The Chemistry of Polynuclear Compounds. Part 31.[1] Synthesis of Undecacarbonylhydridotriosmate(1−) and its Reaction with Octadecacarbonylhexaosmium to give a Carboxylate-bridged Anionic Enneaosmium Species

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Treatment of $[Os_3(CO)_{12}]$ with KOH in MeOH gives the anion $[Os_3H(CO)_{11}]^-$; low-temperature ^{13}C n.m.r. spectroscopy reveals that the structure of this hydrido-cluster is the same as that established for $[Fe_3H(CO)_{11}]^-$ in the solid state; at higher temperatures, fluxional behaviour similar to that previously observed for $[Fe_3H(CO)_{11}]^-$ occurs. The $[Os_3H(CO)_{11}]^-$ anion reacts with $[Os_6(CO)_{18}]$ to produce the Os_9 anion $[(OC)_{10}HOs_3(\mu\text{-}CO_2)\text{-}Os_6(CO)_{17}]^-$ which contains an Os_3 and Os_6 unit linked by a CO_2 group. Carbon-13 n.m.r. spectroscopic studies reveal that the C atom of the CO_2 linkage arises from the $[Os_6(CO)_{18}]$.

PREVIOUS workers in this group have shown[2] that reaction of $[Os_3(CO)_{12}]$ with base followed by acidification gives the hydrido-complexes $[Os_3H_2(CO)_{10}]$ and $[Os_3H(OH)(CO)_{10}]$ in moderate amounts together with trace amounts of $[Os_4H_2(CO)_{13}]$ and $[Os_4H_4(CO)_{12}]$. Anionic species were regarded as reaction intermediates but were not characterised. The reactions of polynuclear metal clusters and their relevance to those occurring on metal surfaces (and possible catalytic reactions thereon) have encouraged the development of synthetic routes to the higher metalloclusters, in particular those containing six or more metal atoms.

Thermal cracking provides one general approach but, as in for example the pyrolysis of $[Os_3(CO)_{12}]$,[3] is non-selective. A classical approach to the general synthesis of clusters involves mixed-oxidation-state condensation.[4] The hexaosmium cluster $[Os_6(CO)_{18}]$ behaves as an electron acceptor and is reduced under a variety of conditions to give $[Os_6(CO)_{18}]^{2-}$. At the onset of this work we considered that treatment of $[Os_6(CO)_{18}]$ with a suitable osmium carbonyl anion would provide a general synthetic route to the larger polynuclear osmium carbonyls. In this paper we report the isolation of the anionic species $[Os_3H(CO)_{11}]^-$ and its reaction with $[Os_6(CO)_{18}]$ to give a complex containing nine osmium atoms. Some structural details of this complex have been published;[5] we report the full experimental details together with some variable-temperature ^{13}C n.m.r. data.

RESULTS AND DISCUSSION

Dodecacarbonyl-*triangulo*-triosmium, $[Os_3(CO)_{12}]$, when stirred with a solution of potassium hydroxide in methanol under nitrogen, slowly dissolves to give a red solution. On addition of $[N(PPh_3)_2]Cl$ or $[NMe_4]Cl$ in methanol (or water) to this solution red microcrystalline salts are precipitated. These red salts must be

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[1] Part 30, C. R. Eady, B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, K. Wong, and M. McPartlin, *J.C.S. Dalton*, 1978, 673.

[2] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc.* (*A*), 1968, 2859.

[3] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1975, 2606.

[4] E. L. Muetterties and W. H. Knoth, ' Polyhedral Boranes,' Marcel Dekker, New York, 1968.

[5] 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, 602.

separated rapidly by filtration and quickly washed with water to remove all traces of base. They are stable in the solid state but rapidly decompose in solution. In Table 1 are presented the data which enabled us to show that these salts contained the anion $[Os_3H(CO)_{11}]^-$. On the basis of these data, $[Os_3H(CO)_{11}]^-$ is considered to be isostructural with its iron analogue, $[Fe_3H(CO)_{11}]^-$.[6] This is confirmed by a variable-temperature ^{13}C n.m.r. study (*ca.* 40% ^{13}CO enriched) of the salt $[N(PPh_3)_2]$-$[Os_3H(CO)_{11}]$, details of which are shown in Figure 1. The low-temperature-spectra [Figure 1(*a*) and 1(*b*)] are consistent with the structure given in Figure 2 with assignments as shown.

