

# The photochemical reaction of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)$ , a triosmium cluster carrying a $\gamma$ -pyrone ligand, with dimethylacetylenedicarboxylate: formation of isomeric clusters

Qi Lin, Weng Kee Leong \*

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

Received 18 August 2004; accepted 15 September 2004

Available online 30 November 2004

## Abstract

The reaction of the cluster  $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)$  (**1**), with DMAD under UV irradiation afforded three isomers of the monosubstituted product,  $\text{Os}_3(\text{CO})_9(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-MeO}_2\text{CCHCCO}_2\text{Me})$  (**2**), and a disubstituted product,  $\text{Os}_3(\text{CO})_8(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-MeO}_2\text{CCHCCO}_2\text{Me})(\mu\text{-MeO}_2\text{CCCCO}_2\text{Me})$  (**3**). The formation of **3** suggests that flipping of the O-heterocycle can occur.

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**Keywords:** Osmium; Clusters; Pyrones; Alkyne

## 1. Introduction

That the cluster core may impart unusual reactivity to a cluster-bound organic substrate has been demonstrated in the quinoline system by Rosenberg [1]. We have for some time been interested in the chemistry of cluster-bound organic substrates [2]. One of the substrates which we have recently turned our attention to are the  $\gamma$ -pyrones. We have earlier reported our investigations into the binding of pyrones onto a triosmium cluster [3]; as well as the reaction of one of these clusters, viz.,  $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)$  (**1**), with alkynes [4]. What we have found was that the presence of the  $\gamma$ -pyrone ligand affected the reactivity of the triosmium cluster towards alkynes; photochemical activation generally led to retention of the pyrone ligand and metal–metal bond scission, resulting sometimes in the formation of dinuclear products. We wish to report here our investigations into the reactivity of **1** with

DMAD, which did not proceed like that observed for the other alkynes.

## 2. Results and discussion

The UV photolysis of **1** with excess DMAD in a cyclohexane/toluene mixture led to the isolation of three isomers of the DMAD-monosubstituted cluster  $\text{Os}_3(\text{CO})_9(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-MeO}_2\text{CCHCCO}_2\text{Me})$ , viz., **2a–c**, and a disubstituted cluster  $\text{Os}_3(\text{CO})_8(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-MeO}_2\text{CCHCCO}_2\text{Me})(\mu\text{-MeO}_2\text{CCCCO}_2\text{Me})$  (**3**). A similar irradiation with visible light yielded only small amounts of products and mainly unreacted **1** even after 4 days. This is in contrast to the reactions with the other alkynes and suggests that the reaction is initiated by CO ejection rather than Os–Os bond scission. The structures of all four clusters have been determined by single crystal X-ray diffraction studies; the ORTEP diagrams for **2a**, **2b**, **2c** and **3** are given in Figs. 1–4, respectively, and a common atomic numbering scheme and selected bond parameters for all four clusters are given in Table 1.

\* Corresponding author. Tel.: +65 68745131; fax: +65 67791691.  
E-mail address: [chmlwk@nus.edu.sg](mailto:chmlwk@nus.edu.sg) (W.K. Leong).

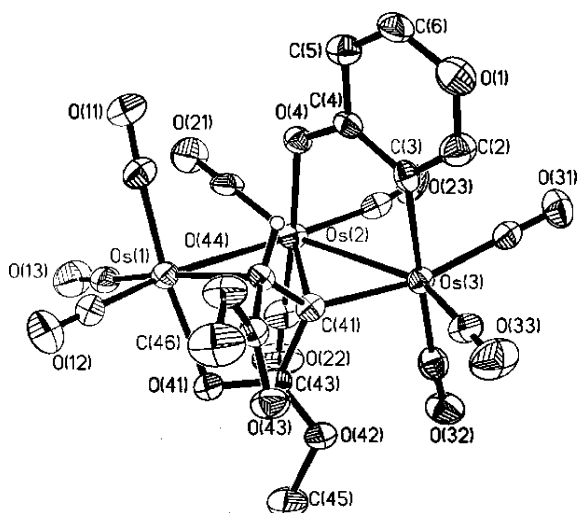


Fig. 1. ORTEP diagram of **2a** (50% probability thermal ellipsoids; methyl and pyrone hydrogens omitted).

