Synthesis, structural characterization and reactivity of triosmium carbonyl clusters containing oxime ligands

Janet Shuk-Yee Wong and Wing-Tak Wong*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. E-mail: wtwong@hkucc.hku.hk

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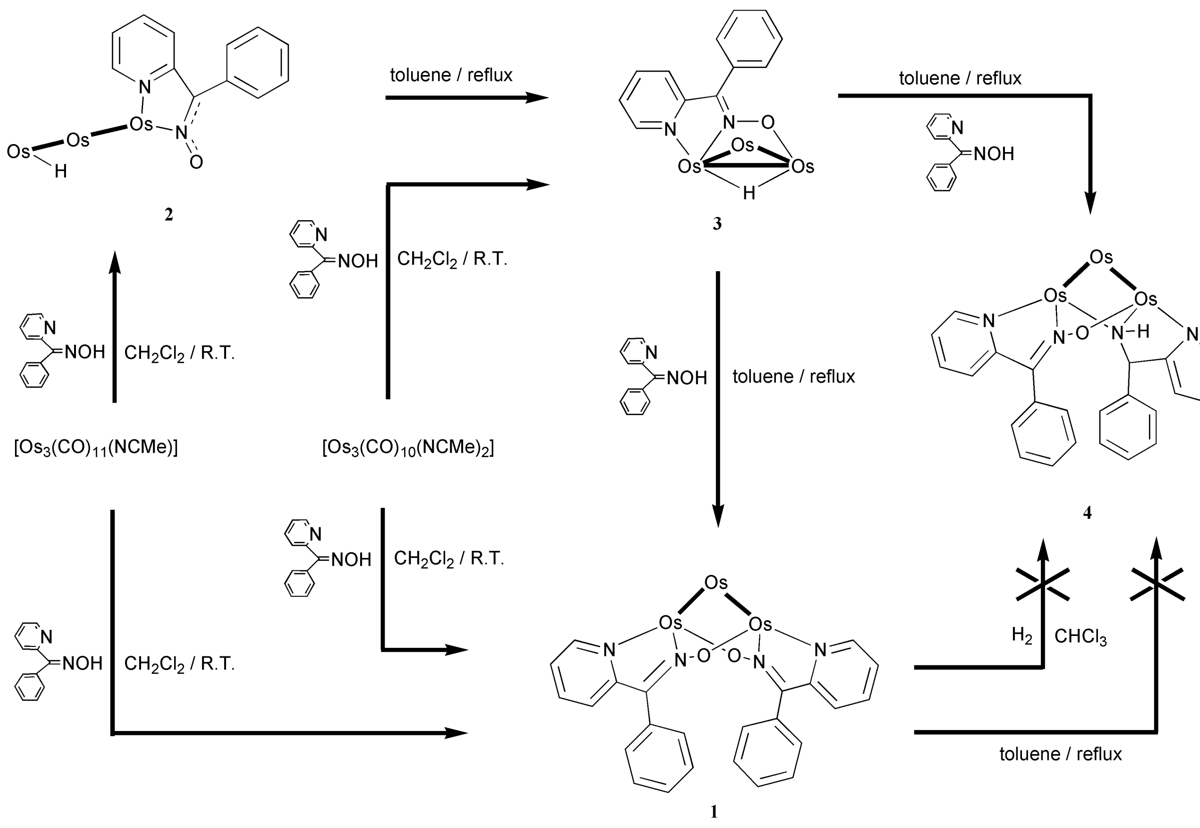
Reaction of $[Os_3(CO)_{11}(NCMe)]$ with phenyl 2-pyridyl ketoxime produced the clusters $[Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}ON{=}CPh(NC_5H_4)\}_2]$ **1** and $[Os_3H(CO)_{11}\{\eta^2\text{-}ON{=}CPh(NC_5H_4)\}]$ **2** in 4 and 17% yields, respectively. Oxidative addition of the oximes to the clusters with O–H bond cleavage and the loss of labile acetonitrile groups, and in the case of complex **1** decarbonylation, are observed. Cluster **2** possesses an open linear metal skeleton attached to both the pyridine nitrogen and oximato nitrogen on one terminal Os atom. Heating **2** in refluxing toluene gave $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}\eta^3\text{-}ON{=}CPh(NC_5H_4)\}]$ **3** in 13% yield. Treatment of a CH_2Cl_2 solution of $[Os_3(CO)_{10}(NCMe)_2]$ with phenyl 2-pyridyl ketoxime at ambient conditions afforded the bridging oximato clusters **1** and **3** in moderate yields. Cluster **3** and 1 equiv. of phenyl 2-pyridyl ketoxime in refluxing toluene led to conversion to clusters **1** and $[Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}ON{=}CPh(NC_5H_4)\}\{\mu\text{-}\eta^2\text{-}N(H)CHPh(NC_5H_4)\}]$ **4** in 12 and 16% yields, respectively. In cluster **4**, one of the oximato moieties is deoxygenated with N–O bond cleavage. Treatment of another oxime ligand, benzophenone oxime, with $[Os_3(CO)_{10}(NCMe)_2]$ gave $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^2\text{-}ON{=}CPh_2\}]$ **5** in moderate yield. On thermolysis of **5** in toluene, $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu\text{-}\eta^3\text{-}ON{=}CPh(C_6H_4)\}]$ **6** and $[Os_3(CO)_{10}(\mu\text{-}OH)\{\mu\text{-}N{=}CPh_2\}]$ **7** were isolated in 27 and 21% yields, respectively. The oxime ligand in **6** is converted to a tridentate ligand. In addition to the μ-η^2-oximato N–O bridge, the phenyl carbon on the ligand coordinates to the cluster core by *ortho*-metallation. Cluster **5** isomerizes thermally to **7**, which is formed by oxidative addition of the oxime with N–O bond cleavage. A μ_4-oxo hexaosmium cluster, $[Os_6(CO)_{16}(\mu_4\text{-}O)\{\mu\text{-}\eta^3\text{-}N{=}CPh(C_6H_4)\}_2]$ **8**, was isolated in low yield upon refluxing **5** in octane. Vacuum pyrolysis of **5** in 140 °C yielded a pentaosmium carbonyl cluster, $[Os_5(CO)_{15}\{\mu\text{-}\eta^3\text{-}N{=}CPh(C_6H_4)\}]$ **9**. All these clusters have been fully characterized by both spectroscopic and crystallographic techniques.

The coordination chemistry of oxime (hydroxyimine), $RR'{=}NOH$, has been well documented.[1–7] Often oximato groups act as bi- or multidentate ligands that are attached to a single metal atom. The oxime group may coordinate to metals either through a nitrogen or an oxygen atom or both. Reactivity observed for coordinated oxime ligands on transition metals includes (a) oxidative deoximation to a ketone,[3] (b) reduction to an imine,[4,5] (c) dehydroxylation to a ligated methyleneamide,[4] (d) dehydration to a nitrile,[4] (e) oxidation to a nitrosoalkane[6] and (f) coupling with nitrile to give imino-acylated species.[7] Metal clusters containing bridging oximato ligands are also known, however, their chemical properties have not been well developed. To our knowledge, reports concerning the cluster chemistry of oximes are rather rare. Deeming and co-workers reported that the O–H bond cleavage in the oxidative addition of $Me_2C{=}NOH$ to the osmium cluster $[Os_3(CO)_{10}(NCMe)_2]$ gives $[Os_3(\mu\text{-}H)(\mu\text{-}Me_2C{=}NO)(CO)_{10}]$, which thermally isomerizes to the hydroxo isomer $[Os_3(\mu\text{-}OH)(\mu\text{-}Me_2C{=}N)(CO)_{10}]$.[8] Lu and co-workers also reported the first example containing a μ_2-η^1-*O*-oximato coordinating group in $[(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-}OC_9H_6N_2Cl)]$.[9] The reactivity of oximes towards triosmium clusters is one of our current interests. In this paper, the synthesis and spectroscopic studies of triosmium clusters with oxime ligands are reported.

Results and discussion

Reaction of $[Os_3(CO)_{11}(NCMe)]$ with phenyl 2-pyridyl ketoxime

Treatment of $[Os_3(CO)_{11}(NCMe)]$ with 1 equiv. of phenyl 2-pyridyl ketoxime at room temperature afforded $[Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}ON{=}CPh(NC_5H_4)\}_2]$ **1** and $[Os_3H(CO)_{11}\{\eta^2\text{-}ON{=}CPh(NC_5H_4)\}]$ **2** in low yields upon TLC separation (Scheme 1). The spectroscopic data of **1** and **2** (and all other products) are listed in Table 1. The molecular structure of **1** was established by X-ray analysis using a red, air stable crystal that was obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution at −20 °C. Fig. 1 shows the perspective view and the numbering scheme for the resulting molecular configuration. Selected bond parameters are given in Table 2. The cluster consists of an open triosmium triangle [Os(1)–Os(2) 2.8472(6) Å] with two oximato ligands spanning the open Os···Os edge (3.60 Å) *via* the N–O group in a μ-η^2 fashion and is similar to the cluster $[Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}\eta^2\text{-}ONPh)_2(CO)_7]$.[10] Cluster **1** possesses C_2 symmetry with the principal axis passing through Os(2) and bisecting the open triangular metal framework. The molecule of **1** contains two oximato ligands that chelate to the metal core in a μ-η^3 manner. The ligand is bound to the cluster by coordination of the pyridine nitrogen lone pair [Os(1)–N(1)



Scheme 1

2.165(9) Å] and the oximato oxygen and nitrogen atoms [Os(1*)–O(5) 2.115(7), Os(1)–N(2) 2.146(9) Å]. The oximato oxygen atoms span to the neighbouring metal centre over the open metal···metal edge. The N–O bond distance is 1.35(1) Å. Most of the reported complexes with a μ-η^2-coordinated oximato N–O unit are dimetallic or trimetallic in nature with the metal–metal bond remaining intact.[1,8,9] Opening up of the Ru–Ru bond by coordination of the μ-η^2-nitrosobenzene ligand has been reported.[10] In cluster **1**, one Os–Os bond is opened up by the oximato ligands. The oximato ligands in **1** act as 5e$^-$ donors. Together with the eight terminal carbonyls, cluster **1** is electron precise with a cluster valence electron (CVE) count of 50, which is expected for a trinuclear cluster with two metal–metal bonds.