TABLE 1

Characteristic data for $[Os_3H(CO)_{11}]^-$

$[N(PPh_3)_2][Os_3H(CO)_{11}]$	Found: C, 39.7; H, 2.30; N, 0.90% Calc.: C, 39.8; H, 2.20; N, 0.90% ν(CO) in CH_2Cl_2:* 2 038w, 2 021s, 1 996s, 1 951ms, 1 667w, br cm^{-1} ^1H Fourier-transform n.m.r. τ 2.4 (m), 23.58 (s) in CD_2Cl_2 at 35 °C
$[NMe_4][Os_3H(CO)_{11}]$	Found: C, 18.4; H, 1.40; N, 1.55% Calc.: C, 18.9; H, 1.35; N, 1.45%

* The $[NMe_4]^+$ salt shows a similar spectrum in acetone.

In spectrum 1(*a*) the doublet of intensity one centred at 273.4 p.p.m. may be assigned to the bridging group a. Doublets of intensity two centred at 185.8 and 181.1 p.p.m. together with a broad resonance (doublet?) at 173.9 p.p.m. also of intensity two may be associated with the three carbonyl ligands e, b, and g although no precise assignment can be made. The two singlets at 184.2 and 182.9 p.p.m. of relative intensity one may be attributed to carbonyls c and d which leaves, finally, the singlet of intensity two at 177.3 p.p.m. which can only be assigned to the two equivalent CO ligands f. We believe that the small but significant ^{13}C–^1H coupling associated with CO^c arises from a through-space effect arising from the close proximity of this group and the hydride ligand.

As the temperature is increased the resonances collapse and at —85 °C two broad signals are observed [Figure 1(*c*)] which at —50 °C have sharpened to one resonance at 179.0 p.p.m. This spectrum may be compared with that of $[Fe_3H(CO)_{11}]^-$ which at —30 °C shows two resonances of relative intensity 10 : 1; these coalesce at 0 °C and at 40 °C a sharp singlet is observed.[7] This n.m.r. study has established that the structure of $[Os_3H(CO)_{11}]^-$, in solution, is the same as that found for $[Fe_3H(CO)_{11}]^-$ in the solid state. The signal at *ca.* 179.0 p.p.m. in the —50 °C spectrum appears to be the average of the signals from all the non-bridging CO ligands although a resonance due to the CO bridge is not observed. By analogy with $[Fe_3H(CO)_{11}]^-$ we might assume that at —50 °C the ten terminal CO groups are fluxional and at higher temperatures this fluxionality also includes the bridging CO group.

The salt $[N(PPh_3)_2][Os_3H(CO)_{11}]$, when treated with 80% H_3PO_4 followed by extraction into chloroform, gives in good yield a yellow solid which has been characterised as $[Os_3H(OH)(CO)_{10}]$. Alternatively, acidification under anhydrous conditions using gaseous hydrogen chloride gives $[Os_3H_2(CO)_{11}]$[8] which loses carbon monoxide to give $[Os_3H_2(CO)_{10}]$. Addition of iodine to the same salt gives $[Os_3H(I)(CO)_{10}]$. Attempts to use the anion to produce larger clusters by treating it with $[Os_3(CO)_{12}]$ gave only trace amounts of $[Os_6(CO)_{18}]^{2-}$. However, the reaction of $[N(PPh_3)_2][Os_3H(CO)_{11}]$ with a stoicheiometric amount of $[Os_6(CO)_{18}]$ in dichloromethane under nitrogen gave, after purification by thin-layer chromatography (t.l.c.) and recrystallisation, brown-black air-stable crystals in good yield (*ca.* 80%). The

