

Addition of diphenyl diselenide (PhSeSePh) to the clusters
[Os₃(CO)₁₀(μ-dppm)] and [(μ-H)Os₃(CO)₈{Ph₂PCH₂P(Ph)C₆H₄}]:
X-ray structures of [Os₂(CO)₄(μ-SePh)₂(μ-dppm)],
[Os₃(CO)₆(μ-CO)(μ-Se)₂(μ-C₆H₄)(μ-dppm)]
and two isomers of [Os₃(CO)₈(μ-SePh)₂(μ-dppm)]

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Abstract

The reaction of [Os₃(CO)₁₀(μ-dppm)] (**4**) with diphenyldiselenide in refluxing toluene at 110 °C affords the dinuclear compound [Os₂(CO)₄(μ-SePh)₂(μ-dppm)] (**5**), three 50 electron isomeric triosmium compounds **6**, **7** and **8** with the formula [Os₃(CO)₈(μ-SePh)₂(μ-dppm)], two triosmium benzyne compounds [Os₃(CO)₆(μ-CO)(μ-η²-Se)₂(μ-C₆H₄)(μ-dppm)] (**9**) and [Os₃(CO)₉(μ-SePh)₂(μ-η²-C₆H₄)(μ-dppm)] (**10**) in 11%, 19%, 15%, 5%, 18% and 6% yields, respectively. Thermolysis of both **6** and **8** in refluxing toluene gives the dinuclear compound **5** in moderate yield, whereas a similar thermolysis of **7** yields **5** and **9** in 20% and 27% yields, respectively. Compound **10** converts to **9** refluxing in octane. Treatment of the unsaturated compound [(μ-H)Os₃(CO)₈{Ph₂PCH₂P(Ph)C₆H₄}] (**11**) with diphenyldiselenide in refluxing benzene gives **5**, **6**, **7** and **8** in 8%, 20%, 25% and 10% yields, respectively. The molecular structures of **5**, **6**, **7** and **9** have been determined by single crystal X-ray diffraction studies. The molecular structure of **5** shows classical “sawhorse” structure with two bridging phenylselenido ligands as well as a dppm ligand. The solid-state structure of **6** reveals that two SePh groups span the open Os–Os edges of the Os₃ triangle, while the dppm ligand bridges one of the closed Os–Os edges. In compound **7**, one SePh spans the open Os–Os site, while the other spans one of the two closed Os–Os edges and the dppm ligand bridges the third Os–Os vector. Compound **9**, which exists as a mixture of two isomers in solution, contains two triply bridging selenido ligands and a benzyne ligand, which are believed to have been formed by the cleavage of Se–Se bond of the PhSeSePh ligand followed by C–Se and C–H activation of the SePh group. The 54 electron compound **10** has been characterized by elemental analysis, IR, ¹H NMR, ³¹P{¹H} NMR and mass spectroscopic data.

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1. Introduction

Chalcogenide ligands have been shown to be of great value for the synthesis and stabilization of polynuclear

transition metal complexes [1]. Transition-metal carbonyl complexes containing chalcogenide atoms as bridging ligands are of interest because they are often used to facilitate the synthesis of high nuclearity metal complexes [2–4]. There are numerous examples of the synthesis and reactivity of simple trinuclear clusters of iron and ruthenium and their monophosphine derivatives containing capping chalcogenido ligands [5–8].

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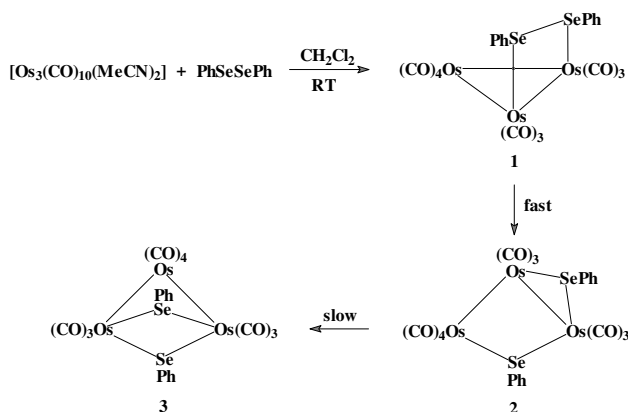
Taking advantage of the frailty of the $\text{Ph}_3\text{P}=\text{Se}$ bond, Adams et al. [9] have recently reported some manganese and mixed iron–manganese carbonyl clusters containing a triply bridging selenido ligand. The synthesis and reactivity of dppm , dppe and bis(diphenylphosphino)ferrocene (dppf) substituted triruthenium and triiron complexes containing capping chalcogenide elements have recently been reported from the reactions of $[\text{M}_3(\text{CO})_{12}]$ ($\text{M} = \text{Ru}, \text{Fe}$) with dppmSe_2 , dppeSe_2 and dppfSe_2 [10]. On the other hand, there are only a few reports concerning the synthesis and reactivity of diphosphine substituted selenido triosmium carbonyl clusters. We have recently demonstrated the synthesis and reactivity of some dppm substituted triosmium clusters containing capping selenido ligand from the reactions of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with dppmSe_2 and dppmSe through oxidative transfer of selenium atom from the dppm ligand to the zero-valent osmium atom [11]. Another approach to the synthesis of bridging selenido metal carbonyl clusters is the cleavage of Se–Se bond of diaryldiselenide [12–14]. For example, Lewis and coworkers [12] reported that the lightly stabilized cluster $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ reacts with PhSeSePh at room temperature to give the 50-electron cluster $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ (**3**) by the cleavage of Se–Se bond of the diselenide. Deeming and coworkers [13,14] also investigated the reactions of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with RSeSeR and obtained the transient intermediate compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-PhSe}_2\text{Ph})]$ (**1**) with an intact Se–Se bond which readily forms $[\text{Os}_3(\text{CO})_{10}(\mu\text{-SePh})_2]$ (**2**) by cleavage of the Se–Se bond of the ligand and then thermally isomerizes to **3** (Scheme 1).

