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Substitution effects at bridging vinyl ligands: molecular structures of $[Os_3H(CH{=}CHR)(CO)_{10}]$ where R = OEt or ferrocenyl

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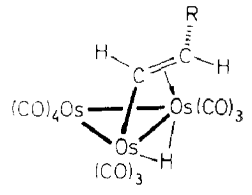
Abstract

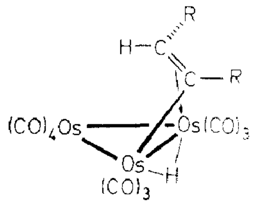
The two related compounds $[Os_3H(\mu,\eta^2\text{-}trans\text{-}CH{=}CHR)(CO)_{10}]$ (R = OEt or ferrocenyl $C_5H_4FeC_5H_5$, Fc), have been prepared, the first by insertion of ethyl ethynyl ether ($CH{\equiv}COEt$) into $[Os_3H_2(CO)_{10}]$ and the second by oxidative addition of ethenylferrocene ($CH_2 = CHFc$) to $[Os_3(CO)_{10}(MeCN)_2]$ respectively. Spectroscopically both compounds are similar to known related compounds with alkyl- or aryl-substituted vinyl ligands. A single-crystal X-ray structural study of each was made in an attempt to detect any structural effects of π-donation by the substituents at the vinyl group, such as was observed for $[Os_3H(CHCHNEt_2)(CO)_{10}]$. The latter compound has been shown to have a zwitterionic structure with an alkylidene bridge between two osmium atoms rather than the normal μ,η^2-vinyl mode of bonding. The two compounds studied here have essentially normal μ,η^2-vinyl bridges, but with some distortion towards the alkylidene bonding type, more pronounced for R = OEt.

Introduction

The vinyl complex $[Os_3H(CH{=}CH_2)(CO)_{10}]$ has been synthesized by the insertion of C_2H_2 into $[Os_3H_2(CO)_{10}]$ [1] and by oxidative addition of C_2H_4 to $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{10}(MeCN)_2]$ [1,2]. A range of other substituted vinyl compounds $[Os_3H(CH{=}CHR)(CO)_{10}]$ have been synthesised and crystal structures have been determined by X-ray diffraction for R = H [3] Et [4] and ^{t}Bu [5], and by neutron diffraction for R = H [6]. These compounds adopt the μ,η^2-vinyl structure



(A)



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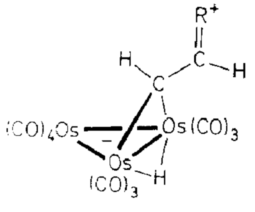
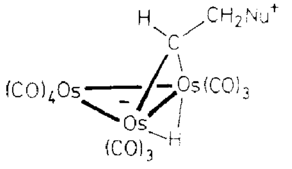


(C)



(D)

A with the *trans* configuration. The related *cis* PhC=CHPh complex [7] and the furyl ($\overline{\text{C=CHCH=CHO}}$) complex [8] are similar, except that they adopt the alternative configurations **B** in which a clash of the 1-substituent with an axial CO at the Os(CO)$_4$ unit is avoided.

More severe modification occurs when the substituent is a good π-donor such as NEt$_2$, in which case the π-system of the ligand is re-organised to give the zwitterionic compound of the type **C** (R = NEt$_2$) [9]. Related zwitterionic alkylidene compounds **D** are formed by the addition of neutral nucleophiles Nu, such as PMe$_2$Ph [10–12] or pyridine [13], to the μ,η^2-vinyl complex to give [Os$_3$H(CHCH$_2$ Nu)(CO)$_{10}$] **D**. Stable adducts are formed with PMe$_2$Ph, while pyridine adducts are implicated in the pyridine-catalysed *cis–trans* isomerisation of [Os$_3$H(CH=CHD) (CO)$_{10}$] [13]. It seems that any substituent that stabilizes carbocationic character at the 2-position of the vinyl by forming p_π–p_π bonds to it will stabilize the zwitterionic μ-alkylidene form **C**. Two substituents that might have some such effect, although to a much lesser extent than NEt$_2$, are OEt or ferrocenyl (Fc, $C_5H_4FeC_5H_5$). In the course of synthesising a range of substituted C$_2$-ligand clusters we have examined the reactions of CH≡COEt and CH≡CFc with triosmium clusters. Some of the ethoxyethyne work has been described previously [14], and we [15] and others [16] have described some Os$_3$ chemistry involving CH≡CFc. We describe here the synthesis and X-ray structures of [Os$_3$H(CH=CHR)(CO)$_{10}$] (R = OEt or Fc).

