

Dinuclear and trinuclear osmium complexes incorporating  
1,2-bis(2-pyridyl)ethene as doubly and triply bridging ligands:  
crystal structures of  $[\text{Os}_2(\mu\text{:}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$ ,  
 $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{:}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  and  
 $[\text{Os}_3(\mu\text{-H})(\mu^3\text{:}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$

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## Abstract

Treatment of *trans*-1,2-bis(2-pyridyl)ethene ( $\text{C}_{12}\text{H}_{10}\text{N}_2$ ) with the labile cluster  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  in refluxing THF generated the products:  $[\text{Os}_2(\mu\text{:}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  (**1**) and  $[\text{Os}_3(\mu\text{:}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_{10}]$  (**2**). When the reaction is carried out in refluxing acetonitrile the products  $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{:}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**3**),  $[\text{Os}_3(\mu\text{-H})(\mu_3\text{:}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$  (**4**) and  $[\text{Os}_3(\mu\text{-CO})(\mu_3\text{:}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**5**) are obtained in addition to compounds **1** and **2**. The X-ray structures for **1**, **3** and **4** are reported. We have established that both pyridine nitrogen atoms are co-ordinated in all five complexes. **1** and **2** contain the ligand incorporated in a doubly-bridging manner, and for clusters **3**, **4** and **5** hydrogen atom transfer at the central ethene group has led to bridging alkylidene and vinyl systems within triply-bridging ligands.

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## 1. Introduction

The design and synthesis of polydentate ligands incorporating aromatic nitrogen heterocycles (pyridine in particular) have played a major role in the development of coordination chemistry [1]. Ligands have been designed to include 2-pyridyl groups to enhance by chelation the coordination of 2-substituents. Reports have appeared on the preparation and characterization

of mono- and bi-metallic compounds with the aromatic nitrogen heterocycles as components of a bridging ligand [2]. Bipyridyls incorporating an alkene function have been widely used to construct polynuclear complexes [3]. Such complexes may exhibit metal–metal interactions associated with the bridging ligand, which might be a multidentated aromatic nitrogen heterocycle [4]. Communication between the metal centres commonly takes place via the  $\pi$  system of the bridging ligand; strong metal-to-ligand charge-transfer (MLCT) in metal–pyridyl complexes is potentially useful in nonlinear optics and other related electronic effects.

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We are interested in interactions of  $\pi$ -delocalised organic ligands with the complex  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ , in order to obtain new complexes that can be used as models for bio-inorganic systems such as some metallo-proteins, or to find some applications as catalysts for photosensitization. In this work, we wish to report the synthesis and characterization of new osmium clusters derived from the interaction of the labile  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  with *trans*-1,2-bis(2-pyridyl)ethene.

$[\text{Os}_3(\text{CO})_{12}]$  reacts at high temperatures with pyridine to give the *ortho*-metallated  $\mu_2$ -pyridyl derivative  $[\text{Os}_3\text{H}(\mu_2\text{-NC}_5\text{H}_4)(\text{CO})_{10}]$  [5], and the same result is observed for room temperature reactions using the more labile clusters  $[\text{Os}_3(\text{CO})_{10}\text{L}_2]$  (L = cyclooctene [6,7],  $\text{CH}_3\text{CN}$  [7]). Likewise, reaction with ethene gives an oxidative addition product, the  $\mu$ -ethenyl derivative  $[\text{Os}_3\text{H}(\mu_2\text{-CH=CH}_2)(\text{CO})_{10}]$  [8] on reaction with  $[\text{Os}_3(\text{CO})_{10}\text{L}_2]$  [7] or  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  [9]. When an pyridinic nitrogen and a alkenyl function are available on the same ligand as in 2-ethenylpyridine ( $\text{NC}_5\text{H}_4\text{CH=CH}_2$ ), coordination through the nitrogen atom and C–H oxidative addition occur to give the  $\eta^2$ -alkenyl species  $[\text{Os}_3\text{H}(\mu_2\text{-NC}_5\text{H}_4\text{CH=CH})(\text{CO})_{10}]$  [10], in which only two Os–Os bonds are observed (Os–Os–Os angle about  $160^\circ$ ).

We previously studied the interaction of *trans*-1,2-bis(2-pyridyl)ethene with the labile compound  $[\text{Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2]$  in THF at room temperature [11] to give the complex  $[\text{Re}_2(\mu:\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  and the oxidative-addition product  $[\text{Re}_2(\mu\text{-H})(\mu:\eta^3\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_7]$ . Carrying out the reaction in refluxing THF gave, besides the two compounds above, the oxidative-addition product  $[\text{Re}_2(\mu\text{-H})(\mu:\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_6]$ , the insertion product  $[\text{Re}_2(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  and  $[\text{Re}_2(\mu:\eta^6\text{-C}_{24}\text{H}_{18}\text{N}_4)(\text{CO})_6]$ . This last complex contains the organic ligand *tricyclo*-tetrakis(2-pyridyl)cyclobutandiyli derived by [2 + 2] cycloaddition of 1,2-bis(2-pyridyl)ethene mediated by co-ordination to the dinuclear framework.

In this paper, we have evaluated the co-ordination ability of 1,2-bis(2-pyridyl)ethylene with the labile triosmium cluster  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ , and have found that coordination occurs through the nitrogen atoms of the pyridine rings, and C–H bonds of the ethenyl function are cleaved rather than those of the pyridine rings. This is broadly in line with earlier observations on the reaction of 2-ethenylpyridine with  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ .

## 2. Experimental

All reactions were performed under dried purified nitrogen using standard Schlenk techniques. Solvents were purified and dried by common procedures prior to use [12].  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  was prepared as de-

scribed previously [13] and 1,2-bis(2-pyridyl)ethene was used as supplied from Aldrich. Reactions were followed by IR monitoring in the range  $2200\text{--}1750\text{ cm}^{-1}$  and products were separated by TLC on silica (Merck 60  $\text{HF}_{254}$ ). IR spectra were recorded on a Nicolet 5DXC FT IR spectrometer using 0.5 mm calcium fluoride solution cells.  $^1\text{H}$  NMR spectra were obtained on a Bruker Avance 300 MHz spectrometer, and chemical shifts are reported in  $\delta$  (ppm) using  $\text{CD}_3\text{COCD}_3$  as solvent and internal standard.