The mass and IR spectra show that **2** is a triosmium compound with terminal carbonyls only. The ^{1}H NMR signal at δ -10.09 is attributed to a terminal metal hydride. In order to establish the molecular structure of **2** the compound was

Table 1 Spectroscopic data for compounds **1**–**9**

Cluster	IR spectra[a] ν(CO)/cm^{-1}	Mass spectra[b] m/z	H NMR spectra[c] δ, J/Hz
1	2072m, 1995vs, 1925w, 1922w, 1914w (CH_2Cl_2)	1189	8.86 (d, $J=6.7$, 4H, Py), 7.81 (td, $J=6.7$, 1.3, 4H, Py), 7.31 (t, $J=7.0$, 6H, Ph), 7.06 (d, $J=7.0$, 4H, Ph)
2	2122w, 2084s, 2064w, 2049m, 2041w, 2028vs, 2018s, 1999s, 1987w	1077	8.73 (dd, $J=6.2$, 1.2, 1H, Py), 7.61 (m, 1H, Py), 7.45 (m, 5H, Ph), 7.29 (dd, $J=8.3$, 1.0, 1H, Py), 7.04 (m, 1H, Py), -10.09 (s, 1H, Os–H)
3	2053s, 2016vs, 2006w, 1993s, 1970s, 1952m	1021	9.02 (dd, $J=6.2$, 1.1, 1H, Py), 7.72 (td, $J=6.5$, 1.1, 1H, Py), 7.54 (dd, $J=6.5$, 1.4, 1H, Py), 7.49 (m, 5H, Ph), 7.25 (td, $J=6.2$, 1.4, 1H, Py), -18.20 (s, 1H, Os–H)
4	2066m, 1989s, 1978sh, 1900w (CH_2Cl_2)	1175	9.02 (d, $J=6.5$, 1H, Py), 8.75 (d, $J=6.0$, 1H, Py), 7.88 (t, $J=7.0$, 1H, Py), 7.53 (t, $J=6.4$, 1H, Py), 7.46 (t, $J=6.5$, 1H, Py), 7.35 (m, 4H, Ph), 7.26 (m, 2H, Ph), 7.22 (d, $J=7.0$, 1H, Py), 6.96 (t, $J=6.0$, 1H, Py), 6.86 (m, 4H, Ph), 6.74 (d, $J=6.4$, 1H, Py), 4.38 (d, $J=4.8$, 1H, NH), 2.51 (d, $J=4.8$, 1H, C–H)
5	2109m, 2072s, 2059s, 2026vs, 2014s, 2003m, 1981m	1048	7.49 (m, 3H, Ph), 7.39 (m, 2H, Ph), 7.23 (m, 5H, Ph), -11.64 (s, 1H, Os–H)
6	2128w, 2082s, 2051vs, 2039s, 2028w, 2008w, 1991m, 1974m	1020	7.85 (d, $J=7.4$, 1H, Ph), 7.34 (m, 3H, Ph), 7.24 (m, 2H, Ph), 7.06 (t, $J=7.4$, 1H, Ph), 6.97 (d, $J=7.9$, 1H, Ph), 6.84 (t, $J=7.9$, 1H, Ph), -13.05 (d, $J=1.7$, 1H, Os–H, -14.38 (d, $J=1.7$, 1H, Os–H)
7	2101w, 2069vs, 2049m, 2014s, 2003s, 1987m, 1976w	1048	7.45 (m, 8H, Ph), 7.37 (m, 2H, Ph), -0.10 (s, 1H, OH)
8	2097w, 2078vs, 2064vs, 2049w, 2018vs, 2008m, 1997m, 1993m, 1968w	1964	7.77 (d, $J=7.1$, 2H, Ph), 7.56 (m, 6H, Ph), 7.36 (m, 4H, Ph), 7.18 (m, 4H, Ph), 7.03 (dd, $J=6.1$, 2.2, 2H, Ph)
9	2099w, 2072s, 2033vs, 2008w, 1997w	1550	8.05 (d, $J=7.5$, 1.4, 1H, Ph), 7.44 (m, 3H, Ph), 7.34 (td, $J=7.5$, 1.4, 1H, Ph), 7.02 (m, 3H, Ph), 6.58 (dd, $J=7.7$, 1.4, 1H, Ph)

[a] In *n*-hexane unless otherwise stated. [b] Parent ion peak; the observed value is the same as that calculated from the molecular formula. [c] In CD_2Cl_2.

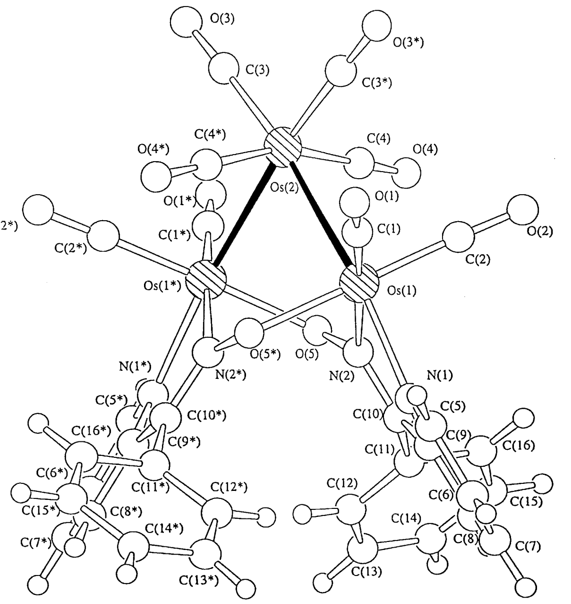


Fig. 1 Molecular structure of $[Os_3(CO)_8\{\mu\text{-}\eta^3\text{-}ON{=}CPh(NC_5H_4)\}_2]$ **1** and the atom numbering scheme.

characterized by X-ray crystallographic analysis (Fig. 2). Selected bond parameters are presented in Table 3. This molecule contains an open linear $Os_3(CO)_{11}$ cluster [Os(1)–Os(2)–Os(3) 175.79(2)°] attached to both the pyridine nitrogen and oximato nitrogen atoms on the terminal Os atom [Os(1)–N(1) 2.11(1), Os(1)–N(2) 2.10(1) Å]. The metal core of **2** is similar to $[Os_3(CO)_{11}(\mu_3\text{-}FcC_4Fc)]$ in which the bond angle of Os(1)–Os(2)–Os(3) is 162.65(4)°.[11] The oxime moiety acts as a bidentate ligand that coordinates to the Os(1) at the axial and equatorial positions *via* the pyridine nitrogen and oximato nitrogen atoms, respectively, to form a five-memebered chelated ring, while the oximato oxygen atom remains non-coordinating. The ligand groups on Os(1), Os(2) and Os(3) are staggered with respect to the ligands on the adjacent metal so as to minimize steric crowding. A similar effect is observed in other linear clusters.[12–14] The N–O bond distance of the oximato group is 1.28(1) Å, which is within the range found in most metal complexes with N-bonded nitroso group[15–17] but is comparably shorter than the corresponding value observed in complex **1**, since both N and O are coordinated in **1** but not in **2**. The oxime ligand in **2** acts as a $3e^-$ donor rather than a $5e^-$ donor as in the case for **1**. Together with the eleven terminal carbonyls, cluster **2** retains a CVE count of 50.

Thermolysis of 2 in toluene

Heating **2** in refluxing toluene for 3 h gave $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}\eta^3\text{-}ON{=}CPh(NC_5H_4)\}]$ **3** in low yield along with decomposition of the starting material. Crystals of **3** suitable for X-ray analysis were obtained by slow evaporation from an *n*-hexane–$CHCl_3$ solution at −20 °C. The molecular structure of **3** is depicted in Fig. 3, and selected bond parameters are given in Table 4. Cluster **3** consists of a triangular metal core [Os(1)–Os(2) 2.8800(5), Os(2)–Os(3) 2.8470(5), Os(1)–Os(3) 2.8473(5) Å] in which the Os(1) and the Os(3) atoms are edge-bridged by a hydride and an oximato ligand. The molecule of **3** contains one oximato ligand that chelates to the metal framework in a similar manner, μ-η^3, as in **1** [Os(1)–N(1) 2.092(8), Os(3)–O(10) 2.166(6), Os(1)–N(2) 2.039(7) Å]. The pyridyl nitrogen N(1) and the oximato nitrogen N(2) chelate to Os(1) and form a five-membered metallacyclic ring [Os(1), N(1), C(14), C(15), N(2)] with a mean deviation of 0.048 Å from the least-squares plane. The metallacyclic ring is fused to the four-membered ring containing Os(1), Os(3), N(2) and O(10) and pyridyl ring containing N(1), C(10), C(11), C(12), C(13) and C(14) with dihedral angles of 23.46° and 174.78°, respectively. The presence of the bridging hydride on the metal core is supported by the signal at δ − 18.20 in the ^1H NMR spectrum. The bond lengths of N(2)–O(10) and N(2)–C(15) are 1.348(10) and 1.30(1) Å, respectively, which indicates their partial double-bond character. The sp^2 hybridization associated with the N(2) and C(15) centers was confirmed by the sum of the bond angles at N(2) (359.9°) and at C(15) (360.0°). This type of oximato bridge has been observed before in the clusters $[Os_3(\mu\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}]$ and $[(\mu\text{-}H)Os_3(CO)_{10}\{\mu_2\text{-}\eta^2\text{-}ON\text{-}C_9H_6NCl)]$.[8,9] The conversion of cluster **2** to cluster **3** may involve the loss of CO under high temperature, which is followed by the coordination of the oximato oxygen to another terminal Os atom and the formation of an Os–Os bond. Therefore, cluster **2** should be an intermediate in the formation of cluster **3**.

