Some Reactions of Tetracarbonyldihydrido-osmium, Octacarbonyldihydridodiosmium, and Dodecacarbonyldihydridotriosmium

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The reactions of $[\{Os(CO)_4\}_nH_2]$ (n = 2 or 3) with carbon tetrahalides yield the corresponding dihalides $[\{Os(CO)_4\}_nX_2]$ (X = Cl or Br). Heating $[Os_2X_2(CO)_8]$ (X = Cl or Br) in n-heptane solution affords the hexacarbonyl compounds $[Os_2X_2(CO)_6]$. The reactions of tin tetrachloride with $[\{Os(CO)_4\}_nH_2]$ (n = 1—3) are reported; for n = 1 or 2, the compounds $[\{Os(CO)_4\}_nH(SnCl_3)]$ (n = 1 or 2) have been isolated. The reaction of $[Os_2(CO)_8H_2]$ with triphenylphosphine yields the compounds $[Os_2(CO)_7H_2(PPh_3)]$, $[Os_2(CO)_6H_2(PPh_3)_2]$, $[Os(CO)_4(PPh_3)]$, and $[Os(CO)_3H_2(PPh_3)]$. Thermolysis of either $[Os_3(CO)_{12}H_2]$ or $[Os_2(CO)_8H_2]$ gives a mixture of the hydrides $[\{Os(CO)_4\}_nH_2]$ (n = 1—4) as well as $[Os_3(CO)_{10}H_2]$ and $[Os_3(CO)_{12}]$. Mechanisms are discussed for these thermolyses. Heating an n-heptane solution of $[Os(CO)_4H_2]$ produces a moderate yield of $[Os_4(CO)_{12}H_4]$. Reactions of $[\{Os(CO)_4\}_nH_2]$ (n = 1—3) with C_2F_4 have been studied, but only in the case of $[Os(CO)_4H_2]$ have products, namely *cis*- and *trans*-$[Os(C_2F_4H)_2(CO)_4]$, been isolated. I.r., n.m.r., and mass spectra of the compounds are reported and discussed.

In recent years, many new carbonyl hydrides of osmium have been prepared.[1-4] Following on from convenient syntheses[5,6] of $[Os(CO)_4H_2]$, some reactions of this compound have been reported.[5,7,8] A high-yield synthesis of $[Os_3(CO)_{10}H_2]$ has also been reported[9] and recently the chemistry of this polynuclear hydride has received considerable attention.[3,4,10-12] The reactivity of other carbonyl hydrides of osmium has, however, been little studied.

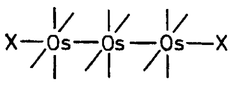
We have prepared the compounds $[Os_2(CO)_8H_2]$[13] and $[Os_3(CO)_{12}H_2]$[14] and we now describe and compare some reactions of the hydrides of the homologous series $[\{Os(CO)_4\}_nH_2]$ (n = 1—3). The hydrides of this series (where n = 2 or 3) are rare examples of polynuclear hydrides which we believe to contain terminal metal–hydrogen bonds. Preliminary reports of some of the reactions described have already appeared.[13-15]

RESULTS AND DISCUSSION

Reaction with Carbon Tetrahalides.—Both $[Os_2(CO)_8H_2]$ and $[Os_3(CO)_{12}H_2]$ react almost quantitatively [equation (1)] with carbon tetrahalides to yield the corresponding halides, as does $[Os(CO)_4H_2]$.[5]

$$[\{Os(CO)_4\}_nH_2] + CX_4 \longrightarrow [\{Os(CO)_4\}_nX_2] \quad (n = 1\text{—}3;\ X = Cl \text{ or } Br) \quad (1)$$

The trinuclear halides have previously been reported as products of the reactions of the halogens with $[Os_3(CO)_{12}]$.[16] The linear structure (1) was suggested for these compounds, mainly on the basis of three strong bands in the ν(CO) region of the i.r. spectra.[16] Our i.r. data (Table 1) are not consistent with structure (1) ‡ and we suggest that (2) or (3) are more probable. A single-crystal X-ray study has shown that $[Os_3(CO)_{12}I_2]$ has structure (2; X = I).[17]



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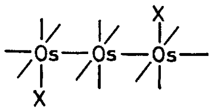

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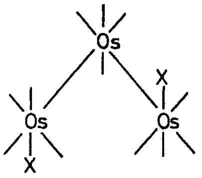

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The binuclear halides $[Os_2(CO)_8X_2]$ (X = Cl or Br) had not previously been characterized, although the iodide of this series was recently reported as a product of the reaction of $[Os_3(CO)_{12}]$ with iodine or CF_3I.[18] Structure (4) was suggested for these binuclear dihalides on the basis of their i.r. spectra[13,18] (Table 1), and this has now

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‡ Structures in this paper are represented schematically in the eclipsed form for clarity, although staggered conformers are expected. Carbonyl groups are omitted for clarity.

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TABLE 1

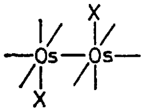
Bands (cm^{-1}) in the carbonyl-stretching frequency region [a]

