

Two isomeric products $[\text{Os}_3(\mu\text{-H})(\text{C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$ formed by orthometallation of the cluster $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$ containing the chelating ligand 2,3-bis(2-pyridyl)pyrazine

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Abstract

Treatment of the labile compound $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ with 2,3-bis(2-pyridyl)pyrazine ($\text{C}_{14}\text{H}_{10}\text{N}_4$) in dichloromethane at room temperature gave the cluster $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$ (**1**), which contains the chelating ligand co-ordinated axially through one of the pyridine rings and equatorially through a pyrazine nitrogen atom while one of the pyridine rings remains unco-ordinated. Thermolysis of **1** leads to loss of CO and yields two structural isomers of $[\text{Os}_3(\mu\text{-H})(\mu,\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$ (**2**) and (**3**). Isomer **2** contains an orthometallated 2-pyridyl group and a co-ordinated 2-pyridyl which is not orthometallated. A seven-membered chelate ring is formed and the pyrazine ring is uncoordinated. On the other hand, isomer **3** contains a 2-pyridyl-1,4-pyrazine fragment metallated in the pyrazine ring to form a five-membered chelate ring with the one pyridine ring remaining unco-ordinated. The molecular structures of **1–3** were confirmed by X-ray crystallographic studies.

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1. Introduction

There is currently much interest [1] in photophysical and photochemical properties of transition metal complexes linked together by bridging ligands, commonly nitrogen-containing aromatic heterocycles [2]. Such complexes can exhibit metal–metal interactions, where the bridging ligand may mediate electronic communication between the metal atoms [3]. The communication between metal centres generally takes place via the ligand π -system, and strong MLCT commonly present in

poly-pyridine complexes is believed to be potentially useful in generating nonlinear optics.

We are generally interested in the interaction of π -delocalised aromatic ligands with metal clusters, believing that the combination of metal clusters and polycyclic aromatics would produce novel systems with interesting electronic properties. Here, we wish to report the synthesis and characterization of new complexes of osmium derived from interaction of the labile trinuclear cluster $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ with the ligand 2,3-bis(2-pyridyl)pyrazine, which has the potential to chelate, bridge, orthometallate and to combine with more than one cluster since it has four donor nitrogen atoms.

Various oxidative additions involving polynuclear metal carbonyl systems have been studied in the last

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few years [3]. The α -diimine ligands (1,4-disubstituted-1,4-diaza-1,3-butadienes = R-DBA) in trimetallic clusters adopt various coordination modes by bridging metal centres: σ, σ - N, N chelating, σ - N, μ_2 - N' , η^2 - $C \equiv N$ and σ, σ - N, N' , η^2, η^2 - $C \equiv N, C \equiv N'$ [4]. Pyridine-2-carbaldimines (6- RC_5H_3N -2- $CH=NR$ abbreviated to R-Pyca) react with $[Os_3(CO)_{10}(CH_3CN)_2]$ to yield two isomers formulated as $[Os_3(CO)_{10}(R-Pyca)]$, with different ligand co-ordination modes, the ligands donating 4 and 6 electrons, respectively. Thermolysis of these compounds gives $[Os_3(\mu-H)(C_5H_3N-2-CH=N-iPr)(CO)_9]$ and $[Os_2(CO)_6(R-Pyca)]$, with ligands donating 5 and 6 electrons, respectively [5]. The triosmium cluster $[Os_3(CO)_{12}]$ reacts at high temperatures [6] and more reactive ones like $[Os_3(CO)_{10}L_2]$ (L = cyclooctene [7,8] or CH_3CN [8]) react at room temperature with pyridine by orthometallation to give the μ -2-pyridyl cluster $[Os_3H(\mu-2-C_5H_4N)(CO)_{10}]$ and related species. 2-Alkyl-substituted pyridines react with $[Os_3(CO)_{10}(L)_2]$ (L = cyclooctene) to yield the same type of product $[Os_3H(\mu-2-RC_5H_3N)(CO)_{10}]$ (R = Me, $PhCH_2$) [7], while diazines react with $[Os_3(CO)_{12}]$ to give the related complex $[Os_3H(C_4H_3N_2)(CO)_{10}]$ [7]. The treatment of 2,2'-bipyridyl with $[Os_3(CO)_{12}]$ leads to the complex $[Os_3H(C_{10}H_7N_2)(CO)_9]$ [7], which contains the chelating/bridging orthometallated bipy ligand. The interaction of 2,3-bis(2-pyridyl)pyrazine with the labile compound $[Re_2(CO)_8(CH_3CN)_2]$ [9] gives the complexes $[Re_2(C_{14}H_{10}N_4)(CO)_8]$ and $[Re_2(CO)_8(\mu-C_{14}H_{10}N_4)Re_2(CO)_8]$, this latter compound contains the 2,3-bis(2-pyridyl)pyrazine ligand σ, σ - N, N -coordinated to each dinuclear rhenium group.

