

Oxygen-hydrogen versus nitrogen-oxygen bond cleavage in the oxidative addition of oximes to $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$: crystal structures of the isomers $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ and $[\text{Os}_3(\text{OH})(\text{Me}_2\text{C}=\text{N})(\text{CO})_{10}]$

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(Received May 16th, 1990)

Abstract

Acetone oxime ($\text{Me}_2\text{C}=\text{NOH}$) reacts with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ to give the bridging oximato cluster $[\text{Os}_3(\mu\text{-H})(\mu\text{-Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (**1**) resulting from oxidative addition with O-H bond cleavage. An X-ray crystal structure determination showed that the oximato ligand is bridging two osmium atoms by bonding to one Os atom through the N-atom and to another through the O-atom. A range of clusters with similarly bonded oximato ligands were synthesised from the oximes derived from benzophenone ($\text{Ph}_2\text{C}=\text{NOH}$), cyclohexanone ($\text{C}_6\text{H}_{10}\text{NOH}$), acetaldehyde ($\text{MeCH}=\text{NOH}$), benzaldehyde ($\text{PhCH}=\text{NOH}$) (two isomers obtained), and formamide ($\text{NH}_2\text{CH}=\text{NOH}$). Compound **1** isomerises at 125°C to the non-hydrido isomer $[\text{Os}_3(\mu\text{-OH})(\mu\text{-Me}_2\text{C}=\text{N})(\text{CO})_{10}]$ (**2**) which was characterised spectroscopically and crystallographically and shown to contain the bridging hydroxy and the iv-bonded $\text{Me}_2\text{C}=\text{N}$ ligands. Overall oxidative addition of the oxime with N-O bond cleavage has been achieved by an initial oxidative addition with O-H cleavage followed by isomerisation.

Introduction

Bidentate and polydentate ligands incorporating oximato groups have commonly been used to bind to a single metal atom but there are only a few examples of bridging oximato ligands [**1**]. We describe here a general route to bridging oximato ligands by oxidative addition of oximes to $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$. The initial product from $\text{Me}_2\text{C}=\text{NOH}$ is formed by O-H bond cleavage but this isomerises thermally to a species containing OH and $\text{Me}_2\text{C}=\text{N}$ bridges. This latter isomer is effectively formed by oxidative addition of the oxime with N-O cleavage.

Results and discussion

The bis-acetonitrile compound $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ is a ready source of the $\text{Os}_3(\text{CO})_{10}$ unit in reactions leading to the coordination of ligands L to give $[\text{Os}_3(\text{CO})_{10}\text{L}_2]$ (for example, L = tertiary phosphine) [2] or oxidative addition of HX to give compounds of the type $[\text{Os}_3(\mu\text{-H})(\mu\text{-X})(\text{CO})_{10}]$ [3]. Commonly the second reaction occurs in preference to the first; for example pyridine does not give $[\text{Os}_3(\text{CO})_{10}(\text{py})_2]$ as an isolable compound but undergoes *ortho-metallation* to give $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_5\text{H}_4\text{N})(\text{CO})_{10}]$ containing the $\mu\text{-2-pyridyl}$ ligand [4,5]. Alcohols add to give $[\text{Os}_3(\mu\text{-H})(\mu\text{-OR})(\text{CO})_{10}]$ [6] so that, in principle, oximes $\text{R}_2\text{C}=\text{NOH}$ could give $[\text{Os}_3(\text{CO})_{10}(\text{R}_2\text{C}=\text{NOH})_2]$ with coordination through nitrogen atoms, $[\text{Os}_3(\mu\text{-H})(\text{R}_2\text{C}=\text{NO})(\text{CO})_{10}]$ with O-H bond cleavage, or $[\text{Os}_3(\mu\text{-H})(\mu\text{-RC}=\text{NOH})(\text{CO})_{10}]$ if the R group *trans* to OH in the oxime is a H-atom. The latter reaction is analogous to the orthometallation of pyridine or the known reactions of the **imines** $\text{RCH}=\text{NR}'$ [7].

Our results show that the primary products from the reactions of oximes with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ are all derived in the same way by from oxidative addition with O-H bond cleavage. For example, acetone oxime ($\text{Me}_2\text{C}=\text{NOH}$) reacts at room temperature to give $[\text{Os}_3(\mu\text{-H})(\mu\text{-Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (**1**) in 46% yield and no other products could be isolated. All the oximes we have studied gave compounds analogous to this (spectroscopic data in Table 1; synthetic methods and analytical data in the Experimental Section). Yields were always less than 60% and sometimes much lower but we were never able to isolate and **characterise** the byproducts. Compound **1** was also obtained by reaction of $\text{Me}_2\text{C}=\text{NOH}$ with $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ but the reaction was slower and was carried out in refluxing THF. Because of the higher temperatures used we also isolated the oxime-substituted derivative of **1**: $[\text{Os}_3(\mu\text{-H})(\text{Me}_2\text{C}=\text{NO})(\text{CO})_9(\text{Me}_2\text{C}=\text{NOH})]$ (**3**) and believe that this is formed from **1** by carbonyl substitution.

