Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 691 (2006) 2048–2054

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Reaction of the heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ with toluene

Yong Leng Kelvin Tan, Weng Kee Leong *

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

Received 26 November 2005; received in revised form 9 January 2006; accepted 9 January 2006
Available online 14 February 2006

Abstract

The heteronuclear cluster $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**4**) reacts with refluxing toluene to form the clusters $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$ (**5**) $RuOs_3(CO)_9(\mu\text{-}CO)_2(\eta^6\text{-}C_6H_5Me)$ (**6**) and $Ru_2Os_3(CO)_{12}(\mu\text{-}CO)(\eta^6\text{-}C_6H_5Me)$ (**7**). Cluster **5** exists as a mixture of five isomers. The inter-relationship among the clusters has also been investigated.

Keywords: Heterometallic complexes; Ruthenium; Osmium; Isomers; Toluene

1. Introduction

Heteronuclear clusters in which the two metals are from the same triad provide an opportunity to investigate any subtle synergistic effects that may be present in such juxtaposition of two similar metals. It also allows comparison of the relative reactivity of the two metals which are expected to have very similar chemical behaviour. Towards this end, we had earlier developed a high-yield synthesis of the hetero group 8 tetranuclear cluster $Os_3Ru(\mu\text{-}H)_2(CO)_{13}$ (**4**) via a synthetic route depicted in Scheme 1, and investigated its reactivity with group 15 ligands [1]. Other work on this cluster was on its synthesis and structure [2], and its employment as a catalyst precursor supported on alumina for a number of catalytic reactions including alkene isomerisation and hydrogenation [3], and CO hydrogenation [4]. In the course of our investigations into its reactivity, we have had recourse to the use of aromatic solvents such as toluene. We found that **4** reacted quite readily with toluene to form novel cluster species. Our investigations on this are reported here.

2. Results and discussion

When **4** was refluxed for 12 h in toluene, the colour of the solution changed from orange to brown. Besides unreacted **4**, TLC separation afforded **3** (probably a decomposition product of **4**), and two novel clusters, viz., $RuOs_3(CO)_9(\mu\text{-}CO)_2(\eta^6\text{-}C_6H_5Me)$ (**6**) and $Ru_2Os_3(CO)_{12}(\mu\text{-}CO)(\eta^6\text{-}C_6H_5Me)$ (**7**) in 29% and 35% yields (calculated with respect to consumed **4**), respectively. Shortening the reaction time afforded **6** (20% yield) but no **7**, and another cluster $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$ (**5**). All three clusters **5**–**7** have been characterised completely, including by single crystal X-ray structural analyses; the ORTEP plots showing their molecular structure, together with selected bond parameters, are given in Figs. 1–3, respectively.

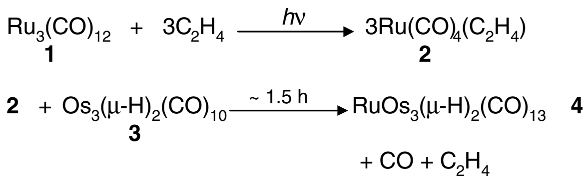
Cluster **5** was also obtained in trace amounts from the synthesis of cluster **4**. Attempts at a high yield synthesis by reacting **4** with excess **2** under both ambient and elevated temperatures were unsuccessful. Similarly, the reaction of **4** with **1** in refluxing hexane also failed to produce the desired product.

Cluster **5** is formally a 74-valence electron cluster, consistent with the observed edge-bridged tetrahedral metal core [5]. The structural parameters are similar to those of its known homonuclear analogue, $Os_5(\mu\text{-}H)_2(CO)_{16}$ (**5a**) [6]. Other reported dihydrido-ruthenium or osmium carbonyl cluster complexes with an edge-bridged tetrahedral metal framework are $H_2Os_4Rh(CO)_{13}(\eta^5\text{-}C_5R_5)$ (R = H, Me) [7], and $H_2RuOs_4(CO)_{13}(\eta^6\text{-}C_6H_6)$ [8], which contain organic ligands as well as hydride and carbonyl groups. The two hydride ligands in **5** bridge the elongated Os(1)–Ru(5) and Os(2)–Ru(5) edges. The structure possessed

---

* Corresponding author.
E-mail address: chmlwk@nus.edu.sg (W.K. Leong).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.01.008



$$\underset{\mathbf{1}}{Ru_3(CO)_{12}} + 3C_2H_4 \xrightarrow{h\nu} \underset{\mathbf{2}}{3Ru(CO)_4(C_2H_4)}$$

$$\mathbf{2} + \underset{\mathbf{3}}{Os_3(\mu\text{-}H)_2(CO)_{10}} \xrightarrow{\sim 1.5\ h} RuOs_3(\mu\text{-}H)_2(CO)_{13}\ \mathbf{4} + CO + C_2H_4$$

Scheme 1.