### 2.1. Reaction of *trans*-1,2-bis(2-pyridyl)ethene with $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$ . Synthesis of the complexes 1–5

A solution of  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  (0.200 g, 0.214 mmol) and 1,2-bis(2-pyridyl)ethene (0.038 g, 0.214 mmol) in  $\text{CH}_3\text{CN}$  ( $50\text{ cm}^3$ ) was refluxed for 8 h, during which time the colour of the solution changed from pale yellow to red. The solvent was removed under reduced pressure and the residue separated by TLC eluting with dichloromethane:*n*-hexane (3:7 vol:vol) to give five compounds:  $[\text{Os}_2(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  (**1**) (yellow, 0.025 g, 16%),  $[\text{Os}_3(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_{10}]$  (**2**) (yellow, 0.010 g, 5%),  $[\text{Os}_3(\mu\text{-H})_2(\mu:\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**3**) (yellow, 0.027 g, 13%),  $[\text{Os}_3(\mu\text{-H})(\mu:\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$  (**4**) (red, 0.025 g, 12%) and  $[\text{Os}_3(\mu\text{-CO})(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**5**) (yellow, 0.009 g, 4%). Complexes **1** and **2** were obtained as yellow crystals after recrystallization from dichloromethane:cyclohexane (1:3 by volume). Yellow crystals of **3** were obtained after recrystallization from an ethanol:cyclohexane mixture (1:3 by volume) and red crystals of compound **4** were obtained from a dichloromethane:cyclohexane mixture (1:3 by volume). Carrying out the same reaction in refluxing THF for 5 h only gave  $[\text{Os}_2(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  **1** and  $[\text{Os}_3(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_{10}]$  **2** (38% and 12%, respectively) Anal. Found for **1**: C, 29.87; H, 1.45; N, 3.75. Calc. for  $\text{C}_{18}\text{H}_{10}\text{N}_2\text{O}_6\text{Os}_2$ : C, 29.57; H, 1.37; N, 3.83%. Anal. Found for **2**: C, 25.87; H, 1.04; N, 2.66%. Calc. for  $\text{C}_{22}\text{H}_{10}\text{N}_2\text{O}_{10}\text{Os}_3$ : C, 25.56; H, 0.97; N, 2.71. Anal. Found for **3**: C, 24.84; H, 1.29; N, 2.82%. Calc. for  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_8\text{Os}_3$ : C, 24.52; H, 1.23; N, 2.86. Anal. Found for **4**: C, 24.87; H, 1.10; N, 2.81%. Calc. for  $\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_8\text{Os}_3$ : C, 24.58; H, 1.02; N, 2.87. Anal. Found for **5**: C, 25.72; H, 1.09; N, 2.76%. Calc. for  $\text{C}_{21}\text{H}_{10}\text{N}_2\text{O}_9\text{Os}_3$ : C, 25.39; H, 1.01; N, 2.82.

### 2.2. Thermal treatment of $[\text{Os}_3(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_{10}]$ (**2**) in cyclohexane

A solution of compound **2** (0.010 g; 0.010 mmol) in cyclohexane ( $30\text{ cm}^3$ ) was heated under reflux for 8 h. The solvent was removed under reduced pressure and TLC of the residue (eluent: dichloromethane:*n*-hexane, 7:3 vol:vol) gave  $[\text{Os}_2(\mu:\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  **1** as yellow crystals (0.005 g; 68%).

### 2.3. Thermal treatment of $[\text{Os}_3(\mu\text{-CO})(\mu_3\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$ (**5**) in cyclohexane

A solution of compound **5** (0.010 g; 0.010 mmol) in cyclohexane (30 cm<sup>3</sup>) was refluxed for 8 h. The solvent was removed under reduced pressure and TLC of the residue (eluent: dichloromethane:*n*-hexane, 7:3 vol:vol) gave  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$  (**4**) as red crystals (0.006 g; 61%).

### 2.4. X-ray single-crystal structure determinations for the compounds **1**, **3** and **4**

Data for compound **1** were registered by using a Rigaku AFC7S diffractometer, whereas those for **3** and **4** were recorded using a Bruker SMART APEX CCD equipment. Both diffractometers were provided with a graphite monochromated Mo K $\alpha$  radiation (0.71073 Å). Details of the crystal data and structure refinements are collected in Table 1. A semi-empirical absorption correction [14] was applied to data from **1**. For **3** and

**4**, the absorption was corrected by using the program SADABS [15]. In all cases, data were corrected for Lp effects. Crystal structures were solved by direct methods for **1** and **4** and using Patterson methods for **3** [16]. In all of them, the final models were reached by Fourier techniques [16]. All non-H atoms were refined with anisotropic displacement parameters. In each structure the H-atoms were included in the last cycle in their calculated positions and refined using a riding model. The isotropic displacement parameters for the H-atoms were considered 1.2 times of their attached C-atoms. The hydride ligands in **3** and **4** were included in their found positions (see below) and refined using fixed isotropic displacement parameters. The final cycle of full-matrix least-squares was based on  $F^2$ . In **1**, the first six picks with residual density between 0.96 and 2.09 e Å<sup>-3</sup> are close to Os atoms. Data reduction for **1** was carried out using the TEXSAN program [17], whereas data reduction and integration for **3** and **4** were performed with SAINT<sup>+</sup> [18]. All structure solutions and refinements were made using SHELXTL-PLUS package [16].