The chemistry of the bridging dppm triosmium cluster $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (**4**) and its orthometallated, unsaturated derivative $[(\mu\text{-H})\text{Os}_3(\text{CO})_8\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ (**11**) has been studied by several groups [15] and continues to be the focus of considerable attention. The interest in these complexes is not only due to the special

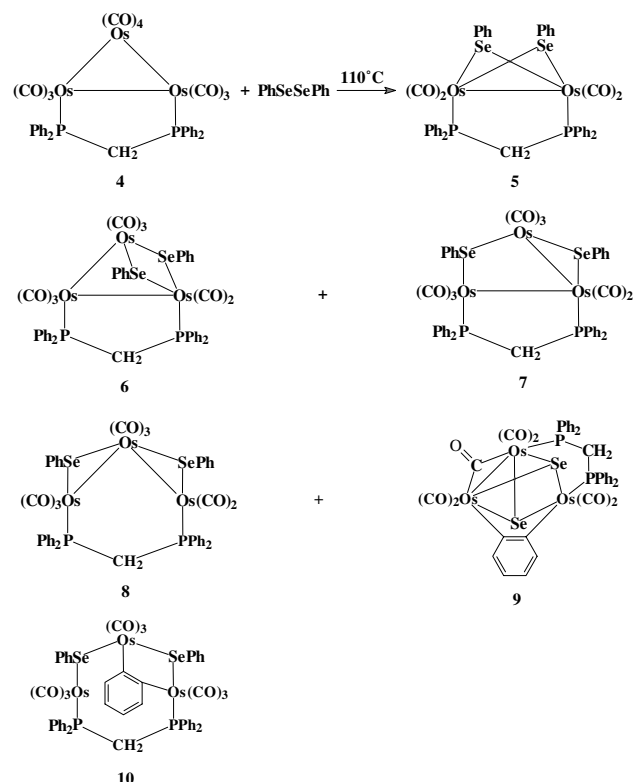
ability of the diphosphine ligand to maintain the metal cluster framework intact during chemical reactions but also because of the unsaturated character of **11** which allows it to react with various small inorganic and organic molecules under mild conditions to give many interesting and potentially useful compounds. Following the above observations we set out to investigate the reactivity of **4** and **11** with PhSeSePh with the intent of synthesizing clusters related to $[\text{Os}_3(\text{CO})_8(\text{SePh})_2(\mu\text{-dppm})]$, and to establish whether starting with the electron precise, **4** or the electronically unsaturated cluster, **11** influences the course of the reaction.

2. Results and discussion

Treatment of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (**4**) with PhSeSePh in refluxing toluene results in the isolation of a diosmium compound $[\text{Os}_2(\text{CO})_4(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**5**), three isomeric triosmium compounds **6**, **7** and **8** with the formula $[\text{Os}_3(\text{CO})_8(\mu\text{-SePh})_2(\mu\text{-dppm})]$, and two triosmium benzyne compounds $[\text{Os}_3(\text{CO})_6(-\text{CO})(\mu\text{-Se})_2(\mu\text{-}\eta^2\text{-C}_6\text{H}_4)(\mu\text{-dppm})]$ (**9**) and $[\text{Os}_3(\text{CO})_9(\mu\text{-SePh})_2(\mu\text{-}\eta^2\text{-C}_6\text{H}_4)(\mu\text{-dppm})]$ (**10**) (Scheme 2) in 11%, 19%, 15%, 5%, 18% and 6% yields respectively. The molecular structures of **5**, **6**, **7** and **9** have been



Scheme 1.



Scheme 2.

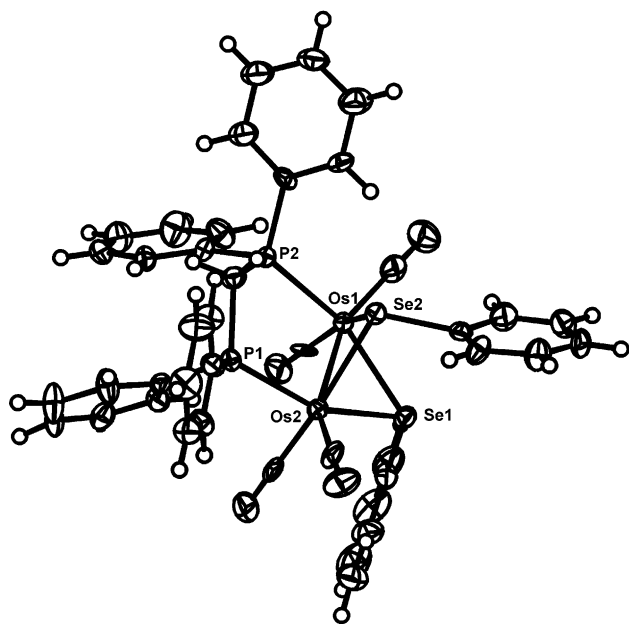


Fig. 1. The molecular structure of $[\text{Os}_2(\text{CO})_4(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**5**). Ellipsoids are shown at the 35% probability level.

fully elucidated by a combination of spectroscopic data and single crystal X-ray diffraction analyses. Compound **10** has been characterized by elemental analysis, IR, ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR and mass spectroscopic data.

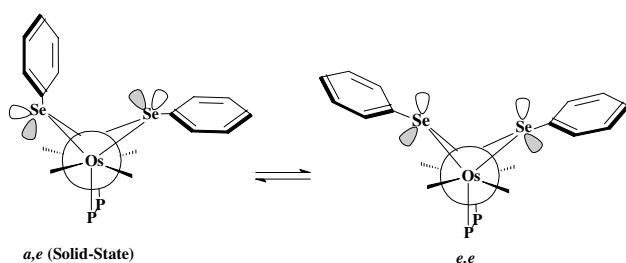
The molecular structure of **5** is shown in Fig. 1, crystal data are listed in Table 1 and selected bond distances and angles are collected in Table 2. The structure consists of an osmium–osmium backbone, ligated terminally by four carbonyl ligands adopting the $\text{Os}_2(\text{CO})_4$ classical “sawhorse” arrangement. This binuclear fragment is bridged by two phenylselenido ligands as well as the dppm ligand. The phenylselenido and the dppm ligands are approximately transoid to each other and the selenido ligands are perpendicular to the Os–Os vector. The Os(1)–Os(2)–P(1)–P(2) plane would define a plane of symmetry for the molecule except that in the solid state the phenyl groups on selenium are situated in an *a, e*-configuration (Scheme 3). This configuration has been shown to be the most stable for related $[\text{Fe}_2(\text{CO})_6(\mu\text{-SR})_2]$ complexes [16]. The phenylselenido ligand spans the two Os atoms nearly in a

Table 1
Crystal data and structure refinement for compounds **5**, **6**, **7** and **9**