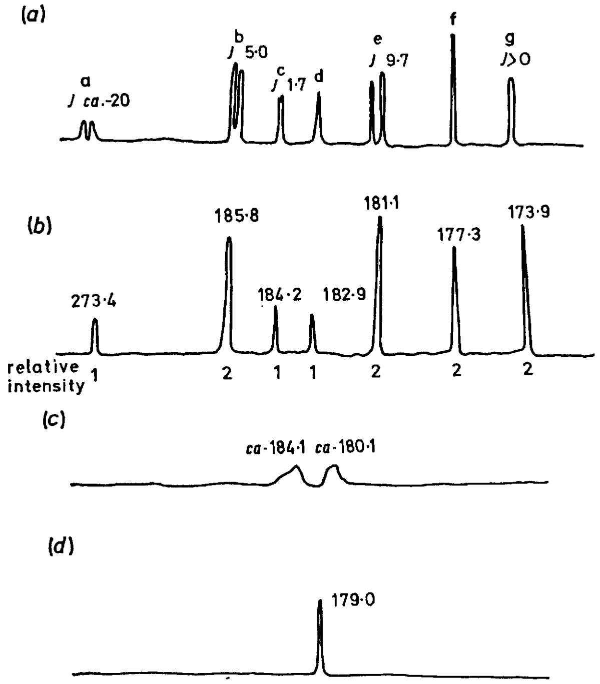

FIGURE 1 Variable-temperature ^{13}C(CO) n.m.r. spectra of $[N(PPh_3)_2][Os_3H(CO)_{11}]$: (*a*) at —105 °C, without ^1H spin decoupling; (*b*) at —105 °C, with ^1H spin decoupling; (*c*) at —85 °C, with ^1H spin decoupling; and (*d*) at —150 °C, with ^1H spin decoupling. Chemical-shift values are in p.p.m. downfield relative to $SiMe_4$, $J(^{13}C-^1H)$ in Hz

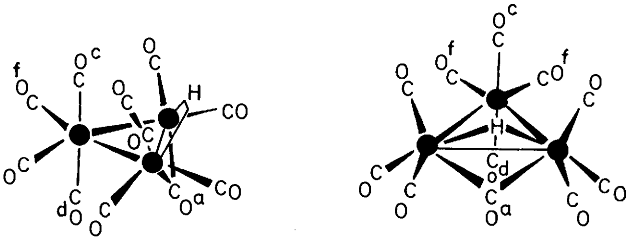

FIGURE 2 Structure of $[Os_3H(CO)_{11}]^-$

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[6] L. F. Dahl and J. F. Blount, *Inorg. Chem.*, 1965, **4**, 1373.

[7] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042.

[8] J. R. Shapley, J. B. Keister, M. R. Churchill, and B. G. de Boer, *J. Amer. Chem. Soc.*, 1975, 4145.

salt $[NMe_4][Os_3H(CO)_{11}]$ (using acetone as solvent) gave a similar product. In Table 2 are presented data for these products which have been characterised as salts of the anion $[(OC)_{10}HOs_3(\mu\text{-}O_2C)Os_6(CO)_{17}]^-$, and in Figure 3 is shown the structure of the $[N(PPh_3)_2]^+$ salt established from a single-crystal *X*-ray diffraction study.[5,9] The complex is not an Os_9 cluster, but consists instead of an Os_3 unit linked to an Os_6 unit by a CO_2 bridge; this bridging group forms a symmetrical ring (within the limits of experimental accuracy) described by atoms Os(2)–O(1)–C–O(2)–Os(3). The strong i.r. band observed at 1 265 cm^{-1} is consistent with this symmetrical arrangement.