In this article, we describe the isolation and characterization of the two isomeric triosmium clusters $[Os_3(\mu-H)(\mu:\eta^3-C_{14}H_9N_4)(CO)_9]$ **2** and **3** formed as thermolysis products of the cluster $[Os_3(C_{14}H_{10}N_4)(CO)_{10}]$ **1**, itself obtained by treatment of $[Os_3(CO)_{10}(CH_3CN)_2]$ with 2,3-bis(2-pyridyl)pyrazine. Our initial objective of linking two triosmium clusters in the way that two dirhenium units were linked remains unfulfilled.

2. Experimental

All reactions were carry out under dried and purified nitrogen. Solvents were purified by standard procedures and distilled prior to use [10]. The cluster $[Os_3(CO)_{10}(CH_3CN)_2]$ was prepared by known methods [11]. 2,3-bis(2-pyridyl)pyrazine was obtained from Aldrich and used as supplied. Reactions were monitored by FTIR in the range 2200–1750 cm^{-1} and products were separated by TLC (SiO_2 , Merck 60 HF_{254}). FTIR spectra were recorded on a Nicolet 5DXC FTIR spectrometer, using 0.5 mm calcium fluoride solution cells. 1H NMR spectra were obtained using a Bruker 300 MHz spectrometer. Crystals for X-ray diffraction analy-

sis were obtained by slow evaporation of saturated dichloromethane-cyclohexane solutions (1:3 by volume).

2.1. Treatment of $[Os_3(CO)_{10}(CH_3CN)_2]$ with 2,3-bis(2-pyridyl) pyrazine: synthesis of the complex $[Os_3(C_{14}H_{10}N_4)(CO)_{10}]$ **1**

The cluster $[Os_3(CO)_{10}(CH_3CN)_2]$ (0.200 g, 0.214 mmol) was added to a solution of 2,3-bis(2-pyridyl)pyrazine (0.050 g, 0.214 mmol) in dichloromethane (50 cm^3). The yellow solution turned deep blue within minutes. After the solution was stirred for 3 h at room temperature, the solvent was removed under reduced pressure and the residue separated by TLC, eluting with dichloromethane:*n*-hexane (8:2 by volume) to give the cluster $[Os_3(C_{14}H_{10}N_4)(CO)_{10}]$ **1** (0.195 g, 84%). Complex **1** was derived from blue solutions and dissolves to give blue solutions but was obtained as orange crystals after recrystallization from dichloromethane/cyclohexane (1:3 by volume). XRD studies were carried out on an orange crystal. Anal. Found for **1**: C, 26.57; H, 0.93; N, 5.16%. Calc. for $C_{24}H_{10}N_4O_{10}Os_3$: C, 26.03; H, 1.00; N, 5.05.

2.2. Thermal treatment of $[Os_3(\eta^1:\eta^1-C_{14}H_{10}N_4)(CO)_{10}]$ (**1**)

A solution of compound **1** (0.100 g, 0.092 mmol) in octane (30 cm^3) was heated under reflux for 3 h. The solvent was removed under reduced pressure and TLC of the residue (eluent: dichloromethane:*n*-hexane, 7:3 by volume) gave two compounds: yellow cluster **2** (0.051g, 52%) and red cluster **3** (0.039 g, 40%), both of which are formulated as $[Os_3(\mu-H)(\mu:\eta^3-C_{14}H_9N_4)(CO)_9]$. For XRD analysis, **2** and **3** were obtained as yellow and red crystals, respectively, from dichloromethane-cyclohexane mixtures (1:3 by volume). Anal. Found for **2**: C, 26.45; H, 1.01; N, 5.14%. Calc. for $C_{23}H_{10}N_4O_9Os_3$: C, 26.14; H, 0.95; N, 5.30. Anal. Found for **3**: C, 26.71; H, 1.03; N, 5.12%. Calc. for $C_{23}H_{10}N_4O_9Os_3$: C, 26.14; H, 0.95; N, 5.30.