	6	7	9	5
Empirical formula	$\text{C}_{45}\text{H}_{32}\text{O}^8\text{Os}_3\text{P}_2\text{Se}_2$	$\text{C}_{45}\text{H}_{32}\text{O}_8\text{Os}_3\text{P}_2\text{Se}_2$	$\text{C}_{38}\text{H}_{26}\text{O}_7\text{Os}_3\text{P}_2\text{Se}_2$	$\text{C}_{41}\text{H}_{32}\text{O}_4\text{Os}_2\text{P}_2\text{Se}_2$
Formula weight	1491.17	1491.17	1385.05	1188.97
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$Pbca$	$P\bar{1}$	$P2(1)/n$
<i>Unit cell dimensions</i>				
<i>a</i> (Å)	11.899(5)	21.865(4)	13.3347(16)	12.787(3)
<i>b</i> (Å)	12.109(5)	17.966(2)	13.8919(16)	22.623(4)
<i>c</i> (Å)	17.827(5)	22.706(3)	14.1230(16)	13.914(3)
α (°)	77.690(5)	90	95.929(2)	90
β (°)	82.580(5)	90	113.941(2)	98.40(2)
γ (°)	75.470(5)	90	115.001(2)	90
<i>V</i> (Å ³)	2421.5(16)	8920(2)	2044.3(4)	3981.9(15)
<i>Z</i>	2	8	2	4
<i>D</i> _{calc} (Mg m ⁻³)	2.045	2.221	2.250	1.983
Absorption coefficient (mm ⁻¹)	9.468	10.282	11.204	8.324
<i>F</i> (000)	1384	5536	1272	2240
Crystal size (mm)	0.39 × 0.25 × 0.16	0.45 × 0.36 × 0.15	0.3 × 0.3 × 0.2	0.31 × 0.22 × 0.264
θ range for data collection (°)	2.05–17.50	1.79–17.50	1.67–26.44	2.02–20.00
Limiting indices	$-9 \leq h \leq 1$ $-10 \leq k \leq 9$ $-15 \leq l \leq 15$	$0 \leq h \leq 18$ $0 \leq k \leq 15$ $0 \leq l \leq 19$	$-16 \leq h \leq 14$ $-17 \leq k \leq 17$ $0 \leq l \leq 17$	$-9 \leq h \leq 9$ $0 \leq k \leq 21$ $0 \leq l \leq 13$
Reflections collected	3674	2510	8163	3450
Independent reflections	3019	2510	8163	3450
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3019/291/466	2510/459/531	8163/0/469	3450/366/460
Goodness-of-fit on <i>F</i> ²	0.959	1.070	1.015	1.136
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	$R_1 = 0.0572$, $wR_2 = 0.1546$	$R_1 = 0.0592$, $wR_2 = 0.1523$	$R_1 = 0.0551$, $wR_2 = 0.1432$	$R_1 = 0.0501$, $wR_2 = 0.1281$
<i>R</i> indices (all data)	$R_1 = 0.0625$, $wR_2 = 0.1601$	$R_1 = 0.0813$, $wR_2 = 0.1701$	$R_1 = 0.0829$, $wR_2 = 0.1646$	$R_1 = 0.0691$, $wR_2 = 0.1476$
Largest difference peak and hole (e Å ⁻³)	3.737 and -1.996	1.088 and -1.710	2.923 and -2.602	1.315 and -1.835

Table 2
Selected bond distances (Å) and angles (°) for **5**

Bond lengths			
Os(1)–Os(2)	2.7454(12)	Os(2)–P(1)	2.314(5)
Os(1)–Se(1)	2.532(2)	Os–C(CO)(average)	1.85(7)
Os(1)–Se(2)	2.563(2)	C–O(average)	1.15 (2)
Os(2)–Se(1)	2.521(2)	P–C(average)	1.83(3)
Os(1)–P(2)	2.331(5)		
Os(2)–Se(2)	2.559(2)		
Bond angles			
Os(1)–Se(1)–Os(2)	65.82 (5)		
Os(1)–Se(2)–Os(2)	64.82(5)		
P(1)–C(1)–P(2)	114.0(10)		



Scheme 3.

symmetric fashion {Os(1)–Se(1) = 2.532(2) Å, Os(1)–Se(2) = 2.563(2) Å, Os(2)–Se(1) = 2.521(2) Å, Os(2)–Se(2) = 2.559(2) Å}. The Os(1)–Os(2) bond distance of 2.7454(12) Å in **5** is comparable to the Os–Os distances found in the related dinuclear compounds [Os₂(CO)₆(μ-1,2-S₂C₆H₄)] {2.686(2) Å} [17] and [Os₂(CO)₆(μ-SCH₂CH₂S)] {2.710(1) Å} [18] but is significantly shorter than that observed in [Os₂(CO)₆(μ-Se)(μ-dppm)] {2.8933(2) Å} [11]. The Os–Se–Os angles are highly acute with the values of 65.82(5)° and 64.82(5)° at Se(1) and Se(2). The P(1)–C(1)–P(2) angle of 114.0(10)° is exactly the same as found in [Ru₂(CO)₄(μ-SCH₂CH₂CH₂S)(μ-dppm)] {P(1)–C(5)–P(2) = 114(2)°} [19] and does not indicate any strain for the dppm ligand. The phenylselenido ligands donate three electrons to make **5** a 34-valence-electron saturated dinuclear compound with each metal atom achieving the expected 18-electron configuration.

The spectroscopic data for **5** indicate that the compound exists as two isomers in solution. The infrared spectrum exhibits four carbonyl stretching bands at 1994 m, 1969 vs, 1923 s and 1910 m cm⁻¹ indicating the presence of more than one isomer in solution. The ³¹P{¹H} NMR spectrum shows two doublets at δ 14.6 (*J* = 70.5 Hz) and –2.8 (*J* = 70.5 Hz) and a singlet at δ –11.8 in a relative intensity of 1:1:8, respectively, indicating the presence of two isomers in solution. The doublets at δ 14.6 and –2.8 are due to minor isomer

while the singlet at δ –11.8 is due to the major isomer. Thus the minor isomer has non-equivalent ³¹P nuclei which are equivalent in the major isomer. In addition to the usual resonances for the phenyl protons, the ¹H NMR spectrum in the aliphatic region shows four multiplets centered at δ 4.79, 4.72, 4.62 and 4.11 indicating the presence of two isomers. If the solid-state structure of **5** corresponds to the major isomer, then the likely structure for the minor isomer is the *e, e*-configuration (Scheme 3) which has been shown to be the next most stable configuration for the iron analogs referred to above [16]. In order for the two phosphorus atoms to be magnetically non-equivalent the *e, e* configuration must have the phenyl groups in a *Z* orientation with respect to the selenium-selenium vector (Scheme 3). Again, this is the preferred orientation for the related iron-alkyl thiolate dinuclear complexes [16]. One might expect the two proposed isomers of **5** to interconvert. Unfortunately, compound **5** was soluble only in methylene chloride which boils well below the temperature at which one would anticipate the expected dynamic behavior to be observed. The FAB mass spectrum contains a molecular ion peak at *m/z* 1188, which undergoes fragmentation by sequential loss of four CO groups.

