Journal of Organometallic Chemistry, 114 (1976) 313—324

ADDITION REACTIONS OF A POLYNUCLEAR OSMIUM HYDRIDO COMPOUND LEADING TO ASSOCIATIVE CARBONYL SUBSTITUTION AND CATALYTIC ALKENE ISOMERISATION *

A.J. DEEMING and S. HASSO

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)

(Received February 3rd, 1976)

Summary

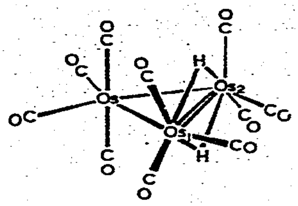
The ability of $H_2Os_3(CO)_{10}$ to undergo addition reactions under mild conditions allows associative CO substitution via isolable intermediates of the type $H_2Os_3(CO)_{10}L$ (L = CO, PMe_2Ph, PPh_3 or PhCN) whose spectra and structures are discussed. It is probable that simple addition of alkenes to $H_2Os_3(CO)_{10}$ is in part responsible for its facile catalysis of alkene isomerisation. The kinetics of catalytic conversion of terminal to internal alkenes and of allylic alcohols to aldehydes or ketones are reported and discussed. The reactions of $H_2Os_3(CO)_{10}$ with allylic halides to give the complexes $HOs_3X(CO)_{10}$ and $Os_3X_2(CO)_{10}$ where X = Cl, Br or I are described. Compound $H_2Os_3(CO)_{10}$ complies with the 18*e*-rule but nevertheless has a chemistry much like that of coordinatively unsaturated molecules.

Introduction

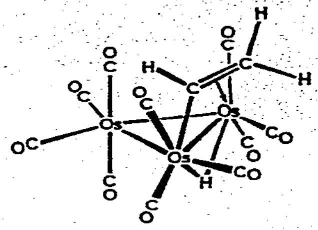
Ethylene at atmospheric pressure and room temperature reacts with $H_2Os_3(CO)_{10}$ (I) to give $HOs_3(CH{=}CH_2)(CO)_{10}$ (II) and ethane [1,2]. The vinyl compound was originally prepared by the action of acetylene on compound I [1,3]. Insertion of ethylene into an Os—H bond of I would give an hydrido-ethyl intermediate which readily eliminates ethane while reacting with another ethylene molecule. Keister and Shapley [2] have suggested a unimolecular decomposition of $HOs_3(Et)(CO)_{10}$ to give the highly reactive $Os_3(CO)_{10}$ to which ethylene read-

---

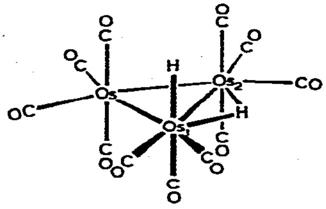
* No reprints available.



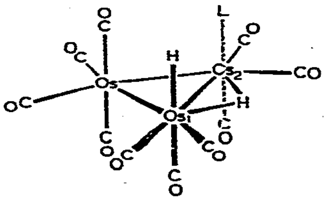
(I)



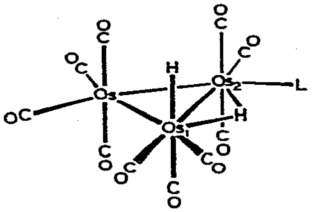
(II)



(III L = CO)



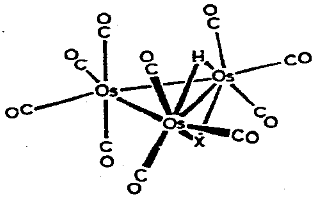
(IIIa)



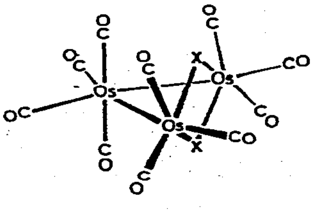
(IIIb)

$H{-}[Os(CO)_4]_n{-}H$

(IV)



(V)



(VI)

ily adds oxidatively giving compound II. We have proposed [1,4] that the double bond between two osmium atoms [5] is responsible for the facile insertion reactions of $H_2Os_3(CO)_{10}$. Direct nucleophilic additions to compound I occur enabling it to readily insert alkynes to give vinyl compounds [1,3,4,6,7], to undergo carbonyl substitution by associative mechanisms and to catalyse alkene isomerisations; our results on the latter two aspects of its chemistry are discussed here. These reactions occur at room temperature, while other triosmium hydrides show none of this chemistry. For example, the complexes $HOs_3(X)(CO)_{10}$ (X = 3*e*-donor such as Br) do not react with tertiary phosphines at room temperature nor do they catalyse alkene isomerisation. $H_2Os_3(CO)_{10}$, unlike these compounds, shows behaviour like that of coordinatively unsaturated molecules. Preliminary results on the formation of simple adducts of compound I have been published [8,9].