2.3. X-ray crystal structure determinations for compounds **1–3**

Single crystals of compounds **1–3** were mounted on glass fibers and all geometric and intensity data were obtained on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $295 \pm 2 \text{ K}$ for **1** and $150 \pm 2 \text{ K}$ for **2** and **3**. Data reduction and integration was carried out with SAINT+ and absorption corrections were applied using the programme SADABS [12,13]. Structures were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were

refined anisotropically. Hydrogen atoms, except those bonded to osmium, were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Hydrogen atoms bridging the osmium atoms were located and their positions refined using fixed isotropic thermal parameters. The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [14] see Table 1.

3. Results and discussion

The general synthetic route to the osmium derivatives 1–3 is depicted in Scheme 1. Treatment of $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ with 2,3-bis(2-pyridyl)pyrazine in dichloromethane solution at room temperature affords compound $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$ **1** in quite good yield (84%). Although crystals of **1** were obtained from blue solutions and redissolving gave blue solutions, the crystals are orange and XRD work was carried out on these orange crystals. We are uncertain about the nature of the blue solute. Our next objective was to obtain a compound in which the organic ligand is coordinated to two triosmium subunits. By treating compound **1** with an excess of $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ in dichloromethane solu-

tion, we hoped to link another Os_3 unit to the two non co-ordinated nitrogen atoms in **1**. Unfortunately, this treatment which was carried out at room temperature and up to reflux temperature, did not lead to any product of the expected type. However, applying forcing conditions, we obtained clusters **2** and **3**, in which orthometallation of a pyridine ring and the pyrazine ring have occurred, respectively, by heating a solution of **1** in refluxing octane (125 °C). The structural isomers **2** and **3** of molecular formula $[\text{Os}_3(\mu\text{-H})(\mu:\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$ were separated by TLC and characterized by the ^1H NMR and IR data shown in Table 2. Single-crystal structure determinations were also carried out on the two isomers. Furthermore treatment of clusters **2** and **3** with an excess of $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ did not lead to cluster-linked products so our initial objective of linking two Os_3 clusters was not achieved.

