

# Formation of hexaosmium raft clusters from $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$ : synthesis, structural characterisation and reactivities of $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})_2]$ and $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})]$

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Reaction of  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$  with 1 equivalent of 2-Aldrithol in  $\text{CH}_2\text{Cl}_2$  under ambient conditions afforded two new raft clusters  $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})_2]$  **1** and  $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})]$  **2** in moderate and fair yields, respectively. Cyclic voltammograms of compound **1** exhibited two metal-based, one-electron reduction couples at  $E_{1/2} = -0.36$  and  $-0.20$  V together with an irreversible ligand-based anodic wave at ca.  $E_{\text{pa}} = +0.31$  V vs. Ag–AgNO<sub>3</sub>. Protonation of **1** with  $\text{CF}_3\text{CO}_2\text{H}$  produced an unstable species  $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_5\text{NSH})(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_5\text{NS})\text{-}[\text{CO}_2\text{CF}_3]$  **3**, which upon standing in  $\text{CH}_2\text{Cl}_2$  quickly decomposed. All compounds have been fully characterised by spectroscopic methods, while the molecular structures of **1** and **2** were established by crystallographic techniques. Both **1** and **2** contain ‘ladder’-type and edge-fused raft cluster cores, with the sulfur atom in **2** being drawn intimately into the cluster envelope. These clusters serve as good models for substrates adsorbed onto metal surfaces.

## Introduction

Cluster chemistry has received considerable attention over the past few decades and research done on cluster–ligand interactions is vast. By studying the interactions of small organic fragments with molecular clusters, an insight into the behaviour of these molecules on metal surfaces in chemisorption and heterogeneous catalysis may be obtained.<sup>1–5</sup> Our previous work on the reactions of pyrimidine-2-thione (Hpymt)<sup>6</sup> and its derivatives<sup>7</sup> with trinuclear osmium and ruthenium carbonyl clusters has shown a wide range of ligand bonding modes on the cluster framework. The heterocycle has been found to be able to act as a monodentate<sup>8,9</sup> and bridging<sup>7</sup> ligand *via* a sulfur atom or as a chelating<sup>10,11</sup> and bridging<sup>7,12</sup> ligand through both S and N. Facile ligand rearrangement within the metal skeleton has also been demonstrated.<sup>6</sup> These findings clearly show the versatility of cluster–ligand bonding activities.

In this context, we have extended our studies on that type of ligand with higher nuclearity carbonyl clusters. Herein, we report the preparation, structural characterisation, reactivity and electrochemical behaviour of the hexaosmium raft clusters  $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})_2]$  **1** and  $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})]$  **2** bearing pyridine-2-thione moieties. To our knowledge, these are the first examples of raft-like species synthesized from a non-rafted parent cluster  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$ .

## Results and discussion

Nucleophilic substitution reactions of hexanuclear carbonyl

parent cluster derivatives  $[\text{Os}_6(\text{CO})_{21-n}(\text{MeCN})_n]$  ( $n = 0, 1$  or  $2$ ) with desired molecules are a rational way to generate ‘raft’ clusters. As part of our continuing investigation, we have studied the interactions of small organic molecules bearing hetero-donor atoms with the hexaosmium cluster  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$ , and observed the formation of ‘raft’ like species.