Table 1

Crystal data and structure refinement for  $[\text{Os}_2(\text{C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  (**1**),  $[\text{Os}_3\text{H}_2(\text{C}_5\text{H}_4\text{NCH}_2\text{CC}_5\text{H}_4\text{N})(\text{CO})_8] \cdot 0.5$  ethanol (**3**) and  $[\text{Os}_3\text{H}(\text{C}_{14}\text{H}_9\text{N}_4)(\text{CO})_9] \cdot \text{cyclohexane}$  (**4**)<sup>a</sup>

	<b>1</b>	<b>3</b>	<b>4</b>
Chemical formula	C <sub>18</sub> H <sub>10</sub> N <sub>2</sub> O <sub>6</sub> Os <sub>2</sub>	C <sub>21</sub> H <sub>15</sub> N <sub>2</sub> O <sub>8.50</sub> Os <sub>3</sub>	C <sub>26</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub> Os <sub>3</sub>
Formula weight	730.68	1001.95	976.90
Crystal system	Monoclinic	Triclinic	Monoclinic
space group	<i>P</i> 2 <sub>1</sub> <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimension			
<i>a</i> (Å)	8.4724(17)	9.6644(11)	8.4311(4)
<i>b</i> (Å)	17.580(4)	10.3619(12)	14.6312(7)
<i>c</i> (Å)	13.206(3)	25.908(3)	17.9624(8)
$\alpha$ (°)	90	89.825(2)	90°
$\beta$ (°)	100.63(3)	86.666(2)	96.1650(10)°
$\gamma$ (°)	90	69.476(2)	90°
Cell volume (Å <sup>3</sup> )	1933.2(7)	2425.3(5)	2202.98(18)
<i>Z</i>	4	4	4
Calculated density (g/cm <sup>3</sup> )	2.511	2.744	2.945
Absorption coefficient, $\mu$ (mm <sup>-1</sup> )	13.169	15.729	17.310
Crystal colour	Yellow	Pale yellow	Red
Crystal size (mm <sup>3</sup> )	0.36 × 0.30 × 0.28	0.45 × 0.25 × 0.07	0.20 × 0.17 × 0.08
$\theta$ Range for data collection	2.50–25.02	2.10–28.31°	1.80–28.28°
Reflections collected	3639	20699	19231
Independent reflections ( $R_{\text{int}}$ )	3398 (0.0425)	10993 (0.0426)	5267 (0.0315)
Reflections with $F^2 > 2\sigma$	2433	9613	4903
Minimum and maximum transmission	0.0877 and 0.1198	0.0531 and 0.4143	0.1317 and 0.3381
Structure solution	Direct methods	Patterson synthesis	Direct methods
Data/restraints/parameters	3398/0/253	10993/2/606	5267/0/304
Final <i>R</i> indices [ $F^2 > 2\sigma$ ]			
<i>R</i> <sub>1</sub>	0.0419	0.0514	0.0237
<i>wR</i> <sub>2</sub>	0.1002	0.1354	0.0501
<i>R</i> indices (all data)			
<i>R</i> <sub>1</sub>	0.0720	0.0586	0.0269
<i>wR</i> <sub>2</sub>	0.0875	0.1405	0.0510
Goodness-of-fit on $F^2$	1.044	1.062	1.080
Largest shift/su	0.000	0.001	0.001
Largest difference peak/hole (e Å <sup>-3</sup> )	2.090/–1.244	3.140/–3.085	2.177/–1.359

<sup>a</sup> For all three structures: temperature = 293(2) K; radiation, Mo K $\alpha$ ;  $\lambda$  = 0.71073 Å, refinement by full-matrix least-squares on  $F^2$ .

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 241913 for **1**, 243246 for **3** and 243245 for **4**. 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, email deposit@www.ccdc.cam.ac.uk or <http://www.ccdc.ac.uk>)

### 3. Results and discussion

#### 3.1. Synthesis of complexes **1–5** by reaction of 1,2-bis(2-pyridyl)ethene with $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$

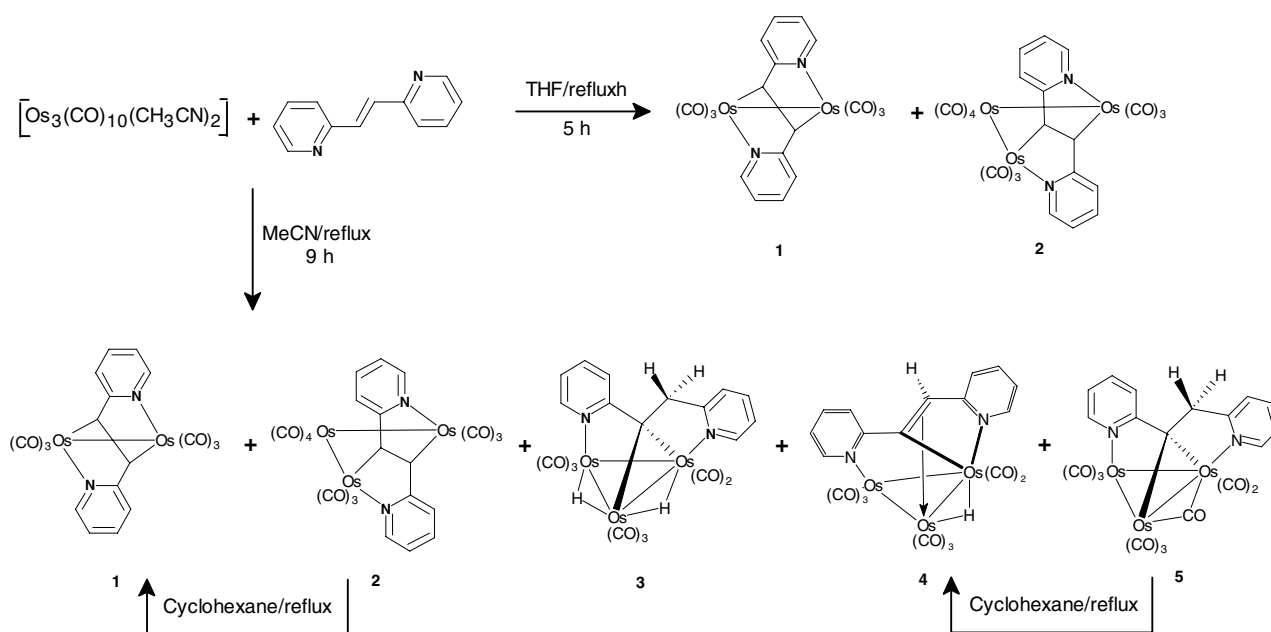
Treatment of  $[\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2]$  with 1,2-bis(2-pyridyl)ethene in refluxing tetrahydrofuran for 5 h gave just two products after TLC separation:  $[\text{Os}_2(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  (**1**), and  $[\text{Os}_3(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_{10}]$  (**2**). However, when refluxing acetonitrile was used as solvent for 8 h, in addition to **1** and **2** the compounds  $[\text{Os}_3(\mu\text{-H})_2(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**3**),  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$  (**4**) and  $[\text{Os}_3(\mu\text{-CO})(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**5**) were obtained in significant yields (Scheme 1).  $^1\text{H}$  NMR and IR data are shown in Table 2. In separate experiments under refluxing cyclohexane cluster **2** converts quantitatively to **1** and compound **5** converts to **4**.