Results and discussion

The compound [Os$_3$H(CH=CHOEt)(CO)$_{10}$] (**1**) is formed together with a small amount of its isomer [Os$_3$H(EtOC=CH$_2$)(CO)$_{10}$] by insertion of CH≡COEt into an Os–H bond of [Os$_3$H$_2$(CO)$_{10}$]. Comparison of the IR and ^{1}H NMR spectra of **1** with those of the CH=CH$_2$ compound, suggests that these are isostructural and that the vinyl ligand is *trans*. The ^{1}H NMR spectrum down to −90 °C shows a simple quartet and triplet for the OEt group, whereas for a static structure the CH$_2$ protons should be diastereotopic. Fluxionality therefore leads to a time-averaged plane of symmetry, as found for its derivatives [Os$_3$H$_2$(C=CHOEt)(CO)$_9$] and

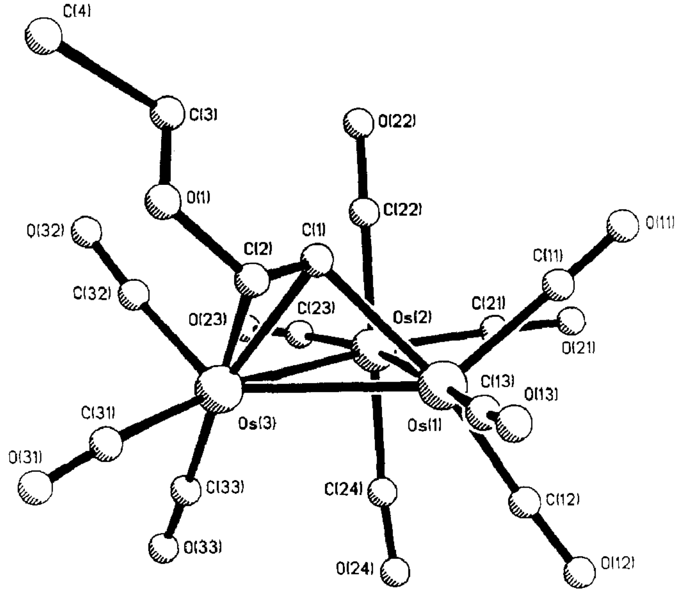


Fig. 1. Molecular structure of $[Os_3H(\textit{trans}\text{-}CH{=}CHOEt)(CO)_{10}]$, compound **1**.

$[Os_3H_2(EtOC_2H)(CO)_9]$ [14]. An oscillation process such as that established for the $CH{=}CH_2$ analogue would account for this [17].

Single red crystals of **1** obtained from n-hexane were suitable for an X-ray diffraction study and the molecular structure revealed is shown in Fig. 1. Atomic coordinates are in Table 1 and selected bond lengths and angles in Table 2. The hydride ligand was not located but is expected to be close to the intersection of the Os(1)–C(11) and Os(3)–C(32) vectors. Overall the structure is as expected, and similar to known structures. The Os(1)–Os(3) distance is the shortest as a result of being bridged by a hydride and a carbon atom. As found for other vinyl compounds of this type, the longer of the other two metal–metal bonds is that to which the vinyl ligand is η^2-coordinated. The *trans* configuration of the vinyl ligand is confirmed and this is found to be σ-bonded through C(1) (C(1)–Os(1) 2.21(3) Å) and has an η^2-coordination to Os(3) (C(1)–Os(3) 2.30(2) and C(2)–Os(3) 2.63(2) Å). The osmium distance to the β-carbon C(2) is much longer than the corresponding distance in the parent $CH{=}CH_2$ compound (2.362(3) Å). A distance as long as 2.63(2) Å raises the question as to whether there is any significant C–Os bonding to C(2) at all, and whether the η^2-description is valid. Because of this we examined the complex $[Os_3H(CH{=}CHFc)(CO)_{10}]$ (**2**) to see whether the ferrocenyl group might have a similar effect to EtO in distorting the μ,η^2-vinyl system.

