

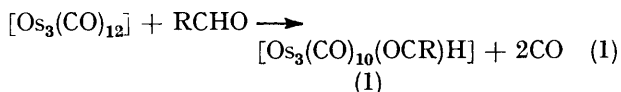
## Triosmium Clusters derived from Aldehydes, Ketones, and Ketens and their Interconversions

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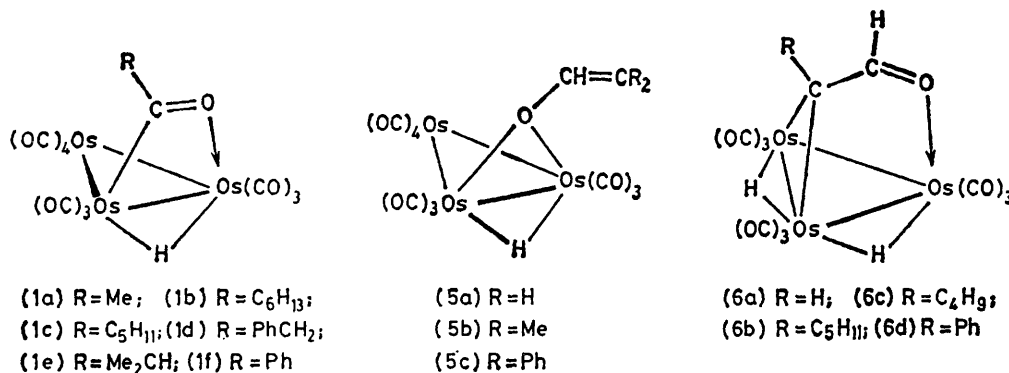
Acyl and enolato-complexes of types  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-OCR})\text{H}]$  ( $\text{R} = \text{CH}_3, \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_{13}, \text{PhCH}_2, \text{Me}_2\text{CH}, \text{or Ph}$ ) or  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-OCH}=\text{CR}'_2)\text{H}]$  ( $\text{R}' = \text{H}, \text{Me}, \text{or Ph}$ ) have been obtained by oxidative addition of aldehydes at  $[\text{Os}_3(\text{CO})_{12}]$  or by insertion of keten or substituted ketens into an Os-H bond of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$ . In certain cases the interconversion of enolato- and acyl complexes was established and in other cases inferred from their reactivity. The acyl complexes where  $\text{R} = \text{CH}_3, \text{Ph}, \text{or Ph}_2\text{CH}$  (derived from isomerisation of the enolato-complex where  $\text{R} = \text{Ph}$ ) decarbonylate at the ligand to give products derived from the alkyl complexes formed. Most acyl complexes ( $\text{R} = \text{CH}_3, \text{C}_5\text{H}_{11}, \text{C}_6\text{H}_{13}, \text{or PhCH}_2$ ) decarbonylate, however, only at the metal with subsequent hydrogen-atom transfer to and from the ligand to give complexes of type  $[\text{Os}_3(\text{CO})_9(\mu_3\text{-R}'\text{CCHO})\text{H}_2]$  containing a co-ordinated formyl group. Analogous species were obtained from cyclohexanone and  $[\text{Os}_3(\text{CO})_{12}]$  or from cyclohexenone and  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$ . All the complexes with organic ligands containing oxygen have Os-O bonds.

By reaction of  $[\text{Os}_3(\text{CO})_{12}]$  or  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  variously with aldehydes, ketones, and ketens we have prepared a range of triosmium clusters including  $\mu$ -acyl and  $\mu$ -vinyloxo-complexes of type  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-X})\text{H}]$  and have studied their interconversions, decarbonylations, and hydrogen-shift reactions. In spite of interest in the role of clusters in catalysis involving carbon monoxide (hydroformylation reactions, Fischer-Tropsch-type chemistry *etc.*) little is known of the nature and behaviour of ligands, such as acyls, that are implicated in these reactions. Prior to our work, the only known acyl cluster was  $[\text{Rh}_6(\text{CO})_{15}(\text{OCR})]^-$  ( $\text{R} = \text{Et}$  or  $\text{Pr}$ ),<sup>1</sup> and since triosmium clusters containing many ligand types

example  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3)\text{H}]$  gives methane and  $[\text{Os}_3(\text{CO})_{10}\text{-L}_2]$  with added ligands L.<sup>5</sup> Instead we used the known facility of substrates to react with  $[\text{Os}_3(\text{CO})_{12}]$  with C-H cleavage and so reacted a range of aldehydes in this way, equation (1). Acyl complexes (1b-f) were formed by



reaction (1) where  $\text{R} = \text{n-C}_6\text{H}_{13}, \text{n-C}_5\text{H}_{11}, \text{PhCH}_2, \text{Me}_2\text{CH}, \text{or Ph}$ . Reaction temperatures were necessarily high (130–150 °C) and yields disappointingly low (12–20%). Often carboxylato- or alkoxo-complexes of



may be generated and easily studied we have chosen to examine oxa-ligands in this system. Preliminary results have been reported,<sup>2-4</sup> but here we will present a complete account of our current work.

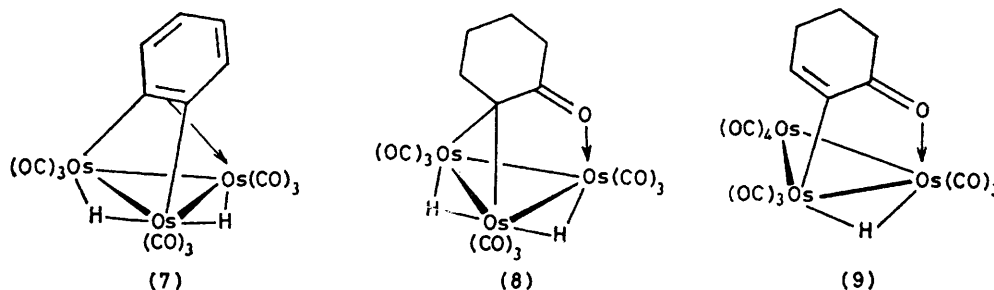
### RESULTS AND DISCUSSION

**Aldehydes.**—Mononuclear acyl complexes are normally synthesised by carbonyl insertion into alkyl-metal bonds or by reaction of acyl halides, for example, with nucleophilic metal centres such as in metal carbonyl anions. Few simple alkyl clusters are known and for triosmium they do not provide an obvious route to acyls, for

known type  $[\text{Os}_3(\text{CO})_{10}(\text{O}_2\text{CR})\text{H}]$  (2) and  $[\text{Os}_3(\text{CO})_{10}\text{-}(\text{OCH}_2\text{R})\text{H}]$  (3) were also formed even though the aldehydes were carefully purified to remove carboxylic acids and alcohols. Direct reaction of acetaldehyde with  $[\text{Os}_3(\text{CO})_{12}]$  gave  $[\text{Os}_2(\text{CO})_8(\text{O}_2\text{CCH}_3)_2]$  (4a) which is readily formed from acetic acid<sup>6</sup> so that complex (1a) ( $\text{R} = \text{CH}_3$ ) could not be formed by reaction (1). Also formaldehyde reacts with  $[\text{Os}_3(\text{CO})_{12}]$  in refluxing xylene to give  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)\text{H}]$  (32%) as the only product we could identify and we believe that the formyl complex  $[\text{Os}_3(\text{CO})_{10}(\text{OCH})\text{H}]$ , if it is formed, readily decarbonylates at this temperature giving  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$

which reacts further with formaldehyde. In a separate reaction we have shown that formaldehyde readily reacts with the dihydride in this way. Other aldehydes also insert into Os-H bonds of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  but less readily