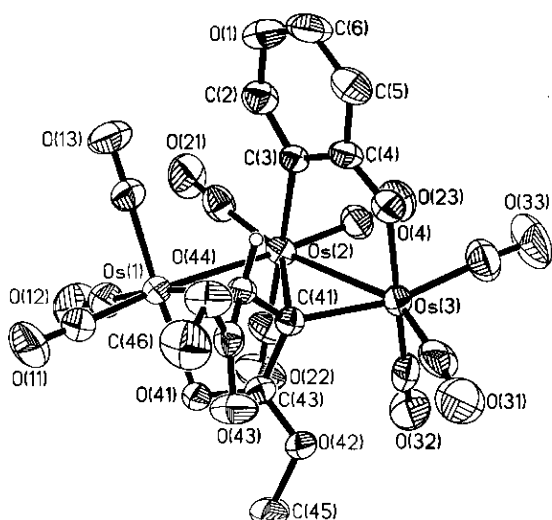


Fig. 2. ORTEP diagram of **2b** (50% probability thermal ellipsoids; methyl and pyrone hydrogens omitted).

The observation of trinuclear products in this reaction can be contrasted with that of  $\text{Os}_3(\text{CO})_{12}$ , for which diosmium compounds were obtained under photochemical conditions [5]; trinuclear compounds with DMAD was obtained via thermal reaction of  $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$  [6].

The carbonyl oxygen of the  $\mu\text{-C}_5\text{H}_3\text{O}_2$  ligand are bonded to the central Os atom in clusters **2a** and **2c**, while it is bonded to a terminal Os in **2b**; the carboxylate group of the  $\mu_3\text{-MeO}_2\text{CCHCO}_2\text{Me}$  ligand in **2a** and **2c** are on different faces, with respect to the  $\mu\text{-C}_5\text{H}_3\text{O}_2$  ligand, of the triosmium framework. The  $\text{MeO}_2\text{CCHCO}_2\text{Me}$  ligands in **2a–c** are coordinated via a  $\mu_3\text{-}\eta_2, \eta_1, \eta_1$  mode to the open triangular osmium core, with C(41) bonding to Os(2) and Os(3), C(42) bonding to Os(1) (Fig. 5), and an additional interaction involving O(41) (of one of the carboxylate groups) with Os(1). The C(41)–C(42) bond lengths (1.512(7)–1.532(8) Å) are typical of an  $\text{sp}^3\text{-sp}^3$  C–C single bond [7]. It thus appears that the hy-

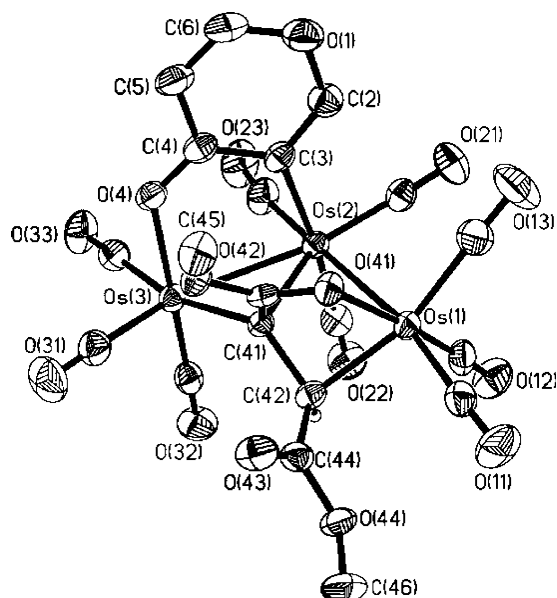


Fig. 3. ORTEP diagram of **2c** (50% probability thermal ellipsoids; methyl and pyrone hydrogens omitted).