Compound	ν(CO)
$[Os_3(CO)_{12}Cl_2]$ [b]	2 150w, 2 120s, 2 085w (sh), 2 063vs, 2 030s, 2 001m
$[Os_3Br_2(CO)_{12}]$ [b]	2 148w, 2 188s, 2 086w (sh), 2 062vs, 2 032s, 2 002m
$[Os_2(CO)_8Cl_2]$	2 121s, 2 082vs, 2 069s, 2 064s, 2 054s, 2 032s
$[Os_2Br_2(CO)_8]$	2 118s, 2 080vs, 2 068s, 2 063s, 2 052s, 2 031s
$[Os_2(CO)_6Cl_2]$	2 107m, 2 077s, 2 022s, 2 013s
$[Os_2Br_2(CO)_6]$	2 104m, 2 074s, 2 020s, 2 012s, 2 009w (sh)
$[Os(CO)_4H(SnCl_3]$	2 155m, 2 095s, 2 078vs, 2 072s
$[Os(CO)_4H(SnBr_3)]$	2 152m, 2 094s, 2 076vs, 2 069s
$[Os_2(CO)_8H(SnCl_3)]$	2 142w, 2 107vs, 2 078s, 2 065s, 2 057 (sh), 2 054s, 2 043vs, 2 032m
$[Os_2(CO)_8Cl(SnCl_3)]$	2 152w, 2 118s, 2 085vs, 2 076s, 2 067s, 2 054vs, 2 048 (sh), 2 034m
$[Os_2Br(CO)_8(SnCl_3)]$	2 151w, 2 118s, 2 084vs, 2 076s, 2 067s, 2 055vs, 2 049m, 2 035m
$[Os_3(CO)_{12}Cl(SnCl_3)]$ [b]	2 152m, 2 124m, 2 086 (sh), 2 069vs, 2 049vs, 2 030m, 2 006m
$[Os_2(CO)_6H_2(PPh_3)_2]$ [b]	2 109vs, 2 073w, 2 029 (sh), 2 008vs, 1 979s, 1 954 (sh), 1 915wbr
$[Os_2(CO)_7H_2(PPh_3)]$	2 110s, 2 057s, 2 044s, 2 026vs, 2 011s, 1 982s, 1 950wbr
$[Os_4(CO)_{12}H_4]$ [c]	2 085s, 2 068vs, 2 022vs, 2 000m
trans-$[Os(C_2F_4H)_2(CO)_4]$	2 085
cis-$[Os(C_2F_4H)_2(CO)_4]$	2 172w, 2 102 (sh), 2 096vs, 2 073 (sh), 2 070s, 2 034vw

[a] n-Heptane solutions; br = broad, sh = shoulder. [b] In dichloromethane. [c] In cyclohexane.

been confirmed by an *X*-ray crystal-structure determination of $[Os_2(CO)_8Cl_2]$.[19]

The mass spectra of $[Os_2(CO)_8Cl_2]$ and $[Os_2Br_2(CO)_8]$ are unusual for metal carbonyl halides containing terminal metal–halogen bonds [20] since there is no competitive loss of carbon mono-oxide and halogen from the parent molecular ions. Similarly, peaks corresponding to $[P - I]^+$ or $[P - I_2]^+$ were not observed in the mass spectrum of $[Os_2(CO)_8I_2]$.[18] In contrast to a previous report,[16] we did not observe competitive loss of CO and halogen from the parent molecular ions of $[Os_3(CO)_{12}X_2]$ (X = Cl or Br). This result may be due to different conditions used for obtaining the spectra. It would thus appear hazardous to assign terminal metal–halogen bonds merely on the basis of mass-spectral data.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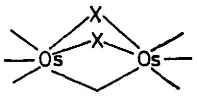
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The di-iodide $[Os_2(CO)_8I_2]$ was reported to form $[Os_2(CO)_6I_2]$ on heating *in vacuo*.[18] We found that heating $[Os_2(CO)_8X_2]$ (X = Cl or Br) *in vacuo* gave a mixture of $[Os_2(CO)_6X_2]$ and $[Os_3(CO)_{10}X_2]$.[21] However, the pure hexacarbonyls were readily obtained by refluxing the octacarbonyl dihalides in heptane; the conversion was almost quantitative. The i.r. spectra given in Table 1 are consistent with structure (5) for these molecules. The mass spectra of the hexacarbonyls showed the parent molecular ions with loss of six carbonyl groups. No halogen loss was observed until all the carbonyl groups were removed. Attempts to prepare a hexacarbonyl dihydride from $[Os_2(CO)_8H_2]$ were unsuccessful.

Reactions with Halogens.—In metal hydride compounds, metal–hydrogen bonds often react with halogens to give the corresponding halides.[22] We found that the reactions of chlorine with $[\{Os(CO)_4\}_nH_2]$ (n = 2 or 3) resulted in good yields of the dichlorides $[Os_2(CO)_8Cl_2]$ or $[Os_3(CO)_{12}Cl_2]$. Bromine, however, reacted with both $[Os_2(CO)_8H_2]$ and $[Os_3(CO)_{12}H_2]$ to cause cleavage of osmium–osmium bonds resulting in the formation of $[OsBr_2(CO)_4]$. Iodine reacted with both hydrides to give a *ca.* 1 : 1 mixture of $[Os(CO)_4I_2]$ and $[Os_2(CO)_8I_2]$.

Reactions with Tin Tetrahalides.—Tin tetrachloride reacted rapidly with a heptane solution of $[Os(CO)_4H_2]$ at room temperature to give the white crystalline product, *cis*-$[Os(CO)_4H(SnCl_3)]$. Similarly, $[Os_2(CO)_8H_2]$ readily reacted with $SnCl_4$ to give $[Os_2(CO)_8H(SnCl_3)]$. Thus, the general reaction can be written as in (2). The

$$SnCl_4 + [\{Os(CO)_4\}_nH_2] \longrightarrow [\{Os(CO)_4\}_nH(SnCl_3)] \quad (n = 1 \text{ or } 2) \qquad (2)$$

osmium–hydrogen stretching frequencies were not detected in the i.r. spectra, but the presence of the hydride ligand in these two compounds was confirmed by the observation of sharp singlets in the high-field region of the n.m.r. spectra (see Table 2). In the case of *cis*-$[Os(CO)_4H(SnCl_3)]$, spin–spin coupling was observed corresponding to $J(^{119}Sn–H)$ 136.0 and $J(^{117}Sn–H)$ 129.5 Hz. No observable coupling of the hydrogen with tin was detected in $[Os_2(CO)_8H(SnCl_3)]$ which is probably a