The products (1) are thermally and air stable at room temperature and easy to isolate by thin-layer chromatography (t.l.c.) ( $\text{SiO}_2$ ) and to characterise. They all show parent molecular ions in their mass spectra and their



and give lower yields of the alkoxo-complexes. Allyl alcohol is catalytically isomerised to propanal by  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  <sup>7</sup> but the catalyst is eventually consumed to give a yellow solution from which we only isolated  $[\text{Os}_3(\text{CO})_9(\text{CEt})\text{H}_3]$ , compound (11b) in 4% yield.

i.r. spectra (around  $2000\text{ cm}^{-1}$ ) are consistent with the structure shown. Their stoichiometry suggests that the acyls are three-electron donors, while  $\nu(\text{CO})(\text{acyl})$  in the range  $1455$  to  $1492\text{ cm}^{-1}$  (Table 1) agrees with bonding to the metal through both C and O atoms. We cannot

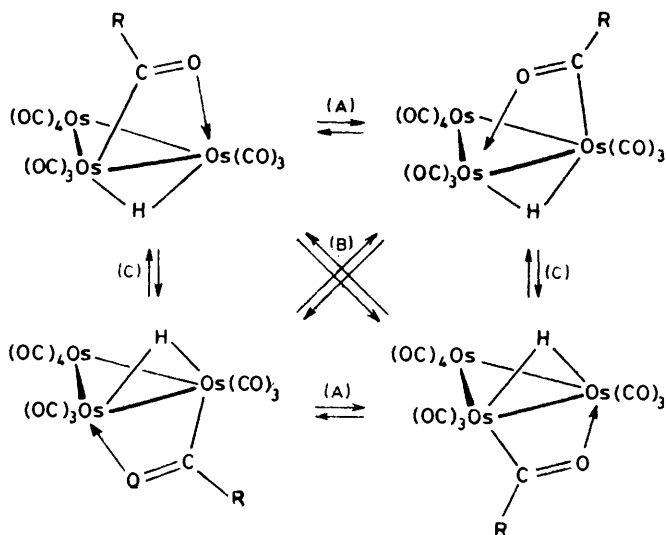
TABLE I  
Infrared and analytical data

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	$\nu(\text{CO})$ or $\nu(\text{C}=\text{C})/\text{cm}^{-1}$	Analysis (%) <sup>b</sup>	
			C	H
(1a)	2 112m, 2 072s, 2 060s, 2 030s, 2 016s, 1 998m, 1 991 (sh), 1 984m	1 492 <sup>c</sup>	16.55 (16.1)	0.60 (0.45)
(1b)	2 111m, 2 072s, 2 059s, 2 029s, 2 015s, 1 998m, 1 992 (sh), 1 984m	1 490 <sup>c</sup>	21.55 (21.15)	1.45 (1.45)
(1c)	2 112m, 2 072s, 2 060s, 2 029s, 2 015s, 1 998m, 1 992 (sh), 1 984m	1 490, <sup>c</sup> 1 478 <sup>c</sup>	21.0 (20.2)	1.35 (1.25)
(1d)	2 111m, 2 073s, 2 061s, 2 030s, 2 015s, 2 013w, 2 000m, 1 992 (sh), 1 985m	1 470 <sup>c</sup>	22.4 (22.25)	0.90 (0.85)
(1e)	2 112m, 2 071s, 2 059s, 2 030s, 2 015s, 1 998m, 1 992 (sh), 1 983m	1 480 <sup>c</sup>	18.45 (18.2)	0.95 (0.85)
(1f)	2 112m, 2 072s, 2 061s, 2 029s, 2 019s, 2 014 (sh), 1 999m, 1 992 (sh), 1 984m	1 455, <sup>c</sup> 1 426 <sup>c</sup>	21.55 (21.35)	0.60 (0.65)
(5a)	2 115w, 2 077s, 2 066s, 2 027vs, 2 009s, 1 993m, 1 988m	1 616 <sup>c</sup>	16.7 (16.1)	0.55 (0.45)
(5b)	2 114w, 2 074s, 2 063s, 2 027vs, 2 006s, 1 991m, 1 986m	1 670 <sup>c</sup>	18.35 (18.2)	0.90 (0.85)
(5c)	2 114w, 2 082 (sh), 2 077s, 2 064s, 2 027vs, 2 023 (sh), 2 005s, 1 990m, 1 987m	1 608, <sup>c</sup> 1 595 <sup>c</sup>	27.45 (27.55)	1.35 (1.15)
(6a)	2 111m, 2 085s, 2 080 (sh), 2 064 (sh), 2 056s, 2 041 (sh), 2 028s, 2 014m, 2 002s, 1 983m	1 500 <sup>c</sup>		
(6b)	2 108m, 2 083s, 2 055s, 2 026s, 2 014m, 2 002s, 1 980m	1 498 <sup>c</sup>	21.05 (20.5)	1.70 (1.50)
(6c)	2 109m, 2 084s, 2 055s, 2 027s, 2 014s, 2 001s, 1 980m	1 490 <sup>c</sup>	19.75 (19.5)	1.40 (1.30)
(6d)	2 113m, 2 087s, 2 059s, 2 027s, 2 017s, 2 003s, 1 990m, 1 985m	1 497 <sup>c</sup>	21.8 (21.65)	0.90 (0.85)
(8)	2 105w, 2 080s, 2 051s, 2 023s, 2 020 (sh), 2 010m, 1 998s, 1 970m	1 496 <sup>d</sup>	20.1 (19.55)	1.00 (1.10)
(9)	2 106m, 2 067s, 2 053s, 2 024s, 2 010m, 2 003s, 1 995m, 1 984w, 1 977m	1 555, <sup>d</sup> 1 536 <sup>d</sup>	20.0 (20.3)	0.75 (0.85)
(10a)	2 107m, 2 082s, 2 053s, 2 024s, 2 012m, 2 000s, 1 982m	1 615, <sup>d</sup> 1 505, <sup>d</sup> 1 494 <sup>d</sup>	20.6 (19.6)	1.15 (0.90)
(10b)	2 090m, 2 056vs, 2 038s, 2 015m, 1 999s, 1 982m, 1 969m	1 600 <sup>c</sup>	19.8 (19.6)	0.90 (0.90)
(11a)	2 083s, 2 021s, 2 010m		14.6 (14.3)	0.55 (0.50)
(11b)	2 080s, 2 021s, 2 008m		16.7 (16.65)	0.85 (0.95)
(12)	2 100m, 2 074s, 2 054m, 2 049 (sh), 2 020s, 2 009s, 1 990w, 1 982w		26.4 (26.7)	1.00 (1.00)