Spectroscopic data for compound **1** (Table 1) are consistent with the formula $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ but there is no easy way to distinguish between forms with the oximate ligand bridging through the oxygen atom alone as in **alkoxy-compounds** such as $[\text{Os}_3\text{H}(\text{OMe})(\text{CO})_{10}]$ [8] or through both the nitrogen and oxygen atoms. A single-crystal X-ray structure determination for **1** established the latter. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are in Table 2. The sum of the bond angles at N is 360.0° and that at C(1) is 359.9° showing that these atoms are planar with sp^2 hybridisation at the C(1) and N atoms. Indeed the whole C(1)C(2)C(3)NO(1) group of atoms is closely planar. The N–O(1) bond length of 1.37(1) Å is in between values for double and single bonds implying some π -bonding in this bond even though there is substantial σ -bonding in the N–C(1) bond which is 1.27(1) Å long. This type of oximate bridge has been observed before in a product from the reaction of $[\text{Co}(\text{C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2]$ with $\text{Ph}_2\text{C}=\text{NOH}$; the X-ray structure of the dinuclear compound $[\text{Co}_2(\text{C}_5\text{H}_5)_2(\mu\text{-Ph}_2\text{C}=\text{N})(\mu\text{-Ph}_2\text{C}=\text{NO})]$ showed that it contains an oximate bridge bonded through oxygen and nitrogen atoms as in compound **1** [1].

Compounds **4-8** are closely related spectroscopically to **1** and are all almost certainly isostructural with it. In the aldehyde oxime derivatives there is the possibility of isomers. The compounds $[\text{Os}_3\text{H}(\text{MeCH}=\text{NO})(\text{CO})_{10}]$ (**6**) and $[\text{Os}_3\text{H}(\text{NH}_2\text{CH}=\text{NO})(\text{CO})_{10}]$ (**8**) were observed in only one **isomeric** form whereas

Table 1

IR and ^1H NMR data for the new oxime cluster derivatives

Compound	$\nu(\text{CO})^a/\text{cm}^{-1}$	$\delta(^1\text{H NMR})^b$
$[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]^c$ (1)	2107m, 2067vs, 2052s, 2022vs, 2104s, 2007sh, 1997m, 1981m.	1.98(s,Me) 1.81(s,Me) -11.72(s,Os ₃ H)
$[\text{Os}_3(\text{OH})(\text{Me}_2\text{C}=\text{N})(\text{CO})_{10}]^c$ (2)	2100w, 2065s, 2047m, 2014s, 2002vs, 1984s, 1974m.	2.39(s,Me ₂) -0.70(s,OH)
$[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_9$ - (Me ₂ C=NOH)] (3)	2094m, 2052s, 2016vs, 2010vs, 1992m, 1976m, 1964w, 1926m.	2.39(s,Me) ^d 2.25(s,Me) 2.09(s,Me) 1.98(s,Me) -10.80(s,Os ₃ H)
$[\text{Os}_3\text{H}(\text{Ph}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (4)	2107m, 2069s, 2057s, 2024vs, 2013s, 2003m, 1982m, 1979m.	7.43(m,Ph) 7.18(m,Ph) -11.75(s,Os ₃ H)
$[\text{Os}_3\text{H}(\text{C}_6\text{H}_{10}=\text{NO})(\text{CO})_{10}]$ (5)	2109w, 2069vs, 2059vs, 2025vs, 2014s, 2008m, 1998m, 1983m, 1979m.	2.36(m,CH ₂) 2.20(m,CH ₂) 1.47(m,br,CH ₂) -11.82(s,Os ₃ H)
$[\text{Os}_3\text{H}(\text{MeCH}=\text{NO})(\text{CO})_{10}]$ (6)	2107m, 2069vs, 2058s, 2023vs, 2014s, 2008sh, 2000m, 1982m.	6.72(q,CH) 1.69(d,Me) -12.24(s,Os ₃ H)
$[\text{Os}_3\text{H}(\text{PhCH}=\text{NO})(\text{CO})_{10}]$ (7a)	2108m, 2069vs, 2059s, 2024vs, 2017s, 2009w, 2002m, 1984m, 1980m.	8.32(s,CH) 7.45(m,Ph) -11.91(s,Os ₃ H)
$[\text{Os}_3\text{H}(\text{PhCH}=\text{NO})(\text{CO})_{10}]$ (7b)	2109m, 2070vs, 2060s, 2024vs, 2018s, 2009m, 2002m, 1984m, 1980m.	7.45(m,Ph) ^e -12.03(s,Os ₃ H)
$[\text{Os}_3\text{H}(\text{NH}_2\text{CH}=\text{NO})(\text{CO})_{10}]$ (8)	2106m, 2065vs, 2055s, 2021vs, 2013s, 2005w, 1997m, 1980m, 1975m.	6.59(t,CH) 4.80(d,NH ₂) -12.22(s,Os ₃ H)

^a Cyclohexane solutions. ^b 200 MHz at room temperature in CDCl_3 unless stated otherwise. ^c NMR in C_6D_6 solution. ^d The OH signal was not assigned. ^e The CH resonance for the second isomer (7b) was not assigned; perhaps it is beneath the Ph resonances.

the oxidative addition of the pure isomer of $\text{PhCH}=\text{NOH}$ with OH *trans* to Ph to the compound $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ gave two isomers of $[\text{Os}_3\text{H}(\text{PhCH}=\text{NO})(\text{CO})_{10}]$ (7). These could be separated by TLC on silica but each slowly reverts to a mixture of the two in solution. Their IR spectra are extremely similar and the hydride NMR signals are at $\delta - 11.91$ and $- 12.03$ respectively. The isomers 7a and 7b almost certainly have the Ph group and the oxygen atom arranged respectively *cis* and *trans* about the C=N bond but we cannot be sure which isomer is which. Energy barriers to rotation about the C=N bonds in oximes are sufficiently high to prevent *cis-trans* isomerisation at room temperature. We believe that there must be a much lower barrier in compound 7 to allow the slow isomerisation between 7a and 7b at room temperature.