Results and discussion

Pathway for carbonyl substitution of $H_2Os_3(CO)_{10}$

Compound I readily undergoes reactions with CO, PhCN, PPh_3 and PMe_2Ph(L) at 20°C to give simple adducts of the type $H_2Os_3(CO)_{10}L$ (III) (see Table 1 for analytical and IR data). We proposed on ^1H NMR evidence that $H_2Os_3(CO)_{11}$ (III; L = CO) had one terminal and one bridging hydride [8] and an X-ray determined structure reported subsequently [9] confirmed this. The hydride positions were deduced from those of the other ligands. In compound I the shortest intermetal distance (Os(1)—Os(2)) is 0.2670 nm, while for compound III; (L = CO) the intermetal distances are 0.2857, 0.2910 and 0.2989 nm. This is consistent with saturation of the Os(1)—Os(2) bond on adding CO to compound I; that is two extra electrons are accommodated in cluster *anti*-bonding orbitals. The presence of a bridging hydrogen atom normally gives a longer than normal Os—Os bond unless there is multiple metal—metal bonding as in compound I.

The site of addition of ligands other than CO is not firmly established except that the strong similarity of the hydride NMR shifts for the whole series of compounds III suggests that they are structurally related (see Table 2). Each compound gives a signal at about τ 20 ppm (terminal H) and another at about τ 29 ppm (bridging H), which coalesce to a single peak at room temperature due to bridge-terminal hydride exchange. In the PMe_2Ph and PPh_3 adducts, only the bridging hydrogen nucleus couples with the ^{31}P nucleus, indicating the structure shown. There is, however, no evidence to determine at which of the four different coordination sites at Os(2), ligand L is bound. Whichever site L enters initially, it is probable that the most stable configuration is adopted, since stereochemical non-rigidity is characteristic of most cluster carbonyls, site exchange occurring via axial—equatorial interchange at one metal atom or by CO transfer between metals. L is expected to migrate to the least crowded coordination site. On steric grounds we would predict either structure IIIa or IIIb with L in the least crowded axial and equatorial sites respectively. Substitution of $M_3(CO)_{12}$ (M = Fe, Ru or Os) leads to ligands bulkier than CO entering the least crowded equatorial positions, while in $H_2Os_3(CO)_{11}$, the terminal hydride (the smaller ligand) enters an axial position. Thus, if all other axial and equatorial ligands are sterically equivalent, small ligands will enter axial and large ones equatorial sites.

TABLE 1

ANALYTICAL AND INFRARED DATA [a] FOR NEW COMPOUNDS

Compound	M.p. (°C)	Analysis Found (calcd.) (%)				ν(CO) (cm⁻¹)				
		C	H	O	P, N or Cl					
$H_2Os_3(CO)_{10}$ (I)						2111vw 1988m	2076s 1973vw	2062s 1957vw	2025vs	2010s
$H_2Os_3(CO)_{11}$ (III; L = CO)	110 (sublim.) decomp. >130	15.6 (15.0)	0.3 (0.25)	19.8 (20.0)		2137vw 2030m 1988m	2088s 2026m	2066vs 2018m	2058vs 2004(sh)	2054vs 2002m
$H_2Os_3(CO)_{10}(PMe_2Ph)$ (III; L = PMe_2Ph)	125–130 (decomp.)	21.95 (21.8)	1.4 (1.3)	16.0 (16.15)	4.0 (3.15)	2106m 2007s	2065s 2001m	2050s 1985m	2024vs 1977m	2016vs
$H_2Os_3(CO)_{10}(PPh_3)$	124–129 (decomp.)	30.45 (30.15)	1.6 (1.55)	14.25 (14.35)	3.1 (2.8)	2105m 2004m	2066s 1983m	2051s 1971m	2025vs	2017vs
$H_2Os_3(CO)_{10}(PhCN)$ [b]	104–109 (decomp.)	22.15 (21.35)	0.85 (0.75)	16.7 (16.75)	1.6 (1.45)	2103w 1985m	2067vs 1966w	2049s	2024vs	2008(sh, br)
$H_2Os_3(CO)_9(PMe_2Ph)$	104–106	21.35 (21.2)	1.45 (1.35)	15.05 (14.95)	3.45 (3.2)	2092m 1984m	2053s 1975m	2014vs 1958m	2005m(sh)	1991m
$H_2Os_3(CO)_9(PPh_3)$	>190	30.05 (29.85)	1.7 (1.6)	13.05 (13.25)	2.9 (2.85)	2093m 1991m	2053s 1976m	2015s(sh) 1962w	2012vs	2004m
$HOs_3Cl(CO)_{10}$		13.65 (13.55)	0.15 (0.1)		3.85 (4.0)	2116w 2015s	2077s 1992(sh)	2068s 1990m	2027vs	2923(sh)
$HOs_3Br(CO)_{10}$		12.25 (12.9)	0.0 (0.1)		[c]	2115w 2015s	2076s 1991m(br)	2068s	2028vs	2024(sh)
$HOs_3I(CO)_{10}$		12.25 (12.25)	0.10 (0.10)		[c]	2112w 2013s	2073s 1990m	2065s	2027vs	2023(sh)

[a] Measured in cyclohexane. [b] Infrared spectrum recorded in cyclohexane containing PhCN in large excess. A solution of the isolated crystals in cyclohexane showed only $H_2Os_3(CO)_{10}$. ν(CN) 2275w (Nujol). [c] Halogen content not established except by mass spectra.