#### 3.2. Complex $[\text{Os}_2(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$ (**1**)

The IR  $\nu(\text{CO})$  absorption spectrum of **1** shows that only terminal CO are present and its pattern is essen-

tially the same as those observed for related dimers of the type  $[\text{M}_2(\text{CO})_6(\alpha\text{-diimine})]$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) [19] containing bridging  $\alpha$ -diimine ligands donating 6 electrons as does  $\text{C}_{12}\text{H}_{10}\text{N}_2$  in **1**. The four aromatic resonances corresponding to eight pyridinic protons in the  $^1\text{H}$  NMR spectrum suggests the equivalence of the pyridine rings. The singlet at  $\delta = 5.54$  ppm integrating for two protons but shifted upfield from the corresponding signal for the free ligand, is consistent with  $\text{C}_2\text{H}_2$  alkene coordination.

An ORTEP picture of **1** determined by single-crystal X-ray analysis is shown in Fig. 1 and selected bond lengths and angles are listed in Table 3. Only two  $\text{Os}(\text{CO})_3$  groups are present [ $\text{Os}\text{--}\text{Os} = 2.7998(8)$  Å] so an  $\text{Os}(\text{CO})_4$  unit has been displaced from the triangular geometry. Although no local crystallographic symmetry is observed, the molecule shows an approximate 2-fold axis through the C6–C7 bond, which accounts for the observed ( $\text{C}_2$ ) symmetry observed in solution. The pyridine rings are N-coordinated to the osmium centers [ $\text{Os1}\text{--}\text{N1} = 2.143(10)$  Å and  $\text{Os2}\text{--}\text{N2} = 2.157(10)$  Å] with a dihedral angle of 85.5 between the mean planes of the heterocycles. The C6–C7 bond distance of 1.535(15) Å strongly indicates a single C–C bond, so hybridization changes of these carbon atoms from  $\text{sp}^2$  to  $\text{sp}^3$  has occurred. These carbon atoms are  $\sigma$ -bonded to the osmium centers with  $\text{Os1}\text{--}\text{C7}$  and  $\text{Os2}\text{--}\text{C6}$  bond distances of 2.189(11) and 2.171(11) Å, respectively. The C6–C7 bond is linked through a di- $\sigma$ ,  $\eta^1$ ,  $\eta^1$  way as found in  $[\text{Os}_2(\text{C}_2\text{H}_4)(\text{CO})_8]$  [20]. The coordination mode of the ligand in **1** was also observed for the complexes  $[\text{Re}_2(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  [10] and  $[(\text{C}_5\text{Me}_5)_4\text{Sm}_2(\mu\text{-}$



Scheme 1.

Table 2  
IR and NMR data for compounds **1–5**

Compound	$\nu$ (CO) <sup>a</sup> (cm <sup>-1</sup> )	<sup>1</sup> H NMR <sup>b</sup> ( $\delta$ , ppm)	<i>J</i> (Hz)	
[Os <sub>2</sub> ( $\mu$ : $\eta^4$ -C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> )(CO) <sub>6</sub> ] <b>1</b>	2061s, 2026vs, 1978vs, 1966s, 1952s	8.67 (ddd, H <sub>a</sub> ) 7.72 (ddd, H <sub>c</sub> ) 7.17 (ddd, H <sub>d</sub> ) 6.90 (ddd, H <sub>b</sub> ) 5.54 (s, H <sub>e</sub> )	ab 5.6 ac 1.6 ad 0.9 bc 7.6 bd 1.3 cd 7.9	
[Os <sub>3</sub> ( $\mu$ : $\eta^4$ -C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> )(CO) <sub>10</sub> ] <b>2</b>	2083m, 2061w, 2051vs, 2032s, 2023w, 1995s, 1983w, 1967s, 1959m	8.67 (ddd, H <sub>a</sub> ) 7.66 (ddd, H <sub>c</sub> ) 7.24 (ddd, H <sub>d</sub> ) 6.91 (dt, H <sub>b</sub> ) 5.51 (s, H <sub>e</sub> )	ab 5.9 ac 1.5 ad 0.8 bc 7.3 bd 1.5 cd 8.2	
[Os <sub>3</sub> ( $\mu$ -H) <sub>2</sub> ( $\mu_3$ : $\eta^3$ -C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> )(CO) <sub>8</sub> ] <b>3</b>	2077s, 2036s, 2010vs, 1996vs, 1981m, 1971m, 1956s, 1947s	9.13 (ddd, H <sub>a</sub> ) 8.57 (ddd, H <sub>c</sub> ) 7.93 (dt, H <sub>e</sub> ) 7.76 (ddd, H <sub>d</sub> ) 7.69 (ddd, H <sub>g</sub> ) 7.35 (dt, H <sub>b</sub> ) 7.01 (ddd, H <sub>h</sub> ) 6.66 (dt, H <sub>f</sub> ) 3.98 (AB q, CH <sub>2</sub> ) -12.13 (s, H <sub>i</sub> ) -18.31 (s, H <sub>j</sub> )	ab 6.0 ac 1.8 ad 0.6 bc 7.6 bd 1.7 cd 7.6 AB 18.5	ef 5.7 eg 1.5 eh 0.8 fg 7.2 fh 1.3 gh 8.3
[Os <sub>3</sub> ( $\mu$ -H)( $\mu_3$ : $\eta^4$ -C <sub>12</sub> H <sub>9</sub> N <sub>2</sub> )(CO) <sub>8</sub> ] <b>4</b>	2070s, 2040vs, 2023w, 2002m, 1994s, 1976s, 1953m, 1923m	8.74 (ddd, H <sub>a</sub> ) 8.57(ddd, H <sub>c</sub> ) 7.75 (dt, H <sub>e</sub> ) 7.59 (dt, H <sub>g</sub> ) 7.43 (ddd, H <sub>d</sub> ) 6.98 (m, H <sub>b</sub> , H <sub>f</sub> ) 6.84 (ddd, H <sub>h</sub> ) 5.56 (br s, H <sub>i</sub> ) -14.68 (d, H <sub>j</sub> )	ab 7.5 ac 1.6 ad 0.9 bc 7.8 bd 1.3 cd 7.8	ef 5.6 eg 1.6 eh 0.8 fg 7.8 fh 1.2 gh 7.8 ij 0.7
[Os <sub>3</sub> ( $\mu$ -CO)( $\mu_3$ : $\eta^3$ -C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> )(CO) <sub>8</sub> ] <b>5</b>	2069s, 2032vs, 1997vs, 1969s, 1952m, 1851m	9.02 (m, H <sub>a</sub> H <sub>c</sub> ) 7.79 (dt, H <sub>e</sub> ) 7.87 (ddd, H <sub>g</sub> ) 7.81 (ddd, H <sub>d</sub> ) 7.30 (dt, H <sub>b</sub> ) 7.25 (ddd, H <sub>h</sub> ) 6.90 (dt, H <sub>f</sub> ) 4.10 (AB q, CH <sub>2</sub> )	ab 5.6 ac 1.2 ad 0.7 bc 7.8 bd 1.1 cd 7.8 AB 20.0	ef 5.7 eg 1.7 eh 0.7 fg 7.4 fh 1.3 gh 8.3