A solution of $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (1) in refluxing octane at 125° for 2 h lead to conversion to a non-hydrido isomer (2); chromatographic work-up gave a 48% yield after all of 1 had been consumed. Similar treatments of the other oximato

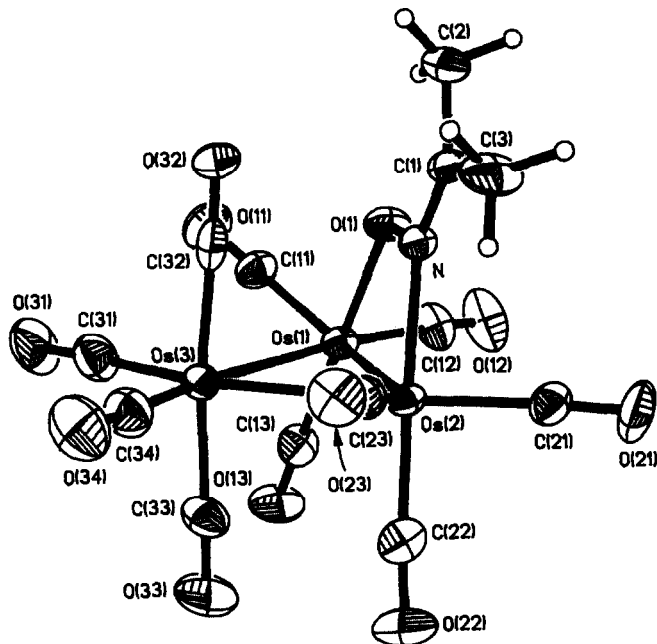


Fig. 1. Molecular structure of the cluster $[\text{Os}_3(\mu\text{-H})(\mu\text{-Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (1). The hydride ligand was not located but bond lengths and angles indicate that it bridges Os(1) and Os(2).

compounds gave no tractable products. The $\nu(\text{CO})$ IR spectrum showed that 2 is structurally similar to 1 with respect to the metal cluster. However, the ^1H NMR spectrum shows that there is a major transformation of the ligands since the singlet at $\delta - 11.72$ in 1 is replaced by a singlet at $\delta - 0.70$ in 2 indicative of a $\mu\text{-OH}$ group [9]. The Me groups are inequivalent in 1 but are equivalent in 2. These

Table 2

Bond lengths (\AA) and angles ($^\circ$) for the compound $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (1)

Os(1)–Os(2)	2.884(1)	N–O(1)	1.37(1)
Os(2)–Os(3)	2.871(1)	N–C(1)	1.27(1)
Os(1)–Os(3)	2.852(1)	C(1)–C(2)	1.49(2)
Os(1)–O(1)	2.080(7)	C(1)–C(3)	1.51(2)
Os(2)–N	2.144(8)		
Range Os–CO	1.90(1)–1.94(1)		
Mean Os–CO	1.912		
Range C–O	1.12(1)–1.16(2)		
Mean C–O	1.135		
Os(1)–Os(2)–Os(3)	59.4(1)	Os(1)–O(1)–N	111.6(5)
Os(1)–Os(3)–Os(2)	60.5(1)	Os(1)–N–O(1)	110.3(5)
Os(2)–Os(1)–Os(3)	60.1(1)	Os(2)–N–C(1)	134.8(7)
Os(3)–Os(1)–O(1)	90.1(2)	O(1)–N–C(1)	115.0(8)
Os(3)–Os(2)–N	87.8(2)	N–C(1)–C(2)	121.9(9)
Os(1)–Os(2)–N	68.2(2)	N–C(1)–C(3)	121(1)
Os(2)–Os(1)–O(1)	69.9(2)	C(2)–C(1)–C(3)	117(1)

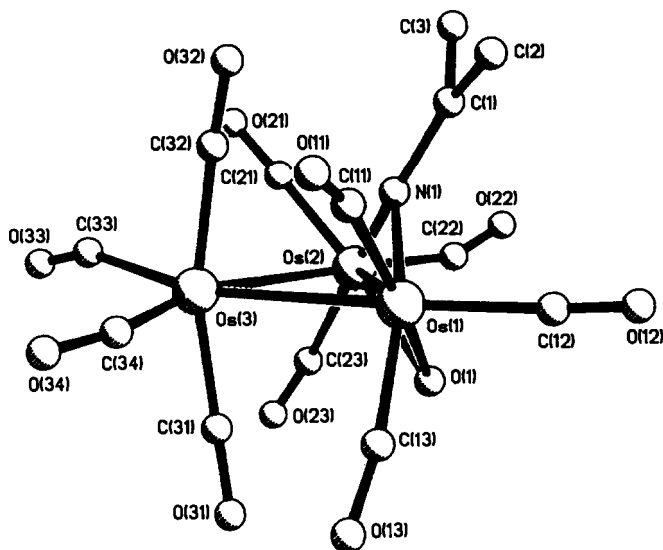


Fig. 2. Molecule **1** of the three independent molecules in the unit cell of $[\text{Os}_3(\mu\text{-OH})(\mu\text{-Me}_2\text{C=N})(\text{CO})_{10}]$ (**2**).