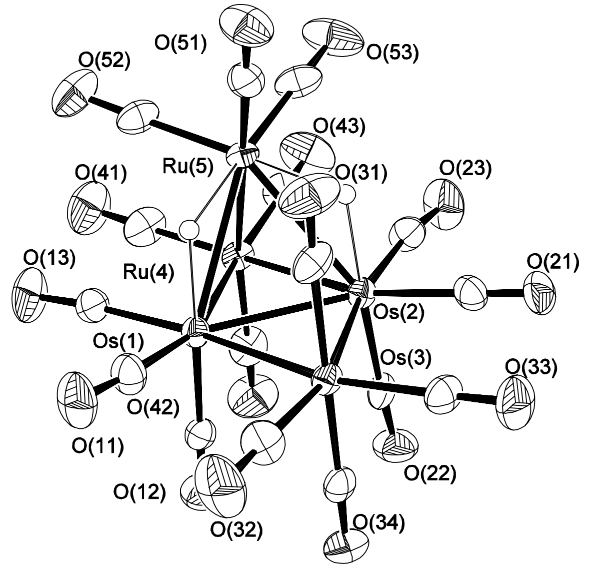


Fig. 1. ORTEP diagram (50% probability thermal ellipsoids) of the main isomer, and selected lengths (Å), for **5**. Os(1)–Os(2) = 2.7909(4); Os(1)–Os(3) = 2.8839(5); Os(1)–Ru(4) = 2.8410(6); Os(1)–Ru(5) = 2.9475(6); Os(2)–Os(3) = 2.8904(5); Os(2)–Ru(4) = 2.8375(6); Os(2)–Ru(5) = 2.9581(6); Ru(4)–Ru(5) = 2.7674(7).

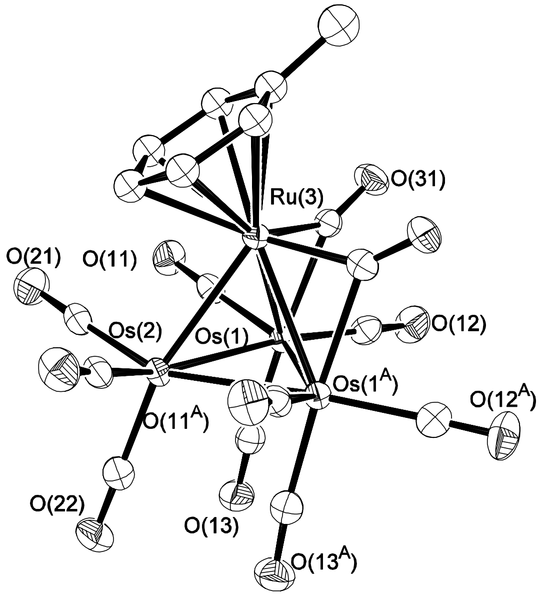


Fig. 2. ORTEP diagram (50% probability thermal ellipsoids, organic hydrogens omitted) and selected lengths (Å) and angles (°) for **6**. Only one orientation of the disordered toluene is shown. Os(1)–Os(2) = 2.7854(4); Os(1)–Ru(3) = 2.8165(7); Os(1)–Os(1A) = 2.9411(5); Os(2)–Ru(3) = 2.7748(8); Os(2)–Os(1A) = 2.7854(4); Os(1)–C(31) = 2.229(7); Ru(3)–C(31) = 1.964(8); Os(1)–C(31)–Ru(3) = 84.1(3).

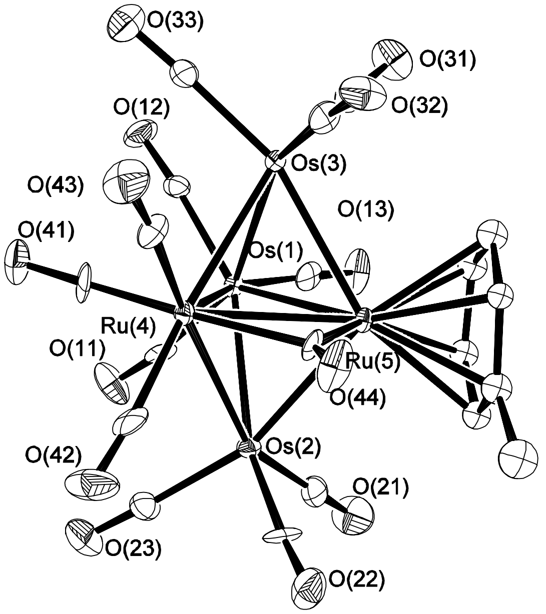


Fig. 3. ORTEP diagram (50% probability thermal ellipsoids, organic hydrogens omitted) of the main isomer, and selected lengths (Å) and angles (°), for **7**. Os(1)–Os(2) = 2.7219(8); Os(1)–Os(3) = 2.7262(8); Os(1)–Ru(4) = 2.7676(11); Os(1)–Ru(5) = 2.7687(13); Os(2)–Ru(5) = 2.7557(13); Os(2)–Ru(4) = 2.8052(11); Os(3)–Ru(5) = 2.7504(13); Os(3)–Ru(4) = 2.7753(11); Ru(4)–Ru(5) = 2.7943(16); Ru(4)–C(44) = 2.179(14); Ru(5)–C(44) = 1.998(15) and Ru(5)–C(44)–Ru(4) = 83.9(5).

