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Hexa- and triosmium carbonyl clusters bearing bridging dppm and capping sulfido ligands

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Abstract

Treatment of $[Os_3(CO)_7(\mu_3\text{-}S)_2(\mu\text{-dppm})]$ (**1**) with Me_3NO in toluene at 80 °C affords the trinuclear cluster $[Os_3(CO)_6(\mu_3\text{-}S)_2(NMe_3)(\mu\text{-dppm})]$ (**2**) and the hexanuclear cluster $[Os_6(CO)_{12}(\mu_3\text{-}S)_4(\mu\text{-dppm})_2]$ (**3**) in 30% and 51% yields, respectively. The reaction of **1** with $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing benzene at 80 °C gives the hexanuclear cluster $[Os_6(CO)_{14}(\mu_3\text{-}S)_2(\mu\text{-dppm})]$ (**4**) in 15% yield. Compound **2** reacts with CO, PPh_3 and $P(OMe)_3$ at room temperature to give **1**, $[Os_3(CO)_6(\mu_3\text{-}S)_2(\mu\text{-dppm})(PPh_3)]$ (**5**) and $[Os_3(CO)_6(\mu_3\text{-}S)_2(\mu\text{-dppm})\{P(OMe)_3\}]$ (**6**), respectively; in high yields indicating that the NMe_3 ligand is weakly bound. Compound **1** reacts with PPh_3 in presence of Me_3NO to afford **5**, **2** and **3** in 53%, 6% and 18% yields, respectively, whereas with $P(OMe)_3$ **1** gives only **6** in 84% yield. Compound **3** reacts with CO at 98 °C to regenerate **1** by the cleavage of the three unsupported osmium–osmium bonds. The molecular structures of **4** and **6** have been unambiguously determined by single crystal X-ray diffraction studies. The hexanuclear compound **3** appears to be a64-electron butterfly core with four triply bridging sulfido ligands and two bridging dppm ligands based on the spectroscopic and analytical data. The metal core of **4** can be described as a central tetrahedral array capped on two faces with two additional osmium atoms. The triply bridging sulfido ligands face cap the two tetrahedral arrays formed by metal capping of the two faces of the central tetrahedron. The dppm ligand bridges one edge of one of the external tetrahedral arrays. Compounds **5** and **6** are formed by the displacement of equatorial carbonyl group of **1** by a PPh_3 and $P(OMe)_3$ ligand respectively and their structures are comparable to that of **1**.

Keywords: Trinuclear; Hexanuclear; Osmium carbonyl clusters; Crystal structures

1. Introduction

The triply bridging sulfido ligand with its lone pair of electrons would seem to be an ideal species for use in cluster size-expansion reactions [1,2]. By using the lone pair of electrons to form coordinative interactions to electron-deficient metal groupings, the sulfido ligand could also facilitate the entry of metal-containing moieties into the cluster [3]. Thus the triply bridging sulfido cluster $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ has served as an important precursor for many aggregation and condensation reactions. For example, Adams et al. [4] reported the synthesis of the mixed-metal cluster $[Os_3(CO)_9(\mu_4\text{-}S)(\mu_3\text{-}S)\{W(CO)_5\}]$ from the photo-induced reaction of $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ with $W(CO)_6$ in which the $W(CO)_5$

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is coordinated through a μ_4-S atom. They also reported that when irradiated in presence of $[W(CO)_5(PMe_2Ph)]$, the compound $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ yields four mixed-metal clusters $[Os_3W(CO)_{12}(\mu_3\text{-}S)_2(PMe_2Ph)]$, $[Os_3W(CO)_{12}(\mu_3\text{-}S)_2(PMe_2Ph)_2]$, $[Os_3W(CO)_{11}(\mu_3\text{-}S)_2(PMe_2Ph)_2]$ and $[Os_3W_2(CO)_{14}(\mu_4\text{-}S)(\mu_3\text{-}S)(PMe_2Ph)_2]$ [5]. The cluster $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ was also found to react with $Os(CO)_5$ under UV irradiation to form $[Os_4(CO)_{13}(\mu_3\text{-}S)_2]$. Adams and coworkers [6] also reported that when irradiated under a rapid purge of nitrogen $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ undergoes a self condensation and forms the hexanuclear compound $[Os_6(CO)_{16}(\mu_3\text{-}S)_4]$ through the removal of two CO ligands. The dimerization is reversed by CO or the dimer can react with H_2 to form $[(\mu\text{-}H)_2Os_3(CO)_8(\mu_3\text{-}S)_2]$. They also demonstrated [7] that $MeCN)_2]$ to form the hexanuclear cluster $[Os_6(CO)_{17}(\mu_4\text{-}S)_2]$. Our interest in chalcogenide containing clusters stems from a desire to understand how the incorporation of main group elements into transition metal clusters would affect their stability, structure and reactivity.