3.1. Complex $[\text{Os}_3(\text{C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$ (**1**)

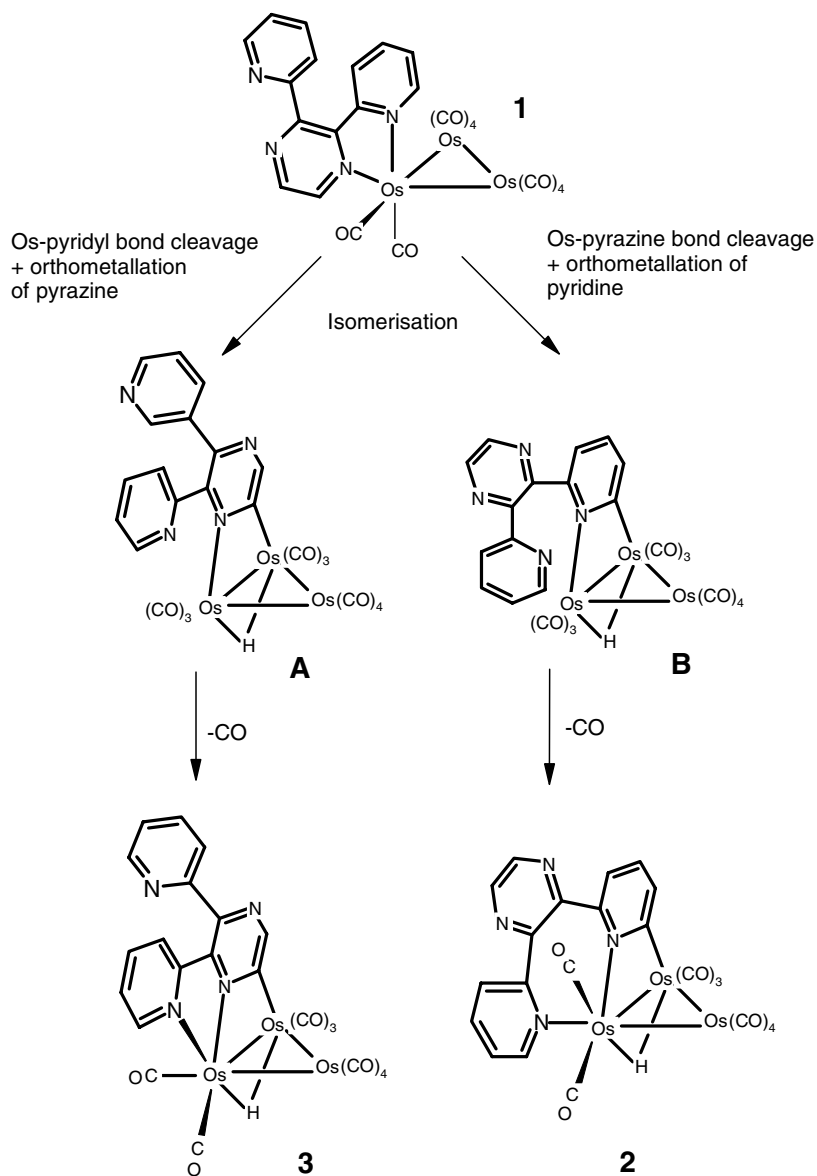
The IR spectrum of **1** around 2000 cm^{-1} revealed a pattern resembling that of $[\text{Os}_3(\text{CO})_{10}(\text{iPr-DAB})]$ [4], the structure of which has been determined by X-ray diffraction. The ^1H NMR spectrum of **1** exhibits two doublets ($\delta = 9.36$ and 8.66) assigned to the pyrazinic protons, and eight different signals in the aromatic

Table 1

Crystal data, data collection and refinement parameters for compounds $[\text{Os}_3(\eta^2\text{-C}_{14}\text{H}_{10}\text{N}_4)(\text{CO})_{10}]$ **1** and $[\text{Os}_3(\mu\text{-H})(\mu:\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$, isomers **2** and **3**

	1	2	3 cyclohexane
Formula	$\text{C}_{24}\text{H}_{10}\text{N}_4\text{O}_{10}\text{Os}_3$	$\text{C}_{23}\text{H}_{10}\text{N}_4\text{O}_9\text{Os}_3$	$\text{C}_{29}\text{H}_{22}\text{N}_4\text{O}_9\text{Os}_3$
<i>M</i>	1084.96	1056.95	1141.11
Crystal size (mm ³)	$0.39 \times 0.19 \times 0.01$	$0.23 \times 0.14 \times 0.06$	$0.41 \times 0.39 \times 0.29$
Colour	Dark red	Yellow	red
Temperature (K)	295 ± 2	150 ± 2	150 ± 2
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
<i>a</i> (Å)	13.6146(9)	9.3649(6)	9.0074(13)
<i>b</i> (Å)	8.5617(6)	10.6368(7)	12.7261(18)
<i>c</i> (Å)	23.5416(16)	14.8754(10)	13.797(2)
α (°)	90	77.7350(10)	81.909(2)
β (°)	104.7800(10)	72.7380(10)	80.417(2)
γ (°)	90	66.1240(10)	87.674(2)
<i>V</i> (Å ³)	2653.3(3)	1286.69(15)	1543.7(4)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	2.716	2.728	2.455
<i>F</i> (000)	1960	952	1048
2 θ Range (°)	1.55–28.31	3.42–49.98	1.51–28.26
μ (mm ⁻¹)	14.395	14.835	12.375
Reflections measured	22702	11288	13427
Independent reflections [<i>R</i> (int)]	6359 [0.0661]	5949 [0.0342]	7040 [0.0238]
Data/restraints/param.	6359/0/370	5949/2/356	7040/0/410
Goodness-of-fit on <i>F</i> ²	1.014	1.082	1.099
Final <i>R</i> index [<i>F</i> ² > 2 σ]	$R_1 = 0.0432$, $wR_2 = 0.0959$	$R_1 = 0.0411$, $wR_2 = 0.1045$	$R_1 = 0.0267$, $wR_2 = 0.0608$
<i>R</i> index (all data)	$R_1 = 0.0575$, $wR_2 = 0.1032$	$R_1 = 0.0429$, $wR_2 = 0.1063$	$R_1 = 0.0293$, $wR_2 = 0.0619$
Index ranges	<i>h</i> –18/18, <i>k</i> –11/11, <i>l</i> –31/31	<i>h</i> –12/12, <i>k</i> –13/13, <i>l</i> –19/19	<i>h</i> –11/11, <i>k</i> –15/16, <i>l</i> –18/18
Max. peak/hole (e Å ⁻³)	1.851 and –1.854	3.649 and –5.951	2.528 and –1.976