<sup>a</sup> Recorded in cyclohexane. <sup>b</sup> Calculated values are given in parentheses. <sup>c</sup> KBr disc. <sup>d</sup> Nujol mull. <sup>e</sup> No other absorption between  $1470$  and  $1969\text{ cm}^{-1}$  due to the organic ligand.

distinguish co-ordination through  $\pi$  CO electrons from that through an oxygen lone pair of electrons, but favour the latter by analogy with dinuclear complexes, e.g.  $[\text{Fe}_2(\text{CO})_6(\text{OCPh})_2]$ <sup>8</sup> and  $[(\text{C}_5\text{H}_5)\text{Ir}(\mu\text{-OCPh})(\mu\text{-OCMe})(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_3]$ .<sup>9</sup> There are, however, analogies for both modes of interaction as in  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-X})\text{H}]$  ( $\text{X} = \text{CH}=\text{CH}_2$ <sup>10</sup> and 2-pyridyl<sup>11</sup> respectively). The complex  $[\text{Os}_3(\text{CO})_{10}(\text{PhC}=\text{NMe})\text{H}]$  also has an *X*-ray structure like that shown for (1).<sup>12</sup>

There is quite a distinct difference in behaviour between  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}=\text{CH}_2)\text{H}]$  and complexes (1) in solution. The vinyl ligand rapidly oscillates between the osmium atoms it bridges, interchanging the  $\sigma$  and  $\eta^2$  linkages, to generate a time-averaged plane of symmetry.<sup>13</sup> This is a rapid enantiomerisation. With complexes (1) enantiomerisation is either slow or does not occur. Thus the <sup>1</sup>H n.m.r. spectrum of complex (1d) shows an AB quartet for the  $\text{CH}_2$  group at  $-130^\circ\text{C}$ . On raising the temperature there is no signal broadening although the two components of the quartet slowly move together to give a singlet at  $30^\circ\text{C}$ . Complex (1c) is a clearer case. The isopropyl methyl groups are diastereotopic giving two clearly resolved sharp <sup>1</sup>H n.m.r. doublets up to  $120^\circ\text{C}$ . Methyl exchange would have occurred either if the acyl and hydride ligands above and below the  $\text{Os}_3$  plane exchanged positions or if the C and O atoms of the  $\mu$ -acyl were interchanged. Both processes (A) and (B) (Scheme 1) are enantiomerisations; the



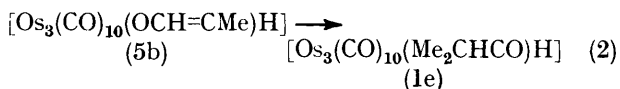
SCHEME 1

only movement which retains the enantiomeric form is (C) but this is highly unlikely to occur in the absence of (A) and (B). The enantiomers might, of course, interconvert slowly enough for the complexes (1) to be resolved. Our preliminary results show that this is more than possible. Diastereoisomers of the amido-bridged complex  $[\text{Os}_3(\text{CO})_{10}(\text{PhCHMeNHCO})\text{H}]$  derived from an enantiomerically pure sample of  $\text{PhCHMeNH}_2$  and  $[\text{Os}_3(\text{CO})_{12}]$  are structurally like (1) and are separable by t.l.c. ( $\text{SiO}_2$ )<sup>14</sup> and we are hoping to separate the isomers

of complex (1) similarly. This is an interesting area because the chirality is not intrinsic to the ligand but results from its geometry of attachment to the cluster.

*Ketens.*—Ketens are dehydro-aldehydes and so their reactions with  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  might be an alternative route to acyl complexes of type (1). Dimethyl-, diphenyl-keten, and keten itself react smoothly at room temperature with  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  to give the  $\mu$ -vinyloxo-complexes  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CR}_2)\text{H}]$  (5a) ( $\text{R} = \text{H}$ ), (5b) ( $\text{R} = \text{Me}$ ), and (5c) ( $\text{R} = \text{Ph}$ ) rather than the isomeric acyl complexes. Infrared, <sup>1</sup>H n.m.r., and mass spectra are totally consistent with the structure shown except that the alternative but less likely arrangement with inversion at oxygen might be adopted. The vinyl group does not interact significantly with the metal atoms. The <sup>1</sup>H n.m.r. spectrum of the vinyl group of (5a) is like those of vinyl ethers but at somewhat higher field and  $\nu(\text{C}=\text{C})$  is at  $1616\text{ cm}^{-1}$ .

These vinyloxo-complexes are isomers of the corresponding acyl compounds. In the considerable work on acyl complexes of transition metals vinyloxo-isomers have not been implicated but our present work on tris-osmium clusters indicates that the interconversion of these ligands is slow but significant to their chemistry. The clearest case we have is the thermal isomerisation of  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CMe}_2)\text{H}]$  (5b) in  $\text{C}_6\text{D}_5\text{CD}_3$  under CO, which we monitored by <sup>1</sup>H n.m.r.; reaction (2). Reaction (2) is

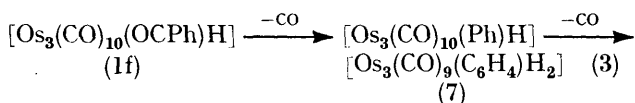


slow even at  $150^\circ\text{C}$  and CO gas seems to be required to prevent decomposition although this causes some conversion to  $\text{Me}_2\text{CHCHO}$  and  $[\text{Os}_3(\text{CO})_{12}]$ . Nevertheless 65% (isolated) of compound (1e) could be obtained from (5b). Even after 20 h at  $150^\circ\text{C}$ , some (5b) is still present in a mixture with (1e) and this may represent equilibrium but the reaction is too slow to be sure of this. Certainly though, (1e) predominates as the more stable isomer. Although (5a) and (5c) also isomerise, only very low yields of acyl complexes were obtained. Apparently in other cases acyl complexes (1) react *via* enolato-isomers of type (5).

Another known isomer of  $[\text{Os}_3(\text{CO})_{10}(\text{OCCH}_3)\text{H}]$  (1a) and  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CH}_2)\text{H}]$  (5a) is the methoxymethylidyne complex  $[\text{Os}_3(\text{CO})_{10}(\text{COCH}_3)\text{H}]$  but this involves an arrangement of C and O atoms without C-C bonding.<sup>15</sup>

*Decarbonylations of Acyl and Enolato-complexes.*—*Decarbonylation of the ligand.* In a few cases, complexes (1) or (5) undergo ligand decarbonylation. In the preparation of  $[\text{Os}_3(\text{CO})_{10}(\text{OCPh})\text{H}]$  (1f) from  $[\text{Os}_3(\text{CO})_{12}]$  and benzaldehyde in refluxing xylene some  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4)\text{H}_2]$  complex (7) (8%) was isolated. Most likely (7) was formed from (1f) because the benzoyl complex in refluxing nonane converts to (7) (63% isolated yield). This proves to be a better synthesis of (7) than the direct thermal reaction of benzene with  $[\text{Os}_3(\text{CO})_{12}]$  at  $190^\circ\text{C}$  which gives low and variable yields.<sup>10</sup> Most probably