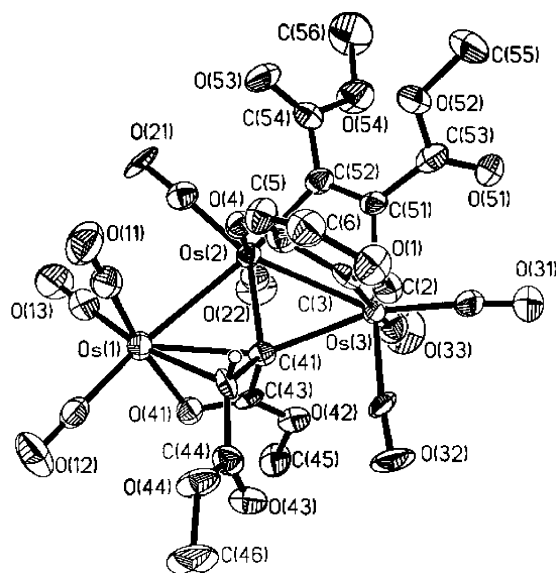
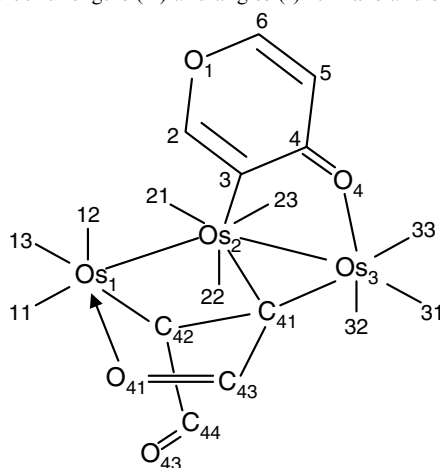


Fig. 4. ORTEP diagram of **3** (50% probability thermal ellipsoids; methyl and pyrone hydrogens omitted).

dride has migrated onto the  $\text{C}\equiv\text{C}$  functionality, which has essentially been reduced to a C–C single bond.

Cluster **3** has one DMAD coordinated as an alkene; the other DMAD is bonded to the triosmium core in a  $\mu_3$  mode, very similar to that in **2**. However, an unusual feature in **3** is the apparent pentacoordination at C(41). The non-bonded C(41)···Os(1) distances for **2a–c** lie between 2.635(7) and 2.659 Å, while the Os–C bonds are in the range 2.084(11) and 2.266(5) Å for the four clusters. Thus the Os(1)–C(41) and Os(3)–C(41) distances of 2.419(11) and 2.425(11) Å, respectively, in **3** are indicative of weak bonding interactions. Furthermore, the C(41)–C(42) bond length

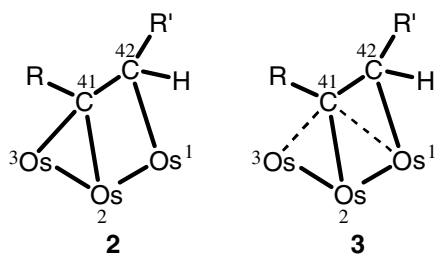
Table 1

Common cluster numbering scheme and selected bond lengths (Å) and angles (°) for **2a–c** and **3**