The molecular structure of **6** is shown in Fig. 2, crystal data are listed in Table 1 and selected bond distances and angles are collected in Table 3. The molecule consists of an open cluster of three metal atoms with two metal–metal bonds and eight linear terminal carbonyl ligands. Among the eight terminal carbonyl groups, three are bonded to each of two osmium atoms Os(2) and Os(3) and two bonded to Os(1). The Os(1)–Os(2) edge is bridged by the dppm ligand and the open Os(1)···Os(3)

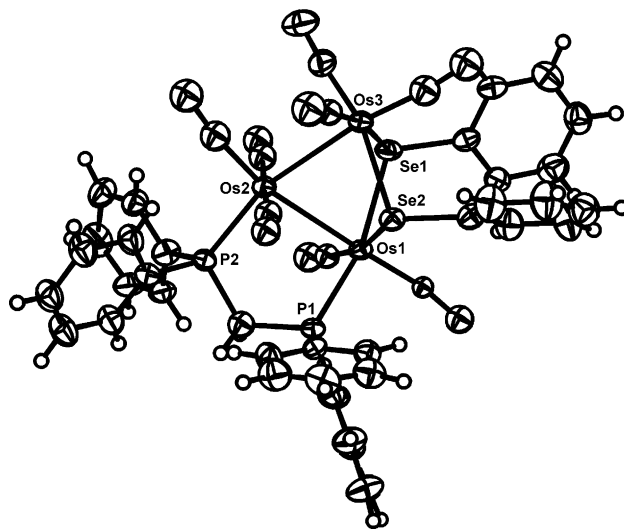


Fig. 2. The molecular structure of [Os₃(CO)₈(μ-SePh)₂(μ-dppm)] (**6**). Ellipsoids are shown at the 35% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths			
Os(1)–Os(2)	2.9406(16)	Os(1)–P(1)	2.324(7)
Os(2)–Os(3)	2.8954(17)	Os(2)–P(2)	2.341(6)
Os(1)–Se(1)	2.575(3)	Os–C(CO)(average)	1.81(5)
Os(1)–Se(2)	2.573(3)	C–O(average)	1.19(3)
Os(3)–Se(1)	2.561(3)	P–C(average)	1.81(5)
Os(3)–Se(2)	2.548(3)		
Bond angles			
P(1)–C(1)–P(2)	118.7(15)	Os(2)–Os(3)–Se(2)	78.58(7)
Os(3)–Se(2)–Os(1)	86.92(9)	Os(2)–Os(1)–Se(2)	77.35(7)
Os(1)–Os(2)–Os(3)	74.26(4)	Os(2)–Os(1)–Se(1)	79.32(7)
Os(3)–Se(1)–Os(1)	86.62(9)	Os(2)–Os(3)–Se(1)	80.42(7)

{Os(1)–Os(3)=3.5217(17)} edge is bridged by two SePh groups. The osmium–osmium bonding distances in **6**, {Os(1)–Os(2)=2.9406(16) Å and Os(2)–Os(3)=2.8954(17) Å} are similar to those of the corresponding distances found in [Os₃(μ-SePh)₂(CO)₁₀] (**3**) {2.947(1) and 2.827(1) Å} [13,14]. The μ-SePh ligands symmetrically span the non-bonding Os(1)··Os(3) edge {Os(1)–Se(1)=2.575(3) Å, Os(3)–Se(1)=2.561(3) Å, Os(1)–Se(2)=2.573(3) Å and Os(3)–Se(2)=2.548(3) Å}. The Os–Se bond lengths are nearly the same as found for the corresponding distances in the analogous open cluster **3** [13,14]. The Os–P bond distances {Os(1)–P(1)=2.324(7) Å and Os(2)–P(2)=2.341(6) Å} are similar to those reported for the parent cluster **1** {2.332(3) Å and 2.312(3) Å} [19]. Both the μ-SePh groups act as three electron donors and as usual the bridging dppm donates four electrons to the cluster which results in a total of 50 valence electrons, and the observation of only two formal Os–Os bonds present in the trinuclear framework is consistent with the electron count. The overall structure of **6** is similar to that of compound **3** if one considers that an equatorial carbonyl group on each of the two metal–metal bonded osmium atoms is replaced by the Ph₂P groups of the dppm ligand.

The spectroscopic data of **6** are consistent with the solid-state structure. The infrared spectrum of **6** exhibits ν(CO) absorption bands in the region characteristic of terminal CO ligands. The FAB mass spectrum exhibits molecular ion peak at *m/z* 1490 and fragments ions formed by the sequential loss of eight carbonyl groups. The ¹H NMR spectrum shows a multiplet centered at δ 7.30 for the phenyl protons of dppm and μ-SePh ligands and two equally intense multiplets at δ 4.70 and 4.12 due to the methylene protons of the dppm ligand. The ³¹P{¹H} NMR spectrum of **6** shows two doublets at δ 14.8 and –2.8 indicating non-equivalence of the ³¹P nuclei.

The molecular structure of **7** is shown in Fig. 3, crystal data are listed in Table 1 and selected bond distances and angles are listed in Table 4. The molecule consists of an open triangular cluster of three osmium

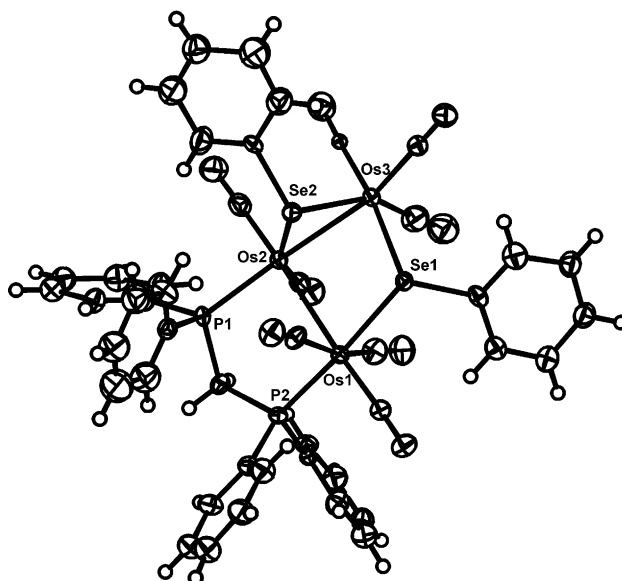


Fig. 3. The molecular structure of [Os₃(CO)₈(μ-SePh)₂(μ-dppm)] (**7**). Ellipsoids are shown at the 35% probability level.