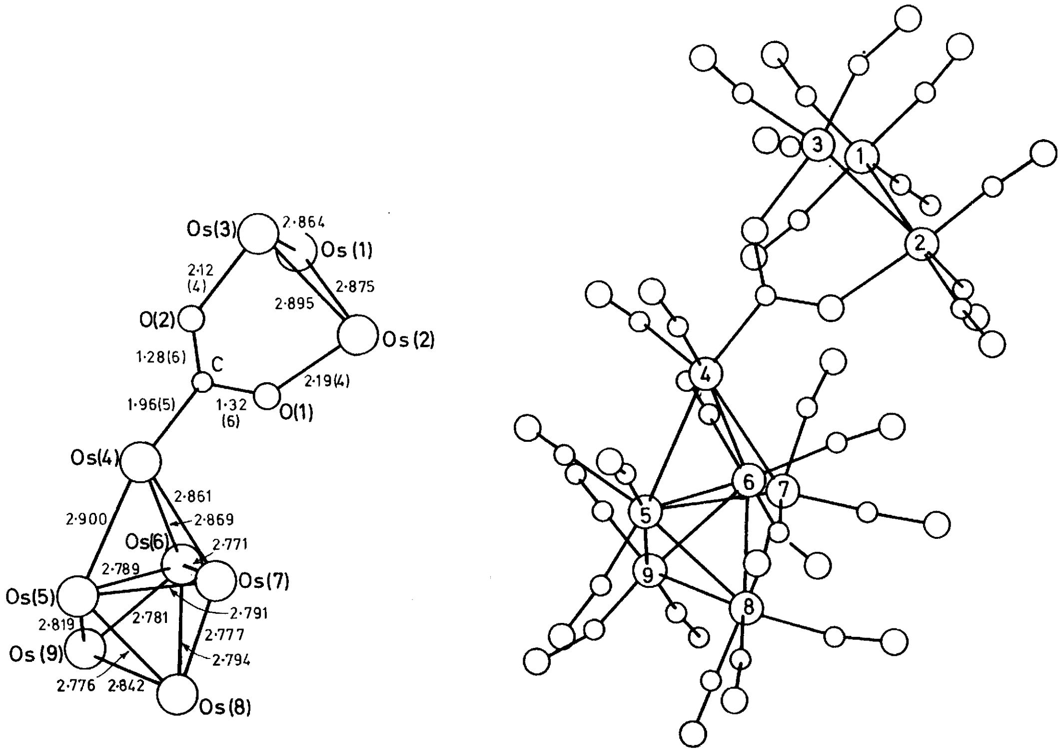

FIGURE 3 Structure of $[(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$ with significant bond lengths (Å). The position of the hydride ligand is not shown but is believed to bridge Os(2)–Os(3)

TABLE 2

Characteristic data for $[(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$

$[N(PPh_3)_2][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$. Found: C, 25.2; H, 1.05; N, 0.50%. Calc.: 25.15; H, 1.0; N, 0.45%; ν(CO) in CH_2Cl_2:[a] 2 111vw, 2 082mw, 2 074m, 2 062mw, 2 047m, 2 028ms, 2 013s, 1 971vw, 1 961vw cm^{-1}; ^1H Fourier-transform n.m.r. spectrum at 32 °C, τ 2.4 (m), 20.4 (s).

$[NMe_4][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$. $\nu(O_2C)$ in KBr[b]: 1 265s cm^{-1}.

[a] The $[NMe_4]^+$ salt shows a similar spectrum. [b] The spectrum of the $[N(PPh_3)_2]^+$ salt is complicated by cation absorption.

In Figure 4 are shown the variable temperature ^{13}C n.m.r. spectra of a sample of $[N(PPh_3)_2][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$ prepared from ^{13}CO-enriched (*ca.* 60%) $[N(PPh_3)_2][Os_3H(CO)_{11}]$. At −85 °C the limiting spectrum is observed [Figure 4(*a*)]. Unfortunately, line broadening is also apparent, but ^1H decoupling clearly indicates that the signals in the region 175.2—174.4 p.p.m. are ^1H-coupled. The most clearly resolved spectrum was recorded at −50 °C. Eight signals at 182.8, 182.2, 177.4, 175.1, 175.0, 174.8, 174.7, and 174.5 p.p.m. of relative intensity 1 : 1 : 2 : 1 : 1 : 2 : 1 : 1 are observed in the ^1H-decoupled spectrum [Figure 4(*c*)]. At −85 °C the signal of intensity two at 177.4 p.p.m. splits into two resonances at 177.7 (1) and 177.6 (1) p.p.m. although some temperature shift is also detected. In total, therefore, the limiting spectrum may be taken as containing nine signals of relative intensity 1 : 1 : 1 : 1 : 1 : 1 : 2 : 1 : 1. The overall symmetry of the complex anion is such (Figure 3) that ten signals might have been expected. We must assume therefore some accidental degeneracy to account for the signal at 174.8 p.p.m. of intensity two. Barring that, the spectra are compatible with the crystallographic structure. The ^1H-decoupling experiments (combined with those for the Os_6 fragment reported below) clearly indicate that the hydride ligand is associated with the Os_3 portion of the molecule and in view of the coupling observed almost certainly lies along the Os(2)–Os(3) bond as suggested from the *X*-ray analysis. This is similar to the location of this ligand in $[Os_3H(CO)_{11}]^-$ (see above). At 40 °C the spectrum simplifies considerably. Again some temperature shift is observed but allowing for this the two resonances at 182.8 and 182.2 p.p.m. in 4(*c*) [corresponding to 183.3 and 182.4 p.p.m. in 4(*d*)] remain unchanged