spectral observations are consistent with the formula $[\text{Os}_3(\text{OH})(\text{Me}_2\text{C=N})(\text{CO})_{10}]$ for **2** with a mirror plane relating the two Me groups.

We had many problems trying to grow crystals of **2** suitable for X-ray structure determination since mostly extremely fine needles were obtained. From one crystalline sample obtained from a hexane-dichloromethane mixture we managed to find a single-crystal block of suitable size but with very distinct grooves in one direction. This diffracted fairly weakly but since it was the best available we went ahead to determine the structure. Diffraction photographs and intensity peak shapes gave no indication of twinning. The unit cell was large [$V = 5831(4) \text{ \AA}^3$] and contained 12 triosmium clusters, three of which were crystallographically independent. In view of these problems we were only able to refine the structure to $R = 0.122$ and the uncertainties in the positions of the lighter atoms are high. The structures of the three independent clusters are the same within these large uncertainties in the molecular parameters. Figure 2 shows the molecular structure of molecule **1** and Table 3 gives selected bond lengths and angles for molecule **1** of **2** together with the corresponding data for molecules **2** and **3**. The structure is consistent with that predicted from spectra with OH and $\text{Me}_2\text{C=N}$ bridges between Os(1) and Os(2) which would be three-electron donors. Electron counting would then require there to be two metal-metal bonds and not three as in **1**. Whereas the Os-Os bond distances in **1** are all very similar [2.884(1), 2.871(1), and 2.852(1) \AA], one is much longer than the others in **2**. The distance Os(1)–Os(2) is 3.036(4) \AA in molecule **1** [corresponding to 3.078(4) and 3.084(4) \AA in molecules **2** and **3**], about 0.2 \AA longer than the other Os-Os distances which are the only metal-metal bonds present. The molecule has a molecular plane of symmetry through Os(3), N(1), and O(1) which is consistent with the observation of a single Me singlet in the ^1H NMR spectrum.

We do not know the mechanism of this conversion but Scheme 1 shows a possible route with the compound $[\text{Os}_3(\text{CO})_{10}(\text{Me}_2\text{C=NOH})]$ being an intermediate

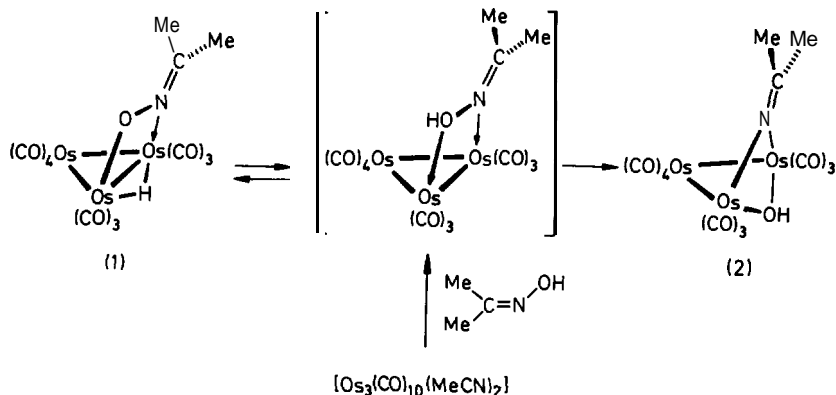
Table 3

Bond lengths (Å) and angles (°) for the compound $[\text{Os}_3(\text{OH})(\text{Me}_2\text{C}=\text{N})(\text{CO})_{10}] (2)^a$

	Molecule 1	Molecule 2	Molecule 3
Os(1)–Os(2)	3.063(4)	3.078(4)	3.084(4)
Os(2)–Os(3)	2.859(4)	2.835(4)	2.852(4)
Os(1)–Os(3)	2.841(4)	2.836(4)	2.849(4)
Os(1)–O(1)	2.18(3)	2.13(4)	2.09(4)
Os(2)–O(1)	2.15(3)	2.04(4)	2.13(4)
Os(1)–N(1)	2.31(5)	2.18(6)	2.17(6)
Os(2)–N(1)	1.67(5)	2.18(6)	2.04(5)
N(1)–C(1)	1.45(8)	1.36(13)	1.28(12)
C(1)–C(2)	1.35(11)	1.65(12)	1.49(12)
C(1)–C(3)	1.52(12)	1.38(14)	1.48(12)
Os(3)–Os(1)–O(1)	85(1)	80(1)	86(1)
Os(3)–Os(2)–O(1)	85(1)	82(1)	85(1)
Os(3)–Os(1)–N(1)	71(1)	82(1)	79(2)
Os(3)–Os(2)–N(1)	79(2)	82(1)	81(2)
Os(1)–O(1)–Os(2)	90(1)	95(2)	94(2)
Os(1)–N(1)–Os(2)	100(2)	90(2)	94(2)
Os(1)–N(1)–C(1)	105(4)	137(6)	127(6)
Os(2)–N(1)–C(1)	153(5)	133(6)	139(6)