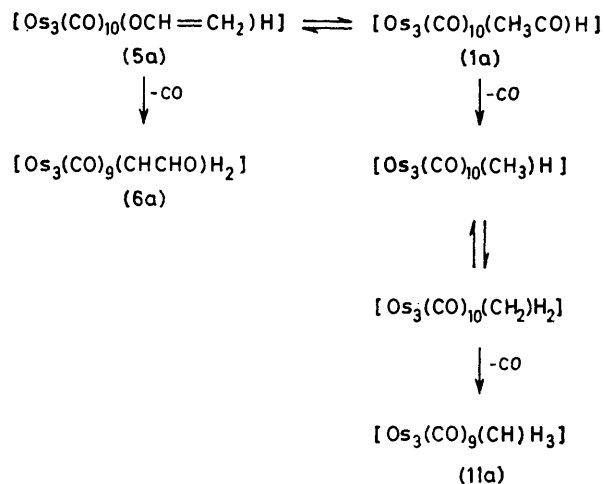
the reaction proceeds as in (3) below. We never observed the intermediate phenyl complex but believe it would be



stable at room temperature if a milder synthetic method could be found. The phenyl complex is of interest because the Ph ligand could adopt a  $\sigma$ ,  $\pi$  bridge as in the corresponding  $\mu$ -CH=CH<sub>2</sub> complex,<sup>16</sup> a three-centre two-electron bridge as in  $[\text{Os}_3(\text{CO})_8\text{Ph}(\text{PPh}_2)(\text{PPhC}_6\text{H}_4)]$ ,<sup>17</sup> or involve C-H-M bonding at the *ortho* position related to that in  $[\text{Os}_3(\text{CO})_{10}(\text{Me})\text{H}]$ .<sup>18</sup> The tautomeric form  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-C}_6\text{H}_4)\text{H}_2]$ , related to  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-CH}_2)\text{H}_2]$ ,<sup>19</sup> might also be involved. The acyl complexes (1) are unfortunately unsuitable to study the details of these hydrogen-transfer reactions because decarbonylation only occurs at elevated temperatures and then to give very stable products such as (7).

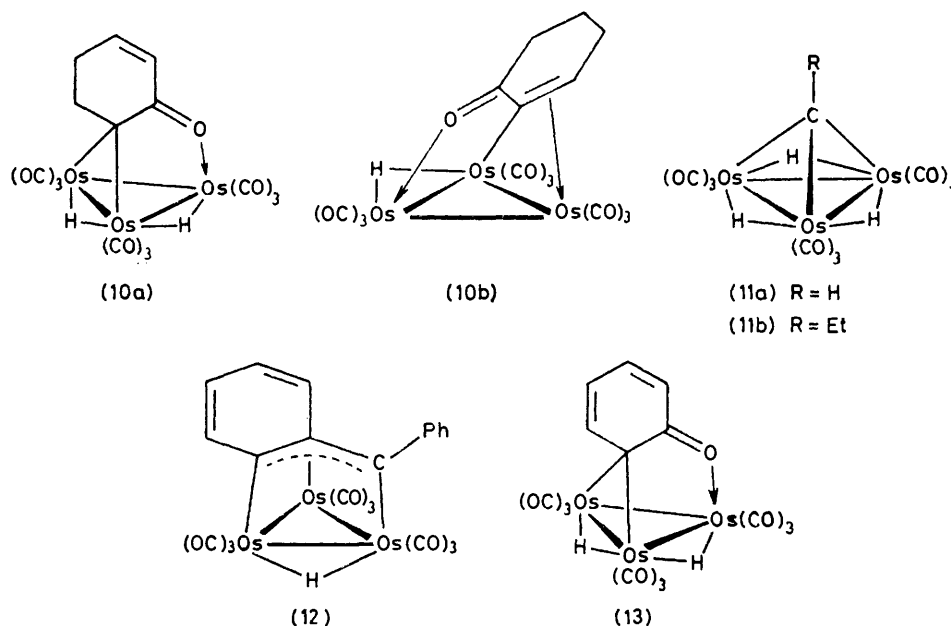
The complex  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CPh}_2)\text{H}]$  (5c) loses CO and H<sub>2</sub> thermally to give a complex (12) of apparent formula  $[\text{Os}_3(\text{CO})_9(\text{CPh}_2)]$  (parent molecular ion observed in the mass spectrum). We presume that it is the acyl tautomer  $[\text{Os}_3(\text{CO})_{10}(\text{Ph}_2\text{CHCO})\text{H}]$  that decarbonylates. Spectroscopically and structurally this product is the osmium analogue of  $[\text{Ru}_3(\text{CO})_9(\text{PhCC}_6\text{H}_4)\text{H}]$  earlier prepared from  $[\text{Ru}_3(\text{CO})_{12}]$  and LiPh and of known X-ray

The enolato-complex (5b) isomerised thermally to the acyl isomer (1e) (see earlier) but gave no identifiable decarbonylation products. However, the simplest enolato-complex (5a) gave in refluxing cyclohexane two distinct decarbonylation products (6a) and (11a) (Scheme 2) as well as traces of the acyl isomer (1a). Complex



SCHEME 2

(1a) also decomposes thermally to a mixture of (6a) and (11a). We propose that (6a) and (11a) are formed from the isomers (5a) and (1a) respectively and that the iso-

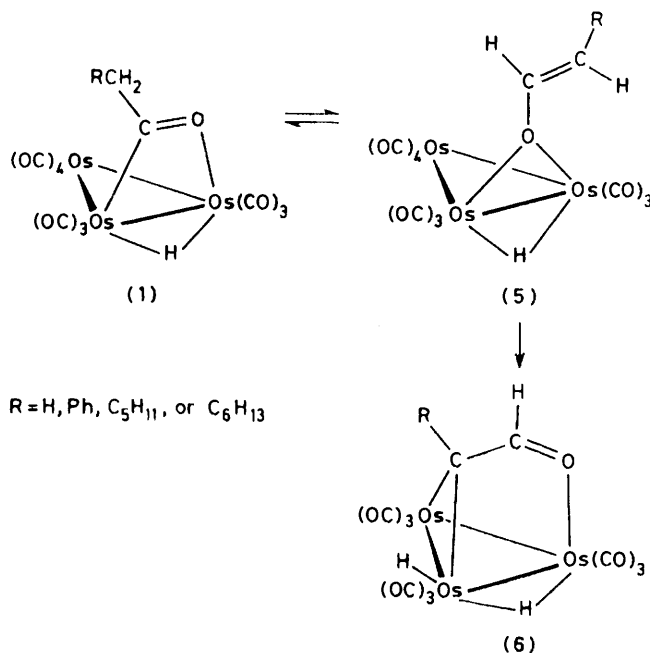


structure.<sup>20</sup> Details of the i.r. spectrum of (12) such as the aromatic C-H deformations (765.5, 759.0, 725.5, and 710.0 cm<sup>-1</sup>) compare well with those reported for the ruthenium compound (767, 757, 723, and 703 cm<sup>-1</sup>). The <sup>1</sup>H n.m.r. spectrum of the ligand covers the range  $\delta$  6.5–7.9 but at 100 MHz we could only assign the signal of the remaining *ortho* hydrogen of the metallated ring ( $\delta$  7.89).