Table 2 Selected bond distances (Å) and angles (°) for cluster **1**

Os(1)–Os(2)	2.8472(6)	N(1)–C(5)	1.36(1)
Os(1)–N(1)	2.165(9)	N(1)–C(9)	1.35(1)
Os(1)–N(2)	2.146(9)	N(2)–C(10)	1.29(1)
Os(1)–O(5*)	2.115(7)	C(9)–C(10)	1.46(1)
N(2)–O(5)	1.35(1)		
Os(1)–Os(2)–Os(1*)	78.52(2)	Os(1)–O(5*)–N(2*)	113.0(6)
Os(2)–Os(1)–N(2)	92.9(2)	N(1)–Os(1)–N(2)	73.9(3)
Os(2)–Os(1)–O(5*)	89.0(2)	N(1)–C(9)–C(10)	115.5(10)
Os(1)–N(1)–C(5)	126.6(9)	N(2)–C(10)–C(9)	115.2(10)
Os(1)–N(1)–C(9)	114.9(7)	N(2)–C(10)–C(11)	121.3(10)
Os(1)–N(2)–O(5)	124.2(6)	O(5)–N(2)–C(10)	117.6(9)
Os(1)–N(2)–C(10)	118.2(7)		

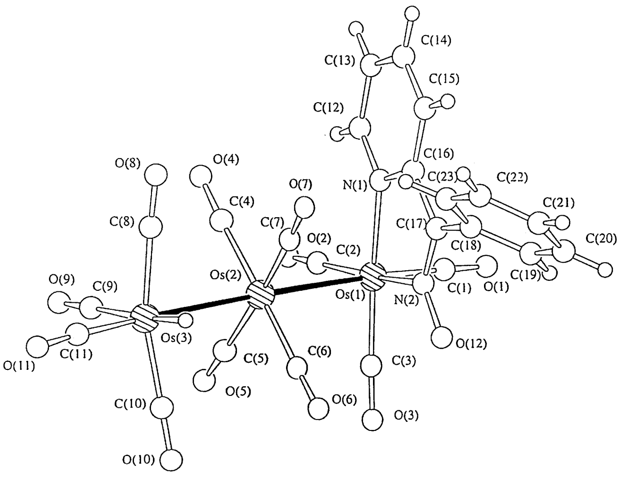


Fig. 2 Molecular structure of $[Os_3H(CO)_{11}\{\eta^2\text{-}ON{=}CPh(NC_5H_4)\}]$ **2** and the atom numbering scheme.

Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with phenyl 2-pyridyl ketoxime

Treatment of a CH_2Cl_2 solution of $[Os_3(CO)_{10}(NCMe)_2]$ with 1 equiv. of phenyl 2-pyridyl ketoxime at ambient conditions

Table 3 Selected bond distances (Å) and angles (°) for cluster **2**

Os(1)–Os(2)	2.9038(7)	N(1)–C(16)	1.35(2)
Os(2)–Os(3)	2.9160(7)	N(2)–O(12)	1.28(1)
Os(1)–N(1)	2.11(1)	N(2)–C(17)	1.34(2)
Os(1)–N(2)	2.10(1)	C(16)–C(17)	1.45(2)
N(1)–C(12)	1.37(2)		
Os(1)–Os(2)–Os(3)	175.79(2)	N(1)–C(16)–C(17)	115(1)
Os(1)–N(1)–C(12)	125.0(10)	N(2)–C(17)–C(16)	114(1)
Os(1)–N(1)–C(16)	115.6(8)	N(2)–C(17)–C(18)	122(1)
Os(1)–N(2)–O(12)	121.1(8)	O(12)–N(2)–C(17)	121(1)
Os(1)–N(2)–C(17)	117.2(8)	C(16)–C(17)–C(18)	122(1)

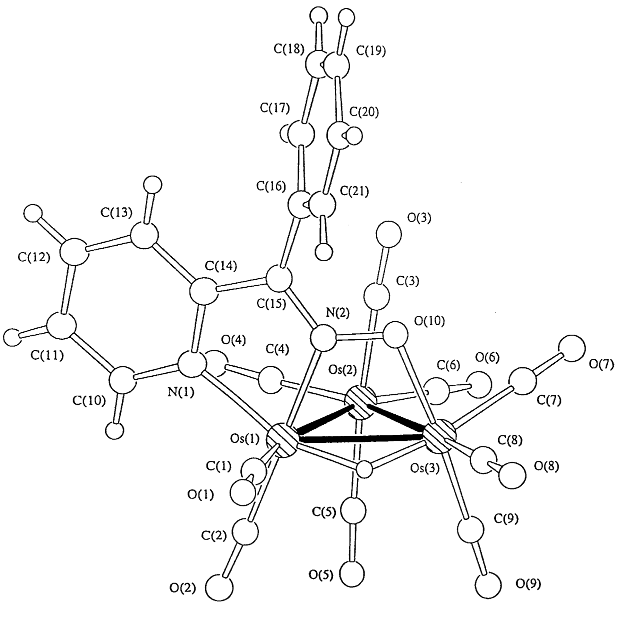


Fig. 3 Molecular structure of $[Os_3(\mu\text{-H})(CO)_9\{\mu\text{-}\eta^3\text{-ON=CPh}(NC_5H_4)\}]$ **3** and the atom numbering scheme.

gave clusters **1** and **3** in moderate yields upon TLC separation (Scheme 1). The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with phenyl 2-pyridyl ketoxime proceeds much faster than that of $[Os_3(CO)_{11}(NCMe)]$ with the same ligand. Cluster **2**, cannot be obtained in the former reaction. This is probably because $[Os_3(CO)_{10}(NCMe)_2]$ contains two labile acetonitrile groups, which favour capping by the pyridine nitrogen and the oximato oxygen and nitrogen atoms of the oxime ligand.

The cluster $[Os_3(CO)_{10}(NCMe)_2]$ is a ready source of $Os_3(CO)_{10}$ fragments in reactions leading to oxidative addition of HX to give compounds of the type $[Os_3(\mu\text{-H})(\mu\text{-X})(CO)_{10}]$. For example, alcohols react to give $[Os_3(\mu\text{-H})(\mu\text{-OR})(CO)_{10}]$.[18] Pyridine undergoes *ortho*-metallation to afford $[Os_3(\mu\text{-H})(\mu\text{-}C_5H_4N)(CO)_{10}]$.[19] Therefore, in principle, oximes $R_2C{=}NOH$ could give $[Os_3(\mu\text{-H})(\mu\text{-}R_2C{=}NO)(CO)_{10}]$ or $[Os_3(\mu\text{-H})(\mu\text{-RC{=}NOH})(CO)_{10}]$ if the R group *trans* to OH in the oxime is an H atom.[8] According to our results, the primary products from the reaction of phenyl 2-pyridyl ketoxime with $[Os_3(CO)_{10}(NCMe)_2]$ are all derived in the same way from oxidative addition with O–H bond cleavage.

Thermolysis of 3 with phenyl 2-pyridyl ketoxime in toluene

A solution of cluster **3** and 1 equiv. of phenyl 2-pyridyl ketoxime in refluxing toluene led to conversion to **1** and $[Os_3(CO)_8\{\mu\text{-}\eta^3\text{-ON=CPh}(NC_5H_4)\}\{\mu\text{-}\eta^2\text{-N(H)CHPh}(NC_5H_4)\}]$ **4** (Scheme 1). Cluster **4** was characterized by various spectroscopic methods (Table 1). The IR spectrum shows the presence of terminal carbonyl ligands and the mass spectrum exhibits molecular ion envelopes that agree with the formula of the compound, with ion peaks corresponding to CO losses also being present. The ^{1}H NMR spectrum of **4** is complicated and consists of proton signals ranging from δ 2.5 to 9.0; no metal hydride could be detected. The proton resonance between δ 6.7 and 9.0 are due to the aromatic ring system, while the two doublets centred at δ 4.38 and 2.51, which are coupled to each other, are attributable to the N–H and C–H protrons, respectively.

Table 4 Selected bond distances (Å) and angles (°) for cluster **3**

Os(1)–Os(2)	2.8800(5)	N(1)–C(10)	1.34(1)
Os(2)–Os(3)	2.8470(5)	N(1)–C(14)	1.37(1)
Os(1)–Os(3)	2.8473(5)	N(2)–O(10)	1.348(10)
Os(1)–N(2)	2.039(7)	N(2)–C(15)	1.30(1)
Os(1)–N(1)	2.092(8)	C(14)–C(15)	1.45(1)
Os(3)–O(10)	2.166(6)		
Os(1)–Os(2)–Os(3)	59.62(1)	Os(1)–N(2)–O(10)	116.8(6)
Os(1)–Os(3)–Os(2)	60.76(1)	Os(1)–N(2)–C(15)	120.3(6)
Os(2)–Os(1)–O(3)	59.61(1)	Os(3)–O(10)–N(2)	103.9(5)
Os(1)–Os(3)–O(10)	69.4(2)	N(1)–Os(1)–N(2)	76.0(3)
Os(2)–Os(3)–O(10)	90.8(2)	N(1)–C(14)–C(15)	114.9(8)
Os(2)–Os(1)–N(2)	84.1(2)	N(2)–C(15)–C(14)	113.2(8)
Os(3)–Os(1)–N(2)	68.0(2)	N(2)–C(15)–C(16)	113.9(8)
Os(1)–N(1)–C(10)	126.5(7)	O(10)–N(2)–C(15)	122.8(8)
Os(1)–N(1)–C(14)	114.6(6)	C(10)–N(1)–C(14)	118.9(8)

Red crystals of **4** suitable for diffraction studies were grown from a saturated solution of *n*-hexane and $CHCl_3$ at $-20\,°C$. The molecular structure of **4** has also been established by X-ray crystallography. There are two independent molecules in each asymmetric unit, which are essentially the same. One of the molecules is depicted in Fig. 4 and selected bond lengths and angles are given in Table 5. One and a half molecules of $CHCl_3$, as a solvent of crystallization, are found in the crystal lattice. Cluster **4** retains the open triangular metal arrangement of **1** with the two Os–Os bonds being almost equi-distance [2.8531(8) *vs.* 2.8170(8) Å], while the Os(1)···Os(3) edge is non-bonded with a separation of 3.31 Å. The molecule contains one oximato ligand and one deoxygenated oximato ligand. The oximato ligand adopts the same coordination mode to the metal centres as those in clusters **1** and **3** [Os(1)–N(1) 2.156(10), Os(3)–O(9) 2.136(9) and Os(1)–N(2) 2.12(1) Å] and the N–O bond distance in **4** is 1.34(1) Å, which is comparable to those in **1** and **3**. The deoxygenated oximato ligand is believed to undergo N–O bond cleavage of the oximato moiety and coordinate to Os(1) and Os(3) through the oximato nitrogen and pyridine nitrogen [Os(1)–N(4) 2.164(10) Os(3)–N(4) 2.155(9) and Os(3)–N(3) 2.138(10) Å], which is similar to the reported ruthenium cluster $[Ru_3(\mu\text{-H})(\mu\text{-HNCHPh}_2)(CO)_{10}]$.[20] The C(26)–N(4) in the deoxygenated ligand has a length of 1.53(1) Å thus is a single C–N bond. The deoxygenated oximato ligand should be a 5e$^-$ donor with the bridging nitrogen and the pyridine nitrogen atoms contributing three and two electrons to the cluster framework, respectively; together with the oximato ligand and eight terminal