approximate mirror symmetry, with the mirror plane passing through Os(3), Ru(4) and Ru(5) and bisecting the Os(1)–Os(2) vector. There was also disorder of the metal framework over three sites, M(3), M(4) and M(5), with osmium occupancies refined to 0.69, 0.14 and 0.17 respectively.

Unlike **5a**, which was reported to exhibit a singlet ^1H resonance at −20.55 ppm, assignable to two equivalent edge-bridging hydrides, the ^1H NMR spectrum of **5** exhibited five sets of signals having varying intensities. There are three singlet resonances at δ −18.72 (H_C), −19.03 (H_E) and −19.25 (H_F), and two sets of doublet resonances at δ −17.92 (H_A) and −18.99 (H_D), and at −18.16 (H_B) and −19.32 (H_G). These are ascribable to the presence of isomers. We have assumed that these isomers differ only in the positions of the hydride ligands. Based on previous observations that the chemical shift for a metal hydride bridging an Os–Os edge would lie in a higher field than that bridging an Os–Ru edge [9], the tentative structures and ^1H NMR assignments are as given in Fig. 4. The coupling giving rise to the doublets assigned to isomers IV and V have been confirmed by selective decoupling, and the relatively large coupling constants suggest that the hydrides share a common metal vertex and are *trans* relative to each other [10]. The isomeric distribution from NMR integration is 0.50:0.15:0.08:0.14:0.14 for I:II:III:IV:V, respectively. This corresponds to a ratio of 0.62:0.28:0.07 for the heavy atom core represented by I/IV, II/V and III, respectively, which quite closely mirrors the solid-state disorder.

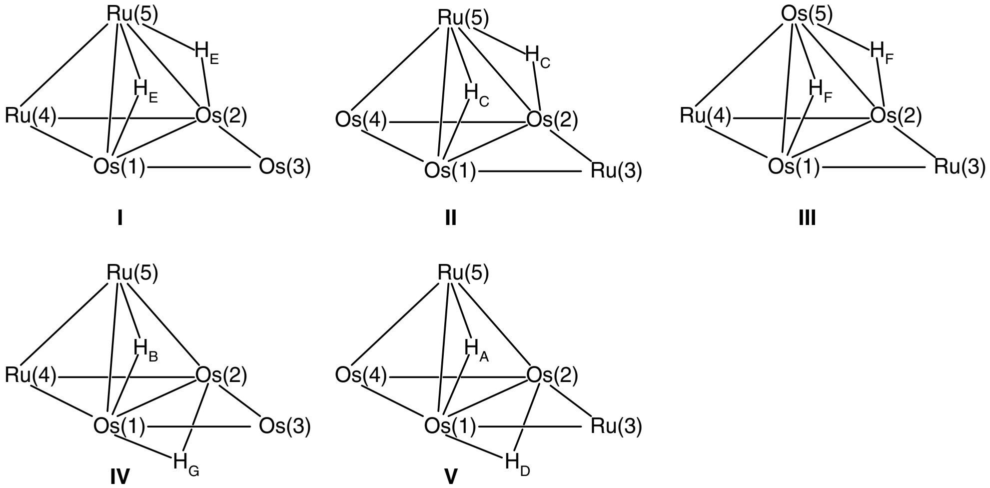


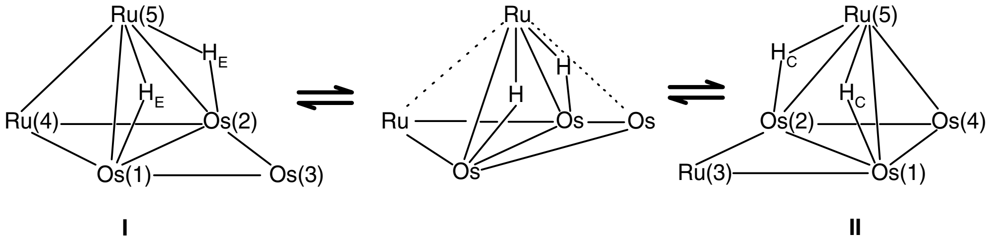
Fig. 4. Possible solution state structures, and their tentative ^{1}H NMR spectroscopic assignments, for cluster **5** (carbonyls omitted).