TABLE 2

Hydrogen-1 n.m.r. data

Compound	τ (for high-field) protons)	Solvent
$[Os(CO)_4H(SnCl_3)]$ [a]	18.37	CH_2Cl_2
$[Os_2(CO)_8H(SnCl_3)]$	19.55	CH_2Cl_2
$[Os(CO)_4H(SnBr_3)]$ [b]	17.93	CH_2Cl_2
$[Os_2(CO)_6H_2(PPh_3)_2]$ [c]	19.46	CH_2Cl_2
$[Os_2(CO)_7H_2(PPh_3)]$	19.11,[d] 19.46 [e]	C_6D_6
$[OsRe(CO)_9H]$	20.37	C_6H_6

[a] $J(^{119}Sn–H)$ 136.0, $J(^{117}Sn–H)$ 129.5 Hz. [b] $J(^{119}Sn–H)$ 135.0, $J(^{117}Sn–H)$ 129.0 Hz. [c] $|^2J(P–Os–H) + {}^3J(P–Os–Os–H)|$ 18.5 Hz. [d] $^2J(P–Os–H)$ 17, $J(H–H)$ 0.7 Hz. [e] $^3J(P–Os–Os–H)$ 1.3, $J(H–H)$ 0.7 Hz.

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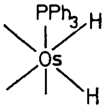
consequence of the trichlorotin and hydride ligands being bonded to different osmium atoms. The reaction of $SnCl_4$ with $[Os_3(CO)_{12}H_2]$ caused cleavage of the osmium–osmium bonds and the major product was *cis*-$[Os(CO)_4H(SnCl_3)]$. This contrasts the reaction of $SnCl_4$ with $[Os_3(CO)_{12}]$ where only one osmium–osmium bond was broken and the major product was $[Os_3(CO)_{12}Cl(SnCl_3)]$. This latter compound possibly has a structure similar to that found for $[Os_3(CO)_{12}I_2]$.[17] The reaction of tin tetrabromide with $[Os(CO)_4H_2]$ was much slower than that with $SnCl_4$ but gave an analogous product, *cis*-$[Os(CO)_4(SnBr_3)]$. All the new tin–osmium derivatives showed a parent molecular ion in their mass spectra, having the expected isotope pattern.

Although *cis*-$[Os(CO)_4H(SnCl_3)]$ does not react readily with carbon tetrahalides, $[Os_2(CO)_8H(SnCl_3)]$ reacted with CCl_4 or CBr_4 to give the products $[Os_2(CO)_8X(SnCl_3)]$ (X = Cl or Br) which were characterized by their i.r. and mass spectra only.



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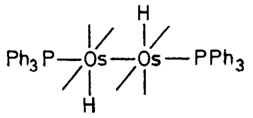

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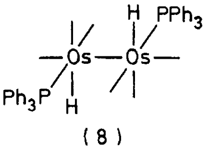

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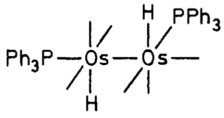

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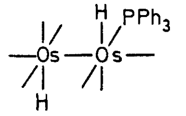

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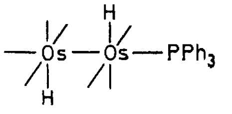

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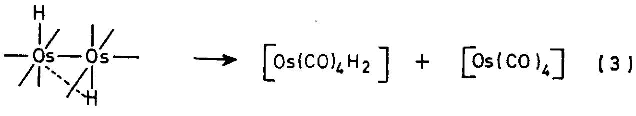
Reactions with Tertiary Phosphines.—The reaction of $[Os(CO)_4H_2]$ with triphenylphosphine has been reported[5] to give the monosubstituted product $[Os(CO)_3H_2(PPh_3)]$ of structure (6). We found that $[Os_2(CO)_8H_2]$ reacted with PPh_3 to yield the four products $[Os_2(CO)_6H_2(PPh_3)_2]$, $[Os_2(CO)_7H_2(PPh_3)]$, $[Os(CO)_3H_2(PPh_3)]$, and $[Os(CO)_4(PPh_3)]$; a possible mechanism for the formation of the last two products is discussed later. Both the new tertiary-phosphine substituted binuclear dihydrides are air-stable, colourless, crystalline solids. A mass spectrum of $[Os_2(CO)_6H_2(PPh_3)_2]$ was not obtained due to the involatility of the sample; however, for $[Os_2(CO)_7H_2(PPh_3)]$ a parent molecular ion was observed. The mass spectra of $[Os(CO)_3H_2(PPh_3)]$ and $[Os(CO)_4(PPh_3)]$ were recorded to aid identification. It is interesting to note that for $[Os(CO)_3H_2(PPh_3)]$ a parent was not observed, but, like the unsubstituted hydride $[Os(CO)_4H_2]$, the highest *m/e* ion corresponds to $[P - 2H]^+$.[23]

The ^1H n.m.r. spectrum of $[Os_2(CO)_6H_2(PPh_3)_2]$ showed a high-field signal centred at τ 19.46, the main feature of which was a doublet $[|{}^2J(\text{P–Os–H}) + {}^3J(\text{P–Os–Os–H})|$ 18.5 Hz]. Other lines were also observed which would be expected for an AA'XX' spin system; however, resolution of these lines was poor due to the low solubility of the compound. The compound $[Os_2(CO)_7H_2(PPh_3)]$ is very soluble in $[^2H_6]$benzene and a good ^1H n.m.r. spectrum was obtained. A complex multiplet at *ca.* τ 2.0 due to the phenyl protons, and two signals at high field were observed. Both high-field signals appeared as doublets of doublets due to phosphorus–hydrogen and hydrogen–hydrogen spin–spin coupling. It is interesting to note that ${}^2J(\text{P–Os–H}) + {}^3J(\text{P–Os–Os–H})$ in $[Os_2(CO)_7H_2(PPh_3)]$ is 18.3 Hz, almost the same as $|{}^2J(\text{P–Os–H}) + {}^3J(\text{P–Os–Os–H})|$ in $[Os_2(CO)_6H_2(PPh_3)_2]$ (*i.e.* 18.5 Hz). Thus ${}^2J(\text{P–Os–H})$ and ${}^3J(\text{P–Os–Os–H})$ are probably of the same sign.