^a Bond lengths and angles are specified for molecule 1 containing Os(1)Os(2)Os(3); corresponding lengths and angles are given for molecule 2 containing Os(4)Os(5)Os(6) and molecule 3 containing Os(7)Os(8)Os(9).

both in the formation of **1** and in its isomerisation to **2**. This implies that this intermediate converts initially to the kinetically controlled product by a fast (and reversible) hydrogen atom transfer from oxygen to osmium. A slower N–O cleavage leads to the thermodynamically stable compound **2**. Similar chemistry could occur with other ligands. For example the as yet unknown nitrite compound $[\text{Os}_3\text{H}(\text{NO}_2)(\text{CO})_{10}]$, analogous to **1**, might isomerise to $[\text{Os}_3(\text{OH})(\text{NO})(\text{CO})_{10}]$ and we are attempting to carry out such transformations.



Scheme 1.

Experimental

The oximes were prepared by standard procedures from hydroxylamine [10] and the corresponding organic carbonyl compound. $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ [11] and $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ [12] were prepared as in the literature.

Reaction of acetone oxime with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

A solution of the bis-acetonitrile compound (0.092 g) and $\text{Me}_2\text{C}=\text{NOH}$ (0.016 g) in dichloromethane (30 cm^3) was stirred at room temperature under nitrogen for 2 h. The solvent was removed under reduced pressure and the residue purified by TLC [SiO_2 ; eluant: light petroleum (b.p. 30–40 °C)/dichloromethane, 9 : 1 v/v] to give one main yellow band which gave $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (1) (0.042 g, 46%) as yellow crystals from hexane/dichloromethane mixtures (found: C, 16.9; H, 0.9; N, 1.65. $\text{C}_{13}\text{H}_7\text{NO}_{11}\text{Os}_3$ calcd.: C, 16.9; H, 0.76; N, 1.5%).

Reaction of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ with acetone oxime

A solution of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ (0.185 g) and $\text{Me}_2\text{C}=\text{NOH}$ (0.035 g) in tetrahydrofuran (40 cm^3) was heated under reflux under nitrogen for 3 h. The solvent was removed under reduced pressure and the residue separated by TLC [SiO_2 ; eluant: pentane/dichloromethane, 10 : 1 v/v] to give compound **1** as yellow crystals (0.066 g, 36%) and $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{Me}_2\text{C}=\text{NOH})(\text{CO})_9]$ (3) (0.050 g, 27%) as yellow-orange crystals. Other oxime derivatives were made from the bis-acetonitrile compound rather than by this route.

Thermal treatment of $[\text{Os}_3\text{H}(\text{Me}_2\text{C}=\text{NO})(\text{CO})_{10}]$

A solution of compound **1** (0.105 g) in n-octane (70 cm^3) was heated under reflux under nitrogen for 2 h. Removal of the solvent under reduced pressure and TLC on silica [eluant: light petroleum (b.p. < 40 °C)/dichloromethane, 9 : 1 v/v] gave several bands but the only one characterised was the main yellow band which gave $[\text{Os}_3(\text{OH})(\text{Me}_2\text{C}=\text{N})(\text{CO})_{10}]$ (2) as yellow crystals (0.050 g, 48%) from hexane/dichloromethane mixtures (found: C, 16.9; H, 0.95; N, 1.45. $\text{C}_{13}\text{H}_7\text{NO}_{11}\text{Os}_3$ calcd.: C, 16.9; H, 0.75; N, 1.5%).

Reactions of other oximes with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

Benzophenone oxime. A solution of the bis-acetonitrile compound (0.250 g) and the oxime (0.100 g) in CH_2Cl_2 (30 cm^3) was refluxed under nitrogen for 3.5 h. TLC work-up as above gave three bands, two of which only contained traces of material. The main band gave $[\text{Os}_3\text{H}(\text{Ph}_2\text{C}=\text{NO})(\text{CO})_{10}]$ (4) as orange crystals (0.158 g, 63%) from pentane-dichloromethane mixtures (found: C, 26.45; H, 1.05; N, 1.3. $\text{C}_{23}\text{H}_{11}\text{NO}_{11}\text{Os}_3$ calcd.: C, 26.35; H, 1.05; N, 1.35%).

Cyclohexane oxime. A solution of the bis-acetonitrile compound (0.200 g) and the oxime (0.050 g) in refluxing dichloromethane (30 cm^3) under nitrogen for 1.5 h gave after TLC work-up the compound $[\text{Os}_3\text{H}(\text{C}_6\text{H}_{10}=\text{NO})(\text{CO})_{10}]$ (5) as yellow crystals (0.121 g, 59%) (found: C, 20.2; H, 1.2; N, 1.45. $\text{C}_{16}\text{H}_{11}\text{NO}_{11}\text{Os}_3$ calcd.: C, 19.95; H, 1.15; N, 1.45%).

