The Enneacarbonyls of Ruthenium and Osmium

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The ultraviolet irradiation of n-heptane solutions of the pentacarbonyls of ruthenium and osmium at −40 °C has been studied. In the case of $[Os(CO)_5]$, the new carbonyl compound $[Os_2(CO)_9]$ has been isolated and is found to decompose only slowly in solution. The product of the low-temperature irradiation of $[Ru(CO)_5]$, which has only been partially characterized as $[Ru_2(CO)_9]$, is extremely unstable in both the solid state and in solution at room temperature. The decompositions of $[Os_2(CO)_9]$ and $[Ru_2(CO)_9]$ in solution have been studied and are discussed. The reaction of $[Os_2(CO)_9]$ with hydrogen gives the known dihydride $[Os_2(CO)_8H_2]$. With PPh_3, the products are $[Os(CO)_4(PPh_3)]$ and $[Os_2(CO)_8H_2]$ but with PEt_3 only $[Os_2(CO)_8H_2]$ is formed. Infrared and mass spectra for $[Ru_2(CO)_9]$ and $[Os_2(CO)_9]$ are reported and discussed.

THE identity of di-iron enneacarbonyl was established in the earliest days of metal-carbonyl chemistry. The decomposition of iron pentacarbonyl by light was first observed by Mond and Langer[1] in 1891 to give a solid iron carbonyl product and carbon monoxide. This compound was formulated as $[Fe_2(CO)_9]$ on the basis of analytical results[2] and this formulation has since been confirmed by *X*-ray crystallographic investigations.[3-5] In 1936, Manchot and Manchot[6] found that ruthenium pentacarbonyl readily decomposes to an orange crystalline compound which they formulated as $[Ru_2(CO)_9]$ by analogy with the well known $[Fe_2(CO)_9]$. Seven years later, Hieber and Stallman[7] reported that the high-pressure carbonylation of osmium tetraoxide yielded a yellow crystalline compound which they suggested was $[Os_2(CO)_9]$. A subsequent *X*-ray crystallographic analysis, however, showed that this compound was the trimer $[Os_3(CO)_{12}]$ and the supposed $[Ru_2(CO)_9]$ was found to be isomorphous with the osmium compound.[8,9] A complete *X*-ray investigation on $[Ru_3(CO)_{12}]$ has been reported.[10] The trimeric nature of $[M_3(CO)_{12}]$ ($M = Ru$ or Os) has also been demonstrated by mass spectrometry where the parent molecular ions have been observed.[11] The existence of $[M_2(CO)_9]$ ($M = Ru$ or Os) therefore became questionable.

We now report the preparation of $[Os_2(CO)_9]$ and present evidence for $[Ru_2(CO)_9]$. We have already described the osmium compound in a preliminary report.[12]

RESULTS AND DISCUSSION

Irradiation of an n-heptane solution of osmium pentacarbonyl at room temperature is known to give the trimer $[Os_3(CO)_{12}]$.[13] We studied the low-temperature irradiation of $[Os(CO)_5]$ in an attempt to gain evidence for the formation of osmium tetracarbonyl, $[Os(CO)_4]$, which we had previously proposed as an intermediate in the thermolysis reactions of $H_2[Os(CO)_4]_n$ ($n = 2$ or 3).[14] We find that a yellow-orange solid is formed on u.v. irradiation of an n-heptane solution of $[Os(CO)_5]$ at −40 °C. This solid is mainly $[Os_2(CO)_9]$ contaminated with $[Os_3(CO)_{12}]$. The crude product was purified by sublimation and obtained as a yellow-orange crystalline solid which melts with decomposition at 64—67 °C. In the solid state, $[Os_2(CO)_9]$ decomposes slowly at room temperature but can be kept for several days at −20 °C. In n-heptane solution it decomposes more rapidly (see later).

