

Synthesis of triosmium alkylidyne clusters incorporating bis(diphenylphosphino)alkane type ligands. Crystal structures of  $[\{\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-C})\}_2(\mu\text{-dppp})]$  (dppp = bis(diphenylphosphino)propane) and  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$

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Abstract

The reaction of triosmium alkylidyne cluster  $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$  with excess bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)propane (dppp) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) yields  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$  **1**,  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$  **2**, and a linking cluster  $[\{\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-C})\}_2(\mu\text{-dppp})]$  **3** respectively in moderate yields. Complexes **1** and **2** are found to undergo ring formation by decarbonylation and formation of an Os–P bond to give new clusters  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$  **4** and  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$  **5**.

Single-crystal X-ray structural analyses of **3** and **4** have shown that there was a phosphine-substituted  $\mu_3\text{-C}$  ligand bonded to one of the triosmium metal cores, giving a five-membered osmacycle complex for **4**, while **3** has the structure of a linking cluster, with the two triosmium alkylidyne cluster units linked by a dppp ligand.

**Keywords:** Osmium; Carbonyl; Clusters; Alkylidyne; Crystal structure; Bis(diphenylphosphino)alkane

1. Introduction

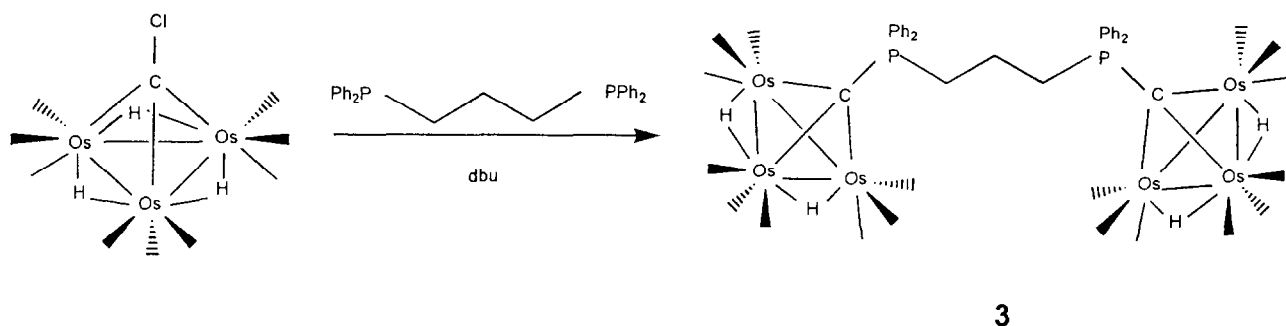
The reaction of triruthenium alkylidyne cluster with triphenylphosphine gives the cluster  $[\text{Ru}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_3)]$  [1]. This has drawn our attention to the reaction of triosmium alkylidyne cluster towards P-donor ligands. We have recently reported the preparation of a triosmium alkylidyne cluster  $(R)\text{-}[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}(\text{Me})\text{CH}_2\text{PPh}_2)]$  [2], which readily undergoes decarbonylation to yield the octacarbonyl cluster  $[(R)\text{-}\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu_3\text{-CPh}_2\text{CH}(\text{Me})\text{CH}_2\text{PPh}_2)]$  via nucleophilic substitution of CO by the uncoordinated P-donor atom, giving a six-membered ring structure (Os–P–C–C–P–C). To further investigate the influence of bis(diphenylphosphino)alkane type ligands upon the reactivities and ring formation properties of triosmium alkylidyne clusters, we have prepared

the new clusters  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$  **1**,  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$  **2**, and  $[\{\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-C})\}_2(\text{PPh}_2(\text{CH}_2)_3\text{PPh}_2)]$  **3**.

2. Results and discussion

The synthesis of complexes **1**, **2**, and **3** was developed by analogy to the deprotonation method used to prepare  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CY})]$  (Y = Lewis base) [3–5]. The reaction of  $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$  [6] with 1 equivalent of the deprotonating agent 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) in the presence of a 10-fold excess of dppm or dppe gives  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$  **1** or  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$  **2** respectively. Both complexes **1** and **2** have very similar solution IR spectral patterns in the carbonyl stretching absorption

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Scheme 1.