Compound **2** was prepared in moderate yield by the oxidative addition of ethenylferrocene ($CH_2{=}CHFc$) to $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing cyclohexane. Relevant spectroscopic and analytical data are in the experimental section. The X-ray crystal structure is shown in Fig. 2 and atomic coordinates are listed in Table 3 and selected bond lengths and angles in Table 4. The structure is as expected.

Crystal structures are now available for the range of vinyl compounds of the type $[Os_3H(CHCHR)(CO)_{10}]$ where R = H, Et, ${}^tBu$, EtO, Fc, and Et_2N. The compound with $R = Et_2N$ is apparently unique in adopting the zwitterionic arrangement **C**

Table 1

Fractional atomic coordinates for [Os$_3$H(CH=CHOEt)(CO)$_{10}$], compound **1**

	x	y	z
Os(1)	0.1513(1)	0.1232(1)	0.2788(1)
Os(2)	0.0155(1)	0.1361(1)	0.3741(1)
Os(3)	−0.0131(1)	0.2208(1)	0.2276(1)
C(1)	0.0289(21)	0.0882(14)	0.1887(15)
C(2)	0.0311(23)	0.1235(27)	0.1199(18)
C(3)	−0.0863(36)	0.0501(32)	0.0600(23)
C(4)	−0.1475(27)	0.0487(31)	−0.0400(19)
O(1)	−0.0308(19)	0.1061(20)	0.0467(16)
C(11)	0.1786(18)	0.0068(22)	0.3119(14)
C(12)	0.2431(24)	0.1701(14)	0.3570(14)
C(13)	0.2332(15)	0.1187(22)	0.2086(15)
C(21)	0.0751(22)	0.0676(14)	0.4539(16)
C(22)	−0.0440(23)	0.0384(19)	0.3246(16)
C(23)	−0.0907(19)	0.1641(19)	0.4113(15)
C(24)	0.0837(20)	0.2384(17)	0.4174(14)
C(31)	−0.0233(25)	0.2924(18)	0.1393(13)
C(32)	−0.1413(18)	0.1953(17)	0.2141(15)
C(33)	−0.0288(20)	0.3155(16)	0.2902(14)
O(11)	0.1905(16)	−0.0594(13)	0.3350(13)
O(12)	0.3062(13)	0.1970(14)	0.4033(12)
O(13)	0.2818(14)	0.1105(14)	0.1653(12)
O(21)	0.1170(18)	0.0252(16)	0.5064(11)
O(22)	−0.0842(19)	−0.0245(17)	0.2965(14)
O(23)	−0.1625(16)	0.1892(17)	0.4287(13)
O(24)	0.1280(16)	0.2940(12)	0.4461(11)
O(31)	−0.0276(18)	0.3397(15)	0.0934(12)
O(32)	−0.2198(18)	0.1737(18)	0.2038(13)
O(33)	−0.0368(20)	0.3747(13)	0.3225(11)

Table 2

Selected bond lengths (Å) and angles (°) for [Os$_3$H(CH=CHOEt)(CO)$_{10}$], compound **1**

Bond lengths			
Os(1)–Os(2)	2.850(1)	Os(3)–C(1)	2.30(2)
Os(1)–Os(3)	2.817(1)	Os(3)–C(2)	2.63(2)
Os(2)–Os(3)	2.882(1)	C(1)–C(2)	1.35(4)
Os(1)–C(1)	2.21(2)	C(2)–O(1)	1.45(4)
	Range	*Average*	
Os–CO	1.85(3)–1.95(3)	1.89	
OsC–O	1.10(3)–1.21(3)	1.16	
Bond angles			
Os(1)–C(1)–Os(3)	77.3(8)	Os(1)–Os(3)–C(1)	49.9(8)
Os(3)–Os(1)–C(1)	52.8(6)	Os(3)–C(1)–C(2)	88(2)
Os(1)–C(1)–C(2)	114(2)	C(1)–C(2)–O(1)	128(4)
	Range	*Average*	
Os–C–O	172(2)–177(3)	174.9	