The magnitude of the phosphorus–hydrogen coupling constants in $[Os_2(CO)_6H_2(PPh_3)_2]$ and $[Os_2(CO)_7H_2(PPh_3)]$ suggests that the PPh_3 ligands are *cis* to the hydride ligands.[5] Since both hydrides are equivalent in $[Os_2(CO)_6H_2(PPh_3)_2]$, the most likely structures are (7) and (8), assuming the equatorial position of the hydride ligands is not changed on substitution; structure (9) cannot be completely ruled out. Similarly, for $[Os_2(CO)_7H_2(PPh_3)]$, structures (10) and (11) would be the most likely.

The reaction of $[Os_3(CO)_{12}H_2]$ with PPh_3 gave a complicated mixture of products and only $[Os(CO)_4(PPh_3)]$ was identified by i.r. spectroscopy.

Thermolysis of $[\{Os(CO)_4\}_nH_2]$ (n = 1—3).—We studied the thermolyses of the hydrides $[\{Os(CO)_4\}_nH_2]$ in sealed tubes, without solvent for n = 2 or 3 and with heptane solvent for n = 1. At *ca.* 160 °C $[Os_3(CO)_{12}H_2]$ gave only $[Os_3(CO)_{12}]$; however, at *ca.* 120 °C many products formed. The volatile product from this thermolysis reaction was shown by i.r. spectroscopy to be $[Os(CO)_4H_2]$. After removal of the volatile product, the residue in the reaction tube was shown by a combination of i.r., n.m.r., and mass spectrometry to contain $[Os_2(CO)_8H_2]$, $[Os_3(CO)_{12}H_2]$, and $[Os_4(CO)_{16}H_2]$ as well as $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{10}H_2]$. Thermolysis of $[Os_2(CO)_8H_2]$ under similar conditions gave a mixture of the same products. The products can be accounted for by a mechanism involving elision of $[Os(CO)_4]$ from the bi- or tri-nuclear hydride by a 1,2 shift of hydrogen [equation (3)]. The co-ordinatively unsaturated $[Os(CO)_4]$ could then insert into the osmium–hydrogen bond of $[Os_2(CO)_8H_2]$ to form $[Os_3(CO)_{12}H_2]$. This trinuclear hydride could also produce $[Os(CO)_4]$ or react with it to form $[Os_4(CO)_{16}H_2]$. Alternative mechanisms involving homolytic cleavage of osmium–osmium and osmium–hydrogen bonds could also account for the observed products in these thermolysis reactions.



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[23] J. R. Moss and W. A. G. Graham, *Inorg. Chem.*, 1977, **16**, in the press.

The thermolysis of $[Os_3(CO)_{12}H_2]$ was undertaken in the presence of $[Re(CO)_5H]$ and it was anticipated that the rhenium hydride might compete with the osmium hydrides for the intermediate $[Os(CO)_4]$. The i.r. spectrum of the products from this thermolysis reaction showed ν(CO) bands which could be attributed to $[Os(CO)_4H\{Re(CO)_5\}]$ as well as bands due to the hydrides $[\{Os(CO)_4\}_nH_2]$ (n = 1—4). The mixed-metal hydride $[OsRe(CO)_9H]$ could not be completely separated from $[Os_2(CO)_8H_2]$ but a parent molecular ion was observed in the mass spectrum, with the expected isotope pattern for $[OsRe(CO)_9H]$, and a signal in the ^1H n.m.r. spectrum was observed at τ 20.37. The compound $[OsRe(CO)_9H]$ reacted with CCl_4 to give the corresponding chloride $[Os(CO)_4Cl\{Re(CO)_5\}]$ which was only identified mass spectrometrically.

The main products of the reaction of $[Os_2(CO)_8H_2]$ with PPh_3 in refluxing benzene are $[Os_2(CO)_6H_2(PPh_3)_2]$ and $[Os_2(CO)_7H_2(PPh_3)]$; however, small amounts of $[Os(CO)_4(PPh_3)]$ and $[Os(CO)_3H_2(PPh_3)]$ were also formed. These minor products can be rationalized on the basis of the elision mechanism, followed by reaction of the intermediates $[Os(CO)_4]$ and $[Os(CO)_4H_2]$, thus formed, with PPh_3 to give the observed products $[Os(CO)_4(PPh_3)]$ and $[Os(CO)_3H_2(PPh_3)]$. The hydride $[Os(CO)_4H_2]$ is known to react with PPh_3 to give $[Os(CO)_3H_2(PPh_3)]$.[5] That these products are not formed from $[Os_2(CO)_6H_2(PPh_3)_2]$ was shown by refluxing $[Os_2(CO)_6H_2(PPh_3)_2]$ in benzene for 5 h, when the starting material was recovered unchanged. Although the reaction of $[Os_3(CO)_{12}H_2]$ with PPh_3 gave a mixture of products which was not separated, the i.r. spectrum of the reaction mixture showed that $[Os(CO)_4(PPh_3)]$ is formed in this reaction.