Table 1  
Spectroscopic data for compounds 1, 2, 3, 4 and 5

Compound	IR ( $\nu_{\text{co}}$ ) <sup>a</sup> (cm <sup>-1</sup> )	<sup>1</sup> H-NMR <sup>b</sup> ( $\delta$ , $J$ (Hz))	<sup>31</sup> P-NMR <sup>c</sup> ( $\delta$ , $J$ (Hz))	MS <sup>d</sup> ( $m/z$ )
1	2093s, 2054vs,	7.23–8.08 (m, 20H, C <sub>6</sub> H <sub>5</sub> )	41.7 (d, <sup>3</sup> $J$ (PP) = 40.7, $\mu_3$ -CPPH <sub>2</sub> )	1222
	2024vs, 1976s,	2.75 (m, 2H, CH <sub>2</sub> )	– 19.9 (d, <sup>3</sup> $J$ (PP) = 40.7, free PPh <sub>2</sub> )	(1222)
	1966s, 1938s	– 20.06 (d, 2H, <sup>3</sup> $J$ (PH) = 2.17, OsH)		
2	2093s, 2054vs,	7.19–7.99 (m, 20H, C <sub>6</sub> H <sub>5</sub> )	49.1 (d, <sup>3</sup> $J$ (PP) = 36.6, $\mu_3$ -CPPH <sub>2</sub> )	1235
	2024vs, 1978s,	2.50 (m, 2H, CH <sub>2</sub> )	– 10.8 (d, <sup>3</sup> $J$ (PP) = 36.6, free PPh <sub>2</sub> )	(1235)
	1955s, 1940s	2.27 (m, 2H, CH <sub>2</sub> )		
		– 20.18 (d, 2H, <sup>3</sup> $J$ (PH) = 2.13, OsH)		
3	2093s, 2056vs,	7.21–7.92 (m, 40H, C <sub>6</sub> H <sub>5</sub> )	44.6 (s, $\mu_3$ -CPPH <sub>2</sub> )	2086
	2025vs, 1975s,	2.12 (t, 4H, 2CH <sub>2</sub> )		(2086)
	1955s, 1937s	1.56 (m, 2H, CH <sub>2</sub> )		
		– 20.16 (d, 2H, <sup>3</sup> $J$ (PH) = 2.10, OsH)		
4	2059s, 2020vs,	7.16–7.83 (m, 20H, C <sub>6</sub> H <sub>5</sub> )	26.2 (s, $\mu_3$ -CPPH <sub>2</sub> )	1194
	1977s, 1957s,	3.5 (m, 2H, CH <sub>2</sub> )	– 24.1 (s, PPh <sub>2</sub> Os)	(1194)
	1925m	– 18.75 (m, 1H, OsH)		
		– 20.67 (m, 1H, OsH)		
		7.19–7.86 (m, 20H, C <sub>6</sub> H <sub>5</sub> )	32.6 (s, $\mu_3$ -CPPH <sub>2</sub> )	1206
5	2056s, 2019vs	3.04 (m, 2H, CH <sub>2</sub> )	– 20.7 (s, PPh <sub>2</sub> Os)	(1206)
	1976s, 1955s,	2.69 (m, 2H, CH <sub>2</sub> )		
	1926m	– 18.73 (m, 1H, OsH)		
		– 20.38 (m, 1H, OsH)		

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> In CDCl<sub>3</sub>. <sup>d</sup> For  $M$ , calculated values in parentheses.