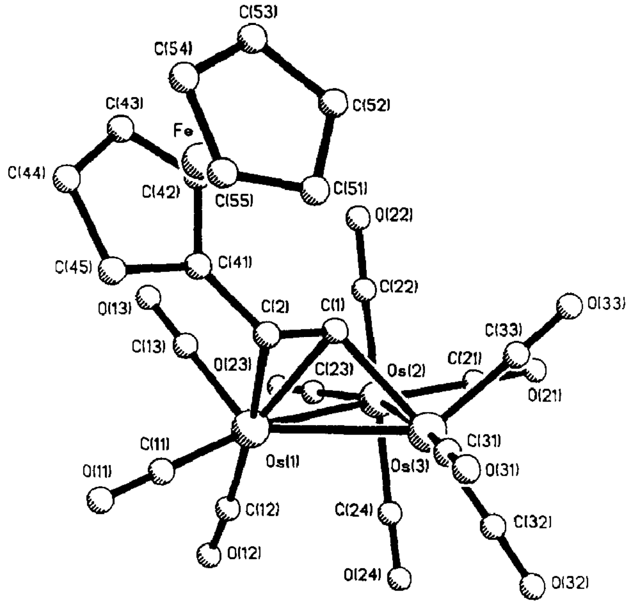


Fig. 2. Molecular structure of $[Os_3H($*trans*-$CH{=}CHC_5H_4FeC_5H_5)(CO)_{10}]$, compound **2**.

with the organic ligand forming an η^1-alkylidene bridge. This is clearly a consequence of the generally observed π-donor properties of Et_2N. For instance, we have found that substitution of H atoms by R_2N groups in hydrocarbon ligands leads to a η^n to η^{n-1} transformation for a range of different bridging ligands (see references 18–20 for examples). Figure 3 shows the obvious geometric relation between angle θ and the distance of the β-carbon atom to osmium. Although the system with $R = Et_2N$ is extreme, other substituents, EtO in particular, cause some opening of the angle θ and a distortion towards the alkylidene form when compared with the structure of the compound with $R = H$. The ferrocenyl group is slightly, but probably not significantly, more effective than simple alkyls (Et or ^{t}Bu) in increasing the angle θ. Steric effects seem insignificant, as judged from a comparison of the data for the compounds with Et and ^{t}Bu. The position of EtO in this series is consistent with that in the alkyne series $[Os_3H_2(CHCR)(CO)_9]$, in which CHCOEt is rotated slightly out of the normal parallel alkyne arrangement towards the perpendicular arrangement found for $CHCNEt_2$ [14,21,22].

As π-donation from the substituent R increases the extent of π-back bonding to the CO ligands should also increase. We have used the average of the three highest wavenumber ν(CO) absorptions as a measure of this effect, and this average is plotted against the distance between osmium and the β-carbon atom in Fig. 4. This seems to confirm that the opening out of the vinyl ligand is associated with some increase in electronic charge at the metal atoms, leading to an energy rise in the metal-centred orbitals. Again the EtO group is intermediate in effect between most substituents and the Et_2N group. Other correlations might be made, for example the correlation between ^{1}H NMR hydride shift and the Os–C(β) distance (Fig. 5), but the physical interpretation of this is more obscure. An expected correlation is that between the kinetic energy barrier to vinyl oscillation and the Os–C(β) distance. The geometric variation indicated in Fig. 3 would correspond to the

