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Reactivity of osmium–rhodium mixed-metal cluster $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ towards vinyl containing ligands

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Abstract

Reaction of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**) with an excess amount of vinylacetic acid gave two new clusters, $[Os_5Rh_2(\mu\text{-}CO)(\eta^6\text{-}C_6H_5CH_3)(CO)_{16}]$ (**2**) and $[Os_2Rh_2(\mu\text{-}CO)_2(\eta^3\text{-}CH_2CHCH_2COO)_2(CO)_7]$ (**3**) in 20 and 40% yields, respectively. Treatment of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ with vinylacetate in refluxing toluene afforded the complexes $[Os_3Rh(\mu_3\text{-}CCH_3)(\eta^6\text{-}C_6H_5CH_3)(CO)_9]$ (**4**) and $[Os_5Rh_2(\mu\text{-}CO)(\eta^6\text{-}C_6H_5CH_3)(CO)_{16}]$ (**2**) in 40 and 20% yields, respectively. Thermolysis of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ in refluxing toluene produced the known cluster compound, $[Os_3Rh(\mu\text{-}H)_3(\eta^6\text{-}C_6H_5CH_3)(CO)_9]$. Treatment of 1-octene with $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ led to the isomerization to give all isomers of octenes. All the new clusters have been fully characterized by both spectroscopic and crystallographic techniques. The isomerization has been examined by GCMS technique. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Osmium; Rhodium; Crystal structure; Vinyl; Isomerization

1. Introduction

Heterometallic carbonyl clusters have caught considerable attention because of their potential of new catalytic and stoichiometric reactions [1]. Adding to this is the recent advances in nanoscale materials that using mixed-metal clusters as precursor [2,3]. We are interested in the mixed-metal clusters of Os and Rh combination due to the fact that metal exhibits significant catalytic reactivity towards a number of chemical process while the osmium metal is well-known for its kinetic stability [4–6]. This metal combination allows the possibility of observing good reactivity and sufficient thermodynamic stability of the cluster intermediates occurred in the catalytic process. In this work, we report the reactivity study of the mixed-metal clusters $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**) towards a series of vinyl containing ligands. Cluster **1** has been synthesized in good yield (60%) from the unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[\{Rh(CO)_2Cl\}_2]$ dimer, and some substitution reaction of CO ligands of **1** was also reported [7]. It would be interesting to explore the possibility of cluster aggregation and catalytic isomerization of alkenes based on the interaction of **1** with some vinyl functionalities.

2. Results and discussion

2.1. Synthesis, structure and spectroscopy

2.1.1. Reaction of $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ with vinylacetic acid

Heating $[Os_3Rh(\mu\text{-}H)_3(CO)_{12}]$ (**1**) with an excess amount of vinylacetic acid in refluxing toluene for 5 h gave $[Os_5Rh_2(\mu\text{-}CO)(\eta^6\text{-}C_7H_8)(CO)_{16}]$ (**2**) and $[Os_2Rh_2(\mu\text{-}CO)_2(\eta^3\text{-}CH_2CHCH_2COO)_2(CO)_7]$ (**3**) (Scheme 1). The spectroscopic data of **2** and **3** are listed in Table 1. The IR spectrum of **2** indicates both terminal and bridging carbonyls are present. The mass spectrum exhibits a daughter peak at $m/z = 1697$ $[M-CO]^+$ rather than a parent isotopic peak (expected $m/z = 1725$). This suggests that cluster **2** may easily undergo fragmentation in the ionization process. The ^{1}H-NMR signals due to the protons of the phenyl ring are observed in the range of δ 5.90–6.30 and the resonance