On heating a solution of $[Os(CO)_4H_2]$ in heptane at 100 °C for 17 h a single product, $[Os_4(CO)_{12}H_4]$,[9,16] was isolated. Recently, it has been shown that the primary product of the thermolysis of $[Os(CO)_4H_2]$ is $[Os_2(CO)_8H_2]$ formed by a binuclear elimination of hydrogen from $[Os(CO)_4H_2]$, and that other polynuclear carbonyl hydrides, *e.g.* $[Os_4(CO)_{12}H_4]$, are formed subsequently.[24]

Reactions with C_2F_4.—The reaction of $[Os(CO)_4H_2]$ with C_2F_4 at 116 °C gave two readily separable products. Both products showed a parent molecular ion at *m/e* 506 corresponding to the simple tetrafluoroethyl insertion product $[Os(C_2F_4H)_2(CO)_4]$. The i.r. spectra suggested that the compounds were *cis*- and *trans*-$[Os(C_2F_4H)_2(CO)_4]$. N.m.r. data for the two complexes are given in Table 3 and are consistent with the *cis* and *trans* isomers. The reactions of $[\{Os(CO)_4\}_nH_2]$ (n = 2 or 3) with C_2F_4 under similar conditions to those for $[Os(CO)_4H_2]$ resulted in a mixture of products from which no pure compounds were separated.

EXPERIMENTAL

The osmium carbonyl hydrides $[\{Os(CO)_4\}_nH_2]$ (n = 1—3) were prepared as described previously.[23] All the reactions were carried out under an atmosphere of nitrogen.

Melting points were determined on a Kofler hot-stage apparatus. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer and in expanded form on a Hewlett–Packard 7127A recorder; spectra were calibrated with gaseous carbon mono-oxide. N.m.r. measurements were made on Varian Associates A56/60A and HA 100 instruments; chemical shifts for ^1H n.m.r. spectra are relative to tetramethylsilane (τ 10.00). Mass spectra were obtained using Associated Electrical Industries MS-9 and MS-12 instruments operating at 70 eV * ionizing voltage. Calculated mass spectra were obtained using a computer program prepared by Drs. R. S. Gay and E. H. Brooks in this department. Accurate masses were determined on the most abundant peak of the parent molecular ion and compared with the mass of the same peak in the calculated spectrum. Microanalyses were by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany, by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by the microanalytical laboratory of this department.

TABLE 3

Nuclear magnetic resonance data for $[Os(C_2F_4H)_2(CO)_4]$ [a]

	^1H		
	τ	$J(F_\alpha$–H)	$J(F_\beta$–H)
cis-Isomer [b]	5.00	57.5	5.0
trans-Isomer	4.96	59.5	5.0

	^{19}F			
	F_α [c]	F_β [c]	$J(F_\alpha$–H)	$J(F_\beta$–H)
cis-Isomer [b]	123.3	75.6	58	5
trans-Isomer [d]	121.9	91.7	59	5

[a] F_α refers to the fluorine atoms closest to the hydrogen atoms, F_β to those furthest away from the hydrogen atoms; coupling constants are given in Hz. [b] In C_6D_6. [c] In p.p.m. to high field of CCl_3F. [d] In n-heptane.

Reactions.—$[Os_2(CO)_8H_2]$ *with carbon tetrachloride*. A solution of $[Os_2(CO)_8H_2]$ (0.12 g) in carbon tetrachloride (5 cm^3) was allowed to stand at room temperature for 10 min. Removal of solvent and recrystallization of the residue from heptane gave octacarbonyldichlorodiosmium, $[Os_2(CO)_8Cl_2]$, as very pale yellow *prisms* (0.10 g, 75%), m.p. 118 °C (decomp.) (Found: C, 14.45; H, 0.00; Cl, 10.25; O, 19.45. $C_8Cl_2O_8Os_2$ requires C, 14.25; H, 0.00; Cl, 10.5; O, 18.95%). The mass spectrum showed the following ions (relative abundances in parentheses): $[P]^+$(21), $[P - CO]^+$ (12), $[P - 2CO]^+$ (100), $[P - 3CO]^+$ (44), $[P - 4CO]^+$ (87), $[P - 3CO - Cl]^+$ (10), $[P - 5CO]^+$ (59), $[P - 4CO - Cl]^+$ (9), $[P - 6CO]^+$ (42), $[P - 5CO - Cl]^+$ (10), $[P - 7CO]^+$ (57), $[P - 6CO - Cl]^+$ (14), $[Os_2Cl_2]^+$ (57), $[P - 7CO - Cl]^+$ (13), $[P - 7CO - O - Cl]^+$ (11), $[Os_2Cl]^+$ (55), $[P - 7CO - O - Cl_2]^+$ (14), $[Os_2]^+$ (28), $[Os(CO)_3Cl]^+$ (39), $[Os(CO)_2Cl]^+$ (27), $[Os(CO)Cl]^+$ (27), $[OsCl]^+$ (41), and $[Os]^+$ (60).

$[Os_3(CO)_{12}H_2]$ *with carbon tetrachloride*. Similarly, reaction of $[Os_3(CO)_{12}H_2]$ (0.054 g) with CCl_4 (10 cm^3) gave on recrystallization from methylene chloride–hexane pale yellow *microprisms* of $[Os_3(CO)_{12}Cl_2]$ (0.058 g, 98%), m.p. 164—170 °C (decomp.) (Found: C, 14.75; Cl, 7.25. $C_{12}Cl_2O_{12}Os_3$ requires C, 15.05; Cl, 7.65%).

$[Os_2(CO)_8H_2]$ *with carbon tetrabromide*. A solution of $[Os_2(CO)_8H_2]$ (0.16 g) in heptane (7 cm^3) was treated with carbon tetrabromide (0.26 g). The solution was set aside

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[24] J. Evans and J. R. Norton, *J. Amer. Chem. Soc.*, 1974, **96**, 7577.