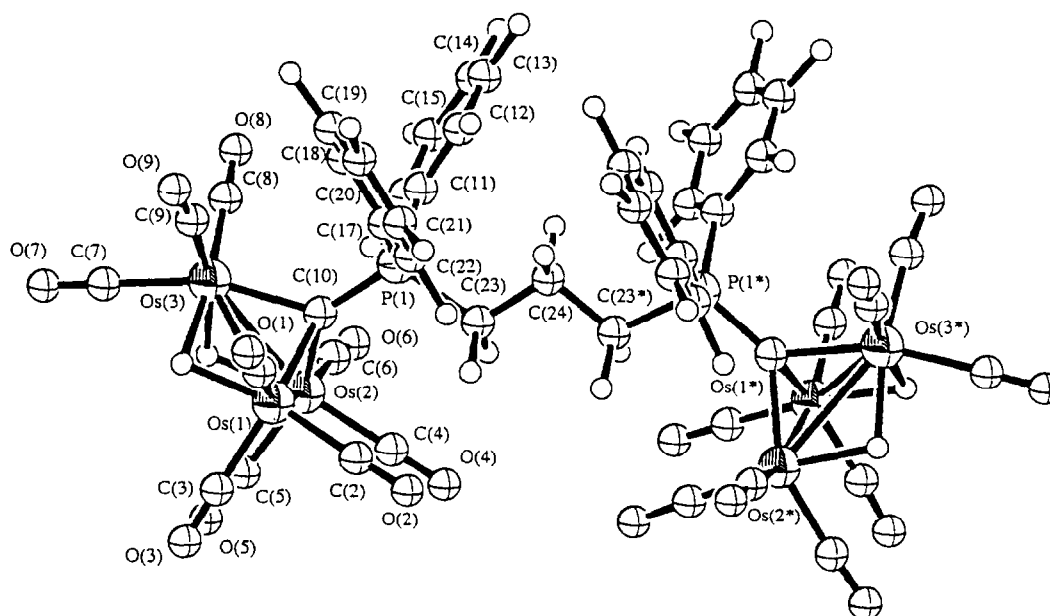


Fig. 1. The molecular structure of  $[\{\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-C})\}_2(\mu\text{-dppp})]$  3.

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

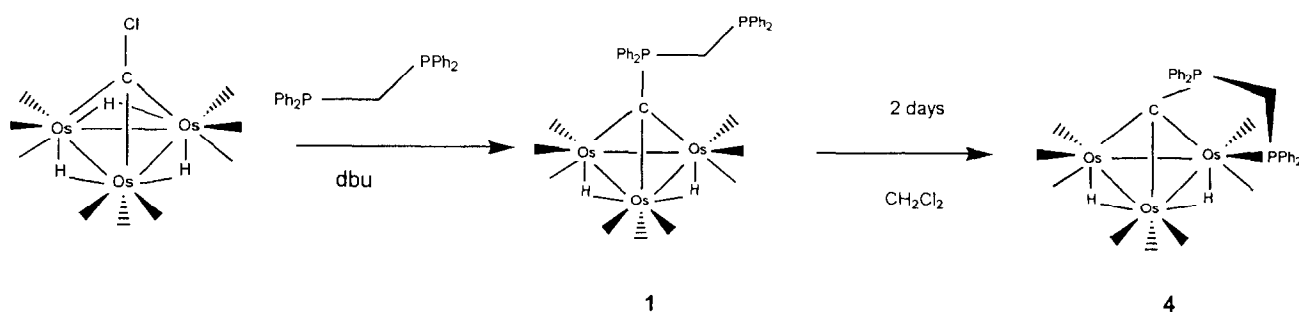
Os(1)–Os(2)	2.9051(9)	Os(1)–Os(3)	2.8896(8)
Os(2)–Os(3)	2.7691(8)	Os(1)–C(9)	2.14(1)
Os(2)–C(9)	2.14(1)	Os(3)–C(9)	2.11(1)
Os(1)–P(1)	2.328(4)	P(1)–C(10)	1.84(1)
P(1)–C(16)	1.84(1)	P(1)–C(34)	1.87(1)
P(2)–C(9)	1.70(1)	P(2)–C(22)	1.83(1)
P(2)–C(28)	1.84(1)	P(2)–C(34)	1.82(1)
Os(2)–Os(1)–Os(3)	57.09(2)	Os(1)–Os(2)–Os(3)	61.17(2)
Os(1)–Os(3)–Os(2)	61.74(2)	Os(1)–C(9)–P(2)	116.3(7)
Os(2)–C(9)–P(2)	122.4(7)	Os(3)–C(9)–P(2)	147.0(7)
C(9)–P(2)–C(22)	117.0(7)	C(9)–P(2)–C(28)	113.8(7)
C(9)–P(2)–C(34)	105.8(6)	P(2)–C(34)–P(1)	108.7(7)
Os(1)–P(1)–C(10)	121.3(5)	Os(1)–P(1)–C(16)	113.9(5)
Os(1)–P(1)–C(34)	107.8(5)		