Table 4
Selected bond lengths (Å) and angles (°) for **7**

Bond lengths			
Os(1)–Os(2)	2.9942(17)	Os(1)–P(2)	2.323(7)
Os(2)–Os(3)	2.8528(3)	Os(2)–P(1)	2.340(7)
Os(1)–Se(1)	2.560(3)	Os–C(CO)	1.946(5)
		(average)	
Os(3)–Se(1)	2.573(3)	C–O(average)	1.13(3)
Os(2)–Se(2)	2.543(3)	P–C(average)	1.82(7)
Os(3)–Se(2)	2.538(3)		
Bond angles			
P(3)–C(1)–P(1)	112.6(14)	Se(2)–Os(3)–Se(1)	79.48(9)
Se(2)–Os(2)–Os(3)	55.59(7)	Se(2)–Os(3)–Os(2)	56.08(7)
Se(2)–Os(2)–Os(1)	88.24(8)	Se(1)–Os(3)–Os(2)	86.36(7)
Os(3)–Os(2)–Os(1)	85.90(4)	Os(1)–Se(1)–Os(3)	101.75(10)
Se(1)–Os(1)–Os(2)	83.55(7)	Os(3)–Se(2)–Os(2)	68.34(8)

atoms with two distinctly different metal–metal bonds, eight terminal carbonyl ligands, two bridging selenido and a bridging dppm ligands. The Os(1) and Os(3) atoms each carry three terminal CO ligands and the Os(2) atom possesses two CO ligands. The open Os(1)–Os(3) edge {Os(1)–Os(3)=3.9822(17) Å} is bridged by one SePh, and another SePh group bridges the Os(2)–Os(3) edge, while the dppm ligand bridges the Os(1)–Os(2) edge, the latter is significantly longer {2.9942(17) Å} than the former {2.8528(3) Å}, which is even shorter than the average Os–Os distance of 2.877(3) Å in [Os₃(CO)₁₂] [21]. The Os(2)–Os(3) bond distance of 2.8528(3) Å, and Os(1)–Os(2) distance of 2.9942(17) Å are comparable with the corresponding Os–Os distances observed in **2** {2.827(1) Å and 2.947(1) Å, respectively} [13,14]. The Os–Se bond distances {Os(2)–Se(2)=2.543(3) Å,

Os(3)–Se(2) = 2.538(3) Å, Os(1)–Se(1) = 2.560(3) Å, and Os(3)–Se(1) = 2.573(3) Å} are nearly equal and comparable to the corresponding Os–Se distances observed in **2** {2.553(2), 2.562(2), 2.531(2) and 2.532(2) Å}. The Os–P bond distances {Os(1)–P(2) = 2.323(7) Å and Os(2)–P(1) = 2.340(7) Å} are similar to those reported for the parent cluster **1** [20]. The molecule contains a total of 50 valence electrons with two formal metal–metal bonds and is thus electron precise. The structure is derived from that of **2** by replacement of one equatorial carbonyl group on each of the two osmium atoms of unbridged metal–metal edge by a PPh₂ group the dpmm ligand.

The spectroscopic data of **7** are consistent with the solid-state structure. The infrared spectrum of **7** in the carbonyl stretching region indicates that all the carbonyl groups are terminally bonded. The ³¹P{¹H} NMR spectrum contains two doublets at δ –4.5 and 18.8 indicating non-equivalent ³¹P nuclei. The ¹H NMR spectrum shows three multiplets centered at δ 7.54, 4.21 and 2.30 in a relative intensity of 30:1:1. The FAB mass spectrum exhibits molecular ion peak at *m/z* 1490 and fragmentation peaks due to the sequential loss of eight carbonyl groups.

We were unable to obtain X-ray quality crystals of compound **8**, therefore, the characterization is based on elemental analysis and infrared, ¹H NMR, ³¹P{¹H} NMR and mass spectroscopic data. The FAB mass spectrum shows the molecular ion peak at *m/z* 1490 corresponding to the formulation [Os₃(CO)₈(μ-SePh)₂(μ-dppm)] and peaks due to the loss of eight CO ligands the same as that observed for **6** and **7**. The ³¹P NMR shows a singlet at δ 10.5, indicating that the phosphorus atoms are equivalent in **8**. The proton NMR of **8** shows a multiplet at 7.35 for the phenyl protons and two multiplets at δ 4.55 and 4.18 due to the methylene protons in a relative intensity of 30:1:1. We believe that **8** is an isomer of **6** and **7** in which each of the two bonded Os–Os edges is bridged by the SePh ligands the dpmm ligand bridges the open osmium–osmium edge.

The molecular structure of **9** is shown in Fig. 4 and selected bond distances and angles are presented in Table 5. The structure consists of an open triangular system of three osmium atoms with one metal–metal bond {Os(2)–Os(3) = 2.8058(7) Å}, six linear terminal carbonyl ligands, of which two are bonded to each osmium atom, one semi-bridging CO ligand, two triply bridging selenido ligands, a bridging dpmm and a benzyne ligand. The open {Os(1)–Os(3)} Os(1)–Os(3) = 3.5725(10) Å} edge is bridged by the benzyne ligand and the other open Os(1)–Os(2) {Os(1)–Os(2) = 3.8575(9) Å} edge is bridged by the dpmm ligand. One carbonyl bound to Os(3) appears to unsymmetrically bridge the Os(2)–Os(3) edge based on the observed Os(2)–CO bond distance {2.421(15)

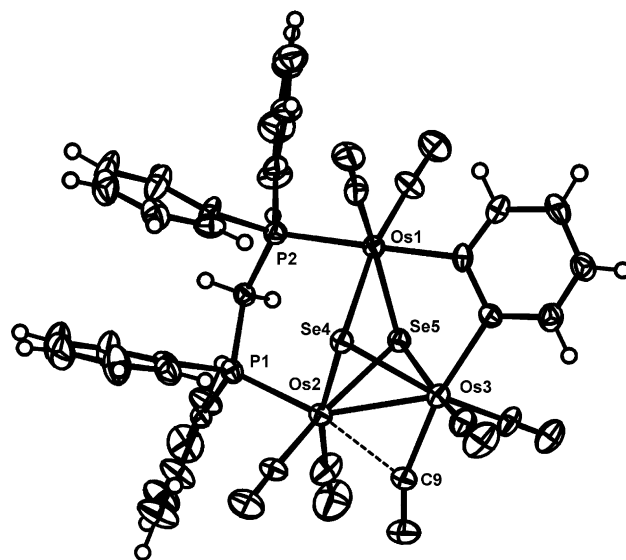


Fig. 4. The molecular structure of [Os₃(CO)₆(μ-CO)(μ-Se)₂(μ-C₆H₄)(μ-dppm)] (**9**). Ellipsoids are shown at the 35% probability level.