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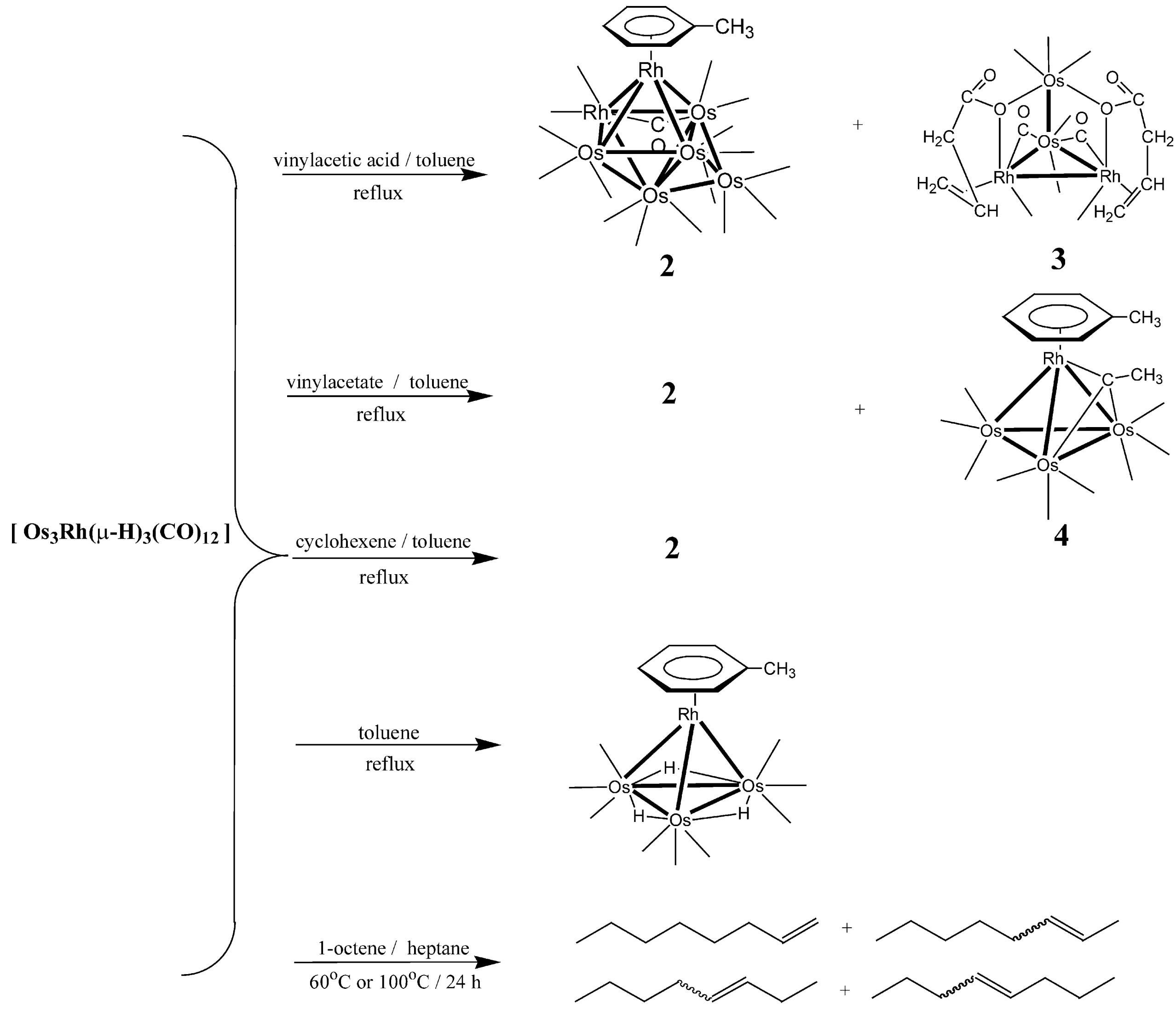


Scheme 1.

for the methyl protons of the tolyl ligand occurs at δ 2.32. The molecular structure of **2** was established by X-ray analysis on a black, air stable crystal that was obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution at −20 °C. Fig. 1 shows the molecular structure of **2** and the numbering scheme for the resulting molecular configuration. The selected bond parameters are given in Table 2. One half of a molecule

Table 1
Spectroscopic data for compounds **2**–**4**

Cluster	IR spectra [a] ν(CO) (cm^{-1})	Mass spectra [b] (*m/z*)	^{1}H-NMR spectra [c] δ, *J* (Hz)
2	2191s, 2057s, 2041s, 2010m, 1976s, 1931m, 1825m	1698 $[M-CO]^+$	6.30 (dt, $J_{HH}=7.7$, 1H, Ph); 6.19 (dt, $J_{HH}=5.7$, 1H, Ph); 6.07 (d, $J_{HH}=7.3$, 1H, Ph); 5.93 (t, $J_{HH}=7.6$, 1H, Ph); 5.90 (d, $J_{HH}=8.1$, 1H, Ph); 2.32 (s, $J_{HH}=6.2$, 3H, CH_3)
3	2097w, 2056vs, 2024s, 1994s (Nujol)	1008 (1008)	7.03(m, 1H, CH); 5.84 (dd, $J_{HH}=15.5$, 1.7 1H, CH); 1.90 (dd, $J_{HH}=6.9$, 1.7 3H, CH_3)
4	2062s, 2020vs, 1987m, 1968m, 1933w	1045(1045)	6.50 (t, $J_{HH}=5.3$, 2H, Ph); 6.35 (d, $J_{HH}=6.1$, 2H, Ph); 6.17 (t, $J_{HH}=6.0$, 1H, Ph); 3.99 (s, $J_{HH}=7.6$, 3H, CH_3); 2.14 (s, 3H, CH_3)

[a] Recorded in CH_2Cl_2 unless otherwise stated.
[b] Positive FAB-MS, calculated values in parentheses.
[c] Recorded in CD_2Cl_2 for **2**, $CDCl_3$ for **3** and **4**.