We have recently reported [8] the synthesis of the hexanuclear selenido cluster $[Os_6(CO)_{12}(\mu_3\text{-}Se)_4(\mu\text{-}dppm)_2]$ from the Me_3NO initiated decarbonylation of $[Os_3(CO)_7(\mu_3\text{-}Se)_2(\mu\text{-}dppm)]$ at 80 °C. Predieri et al. [9] reported the corresponding hexaruthenium compound $[Ru_6(CO)_{12}(\mu_3\text{-}Se)_4(\mu\text{-}dppm)_2]$ from a similar self condensation reaction of $[Ru_3(CO)_7(\mu_3\text{-}Se)_2(\mu\text{-}dppm)]$. As part of our continued interest in cluster expansion reactions, we have been pursuing the chemistry associated with the reactivity of the triply bridging selenido and sulfido triosmium clusters $[Os_3(CO)_7(\mu_3\text{-}Se)_2(\mu\text{-}dppm)]$ and $[Os_3(CO)_7(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ (**1**). In this paper we report the synthesis of $[Os_3(\mu_3\text{-}S)_2(CO)_6(Me_3N)(\mu\text{-}dppm)]$ (**2**) and $[Os_6(CO)_{12}(\mu_3\text{-}S)_4(\mu\text{-}dppm)_2]$ (**3**) by the Me_3NO initiated self condensation reaction of **1**. We also describe the synthesis of the hexanuclear complex $[Os_6(CO)_{14}(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ (**4**) from the reaction of **1** with $[Os_3(CO)_{10}(MeCN)_2]$. These complexes permit the direct comparison of the structures of $[Os_6(CO)_{12}(\mu_3\text{-}Se)_4(\mu\text{-}dppm)_2]$ and $[Os_6(CO)_{14}(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ with those of the unsubstituted complexes $[Os_6(CO)_{16}(\mu_3\text{-}S)_4]$ and $[Os_6(CO)_{17}(\mu_4\text{-}S)_2]$. To further explore the reactivity of $[Os_3(CO)_7(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ (**1**) and $[Os_3(\mu_3\text{-}S)_2(CO)_6(Me_3N)(\mu\text{-}dppm)$ (**2**) we have examined their interactions with CO, PPh_3 and $P(OMe)_3$ and the results are also described in the present paper.