Interestingly, we have found in a ^{1}H EXSY spectrum of **5** taken at ambient temperature clear chemical exchange crosspeaks for H_A–H_B, H_C–H_E and H_D–H_G. These crosspeaks suggest that there is a fluxional process that involves rearrangement of the cluster metal framework such as shown in Scheme 2, which leads to chemical exchange between H_E and H_C. Such skeletal rearrangements are rare [11], and the clusters $Os_4(CO)_{14}(PMe_3)$ [12], $Pt_4(\mu\text{-}CO)_4(PMe_2Ph)_4$ [13], $Os_3Pt(\mu\text{-}H)_2(CO)_{11}(PCy_3)$ and $Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PCy_3)_2$ [14] are amongst the few known examples where low-energy skeletal rearrangements of the metal geometries have been suggested to account for the observed NMR data. In contrast, there does not appear to be any evidence for hydride migration that may lead to, for example, I ↔ IV isomerisation.

Cluster **6** retains the tetrahedral metal framework of the parent cluster **4**, with the toluene ligand capping the ruthenium atom. The crystal structure of **6** has mirror symmetry; the crystallographic mirror plane passes through the Os(2)–Ru(3) vector and bisects the Os(1)–Os(1A) edge and the toluene ligand. The distance from Ru(3) to the centroid of the arene ring is 1.943(20) Å. The toluene ligand is tilted at an angle of 31.9° with respect to the triosmium basal plane. This may be ascribed to steric interaction with the two bridging carbonyl ligands; the bridging carbonyl ligands enable the cluster to take up the additional electron density from the 'electron rich' $Ru(\eta^6\text{-}C_6H_5Me)$ fragment [15].

Cluster **7** is structurally similar to the reported cluster $RuOs_4(CO)_{13}(\eta^6\text{-}C_6H_6)$ (**7a**) which was synthesized from the reaction of $[Os_4(CO)_{13}]^{2-}$ with $[Ru(C_6H_6)(MeCN)_3]^{2+}$ [15]. The metal core of **7** consists of a trigonal bipyramidal Ru_2Os_3 framework, with a valence electron count of 72, as predicted by the effective atomic number (EAN) rule [16]. The η^6 toluene moiety caps one of the equatorial ruthenium atoms. As observed in **7a** the shortest bonds are between the axial (Os(2) and Os(3)) and the equatorial Os(1) metal atoms, while the longest metal–metal bond is the carbonyl-bridged Ru(4)–Ru(5) edge. Only the product having the toluene group bound to an equatorial metal atom has been isolated; there was no evidence for an isomer with the toluene moiety bound to a metal atom at the axial site. This observation is in line with previous reports on trigonal bipyramidal pentanuclear osmium and ruthenium clusters containing arene or cyclopentadienyl ligands; without exception, the aromatic ligand always occupies an equatorial position on the pentanuclear metal framework. It has been suggested that having the $M(\eta^6\text{-}C_6H_6)$ fragment in the equatorial position enhanced the electron density donation from the equatorial to the axial sites, thereby stabilizing the cluster [15].

The crystal structure of **7** exhibited disorder, which was modelled with one of the ruthenium atoms being disordered over three sites – M(2), M(3) and M(4). The ruthenium occupancies refined to about 0.08, 0.08 and 0.84,



Scheme 2.

respectively, which was then fixed in the final stages of the refinement. This disorder model corresponds to two different isomers (Ru occupation at M(2) and M(3) correspond to the same isomer) and is consistent with the solution phase ^{1}H NMR spectrum. Two identical sets of signals appear in the organic region of the ^{1}H NMR spectrum for **7** in a 82:18 integration ratio. The proposed solution state structures and tentative NMR assignments for the two isomers are shown in Fig. 5.

We have carried out a number of experiments to understand the interrelationship among **4**–**7**; the results are summarised in Scheme 3. Cluster **7** is thermally stable and does not fragment under prolonged heating. It is thus the thermodynamic sink. Thermolysis of **5** in toluene afforded **7** in high yield. The yields of **6** and **7** from the thermolysis of **4** in toluene were dependent on the reaction time; prolonged thermolysis resulted in an increase in the proportion of **7** formed, with complete consumption of **4**. The formation of **5** (and **7**) must involve fragmentation of **4**. Cluster **7** was also obtainable from the co-thermolysis of **4** and **6** in octane, albeit in low yield; in the absence of **4** no conversion of **6** to **7** takes place. In contrast, cluster **7** was not detected when **6** was reacted with **2** at ambient temperature or with **1** in refluxing octane. These suggest that besides toluene, **6** can act as a source of the Ru(η^6-C_6H_5Me) fragment.