For all three structures: Mo K α radiation; $\lambda = 0.71073$ Å, refinement by full-matrix least-squares on *F*².



Scheme 1.

region associated to two different pyridine systems. This indicates that the molecular structure of **1** is likely to involve a 4e-donating σ, σ - N, N' -bonded bis(2-pyridyl)pyrazine ligand and, by analogy with the known structure of $[\text{Os}_3(\text{CO})_{10}(\text{iPr-DAB})]$, one nitrogen is co-ordinated axially and the other equatorially. The crystal structure (Fig. 1 with some lengths and angles in Table 3) confirmed that one nitrogen was coordinated axially (one of the two pyridyl nitrogen atoms) and an equatorial site is occupied by a pyrazine nitrogen atom. The remaining pyridyl is uncoordinated. The structure has no surprising features. The axial CO ligands in $[\text{Os}_3(\text{CO})_{12}]$ and related compounds have longer Os–C bonds than the equatorial CO ligands because of competitive π -bonding effects between mutually *trans* ligands. This effect is also found for the $\text{Os}(\text{CO})_4$ groups in **1**. As expected the axial

CO ligand *trans* to the co-ordinated nitrogen atom N(1) does not show this effect and has in fact the shortest Os–C bond in the cluster [1.856(8) Å], compared with the other axial Os–CO distances [1.947(9), 1.960(10), 1.922(8) and 1.954(9) Å] and the equatorial Os–CO distances [1.878(8), 1.894(9), 1.897(9), 1.900(9) and 1.876(11) Å]. The CO *trans* to nitrogen has favorable π -back bonding. The bidentate ligand shows considerable deviation from planarity. It was expected that the non-coordinated pyridyl group should rotate to minimise unfavourable interactions and the torsional angle C(46)C(47)C(50)N(4) is 43.3(13)° but there is also considerable twisting in the coordinated part of the ligand with the torsional angle C(45)C(46)C(47)C(50) 25.8(14)° and N(1)C(45)C(46)C(47) 171.7(8)°. The pyrazine ring is far from planar as a result (Fig. 1).

Table 2
IR and NMR data for compounds 1–3

Compound	$\nu(\text{CO})^a$ (cm^{-1})		^1H NMR b δ	$J_{\text{H-H}}$ (Hz)	
[Os ₃ (C ₁₄ H ₁₀ N ₄)(CO) ₁₀] 1	2090m	2044 m	9.39 (d, H _a)	ab 3.3	ji 5.9
	2014vs	2000s	8.66 (d, H _b)	cd 4.7	jh 1.3
	1982m	1963m	8.61 (ddd, H _c)	ce 1.5	ig 0.8
	1950 m	1914m	7.62 (ddd, H _d)	cf 0.9	ih 7.2
			7.78 (ddd, H _e)	de 7.6	ig 1.3
			8.06 (dt, H _f)	df 1.1	hg 8.0
			7.37 (dt, H _g)	fe 7.8	
			8.15 (ddd, H _h)		
			7.53 (ddd, H _i)		
			9.60 (d H _j)		
[Os ₃ (μ -H)(μ : η^3 -C ₁₄ H ₉ N ₄)(CO) ₉] 2	2090m	2068m	9.88 (ddd, H _c)	ab 2.5	df 1.6
	2046s	2035m	9.00 (d, H _a)	cd 5.8	ef 7.7
	2012vs	2005s	8.98 (d, H _b)	ce 1.5	gh 7.7
	1994m	1976w	7.68 (ddd, H _d)	cf 0.7	gi 1.4
	1967w	1935 w	8.27 (td, H _e)	de 7.7	hi 7.7
			7.93 (ddd, H _f)		
			7.60 (dd, H _g)		
			7.49 (t, H _h)		
			7.27 (dd, H _i)		
			−13.00 (s, H _j)		
[Os ₃ (μ -H)(μ : η^3 -C ₁₄ H ₉ N ₄)(CO) ₉] 3	2085s	2045s	8.53 (s, H _b)	cd 4.8	gi 1.4
	2009vs	1990m	8.72 (ddd, H _c)	ce 1.8	gh 8.4
	1978m	1966m	7.64 (ddd, H _d)	cf 0.9	gj 0.7
	1947 m		8.15 (td, H _e)	de 7.7	hi 7.5
			7.98 (m, H _f , H _h)	df 1.4	ij 5.7
			7.73 (ddd, H _g)	ef 7.7	
			7.62 (ddd, H _i)		
			9.38 (ddd, H _j)		
		−20.70 (s, H _a)			