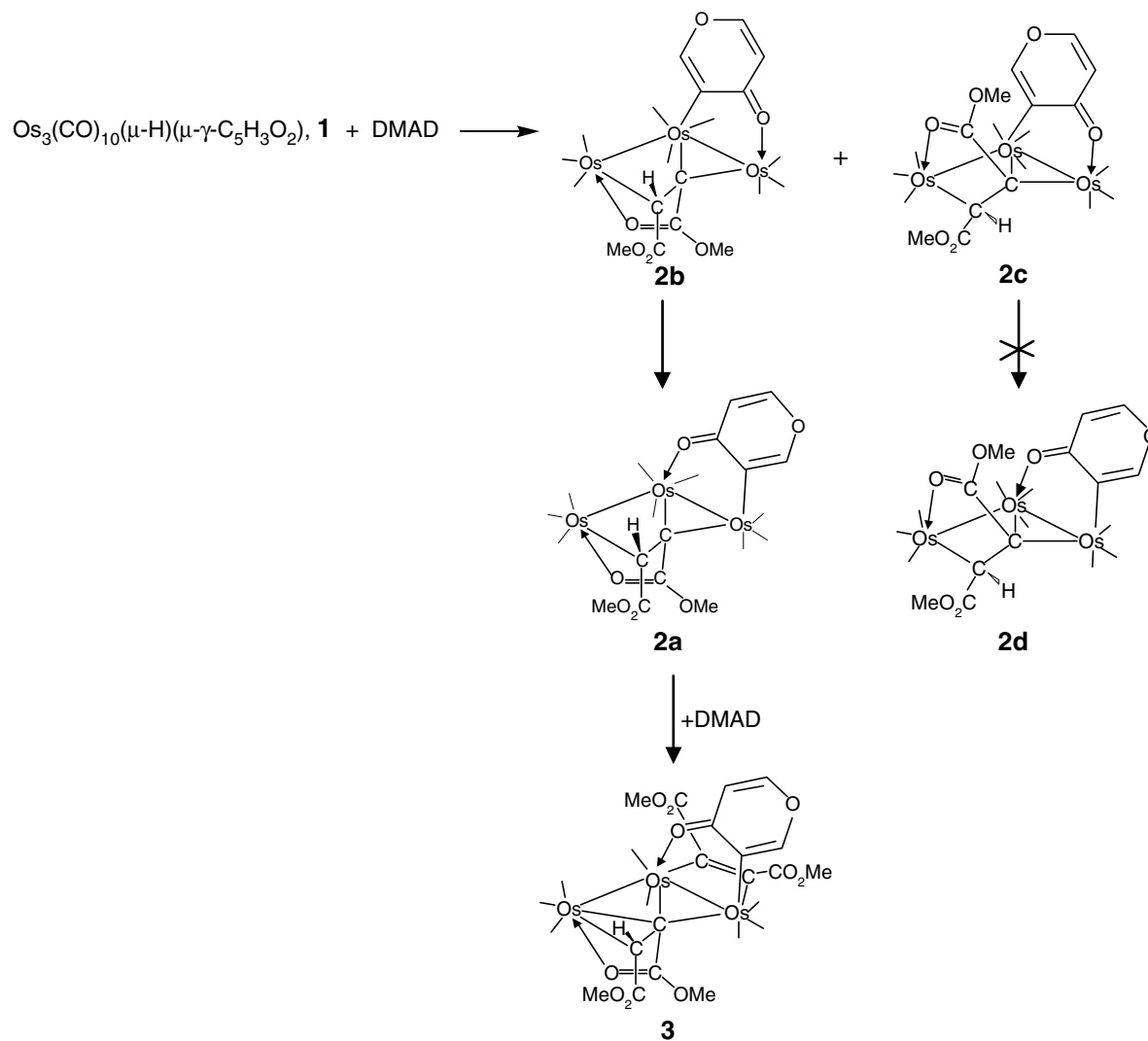
	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3</b>
Bond length (Å)				
Os(1)–Os(2)	2.8741(4)	2.9192(4)	2.9050(3)	2.9013(7)
Os(2)–Os(3)	2.8171(3)	2.8173(4)	2.8129(4)	2.8928(6)
Os(1)–O(41)	2.149(4)	2.154(5)	2.143(4)	2.158(8)
Os(1)···C(41)	2.645(6)	2.635(7)	2.640(6)	2.419(11)
Os(1)–C(42)	2.166(6)	2.203(7)	2.168(6)	2.160(11)
Os(2)/Os(3)–O(4) <sup>a</sup>	2.118(4)	2.111(5)	2.127(4)	2.112(8)
Os(2)–C(41)	2.219(5)	2.263(7)	2.266(5)	2.084(11)
Os(3)–C(41)	2.126(6)	2.102(7)	2.099(5)	2.425(11)
Os(3)/Os(2)–C(3) <sup>b</sup>	2.141(6)	2.172(7)	2.146(6)	2.140(12)
O(4)–C(4)	1.279(6)	1.260(9)	1.263(8)	1.274(14)
C(41)–C(42)	1.512(7)	1.516(9)	1.532(8)	1.480(15)
C(41)–C(43)	1.484(8)	1.462(10)	1.486(7)	1.480(16)
C(42)–C(44)	1.478(7)	1.460(10)	1.488(8)	1.456(18)
C(43)–O(41)	1.243(7)	1.268(8)	1.245(7)	1.257(14)
C(44)–O(43)	1.212(7)	1.218(9)	1.197(8)	1.214(16)
Bond angle (°)				
Os(3)–Os(2)–Os(1)	108.246(10)	106.388(12)	106.896(9)	109.135(19)
O(41)–Os(1)–Os(2)	83.98(11)	85.33(14)	86.92(11)	84.6(2)
C(42)–Os(1)–Os(2)	72.87(14)	73.00(17)	72.61(15)	75.0(3)
Os(2)–C(41)–Os(3)	80.82(19)	80.3(2)	80.14(18)	79.4(4)
C(43)–O(41)–Os(1)	104.9(4)	103.3(4)	104.9(3)	100.6(7)