Table 3

Fractional atomic coordinates for $[Os_3H(CH{=}CHC_5H_4FeC_5H_5)(CO)_{10}]$, compound **2**

	x	*y*	*z*
Os(1)	0.08525(8)	0.15016(5)	0.18297(4)
Os(2)	−0.24598(8)	0.15930(5)	0.13524(4)
Os(3)	−0.16850(8)	0.14828(5)	0.00472(4)
Fe	0.3122(3)	0.4074(2)	0.1003(2)
O(11)	0.427(2)	0.105(1)	0.2403(9)
O(13)	0.176(2)	0.272(1)	0.3277(9)
O(12)	0.078(2)	0.007(1)	0.287(1)
O(22)	−0.216(2)	0.344(1)	0.145(1)
O(21)	−0.607(2)	0.176(1)	0.0199(9)
O(23)	−0.201(2)	0.158(1)	0.3140(9)
O(24)	−0.272(2)	−0.026(1)	0.1169(9)
O(32)	−0.359(2)	−0.008(1)	−0.073(1)
O(31)	−0.047(2)	0.140(1)	−0.116(1)
O(33)	−0.446(2)	0.259(1)	−0.105(1)
C(1)	−0.012(2)	0.246(1)	0.076(1)
C(2)	0.148(2)	0.249(1)	0.102(1)
C(41)	0.256(2)	0.314(1)	0.154(1)
C(51)	0.211(2)	0.381(2)	−0.032(1)
C(42)	0.219(2)	0.393(1)	0.176(1)
C(52)	0.136(3)	0.453(2)	−0.022(2)
C(53)	0.265(3)	0.508(2)	0.030(2)
C(43)	0.360(2)	0.438(1)	0.221(1)
C(44)	0.487(2)	0.395(1)	0.230(1)
C(54)	0.412(3)	0.476(2)	0.049(2)
C(45)	0.431(2)	0.315(1)	0.190(1)
C(55)	0.376(3)	0.398(2)	0.013(1)
C(11)	0.294(2)	0.123(1)	0.217(1)
C(13)	0.144(2)	0.226(1)	0.273(1)
C(12)	0.075(2)	0.062(1)	0.244(1)
C(22)	−0.220(2)	0.272(2)	0.139(1)
C(21)	−0.467(2)	0.169(1)	0.066(1)
C(23)	−0.216(2)	0.158(1)	0.248(1)
C(24)	−0.257(2)	0.043(2)	0.123(1)
C(32)	−0.290(2)	0.053(1)	−0.042(1)
C(31)	−0.092(2)	0.144(1)	−0.066(1)
C(33)	−0.340(2)	0.215(1)	−0.064(1)

trajectory of the vinyl ligand during its oscillation between the bridged metal atoms. The CH=CHOEt compound would be expected to have a very low barrier and the $CH{=}CH_2$ compound the highest; of course the $CHCHNEt_2$ ligand is symmetrical and has no barrier. More quantitative kinetic data would be needed to develop this. Certainly both compounds **1** and **2** appear to have low oscillation barriers. The C_5H_4 group in **2** gives an AA′BB′ spectrum in toluene-d_8 at room temperature consistent with rapid vinyl oscillation. At lower temperatures the triplet fine structure of the AA′BB′ multiplets is lost, but even at −92°C there is no freezing-out into the ABCD spectrum expected for the static structure. Energy differences between the unsymmetrical η^2-mode **A** and a symmetrical mode such as **C** are small.

Table 4

Selected bond lengths (Å) and angles (°) for [$Os_3H(CH{=}CHC_5H_4FeC_5H_5)(CO)_{10}$], compound **2**