The formation of $[Os_2(CO)_9]$ can be considered *via* initial dissociation of CO from $[Os(CO)_5]$ to yield the co-ordinatively unsaturated intermediate $[Os(CO)_4]$ which then reacts with $[Os(CO)_5]$ [equations (1) and (2)].

$$[Os(CO)_5] \xrightarrow{h\nu} [Os(CO)_4] + CO \qquad (1)$$

$$[Os(CO)_4] + [Os(CO)_5] \longrightarrow [Os_2(CO)_9] \qquad (2)$$

Under the present reaction conditions, $[Os_2(CO)_9]$ precipitates from solution. Presumably, at room temperature the solubility of $[Os_2(CO)_9]$ enables further reaction to occur with either $[Os(CO)_5]$ or $[Os(CO)_4]$ to yield the trimer $[Os_3(CO)_{12}]$. The formation of $[Os_2(CO)_9]$ is analogous to the photolysis reactions leading to the complexes $[M_2(\eta\text{-}C_5H_5)_2(CO)_3]$ ($M = Co$[15] or Rh[16]) and $[Re_2(\eta\text{-}C_5H_5)_2(CO)_5]$.[17] These reactions can be represented by the general equations (3) and (4) where $L = CO$ or $\eta\text{-}C_5H_5$.

In a similar apparatus to that used for the preparation of $[Os_2(CO)_9]$ (see Experimental section), the preparation of $[Ru_2(CO)_9]$ was attempted. An orange-brown solid was deposited on the probe during the low-temperature irradiation. The probe was removed from the reaction vessel and any $[Ru(CO)_5]$ or heptane was removed under

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[1] L. Mond and C. Langer, *J. Chem. Soc.*, 1891, **59**, 1090.

[2] J. Dewar and H. O. Jones, *Proc. Roy. Soc.*, 1905, **A76**, 558.

[3] R. Brill, *Z. Krist.*, 1927, **65**, 89.

[4] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 1939, 286.

[5] F. A. Cotton and J. M. Troup, *J.C.S. Dalton*, 1974, 800.

[6] W. Manchot and W. J. Manchot, *Z. anorg. Chem.*, 1936, **226**, 385.

[7] W. Hieber and H. Stallman, *Z. Elektrochem.*, 1943, **49**, 288.

[8] E. R. Corey and L. F. Dahl, *J. Amer. Chem. Soc.*, 1961, **83**, 2203.

[9] E. R. Corey and L. F. Dahl, *Inorg. Chem.*, 1962, **1**, 521.

[10] R. Mason and A. I. M. Rae, *J. Chem. Soc. (A)*, 1968, 778.

[11] B. F. G. Johnson and J. Lewis, *Accounts Chem. Res.*, 1968, **1**, 245.

[12] J. R. Moss and W. A. G. Graham, *Chem. Comm.*, 1970, 835.

[13] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 1967, **6**, 1220.

[14] J. R. Moss and W. A. G. Graham, *J. Organometallic Chem.*, 1970, **23**, C47.

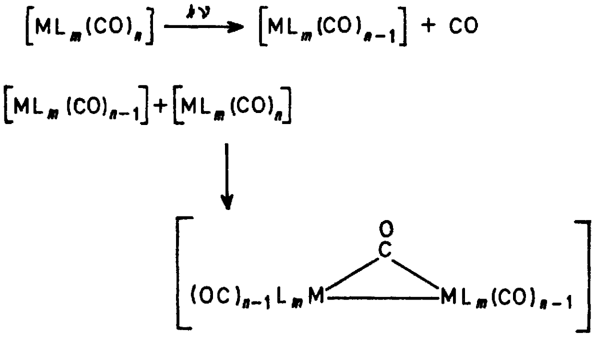
[15] K. P. C. Vollhardt, J. E. Bercaw, and R. G. Bergman, *J. Organometallic Chem.*, 1975, **97**, 283.

[16] J. P. Nice and O. S. Mills, *J. Organometallic Chem.*, 1967, **10**, 337.

[17] J. K. Hoyano and W. A. G. Graham, unpublished work.

reduced pressure. The orange-brown solid thus obtained was very unstable at room temperature, rapidly coating the apparatus with an orange film of $[Ru_3(CO)_{12}]$. An i.r. spectrum of a solution of this solid indicated the presence of only $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$ in approximately equal amounts.

$$[ML_m(CO)_n] \xrightarrow{h\nu} [ML_m(CO)_{n-1}] + CO \qquad (3)$$



(4)

