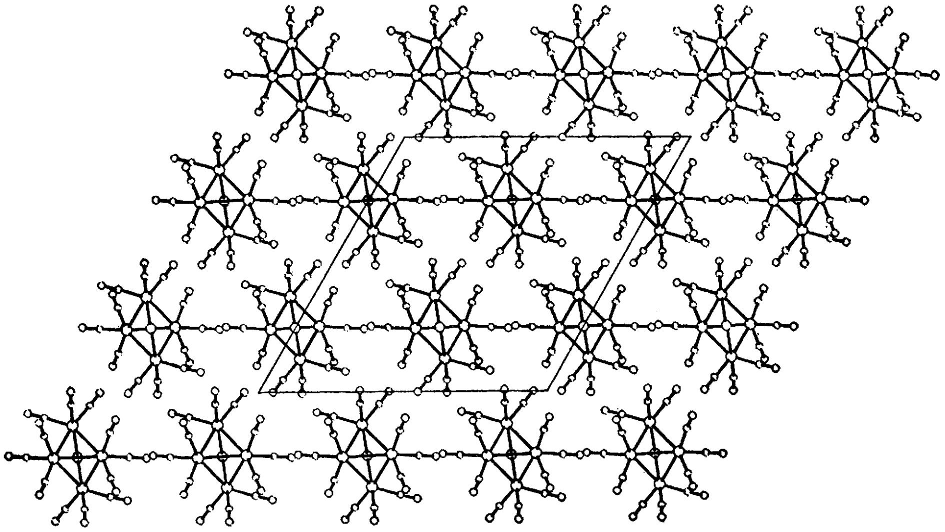

FIGURE 3 Projection of the structure down *b*, showing the molecular packing

EXPERIMENTAL

The compound $[Os_3(CO)_{12}]$ was prepared by a literature method.[12] All the solvents used were of the AnalaR type. Methanol was distilled over magnesium before reaction. All the manipulations were carried out under dry oxygen-free nitrogen. Infrared spectra were recorded on solutions in 0.5-mm NaCl cells on a Perkin-Elmer 257 spectrometer. Mass spectra were obtained using an A.E.I. M.S.12 instrument operating at 70 eV ionising potential. Hydrogen-1 n.m.r. spectra were recorded on Varian XL-100 or CFT-20 spectrometers. Microanalyses were carried out at the University of Cambridge Chemical Laboratory.

Preparations.—$[Os_4(CO)_{12}H_4]$. The compound $[Os_3(CO)_{12}]$ (2 g) in xylene (300 cm^3) was heated for 24 h at 100 °C in an autoclave (2 l) under hydrogen (120 atm at room temperature). A precipitate of $[Os_4(CO)_{12}H_4]$ (1.3 g) was found at the end of the reaction. After filtration, the clear xylene solution was evaporated to dryness. T.l.c. of the above mixture gave only $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{10}H_2]$. No higher osmium clusters were found when the reaction was carried out at higher temperature and pressure. For $[Os_4(CO)_{12}H_4]$: τ 30.5; ν(CO) at 2 085m, 2 066s, 2 020s, and 1 997w cm^{-1}; and *m/e* 1 102 (M^+).

$[NMe_4][Os_4(CO)_{12}H_3]$. The compound $[Os_4(CO)_{12}H_4]$ (50 mg) was stirred in methanolic K[OH] solution (400 mg of K[OH] in 10 cm^3 of MeOH). The $[Os_4(CO)_{12}H_4]$ gradually dissolved to give a yellow solution. Addition of a saturated aqueous solution of $[NMe_4]Cl$ to this solution immediately gave a yellow solid which could be separated by centrifuging. After washing with water, the yellow solid was dried *in vacuo* (yield 40 mg): ν(CO) at 2 048s, 2 022s, 2 000s, and 1 976w at 20 °C, 2 119w, 2 083w, 2 063w, 2 048s, 2 022s, 2 000s, and 1 976w cm^{-1} at −70 °C (Found: C, 16.8; H, 1.5. Calc. for $C_{16}H_{15}NO_{12}Os_4$: C, 16.4; H, 1.0%).

$[N(PPh_3)_2][Os_4(CO)_{11}(CO_2Me)H_4]$. The compound $[Os_4(CO)_{12}H_4]$ (50 mg) was stirred in methanol (10 cm^3) containing Na(OMe) (200 mg). When all the $[Os_4(CO)_{12}H_4]$ had dissolved, $[N(PPh_3)_2]Cl$ (200 mg) was added. On cooling to *ca.* −25 °C a pale yellow solid was deposited. This was washed with water and dried *in vacuo* (yield 30 mg): τ(OMe) 7.0; ν(CO) at 2 085w, 2 053s, 2 037s, 2 021s, 1 995m, and 1 975w cm^{-1} (Found: C, 11.0; H, 1.5. Calc. for $C_{49}H_{37}NO_{13}Os_4P_2$: C, 11.2; H, 1.2%).

$[Os_4(CO)_{12}H_3I]$. The salt $[NMe_4][Os_4(CO)_{12}H_3]$ (50 mg) was dissolved in methanol (10 cm^3). Methanolic iodine (0.1 cm^3, containing the stoicheiometric amount of iodine) was added. A yellow precipitate was immediately formed. The resulting mixture was stirred for another 15 min and then filtered. The yellow solid was recrystallised twice from cyclohexane (yield 20 mg): ν(CO) at 2 085s, 2 067s,

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[7] A. V. Rivera, personal communication.