Table 5
Selected bond distances (Å) and angles (°) for **9**

Bond lengths			
Os(2)–Os(3)	2.8058(7)	Os(2)–C(9)	2.421(15)
Os(1)–Se(5)	2.6041(13)	Os(1)–C(1)	2.125(11)
Os(3)–Se(5)	2.5626(14)	Os(3)–C(6)	2.137(12)
Os(2)–Se(5)	2.5582(13)	Os(1)–P(2)	2.404(3)
Os(1)–Se(4)	2.5918(14)	Os(2)–P(1)	2.315(3)
Os(3)–Se(4)	2.5615(13)	Os–C(CO)	1.99(6)
		(average)	
Os(2)–Se(4)	2.5535(13)	C–O(average)	1.15(2)
Os(3)–C(9)	1.961(14)	P–C(average)	1.834(3)
C(1)–C(2)	1.344(18)		
C(3)–C(4)	1.38(2)		
C(5)–C(6)	1.406(17)		
C(1)–C(6)	1.415(18)		
C(4)–C(5)	1.337(19)		
Bond angles			
Os(2)–Se(5)–Os(3)	66.45(3)	Se(5)–Os(2)–Os(3)	56.85(3)
Os(2)–Se(5)–Os(1)	96.69(4)	C(9)–Os(3)–Se(4)	99.0(4)
Os(3)–Se(5)–Os(1)	87.46(4)	C(9)–Os(3)–Se(5)	101.1(5)
P(2)–C(26)–P(1)	117.5(6)	Se(4)–Os(3)–Se(5)	77.60(4)
P(2)–Os(1)–Se(5)	91.40(8)	Se(4)–Os(3)–Os(2)	56.60(3)
Se(4)–Os(1)–Se(5)	76.33(4)	Se(5)–Os(3)–Os(2)	56.70(3)
P(2)–Os(1)–Se(4)	95.81(9)	Os(2)–Se(4)–Os(3)	66.53(3)
P(1)–Os(2)–Se(4)	100.40(9)	Os(2)–Se(4)–Os(1)	97.12(4)
P(1)–Os(2)–Se(3)	147.55(9)	Os(3)–Se(4)–Os(1)	87.75(4)
Se(4)–Os(2)–Os(3)	56.87(3)	P(1)–Os(2)–Se(5)	98.54(9)
C(9)–Os(2)–Os(3)	43.3(3)	Se(4)–Os(2)–Se(5)	77.87(4)

Å}, about 0.46 Å longer than that of the Os(3) bond distance to the same carbonyl {1.952(16) Å} and the Os–C–O angles with Os(2) and Os(3) {Os(2)–C(9)–O(9) = 125.7(11)° and Os(3)–C(9)–O(9) = 155.4(13)°}. The Os(1)–P(2) distance of 2.404(3) Å is significantly

longer than the Os(2)–P(1) distance of 2.315(3) Å. This is presumably a consequence of the extra electron density on Os(1) due to the attachment of a C₆H₄ moiety. Compound **9** contains a total of 52 valence electrons; with one metal–metal bond, each metal atom achieves an 18-electron configuration. The benzyne moiety is bonded symmetrically to the Os(2)–Os(3) open edge and donates two electrons to the cluster via two σ bonds from C(1) and C(6) {Os(1)–C(1) = 2.125(11) Å, Os(3)–C(6) = 2.137(12) Å}. The C(1)–C(2) bond length of 1.344(18) Å is shortened relative to the bonds in benzene but elongated relative to the expected bond length in a free benzyne. This bond length is significantly shorter than the other bonds in the benzyne ring and suggests localization of electron density in the C(1)–C(2) bond. This bond length is significantly shorter than the related bond length in the μ_3 - η^2 -benzyne ligand in [Os₃(CO)₉(μ_3 - η^2 -C₆H₄) { μ_3 -P(C₅H₄)Fe(C₅H₄) {1.43(1) Å} as expected when going from μ - to μ_3 -coordination of the benzyne ligand [22]. The two μ_3 -capped Se atoms lie above and below the Os₃ plane. The Os–Se distances {2.5535(13)–2.6041(13) Å} are similar to the Os–Se distances in [Os₃(CO)₇(μ_3 -Se)₂(μ -dppm)] {2.4773(13)–2.5757(13) Å} [11].

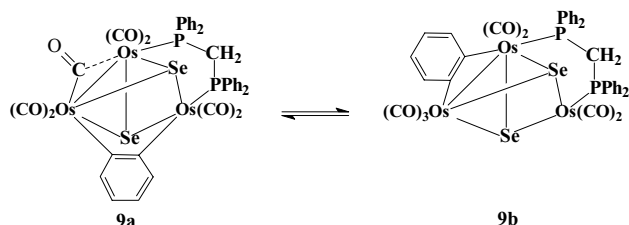
The ³¹P{¹H} NMR spectrum of **9** displays two sets of four doublets which indicates the presence of two isomers in the solution. The doublets at δ –18.1 and –22.9 (J = 122.4 Hz) having the same intensity and coupling constant can be associated with one isomer and the doublets at δ –8.7 and –3.7 (J = 115.5 Hz) with a second isomer. The integration of the ³¹P NMR spectrum revealed a **9a**:**9b** ratio of 3:1. The ¹H NMR spectrum is also consistent with the presence of two isomers in solution. In addition to the usual resonances of the phenyl and benzyl protons, the aliphatic region of the ¹H NMR spectrum contains four multiplets at δ 5.13, 4.84, 4.58 and 4.22 due to the methylene protons of the dppm ligand pointing to the presence of two isomers. The integration of methylene resonances allowed us to associate the resonances at δ 5.13 and 4.84 with the major isomer and the rest of the resonances with the minor isomer. Therefore, the ¹H and ³¹P NMR spectra of **9** indicate the presence of

two isomers in solution in a 3:1 ratio, probably caused by two different dispositions of the benzyne ligand; one on one of the open edges of the cluster, as in the solid state, and one on the metal–metal bonded edge (Scheme 4). The infrared spectrum in the carbonyl stretching region consists of bands characteristic of terminally bonded carbonyl groups and one medium band at 1825 cm^{–1} consistent with the bridging carbonyl ligand in only the major isomer. The mass spectrum shows the molecular ion peak at m/z 1384 and fragment ions due to the sequential loss of seven carbonyl groups.

