Synthesis, Structure, and Dynamic Behaviour of Two Isomeric Triosmium Clusters containing the Ethoxyvinylidene ($C{=}CHOEt$) and Ethoxyethyne ($CH{\equiv}COEt$) Ligands Respectively†

Esther Boyar, Antony J. Deeming,* Mark S. B. Felix, and Shariff E. Kabir
Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ
Trushar Adatia, Ravindra Bhusate, Mary McPartlin,* and Harold R. Powell
Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB

The μ_3-ethynyl compound $[Os_3H(C{\equiv}CH)(CO)_9]$ reacts smoothly with ethanol as the solvent to give two isomeric ethanol adducts: $[Os_3H_2(CCHOEt)(CO)_9]$ (**1**) and $[Os_3H_2(CHCOEt)(CO)_9]$ (**2**), derived by ethoxy-group addition at the β- and α-carbon atoms respectively. Insertion of $CH{\equiv}COEt$ into Os–H bonds of $[Os_3H_2(CO)_{10}]$ gives the vinyl isomers $[Os_3H(CH{=}CHOEt)(CO)_{10}]$ (**3**) and $[Os_3H(CH_2{=}COEt)(CO)_{10}]$ (**4**). Thermal decarbonylation of (**3**) leads to both (**1**) and (**2**) but a similar decarbonylation of (**4**) leads only to (**2**). Compound (**2**) was prepared alternatively by hydrogenation of $[Os_3(\mu_3\text{-}CHCOEt)(CO)_{10}]$ (**5**). *X*-Ray diffraction showed that the structure of (**1**) is closely related to that of the vinylidene compound $[Os_3H_2(\mu_3\text{-}CCH_2)(CO)_9]$, while that of (**2**) contains the μ_3-ethoxyethyne ligand CHCOEt roughly parallel to one Os–Os edge. Although this is related closely to the most common type of μ_3-alkyne bridging, there are considerable distortions from this idealised geometry. Both (**1**) and (**2**) undergo rapid enantiomerisation leading to coalescence of hydride and diastereotopic methylene signals in their ^1H n.m.r. spectra by a single process in each case. A minor isomer of (**1**) detected at low temperatures is more rapidly fluxional than the major one and rapidly interconverts with it at room temperature. Attempting to reverse the addition of ethanol which had given (**1**) and (**2**), these compounds were treated with CF_3CO_2H. Compound (**1**) gave $[Os_3H_2(C{\equiv}CH)(CO)_{10}]^+$ by loss of ethoxide ion, whereas (**2**) was protonated at the metal atoms to give $[Os_3H_3(CHCOEt)(CO)_9]^+$ (**6**).

The ethynyl compound $[Os_3H(\mu_3\text{-}C{\equiv}CH)(CO)_9]$[1] is hydrogenated to the ethylidyne compound $[Os_3H_3(\mu_3\text{-}CMe)(CO)_9]$[2] *via* the vinylidene compound $[Os_3H_2(\mu_3,\eta^2\text{-}C{=}CH_2)(CO)_9]$.[3] There is no evidence for the formation of the alternative (isomeric) ethyne intermediate $[Os_3H_2(\mu_3,\eta^2\text{-}CH{=}CH)(CO)_9]$ in this hydrogenation but this isomer was prepared by another route and was shown not to be hydrogenated. This system provides a very good model for these important simple ligands ($C{\equiv}CH$, $CH{\equiv}CH$, $C{=}CH_2$, and CMe) at metal surfaces and their transformations are models for reactions such as hydrogenation at surfaces. Hydrogen-atom addition to $C{\equiv}CH$ is exclusively to the β-carbon atom as far as we can tell, whereas nucleophilic addition of PMe_2Ph is exclusively at the α-carbon atom. For example, PMe_2Ph addition was shown to give $[Os_3H(CH{=}CPMe_2Ph)(CO)_9]$ (*X*-ray structure) which exists in a zwitterionic form with a phosphonium centre and a negative charge on the metal atoms.[4] We have now established that $[Os_3H(C{\equiv}CH)(CO)_9]$ reacts with a range of nucleophiles with attack predominantly at the α-carbon atom, for example PMe_2Ph, pyridine, NH_3, and $NHEt_2$ all add exclusively in this way.[5] Ethanol on the other hand adds with the ethoxy-group adding predominantly at the α-carbon but with a minor but significant proportion of the attack occurring at the β site. In this paper we describe the formation of $[Os_3H_2(CCHOEt)(CO)_9]$ (**1**) (minor product) and $[Os_3H_2(CHCOEt)(CO)_9]$ (**2**) (major product) by ethanol addition, their single-crystal *X*-ray structures, and the kinetics and mechanism of their fluxional behaviour which contrasts with that of the corresponding CCH_2 and CHCH clusters. Since we published a preliminary communication on this work,[5] Kaesz and Jensen[6] have described the synthesis and structure of the ruthenium analogue of one of the compounds, $[Ru_3H_2(CHCOEt)(CO)_9]$, although this was synthesised by a very different route.

Results and Discussion

Synthesis of the Isomeric Compounds $[Os_3H_2(C_2HOEt)(CO)_9]$, *Clusters* (**1**) *and* (**2**).—The cluster $[Os_3H(C{\equiv}CH)(CO)_9]$ is most easily synthesised by treating $[Os_3(CO)_{10}(MeCN)_2]$ with acetylene at room temperature to give the acetylene compound $[Os_3(\mu_3\text{-}CHCH)(CO)_{10}]$ which thermally decarbonylates with oxidative addition, involving H-atom transfer from carbon to osmium, to give moderate yields of the $C{\equiv}CH$ cluster. A solution of $[Os_3H(C{\equiv}CH)(CO)_9]$ in ethanol reacts slowly at room temperature but rapidly under reflux to give $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**) (21%) and $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) (78%) (Scheme 1). These isomers are easily separated on silica (t.l.c.) and obtained quantitatively as pale yellow crystals; the given yields are after isolation. Solutions of (**1**) and (**2**) in inert solvents (*e.g.* cyclohexane) show no tendency to eliminate ethanol nor to interconvert. We therefore propose that the proportions of (**1**) and (**2**) are given by their rates of formation. This is confirmed by alternative syntheses given below which result in different product distributions.