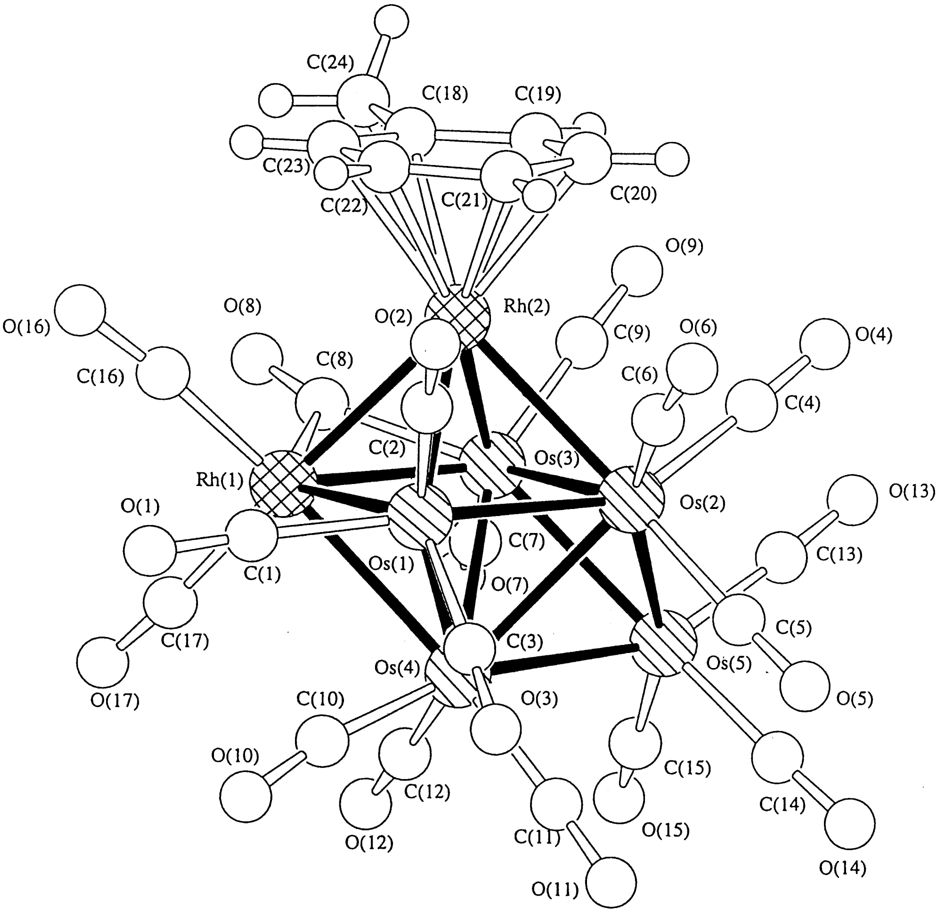
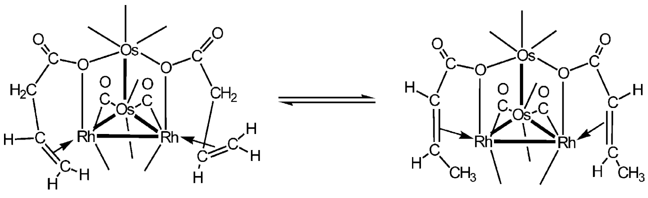


Fig. 1. The molecular structure of $[Os_5Rh_2(\mu\text{-}CO)(\eta^6\text{-}C_6H_5CH_3)(CO)_{16}]$ (**2**) with the atom numbering scheme.

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

Bond distances			
Os(1)–Os(2)	2.8095(8)	Os(1)–Os(4)	2.8516(9)
Os(1)–Rh(1)	2.821(2)	Os(1)–Rh(2)	2.792(1)
Os(2)–Os(3)	2.8077(9)	Os(2)–Os(4)	2.8173(9)
Os(2)–Os(5)	2.8659(9)	Os(2)–Rh(2)	2.772(1)
Os(3)–Os(4)	2.8616(8)	Os(3)–Os(5)	2.7320(8)
Os(3)–Rh(1)	2.736(8)	Os(3)–Rh(2)	2.717(1)
Os(4)–Os(5)	2.8505(8)	Os(4)–Rh(1)	2.847(1)
Rh(1)–Rh(2)	2.720(2)		
Bond angles			
Os(1)–Rh(1)–Os(3)	91.27(4)	Os(1)–Rh(1)–Os(4)	60.40(3)
Os(1)–Rh(1)–Rh(2)	60.47(4)	Os(3)–Rh(1)–Os(4)	61.03(3)
Os(1)–Rh(1)–Os(3)	62.84(3)	Os(1)–Rh(1)–Os(2)	64.63(3)
Os(3)–Rh(1)–Rh(2)	59.73(4′)	Os(4)–Rh(1)–Rh(2)	90.66(5)
Os(1)–Rh(2)–Os(2)	60.66(3)	Os(1)–Rh(2)–Os(3)	92.32(4)
Os(1)–Rh(2)–Rh(1)	61.56(4)	Os(2)–Rh(2)–Os(3)	61.53(3)
Os(2)–Rh(2)–Rh(1)	91.31(5)	Os(3)–Rh(2)–Rh(1)	60.42(4)