merisation has a rate similar to that for the formation of these products and so cannot be studied independently. The major product (11a) almost certainly arises *via* decarbonylation of the acetyl complex to give the CH<sub>3</sub>, CH<sub>2</sub>, and CH complexes successively (Scheme 2). Calvert and Shapley<sup>5</sup> have shown that  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3)\text{H}]$  derived from CH<sub>2</sub>N<sub>2</sub> and  $[\text{Os}_3(\text{CO})_{10}\text{H}]$  at ambient temperatures and below is in tautomeric

equilibrium with  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_2)\text{H}_2]$  at room temperature, and that the equilibrium mixture decarbonylates at higher temperatures to (11a). The rate of this decarbonylation is faster than the initial decarbonylations of (1a) or (5a) which occur without detectable intermediates. Earlier we observed complex (11a) to be formed in the reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with  $\text{PhNMe}_2$ .<sup>21</sup>

*Decarbonylation at the metal with hydrogen transfer at the acyl ligand.* The other acyl complexes (1b—d) do not decarbonylate at the ligand but at the metal alone to give the complexes  $[\text{Os}_3(\text{CO})_9(\text{CRCHO})\text{H}_2]$  (6b—d) analogous to the minor product (6a) derived from the acetyl complex (1a). Complexes (6b—d) contain as part of the  $\mu_3$ -ligand a co-ordinated formyl group which is characterised by  $^1\text{H}$  n.m.r. singlets in the range  $\delta$  11.2 to 11.6 and  $\nu(\text{CO})$  in the range 1490—1500  $\text{cm}^{-1}$ . The formation of complexes (6) is only possible for acyl complexes (1) having a  $\beta$ - $\text{CH}_2$  group, and except for (1a) this then appears to be the dominant mode of decarbonylation. Complexes (6) have  $\nu(\text{CO})$  spectra around 2000  $\text{cm}^{-1}$  remarkably similar to that of complex (13) derived from phenol and having the dienone structure shown as established by X-ray diffraction of the 3-benzyl substituted complex.<sup>22</sup> Their formation from (1) can be understood if there is a vinylxo-intermediate as in Scheme 3; hydrogen transfer from the  $\beta$ -carbon would



SCHEME 3

then correspond with *ortho* metallation of  $[\text{Os}_3(\text{CO})_{10}(\text{OPh})\text{H}]$  to give complex (13). The overall formation of complexes (6) from the aldehydes  $\text{RCH}_2\text{CHO}$  is equivalent to a double oxidative addition at the  $\text{CH}_2$  group.

Complexes (6b—d) are well characterised and show single sets of  $^1\text{H}$  n.m.r. signals with two sharp hydride doublets and are presumed to have the isomeric form shown analogous to that for (13). However, there is a problem in interpreting the spectrum of (6a) (R = H)

because there are two sets of  $^1\text{H}$  n.m.r. signals, each having a pair of doublets for the organic ligand and a pair of hydride doublets, the relative intensity of the two sets varying with solvent and temperature. One set of signals is favoured at higher temperatures or on changing the solvent from  $\text{CDCl}_3$  to  $\text{CD}_3\text{COCD}_3$ . The close correspondence of the sets of signals suggests the species giving them are isomers, (I) and (II) (Table 2), but we cannot suggest an origin for the isomerism. The yields of (6a) are so very low and the sample is not analytically pure so we have been unable to pursue this problem easily.

*Ketones.* Although aldehydes undergo initial formyl C-H cleavage with  $[\text{Os}_3(\text{CO})_{12}]$ , a subsequent rearrangement to (6) amounts to an overall cleavage of the  $\alpha$ - $\text{CH}_2$  bonds, hence one might expect ketonic analogues of (6) to be formed, but by a different route, of course. We have attempted to prepare analogues of the phenol derivative (13)<sup>22</sup> but with saturated rings. Indeed cyclohexanone does react with  $[\text{Os}_3(\text{CO})_{12}]$  directly but slowly in refluxing decane to give a 17% yield of the expected product  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_8\text{O})\text{H}_2]$ , compound (8), easily characterised as an analogue of (6) and (13). A similar yield (20%) of the same compound was similarly obtained from cyclohexenone by some unspecified hydrogen-transfer reaction. In an alternative approach at synthesising  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_8\text{O})\text{H}_2]$  compound (10a), cyclohexenone was reacted with  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  under milder conditions (refluxing cyclohexane) to give a moderate yield of the decarbonyl  $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_7\text{O})\text{H}]$ , compound (9). We assumed, but did not establish, that cyclohexanone was a by-product by consideration of the reaction of ethylene with  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  to give  $[\text{Os}_3(\text{CO})_{10}(\text{CH}=\text{CH}_2)\text{H}]$  and ethane.<sup>13</sup> Compound (9) contains a  $\sigma$  vinyl group but bridging is through the ketone rather than through the alkene. We have also synthesised a simple acyclic analogue of (9) from  $\text{HC}\equiv\text{CCOMe}$  and  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  which we will describe elsewhere.<sup>23</sup>

It is remarkable that oxidative addition of cyclohexenone to give (9) occurs at the vinyl group and at the 2-position rather than at the 3- or 6-positions of the ring; cyclohexenone is not normally substituted at this position. This is another example of oxidative addition at tris-osmium clusters occurring at vinylic in preference to allylic or other more generally reactive positions. The site of attack seems to be geometrically controlled, in this case to give a stable three-atom bridge between osmium atoms.

Hoping to synthesise (10a) by a double oxidative addition, the initial oxidative addition seems to have occurred in quite the wrong position. In spite of this, decarbonylation of (9) occurs smoothly in refluxing octane to give two isomeric products: yellow crystals of  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_8\text{O})\text{H}_2]$  compound (10a) (74%) and red crystals of  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_7\text{O})\text{H}]$  compound (10b) (21%). These isomers do not interconvert under the reaction conditions. The major product (10a) is the complex we hoped to synthesise but its formation from (9) requires extensive and unexpected rearrangement and we do not