Reaction of $[Os_3H_2(CO)_{10}]$ with the alkyne $CH{\equiv}COEt$ at room temperature gave the isomeric ethoxyvinyl compounds $[Os_3H(\mu\text{-}CH{=}CHOEt)(CO)_{10}]$ (**3**) (59%) and $[Os_3H(\mu\text{-}CH_2{=}COEt)(CO)_{10}]$ (**4**) (10%) by addition of Os–H in the two possible directions across the alkyne triple bond (Scheme 2). These compounds have ν(CO) bands around 2 000 cm^{-1} (Table 1) very like those of $[Os_3H(CH{=}CH_2)(CO)_{10}]$ and are believed to be isostructural with it, containing μ,η^2-vinyl ligands rather than having co-ordinated ether functions as was found for $[Os_3H(\mu\text{-}MeCHOMe)(CO)_{10}]$ which is the saturated form of the vinyl compound (**4**).[7] We have illustrated (**3**) in Scheme 2 in

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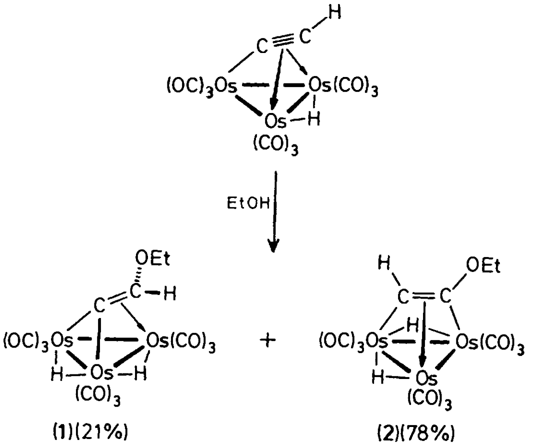
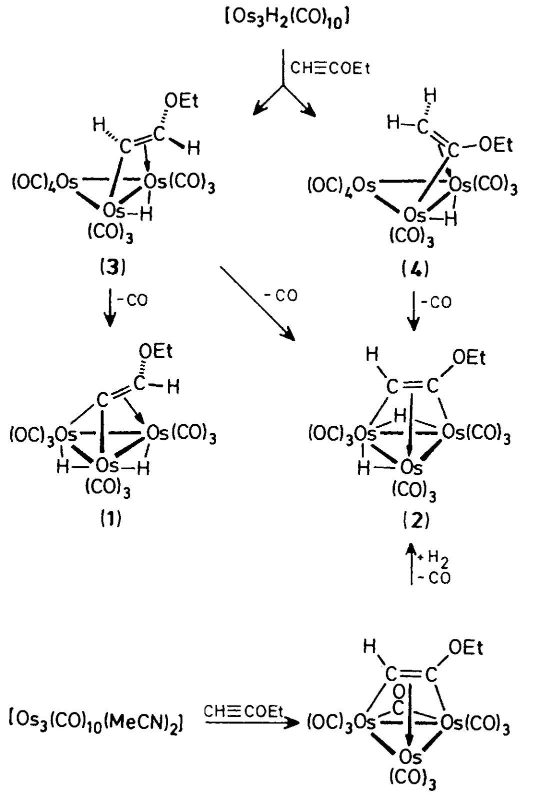
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

the configuration found for $[Os_3H(CH{=}CH_2)(CO)_{10}]$[8] and for terminally substituted compounds of type $[Os_3H(CH{=}CHR)(CO)_{10}]$.[9] Compound (3) contains the *trans*-alkene (J_{HH} across the double bond = 12.3 Hz) and we assume it has the normal configuration. On the other hand we have shown (4) with the different configuration found for $[Os_3H(PhC{=}CHPh)(CO)_{10}]$[10] and for the furanyl compound $[Os_3H(C_4H_3O)(CO)_{10}]$.[11] A clash of a 1 substituent at the vinyl with an axial CO ligand prevents the configuration found for (3) so by analogy we believe (4) adopts a configuration with the ethoxy-group remote from the axial CO ligand of the $Os(CO)_4$ group.

Thermal decarbonylation of (3) in refluxing octane gives cluster (1) (67%) and a small amount of cluster (2) (7%). This is



Scheme 1.



Scheme 2.

Table 1. I.r. and ^1H n.m.r. data

Compound	$\nu(CO)^a/cm^{-1}$	δ^b/p.p.m.	Assignment	J/Hz
(1) $[Os_3H_2(C{=}CHOEt)(CO)_9]$	2 104m, 2 076vs, 2 050vs, 2 026vs,	8.31(s)	C=CHOEt	
	2 015s, 2 010vs, 1 993s, 1 978s	3.86(m)	CH_2CH_3	
		3.58(m)	CH_2CH_3	
		1.19(t)	CH_3	6.9
		−18.98(d)	OsH	1.6
		−21.22(d)	OsH	1.6
(2) $[Os_3H_2(CH{=}COEt)(CO)_9]^c$	2 106m, 2 078vs, 2 052vs, 2 025vs,	6.24(s)	CH=COEt	
	2 007s, 2 002s, 1 995s, 1 982m	3.98(m)	CH_2CH_3	
		3.64(m)	CH_2CH_3	
		1.28(t)	CH_2CH_3	6.9
		−18.02(s)	OsH	
		−21.18(s)	OsH	
(3) $[Os_3H(CH{=}CHOEt)(CO)_{10}]$	2 100w, 2 055vs, 2 046s, 2 016vs,	6.61(d)	CH=CHOEt	12.3
	2 009, 2 002m, 1 985m, 1 980m	5.57(dd)	CH=CHOEt	12.3, 2.2
		4.02(q)	CH_2	7.1
		1.37(t)	CH_3	7.1
		−17.78(d)	OsH	2.2
(4) $[Os_3H(CH_2{=}COEt)(CO)_{10}]$	2 102w, 2 060vs, 2 048s, 2 019vs,	4.18(q)	CH_2	7.0
	2 004m, 1 976w, 1 963vs, 1 949vw	3.88(dd)	C=CH	6.7, 0.9
		1.35(t)	CH_3	7.0
		−17.33(dd)	OsH	3.0, 1.1
(5) $[Os_3(CH{=}COEt)(CO)_{10}]$	2 098m, 2 060vs, 2 045vs, 2 023vs,	7.50(s)	CH=COEt	
	2 001s, 1 992s, 1 974m, 1 848br,w	3.72(q)	CH_2	7.1
		1.32(t)	CH_3	7.1
(6) $[Os_3H_3(CH{=}COEt)(CO)_9]^+$	2 143m, 2 123vs, 2 116vs, 2 107s,	6.83(s)	CH=COEt	
	2 068vs, 2 051s, 2 015m	4.41(m)	CH_2	
		1.50(t)	CH_3	7.1
		−17.76(t)	OsH	1.6
		−20.40(d)	OsH	1.6

[a] In cyclohexane except (6) which is in dichloromethane. [b] In CD_2Cl_2 at −99 °C for (1) and (2); other compounds in $CDCl_3$ or CD_2Cl_2 at 22 °C. [c] N.m.r. data for major isomer only.

almost the opposite product distribution to that formed in the reaction of ethanol with $[Os_3H(C{\equiv}CH)(CO)_9]$. This difference is to be expected since nucleophilic addition is preferentially at the 1 position of the μ_3,η^2-C≡CH ligand whereas H atoms are preferentially transferred to osmium from the 1 position of the vinyl group μ,η^2-CH=CHR. Thermolysis of isomer (**4**) gave only cluster (**2**) and none of (**1**), again as expected if (**1**) and (**2**) do not interconvert.