region. The  $^1\text{H-NMR}$  spectrum of each complex consists of a doublet near  $\delta -20.0$  due to the two bridging hydride ligands coupled to the phosphorus atom attached to the  $\mu_3$ -carbon. The  $^{31}\text{P-NMR}$  spectrum of complex **1** gives two doublets at  $\delta 41.67$  and  $-19.87$  with  $^3J_{\text{PP}} = 40.7$  Hz, while complex **2** shows two doublets at  $\delta 49.06$  and  $-10.84$  with  $^3J_{\text{PP}} = 30.6$  Hz. The low-field doublets of both complexes **1** and **2** are assigned to the  $\text{PPh}_2$  group co-ordinated to the  $\mu_3$ -carbon atom of the electron-withdrawing  $\text{Os}_3\text{C}$  core. The other doublet is attributable to the free  $\text{PPh}_2$  group. The P–P coupling  $^3J_{\text{PP}}$  of complexes **1** and **2** is within the expected range. The FAB mass spectra of **1** and **2** show the parent ion peaks at  $m/z$  1222 and 1236 respectively. The values differ by 14 a.m.u. (one  $\text{CH}_2$  unit), and both of them also show the stepwise loss of nine carbonyl groups.

The reaction of  $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$  with 1 equivalent of dbu in the presence of a 10-fold excess of bis(diphenylphosphino)propane gives a yellow crystalline compound  $[\{\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-C})\}_2(\mu\text{-dppp})]$  **3** (Scheme 1). The spectroscopic data of complex **3** are summarised in Table 1. The  $\nu_{\text{CO}}$  of complex **3** is very similar to that of complexes **1** and **2**. The  $^1\text{H-NMR}$  spectrum of complex **3**, like complexes **1** and **2**, shows

a doublet at  $\delta -20.1$ . But, in the  $^{31}\text{P-NMR}$  spectrum, it only shows a singlet at  $\delta 44.57$ , and the FAB mass spectrum shows a molecular ion at  $m/z = 2086$ . The molecular structure of **3** has been established by X-ray structural analysis. A single crystal of complex **3** suitable for diffraction experiments was grown by slow evaporation of a  $\text{CH}_2\text{Cl}_2/n\text{-hexane}$  solution of complex **3** at room temperature for a period of 2 days. A perspective view of complex **3** together with the atomic labelling scheme are shown in Fig. 1; selected bond lengths and angles are summarised in Table 2. Complex **3** is a hexaosmium cluster containing two triosmium alkyldiene cluster units linked by the dppp. Half of the molecule is related by crystallographic two-fold axis to C(24) on the symmetry axis. Linking clusters of alkyldiene type are not common, although other triosmium linking clusters are well known [7–10]. The P(1)–C(10) bond (1.72(2) Å) is comparable with the previously reported  $[\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CPR}_3)]$  (1.80(3) Å) [2]. The Os(1)–Os(2) bond (2.751 Å) is shorter than the other two Os–Os bonds (2.881(1) and 2.897(1) Å), which is attributable to the bridging effect of two hydrides between Os(1)–Os(3) and Os(2)–Os(3) respectively.

Complexes **1** and **2** readily undergo decarbonylation at ambient temperature to give new clusters, namely



Scheme 2.

Table 3  
Selected bond distance (Å) and angles (°) for **4**

Os(1)–Os(2)	2.751(1)	Os(1)–Os(3)	2.881(1)
Os(2)–Os(3)	2.897(1)	Os(1)–C(10)	2.16(2)
Os(2)–C(10)	2.13(2)	Os(3)–C(10)	2.12(2)
P(1)–C(10)	1.72(2)	P(1)–C(11)	1.85(2)
P(1)–C(17)	1.83(2)	P(1)–C(23)	1.81(2)
C(23)–C(24)	1.56(2)		
Os(2)–Os(1)–Os(3)	61.85(3)	Os(1)–Os(2)–Os(3)	61.29(3)
Os(1)–Os(3)–Os(2)	56.85(3)	Os(1)–C(10)–P(1)	123.5(9)
Os(2)–C(10)–P(1)	132.6(10)	Os(3)–C(10)–P(1)	132.0(9)
C(10)–P(1)–C(11)	113.7(8)	C(10)–P(1)–C(17)	112.7(9)
C(10)–P(1)–C(23)	112.2(8)	P(1)–C(23)–C(24)	112(1)
C(23)–C(24)–C(23)	107(1)		

[Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-CPPh<sub>2</sub>CH<sub>2</sub>)PPh<sub>2</sub>]**4** and [Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-CPPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)PPh<sub>2</sub>]**5**. The IR spectroscopic data are summarized in Table 1. The conversion takes two days for **4** (Scheme 2) and 14 days for **5** to complete, as monitored by both IR and <sup>1</sup>H-NMR techniques. The <sup>1</sup>H-NMR spectra of complexes **4** and **5** give two multiplet signals of hydride at δ –18 and –20, indicating that the two hydrides in the triosmium alkylidyne cluster exist in very different environments. Also, the <sup>31</sup>P-NMR spectra of complexes **4** and **5** give two singlet signals in the ranges δ 25 to 35 and δ –20 to –24. The signals in the negative region are attributed to co-ordination of the Os(1)–P(1) bond. In the FAB mass spectra of complexes **4** and **5**, the molecular ions differ by 28 a.m.u. to those of the complexes **1** and **2** respectively. This difference indicates the loss of a carbonyl group in the complexes **4** and **5** compared with the complexes **1** and **2**.