of CH_2Cl_2, as a solvent of crystallization, is found in the asymmetric unit. The cluster consists of octahedral metal core [Os(1), Os(2), Os(3), Os(4), Rh(1) and Rh(2)] with a CO ligand bridged across the Rh(1)–Os(3) bond [2.736(1) Å]. An additional Os atom, Os(5) was found to cap on the [Os(2)–Os(3)–Os(4)] triangular face. The essentially planar tolyl ligand in **2** is in a η^6-bonding mode and bonded to the Rh(2) atom. This unusual coordination of the η^6-tolyl ligand from the solvent has been reported [8,9]. The IR spectrum of **3** shows the presence of terminal carbonyls only and the signal of the bridging carbonyl ligand may be too weak to be observed. The mass spectrum shows a molecular peak at m/z 1008, together with daughter ions due to the sequential losses of terminal carbonyl ligand. The ^1H-NMR spectrum of **3** obtained showed features that are not compatible with the structure observed in the solid-state structure. The presence of two double doublets with integral ratio of 1:3 at δ 5.84 and 1.90 suggested the possibility of isomerization of vinyl moieties to give a terminal methyl substituent via a 1,3-hydrogen shift (see Scheme 2). A similar process has been observed for $[Mo\{\eta^3\text{-}CH_2C(Ph)CH(Ph)\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ [10]. Red crystals of **3** suitable for X-ray diffraction analysis were grown from a saturated solution of n-hexane and CH_2Cl_2 at −20 °C. The molecular structure of **3** is shown in Fig. 2 and bond distances and angles are listed in Table 3. Cluster **3** contains four metal atoms in which three of them [Os(1)–Rh(1)–Rh(2)] arrange in a triangle



Scheme 2.

with two CO ligands bridged across each Os–Rh edge. The Os(2) is bonded to Os(1) together via two supporting acetate group. The complex contains two (CH_2CHCH_2COO) groups, which are derived from the deprotonation of the vinylacetic acid ligands. The two (CH_2CHCH_2COO) units bridge to the metal atoms [Os(2)–Rh(2), Os(2)–Rh(1), respectively] via the oxygen atom. Each of the two (CH_2CHCH_2COO) units, act as a $5e^-$ donor. Together with seven terminal and two bridging carbonyls make up the valence electron count to 62, which is two electrons less than required by the effective atomic number (EAN) rule. This type of skeleton is not commonly observed and the established example included [$Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})(\eta^1(O)$, $\eta^2(C,C)\text{-}OCOCH_2CH{=}CH_2)(PMe_3)$] and [$Pd(OCOCH_2C{=}CH_2)(PMe_3)$] [11,12].

2.1.2. *Reaction of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with vinylacetate*

A solution of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with an excess amount of vinylacetate in refluxing toluene for 2 h led to cluster **2** and [$Os_3Rh(\mu_3\text{-}CCH_3)(\eta^6\text{-}C_6H_5CH_3)(CO)_9$] (**4**). Cluster **4** was characterized by various spectroscopic methods (Table 1). The IR spectrum exhibits peaks of terminal carbonyl ligand. The mass spectrum shows molecular ion envelopes that agree with the formulae of the compounds. The ^{1}H-NMR spectrum contains the phenyl proton resonance at δ 6.17–6.50, a singlet for the methyl proton of the tolyl ligand at δ 3.99 and signal at δ 2.14 for the methyl proton of the methlidyne ligand. In order to elucidate its molecular structure so as to find out the coordination geometry of the ligands, X-ray analysis was carried out on a black crystal of complex **4**, obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution at −20 °C. The molecular structure and selected bond parameters of complex **4** is shown in Fig. 3 and Table 4, respectively. The three osmium atoms and one rhodium atom define a distorted tetrahedron with a tolyl ligand bonding to it in a η^6-bonding mode via the Rh(1) atom with a mean deviation of 0.0217 Å from the least-square plane. This type of bonding mode has been observed in a closely related