Structure and Dynamic Behaviour of Compound (**1**).—In the original communication of this work [5] the structures of (**1**) and (**2**) were based on i.r. and n.m.r. data (Table 1). The only spectroscopic features really distinguishing these isomers are the ^1H n.m.r. shifts of the C=C*H*OEt and C*H*=COEt atoms. Chemical shifts for μ_3-RC_2H ligands in triosmium clusters are normally around δ 9—10 so the isomer with the signal at δ 8.31 was assigned to the CH=COEt species and that with δ 6.24 to the C=CHOEt isomer. The present single-crystal *X*-ray structure analyses of (**1**) and (**2**) confirm the existence of the two proposed isomers but require their assignments to be reversed from those we gave earlier.[6] The molecular structures of clusters (**1**) and (**2**) are shown in Figures 1 and 2 and atomic co-ordinates are given in Table 2 and selected bond lengths and angles in Table 3. The observation of an unprecedentedly low δ value for the μ_3-alkyne CH=COEt (δ 6.24) is difficult to explain

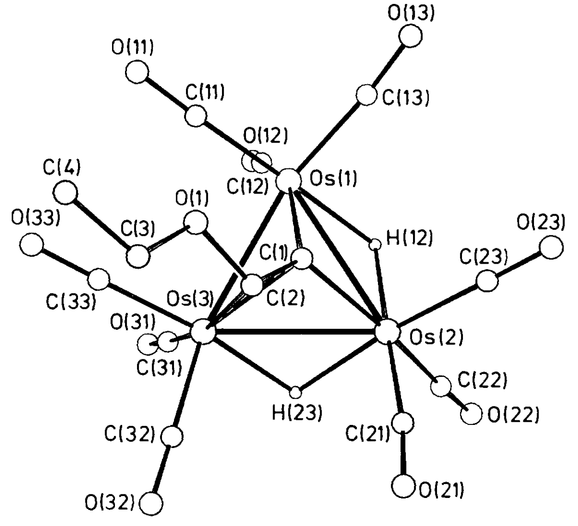


Figure 1. Molecular structure of $[Os_3H_2(CCHOEt)(CO)_9]$, (**1**), with the numbering scheme used in the *X*-ray structure determination

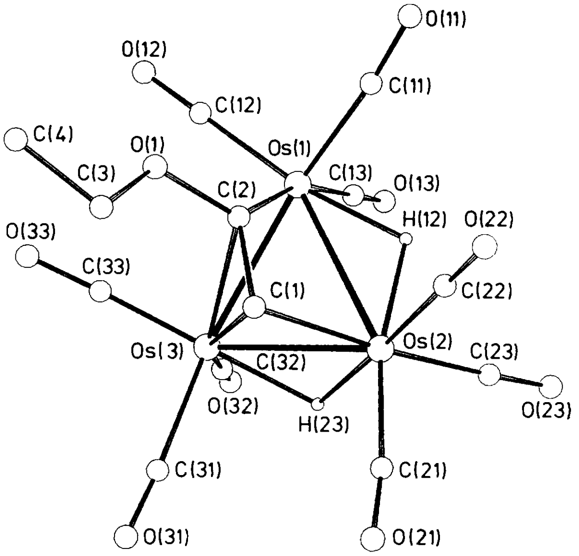


Figure 2. Molecular structure of $[Os_3H_2(CHCOEt)(CO)_9]$, (**2**), with the numbering scheme used in the *X*-ray structure determination

Table 2. Fractional atomic co-ordinates for complexes (**1**) and (**2**)

$[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**)				$[Os_3H_2(CHCOEt)(CO)_9]$ (**2**)			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	−0.132 78(4)	−0.173 50(6)	−0.516 7(9)	Os(1)	0.000 00	0.114 43(13)	0.000 00
Os(2)	−0.202 08(4)	−0.309 60(6)	−0.316 06(9)	Os(2)	0.075 73(11)	0.390 64(13)	0.044 53(15)
Os(3)	−0.068 60(4)	−0.198 26(6)	−0.195 13(9)	Os(3)	0.122 52(13)	0.216 55(13)	−0.101 89(17)
C(11)	−0.045 3(12)	−0.144 4(16)	−0.573 0(23)	C(11)	−0.046 0(34)	0.080 2(45)	0.122 0(43)
O(11)	0.006 3(8)	−0.125 6(14)	−0.606 7(20)	O(11)	−0.071 1(24)	0.043 2(32)	0.198 8(28)
C(12)	−0.160 8(10)	−0.006 4(15)	−0.534 7(24)	C(12)	0.003 1(25)	−0.059 6(37)	−0.031 5(33)
O(12)	−0.178 3(8)	0.080 8(11)	−0.533 1(21)	O(12)	0.010 7(20)	−0.169 2(30)	−0.062 8(31)
C(13)	−0.176 6(10)	−0.221 1(21)	−0.724 9(30)	C(13)	−0.126 1(31)	0.143 2(41)	−0.102 8(41)
O(13)	−0.197 8(9)	−0.255 1(14)	−0.851 1(18)	O(13)	−0.183 9(20)	0.172 0(34)	−0.171 9(31)
C(21)	−0.186 9(10)	−0.427 7(18)	−0.165 6(28)	C(21)	0.163 3(33)	0.529 4(47)	0.055 6(41)
O(21)	−0.175 9(9)	−0.495 4(14)	−0.065 5(21)	O(21)	0.214 8(32)	0.604 5(36)	0.058 4(43)
C(22)	−0.282 8(12)	−0.247 0(14)	−0.250 9(24)	C(22)	0.097 1(28)	0.405 6(39)	0.199 2(37)
O(22)	−0.331 7(9)	−0.208 5(13)	−0.217 9(23)	O(22)	0.101 1(25)	0.404 2(45)	0.295 1(35)
C(23)	−0.253 9(10)	−0.413 5(17)	−0.479 1(29)	C(23)	−0.027 2(25)	0.512 2(36)	0.005 7(32)
O(23)	−0.282 0(8)	−0.474 4(14)	−0.571 7(21)	O(23)	−0.092 5(22)	0.573 8(29)	−0.023 7(33)
C(31)	−0.083 8(10)	−0.044 3(19)	−0.145 5(23)	C(31)	0.233 5(46)	0.317 6(61)	−0.121 6(56)
O(31)	−0.096 6(8)	0.053 8(13)	−0.122 1(19)	O(31)	0.298 1(33)	0.370 3(39)	−0.133 8(39)
C(32)	−0.034 6(11)	−0.260 4(18)	0.006 4(25)	C(32)	0.033 2(31)	0.223 7(42)	−0.243 8(40)
O(32)	−0.013 1(9)	−0.305 2(15)	0.129 4(20)	O(32)	−0.010 8(31)	0.245 8(37)	−0.320 3(32)
C(33)	0.022 0(11)	−0.158 3(18)	−0.227 9(24)	C(33)	0.159 5(34)	0.054 1(49)	−0.121 4(45)
O(33)	0.075 6(7)	−0.128 5(15)	−0.237 6(21)	O(33)	0.191 1(27)	−0.052 5(27)	−0.131 4(24)
C(1)	−0.108 9(9)	−0.321 7(14)	−0.390 9(20)	C(1)	0.177 1(24)	0.243 8(34)	0.085 7(32)
C(2)	−0.048 7(10)	−0.381 8(15)	−0.315 9(26)	C(2)	0.126 4(33)	0.125 9(42)	0.075 9(44)
O(1)	0.009 9(7)	−0.378 3(10)	−0.384 8(17)	O(1)	0.192 5(18)	0.005 2(26)	0.124 4(23)
C(3)	0.071 6(10)	−0.430 3(20)	−0.288 1(33)	C(3)	0.293 0(25)	0.021 7(35)	0.169 9(32)
C(4)	0.132 8(11)	−0.405 0(25)	−0.355 0(36)	C(4)	0.327 9(33)	−0.117 2(46)	0.183 3(42)