<sup>a</sup> In C<sub>6</sub>H<sub>12</sub>.

<sup>b</sup> In CD<sub>3</sub>COCD<sub>3</sub>.

$\eta^2$ : $\eta^2$ -pyCHCHpy) [21], so the ligand in **1** acts as a six-electron donor (3 electrons to each metal atom).

### 3.3. Complex [Os<sub>3</sub>( $\mu$ : $\eta^4$ -C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>)(CO)<sub>10</sub>] (**2**)

The IR spectrum of **2** shows that only terminal CO ligands are present. Its <sup>1</sup>H NMR spectrum is very similar to that of compound **1**, regarding the pattern of the aromatic region and the singlet at  $\delta$  5.51 for the central CHCH moiety. This evidence strongly suggests that 1,2-bis(2-pyridyl)ethene is bonded as in **1** which is also similar to the bonding observed in the complex [Os<sub>3</sub>(CO)<sub>10</sub>(CH<sub>3</sub>OCONNCOOCH<sub>3</sub>)] [22]. Therefore, in **2** we expected the ligand to span the edge of the triosmium cluster that does not support an osmium–osmium

bond. This is also consistent with the easy thermal conversion observed for **2** to **1** by loss of a Os(CO)<sub>4</sub> group with formation of an Os–Os bond between the two bridged osmium atoms.

This mode of coordination for the organic ligand in **2** was confirmed by a single-crystal X-ray diffraction analysis [23]. A graphic representation of the molecular structure of **2** shown in Fig. 2 suggest these conclusions [Os1–Os3 = 2.98(1) and Os2–Os3 = 2.94(1)], but the low quality of the crystals resulted in very poor unpublished data, so we refrain from comparing intramolecular parameters. The complex contains an approximate 2-fold axis which bisects the C6–C7 bond, consistent with the observed symmetry in solution.

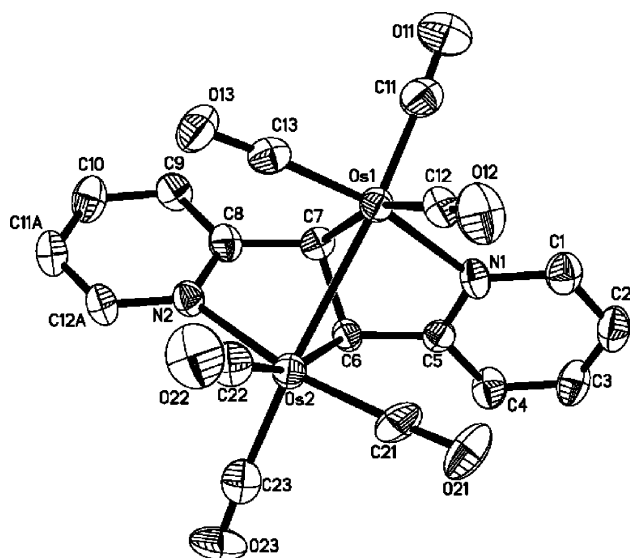


Fig. 1. ORTEP view (35% probability, H atoms omitted for clarity) of the molecular structure of **1** in the crystal.