It is probable that the Ru(η^6-C_6H_5Me) moiety caps onto an $RuOs_2$ face in **4** and subsequent polyhedral rearrangement, via a Berry pseudo-rotation [15], places that fragment into an equatorial position. Such a reaction sequence is corroborated by: (i) Isolation of the cluster $H_3Os_4Rh(MeC{=}NH)(CO)_{11}(\eta^5\text{-}C_5Me_5)$ from the reaction of $[H_4Os_4(CO)_{11}]^{2-}$ with $[Rh(\eta^5\text{-}C_5Me_5)(NCMe)_3]^{2+}$, in which the MeC=NH group is derived from an acetonitrile group of the rhodium moiety. This suggests a stepwise capping of the tetrahedral cluster by a mononuclear substrate [17]. (ii) The reaction of '$Os(C_6H_6)^{2+}$', with $[H_2Os_4(CO)_{12}]^{2-}$ afforded a trigonal bipyramidal cluster in which the arene was initially at an axial site but which subsequently transformed into the more stable equatorial isomer [8,18].

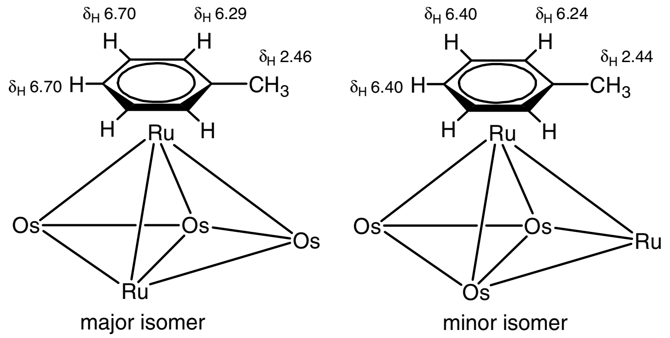


Fig. 5. Proposed solution state structures and tentative NMR assignments for **7** (carbonyls omitted).

3. Concluding remarks

We have thus shown that cluster **4** reacts readily with toluene, initially to form **6**. The latter subsequently fragments to afford an Ru(η^6-C_6H_5Me) fragment which can then undergo capping reaction with **4** to afford **7**. The pathway through **5** appears to be a relatively minor route. Both **5** and **7** exist as isomeric mixtures in solution; there are five isomers for **5** and two for **7**.

4. Experimental

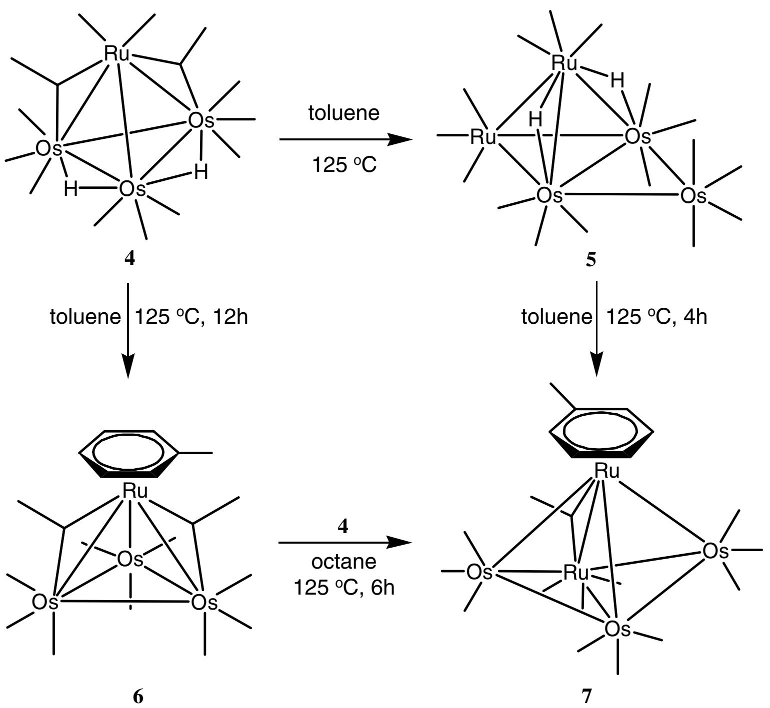
4.1. General procedures

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. Routine NMR spectra were acquired on a Bruker ACF300 NMR spectrometer. Selective decoupling experiments and 2D NMR spectra were acquired on a Bruker Avance DRX500 or Bruker AMX500 machine. EXSY spectra were recorded with a mixing time of 0.5 s unless otherwise stated. The solvent used was deuterated chloroform unless otherwise stated. Chemical shifts reported are referenced to that for the residual proton of the solvent for ^{1}H. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in an *m*-nitrobenzyl alcohol matrix. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The cluster $Os_3(\mu\text{-}H)_2(CO)_{10}$ (**3**) was prepared according to the literature method [19]. $Ru_3(CO)_{12}$ (**1**) was purchased from Oxkem Ltd.; all other reagents were from commercial sources and used as supplied.