Table 3. Selected bond lengths (Å) and angles (°) for $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**) and $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**)

	(**1**)	(**2**)
Os(1)–Os(2)	2.883(1)	3.006(2)
Os(1)–Os(3)	2.774(1)	2.770(2)
Os(2)–Os(3)	2.863(1)	2.824(2)
Os(1)–C(1)	2.01(2)	
Os(1)–C(2)		1.86(5)
Os(2)–C(1)	2.06(2)	2.08(3)
Os(3)–C(1)	2.21(2)	2.32(4)
Os(3)–C(2)	2.43(2)	2.45(5)
C(1)–C(2)	1.39(2)	1.40(5)
C(2)–O(1)	1.40(3)	1.58(5)
O(1)–C(3)	1.43(2)	1.46(4)
C(3)–C(4)	1.47(4)	1.49(6)
Os(3)–Os(1)–Os(2)	60.8(1)	58.4(1)
Os(2)–Os(3)–Os(1)	61.5(1)	65.0(1)
Os(3)–Os(2)–Os(1)	57.7(1)	56.6(1)
C(11)–Os(1)–Os(3)	93.1(6)	155(1)
C(12)–Os(1)–Os(3)	103.3(6)	101(1)
C(11)–Os(1)–Os(2)		103(1)
C(13)–Os(1)–Os(2)	104.1(7)	103(1)
C(21)–Os(2)–Os(3)	95.1(6)	102(1)
C(22)–Os(2)–Os(1)	119.7(5)	102(1)
C(31)–Os(3)–Os(2)	109.4(6)	99(2)
C(32)–Os(3)–Os(2)	105.4(7)	112(1)
C(33)–Os(3)–Os(1)	92.5(6)	90(2)
Os(2)–C(1)–Os(1)	90.1(7)	
Os(2)–C(1)–Os(3)	84.2(7)	80(1)
Os(3)–C(1)–Os(1)	82.0(6)	
C(2)–C(1)–Os(1)	138(1)	
C(2)–C(1)–Os(3)	81(1)	78(3)
C(2)–C(1)–Os(2)	127(1)	104(3)
C(1)–C(2)–Os(1)		123(3)
O(1)–C(2)–C(1)	118(2)	111(3)

but the relatively high δ value for C=CHOEt (δ 8.31) is attributable to the proximity of the OEt group.

The most important part of the structures is the geometry of the μ_3 ligands at the metal triangles. The H atoms of the C=CHOEt and CH=COEt ligands in (**1**) and (**2**) respectively were not located directly in the *X*-ray analyses but these ligands are clearly defined from the positions of the heavier atoms. For example, C(1) in compound (**1**) is approximately centrally placed with distances of 2.01(2) Å to Os(1), of 2.06(2) Å to Os(2), and of 2.21(2) Å to Os(3). In contrast C(2) is bonded only to Os(3) with a rather long 2.43(2) Å; the other distances are even longer [C(2) ··· Os(1) 3.18 and C(2) ··· Os(2) 3.09 Å] and clearly indicate non-bonding contacts. The representation of cluster (**1**) in the Schemes with a H atom and an EtO group both bonded to C(2) is consistent with these distances, the σ-Os–C bonds being shorter than those in η^2 interaction as expected. Indeed cluster (**1**) has a structure quite close to that of $[Os_3H_2(C{=}CH_2)(CO)_9]$.[3] The hydride ligands are non-equivalent (^1H n.m.r. evidence in Table 1) and Os–Os distances and CO positions are consistent with their bridging the Os(1)–Os(2) and Os(2)–Os(3) edges. Potential-energy minimisation gave positions for the hydrogen atoms in the expected sites. The C(1)–C(2) distance [1.39(2) Å] is consistent with an η^2-alkene. The vinylidene ligand is rather unsymmetrically bonded to the Os_3 triangle. The C(2)–C(1)–Os(1) angle [138(1)°] is greater than C(2)–C(1)–Os(2) [127(1)°] but it is not possible to tell whether this is a result of a hydride ligand being located on one side between Os(2) and Os(3) producing an intrinsic asymmetry or whether it is a result of the differences between H and OEt as substituents at C(2) of the μ_3 ligand.

In view of the mobility of the μ_3 ligand in (**1**) (see later) either of two configurations might have been adopted: the one found in the crystal and another with the H and the OEt groups interchanged. The low-temperature ^1H n.m.r. spectrum (Figure 3) indicates the presence of these two isomers, the minor one never being more than 10% populated and decreasing at the lowest temperatures studied (−99 °C). Probably the major isomer detected in solution corresponds to the form in the crystal.

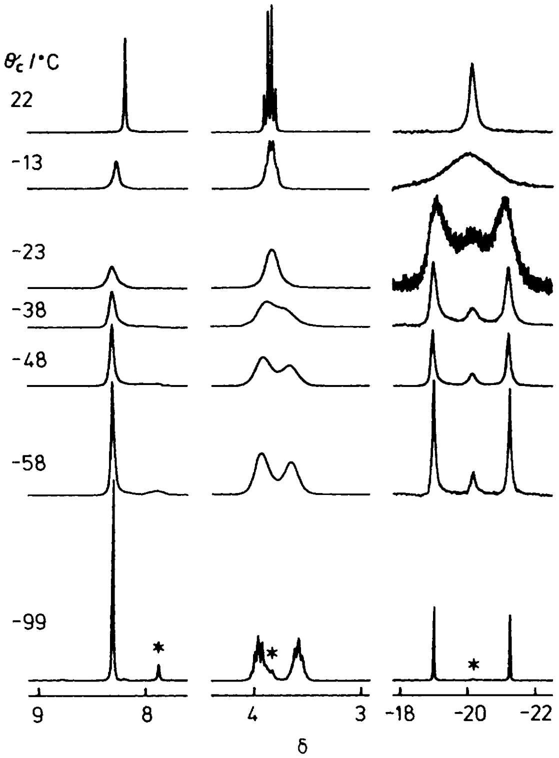


Figure 3. Proton n.m.r. spectra of $[Os_3H_2(C{=}CHOEt)(CO)_9]$, (**1**) recorded in $CDCl_3$ at 200 MHz, * indicates the signals for the minor isomer