^a In C₆H₁₂.

^b In CD₃COCD₃, 298 K.

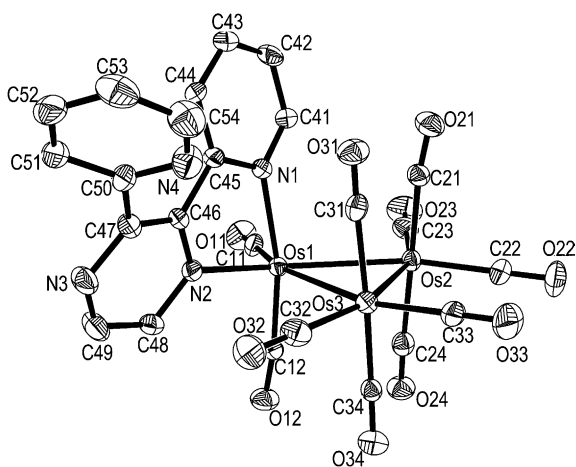


Fig. 1. ORTEP view (30% probability, H atoms omitted for clarity) of the molecular structure of complex [Os₃(C₁₄H₁₀N₄)(CO)₁₀] **1** in the crystal.

3.2. Isomer [Os₃(μ -H)(μ : η^3 -C₁₄H₉N₄)(CO)₉] (**2**)

The ^1H NMR spectrum shows two doublets corresponding to pyrazinic protons and signals in the aromatic region integrating for seven rather than eight

Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for [Os₃(η^2 -C₁₄H₁₀N₄)(CO)₁₀] **1**

Os1–Os2	2.8359(5)	Os3–C32	1.876(11)
Os2–Os3	2.8835(4)	Os3–C33	1.900(9)
Os1–Os3	2.8876(4)	Os3–C34	1.922(8)
Os1–N1	2.152(6)	Os3–Os1–N1	94.97(16)
Os1–N2	2.095(7)	Os2–Os1–N1	98.35(17)
Os1–C11	1.878(8)	Os3–Os1–N2	93.01(18)
Os1–C12	1.856(8)	Os2–Os1–N2	152.34(17)
Os2–C21	1.947(9)	Os1–N1–C45	116.1(5)
Os2–C22	1.897(9)	N1–C45–C46	114.1(7)
Os2–C23	1.894(9)	C45–C46–N2	113.2(8)
Os2–C24	1.960(10)	C46–N2–Os1	117.6(5)
Os3–C31	1.954(9)	N1–Os1–N2	74.6(2)

protons for two pyridine rings. The loss of one pyridinic proton and a singlet at $\delta = -13.00$ for a bridging hydride indicates that one of the pyridine rings has been orthometalated.

The molecular structure of **2** was determined by a single-crystal X-ray study. The solid-state molecular structure of **2** is illustrated in Fig. 2 and selected bond distances and angles are given in Table 4. The molecular structure of **2** is the same as shown in Scheme 1. Atom

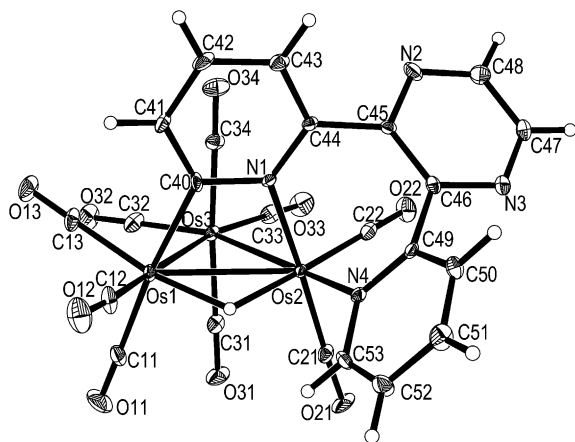


Fig. 2. ORTEP view (30% probability ellipsoids) of the molecular structure of cluster $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$ isomer **2** in the crystal.