Low-temperature Irradiation of $[M(CO)_5]$ (M = Ru *or* Os) *in an I.r. Cell.*—In order to follow the low-temperature irradiation of $[Os(CO)_5]$ by i.r. spectroscopy, a solution of $[Os(CO)_5]$ in n-heptane was cooled to −30 °C with a variable-temperature chamber. The solution was then irradiated for periods of 5 min (to a total irradiation time of 40 min) and the i.r. spectrum recorded after each irradiation. The spectra showed the appearance of new bands, some of which correspond to $[Os_3(CO)_{12}]$ and others which can be assigned to $[Os_2(CO)_9]$ (see Table 1). A similar experiment was carried out with $[Ru(CO)_5]$ in n-heptane and new ν(CO) bands were observed at 2 077 and 2 018 cm^{-1} and a single bridging band at 1 814 cm^{-1}. These bands are probably some of the bands due to $[Ru_2(CO)_9]$; ν(CO) bands of $[Ru_3(CO)_{12}]$ also appeared during the irradiation so that all the bands of $[Ru_2(CO)_9]$ could not be observed (Table 1).

TABLE 1

Infrared carbonyl-stretching bands (cm^{-1}) after irradiation of n-heptane solutions of $[M(CO)_5]$ (M = Ru or Os) at −30 °C for 10 min in an i.r. cell

Compound	ν(CO)
$[Os(CO)_5]$	2 100vw,[a] 2 080m,[b] 2 069s,[c] 2 036vs,[b–d] 2 023m,[b] 2 013s,[b,c] 2 003 (sh),[c] 1 993vs,[d] 1 776w [b]
$[Ru(CO)_5]$	2 077m,[e] 2 061m,[c] 2 038vs,[c,d] 2 032 (sh), 2 029 (sh),[c] 2 018m,[e] 2 001vs,[d] 1 814w [e]

[a] Bands due to unknown species. [b] Bands attributable to $[Os_2(CO)_9]$. [c] Bands attributable to $[M_3(CO)_{12}]$ (M = Ru or Os). [d] Bands attributable to $[M(CO)_5]$ (M = Ru or Os). [e] Bands assignable to $[Ru_2(CO)_9]$.

Mass Spectra.—The mass spectrum of $[Os_2(CO)_9]$ was obtained using a direct probe and a source temperature of 10 °C. The spectrum (Figure 1) showed a parent molecular ion at *m/e* 634 with the expected isotope pattern, and an accurate mass of the most abundant peak of this parent ion was found to be 633.874 (calc. 633.875). Loss of nine carbonyl groups was observed from the parent molecular ion. Carbide peaks due to the series $[Os_2C(CO)_m]^+$ (m = 0—3) were observed as would be expected.[11] Mononuclear ions of the series $[Os(CO)_m]^+$ (m = 0—5) were observed which is consistent with the presence of a bridging carbonyl group,[11] five carbonyl groups being associated with each osmium. Doubly charged ions of the series $[Os_2(CO)_m]^{2+}$ (m = 0—7) were also observed. The peaks of the mononuclear series $[Os(CO)_m]^+$ (m = 0—5) were weak compared to the peaks of the series $[Os_2(CO)_m]^+$ (m = 0—9) (Figure 1). This is in contrast to the spectrum of $[Fe_2(CO)_9]$ where the peaks due to binuclear ions are extremely weak; [11] however, this may be a consequence of the low volatility of $[Fe_2(CO)_9]$.

Very weak peaks corresponding to the series $[Os_3(CO)_m]^+$ (m = 3—12) were observed in mass spectra of $[Os_2CO)_9]$. These peaks are probably a result of some decomposition of $[Os_2(CO)_9]$. The intensity ratio of the peaks due to $[Os_2(CO)_9]$ and $[Os_3(CO)_{12}]$ varied with the sample and the proportion of the most abundant peak of $[Os_3(CO)_{12}]$ to that of $[Os_2(CO)_9]$ was less than 1% in the best samples. The fact that the intensity ratio of the peaks of $[Os_2(CO)_m]^+$ (m = 0—9) and $[Os_3(CO)_m]^+$ (m = 3—12) is variable is strong evidence that two compounds were present, *i.e.* $[Os_2(CO)_9]$ and $[Os_3(CO)_{12}]$. This is good support for the formulation $[Os_2(CO)_9]$ rather than a new isomer of $[Os_3(CO)_{12}]$ containing a bridging carbonyl band, which might have given a strong series of peaks due to $[Os_2(CO)_m]^+$ (m = 0—9). In the mass spectrum of $[Os_3(CO)_{12}]$, no peaks due to mono- or bi-nuclear species are observed.[11]