<sup>a</sup> Os(2)–O(4) for **2a** and **3**; Os(3)–O(4) for **2b** and **2c**.<sup>b</sup> Os(3)–C(3) for **2a** and **3**; Os(2)–C(3) for **2b** and **2c**.

(1.478(13) Å) in **3** is shorter than those in **2a–c**, and is more typical of  $sp^2$ – $sp^2$  or  $sp^3$ – $sp^2$  C–C single bonds [7]. Thus, the bonding description depicted in Fig. 5 is probably appropriate for **3**.

Fig. 5. Bonding interaction of the DMAD with the metal centres in **2** and **3**.

A solution of cluster **2b** was found to isomerise to **2a** on standing at room temperature, as observed by  $^1\text{H}$  NMR monitoring. Furthermore, UV irradiation of a solution of **2b** with excess DMAD gave **2a** and **3**, and similar treatment with **2a** also gave **3** (by monitoring via  $^1\text{H}$  NMR spectroscopy, and also by IR spectroscopic characterisation after subsequent work-up.) The difference in the structures of clusters **2b** and **3** suggests that the formation of **3** from the reaction of **2b** and **3** involves two steps: DMAD attachment and O-heterocycle flipping or rotation. It is likely that O-heterocycle flipping occurs first since steric hindrance by the second DMAD would make the flipping unfavourable if DMAD attachment occurred first. It is not clear at this point how this heterocycle flipping occurs. The observations suggest that **2b** is the precursor to **2a** (although for-



Scheme 1.

mation of **2a** directly from **1** cannot be ruled out entirely), and the latter is in turn the precursor to **3** via reaction with a further equivalent of DMAD (Scheme 1). On the other hand, photolysis of **2c** did not afford the expected **2d**; presumably, flipping of the O-heterocycle was prevented by steric hindrance from the  $\text{MeO}_2\text{CCHCCO}_2\text{Me}$  group on the same side of the cluster frame.

### 3. Conclusions

The reaction of the triosmium cluster **1** which carries a  $\gamma$ -pyrone ligand with DMAD gave triosmium chain products which incorporated the DMAD. These products can be regarded as essentially CO substitution derivatives with scission of a metal–metal bond. The three monosubstitution products are stereoisomers

which differ in their relative orientations of the pyrone and DMAD. The pyrone ligand can undergo flipping or rotation about the metal chain and this appears to be a prerequisite for the second substitution by DMAD.