Table 4
Selected bond lengths (Å) and angles (°) for $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$, isomer **2**

Os1–Os2	2.9377(4)	C41–Os1–Os2	67.69(17)
Os2–Os3	2.8266(3)	C40–Os1–Os3	87.30(16)
Os1–Os3	2.8793(4)	N1–Os2–Os1	68.63(14)
Os1–C40	2.106(7)	N1–Os2–Os3	88.53(14)
N1–C40	1.363(8)	N4–Os2–Os1	108.38(14)
Os2–N1	2.126(5)	N4–Os2–Os3	166.96(14)
N1–C44	1.364(8)	C44–N1–Os2	128.6(4)
C44–C45	1.487(9)	C49–N4–Os2	123.2(4)
C45–C46	1.398(9)	N1–C40–Os1	113.6(5)
C46–C49	1.493(9)	C40–N1–Os2	110.0(4)
N4–C49	1.348(8)	N1–C44–C45	117.9(6)
Os2–N4	2.168(5)	N4–C49–C46	120.6(5)

Os(3) is linked to four terminal CO, Os(2) is linked to two CO and the nitrogen atoms of pyridine rings [Os(2)–N(1) = 2.126(5) Å and Os(2)–N(4) = 2.168(5) Å], while Os(1) is linked to three CO and a carbon atom of the orthometallated pyridine [Os(1)–C(40) = 2.106(7) Å]. Consequently, the seven-membered chelate ring, Os(2)N(4)C(49)C(46)C(45)C(44)N(1), at Os(2) is fused with the four-membered metalocycle ring Os(1)–Os(2)N(1)C(40). The hydride ligand is normally found to bridge the same Os–Os bond as the orthometallated pyridine, and this is the case here. The hydride ligand was located from the XRD data and this was substantiated by the Os–Os distances, the longest being associated with the bridging hydride [Os(1)–Os(2) = 2.9377(4) Å, Os(2)–Os(3) = 2.8266(3) Å and Os(1)–Os(3) = 2.8793(4) Å]. Complex **2** is of interest, since to the best of our knowledge it is first example of a Os₃ cluster that contains an orthometallated pyridine ligand system that is also part of a seven-membered chelate ring. Note that the non-metallated pyridine ring is co-ordinated equatorially *trans* the Os(2)–Os(3) bond. This allows the 7-membered ring to fold considerably

to reduce strain that co-ordination in any other position would require.

3.3. Isomer $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_{10}]$ (**3**)

The $\nu(\text{CO})$ absorption spectrum of **3** shows only terminal CO and its pattern resembles those of $[\text{Os}_3(\mu\text{-H})(\text{C}_5\text{H}_3\text{N}\text{-}2\text{-CH=N}^i\text{-Pr})(\text{CO})_9]$ [**5a**] and $[\text{Os}_3(\mu\text{-H})(\text{C}_{10}\text{H}_7\text{N}_2)(\text{CO})_9]$ [**7**]. The ¹H NMR spectrum exhibits signals for eight protons assigned to pyridinic rings, a singlet at δ 8.53 for the pyrazine ring and at δ –20.70 for a bridging hydride Os–H–Os. This supports metallation of the pyrazine ring with one pyridine co-ordinated and the other free.