TABLE 2

^{1}H NMR DATA FOR COMPLEXES (AT 100 MHz IN $CDCl_3$)

Compound	Temperature (°C)	Hydride resonances		Other resonances	
		τ (ppm)	J(Hz)	τ (ppm)	J(Hz)
$H_2Os_3(CO)_{10}$	27	21.36s			
$H_2Os_3(CO)_{11}$ [a]	−82	20.24d 29.97d	J(HH) 3.6		
$H_2Os_3(CO)_{10}(PMe_2Ph)$	−62	20.53s [b] 30.45d [b]	 J(PH) 12.0		
	27	25.27br		2.95(br)(Ph) 8.48d(Me)	 J(PH) 9.5
$H_2Os_3(CO)_{10}(PPh_3)$	−54	20.11d 29.72dd	J(HH) 4.1 J(PH) 10.7		
	27	24.85br			
$H_2Os_3(CO)_9(PMe_2Ph)$	27	20.74d [c]	J(PH) 6.5	2.55(br)(Ph) 7.70d(Me)	 J(PH) 10.1
$H_2Os_3(CO)_9(PPh_3)$	35	20.06d	J(PH) 7.0		
$H_2Os_3(CO)_{10}(PhCN)$	−58	19.91d 27.05d	J(HH) 4.0		
$HOs_3Cl(CO)_{10}$	27	24.16s			
$HOs_3Br(CO)_{10}$	27	24.92s			
$HOs_3I(CO)$	27	25.24s			

[a] Recorded in CH_2Cl_2. At room temperature only a weak signal due to a small amount of $H_2Os_3(CO)_{10}$ in the solution was detected: the signal due to $H_2Os_3(CO)_{11}$ was too broad to detect at this temperature. [b] J(HH) 4.0 Hz was observed by others [9]. [c] A single sharp doublet was observed at room temperature. The asymmetry and further fine structure at −50° C implies either non-equivalent hydride ligands or isomers are present which exchange rapidly at room temperature.

However, with the small terminal hydride in an axial site, the other axial sites may now be less crowded so we cannot predict whether one would get IIIa or IIIb. A *cis*-arrangement of bridging hydride and L is presumably required for insertion to occur (see later).

Tertiary phosphine adducts of complex I are rapidly formed; for instance, equimolar addition of PMe_2Ph to complex I in hexane gives an immediate colour change from purple to yellow followed by slow precipitation of $H_2Os_3(CO)_{10}(PMe_2Ph)$ (III; L = PMe_2Ph) as yellow plates, which is indefinitely stable in solution in air at room temperature. The consequence of heating solutions of III depends upon L. In refluxing hexane there is a slow loss of CO from III (L = PMe_2Ph or PPh_3) to give purple $H_2Os_3(CO)_9L$. Thus there is overall CO substitution by an associative pathway with CO loss as the slow second step. In contrast to this, the compound $HOs_3(SPh)(CO)_{10}$ does not react with tertiary phosphines at room temperature and carbonyl substitution only occurs at elevated temperatures (80° C) [10] to give mono-, di- and most likely tri-substituted derivatives and not specifically the mono-substituted compound as from compound I under the conditions we used.

With phenyl cyanide no substitution was achieved by heating the adduct III since PhCN rather than CO is lost. Indeed compound III (L = PhCN) exists only in solutions containing PhCN in excess and yellow crystals of the compound dissolve in chloroform or cyclohexane to give purple solutions of compound I as the only osmium species. Similarly, $H_2Os_3(CO)_{11}$ is stable only in solutions containing dissolved CO and, if N_2 is bubbled through to remove this, purple complex I is regenerated. As expected, a lowering of the temperature of a solution containing $H_2Os_3(CO)_{11}$, $H_2Os_3(CO)_{10}$ and CO gives more of the undecacarbonyl compound. Compound III (L = CO) reacts further when CO is bubbled through a refluxing hexane solution to give $Os_3(CO)_{12}$ quantitatively (eq. 1 and 2).