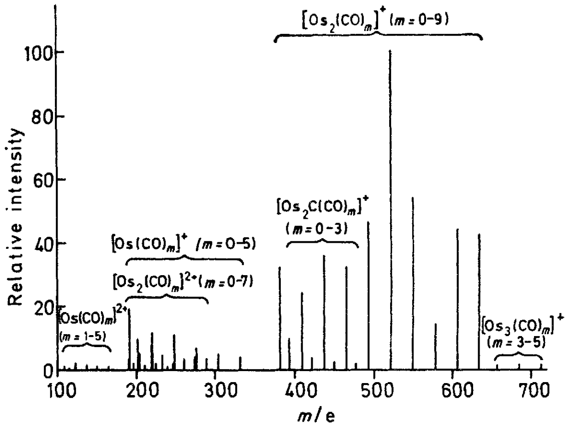


FIGURE 1 Schematic representation of the mass spectrum of $[Os_2(CO)_9]$. For clarity, the patterns for each of the ions have been reduced to a single line by taking the height of the most abundant peak of each particular ion relative to the strongest peak in the spectrum as 100. Thus relative intensity refers to the relative heights of the most abundant peaks of the particular ions

Further evidence for the existence of $[Ru_2(CO)_9]$ was obtained by mass spectrometry. The last traces of solvent and $[Ru(CO)_5]$ were removed under reduced pressure from the orange-brown solid obtained on the probe during the low-temperature irradiation of $[Ru(CO)_5]$. This solid was then introduced by direct probe into the mass spectrometer and a spectrum was recorded at a source temperature of 18 °C. The spectrum clearly showed a parent molecular ion corresponding to $[Ru_2(CO)_9]$ at *m/e* 455 and peaks of the series $[Ru_2(CO)_m]^+$ (m = 0—9). The sample, however, was contaminated with $[Ru_3(CO)_{12}]$ and peaks of the series $[Ru_3(CO)_m]^+$ ($m = 0$—12) were also observed. The intensity ratio of the peaks of $[Ru_2(CO)_m]^+$ ($m = 0$—9) to $[Ru_3(CO)_m]^+$ ($m = 0$—12) varied with the sample {as for $[Os_2(CO)_9]$} suggesting that two compounds are present, *i.e.* $[Ru_2(CO)_9]$ and $[Ru_3(CO)_{12}]$. Although the spectrum of $[Ru_3(CO)_{12}]$ shows binuclear and mononuclear fragments,[11] these peaks are weak compared to the trinuclear series $[Ru_3(CO)_m]^+$ ($m = 0$—12). In our spectrum of the orange-brown solid, the ratio of the height of the most abundant peak of the binuclear series, *i.e.* $[Ru_2(CO)_5]^+$, to the most abundant peak of the trinuclear series, *i.e.* $[Ru_3(CO)_8]^+$, is 1.27 : 1. We find this same ratio of peaks for a pure sample of $[Ru_3(CO)_{12}]$ is 1 : 30.

TABLE 2

Infrared carbonyl-stretching bands (cm^{-1}) for $[Os_2(CO)_9]$

Solvent	ν(CO)
n-Heptane	2 080s, 2 038vs, 2 024m, 2 013s, 2 000w, 1 778m
Nujol	2 132w, 2 084s, 2 060 (sh), 2 044 (sh), 2 036 (sh), 2 020vs, 1 990s, 1 982s, 1 972 (sh), 1 953 (sh), 1 748s, 1 737m

I.r. Spectra.—Diosmium enneacarbonyl, in marked contrast to $[Fe_2(CO)_9]$, is soluble in organic solvents. Thus i.r. spectra of $[Os_2(CO)_9]$ in solution and in the solid state could be obtained (see Table 2 and Figure 2).