### 4. Experimental

#### 4.1. General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use. IR spectra were recorded as hexane solutions unless otherwise stated. NMR spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer as  $\text{CDCl}_3$  solutions unless

otherwise stated.  $^1\text{H}$  chemical shifts reported are referenced against the residual proton signals of the solvents. ESI spectra were obtained on a Finnigan MAT LCQ, with a spray voltage of 4.5 kV and capillary temperature of 353 K, as  $\text{CH}_3\text{CN}$  solutions. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The preparation of  $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\gamma\text{-C}_5\text{H}_3\text{O}_2)$  (**1**), has been described previously [3]. The cluster  $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$  was prepared according to a literature method [8]. All other reagents were from commercial sources and used as supplied. TLC separations were on silica plates of 0.25 or 0.5 mm thickness, and extracted with dichloromethane. Photochemical reactions were performed with a Hanovia 450 W UV lamp, with a nominal  $\lambda_{\text{max}}$  of 254 nm.

#### 4.2. Photochemical reactions of **1** with DMAD

A solution of cluster **1** (23.1 mg, 0.024 mmol) and DMAD (10 drops) in a solvent mixture of cyclohexane (15 mL) and toluene (5 mL) was degassed in a quartz Carius tube by three freeze-pump-thaw cycles and then irradiated with a UV lamp at RT for 5 h. The solvent was removed under reduced pressure and the residue obtained was re-dissolved in the minimum volume of dichloromethane and chromatographed on TLC plates. Elution with hexane/ $\text{CH}_2\text{Cl}_2$  (3/2, v/v) gave, other than a trace of unreacted **1**, four major bands.

Band 1 ( $R_f = 0.23$ ) gave red crystalline  $\text{Os}_3(\text{CO})_9(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-}R,S\text{-MeO}_2\text{CCHCCO}_2\text{Me})$  (**2a**) (yield = 6.2 mg, 24%): IR  $\nu_{\text{CO}}$  2089w, 2067s, 2035m, 2000s, 1990m(sh);  $^1\text{H}$  NMR  $\delta$  7.84 (1H, s, H2), 7.66 (1H, d,  $^3J_{56} = 5.0$  Hz, H6), 6.11 (1H, d, H5), 3.73 (3H, s, OMe), 3.68 (3H, s, OMe), 2.77 (1H, s, =CH). Calculated for  $\text{C}_{20}\text{H}_{10}\text{O}_{15}\text{Os}_3$ : C, 22.64; H, 0.95. Found: C, 22.46; H, 1.07%.

Band 2 ( $R_f = 0.19$ ) gave yellow crystalline  $\text{Os}_3(\text{CO})_9(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-}R,S\text{-MeO}_2\text{CCHCCO}_2\text{Me})$  (**2b**) (yield = 3.0 mg, 12%): IR  $\nu_{\text{CO}}$  2089w, 2071s, 2034s, 2000s, 1989s, 1965w;  $^1\text{H}$  NMR  $\delta$  7.72 (1H, s, H2), 7.62 (1H, d,  $^3J_{56} = 5.0$  Hz, H6), 6.26 (1H, d, H5), 3.76 (3H, s, OMe), 3.72 (3H, s, OMe), 2.96 (1H, s, =CH). Calculated for  $\text{C}_{20}\text{H}_{10}\text{O}_{15}\text{Os}_3$ : C, 22.64; H, 0.95. Found: C, 22.96; H, 0.70%.