Table 3  
Selected bond lengths (Å) and angles (°) for compound  $[\text{Os}_2(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_6]$  (**1**)

Bond lengths		Bond angles	
Os1–Os2	2.7998(8)	C6–C7–Os1	95.2(7)
Os1–N1	2.143(10)	C7–C6–Os2	96.1(7)
Os2–N2	2.157(10)	N1–Os1–C7	76.3(4)
Os1–C7	2.189(11)	N2–Os2–C6	76.4(4)
Os2–C6	2.171(11)	C8–N2–Os2	110.3(8)
C6–C7	1.535(15)	C5–N1–Os1	111.5(7)
		C8–C7–C6	108.0(10)
		C5–C6–C7	108.4(9)
		C8–C7–Os1	111.6(8)
		C5–C6–Os2	112.1(8)
		N1–Os1–Os2	83.4(3)
		N2–Os2–Os1	84.0(2)

### 3.4. Complex $[\text{Os}_3(\mu\text{-H})_2(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$ (**3**)

The  $\nu(\text{CO})$  absorption spectrum of **3** shows only terminal CO and resembles that for  $[\text{Os}_3\text{H}_2(6\text{-CHC}_5\text{H}_3\text{-N-2C(H)=N}^i\text{Pr})(\text{CO})_8]$  [24]. The  $^1\text{H}$  NMR spectrum exhibits a sharp AB quartet (at  $\delta$  3.98 ppm,  $J_{\text{AB}} = 18.5$  Hz) corresponding to a  $\text{sp}^3$ -methylene group, suggesting that the carbon–carbon double bond has been reduced. Eight different signals are observed in the aromatic region associated with two different coordinated pyridine rings. No orthometallation has occurred and the high symmetry observed for compounds **1**, **2** or the free ligand is not present. Compound **3** is a dihydride which is clear from the singlets at  $\delta$  –12.13 and –18.31 ppm.

The molecular structure of **3** was determined by a single-crystal X-ray study (Fig. 3), and selected bond lengths and angles are in Table 4. The triangular array of osmium atoms is supported by three Os–Os bonds [2.9066(6), 2.8250(6) and 2.8010(6) Å]. Os1 bears two

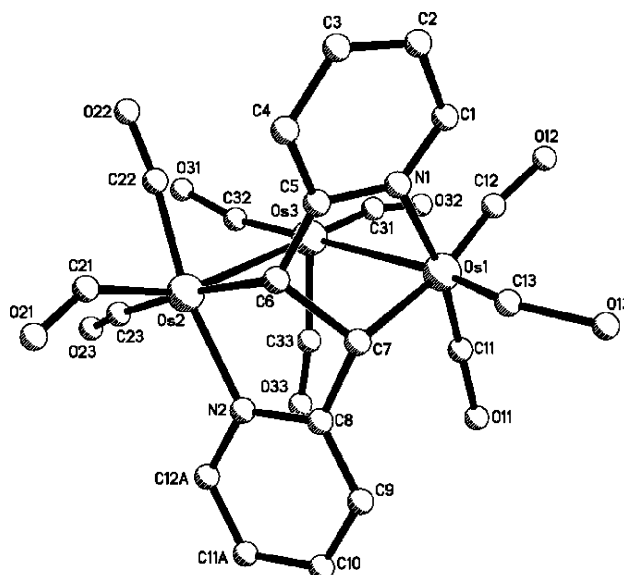


Fig. 2. Ball and stick plot of crystallographically characterized complex  $[\text{Os}_3(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_{10}]$  **2**.

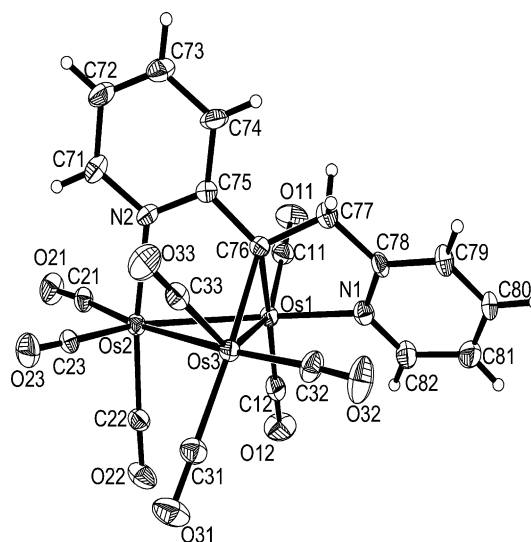


Fig. 3. ORTEP view (30% probability ellipsoids) of the molecular structure of **3** in the crystal.

terminal CO, one pyridine ring [Os1–N1 = 2.112(4) Å] and one  $\sigma$ -bond to a carbon atom of the  $\mu$ -alkylidene group [Os1–C76 = 2.115(9) Å]. Os2 is linked to three CO and to the second pyridine ring [Os2–N2 = 2.151(9) Å] while Os3 is linked to three CO and one  $\sigma$ -bond to the  $\mu$ -alkylidene group [Os3–C76 = 2.210(10) Å].

The hydrides in **3** were not located, but their position can be deduced from structural factors [25] and by comparing its structure with that of  $[\text{Os}_3\text{H}_2(\mu\text{-CH}_2)(\text{CO})_{10}]$  [26], of which the neutron-diffraction structure is known. One hydride bridges the Os1–Os3 bond, probably below the Os<sub>3</sub> plane and opposite to the alkylidene bridge as in

Table 4  
Selected bond lengths (Å) and angles (°) for compound  $[\text{Os}_3(\mu\text{-H})_2(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$  (**3**)

Bond lengths		Bond angles	
Os1–Os2	2.9066 (6)	N1–Os1–Os3	89.0 (2)
Os1–Os3	2.8250 (6)	N1–Os1–Os2	147.0 (2)
Os2–Os3	2.8010 (6)	N1–Os1–C76	79.8 (4)
Os1–N1	2.112 (9)	C76–Os1–Os3	50.7 (3)
Os1–C76	2.115 (9)	C76–Os1–Os2	75.1 (3)
Os3–C76	2.210 (10)	N2–Os2–Os3	82.6 (2)
Os2–N2	2.151 (9)	N2–Os2–Os1	83.9 (2)
C76–C77	1.523 (15)	C75–C76–C77	113.6 (9)
		N2–C75–C76	117.1 (9)
		N1–C78–C77	115.9 (9)

$[\text{Os}_3\text{H}_2(\mu\text{-CH}_2)(\text{CO})_{10}]$ . It will lie close to the intersection of the vectors Os1–C11 and Os3–C33. The large angles of the axial carbonyl ligands on Os1 and Os3 around this bond [ $\text{Os1Os3C31} = 120.4(4)^\circ$  and  $\text{Os3Os1C12} = 118.4(4)^\circ$ ] support this view. The second hydride bridging Os1–Os3 [the Os1–Os2 bond length of 2.9066(6) Å is considerably longer than the other possible edge, Os2–Os3, 2.8010(6) Å] is probably close to the Os3 plane as in  $[\text{Os}_3\text{H}_2(\mu\text{-CH}_2)(\text{CO})_{10}]$  [26] and close to the intersection of the vectors Os1–N1 and Os2–C23. The Os1–Os2 bond length of 2.9066(6) Å is significantly longer due to the bridging hydrogen whereas the Os1–Os3 bond of 2.8250(6) Å has not been significantly lengthened by the bridging hydrogen atom due to the alkylidene group bridging the Os1–Os3 bond.