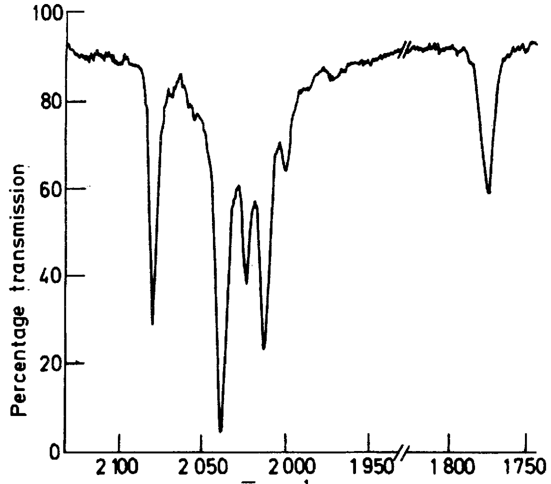
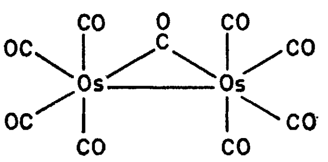


FIGURE 2 Infrared spectrum of an n-heptane solution of $[Os_2(CO)_9]$

Because of decomposition, the spectrum in heptane solution had to be recorded immediately after the solution had been made up (see later). The spectrum of $[Os_2(CO)_9]$ in heptane showed five terminal and one bridging carbonyl-stretching bands (Figure 2), thus an $[Fe_2(CO)_9]$-type structure can be ruled out. The spectrum of $[Os_2(CO)_9]$ as a Nujol mull (Table 2) is considerably different from that of solid $[Fe_2(CO)_9]$.[18] Due to the insolubility of $[Fe_2(CO)_9]$ in all the solvents, a solution spectrum of this molecule is not available for comparison with that of $[Os_2(CO)_9]$. A reasonable structure for $[Os_2(CO)_9]$ is that of C_{2v} symmetry as shown in (I). On local symmetry arguments, four terminal ν(CO) bands would be expected and this is the number observed if the weak band at 2 000 cm^{-1} is due to $\nu(^{13}CO)$. A structure similar to (I) has recently been found for the compound $[Fe_2(CO)_7(Ph_2PCH_2PPh_2)]$.[19] Here, the five ligand atoms surrounding each metal atom are in an approximately trigonal-bipyramidal arrangement and there is a slight twisting about the Fe–Fe bond. Diosmium enneacarbonyl represents a rare example of a compound of the third-row transition metals which has a bridging carbonyl group. The complex $[Os_3(CH{:}CMe)(CO)_{10}]$ has also been shown to have a bridging carbonyl group.[20] The difference in the structures of $[Fe_2(CO)_9]$ and $[Os_2(CO)_9]$ is probably a consequence of a longer metal–metal bond in the later compound which favours the structure with a single bridging carbonyl group.



(I)

Due to the instability of $[Ru_2(CO)_9]$, an i.r. spectrum in heptane solution at room temperature showed only ν(CO) bands due to $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$. However, new bands appeared at 2 077, 2 018, and 1 814 cm^{-1} during the low-temperature irradiation of $[Ru(CO)_5]$ in an i.r. cell, as well as bands assignable to $[Ru_3(CO)_{12}]$, and these bands may be attributed to $[Ru_2(CO)_9]$. The structure of $[Ru_2(CO)_9]$, while it is of considerable interest, cannot be inferred from this data.

Reactions of $[Os_2(CO)_9]$.—Diosmium enneacarbonyl reacted with hydrogen under fairly mild conditions (33 atm * hydrogen, 30 °C for 14 h) to yield the known binuclear hydride $[Os_2(CO)_8H_2]$ [21] [equation (5)]. These

$$[Os_2(CO)_9] + H_2 \longrightarrow [Os_2(CO)_8H_2] + CO \quad (5)$$

conditions are similar to those used to prepare $[Co(CO)_4H]$ from $[Co_2(CO)_8]$ and hydrogen.[22] The reaction of $[Os_2(CO)_9]$ with hydrogen probably represents the first example of a binuclear metal carbonyl reacting with hydrogen to give a binuclear carbonyl hydride. A possible mechanism for this reaction may involve initial dissociation of CO from $[Os_2(CO)_9]$ to yield the intermediate $[Os_2(CO)_8]$, which would require a double osmium–osmium bond from the effective atomic-number rule, followed by addition of H_2 across this double bond.