Acetaldehyde oxime. A solution of the bis-acetonitrile compound (0.155 g) and the oxime (0.2 cm^3) in dichloromethane (30 cm^3) was stirred at room temperature under nitrogen for 40 h. Removal of the solvent gave a green-yellow powder which

was recrystallised from dichloromethane-light petroleum at -30°C to give $[\text{Os}_3\text{H}(\text{MeCH}=\text{NO})(\text{CO})_{10}]$ (6) as yellow crystals (Found: C, 16.1; H, 0.8; N, 1.55. $\text{C}_{12}\text{H}_5\text{NO}_{11}\text{Os}_3$ calcd.: C, 15.85; H, 0.55; N, 1.55%).

Benzaldehyde oxime. A solution of the bis-acetonitrile compound (0.155 g) and the oxime (isomer with OH *trans* to Ph, 0.100 g) in dichloromethane (30 cm^3) was stirred at room temperature under nitrogen for 1.5 h. Removal of the solvent and TLC work-up [SiO_2 ; eluant: dichloromethane/light petroleum (b.p. $< 40^{\circ}\text{C}$), v/v 1: 9] to give two yellow bands which gave yellow crystals characterised as isomers of $[\text{Os}_3\text{H}(\text{PhCH}=\text{NO})(\text{CO})_{10}]$, isomer **7a** (0.021 g, 13%) (found: C, 21.2; H, 0.9; N, 1.4. $\text{C}_{17}\text{H}_7\text{NO}_{11}\text{Os}_3$ calcd.: C, 21.0; H, 0.7; N, 1.45%) and isomer **7b** (0.025 g, 15%) (found: C, 21.2; H, 1.0; N, 1.4%).

Formamide oxime. a solution of the bis-acetonitrile compound (0.150 g) and the oxime (0.050 g) in dichloromethane (30 cm^3) was refluxed under nitrogen for 2 h. TLC work-up as above gave $[\text{Os}_3\text{H}(\text{NH}_2\text{CH}=\text{NO})(\text{CO})_{10}]$ (8) as yellow crystals (0.059 g, 39%) (found: C, 14.85; H, 0.65; N, 3.1 $\text{C}_{11}\text{H}_4\text{N}_2\text{O}_{11}\text{Os}_3$ calcd.: C, 14.5; H, 0.45; N, 3.05%).

Table 4

Crystal data and details of intensity measurements and structure solution and refinement for isomers 1 and 2

	Compound 1	Compound 2
Formula	$\text{C}_{13}\text{H}_7\text{NO}_{11}\text{Os}_3$	$\text{C}_{13}\text{H}_7\text{NO}_{11}\text{Os}_3$
$M/\text{g mol}^{-1}$	923.81	923.81
Crystal size/ mm^3	0.3 x 0.2 x 0.1	0.45x0.20x0.15
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
$a/\text{\AA}$	7.381(1)	15.407(8)
$b/\text{\AA}$	9.601(1)	8.863(3)
$c/\text{\AA}$	13.996(2)	42.72(2)
$\alpha/^\circ$	91.40(1)	90
$\beta/^\circ$	96.04(1)	91.54(4)
$\gamma/^\circ$	96.59(1)	90
$V/\text{\AA}^3$	979.0(2)	5831(4)
Z	2	12
$D_c/\text{g cm}^{-3}$	3.13	3.16
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	194.9	196.5
$F(000)$	816	4896
Collection range/ $^\circ$	$5 \leq 2\theta \leq 50$	$5 \leq 2\theta \leq 50$
No. unique data	3464	10146
Rejection criterion	$F_o > 3\sigma(F_o)$	$F_o > 6\sigma(F_o)$
No. reflections used in refinement	3142	6833
Parameters refined	253	382
R^a	0.0349	0.122
R_w^b	0.0364	0.127
g in weighting scheme c	0.00047	0.0005
Largest peak in final Fourier map/ $e\text{\AA}^3$	1.66	5.1

$^a R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. $^c 1/[\sigma^2(F_o) + gF_o^2]$.

X-ray structure determinations for [Os₃(H)(Me₂C=NO)(CO)₁₀] (I) and [Os₃(OH)(Me₂C=N)(CO)₁₀] (2)

Compound I. Measurements were made on a yellow crystal of C₁₃H₇NO₁₁Os₃ from a hexane/dichloromethane mixture, size 0.3 x 0.2 x 0.1 mm³, at 290 K using a Nicolet R3v/m diffractometer operating in the θ -2 θ scan mode with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal data and details of the data collection, structure solution, and refinement are in Table 4. A total of 3464 unique intensity data were corrected for Lorentz and polarisation effects and a decay correction calculated from the intensities of three standard reflections collected periodically throughout the experiment was also applied. The data were corrected for absorption using the azimuthal scan method, $\mu(\text{Mo-K}\alpha) = 194.9 \text{ cm}^{-1}$.

The structure was solved by direct methods and a model containing 253 parameters was refined by alternating cycles of full-matrix least-squares and by difference-Fourier syntheses. All non-hydrogen atoms were refined anisotropically and methyl hydrogen atoms included in the model for structure factor calculations in idealised positions but their positions were not refined. The function minimised was $[\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ with the weight w defined as $1/[\sigma^2(F_o) + 0.00047F_o^2]$. Atomic coordinates are in Table 5.