The behaviour in solution leading to the coalescences in Figure 3 is probably intramolecular. Certainly we can rule out the reversible loss of ethanol or ethoxide ion since this would lead to the interconversion of isomers (**1**) and (**2**) which does not occur at room temperature. Neither can the changes in the ^1H n.m.r. spectra be explained by hydride migrations alone, as found for $[Os_3H_2(C{=}CH_2)(CO)_9]$ and related compounds,[3,12] but these require motion of the C=CHOEt ligand with respect to the Os_3 triangle. At −99 °C the spectrum of the major isomer is frozen out and corresponds with the chiral geometry found for the crystal structure. In contrast, the minor isomer is still fluxional at this temperature giving single hydride (δ −20.20) and CH_2 (δ 3.8) signals [as well as a C=C*H*OEt signal (δ 7.88)]. Our interpretation is that the enantiomerisation (A) in Figure 4 is very rapid even at −99 °C preventing the spectrum of the minor isomer being frozen out and is faster than the corresponding process (B) for the major isomer. These processes require intermediates (or transition states) with vinylidene ligands in tilted orientations but with molecular symmetry planes, *i.e.* with the C=CHOEt plane perpendicular to the metal plane. Process (A) is presumably faster than (B) because it allows the OEt groups to move away from the $Os(CO)_3$ groups.

Above −99 °C all signals start to broaden and a single set of resonances is observed at room temperature (Figure 3) resulting from rapid enantiomerisation of the major isomer together with the interconversion of isomers. These appear to occur at the same or about the same rate. We have estimated $\Delta G^\ddagger$ at the coalescence temperatures for hydride exchange in the major

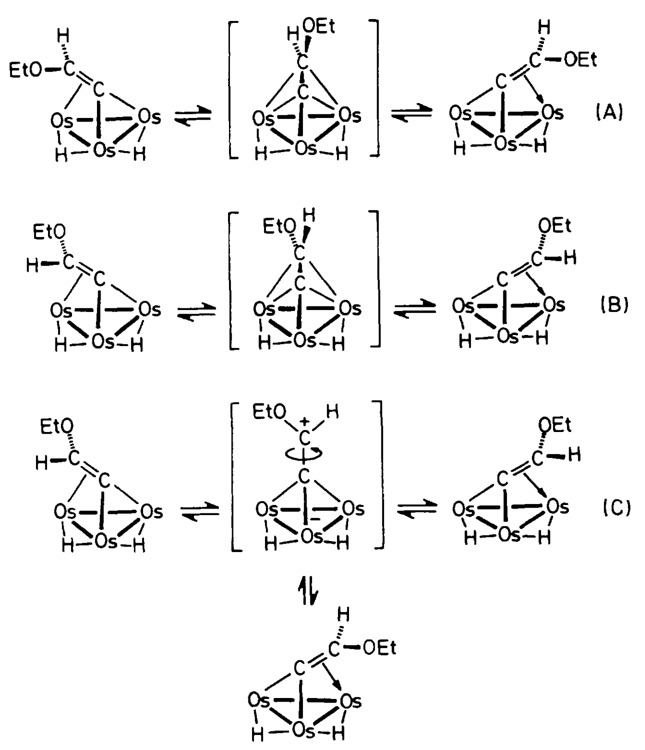


Figure 4. Proposed processes to account for enantiomerisation of the minor isomer of (**1**) (A), of the major isomer (**B**), and for the interconversion of isomers/enantiomerisation of the major isomer (C)

isomer to be 48 ± 2 kJ mol^{-1} (T_c = -18 ± 5 °C for signals at δ −18.98 and −21.22) and for CH_2 exchange in this isomer to be 46 ± 2 kJ mol^{-1} (T_c = -38 ± 5 °C for signals at δ 3.86 and 3.58). Although these are only approximate values, it seems likely that enantiomerisation of the major isomer as well as the interconversion of isomers of (**1**) occur by the same process. Process (B) would not lead to isomer exchange while (C) involving a vertical vinylidene orientation would lead to both enantiomerisation of the major isomer and interconversion of isomers. A similar enantiomerisation has been observed in the related cationic cluster $[Co_3(C{=}CHCHMe_2)(CO)_9][FSO_3]$.[13] Motions of the μ_3 ligand in $[Os_3H_3(C{=}CCH_2CH_2CH_2)(CO)_9]^+$ and the associated theory of such motions have also been described.[14] However, the parent osmium compound $[Os_3H_2(C{=}CH_2)(CO)_9]$[3] is much less fluxional than the C=CHOEt one. Separate hydride signals are observed for the $C{=}CH_2$ compound even at 125 °C. The barrier to ligand motions such as in Figure 4 is very much higher for the $C{=}CH_2$ compound since these would result in hydride site exchange. There can be, of course, no steric reason for this and we believe that the π-donor properties of OEt favour ligand mobility. Certainly the generation of carbocationic character at C(2) as in process (C) (Figure 4) would be favoured by the OEt substituent. In $[Os_3H_2(C{=}CH_2)(CO)_9]$ hydride migration alone can account for observed coalescence of the $C{=}CH_2$ ^1H n.m.r. signals.

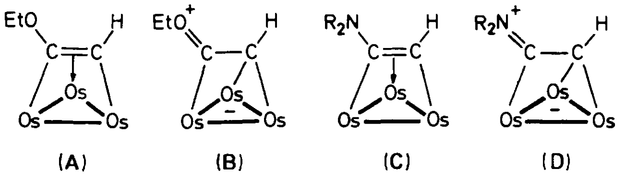


Figure 5. Effect of p_π donation from EtO or R_2N on the attachment of $EtOC{\equiv}CH$ or $R_2NC{\equiv}CH$ ligands in Os_3 clusters