Reaction with Tertiary Phosphines.—The reaction of $[Os_2(CO)_9]$ with triphenylphosphine was carried out in

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* 1 atm = 101 325 Pa.

[18] A. D. Liehr, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

[19] F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, 1974, **96**, 4422.

[20] A. J. Deeming, S. Hasso, and M. Underhill, *J.C.S. Dalton*, 1975, 1614.

[21] J. R. Moss and W. A. G. Graham, *Chem. Comm.*, 1969, 800.

[22] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

an i.r. cell in the dark. After *ca.* 5 h, most of the $[Os_2(CO)_9]$ had reacted and the i.r. spectrum suggested that only two products, *viz.* $[Os(CO)_4(PPh_3)]$ [23] and $[Os_2(CO)_8H_2]$,[21] were formed. No ν(CO) bands of $[Os(CO)_5]$ were observed and we have shown that $[Os(CO)_5]$ does not react with PPh_3 under these conditions. Thus, $[Os(CO)_4(PPh_3)]$ may result from the decomposition of an unstable substitution product of $[Os_2(CO)_9]$ or from the reaction of PPh_3 with the intermediate, $[Os(CO)_4]$, formed in the decomposition of $[Os_2(CO)_9]$. The reaction of triethylphosphine with $[Os_2(CO)_9]$ was complete in *ca.* 10 min and the i.r. spectrum of the reaction solution suggested that only $[Os_2(CO)_8H_2]$ was formed. The reaction of PEt_3 with $[Os_2(CO)_9]$ in $CD_3C_6D_{11}$ also gave $[Os_2(CO)_8H_2]$ which is strong evidence that the hydrogen originates from the phosphine and not the solvent. Other workers have described hydrogen-abstraction reactions by triosmium carbonyl species; however, the present reactions occur under much milder conditions than those previously reported.[24]

Decomposition of $[Os_2(CO)_9]$ *in Heptane Solution.*—The decomposition of n-heptane solutions of $[Os_2(CO)_9]$ was carried out in an i.r. cell in the dark and followed by observing the changes in the i.r. spectrum in the ν(CO) region. The carbonyl bands of $[Os_2(CO)_9]$ gradually decreased in intensity with the formation of new bands. some of which may be assigned to $[Os_3(CO)_{12}]$ (see Table 3). A new band at 2 077 cm^{-1} was clearly observed. The species giving rise to this band increased in concentration then decreased, leaving finally bands of $Os_3(CO)_{12}]$. This species thus appears to be an intermediate in the formation of $[Os_3(CO)_{12}]$ from $[Os_2(CO)_9]$ and may be $[Os_2(CO)_8]$ [equation (6)]. In order to

$$[Os_2(CO)_9] \longrightarrow [Os_2(CO)_8] + CO \qquad (6)$$

comply with the effective atomic-number rule $[Os_2(CO)_8]$ would require a double osmium–osmium bond. When the decomposition of $[Os_2(CO)_9]$ was followed in the presence of added $[Os(CO)_5]$ no band at 2 077 cm^{-1} was observed in the i.r. spectrum. Therefore either $[Os_2(CO)_9]$ or the intermediate reacts with $[Os(CO)_5]$.

TABLE 3

Infrared carbonyl-stretching bands (cm^{-1}) of a solution of $[Os_2(CO)_9]$ in n-heptane as a function of time [a]

t/h	ν(CO)
0	2 080s, 2 038vs, 2 024m, 2 013s, 2 000w, 1 778m
1	2 101w, 2 080s, 2 077m, 1 069w, 2 054w, 2 038vs, 2 024m, 2 013s, 2 000w, 1 778m
2	2 101w, 2 080m, 2 077s, 2 069m, 2 055m, 2 038vs, 2 023m, 2 013s, 2 000w, 1 778m
3.5	2 101w, 2 080m (sh), 2 077s, 2 069m, 2 055m, 2 038vs, 2 024m, 2 013s, 1 778w
6	2 101w, 2 080w (sh), 2 077s, 2 069s, 2 054m, 2 037vs, 2 023m, 2 013s, 1 778w
24 [b]	2 101w, 2 077w, 2 069s, 2 037vs, 2 016m, 2 005m

[a] Solutions were kept in the i.r. cells in the dark during the decomposition. [b] The compound $[Os_3(CO)_{12}]$ exhibits bands in n-heptane at 2 069s, 2 037s, 2 016m, and 2 005m cm^{-1}

The decomposition of the product from the low-temperature irradiation of $[Ru(CO)_5]$ was rapid in heptane solutions. The presence of intermediates was not detected and only bands due to $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$ were observed.