$$H_2Os_3(CO)_{10} + CO \rightarrow H_2Os_3(CO)_{11} \quad (1)$$

$$H_2Os_3(CO)_{11} + CO \rightarrow Os_3(CO)_{12} + H_2 \quad (2)$$

These are the reverse of the reactions by which $H_2Os_3(CO)_{10}$ (I) was formed from H_2 and $Os_3(CO)_{12}$ [11]. The rapid exchange of bridging and terminal hydride in $H_2Os_3(CO)_{11}$ [8,9] is likely to involve the same intermediate with both hydrides terminal that is involved in the displacement of H_2. Neither the known trinuclear species $H_2Os_3(CO)_{12}$ (IV; $n = 3$), [12] nor any of the other known osmium carbonyl hydrides, are formed in this reaction. Note that $Os_3Cl_2(CO)_{12}$ may be formed by the action of CO (high pressure and temperature) on $Os_3Cl_2(CO)_{10}$ [13]. Osmium is now known to form the interesting series of trinuclear hydrides, $H_2Os_3(CO)_x$ ($x = 10$, 11 or 12) in which there are 4,3 and 2 osmium—osmium bonds respectively, as predicted by the 18*e*-rule, as well as $H_2Os(CO)_4$, $H_2Os_2(CO)_8$, $H_2Os_4(CO)_{13}$, $H_4Os_4(CO)_{12}$ and hydrido-carbonyls of higher molar mass. This is a particularly rich area of hydride chemistry.

Mass spectra of compounds III

The spectra of these compounds are consistent with their observed chemistry. Compound III (L = PhCN) gave osmium-containing ions corresponding to the formation of $H_2Os_3(CO)_{10}$ and of the series only compound III (L = CO) showed the parent molecular ion (source temperature 98° C). Even in this spectrum M^+ is much less abundant than $[M - CO]^+$ and a trace of $[Os_3(CO)_{12}]^+$ and derived ions was observed. The dodecacarbonyl was not an impurity and it is probable that decomposition prior to ionisation by reactions 1 and 2 had occurred. Similarly compounds III; (L = PPh_3 or PMe_2Ph) gave spectra due to $H_2Os_3(CO)_9L$ and $Os_3(CO)_{11}L$ alone (source temperatures 115—160° C). The spectrum of $H_2Os_3(CO)_9L$ showed an initial loss of 30 mass units (H_2 + CO) from the parent molecular ion.

Alkene insertion reactions of $H_2Os_3(CO)_{10}$ and catalytic alkene isomerisation

Ethylene reacts at atmospheric pressure with $H_2Os_3(CO)_{10}$ over several days at room temperature to give ethane and $HOs_3(CH{=}CH_2)(CO)_{10}$, [1,2]. The presumed intermediate $HOs_3(CH_2CH_3)(CO)_{10}$, like $H_2Os_3(CO)_{10}$, requires a double Os—Os bond and is expected to undergo similar addition reactions. Thus the elimination of ethane is likely to follow coordination of ethylene, reactions 3—6, rather than by a unimolecular process to give $Os_3(CO)_{10}$ believed by others [9,14] to be formed as a reactive intermediate which reacts readily with ethylene to give $CH{=}CH_2$ compound.

$$H_2Os_3(CO)_{10} + C_2H_4 \rightarrow H_2Os_3(CO)_{10}(C_2H_4) \quad (3)$$

$$H_2Os_3(CO)_{10}(C_2H_4) \rightarrow HOs_3(CH_2CH_3)(CO)_{10}\ . \tag{4}$$

$$HOs_3(CH_2CH_3)(CO)_{10} + C_2H_4 \rightarrow HOs_3(CH_2CH_3)(CO)_{10}(C_2H_4) \tag{5}$$

$$HOs_3(CH_2CH_3)(CO)_{10}(C_2H_4) \rightarrow HOs_3(CH{=}CH_2)(CO)_{10} + C_2H_6 \tag{6}$$

We believe that the kinetically significant species in triangulo-triosmium systems will be those with either single or double Os—Os bonds. The loss and uptake of ligands is allowed by varying the metal—metal bond order so that no CO groups need be displaced as in monomeric carbonyl catalysts and all intermediates may conform with the 18*e*-rule. If the alkene addition and insertion (reactions 3 and 4) are reversible and faster than reactions of type 5 and 6, then catalytic isomerisation of alkenes becomes possible if hydrogen atoms are added to one but removed from another carbon atom. Indeed compound I catalyses the isomerisation of 1-alkenes to internal alkenes and of allylic alcohols to aldehydes or ketones, examples of which are given in Table 3. Addition of $H_2Os_3(CO)_{10}$ (0.075 g) to neat 3-phenylpropene (95 cm^3) gave 6.6% conversion to *trans*-1-phenylpropene over 24 h, by which time the solution had changed from purple to yellow and the catalyst was no longer active. Nevertheless, 5400 mol reaction had occurred per mol catalyst.