Band 3 ( $R_f = 0.14$ ) gave yellow crystalline  $\text{Os}_3(\text{CO})_9(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-}S,R\text{-MeO}_2\text{CCHCCO}_2\text{Me})$  (**2c**) (yield = 5.2 mg, 20%): IR  $\nu_{\text{CO}}$  2090w, 2071s, 2038m, 2003s, 1991m(sh), 1985w(sh), 1967w;  $^1\text{H}$  NMR  $\delta$  8.04 (1H, s, H2), 7.61 (1H, d,  $^3J_{56} = 5.0$  Hz, H6), 6.14 (1H, d, H5), 4.08 (1H, s, =CH), 3.82 (3H, s, OMe), 3.18 (3H, s, OMe). Calculated for  $\text{C}_{20}\text{H}_{10}\text{O}_{15}\text{Os}_3$ : C, 22.64; H, 0.95. Found: C, 22.70; H, 0.83%.

Band 4 ( $R_f = 0.09$ ) gave red crystalline  $\text{Os}_3(\text{CO})_8(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu_3\text{-}R,S\text{-MeO}_2\text{CCHCCO}_2\text{Me})(\mu\text{-MeO}_2\text{CCCC-$

$\text{O}_2\text{Me})$  (**3**) (yield = 4.3 mg, 15%): IR  $\nu_{\text{CO}}(\text{CH}_2\text{Cl}_2)$  2098w(sh), 2086s, 2027s, 2018m(sh), 1956w;  $^1\text{H}$  NMR  $\delta$  7.65 (1H, s, H2), 7.60 (1H, d,  $^3J_{56} = 5.0$  Hz, H6), 5.91 (1H, d, H5), 3.88 (3H, s,  $\mu_3\text{-OMe}$ ), 3.82 (3H, s,  $\mu_3\text{-OMe}$ ), 3.80 (6H, s,  $\mu\text{-OMe}$ ), 3.31 (1H, s, =CH). ESI-MS ( $m/z$ ) 1161  $[\text{M} - \text{Me}]^-$ . Calculated for  $\text{C}_{25}\text{H}_{16}\text{O}_{18}\text{Os}_3 \cdot 1/4\text{C}_6\text{H}_{12}$ : C, 26.61; H, 1.60. Found: C, 26.71; H, 1.68%. Presence of hexane in the crystalline samples used for microanalysis was confirmed by  $^1\text{H}$  NMR spectroscopy.

#### 4.3. Reaction of **2a** or **2b** with DMAD

Into a solution of **2a** (17.1 mg, 0.016 mmol) in  $\text{CDCl}_3$  (0.6 mL) placed in an NMR tube fitted with a Teflon valve was added DMAD (three drops). The solution was degassed by three freeze-pump-thaw cycles and irradiated with a UV lamp at 5 °C for 9 h. The solvent was removed under reduced pressure and the residue obtained was re-dissolved in the minimum volume of dichloromethane and chromatographed on TLC plates. Elution with hexane/ $\text{CH}_2\text{Cl}_2$  (1/1, v/v) gave unchanged **2a** (1.5 mg) and **3** (yield = 6.2 mg, 32%); both identified by their IR spectra.

A similar reaction of **2b** (6.5 mg, 0.006 mmol) with DMAD (three drops) gave **2a** (yield = 0.3 mg, 4.6%), unchanged **2b** (0.7 mg), both identified by their  $^1\text{H}$  NMR spectra, and **3** (yield = 1.0 mg, 14%) which was identified by its IR spectrum.

#### 4.4. Crystal structure determinations

Crystals were grown from dichloromethane (or dibromomethane)/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo  $K\alpha$  radiation, with the SMART suite of programs [9]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [10], and for absorption effects with SADABS [11]. Structural solution and refinement were carried out with the SHELXTL suite of programs [12]. Crystal and refinement data are summarised in Table 2.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic hydrogens were placed in calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model (but see below). Metal hydrides were placed in positions calculated with XHYDEX [13] and refined with a fixed isotropic thermal parameter and riding on one of the osmium atoms it is attached to.

A  $\text{CH}_2\text{Br}_2$  solvent molecule was found in **2a**.