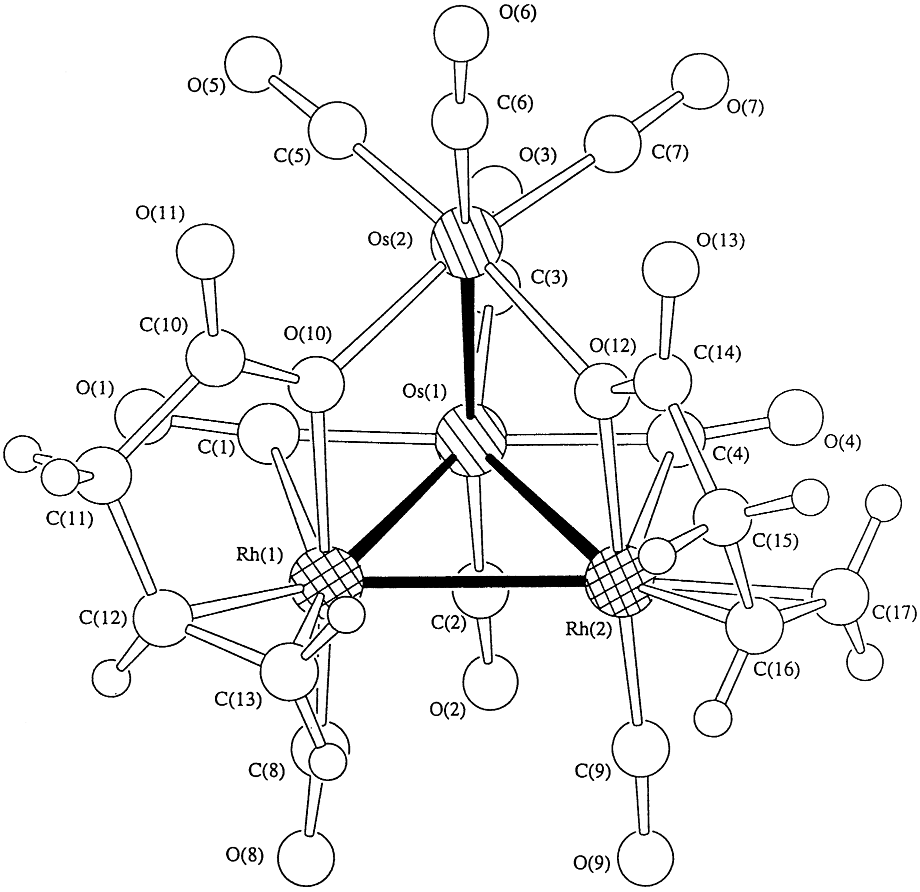


Fig. 2. The molecular structure of [$Os_2Rh_2(\mu\text{-}CO)_2(\eta^3\text{-}CH_2CHCH_2COO)_2(CO)_7$] (**3**) with the atom numbering scheme.

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

Bond distances			
Os(1)–Os(2)	2.8692(8)	Os(1)–Rh(1)	2.824(1)
Os(1)–Rh(2)	2.831(1)	Os(1)–C(4)	1.95(2)
Os(2)···Rh(1)	3.490(1)	Os(2)···Rh(2)	3.540(1)
Os(2)–O(10)	2.112(9)	Os(2)–O(12)	2.106(9)
Rh(1)–Rh(2)	2.807(2)	Rh(1)–O(10)	2.086(10)
Rh(1)–C(12)	2.18(1)	Rh(1)–C(13)	2.22(2)
Rh(2)–O(12)	2.073(9)	Rh(2)–C(16)	2.20(2)
Rh(2)–C(17)	2.20(2)	O(10)–C(10)	1.31(2)
O(11)–C(10)	1.17(2)	O(12)–C(14)	1.33(2)
O(13)–C(14)	1.21(2)	C(10)–C(11)	1.53(2)
C(11)–C(12)	1.51(2)	C(12)–C(13)	1.36(2)
C(14)–C(15)	1.50(2)	C(15)–C(16)	1.45(2)
C(16)–C(17)	1.31(3)		
Bond angles			
Os(1)–Os(1)–Rh(1)	75.68(3)	Os(2)–Os(1)–Rh(2)	76.73(3)
Rh(1)–Os(1)–Rh(2)	59.51(4)	Os(1)–Os(2)–O(10)	82.9(3)
Os(1)–Os(2)–O(12)	82.4(2)	O(10)–Os(2)–O(12)	80.5(4)
Os(1)–Rh(1)–Rh(2)	60.36(4)	Os(1)–Rh(1)–O(10)	84.5(3)
Rh(2)–Rh(1)–O(10)	92.5(3)	Rh(2)–Rh(1)–C(8)	92.0(6)
Rh(2)–Rh(1)–C(12)	134.4(5)	Rh(2)–Rh(1)–C(13)	99.3(6)
O(10)–Rh(1)–C(12)	79.0(5)	O(10)–Rh(1)–C(13)	86.9(5)
Os(1)–Rh(2)–Rh(1)	60.13(4)	Os(1)–Rh(2)–O(12)	84.0(2)
Rh(1)–Rh(2)–O(12)	85.1(3)	Os(2)–O(10)–Rh(1)	112.6(4)
Rh(1)–O(10)–C(10)	119.4(10)	Os(2)–O(12)–Rh(2)	115.7(4)
Rh(2)–O(12)–C(14)	117.3(9)	C(10)–C(11)–C(12)	113(1)
C(11)–C(12)–C(13)	124(1)		

cluster [$Os_3Rh(\mu\text{-}H)_3(\eta^6\text{-}C_6H_5CH_3)(CO)_9$] [8]. A methylidyne unit is capped on the triangular face [Os(1)–Os(2)–Rh(1)] of the metal core. The vinyl group is believed to coordinate to the metal core first and followed by the rearrangement to give the ethylidyne moiety via vinylidene and hydride formation [13–15]. In cluster **4**, the tolyl ligand acts as a $6e^-$ donor, while the methylidyne unit donates $3e^-$ to the metal core. Together with nine terminal carbonyl ligands, a CVE count of 60 is obtained, which is electron precise according to the EAN rule.