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 mmHg ≈ 13.6×9.8 Pa.

for 15 min at 0 °C and the solid which was precipitated was recrystallized from heptane to give dibromo-octacarbonyldiosmium, $[Os_2Br_2(CO)_8]$, as pale yellow *prisms* (0.14 g, 70%), m.p. 121—126 °C (decomp.) (Found: C, 12.45; H, 0.00; Br, 21.35; O, 17.25. $C_8Br_2O_8Os_2$ requires C, 12.55; H, 0.00; Br, 20.9; O, 16.75%). The mass spectrum showed the following ions (relative abundances in parentheses): $[P^+]$(16), $[P - CO]^+$ (14), $[P - 2CO]^+$ (100), $[P - 3CO]^+$ (27), $[P - 4CO]^+$ (65), $[P - 3CO - Br]^+$ (9), $[P - 5CO]^+$ (48), $[P - 4CO - Br]^+$ (5), $[P - 6CO]^+$ (37), $[P - 5CO - Br]^+$ (5), $[P - 7CO]^+$ (48), $[P - 6CO - Br]^+$ (7), $[P - 7CO - O - Br]^+$ (10), $[Os_2Br]^+$ (48), $[P - 7CO - O - Br_2]^+$ (14), $[Os_2]^+$ (36), $[OsBr(CO)_3]^+$ (34), $[OsBr(CO)_2]^+$ (22), $[OsBr(CO)]^+$ (24), $[OsBr]^+$ (50), $[Os(CO)]^+$ (11), $[OsC]^+$ (22), and $[Os]^+$ (68).

$[Os_3(CO)_{12}H_2]$ *with carbon tetrabromide*. Similarly, reaction of $[Os_3(CO)_{12}H_2]$ (0.11 g) with CBr_4 (0.50 g) in hexane (25 cm^3) gave on recrystallization from methylene chloride–hexane pale yellow *prisms* of $[Os_3Br_2(CO)_{12}]$ (0.10 g, 78%), m.p. 145—155 °C (decomp.) (Found: C, 13.75; Br, 15.3. $C_{12}Br_2O_{12}Os_3$ requires C, 13.5; Br, 14.95%).

$[Os_2(CO)_8H_2]$ *with chlorine*. Chlorine was bubbled through a solution of $[Os_2(CO)_8H_2]$ (0.20 g) in hexane (10 cm^3) for 1 min. The solid product was filtered off and washed with hexane. The i.r. spectrum of this solid (0.19 g, 86%) was identical to that of an authentic sample of $[Os_2(CO)_8Cl_2]$.

$[Os_3(CO)_{12}H_2]$ *with chlorine*. In a similar procedure, $[Os_3(CO)_{12}H_2]$ (0.043 g) gave microprisms (0.037 g, 80%) which were shown by i.r. spectroscopy to be $[Os_3(CO)_{12}Cl_2]$.

$[Os_2(CO)_8H_2]$ *with bromine*. A solution of $[Os_2(CO)_8H_2]$ (0.066 g) in hexane (10 cm^3) was treated with a solution of bromine in hexane until the bromine colour persisted. The precipitate was filtered off to give white microprisms (0.072 g, 72%), the i.r. spectrum of which was identical to that of an authentic sample of $[OsBr_2(CO)_4]$.[5]

$[Os_3(CO)_{12}H_2]$ *with bromine*. In a similar procedure, $[Os_3(CO)_{12}H_2]$ (0.041 g) gave off-white microprisms (0.038 g, 61%) of $[OsBr_2(CO)_4]$.

$[Os_2(CO)_8H_2]$ *with iodine*. The compound (0.036 g) in hexane (5 cm^3) when treated with iodine gave only a very small amount of precipitate. The solution was filtered and the solvent removed to give a yellow-white solid (0.046 g), the i.r. spectrum of which corresponded to a mixture of $[Os(CO)_4I_2]$ [25] and $[Os_2(CO)_8I_2]$.[18]

$[Os_3(CO)_{12}H_2]$ *with iodine*. Similarly, $[Os_3(CO)_{12}H_2]$ (0.030 g) gave a yellow-white crystalline solid (0.042 g) shown to be a mixture of $[Os(CO)_4I_2]$ and $[Os_2(CO)_8I_2]$.

$[Os(CO)_4H_2]$ *with tin tetrachloride*. A solution of $[Os(CO)_4H_2]$ (0.15 g, 0.5 mmol) in heptane (10 cm^3) was stirred with tin tetrachloride (0.258 g, 1.0 mmol) for 10 min, then allowed to stand at 0 °C for 1 h. The solid was filtered off and washed with hexane (2 × 5 cm^3) to give *cis*-tetracarbonylhydrido(trichlorostannio)osmium, $[Os(CO)_4H(SnCl_3)]$ (0.25 g, 96%), as colourless *needles* from methylene chloride–hexane, m.p. 101—104 °C [Found: C, 9.05; H, 0.00; Cl, 20.1; O, 12.1; *M* (mass spectrometrically) 529.758. $C_4HCl_3O_4OsSn$ requires C, 9.10; H, 0.20; Cl, 20.15; O, 12.1%; *M* 529.754].

$[Os(CO)_4H_2]$ *with tin tetrabromide*. A solution of $[Os(CO)_4H_2]$ (0.15 g, 0.5 mmol) in heptane (10 cm^3) was stirred with tin tetrabromide (0.60 g, 1.4 mmol) for 3 d. The reaction solution was cooled to −20 °C and filtered to give *cis*-tetracarbonylhydrido(tribromostannio)osmium, $[Os(CO)_4H(SnBr_3)]$ (0.27 g, 83%), as colourless *plates* from heptane, m.p. 87—91 °C (Found: C, 7.60; H, 0.50; Br, 35.75. $C_4HBr_3O_4OsSn$ requires C, 7.25; H, 0.20; Br, 36.2%).

$[Os_2(CO)_8H_2]$ *with tin tetrachloride*. A solution of $[Os_2(CO)_8H_2]$ (0.15 g, 0.25 mmol) in heptane (10 cm^3) was stirred with $SnCl_4$ (0.22 g, 0.84 mmol) for 5 min when a white solid precipitated. The solvent was removed under reduced pressure to give octacarbonylhydrido(trichlorostannio)diosmium, $[Os_2(CO)_8H(SnCl_3)]$ (0.20 g, 97%), as colourless *needles* from methylene chloride–pentane, m.p. 118—121 °C (decomp.) [Found: C, 12.7; Cl, 12.85; O, 15.3; *M* (mass spectrometrically) 831.704. $C_8HCl_3O_8Os_2Sn$ requires C, 11.55; Cl, 12.8; O, 15.4%; *M* 831.532].