Table 2  
Crystal data for clusters **2a–c** and **3**

Compound code	<b>2a</b>	<b>2b</b>	<b>2c</b>	<b>3</b>
Empirical formula	C <sub>20</sub> H <sub>10</sub> O <sub>15</sub> Os <sub>3</sub> · CH <sub>2</sub> Br <sub>2</sub>	C <sub>20</sub> H <sub>10</sub> O <sub>15</sub> Os <sub>3</sub>	C <sub>20</sub> H <sub>10</sub> O <sub>15</sub> Os <sub>3</sub>	C <sub>25</sub> H <sub>16</sub> O <sub>18</sub> Os <sub>3</sub>
Formula weight	1234.73	1060.88	1060.88	1174.98
Temperature (K)	223(2)	223(2)	223(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>C</i> <sub>2</sub> / <i>c</i>	<i>P</i> <sub>2</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	37.907(2)	17.1523(9)	9.3493(5)	8.9631(4)
<i>b</i> (Å)	10.3335(6)	8.9749(5)	10.5178(6)	9.1078(4)
<i>c</i> (Å)	14.9480(9)	17.8415(9)	12.9335(8)	19.7575(10)
$\alpha$ (°)	90	90	92.899(1)	103.163(2)
$\beta$ (°)	104.159(1)	113.036(1)	96.155(1)	95.034(2)
$\gamma$ (°)	90	90	103.647(1)	104.243(2)
Volume (Å <sup>3</sup> )	5677.4(6)	2527.5(2)	1224.98(12)	1504.47(12)
<i>Z</i>	8	4	2	2
<i>D</i> <sub>calc.</sub> (Mg/m <sup>3</sup> )	2.889	2.788	2.876	2.594
Absorption coefficient (mm <sup>-1</sup> )	16.280	15.117	15.596	12.720
<i>F</i> (000)	4448	1912	956	1076
Crystal size (mm <sup>3</sup> )	0.36 × 0.30 × 0.20	0.04 × 0.10 × 0.32	0.04 × 0.16 × 0.20	0.32 × 0.26 × 0.14
$\theta$ Range for data collection (°)	2.05–30.60	2.11–30.54	2.00–30.46	1.07–29.74
Reflections collected	43,219	33,799	15,492	12,682
Independent reflections [ <i>R</i> <sub>int</sub> ]	8418 [0.0610]	7309 [0.0599]	6845 [0.0564]	7612 [0.0563]
Completeness, % ( $\theta$ , °)	96.4 (30.60)	94.3 (30.54)	91.9 (30.46)	99.7 (24.71)
Maximum and minimum transmission	0.135 and 0.065	0.493 and 0.259	0.337 and 0.172	0.405 and 0.149
Data/restraints/parameters	8418/0/370	7309/0/345	6845/0/345	5114/0/415
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.978	1.089	1.035	1.060
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0336, <i>wR</i> <sub>2</sub> = 0.0719	<i>R</i> <sub>1</sub> = 0.0433, <i>wR</i> <sub>2</sub> = 0.0923	<i>R</i> <sub>1</sub> = 0.0372, <i>wR</i> <sub>2</sub> = 0.0850	<i>R</i> <sub>1</sub> = 0.0497, <i>wR</i> <sub>2</sub> = 0.1342
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0464, <i>wR</i> <sub>2</sub> = 0.0743	<i>R</i> <sub>1</sub> = 0.0565, <i>wR</i> <sub>2</sub> = 0.0967	<i>R</i> <sub>1</sub> = 0.0423, <i>wR</i> <sub>2</sub> = 0.0878	<i>R</i> <sub>1</sub> = 0.0551, <i>wR</i> <sub>2</sub> = 0.1380
Largest difference peak and hole (Å <sup>-3</sup> )	2.357 and -1.482	2.987 and -0.858	2.338 and -1.813	4.105 and -2.657

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication Nos. CCDC 247694–247697. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Acknowledgements

This work was supported by the National University of Singapore (Research Grant No. R143-000-149-112) and one of us (Q.L.) thanks the University for a Research Scholarship.

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