TABLE 2  
Hydrogen-1 n.m.r. data <sup>a</sup>

Compound	Ligand signals			Os-H $\delta$
	$\delta$	$J$	Assignment	
(1a)	2.20(s)		CH <sub>3</sub>	-13.93(s)
(1b)	2.44(m)		CH <sub>2</sub> CO	-13.80(s)
	1.25(m)		(CH <sub>2</sub> ) <sub>4</sub>	
	0.88(m)		CH <sub>3</sub>	
(1c)	2.44(m)		CH <sub>2</sub> CO	-13.96(s)
	1.25(m)		(CH <sub>2</sub> ) <sub>3</sub>	
	0.84(m)		CH <sub>3</sub>	
(1d)	7.2(m)		C <sub>6</sub> H <sub>5</sub>	-14.04(s)
	4.81(d) <sup>b</sup>	18.0	CH <sub>2</sub>	
	4.62(d) <sup>b</sup>	18.0		
(1e)	2.03(m)		CH	-13.84(s)
	1.19(d)	7.1	CH <sub>3</sub>	
	0.91(d)	7.1	CH <sub>3</sub>	
(1f)	7.2-7.8		C <sub>6</sub> H <sub>5</sub>	-13.64(s)
(5a)	5.90(dd)	$J_{13}$ 13.0	CH <sup>1</sup> =CH <sup>2</sup> H <sup>3</sup>	-12.35(s)
	3.98(dd)	$J_{23}$ 2.4	CH <sup>1</sup> =CH <sup>2</sup> H <sup>3</sup>	
	3.82(dd)	$J_{12}$ 5.8	CH <sup>1</sup> =CH <sup>2</sup> H <sup>3</sup>	
(5b)	5.26(m)		OCH	-11.94(s)
	1.59(s)		CH <sub>3</sub>	
	1.48(s)		CH <sub>3</sub>	
(5c)	6.9-		(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	-11.83(s)
	7.6(m)			
	6.59(s)		OCH	
(6a) Isomer (I) <sup>c</sup>	11.59(d)		CHO	-12.55(d),
	4.13(d)		CH	-14.42(d)
Isomer (II) <sup>c</sup>	11.49(d)		CHO	-12.80(d),
	3.98(d)		CH	-14.53(d)
Isomer (I) <sup>d</sup>	10.78(d)		CHO	-12.90(d),
	3.21(d)		CH	-14.88(d)
Isomer (II) <sup>d</sup>	10.68(d)		CHO	-13.08(d),
	3.11(d)		CH	-14.88(d)
(6b)	11.44(s)		CHO	-12.06(d),
	2.08(m)		CH <sub>2</sub>	-14.00(d)
	1.24(m)		(CH <sub>2</sub> ) <sub>3</sub>	
	0.88(m)		CH <sub>3</sub>	
(6c)	11.36(s)		CHO	-12.18(d),
	2.12(m)		CH <sub>2</sub>	-14.05(d)
	1.24(m)		(CH <sub>2</sub> ) <sub>2</sub>	
	0.87(m)		CH <sub>3</sub>	
(6d)	11.27(s)		CHO	-11.79(d),
	6.9-		C <sub>6</sub> H <sub>5</sub>	-13.88(d)
	7.7(m)			
(8)	2.30(m)		CH <sub>2</sub>	-12.36(d),
	1.3-		(CH <sub>2</sub> ) <sub>3</sub>	-14.03(d)
	1.9(m)			
(9)	7.85(t)	3.9	CH=	-12.84(s)
	2.53(m)		CH <sub>2</sub>	
	2.26(m)		CH <sub>2</sub>	
	1.77(m)		CH <sub>2</sub>	
(10a)	5.81(d)	9.6	CH=	-12.27(d),
	4.94(dt)	9.6, 4.3	CH=	-14.02(d)
	2.44(m)		CH <sub>2</sub>	
(10b)	1.78(m)		CH <sub>2</sub>	
	3.88(t)	4.4	CH=	
	2.64(m)		CH <sub>2</sub>	
(11a)	1.72(m)		(CH <sub>2</sub> ) <sub>2</sub>	
	0.27(q)	1.2	CH	-19.43(d)
(11b)	4.27(q)		CH <sub>2</sub>	-19.06(s)
	1.57(t)		CH <sub>3</sub>	
(12)	7.89(m)		1 H	-18.05(s)
	6.85-		6 H	
	7.39(m)			
	6.51(m)		2 H	

<sup>a</sup> Recorded at 100 MHz at 27 °C in CDCl<sub>3</sub> unless stated otherwise. <sup>b</sup> AB quartet recorded at -130 °C in CHCl<sub>2</sub>F. Singlet observed in CDCl<sub>3</sub> at 27 °C. <sup>c</sup> In CD<sub>3</sub>COCD<sub>3</sub> at 30 °C. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub> at 30 °C.

yet know whether the same carbon remains bound to osmium in (9) and (10a); we suspect that it does not. The minor red product contains the same ligand as in (9) but with modified co-ordination to the cluster. As implied by the metal decarbonylation the C=C bond which was free in (9) is now co-ordinated; the <sup>1</sup>H n.m.r. triplet for the vinylic hydrogen has shifted upfield by 4 p.p.m. We do not know the geometrical arrangement of the five-electron-donating C<sub>6</sub>H<sub>7</sub>O ligand in (10b) but that illustrated is a good possibility.

*Conclusion.*—It seems that the  $\mu$ -enolato-isomers are thermodynamically less favourable than the  $\mu$ -acyl isomers, as with mononuclear complexes, but not so much so that they are not accessible as reaction intermediates. Probably this allows the acyl complexes described here to decompose quite differently in general to mononuclear complexes. Usually low-valent metal compounds, especially of third-row metals, have little affinity for oxygen and yet all the organic ligands containing oxygen described here form stable complexes containing O-Os bonds and many are extremely robust. Complex (13), for example, does not react with CO to give [Os<sub>3</sub>(CO)<sub>10</sub>(C<sub>6</sub>H<sub>4</sub>O)H] containing a free ketone group and analogous to [Os<sub>3</sub>(CO)<sub>10</sub>(CH<sub>2</sub>)<sub>2</sub>H<sub>2</sub>] but rather to give [Os<sub>3</sub>(CO)<sub>10</sub>(OPh)H]. It is too early to assess the significance of our results to possible organic synthesis using clusters.

#### EXPERIMENTAL

Aldehydes were purified to remove acids and alcohols before use.<sup>24</sup> All reactions at high temperature were under nitrogen. Products were generally isolated by preparative t.l.c. using Merck SiO<sub>2</sub> (HF254, type 60).

*Reactions of [Os<sub>3</sub>(CO)<sub>12</sub>] with Aldehydes.*—*n*-Heptanal. A solution of [Os<sub>3</sub>(CO)<sub>12</sub>] (1.00 g) and purified heptanal (6 cm<sup>3</sup>) in sodium-dried xylene (300 cm<sup>3</sup>) was refluxed under nitrogen for 35 h. Unreacted metal carbonyl precipitated at room temperature (0.160 g) and work-up involving t.l.c. (SiO<sub>2</sub>) gave [Os<sub>3</sub>(CO)<sub>10</sub>(OCC<sub>6</sub>H<sub>13</sub>)H], complex (1b) (0.180 g, 21%), as yellow crystals and [Os<sub>3</sub>(CO)<sub>10</sub>(O<sub>2</sub>CC<sub>6</sub>H<sub>13</sub>)H], complex (2b) (0.117 g, 14%), as a yellow oil which could not be crystallised.

*n*-Hexanal. A similar treatment with a 72 h reflux gave [Os<sub>3</sub>(CO)<sub>10</sub>(OCC<sub>5</sub>H<sub>11</sub>)H], complex (1c) (48%), and [Os<sub>3</sub>(CO)<sub>10</sub>(O<sub>2</sub>CC<sub>5</sub>H<sub>11</sub>)H], complex (2c) (12%), both as yellow crystals.