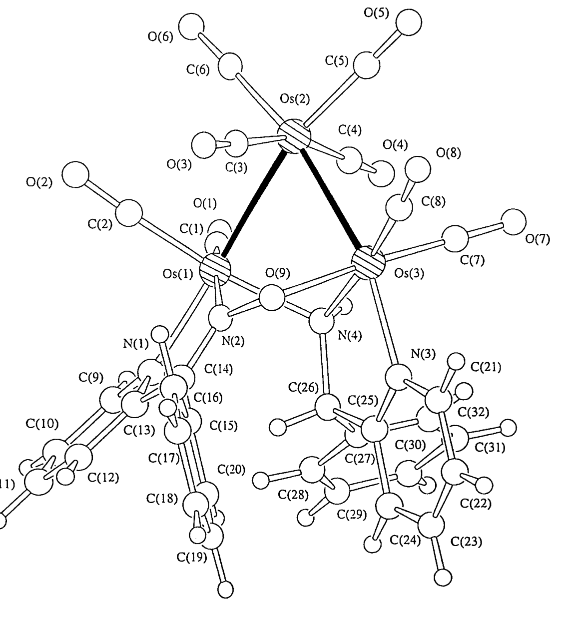


Fig. 4 Molecular structure of $[Os_3(CO)_8\{\mu\text{-}\eta^3\text{-ON=CPh}(NC_5H_4)\}\{\mu\text{-}\eta^2\text{-N(H)CHPh}(NC_5H_4)\}]$ **4** and the atom numbering scheme.

Table 5 Selected bond distances (Å) and angles (°) for cluster **4**

	Molecule 1	Molecule 2
Os(1)–Os(2)	2.8531(8)	2.8624(8)
Os(2)–Os(3)	2.8170(8)	2.8166(8)
Os(1)–N(1)	2.156(10)	2.13(1)
Os(1)–N(2)	2.12(1)	2.093(10)
Os(1)–N(4)	2.164(10)	2.16(1)
Os(3)–N(3)	2.138(10)	2.12(1)
Os(3)–N(4)	2.155(9)	2.14(1)
Os(3)–O(9)	2.136(9)	2.099(8)
N(1)–C(13)	1.38(1)	1.34(1)
N(2)–O(9)	1.34(1)	1.35(1)
N(2)–C(14)	1.32(1)	1.32(1)
N(3)–C(21)	1.35(2)	1.36(2)
N(3)–C(25)	1.33(1)	1.35(2)
N(4)–C(26)	1.53(1)	1.51(2)
C(13)–C(14)	1.44(2)	1.46(2)
C(25)–C(26)	1.52(2)	1.52(2)
Os(1)–Os(2)–Os(3)	71.45(2)	71.83(2)
Os(2)–Os(1)–N(1)	170.2(3)	166.6(3)
Os(2)–Os(1)–N(2)	95.8(3)	93.2(3)
Os(2)–Os(1)–N(4)	82.4(2)	82.6(3)
Os(2)–Os(3)–N(3)	160.5(3)	160.9(3)
Os(2)–Os(3)–N(4)	83.5(2)	84.0(3)
Os(2)–Os(3)–O(9)	91.5(2)	89.3(2)
Os(1)–N(1)–C(13)	113.9(8)	114.5(8)
Os(1)–N(2)–O(9)	120.0(8)	120.7(7)
Os(1)–N(2)–C(14)	118.2(9)	118(1)
Os(1)–N(4)–Os(3)	100.1(4)	101.4(4)
Os(1)–N(4)–C(26)	118.6(7)	115.0(8)
Os(3)–N(3)–C(21)	124.8(8)	125.9(10)
Os(3)–N(3)–C(25)	117.0(8)	117.0(8)
Os(3)–N(4)–C(26)	114.8(7)	115.0(8)
Os(3)–O(9)–N(2)	111.5(7)	112.0(6)
N(1)–C(13)–C(14)	115(1)	116(1)
N(2)–C(14)–C(13)	115(1)	112(1)
N(3)–C(25)–C(26)	120(1)	119(1)
N(4)–C(26)–C(25)	109.1(10)	109(1)
O(9)–N(2)–C(14)	120(1)	118(1)

carbonyls a CVE count of 50 is obtained, which is electron precise for a triosmium cluster containing two metal–metal bonds in accordance with the effective atomic number (EAN) rule.

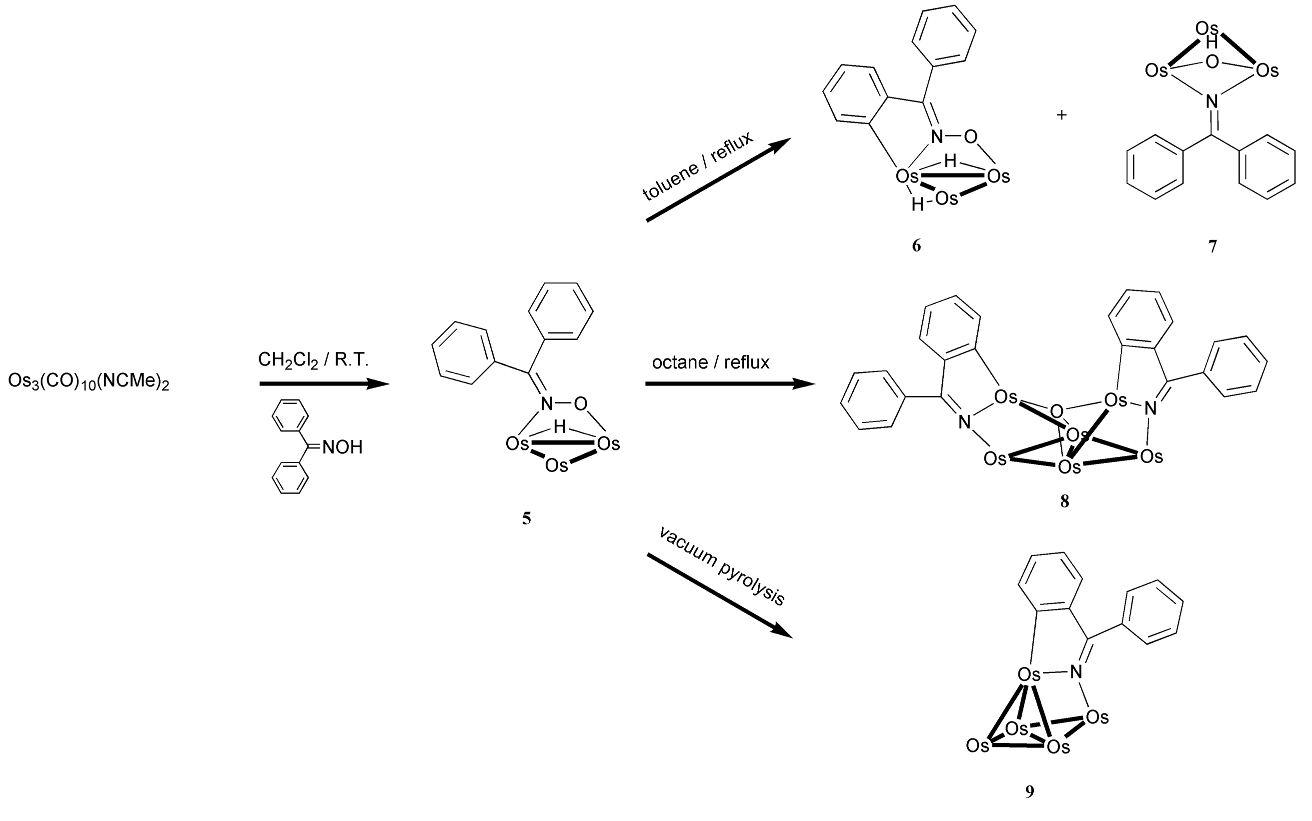
Attempted thermolysis and hydrogenation of 1

Heating complex **1** in refluxing toluene for 2 days results in no observable change in the IR spectrum and spot TLC monitoring. Cluster **1** is thermally stable up to the boiling point of toluene without any molecular rearrangement or bond cleavage.

Hydrogenation of complex **1** was attempted in refluxing $CHCl_3$, monitored by IR and TLC. However, no reaction was observed after 5 h. Thermolysis and hydrogenation of **1** failed to give complex **4**. Therefore, complexes **1** and **4** may be formed *via* different pathways.