No single-crystals suitable for X-ray diffraction studies could be obtained for compound **10**, so its structure is based on analytical and spectroscopic data. The infrared spectrum shows bands characteristic of terminal carbonyl ligands. The trinuclear formulation of **10** was indicated by its microanalysis (C, H) and FAB mass spectrum, which exhibits the molecular ion peak at m/z 1594 and fragment ions peaks due to the successive loss of nine carbonyl groups. The ¹H NMR spectrum shows three multiplets centered at δ 7.20, 4.50 and 4.24 in a relative intensity of 34:1:1. The multiplet at δ 7.20 is due to the C₆H₄ protons and phenyl protons of dppm and two SePh ligands, while multiplets at δ 4.50 and 4.24 are due to the methylene protons of the dppm ligand. The ³¹P{¹H} NMR spectrum of **10** contains two doublets at δ 11.6 and 6.1 indicating non-equivalent ³¹P nuclei. A tentative structure for **10** based on these data is shown in Scheme 2. If correct, this structure represents an unusual example of a 54 electron trinuclear cluster with no supporting metal–metal bonds.

When heated to 110 °C, compound **7** is transformed into **5** and **9**, suggesting that **7** may be an intermediate in the formation both **5** and **9**. The formation of **9** proceeds by the cleavage of Se–C and C–H bonds, followed by loss of a benzene molecule. The fate of the benzene molecule has not been established in this reaction. A similar thermolysis of compound **6** affords only the dinuclear compound **5**. Compound **5** is formed by an extrusion of Os(CO)₃ group from the compounds **6** and/or **7** associated with an edge-to-edge shift of SePh. Compound **9** contains two fewer CO ligands than **10** and it has two triply bridging selenido ligand whereas **10** has two triply bridging SePh ligands. Thus compound **9** may have been formed from **10** by the cleavage of SePh bonds and removal of two CO groups followed by the formation of a metal metal bond. As expected thermolysis of **10** in octane at 128 °C leads to the formation of **9** in 43% yield.

In an attempt to synthesize an earlier intermediate of **6**, **7** and **8** containing intact PhSeSePh moiety we have investigated its reaction with the unsaturated compound [(μ -H)Os₃(CO)₈{Ph₂PCH₂P(Ph)C₆H₄} (**11**). Compound **11** does not react with PhSeSePh at ambient temperature,



Scheme 4.

but does react in refluxing benzene at 80 °C to give **5**, **6**, **7** and **8** in 8%, 20%, 25% and 10% yields, respectively.

3. Experimental

Unless specified otherwise, all reactions were routinely performed under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents were dried and distilled prior to use by standard methods. PhSeSePh was purchased from Aldrich and used as received. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer. The compounds $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (**1**) and $[(\mu\text{-H})\text{Os}_3(\text{CO})_8\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$ (**11**) were prepared according to the literature procedures [23].

3.1. Reaction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-dppm})]$ (**4**) with PhSeSePh

To a toluene solution (20 ml) of **4** (0.100 g, 0.081 mmol) was added PhSeSePh (0.051 g, 0.160 mmol) and the reaction mixture was heated to reflux for 1.5 h. The solvent was removed under reduced pressure and the residue was separated by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed five bands. The first band afforded $[\text{Os}_2(\text{CO})_4(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**5**) (0.011 g, 11%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -15 °C (Anal. Calc. for $\text{C}_{41}\text{H}_{32}\text{O}_4\text{Os}_2\text{P}_2\text{Se}_2$: C, 41.41; H, 2.72. Found: C, 41.62; H, 2.88%). IR (ν CO, CH_2Cl_2): 1994 m, 1969 vs, 1923 s 1910 sh cm^{-1} ; ^1H NMR (CD_2Cl_2): 7.30 (m, 30H), 4.79 (m, 1H), 4.62 (m, 1H), 4.72 (m, 1H), 4.12 (m, 1H) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.6 (d, $J = 70.5$ Hz), -2.8 (d, $J = 70.5$ Hz), -11.8 (s) ppm; mass spectrum: m/z 1188. The second band gave $[\text{Os}_3(\text{CO})_8(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**6**), (0.023 g, 19%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -15 °C (Anal. Calc. for $\text{C}_{45}\text{H}_{32}\text{O}_8\text{Os}_3\text{P}_2\text{Se}_2$: C, 36.24; H, 2.17. Found: C, 36.44; H, 2.29%). IR (ν CO, CH_2Cl_2): 2066 vs, 2019w, 1988vs, 1979 m, 1925 w; ^1H NMR (CDCl_3): δ 7.30 (m, 30H), 4.70 (m, 1H), 4.12 (m, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.6 (d, $J = 50.6$ Hz), -2.8 (d, $J = 50.6$ Hz); mass spectrum: m/z 1490 (M^+). The third band gave $[\text{Os}_3(\text{CO})_8(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**7**), (0.018 g, 15%) as orange crystals after recrystallization from hexane/ CH_2Cl_2 at -15 °C (Anal. Calc. for $\text{C}_{45}\text{H}_{32}\text{O}_8\text{Os}_3\text{P}_2\text{Se}_2$: C, 36.24; H, 2.17. Found: C, 36.31; H, 2.36%). IR (ν CO, CH_2Cl_2): 2058 m, 2039 s, 1975 s (br) cm^{-1} ; ^1H NMR (CD_2Cl_2): δ 7.54 (m, 30H), 4.21 (m, 1H), 2.30 (m,