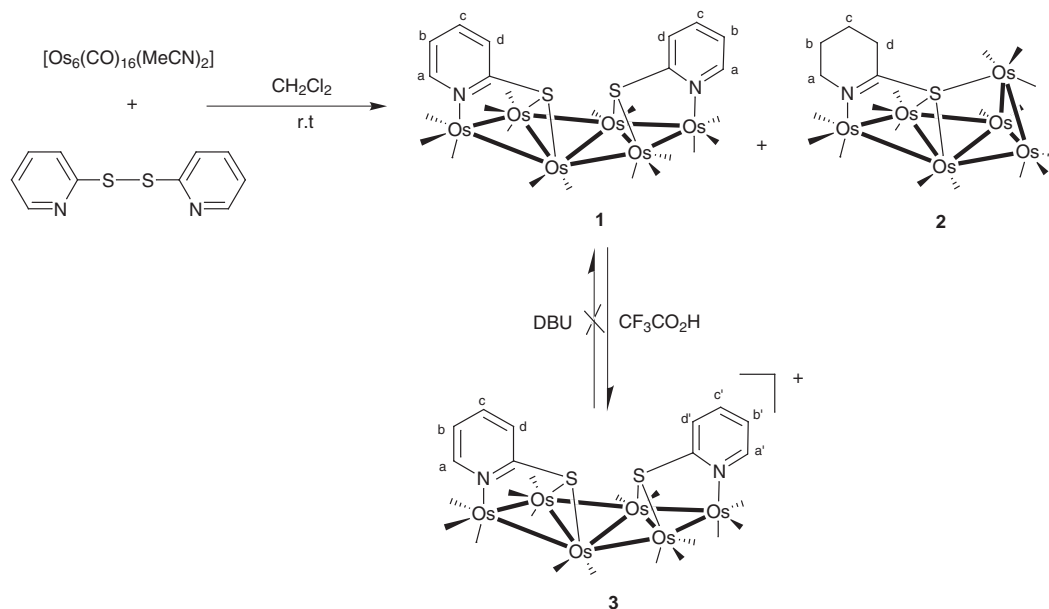
Treatment of the activated cluster  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$  with 2-Aldrithol (di-2-pyridyl disulfide) in  $\text{CH}_2\text{Cl}_2$  at ambient temperature for 24 h, followed by TLC purification, leads to the isolation of two air-stable clusters  $[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})_2]$  **1** and  $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})]$  **2** in moderate and fair yields, respectively (Scheme 1). Both new compounds were formulated and fully characterised by conventional spectroscopic and crystallographic techniques. Their formulae were first established by FAB MS, <sup>1</sup>H NMR spectroscopy (Table 1) and eventually confirmed by X-ray crystallography.

The molecular structure of cluster **1** with an atomic numbering scheme is shown in Fig. 1 and selected bond parameters are presented in Table 2. The molecule consists of four osmium triangles arranged in a chain sharing three common edges. Unlike the previously reported compounds  $[\text{Os}_6(\text{CO})_{20}\text{-}\{\text{C}=\text{C}(\text{H})\text{Ph}\}]$ <sup>13</sup> and  $[\text{Os}_6(\text{CO})_{20}(\text{O}_2\text{CCF}_3)_2]$ ,<sup>14</sup> **1** possesses a ‘zig-zag’ metal skeleton, with significant deviations amongst their least square planes. Fig. 3 presents the metal core architecture and the angle values of the corresponding dihedral planes. Despite this irregularity, the structure has a non-crystallographic twofold axis of symmetry passing through the mid-points of the Os(3)–Os(4) and S(1)–S(2) vectors. The dipyriddy

**Table 1** Spectroscopic data for clusters **1** to **3**

Compound	IR, $\nu(\text{CO})^a/\text{cm}^{-1}$	<sup>1</sup> H NMR, $\delta(\text{J}/\text{Hz})^b$	Mass spectrum, $m/z^c$
<b>1</b>	2087ms, 2064s, 2031vs, 2005s, 1983ms, 1966w, 1943ms, 1923vw	9.24 (2H <sub>a</sub> , dd, $J = 7.4, 2.0$ ), 7.86 (2H <sub>b</sub> , m), 7.65 (2H <sub>a</sub> , dd, $J = 7.1, 1.8$ ) 7.23 (2H <sub>c</sub> , m)	1809(1809)
<b>2</b>	2099vw, 2089vw, 2074vs, 2064vs, 2045s, 2031w, 2020vs, 2003s	9.17 (2H <sub>a</sub> , dd, $J = 7.4, 2.0$ ), 7.80 (2H <sub>b</sub> , m), 7.71 (2H <sub>a</sub> , dd, $J = 7.1, 1.8$ ), 7.32 (2H <sub>c</sub> , m), $-14.60$ (1H, s, OsH)	1729(1729)
<b>3</b>	2088ms, 2066s, 2034vs, 2008s, 1986ms, 1968w, 1945ms, 1924vw	9.22 (H <sub>a</sub> , dd, $J = 7.4, 2.0$ ), 9.02 (H <sub>d</sub> , dd, $J = 7.4, 2.0$ ), 7.85 (H <sub>b</sub> , m), 7.73 (H <sub>b</sub> , m), 7.64 (H <sub>a</sub> , dd, $J = 7.1, 1.8$ ), 7.32 (H <sub>a</sub> , dd, $J = 7.1, 1.8$ ), 7.23 (H <sub>c</sub> , m), 7.05 (H <sub>c</sub> , m)	<sup>d</sup>

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup> In  $\text{CD}_2\text{Cl}_2$ . <sup>c</sup> Simulated values given in parentheses. <sup>d</sup> No satisfactory mass spectrum.