To obtain the molecular structure of complex **4**, X-ray structural analysis was carried out on a single crystal of complex **4**, obtained from slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane solution for two days. An atomic labelling scheme of **4** is shown in Fig. 2; selected bond lengths and angles are summarised in Table 3. The molecular structure of complex **4** shows that it contains an Os(1)–P(1) bond (2.328 (4) Å) and only eight terminal carbonyl groups. The Os(1)–P(1) bond is comparable with previous related species [(*R*)–Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>{μ<sub>3</sub>-CPPh<sub>2</sub>CH(Me)CH<sub>2</sub>PPh<sub>2</sub>}] (2.334 (6) Å). The decarbonylation of complex **1** yields complex **4**, which has a five-membered ring structure [Os–C–P–C–P], while complex **5** has a six-membered ring structure [Os–C–P–C–C–P]. The molecular structure of **4** shows that the cyclization gives a non-planar, twisted, five-membered ring. The conversion of complex **1** to **4** takes two days, while the conversion of complex **2** to complex **5** needs about two weeks. This may be because the formation of a five-membered ring is more favourable than a six-membered ring [11], since the torsional strain of a five-membered ring is less than that of a six-membered ring. Therefore, the conversion of complex **1** to **4**

is faster. The cyclization reaction of **2** is also much slower than (*R*)–[Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>9</sub>{μ<sub>3</sub>-CPPh<sub>2</sub>CH(Me)–CH<sub>2</sub>PPh<sub>2</sub>}], although in both cases a six-membered ring is formed. This may be due to the higher nucleophilicity of the P-donor ligand in (*R*)–[Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>9</sub>{μ<sub>3</sub>-CPPh<sub>2</sub>CH(Me)CH<sub>2</sub>PPh<sub>2</sub>}], since an electron-donating methyl substituent is involved. Attempts to speed up the cyclization of **2** at elevated temperatures has led to a complicated mixture of products which cannot be characterised.

### 3. Experimental

None of the compounds reported here is particularly air-sensitive, however, all reactions were carried out under an atmosphere of dry dinitrogen using Schlenk techniques and were monitored by solution IR spec-

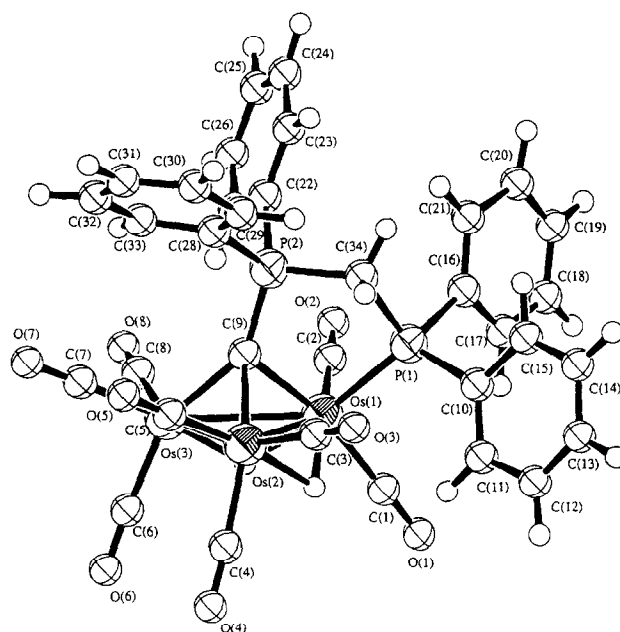


Fig. 2. The molecular structure of [Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-CPPh<sub>2</sub>–CH<sub>2</sub>)PPh<sub>2</sub>]**4**.

troscopy in the carbonyl region on a Bio-rad FTS-7 IR spectrometer using 0.5 mm solution cell. The  $^1\text{H-NMR}$  spectra were recorded on a Bruker DPX 300 NMR spectrometer. The  $^{31}\text{P-NMR}$  spectra were recorded on a JEOL GSX 270 FT-NMR [85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ ]. FAB mass spectra were recorded on a Finnigan MAT 95 instrument with fast atom bombardment technique. Dichloromethane was dried over  $\text{CaH}_2$  and *n*-hexane was distilled from sodium benzophenone ketyl in the presence of tetraethylene glycol dimmer ether.