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[9] J. J. Guy and G. M. Sheldrick, *Acta Cryst.*, in the press.

as does the signal 177.4 p.p.m. [177.7 p.p.m. in 4(*d*)]. The remaining signals collapse to two signals at 175.4 and 175.2 p.p.m. of relative intensity 2 : 4. This spectrum leads to the conclusion that at this temperature a plane of symmetry is generated through the Os_3 triangle. The simplest mechanism to account for this phenomenon involves rotation of the Os_3 unit about the $Os(4)–CO_2$ bond in conjunction with CO scrambling about the Os(4) atom. At 70 °C the spectrum simplifies to two resonances at 176.9 and 176.6 p.p.m.

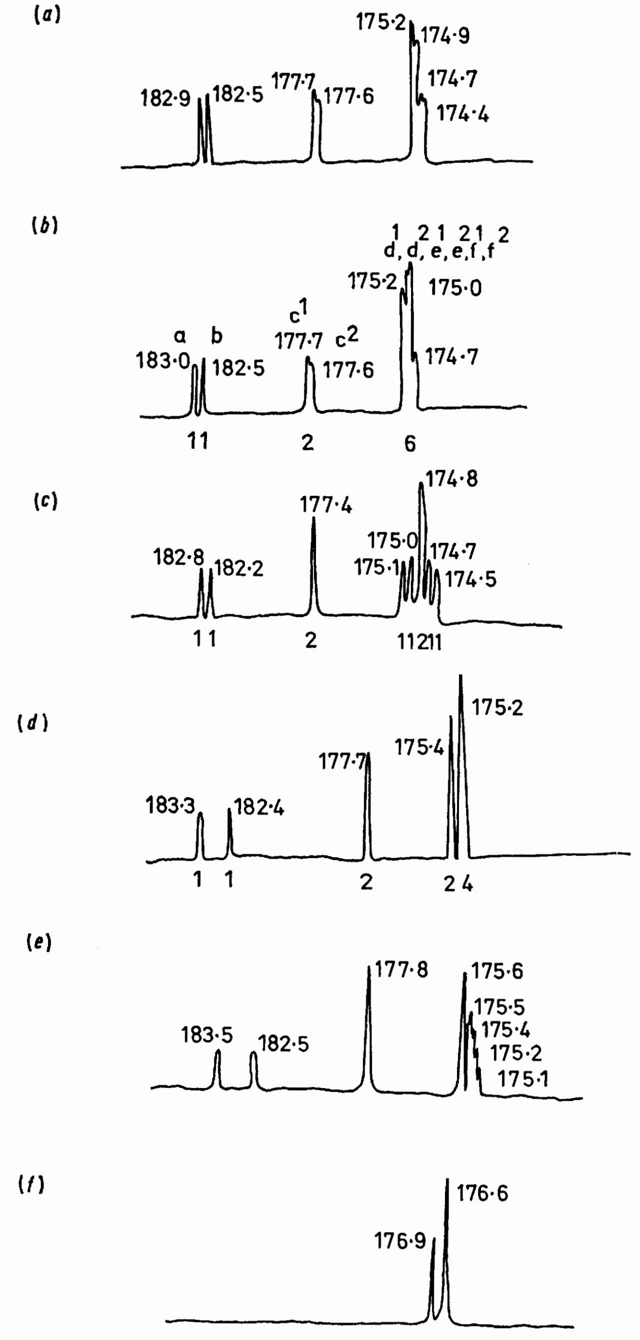

FIGURE 4 Variable-temperature $^{13}C(CO)$ n.m.r. spectra of $[N(PPh_3)_3][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$ synthesised using ^{13}C-enriched $[N(PPh_3)_2][Os_3H(CO)_{11}]$: (*a*) at −85 °C, without ^1H spin decoupling; (*b*) as (*a*) but with ^1H spin decoupling; (*c*) at −50 °C as (*b*); (*d*) 40 °C as (*b*); (*e*) at 40 °C as (*a*); and (*f*) at 70 °C as (*b*). Shifts as in Figure 1