Scheme 1

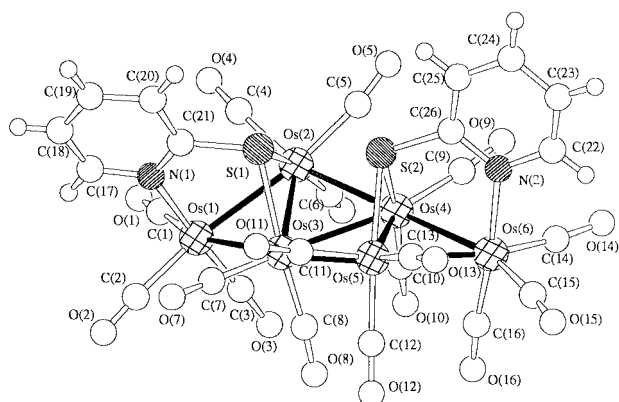


Fig. 1 Molecular structure of cluster **1** showing the atom-labelling scheme for non-hydrogen atoms.

disulfide ligand, in the form of two pyridine-2-thiolate ( $C_5H_4NS$ ) moieties, bridges the osmium triangles at two ends of the rafted skeleton in a  $\mu_3-\eta^2$  fashion. This kind of bridging mode has also been observed in  $[Ru_3(CO)_9(\mu-H)(\mu_3-C_5H_4NS)]^{15}$  and  $[Os_3(CO)_9(\mu-H)(\mu_3-C_5H_4NS)]^{16}$ . All the bonding parameters within the bridging triangles agree satisfactorily with those of the triosmium analogue<sup>16</sup> except the  $Os(2)-Os(3)$  [2.734(1) Å] and  $Os(4)-Os(5)$  [2.715(1) Å] vectors which are comparatively short (*cf.* 2.874(1) Å in  $[Os_3(CO)_9(\mu-H)(\mu_3-C_5H_4NS)]$ ). The non-bonding  $S(1)\cdots S(2)$  separation [3.04 Å] is significantly larger than the average S–S distance found in the complex  $[Cu(C_5H_4NS-SNC_5H_4)_2][ClO_4]^{17}$  (2.04 Å) where a direct S–S bond remains. However, this separation is less than the sum of the van der Waals radii of sulfur [3.60 Å]. The lone-pair lone-pair repulsion results in slightly longer  $Os(2)-Os(4)$  and  $Os(3)-Os(5)$  vectors [2.854(1) and 2.856(1) Å respectively].

In order to study the redox properties of the species, a voltammetric method was used to examine its electrochemical behaviour. The cyclic voltammograms of compound **1** in acetonitrile solution show a pair of quasi-reversible reduction couples at *ca.*  $E_{1/2} = -0.36$  and  $-0.20$  V *vs.* Ag–AgNO<sub>3</sub>. It is likely that these couples are metal-based, generally in line with those obtained by Drake<sup>18</sup> and Goudsmit *et al.*<sup>19</sup> for triangular hexaosmium raft systems. An additional irreversible anodic wave appearing at *ca.* +0.61 V *vs.* Ag–AgNO<sub>3</sub> could be tentatively assigned as arising from the oxidation of a sulfur donor. The absence of such an irreversible oxidation wave for the “free” ligand and another structurally related organic

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

$Os(1)-Os(2)$	2.819(1)	$Os(2)-S(1)$	2.414(6)
$Os(1)-Os(3)$	2.796(1)	$Os(3)-S(1)$	2.422(6)
$Os(2)-Os(3)$	2.734(1)	$Os(4)-S(2)$	2.452(6)
$Os(2)-Os(4)$	2.854(1)	$Os(5)-S(2)$	2.413(7)
$Os(3)-Os(4)$	2.822(1)	$C(21)-S(1)$	1.79(2)
$Os(3)-Os(5)$	2.856(1)	$C(26)-S(2)$	1.78(3)
$Os(4)-Os(5)$	2.715(1)	$Os(1)-N(1)$	2.17(2)
$Os(4)-Os(6)$	2.812(1)	$Os(6)-N(2)$	2.17(2)
$Os(5)-Os(6)$	2.829(1)		
$Os(2)-S(1)-Os(3)$	68.8(2)	$Os(4)-S(2)-Os(5)$	67.8(2)
$S(1)-Os(3)-Os(2)$	55.4(1)	$S(2)-Os(5)-Os(4)$	56.8(2)
$Os(3)-Os(2)-S(1)$	55.7(1)	$Os(5)-Os(4)-S(2)$	55.4(2)