2.1.3. *Thermolysis of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] in toluene*

Heating of **1** in toluene to reflux for 2 h led to the known cluster [$Os_3Rh(\mu\text{-}H)_3(\eta^6\text{-}C_6H_5CH_3)(CO)_9$] in good yield [8]. Hence the formation of higher nuclearity cluster **2** should involve the coordination of vinyl group to the metal core. Reaction of **1** with refluxing toluene in the presence of cyclohexene gave **2** in 20% yield as the only isolable product. It is tempting to suggest that the metal hydrides may interact with the coordinated alkene and open up new paths of **1** other than the substitution of CO by toluene.

2.1.4. *Reaction of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with 1-octene*

Interaction of alkenes with **1** led us to explore the possible catalytic properties of it towards alkene isomerization reactions. Treatment of **1** with an excess amount of 1-octene in *n*-heptane at different temperatures (25, 60 and 100 °C) for 24 h have been investigated. No new cluster compound was obtained as evident from IR and TLC monitoring. Nevertheless, the isomerization of 1-octene occurs at 60 and 100 °C as shown by GCMS technique. At 100 °C, seven peaks were observed in the gas chromatogram, all with $m/z = 112$, which correspond to the isomer of 1-octene:(*E*)-2-octene, (*Z*)-2-octene, (*E*)-3-octene, (*Z*)-3-octene, (*E*)-4-octene and (*Z*)-4-octene in various amounts. This indicated that **1** could catalyze the isomerization of alkenes. However, no optimization of the reaction was performed at this stage of investigation.

3. Experimental

3.1. *General procedures*

All reactions and manipulations were carried out under nitrogen using Schlenk techniques unless otherwise stated. Glassware was pre-dried in an oven (~120 °C) before used. Reactions were monitored by both IR spectroscopy and analytical thin-layer chromatography (Merck Kieselgel 60 F_{254}) and the products were separated by thin-layer chromatography on plates coated with silica (Merck Kieselgel 60 F_{254}). Dichloromethane (Ajax, AR) was distilled over calcium hydride. *n*-Hexane (Ajax, AR) was purified by distillation in the presence of sodium-benzophenone. All other solvents were analytical grade and were used as received. Before use, they were freed from oxygen by degassing and saturating with nitrogen atmosphere.

Starting materials [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] [7], [$Os_3(\mu\text{-}H)_2(CO)_{10}$] [16] and [$\{Rh(CO)_2Cl\}_2$] [17] were prepared according to literature procedures. All chemicals, unless otherwise stated, were purchased commercially and used as received. Infrared spectra were recorded on a Bio-Rad FTS-165 IR spectrometer, using 0.5 mm CaF_2 solution cells. ^{1}H-NMR was obtained on a Bruker DPX400 spectrometer using CD_2Cl_2 or $CDCl_3$ and referenced to $SiMe_4$ ($\delta = 0$). Positive ionization fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, using 3-nitrobenyl alcohol as matrix solvent. GCMS spectra were obtained on a GCD series II gas chromatograph electron ionization detector. Elemental analyses were performed by Department of Chemistry, City University of Hong Kong.

3.2. *Reaction of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with vinylacetic acid*

Compound **1** (100 mg, 0.10 mmol) and an excess amount of vinylacetic acid were stirred at refluxing toluene (50 cm^3) for 5 h. The color gradually turned