Reaction of [$Os_3(CO)_{10}(NCMe)_2$] with benzophenone oxime

To explore the change in the reactivity of the oxime with different substitutents, we investigated the reaction of [$Os_3(CO)_{10}(NCMe)_2$] with benzophenone oxime, in addition to phenyl 2-pyridyl ketoxime. Treatment of 1 equiv. benzophenone oxime with [$Os_3(CO)_{10}(NCMe)_2$] in CH_2Cl_2 at room temperature over a period of 5 h afforded [$Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^2\text{-}ON{=}CPh_2\}$] **5** in 27% yield (Scheme 2). The preparation and the spectroscopic data of cluster **5** have been reported and a structure for **5** proposed by comparing the spectroscopic data with those of the compound [$Os_3(\mu\text{-}H)(\mu_2\text{-}Me_2C{=}NO)(CO)_{10}$].[8] We determined the structure of cluster **5** by both spectroscopic techniques (Table 1) and X-ray diffraction analysis in this work. There are two independent molecules of **5** in each asymmetric unit, which are essentially the same; one of the molecules is depicted in Fig. 5 and relevant bond parameters are in Table 6. The molecule contains a triangular metal core [Os(1)–Os(2) 2.8736(8), Os(2)–Os(3) 2.8740(9), Os(1)–Os(3) 2.8471(8) Å]. The oximato ligand chelates to the metal framework *via* the N–O unit [Os(1)–N(1) 2.155(10), Os(3)–O(11) 2.091(9) Å], in the same way as in the reported cluster [$Os_3(\mu\text{-}H)(\mu\text{-}Me_2C{=}NO)(CO)_{10}$],[8] by oxidative addition with O–H cleavage. The N–O bond distance is found to be 1.35(1) Å, which is comparable with those in previously



Scheme 2

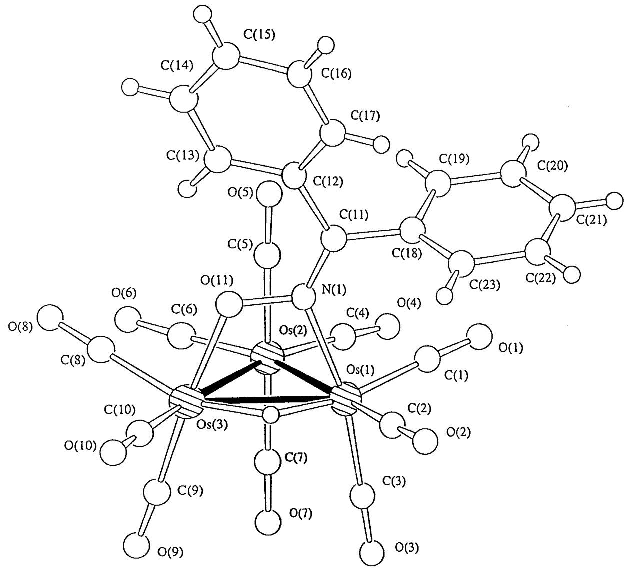


Fig. 5 Molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}\eta^2\text{-}ON{=}CPh_2\}]$ **5** and the atom numbering scheme.

mentioned complexes.[1,8] In contrast to **3**, the oxime ligand in **5** acts as a bidentate ligand and chelates to the metal core in a μ-η^2-manner while the oxime in **3** binds to the cluster in a μ-η^3-fashion, with one more coordination *via* the pyridine nitrogen atom.

Thermolysis of 5 in toluene

Cluster **5** was heated in refluxing toluene until complete consumption was observed by TLC monitoring. Two products, identified as $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu\text{-}\eta^3\text{-}OH{=}CPh(C_6H_4)\}]$ **6** and $[Os_3(CO)_{10}(\mu\text{-}OH)\{\mu\text{-}N{=}CPh_2\}]$ **7**, were isolated in 27 and 21% yields, respectively (Scheme 2). The ^1H NMR signals due to the organic moieties of the two complexes are fully consistent with their structures. The signals of the two hydrides in **6** are observed at δ − 14.38 and − 13.05, while a signal at δ − 0.10 in **7** is assigned to the bridging hydroxy proton. The mass spectra exhibit molecular ion envelopes that agree with the formulae of the compounds (Table 1).

Table 6 Selected bond lengths (Å) and angles (°) for cluster **5**

	Molecule 1	Molecule 2
Os(1)–Os(2)	2.8736(8)	2.8594(9)
Os(2)–Os(3)	2.8740(9)	2.8605(9)
Os(1)–Os(3)	2.8471(8)	2.8747(8)
Os(1)–N(1)	2.155(10)	2.170(10)
Os(3)–O(11)	2.091(9)	2.077(9)
N(1)–O(11)	1.35(1)	1.35(1)
N(1)–C(11)	1.31(2)	1.32(2)
C(11)–C(12)	1.50(7)	1.48(2)
C(11)–C(18)	1.49(2)	1.48(2)
Os(1)–Os(2)–Os(3)	59.39(2)	60.34(2)
Os(1)–Os(3)–Os(2)	60.30(2)	59.81(2)
Os(2)–Os(1)–Os(3)	60.31(2)	59.85(2)
Os(1)–Os(3)–O(11)	69.7(2)	69.4(2)
Os(2)–Os(1)–N(1)	86.4(3)	87.4(3)
Os(2)–Os(3)–O(11)	89.9(3)	90.1(3)
Os(3)–Os(1)–N(1)	68.9(3)	68.4(3)
Os(1)–N(1)–O(11)	108.7(7)	108.4(7)
Os(1)–N(1)–C(11)	132.8(9)	132.1(9)
Os(3)–O(11)–N(1)	112.1(7)	113.5(7)
O(11)–N(1)–C(11)	117(1)	119(1)
N(1)–C(11)–C(12)	124(1)	125(1)
N(1)–C(11)–C(18)	117(1)	118(1)
C(12)–C(11)–C(18)	117(1)	116(1)

Yellow crystals of **6** and **7** suitable for diffraction analysis were obtained by slow evaporation of these compounds in *n*-hexane–CH_2Cl_2 at − 20 °C. Perspective views of the molecular structures of **6** and **7** are shown in Fig. 6 and 7, respectively, and relevant bond parameters in Tables 7 and 8, respectively. Complex **6** retains the same cluster core as **5**. On thermolysis, the oxime was converted into a tridentate ligand by *ortho*-metallation. In addition to the μ-η^2-oximato N–O bridge, the phenyl α-carbon on the ligand coordinates to Os(1) [Os(1)–C(22) 2.11(1) Å] and leads to the formation of a five-membered ring [Os(1), C(22), C(17), C(10), N(1)] with a mean deviation of 0.044 Å from the least-squares plane. The metallacyclic five-membered ring is fused to the four-membered ring containing Os(1), Os(3), N(1) and O(10) and the phenyl ring containing C(17), C(18), C(19), C(20), C(21) and C(22) with dihedral angles of 14.19° and 5.61°, respectively. The coordination mode of the ligand in **6** resembles that in **3** in

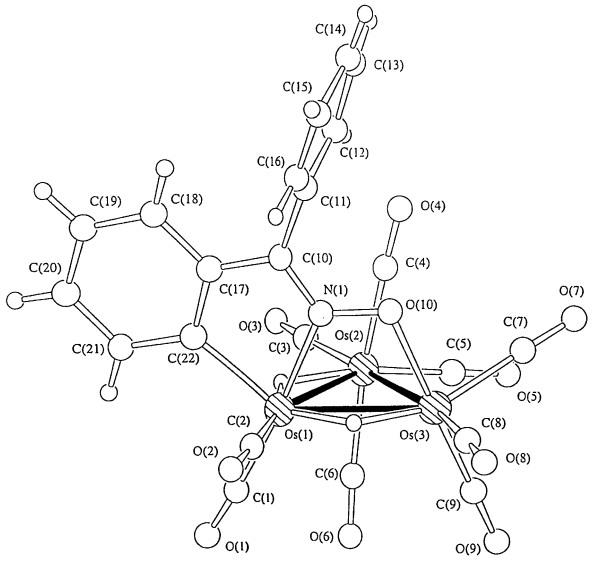


Fig. 6 Molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9\{\mu\text{-}\eta^3\text{-}ON{=}CPh(C_6H_4)\}]$ **6** and the atom numbering scheme.

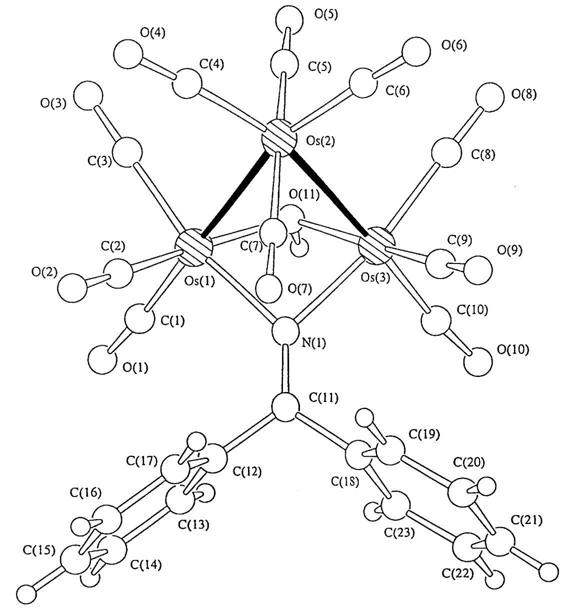


Fig. 7 Molecular structure of $[Os_3(CO)_{10}(\mu\text{-}OH)\{\mu\text{-}N{=}CPh_2\}]$ **7** and the atom numbering scheme.

Table 7 Selected bond lengths (Å) and angles (°) for cluster **6**

Os(1)–Os(2)	3.0327(6)	N(1)–O(10)	1.346(9)
Os(2)–Os(3)	2.8862(6)	N(1)–C(10)	1.31(1)
Os(1)–Os(3)	2.9522(6)	C(10)–C(11)	1.51(1)
Os(1)–N(1)	2.073(7)	C(10)–C(17)	1.46(1)
Os(1)–C(22)	2.11(1)	C(17)–C(22)	1.40(1)
Os(3)–O(10)	2.151(7)		
Os(1)–Os(2)–Os(3)	59.78(1)	Os(1)–C(22)–C(17)	112.6(7)
Os(1)–Os(3)–Os(2)	62.58(1)	Os(1)–C(22)–C(21)	129.4(9)
Os(2)–Os(1)–Os(3)	57.65(1)	Os(3)–O(10)–N(1)	106.7(5)
Os(1)–Os(3)–O(10)	68.5(2)	O(10)–N(1)–C(10)	122.2(7)
Os(2)–Os(1)–N(1)	84.4(2)	N(1)–C(10)–C(11)	123.9(9)
Os(2)–Os(3)–O(10)	91.2(2)	N(1)–C(10)–C(17)	112.5(8)
Os(3)–Os(1)–N(1)	66.3(2)	C(10)–C(17)–C(22)	117.2(9)
Os(1)–N(1)–O(10)	117.6(6)	C(11)–C(10)–C(17)	123.5(9)
Os(1)–N(1)–C(10)	120.2(6)		

Table 8 Selected bond lengths (Å) and angles (°) for cluster **7**

Os(1)–Os(2)	2.8639(5)	Os(3)–O(11)	2.134(6)
Os(2)–Os(3)	2.8587(6)	N(1)–C(11)	1.27(1)
Os(1)–N(1)	2.116(7)	C(11)–C(12)	1.51(1)
Os(1)–O(11)	2.149(7)	C(11)–C(18)	1.51(1)
Os(3)–N(1)	2.112(7)		
Os(1)–Os(2)–Os(3)	65.87(1)	Os(1)–N(1)–C(11)	132.8(6)
Os(2)–Os(1)–O(11)	82.3(2)	Os(3)–N(1)–C(11)	132.4(6)
Os(2)–Os(1)–N(1)	81.8(2)	N(1)–Os(1)–O(11)	74.6(3)
Os(2)–Os(3)–N(1)	82.0(2)	N(1)–Os(3)–O(11)	75.0(3)
Os(2)–Os(3)–O(11)	82.7(2)	N(1)–C(11)–C(12)	123.4(8)
Os(1)–N(1)–Os(3)	94.8(3)	N(1)–C(11)–C(18)	123.1(8)
Os(1)–O(11)–Os(3)	93.2(2)	C(12)–C(11)–C(18)	113.4(8)

which the pyridyl nitrogen atom in **3** is replaced by a phenyl carbon in **6**. The bond lengths of N(1)–O(10) and N(1)–C(10) are 1.346(9) and 1.31(1) Å, respectively, which indicates their partial double-bond character. The sp^2 hybridization associated with the N(1) and C(10) centres was confirmed by the sum of the bond angles at N(1) (360.0°) and at C(10) (359.9°). The N–O bond distance of **6** is comparable to those in the previously mentioned complexes.