In Figure 5 are shown the variable-temperature $^{13}C(CO)$ n.m.r. spectra of $[N(PPh_3)_2][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$ synthesised using ^{13}CO (*ca.* 40%)-enriched $[Os_6(CO)_{18}]$. At −95 °C (the lowest temperature at which the complex remained in solution) 14 resonances of total intensity 15 are observed. As the temperature is increased to −85 °C all the signals undergo a slight drift but more importantly an additional broad resonance of intensity three appears at 182.0 p.p.m. As the temperature is increased to −70 °C this is resolved into a singlet. On the basis of these observations it is clear that even at −95 °C three CO ligands are exchanging; with this in mind, the spectrum at −95 °C is compatible with the established geometry of the Os_6 fragment, with 18 (real and apparent) CO resonances. At >-95 °C additional CO scrambling occurs. Between −95 and −70 °C the signals initially observed at 197.0, 189.1, 188.1, 185.1, 183.9, 183.8, 173.8, and 172.8 p.p.m. of relative intensity 1 : 1 : 1 : 2 : 1 : 1 : 1 : 1 broaden and collapse until at −50 °C [Figure 5(*d*)] they are no longer observed. On further warming a singlet of intensity six appears at 185.1 p.p.m. At this stage eight signals are observed at 193.7 (1), 185.1 (6), 184.5 (1), 182.4 (3), 180.9 (1), 178.9 (1), 178.7 (1), and 173.4 (1) p.p.m. At higher temperatures [see Figure 5(*i*)] the spectrum simplifies further. We assign these spectra as follows. Since the signal at 193.3 p.p.m. remains more or less constant throughout and the C atom is not involved in any fluxional process we assign it to the CO_2 fragment. At higher temperatures when a 1 : 6 : 3 : (3) : (3) : (2) intensity relation of signals may be deduced (values in parentheses being for signals not totally resolved) we believe that the process invoked to account for the fluxional behaviour of the Os_3 unit is also (as it must be) equilibrating Os atoms (5) and (6) about each of which the three CO groups are rapidly equilibrating, producing the signal of intensity six at *ca.* 186 p.p.m. The remaining signals of intensity three may be assigned to the rapidly equilibrating CO ligands on Os(7), Os(8), and Os(9), since these three Os atoms are not equilibrated by the above process; the signal of intensity two which is not observed at 80 °C but is supposed to be resolved into two singlets at low temperatures may be associated with the two equilibrating CO groups bound to Os(4). In summary, therefore, a single process accounts for the limited equilibration of CO groups in both the Os_3 and Os_6 units; this corresponds to a polytopal rearrangement about Os(4). At higher temperatures additional fluxional processes, presumably similar to those found for $[Os_3H(CO)_{11}]^-$, occur in the Os_3 fragment but at no time is definitive evidence found for CO migration from one Os atom to another within the Os_6 fragment. Finally, the carbon atom of the CO_2 linking group clearly arises from $[Os_6(CO)_{18}]$.

In order to locate the resonance associated with the $^{13}CO_2$ carbon atom the spectrum of ^{13}CO-substituted (*ca.* 40%) $[(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$ was recorded over extensive spectral widths. In these experiments the only resonance which remained over all the temperatures was that at **193.3** p.p.m. of intensity one. We assign this signal, therefore, to the carbon dioxide group.