Bond lengths			
Os(1)–Os(2)	2.899(1)	Os(3)–C(1)	2.12(2)
Os(1)–Os(3)	2.830(1)	Os(1)–C(2)	2.48(2)
Os(2)–Os(3)	2.863(1)	C(1)–C(2)	1.38(3)
Os(1)–C(1)	2.27(2)	C(2)–C(41)	1.43(2)
	Range	*Average*	
Os–CO	1.82(3)–1.91(2)	1.87	
OsC–O	1.13(2)–1.20(4)	1.16	
Fe–C(C_5H_4)	2.05(2)–2.06(2)	2.05	
Fe–C(C_5H_5)	1.99(3)–2.09(2)	2.04	
C–C(C_5H_4)	1.37(3)–1.48(3)	1.44	
C–C(C_5H_5)	1.40(3)–1.46(4)	1.42	
Bond angles			
C(2)–C(1)–Os(1)	82(1)	C(1)–Os(3)–Os(1)	52.3(5)
C(2)–C(1)–Os(3)	124(2)	C(1)–Os(1)–Os(3)	47.6(4)
Os(1)–C(1)–Os(3)	80.0(7)	C(2)–C(1)–Os(3)	124(2)
C(41)–C(2)–C(1)	124(2)		
	Range	*Average*	
Os–C–O	173(3)–179(2)	177.0	

From what has been said above, it appears that π-donor substituents at the β-position allow some contribution from form **C** to form **A** so that the β-carbon atom moves away from the osmium atoms. π-Donor substituents at the 1-position as in [$Os_3H(EtOC{=}CH_2)(CO)_{10}$] should have no such effect, but this has not been tested. The furyl compound [$Os_3H(\overline{C{=}CHCH{=}CHO})(CO)_{10}$] (3) has the oxygen

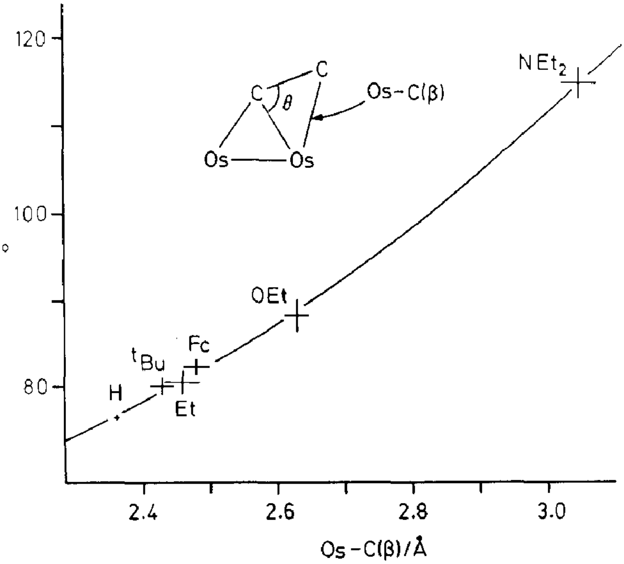


Fig. 3. Graph of the angle θ (defined above) against the distance from osmium to the β-carbon atom of the vinyl group for the series of compounds [$Os_3H(CHCHR)(CO)_{10}$] where R = H, ${}^tBu$, Et, Fc, OEt, NEt_2 (see text for references).

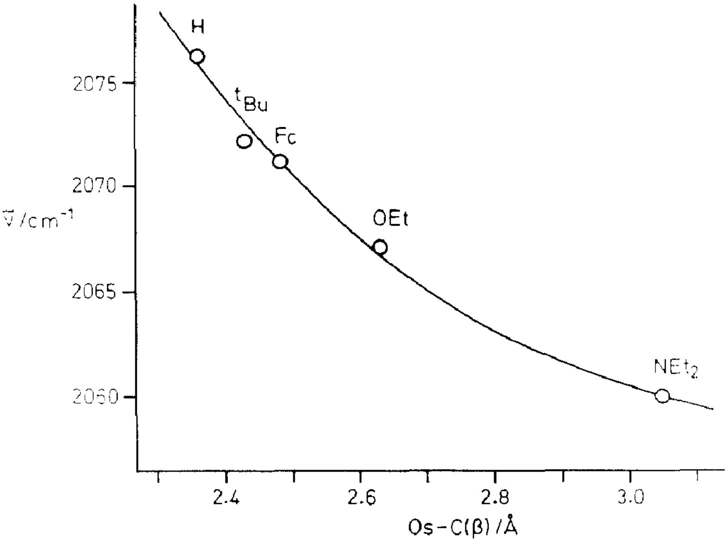


Fig. 4. Graph of $\bar{\nu}$ (cm^{-1}) (the average of the three highest wavenumber CO stretching absorptions) against the distance from osmium to the β-carbon atom in [$Os_3H(CHCHR)(CO)_{10}$] (R = H, Et, Fc, OEt, NEt_2).