4.2. Preparation of $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ and $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$

Cluster **1** (30.1 mg, 0.047 mmol) was placed with hexane (60 mL) into a 100 mL round-bottom flask fitted with a Teflon valve. After three freeze–pump–thaw cycles, ethene gas at ~20 psi was introduced at ambient temperature. The mixture was then irradiated by a 60 W Phillips reflector lamp, while being cooled in an ice-water bath, until the solution became colourless (~2 h). The solution, which now contains **2**, was then poured into a 100 mL Schlenk vessel containing **3** (40.2 mg, 0.047 mmol). The mixture was stirred under a nitrogen atmosphere for 1.5 h, whereupon the colour changed to orange. Removal of the solvent and volatiles in vacuo and column chromatographic separation of the residue, with hexane as eluant, gave three bands. (% yields reported are with respect to the amount of **3** used.) The first two bands were identified from their infrared spectra as **1** (19.1 mg, 0.030 mmol) and $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (**4**) (47.2 mg, 96%), respectively.

Band 3 gave dark brown crystals of $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$ (**5**). Yield = 2.4 mg, 3%. IR (CH_2Cl_2) ν(CO): 2123w, 2083m, 2061s, 2046m, 2009w cm^{-1}. ^{1}H NMR: δ



Scheme 3.

−17.92 (d, $^2J_{HH} = 3.3$ Hz), −18.16 (d, $^2J_{HH} = 2.5$ Hz), −18.72 (s), −18.99 (d, $^2J_{HH} = 3.3$ Hz), −19.03 (s), −19.25 (s), −19.32 (d, $^2J_{HH} = 2.5$ Hz). MS (ESI): *m*/*z* 1195 ($[M - CO]^+$), calcd for M^+: 1223. Anal. Calcd for $C_{16}H_2O_{16}Os_3Ru_2$: C, 15.71; H, 0.16. Found: C, 15.84; H, 0.39%.

4.3. Reaction of $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (4) with toluene

To a Schlenk tube containing **4** (35.8 mg, 0.029 mmol) was added toluene (30 mL). The reaction mixture was refluxed for 12 h after which the solvent was removed on the vacuum line. The residue so obtained was redissolved in the minimum of dichloromethane and chromatographed on TLC plates. Elution with hexane/dichloromethane (7:3, v/v) yielded four bands. The first and second bands were identified from their infrared spectra as **3** (8.6 mg) and unreacted **4** (5.2 mg), respectively.

Band 3 ($R_f = 0.21$) afforded dark brown crystals identified to be $RuOs_3(CO)_9(\mu\text{-}CO)_2(\eta^6\text{-}C_6H_5Me)$ (**6**). Yield = 9.0 mg, 29%. IR (CH_2Cl_2) ν(CO): 2082m, 2062s, 2033s, 2016m, 2002m, 1950w, 1828w(br) cm^{-1}. ^1H NMR: δ 5.86 (m, 5H), 2.30 (s, 3H). MS (FAB): *m*/*z* 1046 ($[M - CO]^+$), calcd for M^+: 1072. Anal. Calcd. for $C_{18}H_8O_{11}Os_3Ru \cdot \frac{1}{2}C_6H_{14}$: C, 22.62; H, 1.34. Found: C, 22.47; H, 1.38%. Presence of hexane in the analytical sample verified by ^1H NMR spectroscopy.

Band 4 ($R_f = 0.13$) afforded dark brown crystals identified to be $Ru_2Os_3(CO)_{12}(\mu\text{-}CO)(\eta^6\text{-}C_6H_5Me)$ (**7**). Yield = 12.3 mg, 35%. IR (CH_2Cl_2) ν(CO): 2083vw, 2073w, 2044s, 2017m, 2009m, 1978mw cm^{-1}. ^1H NMR: δ 6.70 (dd, 3H, $^3J_{HH} = 6.0$ Hz, $^3J_{HH} = 6.0$ Hz), 6.39 (d, 2H, $^3J_{HH} = 6.0$ Hz), 2.46 (s, 3H) [major isomer]; 6.40 (dd, 3H, $^3J_{HH} = 6.0$ Hz, $^3J_{HH} = 6.0$ Hz), 6.24 (d, 2H, $^3J_{HH} = 6.0$ Hz), 2.44 (s, 3H) [minor isomer]. MS (FAB): *m*/*z* 1230 (M^+), calcd for M^+: 1229. Anal. Calcd. for $C_{20}H_8O_{13}Os_3Ru_2$: C, 19.54; H, 0.66. Found: C, 19.55; H, 0.62%.

Decreasing the reaction time to 6 h resulted in the isolation of **3** (2.1 mg), **4** (19.7 mg), **6** (6.2 mg, 20%) and **5** (3.9 mg, 11%).