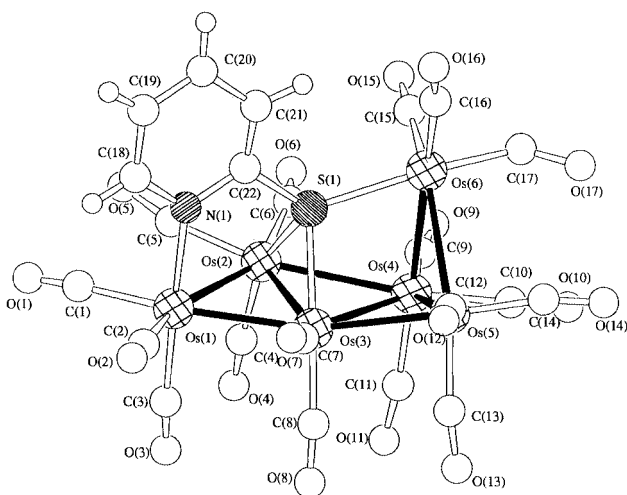
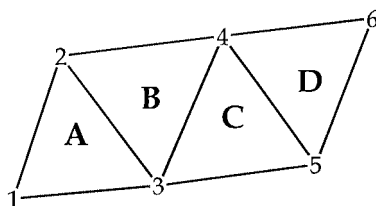
molecule, 2-sulfanylpuridine, provides strong evidence for our suggestion.

The complex was found to undergo protonation in the presence of excess of the strong Brønsted acid  $CF_3CO_2H$  to give a highly unstable cationic cluster **3** which was formulated and characterised on the basis of solution IR and <sup>1</sup>H NMR. Attempts have been made to obtain single crystals for **3**, but the cluster decomposed even at  $-20$  °C. In <sup>1</sup>H NMR analysis, although the SH resonance signal cannot be detected (normally occurs in the range  $\delta -4$  to 4),<sup>20</sup> there are eight instead of four resonance peaks due to aromatic protons. This indicates two pyridine rings in different magnetic environments, which differs from the situation observed in compound **1**. A broad peak at *ca.* 2435  $cm^{-1}$  in the IR spectrum provides evidence for a  $\nu(SH)$ . This value is comparable to bridging S–H vibrations of other metal complexes.<sup>21</sup> Further addition of  $CF_3CO_2H$  did not lead to formation of dicationic species. Using a stronger but more bulky electrophile, such as  $CH_3^+$ , did not give a monocationic species. Heating cluster **3** with an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) did not regenerate compound **1**. Attempts to generate the binary cluster  $[Os_6(CO)_{21}]$  *in situ* by continuous CO bubbling through a solution of **1** only led to cluster decomposition. This again illustrates the importance of the surrounding ligands in cluster stability.<sup>22,23</sup>

A perspective drawing of cluster **2** with the atomic numbering scheme is shown in Fig. 2. Some important bond parameters are in Table 3. Compound **2** exists as two crystallographically independent molecules with comparable bonding parameters. The metal core arrangement is similar to that of **1**, except one end of the  $Os_3$  plane folds up to give a step-like environment for the co-ordination of a sulfur ligand. Com-

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

Os(1)–Os(2)	2.899(4)	Os(4)–Os(6)	2.903(4)
Os(1)–Os(3)	2.744(3)	Os(5)–Os(6)	3.004(4)
Os(2)–Os(3)	2.738(4)	Os(1)–N(1)	2.14(4)
Os(2)–Os(4)	2.985(3)	Os(2)–S(1)	2.34(1)
Os(3)–Os(4)	2.817(3)	Os(3)–S(1)	2.34(2)
Os(3)–Os(5)	2.776(3)	Os(6)–S(1)	2.39(1)
Os(4)–Os(5)	2.877(4)	C(22)–S(1)	1.76(4)
Os(2)–S(1)–Os(3)	71.6(4)	Os(3)–Os(2)–S(1)	54.3(4)
S(1)–Os(3)–Os(2)	54.1(4)		