atom at the α-position and yet the Os–C(β) distance is 2.63(1) Å, the same as in cluster **1**. However, conjugative effects in this case mean that π-effects can also operate through the α-position. Thus a contribution of form **3b** to form **3a** would allow cluster **3** to be distorted towards the alkylidene form. We predict that the pyrrolyl compound corresponding to **3** should therefore show a bigger effect but this compound has not yet been examined *.

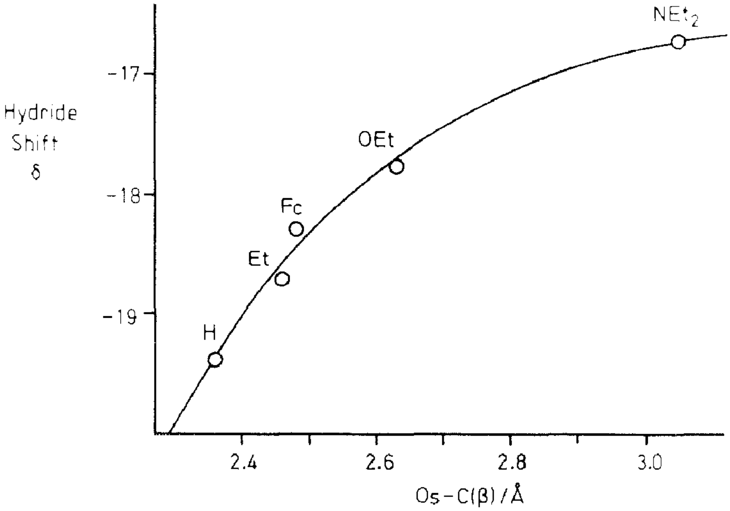


Fig. 5. Graph of ^{1}H NMR hydride chemical shifts against the distance from the β-carbon atom in the compounds [$Os_3H(CHCHR)(CO)_{10}$] (R = H, Et, Fc, OEt, NEt_2).

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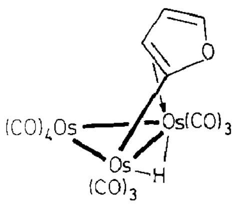
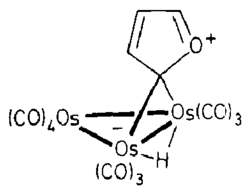
* *Note added in proof*: We have since shown that the *N*-methylpyrrolyl compound [Os_3H-($C{=}CHCH{=}CHNMe)(CO)_{10}$] does indeed adopt an alkylidene-type structure in the crystal corresponding to **3b** (A.J. Arce and A.J. Deeming, unpublished results).



(3a)



(3b)

Experimental

Synthesis of compounds

Compound 1. This compound was synthesised as previously reported [14] by reaction of ethylethynyl ether and $[Os_3H_2(CO)_{10}]$ in n-hexane at room temperature. It was separated from a small amount of the isomer $[Os_3H(EtOC{=}CH_2)(CO)_{10}]$ by TLC. It was recrystallised from n-hexane as ruby-red crystals suitable for a single-crystal X-ray study. IR (cyclohexane) ν(CO): 2100w, 2055vs, 2046s, 2016vs, 2008m, 2002m, 1984m, 1979m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.59d (J 12.2 Hz, CHCHOEt), 5.55dd (J 12.2, 2.2 Hz, CHCHOEt), 4.01q (J 7.1 Hz, CH_2), 1.36t (J 7.1 H_2, CH_3), −17.81d (J 2.2 Hz, Os_3H).