Kinetics and mechanism of alkene isomerisation

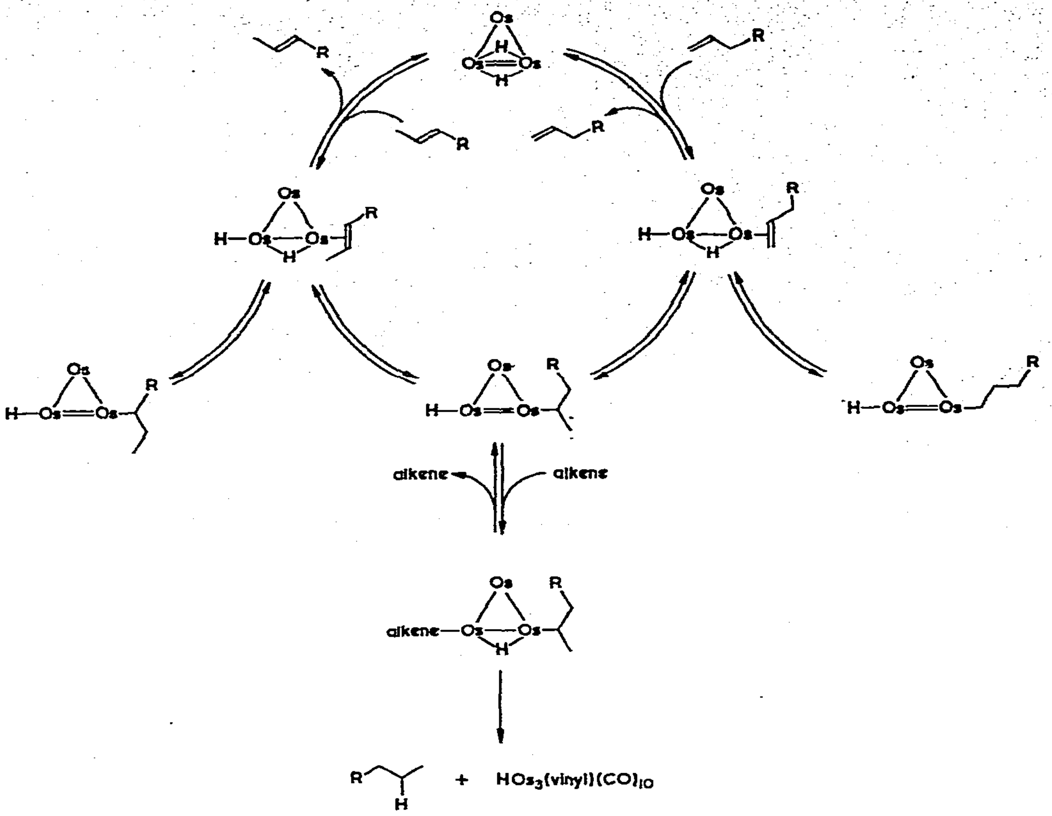
When the alkene is in a large excess over the catalyst, $H_2Os_3(CO)_{10}$, the colour of the solution changes from purple through to yellow as reactions 3 to 6 proceed, although we did not isolate products to confirm this. However, reactions 3 and 4 are sufficiently faster than reactions 5 and 6 (shown as a branch of the catalytic cycle in Scheme 1) for catalytic isomerisation of alkenes to occur and kinetics measured without, in most cases, complications due to catalyst decom-

TABLE 3

$H_2Os_3(CO)_{10}$ CATALYSED ISOMERISATIONS AND ASSOCIATED RATE DATA [a]

Alkene	Isomerised product	k_2 ($l\ mol^{-1}\ s^{-1}$) X 10^3
Hex-1-ene [b]	*cis*- and *trans*-hex-2-ene [e]	7.7 ± 0.4
3-Phenylpropene [b]	*trans*-1-phenylpropene	9.1 ± 0.2
Phenyl(prop-2-enyl)ether [b,c]	*cis*- and *trans*-phenyl(prop-1-enyl)ether	43 ± 2
Prop-3-en-1-ol [d] (allyl alcohol)	propanol	10.7 ± 0.4
But-1-en-3-ol [d]	butan-2-one	10.5 ± 0.4
But-2-en-1-ol [d] (crotyl alcohol)	butanal	0.16 ± 0.01
2-Methylprop-2-en-1-ol (methallyl alcohol)	no reaction at 32.5°C over several days	$<<10^{-1}$

[a] Measured at 32.5°C in $CDCl_3$ (see experimental). [b] k_1 was measured at various concentrations of $H_2Os_3(CO)_{10}$. A plot of k_1 against $H_2Os_3(CO)_{10}$ concentration is a straight line through the origin of slope k_2. [c] The isomerisation of diprop-2-enyl ether to a mixture of *cis, cis*-, *trans, trans*- and *cis,trans*-diprop-1-enyl ether (approximate ratio 1 : 1 : 2) was also observed. [d] k_1 was measured at one $H_2Os_3(CO)_{10}$ concentration and the relation $k_2 = k_1/[H_2Os_3(CO)_{10}]$ assumed. [e] The isomerisation of the hex-1-ene to internal hexenes was observed on interaction with $H_2Os_3(CO)_{10}$ in the presence of hydrogen gas [14]. Hydrogen is unnecessary for the isomerisation.