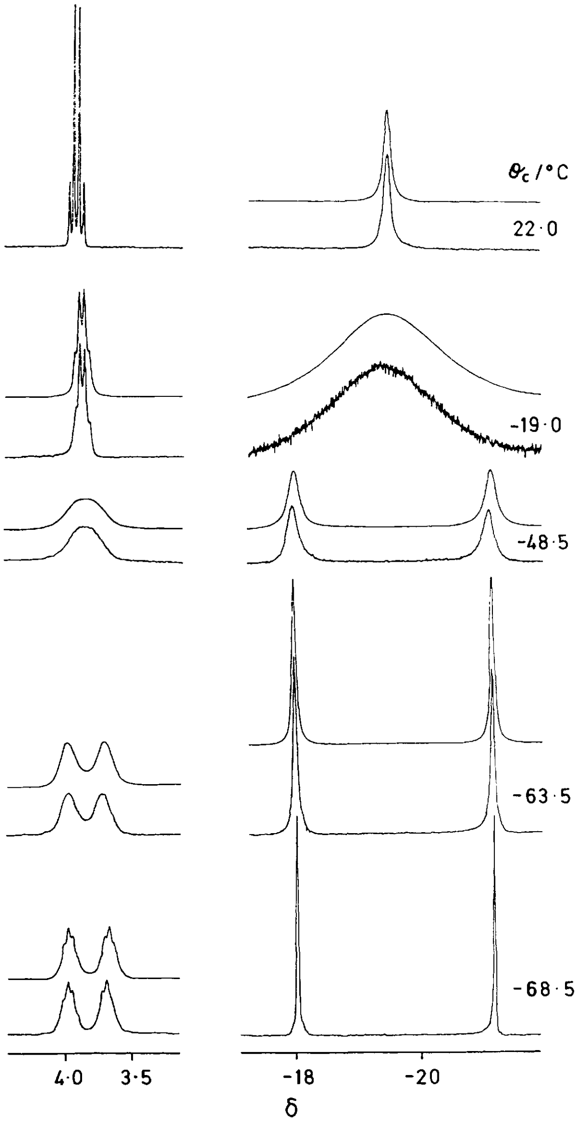


Figure 6. Observed ^1H n.m.r. spectra for the CH_2 and hydride signals of $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) recorded in $CDCl_3$ at 200 MHz with computer simulations above

Structure and Dynamic Behaviour of Compound (**2**).—The triply bridging alkyne in $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**), Figure 2, has C(1)–C(2) approximately parallel to the Os(1)–Os(2) bond, as is normally observed for compounds of the type $[Os_3H_2(\mu_3,\eta^2\text{-alkyne})(CO)_9]$. However, there is a significant twisting of the alkyne out of the strictly parallel orientation. Notably in the η^2 interaction with Os(3), the Os(3)–C(2) distance of 2.45(5) Å is very long for a metal–carbon bond even allowing for distances in η^2-alkene interactions being normally longer than σ-Os–C bonds. Likewise the C(2)–Os(1) σ bond [1.86(5) Å] is shorter than the other one, C(1)–Os(2) [2.08(3) Å]. One possible reason for these distortions is that there is some π donation from the EtO group leading to a contribution from (**B**) (Figure 5). A more extreme case would be the amino-alkyne compound $[Os_3H_2(R_2NCCH)(CO)_9]$ (R = H or Me)[5] which has a higher barrier to rotation about the N–C bond and in which case form (**D**) may be closer to the true representation than (**C**).

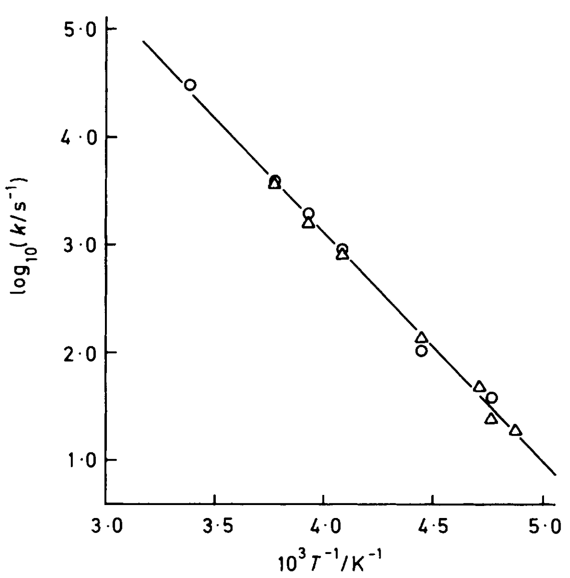
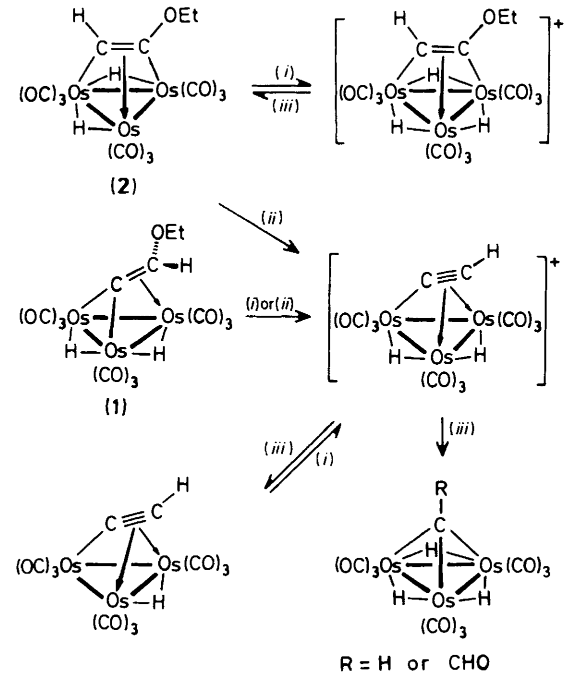


Figure 7. Graph of $\log_{10}(k/s^{-1})$ for hydride exchange (○) and CH_2 exchange (△) against $10^3T^{-1}/K^{-1}$ for compound (**2**) derived from spectra such as in Figure 6

The ^1H n.m.r. spectra for compound (**2**) show that it is fluxional but, in contrast to (**1**), it exists in only one isomeric form giving one set of signals at −99 °C (Figure 6). Exchange of the diastereotopic methylene protons of the CHCOEt ligand can only occur by an enantiomerisation process. This, of course, requires mobility of the ligand with respect to the metal atoms. Figures 6 and 7 show observed and simulated line shapes and the derived kinetic data. Within experimental error the rates of hydride exchange and diastereotopic methylene exchange are equal; see Figure 7 and the Experimental section for data. The probable mechanism is an alkyne rotation from a parallel to a perpendicular orientation with respect one Os–Os edge with the plane of the ligand moving from a tilted orientation to perpendicular to the metal plane. On rotating further, back into a parallel orientation, the opposite face of the organic ligand is involved in the η^2 interaction. This leads to inversion and the process may be regarded as a rotation/flip and has commonly been identified.[15] This motion is at the same rate as hydride exchange, but there is no need to invoke hydride migrations since the alkyne rotation/flip would itself lead to hydride exchange. Hydride migrations in some related molecules are faster than organic ligand motion[15] and this further points to the ethoxy-substituent enhancing the mobility of the ligand. π Donation from the ethoxy-group would stabilise the form with the ligand plane vertical to the metal plane and with the carbon–carbon bond perpendicular to an osmium–osmium edge.