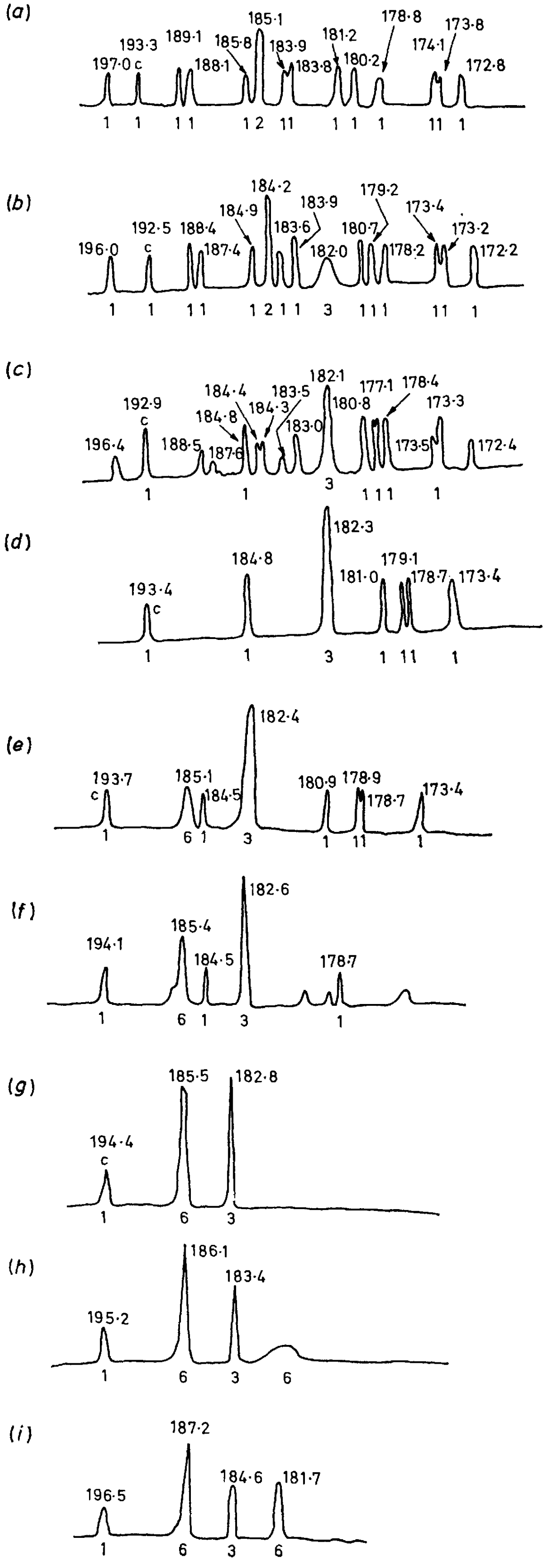

FIGURE 5 Variable-temperature $^{13}C(CO)$ n.m.r. spectra of $[N(PPh_3)_2][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$ synthesised using ^{13}C-enriched $[Os_6(CO)_{18}]$ at (*a*) −95, (*b*) −85, (*c*) −70, (*d*) −50, (*e*) −30, (*f*) −10, (*g*) 10, (*h*) 35, and (*i*) 80 °C. All the spectra are ^1H spin decoupled, shifts as in Figure 1

The mechanism by which $[(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$ is produced from $[Os_3H(CO)_{11}]^-$ and $[Os_6(CO)_{18}]$ is not clear. We have been able to show that under aqueous conditions $[Os_3H(CO)_{11}]^-$ is converted into $[Os_3H(OH)(CO)_{10}]$. We therefore considered the possibility that, in the presence of added base, the anion $[Os_3H(O)(CO)_{10}]^-$ would be produced, which would then attack an electrophilic carbonyl ligand on $[Os_6(CO)_{18}]$. This followed by ring closure would lead to the observed product. However, in a separate experiment we found that $[Os_3H(OH)(CO)_{10}]$ does not react with $[Os_6(CO)_{18}]$ under the conditions employed in the preparation of the Os_9 anion.

The salt $[N(PPh_3)_2][(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]$ is stable in all the common solvents apart from acetonitrile, and only at high temperatures does it show signs of decomposition, *e.g.* in boiling toluene some $[Os_6(CO)_{18}]$ is produced. It reacts with sulphuric acid in dichloromethane to give $[Os_6(CO)_{18}]$ and $[Os_3H(OH)(CO)_{10}]$, with HCl in dichloromethane to give $[Os_6(CO)_{18}]$ and $[Os_3Cl(H)(CO)_{10}]$, and with excess of iodine to give $[Os_6(CO)_{18}]$ as the only isolable product.

EXPERIMENTAL

All the manipulations were carried out under dry oxygen-free nitrogen. Solvents were dried, deoxygenated, and distilled before use according to standard literature methods. The complex $[Os_3(CO)_{12}]$ was prepared by the method of ref. 2.