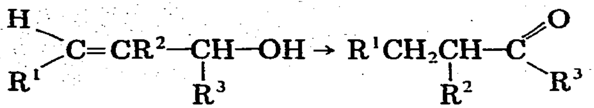


SCHEME 1. Proposed pathway for alkene isomerisation.

position (see Experimental section). Starting with $D_2Os_3(CO)_{10}$ the isomerisation of 3-phenylpropene to 1-phenylpropene was followed by ^{1}H NMR spectra. As the isomerisation occurred, $H_2Os_3(CO)_{10}$ was readily formed, which is consistent with alkene insertion into a D—Os bond with transfer of a H atom back to the metal so that after a few catalytic cycles all D atoms are incorporated into organic products.

The rates of isomerisation are given by $-d[\text{alkene}]/dt = k_2[H_2Os_3(CO)_{10}][\text{alkene}]$, so that the observed first order rate coefficient k_1 is given by $k_1 = k_2[H_2Os_3(CO)_{10}]$. This relation was established in some cases, while in others k_2 was assumed to be given by $k_1/[H_2Os_3(CO)_{10}]$. Values of k_2 for some compounds of type $CH_2{=}CHCH_2R$ ($R = C_3H_7$, Ph, OPh or OH) showed little dependence on R (Table 3). This implies that initial coordination to give $H_2Os_3(CO)_{10}$(alkene) and/or insertion to give $HOs_3(CO)_{10}$(alkyl) are rate determining and not the transfer of H atoms back to osmium.

Allylic alcohols were shown to isomerise to aldehydes or ketones and starting with $CH_2{=}CHCH_2OD$ we obtained $CH_3CHDCHO$ (see Experimental section). This is consistent with coordinated allyl alcohol isomerising to coordinated $CH_3CH{=}CHOD$ which on displacement from the metal rapidly converts from the enol form to $CH_3CHDCHO$. The effect of methyl-substitution at the allyl group on the rate of isomerisation has been studied (eq. 7). For $R^1 = R^2 = H$, the



$$\underset{R^1}{\overset{H}{>}}C=CR^2-\underset{R^3}{CH}-OH \rightarrow R^1CH_2\underset{R^2}{CH}-C\overset{O}{\underset{R^3}{<}} \quad (7)$$

rate of isomerisation is the same with in experimental error whether $R^3 = H$ or Me. Since the rate does not depend on whether a hydrogen atom is removed from a secondary or tertiary carbon, regeneration of $H_2Os_3(CO)_{10}$ from the intermediate $HOs_3(alkyl)(CO)_{10}$ is probably rapid. In agreement with rate-determining alkene coordination and/or insertion into the Os—H bond, substitution at the vinylic positions (R^1 or $R^2 = CH_3$) produced a marked rate reduction. When $R^1 = R^3 = H$ and $R^2 = CH_3$, the complete lack of isomerisation at 32.5°C is probably due to the difficulty of forming tertiary alkylmetal intermediates. This does not preclude reversible insertion to give primary alkyl-species in this and other cases, but this does not lead to isomerisation. A mixture of organic products including more than one aldehyde was obtained after several hours at 60°C. On the other hand internal alkenes isomerise slowly at 32.5°C if they can do so via secondary alkyl intermediates. Thus when $R^1 = CH_3$ and $R^2 = R^3 = H$, isomerisation to butanal proceeds but slower by a factor of 66 than the unsubstituted molecule.

Reactions of $H_2Os_3(CO)_{10}$ with allylic halides

Allyl halides (halide = Cl, Br or I) react with $H_2Os_3(CO)_{10}$ at room temperature by a non-catalytic reaction to give propene (identified by its ^{1}H NMR spectrum) and $HOs_3X(CO)_{10}$ (V) and $Os_3X_2(CO)_{10}$ (VI) as the only osmium-containing compounds. Compounds VI (X = Cl, Br and I) were initially prepared by decarbonylation of the complexes $Os_3X_2(CO)_{12}$ [13] and of the hydrido complexes only $HOs_3Cl(CO)_{10}$ has been prepared previously in very low yield [13]. The ratio of these two species in the product mixture depends on $CH_2{=}CHCH_2X$ as shown in Table 4. We have shown that $HOs_3Cl(CO)_{10}$ does not react with an excess of $CH_2{=}CHCH_2Cl$ so that $Os_3Cl_2(CO)_{10}$ could not have been formed by this route. Neither does $H_2Os_3(CO)_{10}$ react with methyl iodide even under more forcing conditions than those required for allyl halides to react, possibly indicating that an oxidative addition pathway does not occur. Preliminary kinetic results have shown that the rates of the reactions of I with $CH_2{=}CHCH_2X$ depend neither on the concentration nor identity of the allyl halide. We are carrying out further work on the mechanisms of these reactions. One mechanism we are considering

TABLE 4

MOL FRACTIONS OF $HOs_3X(CO)_{10}$ AND $Os_3X_2(CO)_{10}$ AS PRODUCTS OF THE REACTION OF $H_2Os_3(CO)_{10}$ WITH $CH_2{=}CHCH_2X$ (X = Cl, Br OR I) IN PENTANE AT 20°C

X	$HOs_3X(CO)_{10}$	$Os_3X_2(CO)_{10}$
Cl	0.53	0.47
Br	0.43	0.57
I	~1.00	trace

is analogous to that for alkene isomerisation except that a halogen rather than hydrogen atom is transferred back to the metal from the β-carbon.