Reactions of Isomers (**1**) *and* (**2**) with Acids.—The reversible loss of ethanol or ethoxide ions from (**1**) or (**2**) does not occur in solution at room temperature. This would have led to their interconversion but this does not occur. In the light of this we have studied the reactions of these isomers with acids since protonation might be at the ethoxy-group resulting in the displacement of ethanol to give the cation $[Os_3H_2(C{\equiv}CH)(CO)_9]^+$ or at the metal atoms to give the corresponding trihydride. An excess of trifluoroacetic acid reacts with each of the isomers (**1**) and (**2**) in $CDCl_3$, but differently. Isomer (**2**) protonates to give $[Os_3H_3(CH{=}COEt)(CO)_9]^+$ (**6**) which was characterised spectroscopically (Table 1) and which reverts to (**2**) on deprotonation by quenching with an excess of water. We know there is no ethoxide ion loss since ^1H n.m.r. signals for $[Os_3H_2(C{\equiv}CH)(CO)_9]^+$, which may be formed by protonating $[Os_3H(C{\equiv}CH)(CO)_9]$, are not present. However, a similar treatment of the vinylidene isomer (**1**) does give $[Os_3H_2(C{\equiv}CH)(CO)_9]^+$ (Scheme 3). These results seem to correlate with the observation that $[Os_3H(C{\equiv}CH)(CO)_9]$ reacts with ethanol to give predominantly isomer (**2**) with EtO^- addition at the α-carbon atom. Since the α-carbon atom of the C≡CH ligand has a stronger affinity for ethoxide, we might expect (**2**) to be a poorer source of ethoxide than (**1**).



Scheme 3. (*i*) CF_3CO_2H; (*ii*) Ph_3CBF_4; (*iii*) H_2O

The cationic cluster $[Os_3H_2(C{\equiv}CH)(CO)_9]^+$ generated from (**1**) reacts as expected when treated with water.[5] It is partially deprotonated and is partially attacked by H_2O at the α carbon to give $[Os_3H_3(CH)(CO)_9]$, by decarbonylation of the intermediate $[Os_3H_2(CH_2CO)(CO)_9]$, and at the β carbon to give $[Os_3H_3(CCHO)(CO)_9]$ (Scheme 3). This chemistry has been outlined earlier.[5]

Attempting to avoid protonation of isomer (**2**) and to induce the removal of the ethoxide ion instead, we treated it with a Lewis acid, $[Ph_3C][BF_4]$. After quenching with water, some of the starting cluster (**2**) was obtained but also some of $[Os_3H_3(CH)(CO)_9]$ and $[Os_3H(C{\equiv}CH)(CO)_9]$, consistent with the formation of Ph_3COEt and the cation $[Os_3H_2(C{\equiv}CH)(CO)_9]^+$. Isomer (**1**) behaves similarly with the trityl cation (Ph_3C^+).

Experimental

The compounds $[Os_3(CO)_{10}(MeCN)_2]$,[16] $[Os_3H_2(CO)_{10}]$,[17] and $[Os_3H(\mu_3\text{-}C{\equiv}CH)(CO)_9]$[18] were prepared as described in the literature. The alkyne CH≡COEt was used as purchased (Aldrich).

Reaction of $[Os_3H_2(CO)_{10}]$ *with* CH≡COEt.—The compound CH≡COEt (1.0 cm^3, 60% solution in hexane) was added to a hexane solution (100 cm^3) of $[Os_3H_2(CO)_{10}]$ (1.0 g) at 22 °C. Removal of the solvent after 4 h followed by chromatographic separation [t.l.c. (SiO_2); eluant, light petroleum (b.p. 30—40 °C)–CH_2Cl_2 (10:1, v/v)] yielded $[Os_3H(CH{=}CHOEt)(CO)_{10}]$ (**3**) as red crystals (0.639 g, 59%) from a hexane–

CH_2Cl_2 mixture (Found: C, 18.35; H, 1.05. $C_{14}H_8O_{11}Os_3$ requires C, 18.2; H, 0.9%) and $[Os_3H(CH_2{=}COEt)(CO)_{10}]$ (**4**) as red crystals (0.105 g, 10%) from hexane–CH_2Cl_2 (Found: C, 18.35; H, 0.85. $C_{14}H_8O_{11}Os_3$ requires C, 18.2; H, 0.9%).

Reaction of $[Os_3(MeCN)_2(CO)_{10}]$ *with* $CH{\equiv}COEt$.—A similar reaction using $CH{\equiv}COEt$ (0.1 cm^3, 60% solution in hexane) and $[Os_3(MeCN)_2(CO)_{10}]$ (0.180 g) in CH_2Cl_2 (30 cm^3) for 2.5 h gave, after similar work-up, $[Os_3(CH{=}COEt)(CO)_{10}]$ (**5**) as yellow crystals (0.055 g, 31%) from hexane (Found: C, 18.45; H, 0.8. $C_{14}H_6O_{11}Os_3$ requires C, 18.25; H, 0.65%).

Thermolysis of $[Os_3H(CH{=}CHOEt)(CO)_{10}]$ (**3**).—A solution of $[Os_3H(CH{=}CHOEt)(CO)_{10}]$ (0.345 g) in octane (30 cm^3) was refluxed for 4 h under nitrogen. Removal of the solvent and t.l.c. of the residue eluting with light petroleum (b.p. 30—40 °C) gave two colourless bands yielding $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) as pale yellow crystals from methanol (0.024 g, 7%) (Found: C, 17.4; H, 0.9. $C_{13}H_8O_{10}Os_3$ requires C, 17.45; H, 0.9%) and $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**) as pale yellow crystals (0.230 g, 67%) from a pentane–CH_2Cl_2 mixture (Found: C, 17.5; H, 0.95. $C_{13}H_8O_{10}Os_3$ requires C, 17.45; H, 0.9%).

Thermolysis of $[Os_3H(CH_2{=}COEt)(CO)_{10}]$ (**4**).—A hexane solution (10 cm^3) of compound (**4**) (0.023 g) was refluxed for 4 h. Similar work-up as above gave $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) (0.010 g, 45%) and unreacted starting material (0.004 g, 16%). No compound (**1**) was observed.

Hydrogenation of $[Os_3(CH{=}COEt)(CO)_{10}]$ (**5**).—Hydrogen was bubbled into a refluxing hexane solution (30 cm^3) of $[Os_3(CH{=}COEt)(CO)_{10}]$ (0.200 g) for 12 h. The reaction mixture was treated as above to give $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) (0.134 g, 67%) and unreacted compound (**5**) (0.020 g, 10%).

Reaction of $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) *with* $[Ph_3C][BF_4]$.—The salt $[Ph_3C][BF_4]$ (0.212 g, 10 mol per mol Os_3) was added to a dry CH_2Cl_2 solution (25 cm^3) of $[Os_3H_2(CH{=}COEt)(CO)_9]$ (0.054 g) under nitrogen. After 72 h at room temperature the solution was treated with water (200 cm^3) and then extracted twice with CH_2Cl_2. Chromatographic work-up of the CH_2Cl_2 extract [t.l.c. (SiO_2); eluant; pentane] gave $[Os_3H_3(CH)(CO)_9]$ (0.008 g, 16%), $[Os_3H(C{\equiv}CH)(CO)_9]$ (0.008 g, 16%) and unreacted $[Os_3H_2(CH{=}COEt)(CO)_9]$ (0.027 g).