$[Os_2(CO)_9]$ *as a Hydride?*—The facile reaction of $[Os_2(CO)_9]$ with tertiary phosphines to yield $[Os_2(CO)_8H_2]$ suggested that the compound formulated as $[Os_2(CO)_9]$ may be a carbonyl hydride, *e.g.* $[Os_2(CO)_9H_2]$. We therefore examined this possibility.

The failure to observe a parent molecular ion in the mass spectrum due to a hypothetical $[Os_2(CO)_9H_2]$ is inconclusive since other carbonyl hydrides are known, *e.g.* $[Os(CO)_4H_2]$, which show only the parent ion minus two hydrogens.[25] Some evidence that a carbonyl hydride is not involved in the present case is offered by the results of a computer analysis * of the heaviest species observed in the spectrum, namely $[Os_2(CO)_9]^+$. This analysis indicated that no significant hydrogen-containing species had to be invoked in order to achieve the best fit of the observed intensities of the multiplet assigned as $[Os_2(CO)_9]^+$. Had this ion been derived from a carbonyl hydride, some residual hydrogen might have been expected. This was found to be the case with $[Os(CO)_4H_2]$, in which a computer analysis of the ion of highest mass observed in the spectrum {nominally $[Os(CO)_4]^+$} contained significant hydrogen.[25] The composition (%) of the heaviest peaks of the two compounds is given below with standard deviations in parentheses.

	$[P]^+$	$[P-H]^+$	$[P-2H]^+$
$[Os(CO)_4H_2]$	0	4.3 (0.8)	95.7 (0.9)
‘ $[Os_2(CO)_9H_2]$ ’	0.8 (1.8)	1.6 (1.6)	97.5 (1.8)

Moreover, we were neither able to detect a high-field n.m.r. signal in the range τ 14—40 nor any bands in the i.r. spectrum which we could assign to ν(Os–H).

We believe that the balance of evidence favours the formulation of the compound described in this paper as the binary metal carbonyl $[Os_2(CO)_9]$.

EXPERIMENTAL

Osmium tetraoxide was purchased from Englehard Industries, Newark, New Jersey. Carbon mono-oxide was of C.P. grade and purchased from Matheson of Canada Ltd., Whitby, Ontario. All the solvents used were of reagent grade. Reactions other than those at high pressure were carried out under an atmosphere of nitrogen. Melting points were determined on a Kofler hot-stage apparatus.

Osmium pentacarbonyl was prepared by the literature method.[13] In contrast to the reported preparations of $[Os(CO)_5]$,[7,13] we found no evidence for the formation of $[Os(CO)_4H_2]$ in the high-pressure reaction of OsO_4 with CO, presumably due to the absence of significant hydrogen impurity in the CO. Yields of the pentacarbonyl were estimated by weighing the solid $[Os_3(CO)_{12}]$ remaining in the autoclave after distillation of the $[Os(CO)_5]$–heptane solution. Ruthenium pentacarbonyl was prepared by the

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* We thank Dr. A. S. Foust of this department for preparing the computer program for this analysis. We have previously mentioned this program briefly.[25]

[23] F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 1968, **7**, 1290.

[24] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1973, 2727 and refs. therein.

[25] J. R. Moss and W. A. G. Graham, *Inorg. Chem.*, in the press.

high-pressure reaction of CO (133 atm) with $[Ru_3(CO)_{12}]$ at 100 °C for 24 h in n-heptane solution.[26] Yields of $[Ru(CO)_5]$ were almost quantitative.