Table 5

Fractional atomic coordinates ($\times 10^4$) for the compound [Os₃H(Me₂C=NO)(CO)₁₀] (I)

	x	y	z
Os(1)	2184(1)	8451(1)	8377(1)
Os(2)	1472(1)	5847(1)	7257(1)
Os(3)	2(1)	8320(1)	6562(1)
O(1)	162(10)	7115(7)	8932(5)
N	-257(12)	5883(8)	8394(5)
C(1)	-1538(16)	5035(11)	8672(8)
C(2)	-2502(18)	5375(13)	9515(8)
C(3)	-2107(19)	3627(12)	8163(10)
C(11)	1035(17)	10002(12)	8772(8)
C(12)	3751(18)	8339(11)	9548(8)
C(13)	3996(18)	9677(11)	7843(8)
C(21)	2410(16)	4229(11)	7804(8)
C(22)	3259(17)	5954(11)	6373(8)
C(23)	-340(16)	4898(11)	6306(7)
C(31)	-435(21)	10234(13)	6582(8)
C(32)	-1993(19)	7836(12)	7303(8)
C(33)	2208(18)	8715(13)	5925(8)
C(34)	-1423(20)	7650(14)	5379(8)
O(21)	2966(15)	3230(10)	8059(8)
O(33)	3487(15)	8980(11)	5554(7)
O(22)	4443(13)	6019(11)	5900(6)
O(11)	296(17)	10918(10)	9010(7)
O(31)	-699(19)	11385(10)	6562(7)
O(13)	5120(13)	10384(10)	7548(7)
O(12)	4723(16)	8336(9)	10216(6)
O(23)	-1369(12)	4344(9)	5739(6)
O(34)	-2320(16)	7287(11)	4697(6)
O(32)	-3242(12)	7533(11)	7719(7)

Table 6

Fractional aomic coordinates ($\times 10^4$) for the compound $[\text{Os}_3(\text{OH})(\text{Me}_2\text{C}=\text{N})(\text{CO})_{10}]$ (2)

	x	y	z
Os(1)	7895(2)	7503(3)	914(1)
Os(2)	7352(2)	4264(3)	1063(1)
Os(3)	9012(2)	5470(3)	1243(1)
O(1)	7517(24)	5524(38)	639(8)
N(1)	7070(34)	5922(56)	1216(11)
C(1)	6483(48)	6917(77)	1374(15)
C(2)	6365(56)	8400(88)	1429(18)
C(3)	5870(61)	6112(101)	1590(20)
C(11)	8259(34)	9041(54)	1238(11)
O(11)	8583(39)	9847(65)	1357(13)
C(12)	7032(39)	8692(63)	693(12)
O(12)	6575(52)	9440(88)	590(17)
C(13)	8737(55)	7969(90)	603(18)
O(13)	9343(33)	8202(53)	436(11)
C(21)	7382(49)	3391(79)	1460(16)
O(21)	7388(25)	2685(41)	1700(8)
4(22)	6188(55)	3378(83)	927(16)
O(22)	5527(54)	3194(87)	939(17)
C(23)	7763(56)	2274(91)	854(18)
O(23)	8221(30)	1712(47)	749(9)
C(31)	9322(45)	4895(73)	839(15)
O(31)	9507(28)	4483(46)	580(9)
C(32)	8399(36)	6126(58)	1606(12)
O(32)	8073(37)	6783(61)	1799(12)
C(33)	9388(68)	3566(118)	1526(22)
O(33)	9696(37)	2662(66)	1578(12)
C(34)	9963(56)	6555(91)	1245(18)
O(34)	10674(36)	7349(59)	1288(11)
Os(4)	2609(2)	6824(3)	2064(1)
Os(5)	2265(2)	10152(3)	1897(1)
Os(6)	3270(2)	9253(3)	2431(1)
O(2)	2902(27)	8389(43)	1703(8)
N(2)	1463(38)	8260(61)	2037(12)
C(4)	604(71)	8123(115)	2101(23)
C(5)	484(47)	6335(76)	2199(15)
C(6)	48(66)	9258(107)	2002(21)
C(41)	2295(61)	6055(101)	2507(20)
O(41)	2186(39)	5079(63)	2678(13)
C(42)	2178(44)	5177(71)	1783(14)
O(42)	1903(44)	4374(75)	1633(15)
C(43)	3637(83)	5705(128)	2121(25)
O(43)	4356(54)	5561(85)	2119(17)
C(51)	1876(49)	11443(80)	2175(16)
O(51)	1377(32)	12499(53)	2263(10)
C(52)	1592(43)	10517(70)	1556(14)
O(52)	1192(49)	11022(81)	1362(16)
C(53)	3107(37)	11568(58)	1816(11)
O(53)	3702(45)	12434(77)	1750(15)
C(61)	4222(44)	8928(68)	2113(14)
O(61)	4776(37)	9081(59)	1998(12)
C(62)	2206(78)	9334(124)	2563(25)
O(62)	1566(62)	9138(101)	2713(21)