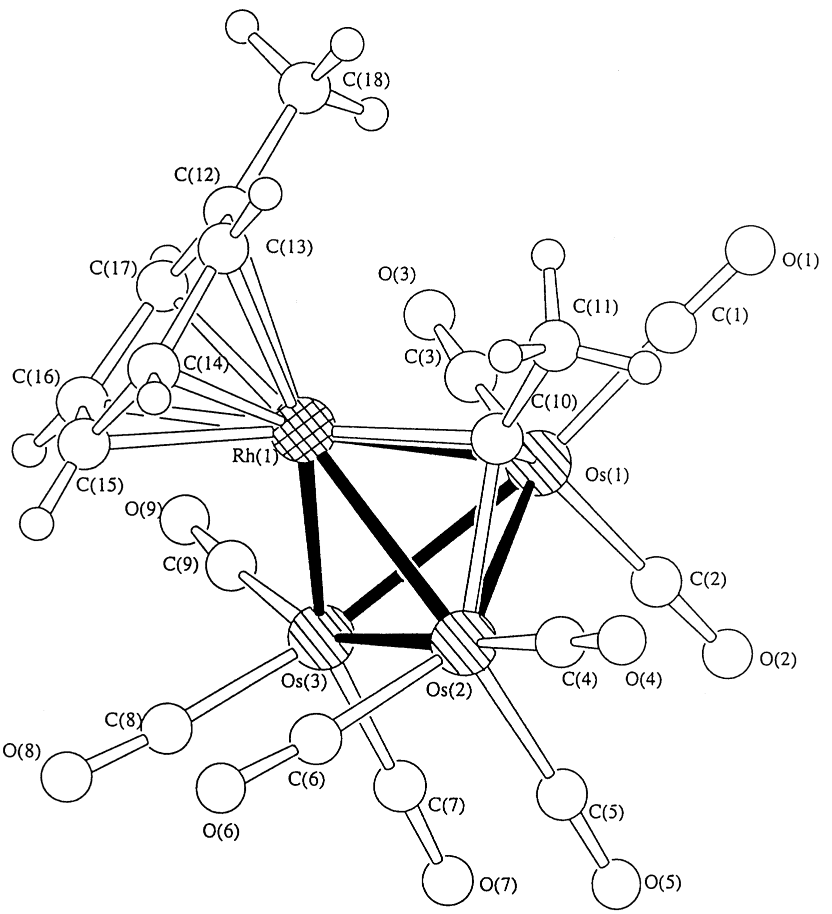


Fig. 3. The molecular structure of [$Os_3Rh(\mu_3\text{-}CCH_3)(\eta^6\text{-}C_6H_5CH_3)(CO)_9$] (**4**) with the atom numbering scheme.

Table 4
Selected bond distances (Å) and angles (°) for cluster **4**

Bond distances			
Os(1)–Os(2)	2.7888(8)	Os(1)–Os(3)	2.7617(7)
Os(1)–Rh(1)	2.706(1)	Os(1)–C(10)	2.07(1)
Os(2)–Os(3)	2.7592(8)	Os(2)–Rh(1)	2.720(1)
Os(2)–C(10)	2.06(1)	Os(3)–Rh(1)	2.719(1)
Rh(1)–C(10)	2.00(1)	C(12)–C(13)	1.41(3)
C(12)–C(17)	1.37(2)	C(12)–C(18)	1.52(2)
C(13)–C(14)	1.43(3)	C(14)–C(15)	1.39(3)
C(15)–C(16)	1.37(3)	C(16)–C(17)	1.45(2)
Bond angles			
Os(2)–Os(1)–Os(3)	59.62(2)	Os(2)–Os(1)–Rh(1)	59.32(3)
Os(2)–Os(1)–C(10)	47.4(4)	Os(3)–Os(1)–Rh(1)	59.63(3)
Os(3)–Os(1)–C(10)	93.1(4)	Rh(1)–Os(1)–C(10)	47.2(3)
Os(1)–Os(2)–Os(3)	59.70(2)	Os(1)–Os(2)–Rh(1)	58.82(3)
Os(1)–Os(2)–C(10)	47.6(4)	Os(3)–Os(2)–Rh(1)	59.49(3)
Os(3)–Os(2)–C(10)	93.3(4)	Rh(1)–Os(2)–C(10)	47.0(3)
Os(1)–Os(3)–Os(2)	60.68(2)	Os(1)–Os(3)–Rh(1)	59.16(2)
Os(2)–Os(3)–Rh(1)	59.53(3)	Os(1)–Rh(1)–Os(2)	61.86(3)
Os(1)–Rh(1)–Os(3)	61.21(3)	Os(1)–Rh(1)–C(10)	49.4(4)
Os(2)–Rh(1)–Os(3)	60.98(3)	Os(2)–Rh(1)–C(10)	48.9(4)
Os(3)–Rh(1)–C(10)	96.0(4)	Os(1)–C(10)–Os(2)	85.0(1)
Os(1)–C(10)–Rh(1)	83.4(5)	Os(2)–C(10)–Rh(1)	84.1(5)
Os(2)–C(10)–C(11)	131(1)	C(13)–C(14)–C(15)	119(1)
C(14)–C(15)–C(16)	120(1)	C(15)–C(16)–C(17)	120(1)

from yellow to brown. The reaction mixture was evaporated to dryness. The residue was then redissolved in CH_2Cl_2 (3 cm^3) and separated by preparative TLC with an eluent of *n*-hexane–CH_2Cl_2 (1:1 v/v) to yield brown complex **2** ($R_f = 0.55$, 0.02 mmol, 20%) and orange complex **3** ($R_f = 0.35$, 0.04 mmol, 40%). Anal. Found for **2**: C, 16.3; H, 0.5. Calc. for $C_{24}H_8O_{17}Os_5Rh_2$: C, 16.7; H, 0.5%. Anal. Found for **3**: C, 20.3; H, 1.0. Calc. for $C_{17}H_{10}O_{13}Os_2Rh_2$: C, 20.3; H, 1.1%.