Ultraviolet irradiations were carried out using a Hanovia Utility Lamp (model 30620, 140 W) at a distance of 15 cm from the reaction vessel. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer and in expanded form on a Hewlett–Packard 7127A recorder. Spectra were calibrated with gaseous CO. Low-temperature studies were made using a variable-temperature chamber (model 104) manufactured by Barnes Engineering Company, Stamford, Connecticut. Mass spectra were obtained using A.E.I. MS-9 and MS-12 instruments, with an ionizing voltage of 70 eV.* Mass spectra were interpreted with the aid of a computer program which calculated exact masses and isotope-combination patterns. Exact masses determined for a particular compound were measured on the most abundant peak of the parent molecular ion. Microanalyses were by the microanalytical laboratory of this department.

The apparatus used for the low-temperature irradiations on the preparative scale was of two types. In the first, a reaction vessel (Pyrex or quartz, volume *ca.* 30 cm^3) was suspended in an unsilvered Dewar (Pyrex or quartz) vessel containing n-heptane kept at −40 °C by a stream of cold nitrogen passing through a copper coil. The reaction solution was stirred magnetically and irradiated through the Dewar. In the second apparatus, the reaction vessel (Pyrex or quartz, volume *ca.* 35 cm^3) was equipped with a cold (−78 °C) probe (length 4 cm, outside diameter 2 cm); the temperature of the reaction solution (*ca.* 15 cm^3) was kept close to −40 °C by rapid magnetic stirring.

Diosmium Enneacarbonyl.—A solution of $[Os(CO)_5]$ (0.68 g) in n-heptane (15 cm^3) was transferred to a Pyrex reaction vessel cooled by a −78 °C probe; the probe kept the reaction solution at *ca.* −40 °C. The solution was irradiated under nitrogen with rapid magnetic stirring. During irradiation the pale yellow n-heptane solution became a brighter yellow and an orange-yellow solid precipitated. After irradiation for 2 h, the reaction vessel was cooled to −78 °C to precipitate all the product and the solution was syringed off. This solution contained mainly $[Os(CO)_5]$, as shown by its i.r. spectrum. During the irradiation, some solid was deposited on the cold probe; this solid was combined with that in the reaction vessel and the last traces of solvent and pentacarbonyl were removed under reduced pressure. The yellow-orange solid remaining (0.15 g, 23%) was mainly $[Os_2(CO)_9]$ with a trace amount of $[Os_3(CO)_{12}]$ as shown by its i.r. spectrum. The crude product was purified by sublimation on to a −20 °C probe (30 °C, 0.01 mmHg) † to give diosmium enneacarbonyl, $[Os_2(CO)_9]$, as orange-yellow *microprisms*, m.p. 64—67 °C [Found: C, 17.4%; *M* (mass spectrometrically) 633.874. $C_9O_9Os_2$ requires C, 17.1%; *M* 633.875].

Reactions of $[Os_2(CO)_9]$.—*With hydrogen.* Freshly sublimed $[Os_2(CO)_9]$ (5 mg) as a solution in n-heptane (15 cm^3) was placed in an autoclave (200 cm^3) and charged with hydrogen (33 atm). The reaction solution was stirred at room temperature for 14 h and the gases vented. The i.r. spectrum in the ν(CO) region showed only bands corresponding to $[Os_2(CO)_8H_2]$.[21]

With tertiary phosphines. The reactions of $[Os_2(CO)_9]$ with both triphenyl- and triethyl-phosphines were carried out in an i.r. cell, in n-heptane solutions in the dark. In the case of PPh_3, the reaction was complete after 23 h as judged by carbonyl-stretching frequencies observed at 2 093s, 2 062s, 2 057 (sh), 2 039s, 2 033s, 2 022 (sh), 2 019s, 1 993w, 1 983m, and 1 946vs cm^{-1}; these bands suggest that the two main products formed are $[Os(CO)_4(PPh_3)]$ [23] and $[Os_2(CO)_8H_2]$. In the case of PEt_3, the reaction was complete after 10 min when ν(CO) bands were observed at 2 132vw, 2 093s, 2 057s, 2 039s, 2 033s, 2 021 (sh), 2 019s, and 1 955wbr cm^{-1}. These bands are identical to those observed for $[Os_2(CO)_8H_2]$.[21]

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* 1 eV ≈ 1.60 × 10^{-19} J.

† 1 mmHg = 13.6 × 9.8 Pa.

[26] R. K. Pomeroy and W. A. G. Graham, unpublished work.