4.4. Reaction of $Ru_2Os_3(\mu\text{-}H)_2(CO)_{16}$ (5) with toluene

To a Carius tube containing toluene (30 mL) was added **5** (14.2 mg, 0.012 mmol). The reaction mixture was degassed by three freeze–pump–thaw cycles, and stirred at 120 °C for 4 h. Subsequent treatment as above yielded three bands which were identified as **3** (0.9 mg), **6** (1.5 mg, 12%) and **7** (10.3 mg, 70%), respectively.

4.5. Reaction of $RuOs_3(\mu\text{-}H)_2(CO)_{13}$ (4) and $RuOs_3(CO)_{11}(\eta^6\text{-}C_6H_5Me)$ (6)

To a Carius tube containing octane (20 mL) was added **4** (7.2 mg, 0.007 mmol) and **6** (6.9 mg, 0.006 mmol). The reaction mixture was degassed by three freeze–pump–thaw cycles, and stirred at 120 °C for 6 h. Subsequent treatment as above yielded four bands which were identified as **3** (1.7 mg), **4** (4.8 mg), **6** (4.0 mg) and **5** (2.1 mg, 32%), respectively.

Table 1
Crystal and refinement data for **5**–**7**

Identification code	**5**	**6**	**7**
Empirical formula	$C_{16}H_2O_{16}Os_3Ru_2$	$C_{18}H_8O_{11}Os_3Ru$	$C_{20}H_8O_{13}Os_3Ru_2$
Formula weight	1222.92	1071.91	1229.00
Temperature (K)	223(2)	223(2)	183(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/m$	$Pna2_1$
a (Å)	8.9782(5)	8.4941(5)	18.2236(6)
b (Å)	10.5651(6)	14.5048(8)	8.5532(3)
c (Å)	13.3130(8)	8.6216(5)	16.3487(5)
α (°)	100.1930(10)	90	90
β (°)	90.2190(10)	95.6650(10)	90
γ (°)	106.7790(10)	90	90
Volume (Å^3)	1187.94(12)	1057.04(11)	2548.27(15)
Z	2	2	4
Density (calculated) (Mg m^{-3})	3.419	3.368	3.203
Absorption coefficient (mm^{-1})	17.305	18.733	16.127
$F(000)$	1084	952	2192
Crystal size (mm^3)	0.03 × 0.13 × 0.21	0.34 × 0.15 × 0.06	0.16 × 0.10 × 0.04
Θ range for data collection (°)	2.05–30.02	2.37–29.46	2.24–29.87
Reflections collected	17705	14495	20329
Independent reflections [R_{int}]	6643 [0.0634]	2857 [0.0345]	6467 [0.0596]
Maximum and minimum transmission	0.316395 and 0.152365	0.3994 and 0.0607	0.5648 and 0.1823
Data/restraints/parameters	6643/1/337	2857/8/146	6467/1/309
Goodness-of-fit on F^2	1.002	1.091	1.057
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0402$, $wR_2 = 0.1066$	$R_1 = 0.0321$, $wR_2 = 0.0768$	$R_1 = 0.0528$, $wR_2 = 0.1070$
R indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.1101$	$R_1 = 0.0347$, $wR_2 = 0.0782$	$R_1 = 0.0584$, $wR_2 = 0.1096$
Largest difference in peak and hole (e Å^{-3})	2.751 and −2.003	2.575 and −2.497	1.929 and −1.777

4.6. X-ray crystal structure determinations

Crystals were mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, at 223 K with the SMART suite of programs [20]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [21], and for absorption effects with SADABS [22]. Structural solution and refinement were carried out with the SHELXTL suite of programs [23]. Crystal and refinement data are summarised in Table 1.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The hydrides in **5** were placed by potential energy calculations with the program XHYDEX [24], given fixed isotropic thermal parameters, and refined riding on the osmium atom to which they are both attached. Organic hydrogen atoms were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model, except for the carbon atoms of the toluene in **6** and **7**.

Cluster **7** was refined as a racemic twin. Clusters **5** and **7** exhibited disorder of the heavy atom positions; the ruthenium atoms (only one of the two for **7**) were modelled as disordered over three sites. The Ru occupancies in **5** were refined to give 0.31, 0.86 and 0.83, respectively, for the Os(3), Ru(4) and Ru(5) sites. In **7**, the Ru occupancies were fixed at 0.09, 0.09 and 0.82, respectively, for Os(2), Os(3) and Ru(4). Cluster **6** exhibited disorder of the toluene ring, which was modelled as two sets of mirror images as the ring lies about a mirror plane.

Acknowledgement

This work was supported by the National University of Singapore (Research Grant No. R143-000-190-112) and one of us (Y.L.K.T.) thanks the University for a Research Scholarship.

Appendix A. Supplementary data

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 290066–290068. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.008.