The starting cluster was prepared following the literature method, where dppm, dppe, and dppp were purchased from Aldrich and used as received without further purification. Routine separations of products were performed in air by thin-layer chromatography (TLC) using plates coated with Merck Kieselgel 60 GF<sub>254</sub>.

### 3.1. Preparation of complexes $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$ **1**, $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$ **2**

The complex  $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$  (87.3 mg, 0.10 mmol) and the ligand dppm (0.384 g, 1 mmol) or dppe (0.398 g, 1 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$ .  $\text{dbu-CH}_2\text{Cl}_2$  solution (0.1 mmol) was added dropwise to give a yellow solution. The mixture was stirred at room temperature for 15 min and subsequently evapo-

rated to dryness under vacuum. The residue was purified by TLC using acetone/*n*-hexane (1:9 v/v) as eluent. Complex **1** was isolated as a pale yellow solid ( $R_f = 0.5$ ), 45% yield (55 mg), while the pale yellow complex **2** was obtained ( $R_f = 0.5$ ) in 50% yield (62 mg).

### 3.2. Preparation of complex $[\{\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-C})\}_2(\mu\text{-dppp})]$ **3**

The complex  $[\text{Os}_3(\mu\text{-H})_3(\text{CO})_9(\mu_3\text{-CCl})]$  (87.3 mg, 0.1 mmol) and the ligand dppp (0.412 g, 1 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$ . Dropwise addition of  $\text{dbu-CH}_2\text{Cl}_2$  (0.1 mmol) gave a yellow solution. The mixture was stirred for 15 min at room temperature, then subsequently evaporated to dryness under vacuum. The residue was purified by TLC using *n*-hexane/ $\text{CH}_2\text{Cl}_2$  (8:2 v/v) as eluent. Complex **3** was isolated as a yellow solid ( $R_f = 0.55$ ) in 40% yield (83.4 mg).

### 3.3. Preparation of complexes $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu_3\text{-CPh}_2\text{CH}_2)\text{PPh}_2]$ **4** and $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_8(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2)\text{PPh}_2]$ **5**

The complex  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{PPh}_2)]$  **1** (61 mg, 0.5 mmol) or  $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\mu_3\text{-CPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)]$  **2** (62 mg, 0.5 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$ . Dropwise addition of  $\text{dbu-CH}_2\text{Cl}_2$  (0.1 mmol) gave a yellow solution. The mixture was stirred for 15 min at room temperature, then subsequently evaporated to dryness under vacuum. The residue was purified by TLC using *n*-hexane/ $\text{CH}_2\text{Cl}_2$  (8:2 v/v) as eluent. Complex **4** was isolated as a yellow solid ( $R_f = 0.55$ ) in 40% yield (83.4 mg).

Table 4  
Crystal data and data collection parameters for **3** and **4**

Compound	<b>3</b>	<b>4</b>
Empirical formula	$\text{Os}_6\text{C}_{47}\text{H}_{30}\text{O}_{18}\text{P}_2$	$\text{Os}_3\text{C}_{34}\text{H}_{24}\text{P}_2\text{O}_8$
<i>M</i>	2085.89	1193.11
Colour, habit	yellow, block	yellow, block
Crystal dimensions (mm <sup>3</sup> )	0.25 × 0.22 × 0.31	0.33 × 0.30 × 0.39
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
<i>a</i> (Å)	15.293(3)	13.801(2)
<i>b</i> (Å)	20.527(3)	21.171(2)
<i>c</i> (Å)	17.578(3)	11.816(3)
$\beta$ (°)	94.65(1)	91.67(2)
<i>U</i> (Å <sup>3</sup> )	5499(1)	3450(1)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	2.519	2.296
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	139.27	111.54
<i>F</i> (000)	3768	2200
<i>T</i> (K)	298	298
Scan range (°)	1.37 + 0.35 tan $\theta$	1.42 + 0.35 tan $\theta$
Reflections collected	3579	4882
Unique reflections	3414	4661
Observed reflections ( $I > 3.00\sigma(I)$ )	2073	3413
Transmission factors	0.611–1.000	0.653–1.000
<i>p</i> in weighting scheme	0.002	0.002
$w = [\sigma_c^2(F_o) + p^2/4(F_o^2)]^{-1}$		
<i>R</i> <sup>a</sup>	0.037	0.033
<i>R</i> <sup>b</sup>	0.035	0.034
Residual electron density (e Å <sup>-3</sup> )	0.95 to -0.84	1.02 to -0.77

<sup>a</sup>  $R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$ . <sup>b</sup>  $R = [(\sum w(|F_o| - |F_c|)^2) / \sum wF_o^2]^{1/2}$ .

CPPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)] **2** (62 mg, 0.5 mmol) was dissolved in 25 ml of CH<sub>2</sub>Cl<sub>2</sub> under dinitrogen to give a pale yellow solution. The mixture was allowed to stir for two days for complex **1** and two weeks for complex **2**. After that, they were evaporated to concentration, and the mixtures were subject to preparative TLC using *n*-hexane/acetone (9:1 v/v) as eluent to afford yellow compounds of [Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-CPPh<sub>2</sub>CH<sub>2</sub>)PPh<sub>2</sub>]**4** (36 mg, 0.3 mmol) in 60% yield and [Os<sub>3</sub>(μ-H)<sub>2</sub>(CO)<sub>8</sub>(μ<sub>3</sub>-CPPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)PPh<sub>2</sub>]**5** for complex **2** (24 mg, 0.2 mmol) in 40% yield.

#### 4. X-ray analyses of **3** and **4**

All pertinent crystallographic data and other experimental details are summarised in Table 4. Intensity data were collected at ambient temperature on a Riguka

Table 5

Atomic coordinates for compound **3** with estimated standard deviations in parentheses

Atom	x	y	z
Os(1)	0.31716(5)	-0.00936(4)	0.70131(5)
Os(2)	0.21166(5)	0.01671(4)	0.57062(5)
Os(3)	0.33563(6)	-0.08989(4)	0.56931(5)
P(1)	0.1536(3)	-0.1227(2)	0.6723(3)
O(1)	0.417(1)	-0.0899(9)	0.828(1)
O(2)	0.202(1)	0.0499(7)	0.8156(9)
O(3)	0.421(1)	0.1164(10)	0.700(1)
O(4)	0.0776(9)	0.0853(7)	0.6632(8)
O(5)	0.310(1)	0.1397(8)	0.5338(9)
O(6)	0.080(1)	0.0098(8)	0.4316(9)
O(7)	0.493(1)	-0.0684(9)	0.473(1)
O(8)	0.248(1)	-0.2001(8)	0.6583(9)
O(9)	0.430(1)	-0.2001(8)	0.6583(9)
C(1)	0.376(2)	-0.059(1)	0.779(1)
C(2)	0.248(1)	0.027(1)	0.775(1)
C(3)	0.385(2)	0.068(1)	0.703(1)
C(4)	0.127(1)	0.0595(9)	0.627(1)
C(5)	0.270(1)	0.094(1)	0.577(1)
C(6)	0.130(1)	0.009(1)	0.481(1)
C(7)	0.437(2)	-0.077(1)	0.510(2)
C(8)	0.282(1)	-0.147(1)	0.495(1)
C(9)	0.388(1)	-0.161(1)	0.622(1)
C(10)	0.227(1)	-0.0715(8)	0.6337(10)
C(11)	0.090(1)	-0.1738(8)	0.6007(10)
C(12)	0.057(1)	-0.2338(9)	0.627(1)
C(13)	0.002(1)	-0.2678(10)	0.575(1)
C(14)	-0.020(1)	-0.248(1)	0.504(1)
C(15)	0.016(2)	-0.191(1)	0.475(1)
C(16)	0.072(1)	-0.1503(10)	0.529(1)
C(17)	0.206(1)	-0.1797(9)	0.742(1)
C(18)	0.246(1)	-0.235(1)	0.713(1)
C(19)	0.291(2)	-0.266(1)	0.839(1)
C(20)	0.291(2)	-0.266(1)	0.839(1)
C(21)	0.253(2)	-0.213(1)	0.871(1)
C(22)	0.210(1)	-0.1674(10)	0.181(1)
C(23)	0.071(1)	-0.0770(8)	0.7187(10)
C(24)	0.000	-0.122(1)	0.750

Table 6

Atomic coordinates for compound **4** with estimated standard deviations in parentheses