$[Os_3(CO)_{12}H_2]$ *with tin tetrachloride*. Similarly, $[Os_3(CO)_{12}H_2]$ (0.048 g, 0.052 mmol) in heptane (10 cm^3) with $SnCl_4$ (0.04 g, 0.16 mmol) gave *cis*-$[Os(CO)_4H(SnCl_3)]$ (0.026 g, 47%), after sublimation (55 °C, 0.01 mmHg), and identified by its i.r. spectrum.

$[Os_3(CO)_{12}]$ *with tin tetrachloride*. A suspension of $[Os_3(CO)_{12}]$ (0.19 g, 0.21 mmol) in benzene (10 cm^3) was stirred with $SnCl_4$ (1.11 g, 4.2 mmol) for 3 h. The white solid that precipitated was filtered off to give dodecacarbonylchloro(trichlorostannio)triosmium, $[Os_3(CO)_{12}Cl(SnCl_3)]$ (0.23 g, 94%), as colourless *microprisms* from methylene chloride–hexane, m.p. 185 °C (decomp.) (Found: C, 12.05; H, 0.00; Cl, 12.1; O, 15.95. $C_{12}Cl_4O_{12}Os_3Sn$ requires C, 12.35; H, 0.00; Cl, 12.1; O, 16.45%).

$[Os_2(CO)_8H(SnCl_3)]$ *with carbon tetrachloride*. A solution of $[Os_2(CO)_8H(SnCl_3)]$ (0.08 g) in CCl_4 (5 cm^3) was heated under reflux for 2 min. The solvent was removed under reduced pressure leaving colourless *needles* (0.07 g, 84%), m.p. 129—132 °C, identified as octacarbonylchloro(trichlorostannio)diosmium, $[Os_2(CO)_8Cl(SnCl_3)]$, by i.r. and mass spectroscopy only.

$[Os_2(CO)_8H(SnCl_3)]$ *with carbon tetrabromide*. A solution of $[Os_2(CO)_8H(SnCl_3)]$ (0.01 g) in benzene (5 cm^3) was heated with CBr_4 (0.015 g) for 2 min. The solvent was removed under reduced pressure and the resulting solid recrystallized from methylene chloride–pentane to give bromo-octacarbonyl(trichlorostannio)diosmium, $[Os_2Br(CO)_8(SnCl_3)]$, as colourless *needles* (0.05 g, 45%), m.p. 128—131 °C (decomp.), identified by i.r. and mass spectroscopy only.

$[Os_2(CO)_8H_2]$ *with triphenylphosphine*. A solution of $[Os_2(CO)_8H_2]$ (0.27 g, 0.44 mmol) and triphenylphosphine (0.23 g, 0.89 mmol) in benzene (25 cm^3) was heated under reflux for 2 h. The solvent was removed under reduced pressure and the solid residue washed with hexane (3 × 25 cm^3) to give hexacarbonyldihydridobis(triphenylphosphine)diosmium, $[Os_2(CO)_6H_2(PPh_3)_2]$, as white *plates* (0.10 g, 21%) from methylene chloride–hexane, m.p. 207—210 °C (Found: C, 46.95; H, 3.20; P, 5.95. $C_{42}H_{32}O_6Os_2P_2$ requires C, 46.9; H, 3.00; P, 5.75%). The combined hexane washings, after removal of $[Os_2(CO)_6H_2(PPh_3)_2]$, were concentrated and chromatographed on a Florisil column. Elution with hexane gave in order: $[Os_2(CO)_8H_2]$; $[Os_2(CO)_7H_2(PPh_3)]$ as colourless *prisms* (0.08 g, 20%), m.p. 99—101 °C, from hexane (Found: C, 38.5; H, 2.90; P, 3.80. $C_{25}H_{17}O_7Os_2P$ requires C, 35.7; H, 2.05; P, 3.70%); and $[Os(CO)_3H_2(PPh_3)]$ (0.02 g) identified by its i.r. and mass spectra. Elution with benzene gave $[Os(CO)_4(PPh_3)]$ (0.02 g) identified [26] by its i.r. and mass spectra.

$[Os(CO)_4H_2]$ *with* C_2F_4. A solution of $[Os(CO)_4H_2]$ (0.22 g,

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[25] L. A. W. Hales and R. J. Irving, *J. Chem. Soc.* (*A*), 1967, 1932.

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

0.72 mmol) and C_2F_4 (0.56 g, 5.60 mmol) in heptane (15 cm^3) was heated in a sealed evacuated Carius tube at 116 °C for 5 h. After cooling, the unchanged tetrafluoroethylene was removed under reduced pressure followed by solvent and volatile reaction products, leaving a pale yellow solid (0.24 g, 65%). This solid was recrystallized from hexane and sublimed (30 °C, 0.01 mmHg) to give *cis*-tetracarbonylbis-(tetrafluoroethyl)osmium, $[Os(C_2F_4H)_2(CO)_4]$, as colourless *needles*, m.p. 81—83 °C (Found: C, 19.05; H, 0.65. $C_8H_2F_8O_4Os$ requires C, 19.05; H, 0.40%). The solvent and volatile reaction products which had been removed under reduced pressure from the Carius tube were cooled to −78 °C when a low yield of colourless prisms was deposited. These crystals were identified as *trans*-tetracarbonylbis-(tetrafluoroethyl)osmium, $[Os(C_2F_4H)(CO)_4]$, by i.r. and mass spectroscopy. The compound sublimes without melting above 60 °C.