*Phenylacetaldehyde.* A similar treatment, refluxing for 17 h, gave [Os<sub>3</sub>(CO)<sub>12</sub>] (59%), [Os<sub>3</sub>(CO)<sub>10</sub>(OCCH<sub>2</sub>Ph)H], compound (1d) (12%), and trace quantities of [Os<sub>3</sub>(CO)<sub>10</sub>(O<sub>2</sub>CCH<sub>2</sub>Ph)H], compound (2d).

*Isobutyraldehyde.* In this case, [Os<sub>3</sub>(CO)<sub>12</sub>] (0.484 g), purified aldehyde (2 cm<sup>3</sup>), and sodium-dried nonane (10 cm<sup>3</sup>) were heated in an evacuated sealed glass tube at 150 °C for 7 days. Chromatographic work-up gave unreacted metal carbonyl (0.379 g), [Os<sub>3</sub>(CO)<sub>10</sub>(OCCHMe<sub>2</sub>)H], compound (1e) (0.009 g), and [Os<sub>3</sub>(CO)<sub>10</sub>(O<sub>2</sub>CCHMe<sub>2</sub>)H], compound (2e) (0.005 g), both as yellow crystals.

*Benzaldehyde.* A solution of [Os<sub>3</sub>(CO)<sub>12</sub>] (0.726 g) and purified aldehyde (5 cm<sup>3</sup>) in sodium-dried xylene was heated under reflux under nitrogen for 28 h. The compound [Os<sub>3</sub>(CO)<sub>12</sub>] (0.160 g) crystallised on cooling and chromatography on SiO<sub>2</sub> gave [Os<sub>3</sub>(CO)<sub>9</sub>(C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>], compound (7) (0.046 g, 8%), and another band containing [Os<sub>3</sub>(CO)<sub>10</sub>-

(OCPh)H], compound (1f), and  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_2\text{Ph})\text{H}]$ , compound (3f), mol ratio = 6 : 1 by  $^1\text{H}$  n.m.r., 0.088 g in total. Pure compound (1f) was obtained as yellow crystals (0.058 g) by repeated fractional crystallisation from pentane at  $-20^\circ\text{C}$ .

*Acetaldehyde.* (i). Vapour of purified acetaldehyde was carried in a slow stream of nitrogen through a refluxing solution of  $[\text{Os}_3(\text{CO})_{12}]$  (0.378 g) in xylene (250 cm<sup>3</sup>) for 14 h. Work-up gave unreacted metal carbonyl (0.040 g) and  $[\text{Os}_2(\text{CO})_6(\text{O}_2\text{CMe})_2]$ , compound (4a), (0.096 g, 28%).

(ii). A mixture of  $[\text{Os}_3(\text{CO})_{12}]$  (0.40 g), purified acetaldehyde (2 cm<sup>3</sup>), and nonane (15 cm<sup>3</sup>), under vacuum in a sealed glass tube, was heated firstly at  $140^\circ\text{C}$  (no apparent reaction) and then at  $170^\circ\text{C}$  for 7 days. Work-up gave  $[\text{Os}_2(\text{CO})_6(\text{O}_2\text{CMe})_2]$ , compound (4a), (0.185 g, 46%) as the only isolable product. Compound (1a) was not observed.

*Formaldehyde.* Formaldehyde from dried paraformaldehyde was passed over  $\text{P}_2\text{O}_5$  and bubbled through a solution of  $[\text{Os}_3(\text{CO})_{12}]$  (0.40 g) in refluxing xylene (250 cm<sup>3</sup>) for 1.5 h. Work-up gave unreacted carbonyl (0.215 g) and  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)\text{H}]$  (0.060 g, 32%) as yellow crystals and traces of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$ . Similar reactions at room temperature using  $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_8)]$  ( $\text{C}_6\text{H}_8$  = cyclohexa-1,3-diene) or  $[\text{Os}_3(\text{CO})_{10}(\text{CH}(\text{CH}_2\text{CO}_2\text{Et})\text{CO}_2\text{Et})\text{H}]$  as precursors for ' $\text{Os}_3(\text{CO})_{10}$ ' gave only low yields of the same two products.

*Reactions of  $[\text{Os}_3(\text{CO})_{10}]$  with Ketones.—Cyclohexanone.* A solution of  $[\text{Os}_3(\text{CO})_{12}]$  (0.300 g) and cyclohexanone (1.0 cm<sup>3</sup>) in decane (20 cm<sup>3</sup>) was heated under reflux under nitrogen for 15 h. Some  $[\text{Os}_3(\text{CO})_{12}]$  precipitated on cooling. Removal of solvent from the dark solution and t.l.c. ( $\text{SiO}_2$ ) of the residue gave a monohydride complex, which might be  $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_{11}\text{O})\text{H}]$  but was not characterised properly, and  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_9\text{O})\text{H}_2]$ , compound (8) (0.051 g, 17%), as yellow crystals.

*Cyclohexenone.* A similar reaction using cyclohexenone (6 h reflux) gave compound (8) (20%), spectroscopically identical to that from cyclohexanone.

*Reactions of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  with the Ketens  $\text{R}_2\text{C}=\text{C}=\text{O}$  (R = H, Me, or Ph).—Keten.* Keten prepared by the method of Andreades and Carlson<sup>25</sup> was bubbled through a solution of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.119 g) in sodium-dried heptane (25 cm<sup>3</sup>) for 5 min and the stoppered solution shaken for 2 h at room temperature. After removal of solvent, the crude red product was purified by t.l.c. ( $\text{SiO}_2$ ) to give  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CH}_2)\text{H}]$ , compound (5a), as yellow crystals (0.048 g, 40%).

*Dimethylketen.* The compound  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.50 g) was added to an approximately 10% solution of  $\text{Me}_2\text{C}=\text{CO}$  in ethyl acetate prepared by the method of Smith and Norton.<sup>26</sup> After the mixture had been shaken for 1.75 h under nitrogen, chromatographic work-up gave  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CMe}_2)\text{H}]$ , compound (5b), as yellow crystals (0.30 g, 60%).

*Diphenylketen.* A solution of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.434 g) and diphenylketen (0.2 cm<sup>3</sup>) in sodium-dried benzene (250 cm<sup>3</sup>) was refluxed under nitrogen for 22 h. Work-up gave unreacted dihydride (0.224 g) and  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CPh}_2)\text{H}]$ , compound (5c) (0.088 g, 42% conversion), as yellow crystals.

*Other Reactions of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$ .—With cyclohexenone.* A solution of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.30 g) and cyclohexenone ( $\text{C}_6\text{H}_8\text{O}$ ) (0.5 cm<sup>3</sup>) in hexane (25 cm<sup>3</sup>) was heated under reflux for 5 h. Removal of solvent and chromatographic work-up gave  $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_7\text{O})\text{H}]$ , compound (9), as yellow crystals (0.106 g, 32%).

*With Formaldehyde.* Formaldehyde was bubbled through

a purple solution of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.20 g) in xylene (250 cm<sup>3</sup>) for 30 min. The yellow solution yielded  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)\text{H}]$  (0.193 g, 95%) as yellow crystals.

*With benzaldehyde.* Reaction in refluxing xylene gave only a very low yield of impure  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_2\text{Ph})\text{H}]$  (3f) and no other characterisable products.