**Fig. 2** Molecular structure of cluster **2**. Details as in Fig. 1.

plane	Dihedral Angle/°	plane	Dihedral Angle/°
A/B	157.0	A/B	178.3
B/C	153.7	B/C	155.6
C/D	158.0	C/D	98.6

$[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})_2]$   $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})]$   
**1** **2**

**Fig. 3** Pictorial representation of the metal skeleton of compounds **1** and **2**. All ligands are omitted for clarity. The numbers represent the metal atoms, while letters define the corresponding dihedral planes.

paratively short Os(2)–S(1) [2.34(1) Å] and Os(3)–S(1) [2.34(2) Å] bond distances along with a relatively large Os(2)–S(1)–Os(3) [71.6(4)°] angle reveal an exocyclic sulfur atom intimately associated with the cluster envelope. This phenomenon is also amplified by a ‘folding up’ of the triangular plane defined by Os(4)–Os(5)–Os(6). A summary of the dihedral plane values is given in Fig. 3. In this regard, the pyridine-2-thiolate ligand can be considered as an adsorbate mimic on a metal surface,<sup>24</sup> which has a high resemblance to the adsorption of a benzenethiol molecule on the Mo(110) plane in desulfurisation processes.<sup>25</sup> It is noteworthy that the pyridine-2-thiolate ligand behaves as a 7-electron donor by bridging four metal atoms. The first example of this kind of bonding mode was reported by Deeming *et al.*<sup>15</sup> in  $[\{\text{Ru}_3(\text{CO})_7(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})\}_3]$ . In accordance with our <sup>1</sup>H NMR experiments, a hydride ligand is present in the cluster. However, this could not be located

crystallographically because of the poor quality of the diffraction data. As far as electron counting is concerned, cluster **2** contains 90 cluster valence electrons (CVEs) and is consistent with the nine metal–metal bonds observed in the structure according to the effective atomic number (EAN) rule.

## Experimental

All reactions and manipulations were carried out in an atmosphere of dry dinitrogen using standard Schlenk techniques. All solvents were purified and dried by standard methods prior to use.<sup>26</sup> Chemicals were purchased from Aldrich chemicals and used as received. Vacuum pyrolysis of  $[\text{Os}_3(\text{CO})_{12}]$  gave hexaosmium cluster  $[\text{Os}_6(\text{CO})_{18}]$ <sup>27</sup> and the compound  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$  was prepared as described in the literature.<sup>28</sup> Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer, using 0.5 mm thick calcium fluoride solution cells, proton NMR spectra on a Bruker DPX 300 NMR spectrometer using  $\text{CD}_2\text{Cl}_2$  with reference to  $\text{SiMe}_4$  ( $\delta$  0) and mass spectra on a Finnigan MAT 95 instrument by the fast atom bombardment technique, using *m*-nitrobenzyl alcohol or  $\alpha$ -thioglycerol as the matrix solvents. Elemental analyses were conducted by Butterworth Laboratories, UK. Routine separation of products in air was performed by thin-layer chromatography (TLC) on plates coated with Merck Kieselgel 60 GF<sub>254</sub>.

All electrochemical measurements were performed under an argon purge to exclude oxygen. Acetonitrile was freshly distilled and deoxygenated prior to use. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium tetrafluoroborate in MeCN. Voltammetric experiments were carried out with a Princeton Applied Research (PAR) model 273A potentiostat connected to an interfaced computer. A standard three-electrode cell consisting of an Ag–AgNO<sub>3</sub> reference electrode (Bioanalytical), a platinum wire counter electrode (Aldrich) and a glassy carbon working electrode (Bioanalytical) was employed.