Thermolyses.—$[Os(CO)_4H_2]$. A solution of $[Os(CO)_4H_2]$ (0.30 g, 1.0 mmol) in heptane (20 cm^3) was heated in a sealed evacuated Carius tube at 100 °C for 17 h. The tube was cooled and the pale yellow crystals filtered off and washed with heptane to give $[Os_4(CO)_{12}H_4]$ (0.15 g, 55%) as pale yellow *microprisms* from benzene, m.p. 232—240 °C (decomp.) [Found: C, 13.25; H, 0.20; O, 17.5; *M* (mass spectrometrically) 1 101.810. $C_{12}H_4O_{12}Os_4$ requires C, 13.1; H, 0.35; O, 17.45%; *M* 1 101.808].

$[Os_2(CO)_8H_2]$. The compound (0.043 g) was heated in a sealed evacuated Carius tube at 135 °C for 20 min. The tube was cooled, opened, and the volatile product {shown by its i.r. spectrum to be $[Os(CO)_4H_2]$} removed under reduced pressure. An i.r. spectrum of a heptane solution of the residue in the tube showed ν(CO) bands of $[Os_2(CO)_8H_2]$, $[Os_3(CO)_{12}H_2]$, $[Os_4(CO)_{16}H_2]$, $[Os_3(CO)_{12}]$, and trace amounts of $[Os_3(CO)_{10}H_2]$.

$[Os_3(CO)_{12}H_2]$. The compound (0.023 g) was heated in a sealed evacuated Carius tube at 120—129 °C for 15 min. The tube was cooled, opened, and the volatile product shown to be $[Os(CO)_4H_2]$ by its i.r. and mass spectra. An i.r. spectrum of the residue in the tube showed this to contain $[Os_2(CO)_8H_2]$, $[Os_3(CO)_{12}H_2]$, $[Os_4(CO)_{16}H_2]$, $[Os_3(CO)_{12}]$, and trace amounts of $[Os_3(CO)_{10}H_2]$. This residue was sublimed (48 °C, 0.01 mmHg) to remove $[Os_2(CO)_8H_2]$, $[Os_3(CO)_{12}H_2]$, and $[Os_3(CO)_{10}H_2]$, and the remaining residue sublimed (55 °C, 0.01 mmHg) for 3 d; this sublimate was shown to be mainly $[Os_4(CO)_{16}H_2]$ and $[Os_3(CO)_{12}]$ by i.r. and mass spectroscopy.

In a similar experiment, $[Os_3(CO)_{12}H_2]$ was heated at 125 °C for 10 min. A saturated solution of the oily residue was made up in benzene (3 cm^3). The ^{1}H n.m.r. spectrum of this solution in the high-field region showed four sharp singlets at τ 18.70, 19.77, 19.87, and 20.12 corresponding to $[Os(CO)_4H_2]$, $[Os_4(CO)_{16}H_2]$, $[Os_3(CO)_{12}H_2]$, and $[Os_2(CO)_8H_2]$ respectively; presumably, the concentration of $[Os_3(CO)_{10}H_2]$ in the products is too low for its high-field n.m.r. signal to be observed. In another experiment, $[Os_3(CO)_{12}H_2]$ was heated at 165 °C for 15 min; the i.r. spectrum of the resulting yellow solid was identical to that of $[Os_3(CO)_{12}]$.

$[Os_3(CO)_{12}H_2]$ *in the presence of* $[Re(CO)_5H]$. A mixture of $[Os_3(CO)_{12}H_2]$ (0.12 g, 0.13 mmol) and $[Re(CO)_5H]$ (0.09 g, 0.28 mmol) was heated in a sealed Carius tube at 117 °C for 30 min. The tube was cooled, opened, and an i.r. spectrum of the volatile product showed this to be a mixture of $[Os(CO)_4H_2]$ and $[Re(CO)_5H]$. An i.r. spectrum of the residue in the tube showed some new ν(CO) bands in addition to those of the osmium carbonyl hydrides obtained from thermolysis of $[Os_3(CO)_{12}H_2]$. The residue was sublimed (30 °C, 0.01 mmHg) to give a pale yellow oil. The mass spectrum of this oil showed a parent molecular ion corresponding to $[OsRe(CO)_9H]$ at *m/e* 630 having the expected isotope pattern; peaks due to $[Os_2(CO)_8H_2]$ were also present. The ^{1}H n.m.r. spectrum of this oil showed a signal at τ 20.09 due to $[Os_2(CO)_8H_2]$ and a signal at τ 20.37 which may be assigned to $[OsRe(CO)_9H]$; the i.r. spectrum in n-heptane solution showed ν(CO) bands due to $[Os_2(CO)_8H_2]$ as well as bands which can be assigned to $[OsRe(CO)_9H]$ at 2 082s, 2 069w, 2 046m, 2 028vs, 2 005s, and 1 983s cm^{-1}.

Hexacarbonyldichlorodiosmium.—A solution of $[Os_2(CO)_8Cl_2]$ (0.14 g) in heptane (20 cm^3) was heated under reflux for 40 min. The solvent was removed under reduced pressure to give a yellow-orange residue which was sublimed (60 °C, 0.01 mmHg) to give $[Os_2(CO)_6Cl_2]$ as yellow *prisms* (0.105 g, 82%), m.p. 82 °C (decomp.) (Found: C, 12.0; Cl, 12.3. $C_6Cl_2O_6Os_2$ requires C, 11.65; Cl, 11.45%).

Dibromohexacarbonyldiosmium.—Similarly, $[Os_2Br_2(CO)_8]$ (0.115 g) gave $[Os_2Br_2(CO)_6]$ as yellow *prisms* (0.095 g, 89%), m.p. 102—105 °C (Found: C, 10.4; Br, 22.9. $C_6Br_2O_6Os_2$ requires C, 10.2; Br, 22.55%).

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