3.3. Reaction of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with vinylacetate

Compound **1** (100 mg, 0.10 mmol) was dissolved in toluene (50 cm^3) and excess amount of vinylacetate was added. The yellow solution was allowed to heat under reflux for 2 h. The reaction mixture changed to brown gradually. The solvent was then removed in vacuo and redissolved in CH_2Cl_2 (3 cm^3). The purification with *n*-hexane–CH_2Cl_2 (1:1 v/v) as eluent gave light brown complex **4** ($R_f = 0.65$, 0.04 mmol, 40%) and brown complex **2** ($R_f = 0.55$, 0.02 mmol, 20%). Anal. Found for **4**: C, 20.4; H, 1.4. Calc. for $C_{18}H_{11}O_9Os_3Rh$; C, 20.7; H, 1.1%.

Table 5
Crystallographic data and data collection parameters for complexes **2**–**4**

	2	**3**	**4**
Empirical formula	$Os_5Rh_2O_{17}C_{24}H_8 \cdot 0.5CH_2Cl_2$	$Os_2Rh_2C_{17}H_{10}O_{13}$	$Os_3RhO_9C_{18}H_{11}$
Formula weight	1746.36	1008.47	1044.79
Crystal dimension (mm)	0.19 × 0.16 × 0.15	0.22 × 0.18 × 0.17	0.22 × 0.21 × 0.19
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (#15)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a (Å)	25.540(2)	10.073(1)	8.698(1)
b (Å)	22.360(2)	18.575(1)	17.544(2)
c (Å)	17.484(1)	12.554(1)	14.506(2)
α (°)			
β (°)	132.25(2)	91.20(1)	92.41(2)
γ (°)			
V (Å^3)	7390(2)	2348.4(3)	2211.6(4)
Z value	8	4	4
D_{calc} (g cm^{-3})	3.139	2.852	3.138
$F(000)$	6148.00	1832.00	1856.00
μ (Mo–K$_\alpha$ (cm^{-1}))	180.81	122.21	179.47
Temperature (K)	298	298	298
Reflection collected	22 750	14 651	13 413
Unique reflection	8439	5449	5095
Observed reflection [$I > 1.50\sigma(I)$]	5746	3654	4249
R	0.044	0.050	0.055
R_w	0.050	0.050	0.069

3.4. Thermolysis of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] in toluene

Compound **1** (100 mg, 0.10 mmol) was refluxed in toluene. The color turned into light brown gradually. The solution was evaporated to dryness and the residue was separated by preparative TLC with solution mixture of n-hexane–CH_2Cl_2 (2:1 v/v) as eluent. The separation yielded a major orange complex ($R_f = 0.65$, 0.04 mmol, 40%).

3.5. Reaction of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with cyclohexene in toluene

Compound **1** (100 mg, 0.10 mmol) and an excess amount of cyclohexene was refluxed in toluene (50 cm^3) under an inert atmosphere, respectively. The colour gradually turns from yellow to brown in the reaction. The brown solution was concentrated under reduced pressure and separated by preparative TLC with n-hexane–CH_2Cl_2 (1:1 v/v) to give a brown complex **2** ($R_f = 0.55$, 0.03 mmol, 30%).

3.6. Reaction of [$Os_3Rh(\mu\text{-}H)_3(CO)_{12}$] with 1-octene

A solution of **1** (100 mg, 0.10 mmol) in n-heptane (40 cm^3) was stirred with excess amount of 1-octene at three different temperatures, i.e. 25, 60 and 100 °C for 24 h, respectively. The reaction mixtures were collected and analyzed by GCMS spectroscopy as indicated above. For the reactions at 60 and 100 °C, GCMS spectra collected at various time intervals showed the presence of isomeric olefins.

3.7. Crystallography

All pertinent crystallographic data and other experimental details are summarized in Table 5. Crystals suitable for X-ray analyses were glued on glass fibers with epoxy resin or sealed in a 0.3 mm glass capillary. Intensity data were collected at ambient temperature on a Bruker AXS SMART CCD diffractometer equipped with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$). All structures were solved by direct methods (SHELX-86 [18] for **2** and **4**; SIR-92 for **3** [19]) and expanded by Fourier-difference technique (DIRDIF-94) [20]. Non-hydrogen atoms were refined anisotropically for **3** and **4**. For **2**, some non-hydrogen atoms were refined anisotropically while the rest were refined isotropically. Hydrogen atoms were generated in their ideal position and included in the structure factor calculations but not refined. Calculations were performed on a Silicon Graphics computer using TEXSAN [21] crystallographic software package.

4. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC

186412; CCDC 186414. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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