The X-ray structure is shown in Fig. 3 and selected bond lengths and angles are in Table 5. Cluster **3** is related to $[\text{Os}_3\text{H}(\mu\text{-C}_5\text{H}_4\text{N})(\text{CO})_{10}]$ [**6**] and $[\text{Os}_3\text{H}(\mu\text{-C}_5\text{H}_3\text{N})(\text{CO})_{10}]$ [**7**]. The organic ligand forms a chelate by means of nitrogen atoms of a pyridine and a pyrazine ring, respectively, [Os(2)–N(2) = 2.103(4) Å and Os(2)–N(1) = 2.033(4) Å]. In this case a 5-membered chelate ring Os(2)N(2)C(45)C(44)N(1) is fused to a 4-membered ring, Os(1)C(41)N(1)Os(2) through the σ -bond [Os(1)–C(41) = 2.111(5) Å] formed by metallation of pyrazine ring. The two non-bridged Os–Os bonds are the same length, 2.8887(4) and 2.8844(4) Å, while the bridged Os–Os bond is rather longer 2.9143(4) Å. The hydride, located in the structure determination, bridges the longest Os–Os bond. Note that in contrast to isomer **2**, the pyridine is co-ordinated axially at Os(2) and *trans* to the metal hydride.

Scheme 1 shows unobserved intermediates **A** and **B** which we suggest are formed in the conversion of **1**

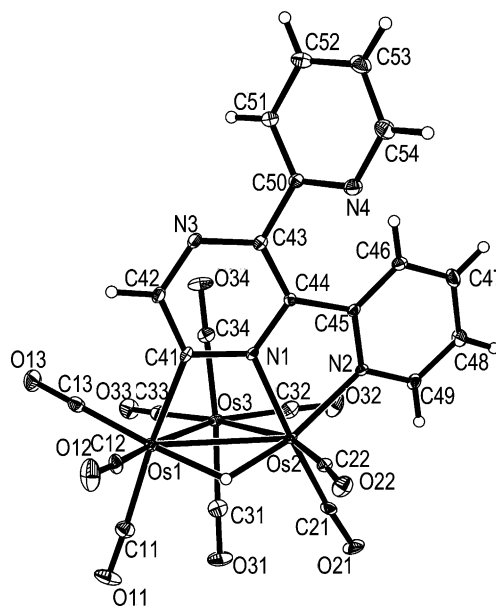


Fig. 3. ORTEP view (30% probability ellipsoids) of the molecular structure of cluster $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$ isomer **3** in the crystal.

Table 5
Selected bond lengths (Å) and angles (°) for $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^3\text{-C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9]$, isomer **3**

Os1–Os2	2.9143(4)	C41–Os1–Os2	67.64(13)
Os2–Os3	2.8844(4)	C41–Os1–Os3	87.84(13)
Os1–Os3	2.8887(4)	Os1–C41–N1	109.4(3)
Os1–C41	2.111(5)	N1–Os2–Os1	68.03(11)
C41–N1	1.355(6)	N1–Os2–Os3	86.14(11)
Os2–N1	2.033(4)	C41–N1–Os2	114.7(3)
Os2–N2	2.103(4)	C44–N1–Os2	121.0(3)
N2–C45	1.363(6)	N2–Os2–Os3	100.67(11)
C44–C45	1.476(6)	N2–Os2–Os1	138.73(11)
N1–C44	1.358(6)	C45–N2–Os2	116.9(3)
		N2–C45–C44	114.0(4)
		N1–Os2–N2	75.15(15)

into **2** and **3**. Opening of a chelate ring in **1** by cleavage of either Os(1)–N(1) or Os(1)–N(2) bonds (see Fig. 1) could control whether **2** or **3** is formed. After chelate-ring opening, orthometallation of the heterocycle that remains co-ordinated, followed by loss of a CO ligand and reformation of a chelate ring would lead to products **2** and **3**. Thus if the initial process in the transformation is ring-opening, an unsaturated cluster would be formed which could undergo orthometallation to give isomers of **1**. Intermediates **A** and **B** are depicted to show the arrangements that would be required to lead to closure of the 5- and 7-membered rings following loss of CO. Intermediate **A** can only give product **3** by 5-membered chelate ring closure, whereas **B** could give pyridyl co-ordination (7-membered chelate ring formation to give **2**) or pyrazine co-ordination (5-membered chelate ring formation, unobserved). Clearly the formation of the 7-membered ring is favoured over the 5-membered ring which is made less favourable by fusion to a 4-membered ring.

4. Supporting material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 243108 for **1**, 243109 for **2** and 243110 for **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail deposit@www.ccdc.cam.ac.uk or <http://www.ccdc.ac.uk>).

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