Experimental

Preparation of compounds

All reactions were carried out under nitrogen unless stated otherwise. Separations were carried out on chromatographic plates (silica).

Reaction of dihydridodecacarbonyltriosmium with dimethylphenylphosphine

PMe_2Ph (0.0181 g; 1.31 × 10^{-4} mol) was added to a solution of $H_2Os_3(CO)_{10}$ (0.119 g; 1.31 × 10^{-4} mol) in n-hexane (35 cm^3). Following an immediate colour change from purple to yellow, the solution was allowed to stand overnight to complete the precipitation of $H_2Os_3(CO)_{10}(PMe_2Ph)$ as yellow plates (0.0997 g; 77%). The PPh_3 compound was prepared similarly.

Pyrolysis of tertiary phosphine adducts

$H_2Os_3(CO)_{10}(PMe_2Ph)$. Over 2 h a solution of this compound (0.133 g) in refluxing hexane (70 cm^3) under N_2 turned from yellow to purple. Removal of the solvent under reduced pressure and chromatography of the residue on silica plates gave one main purple band which gave $H_2Os_3(CO)_9(PMe_2Ph)$ as purple crystals (0.073 g, 66%).

$H_2Os_3(CO)_{10}(PPh_3)$. A solution of the compound (0.114 g) in refluxing hexane (40 cm^3) under N_2 changed from yellow to purple over 1 h 10 min. Some yellow precipitate was removed by filtration and chromatography of the purple solution gave $H_2Os_3(CO)_9(PPh_3)$ as a purple solid (0.074 g, 66%).

Reaction of dihydridodecacarbonyltriosmium with carbon monoxide

(a) CO was bubbled through a solution of $H_2Os_3(CO)_{10}$ (0.111 g; 1.29 × 10^{-4} mol) in pentane (15 cm^3) until it had become yellow (40 min). On standing under CO for 24 h yellow crystals of $H_2Os_3(CO)_{11}$ (0.055 g; 48%) deposited.

(b) The infrared spectrum of a solution was recorded periodically while CO was bubbled through a refluxing solution of $H_2Os_3(CO)_{10}$ (0.064 g) in hexane (45 cm^3). The concentration of starting material decreased, while that of $Os_3(CO)_{12}$ increased. $H_2Os_3(CO)_{11}$ was observed to be in low concentration at intermediate stages, but the absence of absorptions due to $H_2Os_3(CO)_{12}$ was noted. After 125 min complete conversion to $Os_3(CO)_{12}$ was observed.

Reaction of dihydridodecacarbonyltriosmium with benzonitrile

A stoichiometric addition of PhCN to $H_2Os_3(CO)_{10}$ in chloroform gave no reaction whereas $H_2Os_3(CO)_{10}$ dissolves in neat PhCN to give complete reaction. Yellow-orange crystals of $H_2Os_3(CO)_{10}(PhCN)$ deposited overnight from a solution of $H_2Os_3(CO)_{10}$ (0.090 g) and PhCN (0.10 cm^3) in n-hexane (10 cm^3). The product could not be recrystallised in the absence of PhCN since $H_2Os_3(CO)_{10}$ is regenerated.

Reactions of $H_2Os_3(CO)_{10}$ with allyl halide

Allyl iodide. Allyl iodide (0.4 cm^3) was added to a solution of $H_2Os_3(CO)_{10}$

(0.121 g) in pentane (30 cm^3) and the mixture allowed to stand at room temperature for ca. 16 h. The organic materials were removed under reduced pressure (0.01 mmHg) to give an orange solid, the mass spectrum of which indicated that it was $HOs_3I(CO)_{10}$ containing some $Os_3I_2(CO)_{10}$. Chormatography gave $HOs_3I(CO)_{10}$ as orange crystals (>95% yield) together with a trace of $Os_3I_2(CO)_{10}$ which was not obtained pure.

Allyl bromide and chloride. These were reacted in the same manner and the solid residue [containing only $HOs_3X(CO)_{10}$ and $Os_3X_2(CO)_{10}$] was analysed by taking a known mass in $CDCl_3$ solution and integrating the hydride signal in the NMR spectrum against added methyl iodide. Careful chromatography enabled a separation of the two components.

Compound $HOs_3I(CO)_{10}$ showed no reaction with PPh_3 at room temperature in cyclohexane and $HOs_3Br(CO)_{10}$ did not catalyse the isomerisation of 3-phenylpropene under the same conditions as did $H_2Os_3(CO)_{10}$.