Atom	x	y	z
Os(1)	0.60218(4)	0.46967(3)	0.42002(5)
Os(2)	0.76029(4)	0.51849(3)	0.38223(5)
Os(3)	0.72893(4)	0.56981(3)	0.16873(5)
P(1)	0.6278(3)	0.3650(2)	0.2932(3)
P(2)	0.8134(3)	0.4065(2)	0.1911(3)
O(1)	0.3947(8)	0.4866(5)	0.3223(9)
O(2)	0.5333(7)	0.4275(5)	0.0059(9)
O(3)	0.7917(8)	0.4222(6)	0.5719(10)
O(4)	0.6964(9)	0.5518(6)	0.3949(10)
O(5)	0.9754(9)	0.5518(6)	0.3949(10)
O(6)	0.6554(9)	0.7008(6)	0.233(1)
O(7)	0.9373(9)	0.6133(6)	0.136(1)
O(8)	0.6818(8)	0.5745(5)	-0.0865(10)
C(1)	0.474(1)	0.4801(7)	0.293(1)
C(2)	0.558(1)	0.4437(7)	0.097(1)
C(3)	0.776(1)	0.4571(7)	0.500(1)
C(4)	0.720(1)	0.5895(8)	0.472(1)
C(5)	0.893(1)	0.5395(7)	0.390(1)
C(6)	0.684(1)	0.6513(8)	0.205(1)
C(7)	0.858(1)	0.5961(8)	0.145(1)
C(8)	0.702(1)	0.5727(7)	0.008(1)
C(9)	0.7555(9)	0.4756(6)	0.218(1)
C(10)	0.6000(10)	0.3371(7)	0.436(1)
C(11)	0.561(1)	0.3755(7)	0.516(1)
C(12)	0.544(1)	0.3506(8)	0.620(1)
C(13)	0.567(1)	0.2902(8)	0.646(1)
C(14)	0.606(1)	0.2504(7)	0.572(1)
C(15)	0.624(1)	0.2738(8)	0.466(1)
C(16)	0.562(1)	0.3074(7)	0.203(1)
C(17)	0.464(1)	0.3134(8)	0.200(1)
C(18)	0.407(1)	0.2731(9)	0.132(2)
C(19)	0.449(2)	0.227(1)	0.079(2)
C(20)	0.546(2)	0.218(1)	0.081(2)
C(21)	0.607(1)	0.2617(10)	0.144(2)
C(22)	0.8027(10)	0.3761(7)	0.046(1)
C(23)	0.843(1)	0.3180(8)	0.021(1)
C(24)	0.837(1)	0.2955(9)	-0.088(2)
C(25)	0.793(1)	0.3303(9)	-0.169(2)
C(26)	0.753(1)	0.3877(8)	-0.148(1)
C(27)	0.758(1)	0.4123(7)	-0.040(1)
C(28)	0.945(1)	0.4096(7)	0.218(1)
C(29)	0.993(1)	0.3729(9)	0.296(2)
C(30)	1.094(2)	0.379(1)	0.313(2)
C(31)	1.140(1)	0.4219(9)	0.254(2)
C(32)	1.097(1)	0.4577(9)	0.178(2)
C(33)	0.998(1)	0.4510(9)	0.153(2)
C(34)	0.760(1)	0.3481(7)	0.238(1)

AFC7R diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) with a graphite monochromator. The unit cell constants were determined from 25 accurately centred reflections in the range  $10^\circ \leq 2\theta \leq 20^\circ$ . The stability of the crystals was monitored at regular intervals using three standard reflections, and no significant variation was observed. Data were corrected for Lorentz and polarisation effects. Absorption corrections based on  $\psi$ -scan methods were also applied [12]. The struc-

tures were solved by a combination of direct methods (SIR88) [13] and difference Fourier techniques. Refinement was achieved by a full-matrix least-squares technique with Os- and P-assigned anisotropic displacement parameters. The hydrogen atoms of the organic fragment were introduced into their idealised positions (C–H 0.95 Å), while hydride atoms were estimated by potential energy calculations [14]. Calculations were performed on a Silicon Graphics workstation, using the program package TeXsan [15]. Final atomic co-ordinates for the non-hydrogen atoms are given in Tables 5 (for **3**) and 6 (for **4**).

Additional materials available from the Cambridge Crystallographic Data Centre comprise hydrogen atom co-ordinates, thermal parameters and a complete list of bond lengths and angles.

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