Apart from **6**, complex **7** was also obtained upon thermolysis of **5**. The ^{1}H NMR signals due to protons of the phenyl rings are observed in the range δ 7.33–7.48 and the resonance for the bridging hydroxy proton occurs at δ −0.10. The molecule consists of an open triangular array of three osmium atoms [Os(1)–Os(2) 2.8639(5), Os(2)–Os(3) 2.8587(6) Å] with OH and Ph_2C=N bridges on the open Os···Os edge [Os(1)–O(11) 2.149(7), Os(3)–O(11) 2.134(6), Os(1)–N(1) 2.116(7), Os(3)–N(1) 2.112(7) Å]. Compound **5** isomerizes thermally to **7**, which is formed by oxidative addition of the oxime with N–O bond cleavage. The geometry of **7** is similar to $[Os_3(\mu\text{-OH})\{\mu\text{-Me}_2C{=}N)(CO)_{10}]$, which is the product of thermolysis of $[Os_3(\mu\text{-H})\{\mu\text{-Me}_2C{=}NO)(CO)_{10}]$. The mechanism of this conversion has not been studied but a possible route with $[Os_3(\mu\text{-Me}_2C{=}NOH)(CO)_{10}]$ as an intermediate has been suggested before.[8] A reported triruthenium cluster, $[Ru_3(\mu\text{-H})(\mu\text{-N}{=}CPh_2)(CO)_{10}]$, also contains an edge bridging N=CPh_2 unit that is derived from benzophenone imine.[21] The μ-OH and μ-N=CPh_2 units would be three-electron donors. Together with ten terminal carbonyls, cluster **7** is electron precise for a triosmium cluster with two Os–Os bonds.

Thermolysis of 5 in octane

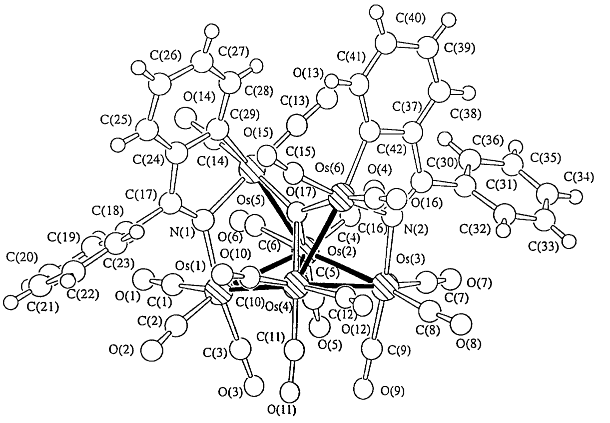


Fig. 8 Molecular structure of $[Os_6(CO)_{16}(\mu_4\text{-O})\{\mu\text{-}\eta^3\text{-N}{=}CPh(C_6H_4)\}_2]$ **8** and the atom numbering scheme.

Heating **5** in refluxing *n*-octane for 1 h afforded $[Os_6(CO)_{16}(\mu_4\text{-O})\{\mu\text{-}\eta^3\text{-N}{=}CPh(C_6H_4)\}_2]$ **8** in low yield (Scheme 2). Dark green crystals of **8** suitable for diffraction studies were grown from a saturated solution of *n*-hexane–*n*-octane at −20 °C. The molecular structure of **8** is depicted in Fig. 8 and relevant structural parameters are listed in Table 9. Complex **8** contains six metal atoms grouped into a central cluster of four, Os(1)–Os(2)–Os(3)–Os(4), which is arranged in the form of a "butterfly tetrahedron" containing five metal–metal bonds. The dihedral angle between the Os(1), Os(2), Os(4) and Os(2), Os(3), Os(4) planes is 27.9°. The two remaining metal atoms are linked to this 4-atom cluster at the "hinge" atoms, one to each, *via* a metal–metal bond [Os(2)–Os(5) 2.862(1), Os(4)–Os(6) 2.914(1) Å]. The bond between the "hinge" atoms, Os(2) and Os(4), is quite short, 2.713(1) Å, which is relatively common in high nuclearity clusters for metals with high coordination numbers.[22,23] In **8**, Os(2) and Os(4) have significantly higher coordination numbers than the other Os atoms. The Os–Os bonds from the Os(2) and Os(4) hinge atoms to the Os(1) and Os(3) "wing-tips" can be grouped into pairs of long [Os(1)–Os(2) 2.891(1), Os(3)–Os(4) 2.885(1) Å] and short [Os(1)–Os(4) 2.842(1), Os(2)–Os(3) 2.825(1) Å] bonds. The hexanuclear metal framework is related to those observed in $[Os_6(\mu_4\text{-S})(\mu\text{-HC}{=}NC_6H_5)_2(CO)_{15}]$ and $[Os_3(CO)_8(\mu_3\text{-S})_2]_2$.[22,23] A novel structural feature of cluster **8** is that a μ_4-oxo atom is embraced in the semi-open environment described by Os(2), Os(4), Os(5) and Os(6) [average Os–O 2.11(1) Å]. The capping modes of μ_3-oxo[24,25] or μ_4-oxo[26] in osmium cluster systems have been reported. Another interesting feature of **8** is the formation of the *ortho*-metallated phenyl ring of the N=CPh_2 units that arises from C–H fission. Complex **8** contains two μ_3 bridging N=CPh_2 groups, which

Table 9 Selected bond lengths (Å) and angles (°) for cluster **8**

Os(1)–Os(2)	2.891(1)	Os(5)–O(17)	2.07(1)
Os(1)–Os(4)	2.842(1)	Os(5)–C(29)	2.06(2)
Os(2)–Os(3)	2.825(1)	Os(6)–N(2)	2.09(1)
Os(2)–Os(4)	2.713(1)	Os(6)–O(17)	2.13(1)
Os(2)–Os(5)	2.862(1)	Os(6)–C(42)	2.03(2)
Os(3)–Os(4)	2.885(1)	N(1)–C(17)	1.30(2)
Os(4)–Os(6)	2.914(1)	N(2)–C(30)	1.29(2)
Os(1)–N(1)	2.10(1)	C(17)–C(18)	1.51(2)
Os(2)–O(17)	2.11(1)	C(17)–C(24)	1.49(2)
Os(3)–N(2)	2.11(1)	C(30)–C(31)	1.49(2)
Os(4)–O(17)	2.13(1)	C(30)–C(37)	1.50(3)
Os(5)–N(1)	2.07(1)		
Os(2)–O(17)–Os(4)	79.7(4)	Os(5)–N(1)–C(17)	114(1)
Os(2)–O(17)–Os(5)	86.6(5)	Os(3)–N(2)–C(30)	131(1)
Os(2)–O(17)–Os(6)	133.8(5)	Os(6)–N(2)–C(30)	114(1)
Os(4)–O(17)–Os(5)	134.4(6)	N(1)–C(17)–C(18)	122(1)
Os(4)–O(17)–Os(6)	86.3(4)	N(1)–C(17)–C(24)	118(1)
Os(5)–O(17)–Os(6)	131.2(6)	N(2)–C(30)–C(31)	125(1)
Os(1)–N(1)–Os(5)	113.3(6)	N(2)–C(30)–C(37)	117(1)
Os(3)–N(2)–Os(6)	113.8(7)	C(18)–C(17)–C(24)	118(1)
Os(1)–N(1)–C(17)	132(1)	C(31)–C(30)–C(37)	116(1)

are derived from the N–O cleavage of the oximato ligands. Each N=CPh$_2$ units bridges to one hinge and one wing-tip osmium *via* the μ$_2$-oximato nitrogen and the phenyl α-carbon [average Os–N 2.09(1), Os–C 2.05(2) Å]. The coordination geometry of the bridging alkylideneimido units in **8** is similar to that in [Ru$_3$(μ-H)$_2$(μ$_3$-N=CPhC$_6$H$_4$)(PPh$_3$)$_2$(CO)$_7$].[27] Assuming that the μ$_4$-O and oxime groups behave as six- and four-electron donors, respectively, then cluster **8** is a 94-electron species, which is consistent with the seven metal–metal bonds observed in the structure according to the EAN rule.