### 3.5. Complex $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$ (**4**)

The  $^1\text{H}$  NMR spectrum shows eight signals due to two non-equivalent pyridine rings. The broad signal at  $\delta$  5.56 integrates for one olefinic hydrogen ( $\text{H}_i$ ). The absence of a second CH olefinic signal and a doublet at  $\delta$  –14.68 ppm for a bridging hydride OsHOs, suggest C–H bond cleavage on the  $\text{HC}=\text{CH}$  fragment. The H–H COSY spectrum revealed that the broad signal for  $\text{H}_i$  is coupled to the hydride ligand. These results indicate metallation at the carbon atom, probably to give a five-membered chelate ring as in  $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{NC}_5\text{H}_4\text{CH}=\text{CH})]$  [10] and  $[\text{Re}_2(\mu\text{-H})(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_7]$  [11].

The X-ray structure of **4** (Fig. 4, selected bonds distances and angles are in Table 5) reveals that the organic fragment is  $\eta^4$  co-ordinated, donating 7e by means of two Os–N bonds [Os1–N1 = 2.140(4) Å] and Os2–N2 = 2.170(4) Å], one  $\sigma$ –Os–C bond [Os1–C47 = 2.096(4) Å] and an C=C  $\pi$ – $\eta^2$  interaction to Os3 [Os3–C47 = 2.217(5) Å, Os3–C46 = 2.326(5) Å]. The distance C46–C47 [1.412(6) Å] is longer than those for uncoordinated C–C double bond lengths [1.39(4) Å] [27] and the cluster could be considered to be derived by substituting two hydrogen atoms of the ethenyl (vinyl) cluster  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^2\text{-CH}=\text{CH}_2)(\text{CO})_{10}]$  [28] by 2-pyridyl

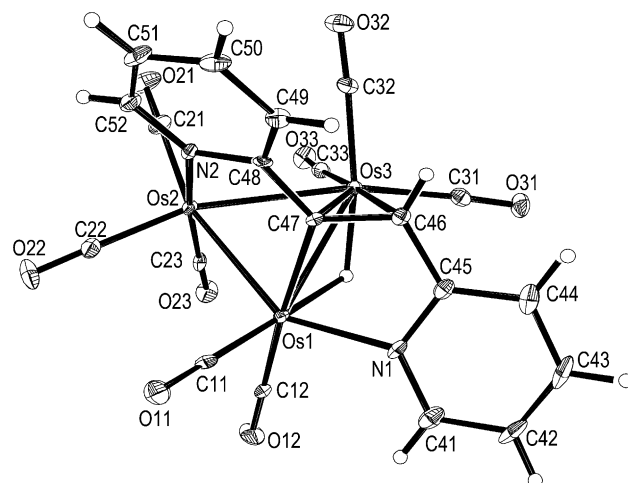


Fig. 4. ORTEP view (30% probability ellipsoids) of the molecular structure of **4** in the crystal.

Table 5  
Selected bond lengths (Å) and angles (°) for cluster  $[\text{Os}_3(\mu\text{-H})(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\text{CO})_8]$  (**4**)

Bond lengths		Bond angles	
Os1–Os2	2.7214 (3)	N1–Os1–Os2	147.01 (11)
Os1–Os3	2.8564 (3)	N1–Os1–Os3	86.09 (11)
Os2–Os3	2.8987 (3)	N2–Os2–Os1	88.58 (10)
Os1–C47	2.096 (4)	N2–Os2–Os3	84.57 (10)
Os3–C47	2.217 (5)	C48–N2–Os2	114.4 (3)
Os3–C46	2.326 (5)	C46–C47–C48	122.14 (4)
Os1–N1	2.140 (4)	C47–Os1–Os3	50.38 (12)
Os2–N2	2.170 (4)	C47–Os3–Os2	68.40 (11)
C46–C47	1.412 (6)	C46–Os3–Os2	104.45 (12)
		C46–Os3–Os1	67.10 (12)
		C46–C47–Os3	76.1 (3)

groups after displacing two CO ligands. The structural features of the complex, including the position of the hydride ligand which was located in the XRD study, are consistent with this description as a  $\mu\text{-}\eta^2$ -alkenyl complex. The co-ordination of the two pyridine groups has led to two fused five-membered rings [Os2N2C48–C47Os1 and Os1N1C45C46C47] along the Os1–C47 bond.