*With acetaldehyde.* The vapour of purified acetaldehyde was passed in a slow stream of nitrogen into a solution of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.061 g) in xylene (100 cm<sup>3</sup>) for 4 h at  $20^\circ\text{C}$ . Work-up gave unreacted dihydride (0.017 g) and  $[\text{Os}_3(\text{CO})_{10}(\text{OEt})\text{H}]$  (0.010 g, 23%) (3a) as a rather impure yellow solid.

*With allyl alcohol.* A solution of  $[\text{Os}_3(\text{CO})_{10}\text{H}_2]$  (0.427 g) and purified allyl alcohol (0.500 cm<sup>3</sup>) in sodium-dried cyclohexane (10 cm<sup>3</sup>) was stirred at room temperature under nitrogen for 48 h. Removal of solvent and t.l.c. of the residual oil gave various products of which we were only able to characterise  $[\text{Os}_3(\text{CO})_9(\text{CC}_2\text{H}_5)_2\text{H}_3]$ , compound (11b) (0.017 g, 4%).

*Thermolysis Reactions of Compounds (1).—Compound (1a).* A solution of  $[\text{Os}_3(\text{CO})_{10}(\text{OCCH}_3)\text{H}]$  (0.002 g) (see later for synthesis) in sodium-dried, distilled nonane was heated under reflux for 30 min under nitrogen. T.l.c. ( $\text{SiO}_2$ ) gave two bands which yielded  $[\text{Os}_3(\text{CO})_9(\text{CH})\text{H}_3]$  (11a) and  $[\text{Os}_3(\text{CO})_9(\text{CHCHO})\text{H}_2]$  (6a), which were unambiguously characterised by their mass and i.r. (around 2 000 cm<sup>-1</sup>) spectra.

*Compound (1b).* A solution of  $[\text{Os}_3(\text{CO})_{10}(\text{OCC}_6\text{H}_{13})\text{H}]$  (0.156 g) in nonane (50 cm<sup>3</sup>) was refluxed under nitrogen for 8 h. Several products were obtained by t.l.c. of which only  $[\text{Os}_3(\text{CO})_9(\text{C}_5\text{H}_{11}\text{CCHO})\text{H}_2]$ , compound (6b) (0.015 g, 10%), was characterised.

*Compound (1c).* A similar treatment of  $[\text{Os}_3(\text{CO})_{10}(\text{OCC}_5\text{H}_{11})\text{H}]$  gave  $[\text{Os}_3(\text{CO})_9(\text{C}_4\text{H}_9\text{CCHO})\text{H}_2]$ , compound (6c) (15%).

*Compound (1d).* A similar treatment of  $[\text{Os}_3(\text{CO})_{10}(\text{OCC}_6\text{H}_5\text{Ph})\text{H}]$  (5 h reflux in nonane) gave  $[\text{Os}_3(\text{CO})_9(\text{PhCCHO})\text{H}_2]$  (6d) as yellow crystals (17%).

*Compound (1f).* The benzoyl complex (0.046 g) in nonane solution was refluxed for 4.5 h and work-up with t.l.c. ( $\text{SiO}_2$ ) gave  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_4)\text{H}_2]$ , compound (7) (0.029 g, 63%), as yellow crystals.

*Thermolysis Reactions of Compounds (5).—Compound (5a).* A solution of  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CH}_2)\text{H}]$  (0.200 g) in sodium-dried cyclohexane (150 cm<sup>3</sup>) was heated under reflux for 65 h. After removal of the solvent, t.l.c. ( $\text{SiO}_2$ ) eluting with pentane gave  $[\text{Os}_3(\text{CO})_9(\text{CH})\text{H}_3]$  (11a) (0.077, 39%) as colourless crystals,  $[\text{Os}_3(\text{CO})_{10}(\text{OCCH}_3)\text{H}]$  (1a) (0.002 g) as yellow crystals, and  $[\text{Os}_3(\text{CO})_9(\text{CHCHO})\text{H}_2]$  (6a) (0.007 g, 3.5%) as a brown solid. A similar reaction in refluxing nonane (30 min) gave (11a) and (6a) in similar yields, but no (1a) was observed. Bubbling CO through a refluxing cyclohexane solution of (5a) (38 h) gave  $[\text{Os}_3(\text{CO})_{12}]$  (11%), unreacted (5a) (16%), (1a) (3%), and a trace of (6a).

Complex (5a) (0.063 g) was sealed with  $\text{C}_6\text{D}_5\text{CD}_3$  (0.5 cm<sup>3</sup>) under CO in an n.m.r. tube. The  $^1\text{H}$  n.m.r. spectrum was recorded periodically after heating the tube at  $90^\circ\text{C}$ . Complex (1a)  $[\text{Os}_3(\text{CO})_{10}(\text{OCCH}_3)\text{H}]$  was apparent after 2.25 h but the spectrum of acetaldehyde was also observed. The compound  $[\text{Os}_3(\text{CO})_{12}]$  (21%) and (1a) (5%) were isolated after 8 h heating.

*Complex (5b).* Complex  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CMe}_2)\text{H}]$  (0.104 g) was sealed with  $\text{C}_6\text{D}_5\text{CD}_3$  (0.5 cm<sup>3</sup>) under CO in an n.m.r. tube and heated at  $150^\circ\text{C}$  for 20 h by which time no further changes were occurring. The n.m.r. spectrum indicated the formation of  $\text{Me}_2\text{CHCHO}$  (2-methylpropanal)

and complex (1e)  $[\text{Os}_3(\text{CO})_{10}(\text{OCCHMe}_2)\text{H}]$ . Work-up gave  $[\text{Os}_3(\text{CO})_{12}]$  (13%), unreacted starting material (9%), and complex (1e) (65%) as yellow crystals. 2-Methylpropanal (21%) was estimated by integration of n.m.r. signals against a weighed amount of added benzyl alcohol.

**Complex (5c).** A solution of  $[\text{Os}_3(\text{CO})_{10}(\text{OCH}=\text{CPh}_2)\text{H}]$  (0.113 g) in sodium-dried, distilled nonane (50 cm<sup>3</sup>) was heated under nitrogen for 3 h. Chromatographic work-up gave  $[\text{Os}_3(\text{CO})_9(\text{PhCC}_6\text{H}_4)\text{H}]$  (12) (0.027 g, 24%) as orange crystals. A similar reaction to those with (5a) and (5b) in a sealed n.m.r. tube under CO gave a complex mixture including  $[\text{Os}_3(\text{CO})_{12}]$  and diphenylacetaldehyde but quantities were low and not determined.

**Thermolysis Reaction of Complex (9).**—Complex  $[\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_7\text{O})\text{H}]$  (0.10 g) in octane (20 cm<sup>3</sup>) was heated under reflux for 2 h. Chromatographic work-up gave the isomeric complexes  $[\text{Os}_3(\text{CO})_9(\text{C}_6\text{H}_6\text{O})\text{H}_2]$ , complex (10a) (0.072 g, 74%), as yellow crystals and complex (10b) (0.020 g, 21%) as red crystals. These were shown not to inter-convert in refluxing octane.

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