Vacuum pyrolysis of 5

Solid state pyrolysis of the triosmium cluster **5** at 140 °C for 1.5 h yielded the pentanuclear cluster [Os$_5$(CO)$_{15}${μ-η^2-N=CPh(C$_6$H$_4$)}] **9** in 15% yield (Scheme 2). The molecular structure of **9** is shown in Fig. 9 together with the atom-numbering scheme adopted. Bond lengths and interbond angles are listed in Table 10. The metal framework of **9** can be described as an edge-bridged tetrahedron, similar to that observed in [Os$_5$H$_3$(CO)$_{14}$(C$_5$H$_4$N)].[28] The μ-η^2-alkylideneimido ligand is bridged through the nitrogen atom to the bridging Os atom and the apex of the tetrahedron while the α-carbon of the phenyl ring is bonded to the same apex. The angle between the planes formed by Os(1), Os(2), Os(3) and Os(2), Os(3), Os(5) is 162.4°, with Os(5) displaced towards the apical Os(4) atom. The bond lengths between the μ-η^2-alkylideneimido ligand and the metal atoms, Os(4)–C(18), Os(4)–N(1), and Os(5)–N(1), are not significantly different from those observed in **8**. Complex **9** has an electron count of 74, consistent with the cluster having the observed edge-bridged tetrahedral geometry. We have been able to obtain four new clusters upon thermolysis of **5** in refluxing toluene or octane and vacuum pyrolysis. Upon the use of high temperature, C–H activation, N–O cleavage of the oxime ligands and cluster build-up have been observed.

Experimental

Methods and materials

All reactions were carried out under an inert atmosphere of argon using standard Sclenck techniques. Solvents were freshly purified by standard procedures prior to use.[29] Commercial chemicals such as phenyl 2-pyridyl ketoxime and benzophenone oxime were used directly as received. The compounds [Os$_3$(CO)$_{10}$(NCMe)$_2$] and [Os$_3$(CO)$_{11}$(NCMe)] were prepared by the literature methods.[30,31] Infrared spectra were recorded on a Bio-Rad FTS-135 IR spectrometer, using 0.5 mm calcium fluoride solutions cells. ^{1}H NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer using CD$_2$Cl$_2$ with reference to SiMe$_4$. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer by fast atom bombardment techniques, using *m*-nitrobenzyl alcohol as the matrix solvent. Routine purification of products was carried out in air by thin layer chromatography (TLC) on plates coated with Merck Kiesegel 60 GF$_{254}$. Elemental analyses were conducted by Butterworth Laboratories, UK.

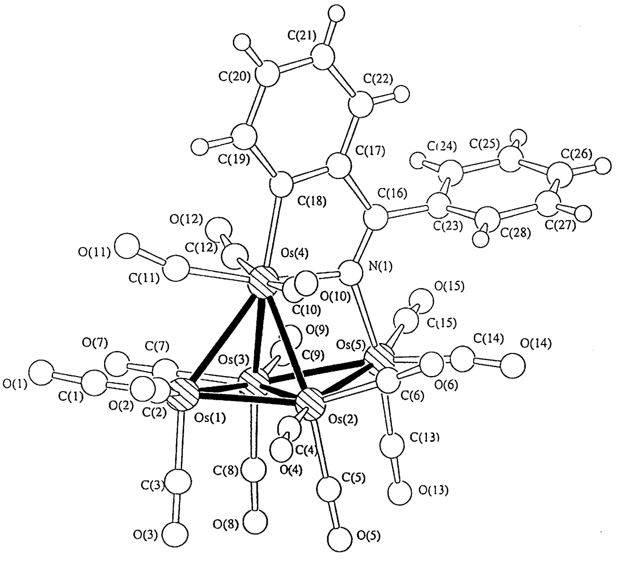


Fig. 9 Molecular structure of [Os$_5$(CO)$_{15}$(μ-η^2-N=CPh(C$_6$H$_4$)}] **9** and the atom numbering scheme.

Table 10 Selected bond lengths (Å) and angles (°) for cluster **9**

Os(1)–Os(2)	2.7528(9)	Os(3)–Os(5)	2.8645(9)
Os(1)–Os(3)	2.7762(9)	Os(4)–N(1)	2.13(1)
Os(1)–Os(4)	2.9180(9)	Os(4)–C(18)	2.11(2)
Os(2)–Os(3)	2.7703(9)	Os(5)–N(1)	2.12(1)
Os(2)–Os(4)	2.8398(9)	N(1)–C(16)	1.30(2)
Os(2)–Os(5)	2.8560(9)	C(16)–C(17)	1.47(3)
Os(3)–Os(4)	2.8453(9)	C(16)–C(23)	1.48(2)
Os(4)–N(1)–Os(5)	110.5(6)	N(1)–C(16)–C(17)	117(1)
Os(4)–N(1)–C(16)	116(1)	N(1)–C(16)–C(23)	121(1)
Os(5)–N(1)–C(16)	133(1)	C(17)–C(16)–C(23)	121(1)

Reactions of triosmium clusters

Reaction of [Os$_3$(CO)$_{11}$(NCMe)] with phenyl 2-pyridyl ketoxime. A solution of [Os$_3$(CO)$_{11}$(NCMe)] (100 mg, 0.109 mmol) in CH$_2$Cl$_2$ was stirred with 1 equiv. of phenyl 2-pyridyl ketoxime (21.6 mg, 0.109 mmol) at room temperature. The reaction mixture gradually changed colour from yellow to deep yellow. The reaction was complete after stirring for 5 h, as monitored by TLC and IR. The reaction solution was concentrated *in vacuo* and separated by TLC using *n*-hexane–CH$_2$Cl$_2$ (1 : 6 v/v) as the eluent to afford a pale orange complex **1** ($R_f \approx 0.50$, 5 mg, 0.004 mmol, 4%) and yellow complex **2** ($R_f \approx 0.20$, 20 mg, 0.019 mmol, 17%). Anal. found for **1**: C, 32.2; H, 1.5; N, 4.5; calc. for C$_{32}$H$_{18}$N$_4$O$_{10}$Os$_3$: C, 32.3; H, 1.5; 1.5; N, 4.7%. Anal. found for **2**: C, 25.5; H, 0.9; N, 2.6; calc. for C$_{23}$H$_{10}$N$_2$O$_{12}$Os$_3$: C, 25.7; H, 0.9; N, 2.6%.

Reaction of [Os$_3$(CO)$_{10}$(NCMe)$_2$] with phenyl 2-pyridyl ketoxime. A solution of [Os$_3$(CO)$_{10}$(NCMe)$_2$] (100 mg, 0.107 mmol) in CH$_2$Cl$_2$ was stirred with 1 equiv. of phenyl 2-pyridyl ketoxime (21.3 mg, 0.107 mmol) at room temperature. An immediate colour change from yellow to dark red was observed. After stirring for 15 min, the solution was concentrated to 5 cm^3 *in vacuo*. Purification was accomplished by TLC using *n*-hexane–CH$_2$Cl$_2$ (2 : 3 v/v) as eluent to afford two bands with $R_f \approx 0.75$ and 0.33, which were extracted from silica to yield complex **1** (11 mg, 0.009 mmol, 8%) and complex **3** (38 mg, 0.037 mmol, 35%), respectively.

Reaction of [Os$_3$(CO)$_{10}$(NCMe)$_2$] with benzophenone oxime. The cluster [Os$_3$(CO)$_{10}$(NCMe)$_2$] (100 mg, 0.107 mmol) and benzophenone oxime (21.1 mg, 0.107 mmol) were allowed to react in CH$_2$Cl$_2$ (30 ml) at room temperature for 5 h to give a deep yellow solution. Evaporation to dryness and separation of the residue by TLC using *n*-hexane–CH$_2$Cl$_2$ (3 : 1 v/v) gave the yellow complex **5** ($R_f \approx 0.50$, 30 mg, 0.029 mmol, 27%). Anal. found: C, 26.4; H, 1.1; N, 1.3; calc. for C$_{23}$H$_{11}$NO$_{11}$Os$_3$: C, 26.4; H, 1.1; N, 1.3%.

Table 11 Crystal data and data collection parameters for compounds **1**–**9**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Empirical formula	$C_{32}H_{18}N_4$-$O_{10}Os_3$	$C_{23}H_{10}N_2$-$O_{12}Os_3$	$C_{21}H_{10}N_2$-$O_{10}Os_3$	$C_{32}H_{20}N_4O_9Os_3\cdot$ $1.5CHCl_3$	$C_{23}H_{11}NO_{11}Os_3$	$C_{22}H_{11}NO_{10}Os_3$	$C_{23}H_{11}NO_{11}Os_3$	$C_{42}H_{18}N_2O_{17}Os_6$	$C_{28}H_9NO_{15}Os_5$
M	1189.11	1076.94	1020.92	1354.20	1047.94	1019.93	1047.94	1963.81	1550.38
Crystal system	Tetragonal	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P4_12_12$ (no. 92)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	13.050(2)	9.982(2)	8.803(2)	12.417(1)	25.233(1)	12.084(1)	10.142(2)	12.960(1)	9.505(2)
b/Å	—	16.596(6)	12.235(1)	15.469(2)	20.658(1)	12.075(1)	10.612(2)	18.167(1)	11.528(3)
c/Å	19.513(1)	8.586(4)	12.380(2)	21.601(2)	10.131(1)	18.003(2)	13.508(1)	18.872(1)	16.272(2)
α/°	—	102.17(3)	81.460(2)	77.57(1)	—	—	97.08(1)	—	85.65(3)
β/°	—	101.34(3)	71.34(1)	82.77(2)	91.60(1)	106.82(2)	99.07(1)	90.67(1)	83.24(1)
γ/°	—	92.27(2)	77.51(2)	82.51(1)	—	—	111.95(2)	—	67.06(2)
U/Å^3	3323.1(6)	1358.4(9)	1228.9(4)	3996.7(8)	5278.9(5)	2514.5(5)	1305.0(5)	4443.0(4)	1629.7(6)
Z	4	2	2	4	8	4	2	4	2
D_c/g cm^{-3}	2.377	2.633	2.759	2.250	2.635	2.694	2.667	2.936	3.159
μ(Mo–Kα)/cm^{-1}	114.98	140.52	155.19	98.64	144.55	151.67	146.20	171.57	194.81
T/K	298	298	298	298	298	298	298	298	298
Reflections collected	20 864	5075	7606	25 032	32 757	15 646	8113	27 603	10 031
Unique reflections	3699	4776	5278	17 331	12 240	5891	5629	10 322	6972
Observed reflections [$I > 1.50\sigma(1)$]	3141	3064	4794	10105	7842	4053	4613	5423	5943
R	0.035	0.039	0.043	0.048	0.052	0.037	0.038	0.051	0.057
R'	0.038	0.042	0.055	0.045	0.050	0.039	0.046	0.046	0.070

Transformations of oxime containing osmium clusters

Attempted thermolysis and hydrogenation of complex 1. Complex **1** (50 mg, 0.042 mmol) was dissolved in toluene (30 ml). The orange solution was heated at 125 °C. Using IR and spot TLC monitoring, no visible change was observed after 2 days.