Compound 2. A suspension of $[Os_3(CO)_{10}(MeCN)_2]$ (0.055 g) and ethenylferrocene ($CH_2{=}CHFc$) (0.026 g) in cyclohexane (25 cm^3) was refluxed under nitrogen for 30 min. The solvent was removed under reduced pressure and the residue extracted into dichloromethane and separated by TLC [SiO_2; eluant: petroleum ether (b.p. 30–40 °C)]. The major band gave $[Os_3H(CH{=}CHFc)(CO)_{10}]$ (**2**) as red crystals (0.035 g, 59%) from dichloromethane. Found: C, 25.15; H, 1.25. $C_{22}H_{12}FeO_{10}Os_3$ calcd.: C, 24.85; H, 1.15%. IR (cyclohexane) ν(CO): 2103m, 2060vs, 2050s, 2020vs, 2010m, 2002m, 1992m, 1985m, 1978m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.27d (J 14.7 Hz, CHCHFc), 7.34dd (J 14.7 Hz, CHCHFc). 4.38m (C_5H_4), 4.19s (C_5H_5), 18.3d (J 1.6 Hz, Os_3H).

Crystal structure determinations

Red crystals of both compounds **1** and **2** were obtained by evaporation of hexane solutions. Diffraction data for compound **1** were collected on a Nicolet R3m/V diffractometer and for compound **2** on an Enraf–Nonius CAD4 diffractometer. Details of data collections, structure solutions, and crystal data for **1** and **2** are given in Table 5. In both cases corrections were made for Lorentz and polarisation effects and for decay by fitting the intensity data to three standard reflections collected periodically throughout the data collection. Empirical absorption corrections were carried out using the azimuthal scan method.

The structures were solved by methods given in Table 5 and were refined by alternating cycles of full-matrix least squares and difference Fourier synthesis. Computations were carried out on a MicroVax II computer using SHELXTL PLUS for compound **1** and SDP/VAX for compound **2**. Anomalous dispersion effects were included in F_c [23] and scattering factors for compound **2** [24] and the values of $\Delta F'$ and $\Delta F''$ [25] were taken from standard sources.

All non-hydrogen atoms of **1** but only the metal atoms of **2** were refined anisotropically; other non-hydrogen atoms were refined isotropically. Hydrogen

Table 5

Data related to structure determination of $[Os_3H(CH{=}CHR)(CO)_{10}]$ compounds **1** (R = OEt) and **2** (R = Fc)

Compound	**1**	**2**
Formula	$C_{14}H_8O_{11}Os_3$	$C_{21}H_{11}FeO_9Os_3$
M/g mol^{-1}	922.81	1033.76
Size/mm^3	$0.2\times0.2\times0.3$	$0.1\times0.3\times0.4$
Crystal system	monoclinic	monoclinic
Space group	$I2/a$	$P2_1/c$
a (Å)	14.472(5)	9.871(2)
b (Å)	15.586(5)	16.404(2)
c (Å)	17.843(6)	18.171(2)
β (°)	101.58(2)	122.66(1)
U (Å^3)	3943(2)	2477(1)
Z	8	4
D_c (g cm^{-3})	3.11	2.77
μ(Mo-K_α) (cm^{-1})	193.3	159.8
F(000)	3262	1852
No. of orientation reflns; 2θ range	15, $12 \leqslant 2\theta \leqslant 27$	25, $12 \leqslant 2\theta \leqslant 23$
Radiation, λ (Å)	Mo, 0.71073	Mo, 0.71073
Temp. (°C)	20	20
Scan mode	$\omega-2\theta$	$\omega-2\theta$
2θ range (°)	$3 \leqslant 2\theta \leqslant 50$	$5 \leqslant 2\theta \leqslant 50$
Total no. data	4353	4706
No. unique data	3508	4531
Structure solution	Direct methods	Patterson
Rejection criterion	$F_o \leqslant 3\sigma(F_o)$	$F_o \leqslant 3\sigma(F_o)$
No. reflns used in refinement	2477	2213
No. parameters in refinement	253	166
R	0.064	0.042
R_w	0.057	0.048
Weight w in weighting scheme	$1/[\sigma^2(F)+0.000311F^2]$	$4F^2/[\sigma(F)^2]^2$
Max. height in final diff. Fourier (eÅ^{-3})	2.05	0.89

atoms were not included in either of the structural models. Tables of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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