Table 6 (continued)

	x	y	z
C(63)	3531(45)	11035(72)	2571(14)
O(63)	3688(46)	12520(77)	2630(15)
C(64)	3884(46)	8102(74)	2714(14)
O(64)	4375(51)	7299(86)	2911(17)
Os(7)	2294(2)	9604(3)	606(1)
Os(8)	2744(2)	6280(3)	749(1)
Os(9)	3978(2)	8374(3)	518(1)
O(3)	2240(28)	8170(46)	995(9)
N(3)	1968(38)	7376(61)	428(12)
C(7)	1432(71)	7059(116)	205(23)
C(8)	935(42)	8063(69)	-13(13)
C(9)	1302(39)	5433(62)	145(12)
C(71)	2369(56)	10652(93)	272(18)
O(71)	2468(48)	11336(79)	55(16)
C(72)	1061(41)	10146(64)	651(12)
O(72)	420(37)	10967(60)	630(12)
C(73)	2862(50)	11128(82)	785(16)
O(73)	3139(33)	12219(55)	1004(11)
C(81)	3232(98)	4345(163)	553(34)
O(81)	3555(50)	4014(82)	296(17)
C(82)	1754(52)	5001(85)	860(16)
O(82)	1410(89)	3544(161)	825(32)
C(83)	3545(33)	5532(54)	1073(10)
O(83)	3949(46)	5229(75)	1274(15)
C(91)	4126(44)	8698(72)	927(14)
O(91)	4300(42)	8956(70)	1211(14)
C(92)	3545(47)	7532(77)	131(15)
O(92)	3252(40)	7581(68)	-149(13)
C(93)	4981(47)	6990(73)	498(14)
O(93)	5581(39)	6360(63)	467(12)
C(94)	4401(102)	10127(179)	255(34)
O(94)	4854(64)	11059(109)	313(21)

Compound 2. Crystallisation of $C_{13}H_7NO_{11}Os_3$ (**2**) from hexane–dichloromethane solutions generally gave very fine needles which were unsuitable for structure determination. On one occasion a poor quality $0.45 \times 0.20 \times 0.15$ mm³ single-crystal block with pronounced striations in one direction was found to diffract but not very strongly. Details of the crystal data, data collection and structure solution and refinement are in Table 4. A total of 11278 intensity measurements were made and corrected as for compound **1**; 10146 of these were unique.

The structure was solved by direct methods and a model containing 382 parameters was refined for 6833 data with $F_o > 6\sigma(F_o)$ by alternating cycles of full-matrix least-squares and by difference-Fourier syntheses. The unit cell contained three independent Os₃ clusters ($Z = 12$). Only the Os atoms were refined anisotropically and no hydrogen atoms were included in the model. The quality of the final refined structure was severely limited by the quality of the crystal and the diffraction data and we were able to refine the structure only to $R = 0.122$. Esd's are approximately

4 times larger than normally expected for a well-refined triosmium cluster. Atomic coordinates are in Table 6.

All calculations were carried out using a MICROVAX II computer running SHELXTL PLUS [13]. Full lists of bond lengths and angles, thermal parameters, and F_o/F_c values for compounds 1 and 2 are in the supplementary data which may be obtained from the authors.

Acknowledgements

We thank the SERC for a grant for the diffractometer, for postdoctoral support (D.W.O) and a studentship (for N.I.P.).

References

- 1 See for example: T. **Carofiglio**, S. Stella, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, (1989) 1957.
- 2 A.J. Deeming, **S. Donovan-Mtunxi**, S.E. Kabir, and P.J. Manning, *J. Chem. Soc., Dalton Trans.*, (1985) 1037.
- 3 A.J. Deeming, *Adv. Organomet. Chem.*, 26 (1986) 1.
- 4 A.J. Deeming, R. Peters, M.B. Hursthouse, and J.D.J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, (1982) 787 and references therein.
- 5 J.R. Shapley, D.E. Samkoff, C. **Bueno**, and M.R. Churchill, *Inorg. Chem.*, 21 (1982) 634 and references therein.
- 6 M. Tachikawa and J.R. Shapley, *J. Organomet. Chem.*, 124 (1977) C19.
- 7 R.D. Adams and N.M. Golembeski, *Inorg. Chem.*, 17 (1978) 1969.
- 8 M.R. Churchill and H.J. Wasserman, *Inorg. Chem.*, 19 (1980) 2391.
- 9 A.J. Deeming, P.J. Manning, I.P. **Rothwell**, M.B. Hursthouse, and N.P.C. **Walker**, *J. Chem. Soc., Dalton Trans.*, (1984) 2039.
- 10 **A.I. Vogel**, *Textbook of Practical Organic Chemistry*, 4th ed., Longmans, 1978.
- 11 C.E. **Anson**, E.J. **Ditzel**, M. Fajardo, H.D. **Holden**, B.F.G. Johnson, J. Lewis, J. **Puga**, and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1984) 2723.
- 12 S.A.R. Knox, J.W. Koepke, M.A. Andrews, and H.D. Kaesz, *J. Am. Chem. Soc.*, 97 (1975) 3942.
- 13 G.M. Sheldrick, *An integrated system for refining and displaying crystal structures from diffraction data*, University of **Göttingen**, 1986.