[8] M. R. Churchill, B. G. DeBoer, J. R. Shapley, and J. B. Kesiter, *J. Amer. Chem. Soc.*, 1976, **98**, 2357.

[9] G. Ferraris and G. Gervasio, *J.C.S. Dalton*, 1974, 1813.

[10] C. R. Eady, J. J. Guy, B. F. G. Johnson, J. Lewis, M. C. Malatesta, and G. M. Sheldrick, *J.C.S. Chem. Comm.*, 1976, 807.

[11] B. E. Reichert and G. M. Sheldrick, *Acta Cryst.*, 1977, **B33**, 173.

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2 023 (sh), 2 020s, 2 010m, and 2 000w cm^{-1}; m/e 1 228 (M^+) (Found: C, 12.0; H, 0.4. Calc. for $C_{12}H_3IO_{12}Os_4$: C, 11.7; H, 0.2%).

X-*Ray Structural Analysis*.—Pale yellow crystals of $[Os_4(CO)_{12}H_3I]$, in the form of elongated rectangular blocks, were obtained from cyclohexane. 5 294 Reflection intensities were measured with a Philips PW 1100 four-circle diffractometer using a crystal of dimensions *ca*. 0.064 × 0.096 × 0.144 mm. Cell constants were derived from angular measurements of 25 strong high-angle reflections. A full hemisphere of data ($3.0 < 2\theta < 60.0°$) was collected using graphite-monochromated Mo-K_α radiation and a θ—2θ scan technique. Weak reflections which gave $I_t - 2(I_t)^{\frac{1}{2}} < I_b$ on the first scan were omitted, I_t being the intensity at the top of the reflection peak for a 10-s count and I_b the mean of two preliminary 5-s background measurements on either side of the peak. The background measuring time was proportional to I_b/I_i, where I_i is the total intensity recorded in the first scan of the reflection peak. A constant scan speed of 0.05° s^{-1} and a variable scan width [θ range = $(0.60 + 0.20\tan\theta)°$] were used. Three standard reflections measured every 3 h during data collection showed no significant variation in intensity.

The variance of the intensity I was calculated [13] as the sum of the variance due to counting statistics and $(0.03I)^2$, where the term in I^2 was introduced to allow for other sources of error.[14] I and $\sigma(I)$ were corrected for Lorentz and polarisation effects, and for extinction. An empirical absorption correction was applied, and reflections for which $I < 2\sigma(I)$ were rejected. Equivalent reflections were averaged to give 2 724 unique observed intensities.

Crystal data. $C_{12}H_3IO_{12}Os_4$, $M = 1\,226.8$, Monoclinic, $a = 17.307(8)$, $b = 8.040(3)$, $c = 17.760(9)$ Å, $\beta = 119.80(2)°$, $U = 2\,144.5$ Å^3, $D_c = 3.799$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 251.1 cm^{-1}, space group $C2/c$ from systematic absences and successful refinement.

The two independent osmium and the iodine atoms were located by multisolution sigma-2 sign expansion, and the carbon and oxygen atoms from a subsequent electron-difference synthesis. The structure was refined by full-matrix least-squares refinement, with anisotropic Os and I, and isotropic C and O. With weights $w = 1.7097/\sigma^2(F)$, $w\Delta^2$ was fairly independent of $|F_o|$ and $\sin\theta$. In the final cycle the mean shift-to-error ratio was 0.008, and residuals were R 0.036 and R' 0.039 ($R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$). A final difference synthesis computed at this stage revealed no significant peaks.

TABLE 3

Fractional atomic co-ordinates (× 10^4)

	x/a	y/b	z/c
Os(1)	788(1)	4 745(1)	3 724(1)
Os(2)	817(1)	2 587(1)	2 447(1)
I(1)	0 *	7 206(1)	2 500 *
C(11)	598(7)	6 064(13)	4 523(7)
O(11)	498(6)	6 796(14)	5 007(7)
C(12)	1 925(7)	5 699(13)	4 045(7)
O(12)	2 590(6)	6 252(12)	4 203(6)
C(13)	1 268(7)	3 016(12)	4 543(7)
O(13)	1 532(6)	2 022(13)	5 055(7)
C(21)	637(6)	1 040(11)	1 534(6)
O(21)	582(7)	61(12)	1 039(7)
C(22)	1 788(8)	3 732(14)	2 503(8)
O(22)	2 404(8)	4 420(14)	2 549(8)
C(23)	1 574(7)	1 138(12)	3 327(7)
O(23)	2 016(6)	128(12)	3 843(7)

* Parameter fixed.

Complex neutral-atom scattering factors [15] were employed. Table 3 lists the final atomic parameters, while details of the thermal parameters, molecular planes, and observed and calculated structure-factor amplitudes may be found in Supplementary Publication No. SUP 22248 (15 pp.).* After initial data processing on the North London Polytechnic ICL computer, all the computing was carried out on the University of Cambridge IBM 370/165 computer, using programs written by G. M. S., and the plotting program PLUTO written by Dr. W. D. S. Motherwell.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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