### 3.6. Complex $[\text{Os}_3(\mu\text{-CO})(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)(\text{CO})_8]$ (**5**)

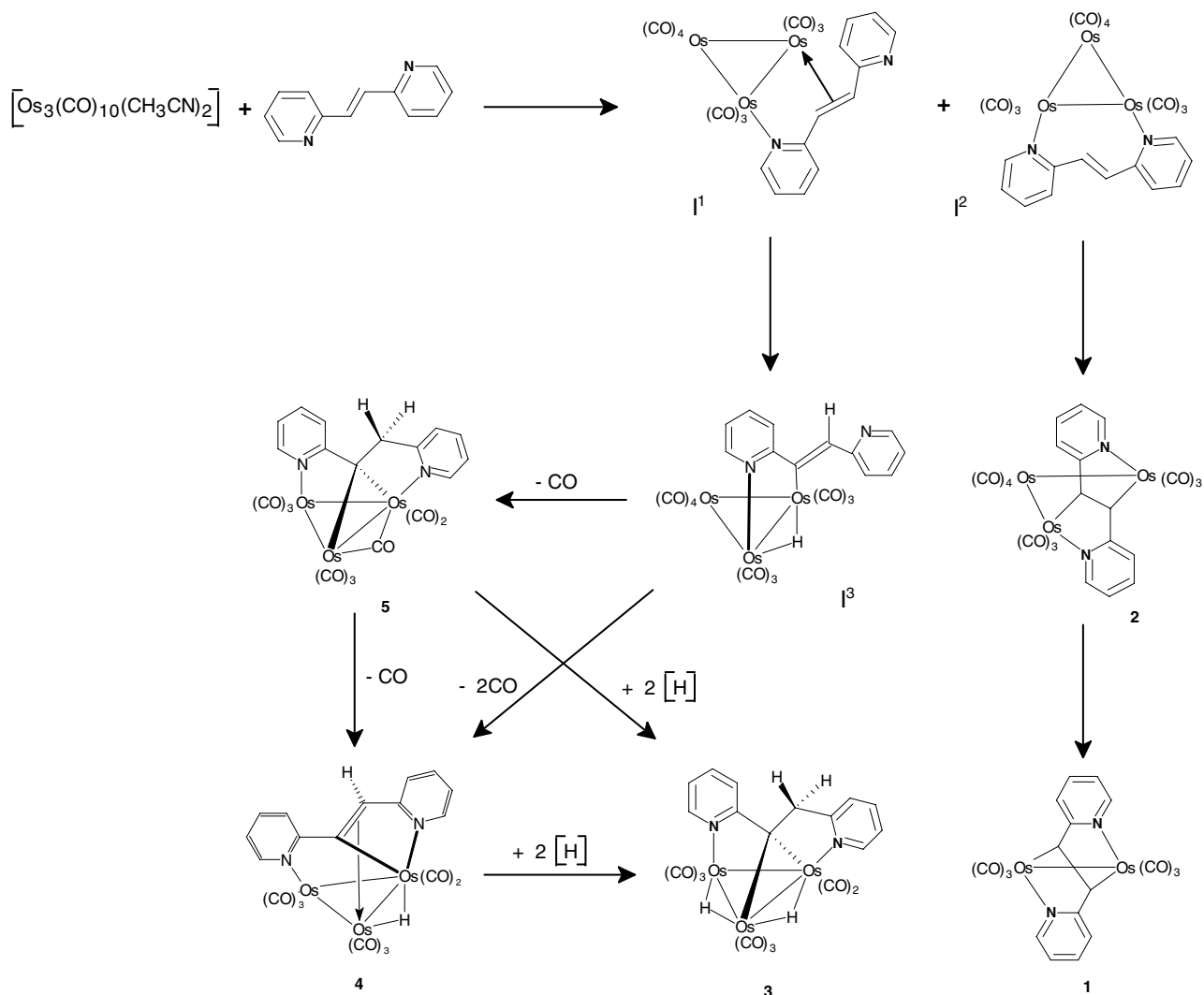
Cluster **5** was obtained in low yield (4%) but this is expected considering its ready conversion to compound **4** in refluxing cyclohexane. Of the five compounds described in this paper, **5** is the only one to contain a bridging CO ligand which is apparent from the IR absorption at  $1851\text{ cm}^{-1}$ . Its  $^1\text{H}$  NMR spectrum in the aromatic region is consistent with two non-equivalent pyridine rings. A sharp, well resolved AB quartet at  $\delta$  4.10 ppm ( $J = 20.0\text{ Hz}$ ) is associated with magnetically non-equivalent protons of a methylene group. Cluster **5** is closely related in this respect to compound

3. We were unable to get suitable crystals for an XRD determination but the structure shown in Scheme 1 is supported by spectroscopic data and from the ready conversion of **5** to **4**. Rupture of an Os–C bond with H migration from the CH<sub>2</sub> group to the metallic triangle to form a hydride and CO elimination can be seen as a facile process for the formation of the  $\mu:\eta^2$ -alkenyl complex **4**.

### 3.7. Possible route to the clusters 1–5

Since **1** and **2** were formed under milder conditions than **3–5**, we initially assumed that those were formed first and that cluster **2** gave the other complexes. However, we have established that **2** only converts to **1** thermally so clusters **3–5** are unlikely to be formed from **2**. Pyridine readily orthometallates on reaction with [Os<sub>3</sub>(CO)<sub>10</sub>(CH<sub>3</sub>CN)<sub>2</sub>] [7] but two co-ordination sites are actually blocked in *trans*-1,2-bis(2-pyridyl)ethene to prevent orthometallation. Two ways the ligand could inter-

act without leaving vacant coordination sites are shown in Scheme 2 (intermediates **I**<sup>1</sup> and **I**<sup>2</sup>). Intermediate **I**<sup>2</sup> is set-up to form **2** by coordination of the alkene and the two pyridine groups and converts to **1** by loss of Os(CO)<sub>4</sub>. However, it seems unlikely that the dipyridine could easily span two osmium atoms as in **I**<sup>2</sup> because of the 8-membered ring so formed and because of the *trans* geometry of the alkene. We therefore favour a route via **I**<sup>1</sup> to all compounds **1** to **5**. Metallation at the alkene group in **I**<sup>1</sup> would generate **I**<sup>3</sup> which could transfer an H-atom to the  $\beta$ -site on the central C<sub>2</sub> unit to give **5**. Alternatively, further nitrogen coordination in **I**<sup>1</sup> would lead to compound **2**, a reaction which is favoured over alkene activation in THF. We suggest that  $\beta$ -elimination at **5** leads to **4**. We are unable to account for the formation of **3** with confidence, because there is needed a source of two H-atoms either from **4** or **5** and there is no obvious source of these. Both **4** and **5** are expected to hydrogenate readily to **3** if a source of hydrogen is present.



Scheme 2.



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