1H) ppm; mass spectrum: m/z 1490 δ . The fourth band gave $[\text{Os}_3(\text{CO})_8(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**8**) as yellow crystals (0.006 g, 5%) after recrystallization from hexane/ CH_2Cl_2 at 4 °C (Anal. Calc. for $\text{C}_{45}\text{H}_{32}\text{O}_8\text{Os}_3\text{P}_2\text{Se}_2$: C, 36.24; H, 2.17. Found: C, 36.48; H, 2.42%). IR (ν CO, CH_2Cl_2): 2062 m, 2035 s, 1995 m, 1978 vs cm^{-1} , ^1H NMR (CD_2Cl_2): δ 7.35 (m, 30H), 4.55 (m, 1H), 4.18 (m, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 10.5 (s) ppm; mass spectrum: m/z 1490. The fifth band afforded $[\text{Os}_3(\text{CO})_6(\mu\text{-CO})(\mu\text{-Se})_2(\mu\text{-C}_6\text{H}_4)(\mu\text{-dppm})]$ (**9**) (0.020 g, 18%) as orange crystals after recrystallization from hexane/ CH_2Cl_2 at -15 °C (Anal. Calc. for $\text{C}_{38}\text{H}_{26}\text{O}_7\text{Os}_3\text{P}_2\text{Se}_2$: C, 32.94; H, 1.88. Found: C, 33.12; H, 1.77%). IR (ν CO, CH_2Cl_2): 2077 s, 2033 w, 2017 vs, 1971 w (br), 1950 m, 1919 vw (br) cm^{-1} , ^1H NMR (CD_2Cl_2): δ 7.20 (m, 34 H), 5.13 (m, 1H), 4.84 (m, 1H), 4.58 (m, 1H), 4.22 (m, 1H) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR δ -8.7 ($J = 115.5$ Hz), -3.7 ($J = 115.5$ Hz), -18.1 (d, $J = 122.4$ Hz), -22.9 (d, $J = 122.4$ Hz) ppm; mass spectrum: m/z 1384 (M^+). The sixth band gave $[\text{Os}_3(\text{CO})_9(\mu\text{-SePh})_2(\mu\text{-C}_6\text{H}_4)(\mu\text{-dppm})]$ (**10**) (0.10 g, 6%) as pale yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -15 °C (Anal. Calc. for $\text{C}_{52}\text{H}_{36}\text{O}_9\text{Os}_3\text{P}_2\text{Se}_2$: C, 39.13; H, 2.28. Found: C, 39.33; H, 2.35%). IR (ν CO, CH_2Cl_2): 2023 vs, 2006 s, 1962 s, 1940 cm^{-1} ; ^1H NMR (CD_2Cl_2): δ 7.20 (m, 24H), 4.50 (m, 1H), 4.24 (m, 1H), 3.44 (m, 1H), 3.20 (m, 1H) ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR δ 11.6 (d, $J = 77.9$ Hz), 6.1 (d, $J = 77.9$ Hz) ppm; mass spectrum: m/z 1594 (M^+).

3.2. Thermolysis of **6**

A toluene (15 ml) solution of **6** (0.015 g, 0.010 mmol) was heated to reflux for 1.5 h. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (5:1, v/v) developed a single band which afforded the dinuclear compound $[\text{Os}_2(\text{CO})_4(\mu\text{-SePh})_2(\mu\text{-dppm})]$ (**5**) (0.007 g, 58%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -15 °C.

3.3. Thermolysis of **7**

A similar thermolysis of **7** (0.012 g, 0.008 mmol) for 6 h followed by similar chromatographic workup afforded **5** (0.002 g, 20%) and **9** (0.003 g, 27%).

3.4. Thermolysis of **8**

A similar thermolysis to that above of **8** (0.008 g, 0.005 mmol) followed by similar chromatographic separation gave **5** (0.003 g, 50%).

3.5. Conversion of **10** to **9**

An octane solution (10 ml) of **10** (0.008 g, 0.005 mmol) was heated to reflux under nitrogen for 2 h. The solvent was removed under reduced pressure and the residue was separated by TLC on silica gel. Elution with hexane/CH₂Cl₂ gave a single band which afforded **9** (0.003 g, 43%).

3.6. Reaction [(μ -H)Os₃(CO)₈{Ph₂PCH₂P(Ph)C₆H₄}] (**11**) with PhSeSePh

A benzene solution (50 ml) of **11** (0.100 g, 0.085 mmol) and PhSeSePh (0.080 g, 0.256 mmol) was heated to reflux at 80 °C for 12 h during which time the colour changed from green to yellow. The solvent was removed under reduced pressure and the residue was separated by TLC on silica gel. Elution with hexane/CH₂Cl₂ (4:1, v/v) developed four bands which afforded the following compounds in order of elution: **5** (0.008 g, 8%), **6** (0.025 g, 20%), **7** (0.032 g, 25%) and **8** (0.012 g, 10%).

3.7. X-ray structural determination of **5**, **6**, **7** and **9**

Crystallographic and other experimental data are summarized in Table 1. Crystallographic data were collected at 293(2) K, using a Bruker P4 diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). Data collection and processing were carried out using XSCANS [24]. The unit cells were indexed on low angle reflections in a θ range of 10–13° and refined using the entire data set. The structures were solved by direct methods (SHELXS-97) [25] and refined on F^2 by full matrix least-squares (SHELXL-97) [26], utilized as incorporated in the WINGX [27] program package using all unique data. Unfortunately, none of the crystals diffracted optimally, limiting the number of reflections that we were able to obtain and resulting in relative low data to parameter ratios. While the data were sufficient to provide relatively accurate atomic positions, unconstrained refinement of the thermal parameters for all four structures were unstable. When possible suitable restraints were applied to the thermal parameters: rigid bond, “similar U_{ij} ”, and/or approximate isotropic restraints were applied using DELU, SIMU, and/or ISOR in SHELXL-97. In cases where this refinement proved unstable, the atoms were refined isotropically. The hydrogen atoms were included in calculated positions (riding model) with U_{iso} set at 1.2 times the U_{eq} of the parent atom.

4. Conclusions

In summary, new di- and triosmium compounds containing bridging SePh and dppm ligands have

been synthesized from the reactions of **4** and **11** with PhSeSePh and characterized by X-ray analysis. The reaction of **4** with PhSeSePh at 110 °C yielded the dinuclear compound **5**, three isomeric compounds **6**, **7** and **8** with the formula [Os₃(CO)₈(μ -SePh)₂(μ -dppm)] and two benzyne compounds **9** and **10**. The reaction of the unsaturated compound **11** with PhSeSePh at 80 °C is more selective affording only **5**, **6**, **7** and **8**. Most probably the presence of bridging dppm ligand prevents cluster fragmentation and allows one to isolate the benzyne complexes **9** and **10**. The principal differences between the three isomers **6**, **7** and **8** arise from different positions of the SePh ligand with respect to the dppm ligand. In **6** both the SePh ligands span the open Os–Os edge and the dppm ligand bridges one of the bonded metal–metal edge while in **7** the two SePh ligands bridging across one bonding and one non-bonding Os–Os edges and the third Os–Os edge is bridged by the dppm ligand. In **8**, the dppm ligand spans the non-bonded Os–Os edge and each of the two SePh ligand bridges one bonded Os–Os edge. That **9** and **10** form only at more elevated temperatures indicates that they result from **6–8**. That the same products are obtained from both **4** and **11** is probably due to the fact that orthometallation in **11** is reversible and gives the same reactive intermediate as **4** after it loses one CO.

Finally, the trends in the non-bonded Os–Os distances observed for **6**, **7** and **9** present some interesting parallels with other bridged open clusters. Thus the two single atom bridges in **6** result in a shorter open edge than the one single atom bridge in **7** and the three atom bridge in **9** results in a longer open edge than the two atom bridge in the same compound.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 226813 for **5**, 226814 for compound **6**, 226815 for compound **7**, and 226816 for compound **9**. Copies of this information may be obtained free of charge from 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](http://www.ccdc.cam.ac.uk)).

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