Kinetics of alkene isomerisation

The rates of alkene isomerisation were calculated from ^1H NMR integrations recorded at various times after preparing solutions of alkene and $H_2Os_3(CO)_{10}$ in $CDCl_3$. For example, with $H_2Os_3(CO)_{10}$ (5.37×10^{-2} mol l^{-1}) and 3-phenylpropene (1.21 mol l^{-1}), the isomerisation to *trans*-1-phenylpropene proceeds with first order dependence on 3-phenylpropene concentration ($k_1 = 4.89 \times 10^{-4}$ s^{-1}; 32.5°C). In a separate experiment the decomposition of $H_2Os_3(CO)_{10}$ in a similar solution was followed by measuring the fall in intensity of the absorption band giving rise to the purple colour of the complex at 552 nm ($\epsilon_{max} = 379$ l mol^{-1} cm^{-1}); 4.2% decomposition having occurred after 1.65×10^4 s. This corresponds to ca. 12 half-lives for the alkene isomerisation and therefore catalyst decomposition can largely be ignored. This was further confirmed, in most cases, by linearity of integrated first-order rate plots for up to over 90% alkene isomerisation. For the isomerisation of prop-3-en-1-ol(allyl alcohol) to propanol the decomposition of $H_2Os_3(CO)_{10}$ occurred more readily so that satisfactory kinetics could only be obtained for low alkene concentrations.

Further, k_1 values are largely independent of the initial alkene concentration; thus for catalyst concentration 2.47×10^{-2} mol l^{-1} and 3-phenylpropene concentrations 0.302, 1.21 and 6.05 mol l^{-1} we obtained values for k_1 (32.5°C): $(2.4 \pm 0.10) \times 10^{-4}$, $(2.24 \pm 0.05) \times 10^{-4}$ and $(2.19 \pm 0.05) \times 10^{-4}$ s^{-1} respectively. If real, this small variation of k_1 could be due to medium effects on going from a 4% to an 80% v/v solution of alkene in $CDCl_3$. By keeping the initial alkene concentration held constant and varying the concentration of $H_2Os_3(CO)_{10}$ we showed that the observed first order rate coefficient $k_1 = k_2[H_2Os_3(CO)_{10}]$, and values for k_2 are given in Table 3.

Isomerisation of $CH_2{=}CHCH_2OD$

A solution of prop-3-en-1-ol (allyl alcohol) (0.2 cm^3) in $CDCl_3$ (1.0 cm_3) was treated successively with D_2O (4×2 cm^3). $H_2Os_3(CO)_{10}$ (ca. 0.01 g) was added to the dried solution which slowly changed from purple to yellow. This treatment with $H_2Os_3(CO)_{10}$ was carried out three more times and the ^1H NMR spectrum of the distilled mixture was recorded. The spectrum showed $CH_3CHDCHO$ with signals due to $C\underline{H}O$ (τ 0.29 ppm; doublet; intensity 0.93 ± 0.04); $C\underline{H}D$

(τ 7.64 ppm; quartet of doublets, intensity 1.12 ± 0.04) and $C\underline{H}_3$ (τ 9.00 ppm; 1 : 1 : 1 triplet of doublets due to $CHDC\underline{H}_3$ (J(HH) 7.55 and J(HD) 1.14 Hz) with a weak underlying 1 : 2 : 1 triplet due to $CH_2C\underline{H}_3$ (J(HH) 7.55); total intensity 3.00).

Acknowledgements

We would like to thank Johnson—Matthey and Co. Ltd. for a very generous loan of osmium tetraoxide.

References

1 A.J. Deeming, S. Hasso and M. Underhill, J. Chem. Soc. Dalton, (1975) 1614.
2 J.B. Keister and J.R. Shapley, J. Organometal. Chem., 85 (1975) C29.
3 W.G. Jackson, B.F.G. Johnson, J.W. Kelland, J. Lewis and K.T. Schorpp, J. Organometal. Chem., 87 (1975) C27
4 A.J. Deeming, S. Hasso and M. Underhill, J. Organometal. Chem., 80 (1974) C53.
5 R. Mason and D.M.P. Mingos, J. Organometal. Chem., 50 (1973) 53.
6 W.G. Jackson, B.F.G. Johnson, J.W. Kelland, J. Lewis and K.T. Schorpp, J. Organometal. Chem., 88 (1975) C17.
7 A.J. Deeming and M. Underhill, J. Chem. Soc. Dalton, (1974) 1415.
8 A.J. Deeming and S. Hasso, J. Organometal. Chem., 88 (1975) C21.
9 J.R. Shapely, J.B. Keister, M.R. Churchill and B.G. DeBoer, J. Amer. Chem. Soc., 97 (1975) 4145.
10 A.J. Deeming, B.F.G. Johnson and J. Lewis, J. Chem. Soc. (A), (1970) 2518.
11 H.D. Kaesz, S.A.R. Knox, J.W. Koepke and R.B. Saillant, Chem. Comm., (1971) 477; S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 97 (1975) 3942.
12 J.R. Moss and W.A.G. Graham, J. Organometal. Chem., 23 (1970) C47.
13 A.J. Deeming, B.F.G. Johnson and J. Lewis, J. Chem. Soc. (A), (1970) 2517.
14 J.B. Keister and J.R. Shapley, J. Amer. Chem. Soc., 98 (1976) 1056.