Infrared spectra were recorded either as solutions in 0.1- or 0.5-mm CaF_2 cells or as KBr discs on a Perkin-Elmer 257 spectrometer using polystyrene as calibrant. Mass spectra were obtained using a A.E.I. MS.12 instrument. Hydrogen-1 n.m.r. spectra were recorded using Varian Associates HA 100 or CFT 20 instruments operating at 100 and 20 MHz respectively. Tetramethylsilane or the solvent were used as internal calibrants. Carbon-13 n.m.r. spectra were recorded using a Varian Associates XL 100 instrument operating in the Fourier-transform mode at 25.2 MHz. Spectra were obtained over a range of spectral widths (10 000, 5 000, and 300 Hz) with appropriate acquisition times and calibrated relative to $SiMe_4$ using the solvent resonances as internal standard. Variation of the standard with temperature remained uncorrected. At $\geqslant -60$ °C, $[Cr(pd)_3]$ (pd = pentane-2,4-dionate) was added as a relaxing agent, having first established over an extended period of time, particularly at high temperature, that the reagent did not chemically alter the ^{13}CO-enriched species. Solvents used: (a) < -85 °C, $CHFCl_2$–CH_2Cl_2 (3 : 1); (*b*) −30 to −85 °C, CH_2Cl_2–CD_2Cl_2 (3 : 1); (*c*) 30—55 °C, $CDCl_3$; (*d*) up to 100 °C, 1,1,2-trichloroethane using an insert of C_6D_6 or C_7D_8 as external calibration and deuterium lock. Microanalyses were performed within these laboratories.

The Preparation of Undecacarbonylhydridotriosmate (1—).—Potassium hydroxide (0.5 g, 0.025 mol) was dissolved in methanol (25 cm^3), left to cool, and $[Os_3(CO)_{12}]$ (0.5 g, 0.55 mmol) added with stirring until it had dissolved. To the red solution was added a solution of $[N(PPh_3)_2]Cl$ (0.350 g, 0.61 mmol) in methanol (3 cm^3). On reducing the solution in volume (10 cm^3) a red microcrystalline precipitate of $[N(PPh_3)_2][Os_3H(CO)_{11}]$ was obtained. This was rapidly filtered off, washed with cold methanol (2 × 3 cm^3), with water rapidly, and then dried, yield 0.540 g (69%). Addition of water to the methanol filtrate gave another precipitate which on purification yielded another 0.14 g (17.8%) of product. The $[NMe_4]^+$ salt was obtained by addition of a saturated aqueous solution (15 cm^3) of $[NMe_4]Cl$ rather than to the solution of $[Os_3(CO)_{12}]$ in methanolic KOH. The pure precipitate was filtered off, washed with water (4 × 5 cm^3), and dried *in vacuo*. The solid was then washed with dichloromethane (2 × 3 cm^3), yield 0.160 g (30%).

Reactions of the Anion $[Os_3H(CO)_{11}]^-$.—(*a*) *Acidification in aqueous media*. The salt $[N(PPh_3)_2][Os_3H(CO)_{11}]$ was treated with excess of H_3PO_4 (80%) and the mixture then extracted with $CHCl_3$ (5 + 5 cm^3); these yellow extracts were washed with water (10 × 2 cm^3), dried over magnesium sulphate and then concentrated to give a yellow solid characterised as $[Os_3H(OH)(CO)_{10}]$ on the basis of its spectroscopic properties (i.r. and mass spectra).

(b) *Acidification under anhydrous conditions*. To a CD_2Cl_2 solution saturated with HCl was added $[NMe_4]$-$[Os_3H(CO)_{11}]$ with stirring. The solution immediately became yellow and ^1H Fourier-transform n.m.r. spectroscopy (−86 °C) clearly revealed the characteristic bands of $[Os_3H_2(CO)_{11}]$[20.51 (d)(1) and 30.03 (d)(1) p.p.m.; *J* 3.5 Hz].

The Preparation of $[(OC)_{10}HOs_3(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$.—The salt $[N(PPh_3)_2][Os_3H(CO)_{11}]$ (47.6 mg, 0.034 mmol) was added in small quantities over a period of 2 h to a solution of $[Os_6(CO)_{18}]$ (50.7 mg, 0.031 mmol) in dichloromethane. Purification by t.l.c. [eluant CH_2Cl_2–cyclohexane (9 : 1)] followed by crystallisation using the same solvents gave brown-black crystals (74.4 mg, 79%) of the required salt.

The $[NMe_4]^+$ salt was obtained by addition of $[NMe_4]$-$[Os_3H(CO)_{11}]$ to a solution of $[Os_6(CO)_{18}]$ in a 1 : 1 mol ratio, dissolved in acetone. Purification by t.l.c. [eluant CH_2Cl_2–Me_2CO(2 : 1)] gave a brown solid which could be characterised, after recrystallisation, as the required salt.

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