## Syntheses

$[\text{Os}_6(\text{CO})_{16}(\mu_3\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})_2]$  **1** and  $[\text{Os}_6(\text{CO})_{17}(\mu\text{-H})(\mu_4\text{-}\eta^2\text{-C}_5\text{H}_4\text{NS})]$  **2**. The cluster  $[\text{Os}_6(\text{CO})_{16}(\text{MeCN})_2]$  [110 mg, 0.066 mmol] was dissolved in  $\text{CH}_2\text{Cl}_2$  (30  $\text{cm}^3$ ) and stirred with addition of one equivalent of 2-Aldrithol at ambient temperature. After the reaction proceeded for 6 h, the solution gradually changed from blackish brown to bright brown. It was then filtered and the volume reduced to *ca.* 5  $\text{cm}^3$  *in vacuo*. The residue was subsequently purified by TLC using hexane– $\text{CH}_2\text{Cl}_2$  (10 : 10 v/v) as the eluent. Two bands of greenish brown **1** ( $R_f$  0.63; 48 mg, 0.027 mmol, 40%) and purple **2** ( $R_f$  0.57; 18 mg, 0.010 mmol, 16%) together with several uncharacterised, low-yield products were eluted consecutively. Purple crystals suitable for diffraction analyses were obtained separately in  $\text{CHCl}_3$ –toluene (1 : 4 v/v) over a period of 2 and 5d respectively for compounds **1** and **2** (Found for **1**: C, 16.2; H, 0.4; N, 1.5; S, 3.5. Calc. for  $\text{C}_{27}\text{H}_9\text{Cl}_3\text{N}_2\text{O}_{16}\text{Os}_6\text{S}_2$ : C, 16.8; H, 0.5; N, 1.5; S, 3.3. Found for **2**: C, 15.1; H, 0.2; N, 0.9; S, 1.9. Calc. for  $\text{C}_{22}\text{H}_5\text{NO}_{17}\text{Os}_6\text{S}$ : C, 15.3; H, 0.3; N, 0.8; S, 1.9%).

**Protonation of compound 1.** To a  $\text{CH}_2\text{Cl}_2$  solution (40  $\text{cm}^3$ ) of compound **1** (50 mg, 0.028 mmol) a twentyfold excess of  $\text{CF}_3\text{CO}_2\text{H}$  (0.043  $\text{cm}^3$ , 0.57 mmol) was added dropwise in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) with rapid stirring. The reaction mixture was sampled and monitored by <sup>1</sup>H NMR and solution IR at regular time intervals over a period of 12 h. The conversion into **3** was quantitatively completed after 24 h.

**Methylation of compound 1.** Complex **1** (80 mg, 0.044 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (40  $\text{cm}^3$ ) to produce a deep green solution. A solution of  $\text{CF}_3\text{SO}_3\text{CH}_3$  (0.05  $\text{cm}^3$ , 0.442 mmol) in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) was added dropwise *via* a syringe over a period

**Table 4** Summary of crystal data and data collection parameters for clusters **1** and **2**

	<b>1</b> ·CHCl <sub>3</sub>	<b>2</b>
Empirical formula	C <sub>27</sub> H <sub>9</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>16</sub> Os <sub>6</sub> S <sub>2</sub>	C <sub>22</sub> H <sub>2</sub> NO <sub>17</sub> Os <sub>6</sub> S
<i>M</i>	1809.2 (1929.05 with solvent)	1728.54
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i> (no. 15)	<i>P2<sub>1</sub>/c</i> (no. 14)
<i>a</i> /Å	38.914(2)	16.731(2)
<i>b</i> /Å	11.667(2)	11.857(1)
<i>c</i> /Å	19.134(1)	32.862(1)
$\beta$ /°	103.35(1)	99.36(2)
<i>U</i> /Å <sup>3</sup>	8452(1)	6432.4(9)
<i>Z</i>	8	8
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	183.10	237.35
No. reflections collected	36197	32117
No. unique reflections	7650	7125
<i>R</i> <sub>int</sub>	0.101	0.145
<i>R</i>	0.063	0.077
<i>R</i> '	0.070	0.075

of 10 min. No changes were detected by <sup>1</sup>H NMR monitoring after stirring for 10 h. Attempts to repeat the experiment at an elevated temperature (refluxing CHCl<sub>3</sub>) led to cluster decomposition.

### Crystallography

Diffraction data of compounds **1** and **2** were collected at ambient temperatures on a MAR research imaging plate diffractometer over exposure periods of 12 and 20 min per frame, respectively. For **1** the solution was refined on *F* by full-matrix least-squares analysis with all atoms refined anisotropically while H and C(27) of the solvent molecule were fixed. All the hydrogen atoms in the ligand were generated in their idealised positions (C–H 0.95 Å). Only Os and S atoms were refined anisotropically, while other light atoms such as C, N and O were refined isotropically in compound **2**. Attempts to include all non-hydrogen atoms in anisotropic refinement cycles gave an unsatisfactory structure solution. A summary of the crystallographic data is listed in Table 4. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.<sup>29</sup>

CCDC reference number 186/1500.

See <http://www.rsc.org/suppdata/dt/1999/2521/> for crystallographic files in .cif format.

### Acknowledgements

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