References

[1] (a) L. Pereira, W.K. Leong, S.Y. Wong, J. Organometallic. Chem. 609 (2000) 104;
(b) L.J. Pereira, K.S. Chan, W.K. Leong, J. Organomet. Chem. 690 (2005) 1033;
(c) L.J. Pereira, W.K. Leong, J. Organomet. Chem, accepted.

[2] (a) A.L. Rheingold, B.C. Gates, J.P. Scott, J.R. Budge, J. Organomet. Chem. 331 (1987) 81;
(b) G.A. Foulds, B.F.G. Johnson, J. Lewis, R.M. Sorrell, J. Chem. Soc., Dalton Trans. (1986) 2515;
(c) G.L. Geoffroy, J.R. Fox, E. Burkhardt, H.C. Foley, A.D. Harley, R. Rosen, Inorg. Synth. 21 (1982) 57;
(d) E.W. Burkhardt, G.L. Geoffroy, J. Organomet. Chem. 198 (1980) 179.

[3] (a) J.P. Scott, J.R. Budge, A.L. Rheingold, B.C. Gates, J. Amer. Chem. Soc. 109 (1987) 7736;
(b) J.R. Budge, J.P. Scott, B.C. Gates, J. Chem. Soc., Chem. Commun. (1983) 342.

[4] (a) J.R. Budge, B.F. Luecke, J.P. Scott, B.C., Gates, in: Proceedings of the 8th International Congress on Catalysis, vol. 5, 1984, p. V89;
(b) J.R. Budge, B.C. Gates, in: Proceedings of the Pan-Pacific Synfuels Conference, vol. 1, 1982, p. 204.

[5] D.M.P. Mingos, D.J. Wales, Introduction to Cluster Chemistry, Prentice Hall, Englewood Cliffs, NJ, 1990.

[6] (a) C.R. Eady, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 57 (1973) C84;
(b) C.R. Eady, B.F.G. Johnson, J. Lewis, J. Chem. Soc., Dalton Trans. (1977) 838;
(c) J.J. Guy, G.M. Sheldrick, Acta Crystallogr., Sect. B. 34 (1978) 1725.

[7] (a) D.Y. Jan, L.Y. Hsu, W.L. Hsu, S.G. Shore, Organometallics 6 (1987) 274;
(b) W. Clegg, N. Feeder, A.M. Martin Castro, S. Nahar, P.R. Raithby, G.P. Shields, S. Teat, J. Organomet. Chem. 573 (1999) 237.

[8] M.R.A. Al-Mandhary, R. Buntem, C. Cathey, J. Lewis, M.C.R. de Arellano, G.P. Shields, C.L. Doherty, P.R. Raithby, Inorg. Chim. Acta 350 (2003) 299.

[9] (a) J.R. Fox, W.L. Gladfelter, T.G. Wood, J.A. Smegal, T.K. Foreman, G.L. Geoffroy, I. Tavanaipour, V.W. Day, C.S. Day, Inorg. Chem. 20 (1981) 3214;
(b) W.L. Gladfelter, G.L. Geoffroy, Inorg. Chem. 19 (1980) 2579.

[10] J.A. Iggo, NMR Spectroscopy in Inorganic Chemistry, Oxford University Press, Great Britain, 1999.

[11] (a) B.F.G. Johnson, R.E. Benfield, in: B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, Chichester, England, 1980;
(b) B.E. Mann, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 2, Pergamon Press, New York, 1982.

[12] L.R. Martin, F.W.B. Einstein, R.K. Pomeroy, J. Am. Chem. Soc. 108 (1986) 338.

[13] A. Moor, P.S. Pregosin, L.M. Venanzi, A. Welch, J. Inorg. Chim. Acta 85 (1984) 103.

[14] P. Ewing, L.J. Farrugia, D.S. Rycroft, Organometallics 7 (1988) 859.

[15] P.R. Raithby, G.P. Shields, Polyhedron 17 (1998) 2829.

[16] R.K. Pomeroy, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, vol. 7, Pergamon Press, New York, 1995 (Chapter 15).

[17] W. Clegg, N. Feeder, A.M.M. Castro, S. Nahar, P.R. Raithby, G.P. Shields, S.J. Teat, J. Organomet. Chem. 573 (1999) 237.

[18] M.R.A. Al-Mandhary, J. Lewis, P.R. Raithby, J. Organomet. Chem. 530 (1997) 247.

[19] H.D. Kaesz, Inorg. Synth. 28 (1990) 238.

[20] SMART version 5.628, Bruker AXS Inc., Madison, WI, USA, 2001.

[21] SAINT+ version 6.22a, Bruker AXS Inc., Madison, WI, USA, 2001.

[22] G.M. Sheldrick, SADABS, University of Gottingen, 1996.

[23] SHELXTL version 5.1, Bruker AXS Inc., Madison, WI, USA, 1997.

[24] A.G. Orpen, XHYDEX, School of Chemistry, University of Bristol, UK, 1997.