Complex **1** (50 mg, 0.042 mmol) was dissolved in $CHCl_3$ (20 ml). Hydrogenation of the pale orange solution at atmospheric pressure was then attempted under reflux at 65 °C for 5 h. The reaction was monitored by IR spectroscopy and spot TLC. However, no change was observed. About 90% of the starting material was recovered upon separation on preparative silica plates.

Thermolysis of complex 2. Complex **2** (50 mg, 0.046 mmol) was refluxed in toluene under an inert atmosphere. The reaction was monitored by TLC and IR and completed after 3 h. The solvent was then removed *in vacuo* and redissolved in CH_2Cl_2 (3 cm^3). TLC purification with *n*-hexane–CH_2Cl_2 (1 : 1 v/v) gave an orange complex **3** ($R_f \approx 0.70$, 6 mg, 0.006 mmol, 13%) and unreacted starting material **2** ($R_f \approx 0.10$, 3 mg, 0.003 mmol, 7%). Anal. found for **3**: C, 24.5; H, 1.0; N, 2.6; calc. for $C_{21}H_{10}N_2O_{10}Os_3$: C, 24.7; H, 1.0; N, 2.7%.

Thermolysis of complex 3 with phenyl 2-pyridyl ketoxime. Complex **3** (50 mg, 0.049 mmol) and phenyl 2-pyridyl ketoxime (10 mg, 0.049 mmol) were stirred at reflux in toluene (30 ml) for 1.5 h. The colour gradually turned from orange to dark red. The reaction mixture was evaporated to dryness. The residue was finally redissolved in CH_2Cl_2 (*ca.* 2 cm^3) and separated by preparative TLC with an eluent of *n*-hexane–CH_2Cl_2 (1 : 2 v/v) to give complex **1** ($R_f \approx 0.80$, 7 mg, 0.006 mmol, 12%) and pale red complex **4** ($R_f \approx 0.60$, 9 mg, 0.008 mmol, 16%). Anal. found for **4**: C, 32.8; H, 1.7; N, 4.9; calc. for $C_{32}H_{20}N_4O_9Os_3$: C, 32.7; H, 1.7; N, 4.7%.

Thermolysis of complex 5 in toluene. Complex **5** (50 mg, 0.048 mmol) was dissolved in toluene and the yellow solution was allowed to heat under reflux for 6 h. The reaction mixture changed colour to deep yellow gradually. The solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (3 cm^3) and separated by preparative TLC with *n*-hexane–CH_2Cl_2 (3 : 1 v/v) to yield yellow complex **6** ($R_f \approx 0.38$, 13 mg, 0.013 mmol, 27%) and yellow complex **7** ($R_f \approx 0.15$, 10 mg, 0.010 mmol, 21%). Anal. found for 6: C, 26.3; H, 1.0; N, 1.3; calc. for $C_{23}H_{11}NO_{11}Os_3$: C, 26.4; H, 1.1; N, 1.3%. Anal. found for **7**: C, 25.7; H, 1.1; N, 1.31; calc. for $C_{22}H_{11}NO_{10}Os_3$: C, 25.9; H, 1.1; N, 1.4%.

Thermolysis of complex 5 in octane. Cluster **5** (50 mg, 0.048 mmol) was refluxed in octane. The colour gradually turned dark brown. The reaction was monitored by TLC and IR and completed after 1 h. The solvent was then removed *in vacuo* and the solid residue redissolved in CH_2Cl_2 (3 cm^3). TLC purification with *n*-hexane–CH_2Cl_2 (1 : 1 v/v) afforded **8** ($R_f \approx 0.85$, 6 mg, 0.003 mmol, 6%). Anal. found: C, 25.7; H, 1.0; N, 1.4; calc. for $C_{42}H_{18}N_2O_{17}Os_6$: C, 25.7; H, 0.9; N, 1.4%.

Vacuum pyrolysis of complex 5. A concentrated CH_2Cl_2 solution (4 cm^3) of **5** (50 mg, 0.048 mmol) was introduced into a Carious tube. The solvent was removed under reduced pressure and the tube was sealed after being dried. The tube was then placed in a furnace at 140 °C for 1.5 h. The dark brown residue was extracted exhaustively with CH_2Cl_2 and the combined extracts, after concentration, were subjected to preparative TLC separation. Elution with *n*-hexane–CH_2Cl_2 (1 : 1 v/v) afforded complex **9** ($R_f \approx 0.50$, 11 mg, 0.007 mmol, 15%). Anal. found: C, 21.6; H, 0.5; N, 0.9; calc. for $C_{28}H_9NO_{15}Os_5$: C, 21.7; H, 0.6; N, 0.9%.

Crystallography

Crystals suitable for X-ray analyses were glued on glass fibres with epoxy resin or sealed in a 0.3 mm glass capillary. Intensity data were collected at ambient temperature on either a Bruker AXS SMART CCD diffractometer (complexes **1**, **3**–**9**) or a Rigaku AFC7R diffractometer (complex **2**) equipped with graphite-monochromated Mo-Kα radiation. Details of the intensity data collection and crystal data are given in Table 11. The diffracted intensities were corrected for Lorentz-polarization effects. Absorption corrections were applied by SADABS for **1** and **3**–**9**,[32] while the Ψ-scan method was employed for semi-empirical absorption corrections in the case of **2**.[33] All structures except complex **3** (by heavy-atom Patterson methods, SAPI91[34]) were solved by direct methods (SHELXS 86[35] for **1**, **6**; SIR 92[36] for **2**, **4**, **5**, **7**–**9**) and expanded by Fourier difference techniques.[37] Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on *F*, with the osmium atoms and non-hydrogen atoms being refined anisotropically. However, attempts to refine all the atoms anisotropically were made in structures **4**, **8** and **9**, but led to negative anisotropic displacement parameters. Therefore some non-hydrogen atoms were refined isotropically. Hydrogen atoms were generated in their ideal positions and included in the structure factor calculations but not refined. Calculations were performed on a Silicon Graphics computer using the teXsan[38] crystallographic software package.

CCDC reference numbers 174851–174859. See http://www.rsc.org/suppdata/nj/b1/b107628k/ for crystallographic data in CIF or other electronic format.

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References

1 T. Carofiglio, S. Stella, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1989, 1957.

2 C. M. P. Ferreira, M. F. C. G. Silva, V. Y. Kukushkin, J. J. R. F. Silva and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 1998, 325.

3 V. Y. Kukushkin, D. Tudela and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1996, **156**, 333.

4 V. Y. Kukushkin and A. J. L. Pombeiro, *Coord. Chem. Rev.*, 1999, **181**, 147.

5 A. K. Das, S. M. Peng and S. Bhattacharya, *J. Chem. Soc., Dalton Trans.*, 2000, 181.

6 V. Y. Kukushkin, D. Tudela, Y. A. Izotova, V. K. Belsky and A. I. Stash, *Inorg. Chem.*, 1996, **35**, 4926.

7 M. L. Kuznetsov, N. A. Bokach, V. Y. Kukushkin, T. Pakkanen, G. Wagner and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2000, 4683.

8 A. J. Deeming, D. W. Owen and N. I. Powell, *J. Organomet. Chem.*, 1990, **398**, 299.

9 M. H. Chao, S. Kumaresan, Y. S. Wen, S. C. Lin, J. R. Hwu and K. L. Lu, *Organometallics*, 2000, **19**, 714.

10 K. K. H. Lee and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1996, 3911.

11 R. D. Adams and B. Qu, *Organometallics*, 2000, **19**, 2411.

12 M. A. Gallop, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Commun.*, 1986, 706.

13 D. B. Firfiray, A. Irving and J. R. Moss, *J. Chem. Soc., Commun.*, 1990, 377.

14 K. L. Lu, M. L. Chung, P. Y. Lu, H. M. Gau, F. E. Hong and Y. S. Wen, *Organometallics*, 1994, **13**, 3177.

15 K. K. H. Lee and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1997, 2987.

16 R. G. Buckley, J. Charalambous, M. J. Kensett, M. McPartlin, P. Mukerjee, E. G. Brain and J. M. Jenkins, *J. Chem. Soc., Perkin Trans. 1*, 1983, 693.

17 J. Charalambous, W. C. Stolen and K. Henrick, *Polyhedron*, 1989, **8**, 103.

18 M. Tachikawa and J. R. Shapley, *J. Organomet. Chem.*, 1977, **124**, C19.

19 J. R. Shapley, D. E. Samkoff, C. Bueno and M. R. Churchill, *Inorg. Chem.*, 1982, **21**, 634.

20 C. Bois, J. A. Cabeza, R. J. Franco, V. Riera and E. Saborit, *J. Organomet. Chem.*, 1998, **564**, 201.

21 J. A. Cabeza, I. del Río, M. Moreno and V. Riera, *Organometallics*, 1998, **17**, 3027.

22 R. D. Adams, Z. Dawoodi, D. F. Foust and B. E. Segmüller, *J. Am. Chem. Soc.*, 1983, **105**, 831.

23 R. D. Adams and I. T. Horváth, *J. Chem. Soc.*, 1984, **106**, 1869.

24 R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1983, 246.

25 K. S. Y. Leung and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1997, 4357.

26 S. L. Ingham, J. Lewis and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1993, 166.

27 P. L. Andreu, J. A. Cabeza, I. del Río and V. Riera, *Organometallics*, 1996, **15**, 3004.

28 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. A. Pearsall, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1987, 327.

29 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 3rd edn., 1998.

30 J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1989, **28**, 232.

31 M. R. Churchill, F. J. Hollander and J. P. Hutchison, *Inorg. Chem.*, 1977, **6**, 2697.

32 R. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.

33 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

34 H. F. Fan, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan, 1991.

35 G. M. Sheldrick, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, Oxford, UK, 1985, p. 175.

36 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, G. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 437.

37 B. T. Beurskens, G. Admiroal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *Technical Report of the Crystallographic Laboratory*, University of Nijmegen, The Netherlands, 1994.

38 teXsan, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, USA, 1985 and 1992.