Reaction of $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**) *with* $[Ph_3C][BF_4]$.—A similar treatment of $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (0.062 g) and $[Ph_3C][BF_4]$ (0.229, 10 mol per mol Os_3) gave $[Os_3H_3(CH)(CO)_9]$ (0.011 g, 19%), $[Os_3H(C{\equiv}CH)(CO)_9]$ (0.009 g, 16%), and unreacted $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (0.035 g).

Protonation of $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) *with* CF_3CO_2H.—Trifluoroacetic acid (0.039 cm^3, 15 mol per mol Os_3) was added to a CD_2Cl_2 solution (0.5 cm^3) of $[Os_3H_2(CH{=}COEt)(CO)_9]$ (0.030 g) in an n.m.r. tube. Proton n.m.r. spectroscopy indicated complete protonation to give $[Os_3H_3(CH{=}COEt)(CO)_9]^+$ which on treatment with water followed by extraction and chromatographic work-up regenerated $[Os_3H_2(CH{=}COEt)(CO)_9]$ (**2**) (0.025 g).

Protonation of $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**) *with* CF_3CO_2H.—Similarly, CF_3CO_2H (0.040 cm^3, 15 mol per mol Os_3) was added to a CD_2Cl_2 solution (0.5 cm^3) of $[Os_3H_2(C{=}CHOEt)(CO)_9]$ (**1**) (0.033 g). The ^1H n.m.r. spectrum of the solution was recorded at various time intervals. Formation of $[Os_3H_2(C{\equiv}CH)(CO)_9]^+$ was complete after 5 d. Treatment of the solution with water and subsequent chromatographic separation of a CH_2Cl_2 extract [t.l.c. (SiO_2); eluant; pentane] gave $[Os_3H_3(CH)(CO)_9]$ (0.005 g, 16%) and $[Os_3H(C{\equiv}CH)(CO)_9]$ (0.005 g, 16%). Eluting further with pentane–methanol (10:1, v/v) gave $[Os_3H_3(CCHO)(CO)_9]$ as pale yellow crystals (0.007 g, 20%) from methanol (Found: C, 15.45; H, 0.6. $C_{11}H_4O_{10}Os_3$ requires C, 15.25; H, 0.45%).

Reaction of $[Os_3H(C{\equiv}CH)(CO)_9]$ *with Ethanol*.—The compound $[Os_3H(C{\equiv}CH)(CO)_9]$ (0.0550 g) was dissolved in ethanol (20 cm^3) by successively shaking the flask and then standing it in an ultrasonic bath. The solvent was removed after 6 h and the residue separated by t.l.c. [SiO_2; eluant, light petroleum (b.p. < 40 °C)] to give two bands yielding $[Os_3H_2(CCHOEt)(CO)_9]$ (**1**) (0.0121 g, 21.2%) and $[Os_3H_2(CHCOEt)(CO)_9]$ (**2**) (0.0444 g, 77.8%), both identified by their i.r. and n.m.r. spectra.

Crystal Structure Determinations.—*Crystal data for* (**1**). $C_{13}H_8O_{10}Os_3$, M = 896.425, monoclinic, space group $P2_1/n$, a = 19.416(2), b = 11.512(3), c = 8.622(3) Å, β = 103.38(2)°, U = 1 874.85 Å^3, $F(000)$ = 1 576, μ(Mo-K_α) = 203.02 cm^{-1}, Z = 4, D_c = 3.16 g cm^{-3}.

Crystal data for (**2**). $C_{13}H_8O_{10}Os_3$, M = 896.425, monoclinic, space group Cc, a = 15.054(3), b = 10.114(2), c = 12.902(3) Å, β = 107.75(2)°, U = 1 870.89 Å^3, $F(000)$ = 1 576, μ(Mo-K_α) = 203.45 cm^{-1}, Z = 4, D_c = 3.17 g cm^{-3}.

Methods of data collection and data processing used for the two isomeric forms of $[Os_3H_2(C_2HOEt)(CO)_9]$ (**1**) and (**2**) were similar to those described previously.[19] The data were collected using single crystals of dimensions 0.35 × 0.24 × 0.10 mm (**1**) and 0.32 × 0.24 × 0.26 mm (**2**) on a Philips four-circle diffractometer, using a scan width of 0.8° and with a θ range 3—25°. Using graphite-monochromated Mo-K_α radiation reflections were recorded with a ω—2θ scan mode, Lorentz polarisation corrections were applied, and equivalent reflections were merged in both data sets to give a total of 2 394 (**1**) and 1 547 (**2**) unique reflections with $I/\sigma(I) > 3.0$. Absorption corrections were applied to the data.[20]

Structure solution and refinement.[21] The position of the three osmium atoms in $[Os_3H_2(CCHOEt)(CO)_9]$ (**1**) and $[Os_3H_2(CHCOEt)(CO)_9]$ (**2**) were located from Patterson syntheses. Subsequent difference-Fourier syntheses enabled location of the remaining non-hydrogen atoms, and the positions of the bridging H ligands were calculated by a potential-energy minimisation routine.[22] Full-matrix refinement of the atomic positions and thermal parameters of the non-hydrogen atoms converged to R = 0.0456, R' = 0.0437 (**1**) and R = 0.0518, R' = 0.0506 (**2**). Anisotropic thermal parameters were assigned to the three metal atoms in both structures during the final stages of refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Kinetics of Intramolecular Exchange in Compound (**2**).—Since only one isomer is present in $CDCl_3$ solutions of $[Os_3H_2(CHCOEt)(CO)_9]$ (**2**), it was easier to obtain rates of hydride exchange (k_H/s^{-1}) and of inversion at the carbon atom C*H*COEt (k_I/s^{-1}) from line shapes of coalescing signals. Figure 6 shows selected ^1H n.m.r. spectra together with those computed using the program DNMR3.[23] Other signals in the spectra are essentially independent of temperature. Rates k_H/s^{-1} (with k_I/s^{-1} in parentheses) at temperatures T/K as obtained from the best fitting of spectra are: 31 000 ± 3 000 at 295.2, 4 000 ± 200 (4 000 ± 500) at 264.6, 2 000 ± 100 (1 700 ± 200) at 254.2, 850 ± 50 (900 ± 100) at 244.5, 110 ± 10 (140 ± 10) at 224.7, (50 ± 2) at 211.8, 40 ± 5 (25 ± 5) at 209.7, and (20 ± 2) at 204.7. These data appear graphically in Figure 7. Activation parameters for hydride exchange are $\Delta G^\ddagger$ (225 K) = 45.7 ± 0.2 kJ mol^{-1}, $\Delta H^\ddagger$ = 41.0 ± 1.6 kJ mol^{-1}, and $\Delta S^\ddagger$ = −(20 ± 6) J K^{-1} mol^{-1} and for methylene hydrogen exchange $\Delta G^\ddagger$ (225 K) = 45.3 ± 0.2 kJ mol^{-1}, $\Delta H^\ddagger$ = 40.1 ± 1.2 kJ mol^{-1}, and $\Delta S^\ddagger$ = −(24 ± 5) J K^{-1} mol^{-1}.

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