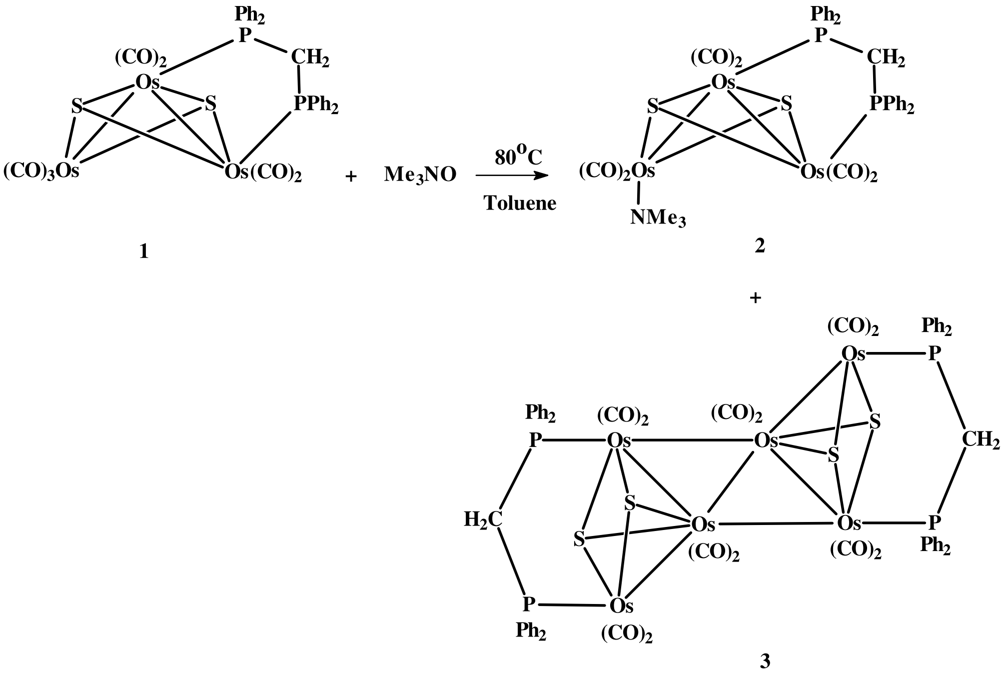
2. Results and discussion

Treatment of $[Os_3(\mu_3\text{-}S)_2(CO)_7(\mu\text{-}dppm)]$ (**1**) with Me_3NO in toluene at 80 °C affords a novel trinuclear cluster $[Os_3(\mu_3\text{-}S)_2(CO)_6(Me_3N)(\mu\text{-}dppm)]$ (**2**) and a hexanuclear cluster $[Os_6(CO)_{12}(\mu_3\text{-}S)_4(\mu\text{-}dppm)_2]$ (**3**) in 30% and 51% yields respectively, after usual chromatographic work-up (Scheme 1).

The formation of **2** constitutes an unambiguous example where oxidation of a cluster bound CO by Me_3NO leads to the corresponding amino derivative. This observation is similar to that reported by Braunstein and coworkers [10] who obtained the NMe_3 substituted compounds $[(\mu\text{-}H)FeCo_3(CO)_{11}(NMe_3)]$ and $[(\mu\text{-}H)FeCo_3(CO)_{10}(PPh_2H)(NMe_3)]$ from the reactions of Me_3NO with $[(\mu\text{-}H)FeCo_3(CO)_{12}]$ and $[(\mu\text{-}H)FeCo_3(CO)_{11}(PPh_2H)]$ respectively. Amine-substituted clusters are rarely amenable to solid-state characterization since the stability of such complexes is limited [11]. Thus we were unable to obtain X-ray quality crystals of compound **2**, therefore, the characterization is based on elemental analysis, infrared, ^1H NMR, $^{31}P\{^1H\}$ NMR and FAB mass spectroscopic data. The infrared spectrum of **2** shows ν(CO) bands characteristic of terminal carbonyl groups. In addition to the usual phenyl proton resonances the ^1H NMR spectrum shows two multiplets at δ 4.61 and 3.48 due to the methylene protons of the dppm ligand and a singlet at δ 2.81 due to the methyl protons of the NMe_3 ligand. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ −13.6 and −14.8 ($J=92.4$ Hz) for the two magnetically non-equivalent ^{31}P nuclei. The FAB mass spectrum shows molecular ion (M^+) peak at *m/z* 1245 and fragment ions formed by the sequential loss of six carbonyl groups.

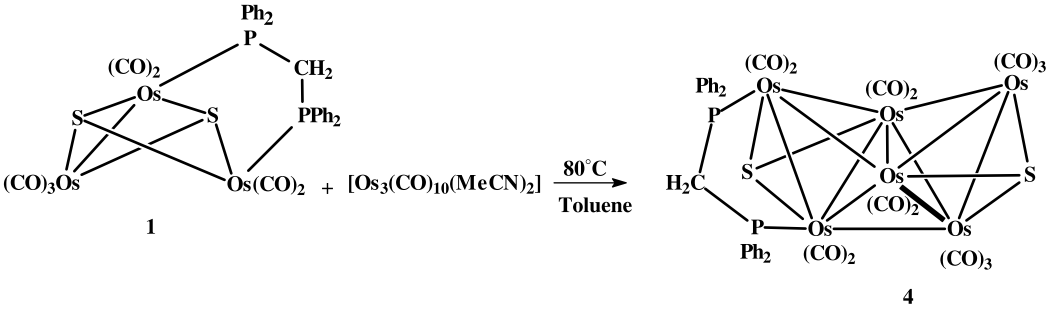
The hexanuclear cluster **3** has been characterized by elemental analysis, infrared, ^1H NMR, $^{31}P\{^1H\}$ NMR and mass spectroscopic data. The spectroscopic data of **3** are in accord with the solid-state structure of the selenium analogue [8]. The infrared spectrum exhibits ν(CO) bands characteristic of terminal carbonyl groups and is exactly the same as the selenium analog. In addition to the usual phenyl proton resonances the ^1H NMR spectrum in the aliphatic region contains two multiplets centered at δ 3.56 and 3.80 due to the methylene protons of the dppm ligand. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at δ −9.8 ($J=17.2$ Hz) and −6.4 ($J=17.\ 2$ Hz), indicating that the ^{31}P nuclei are magnetically non-equivalent. These NMR data are identical in pattern with the selenium analog with only slight variations in the chemical shifts. The FAB mass spectrum shows a molecular ion peak at *m/z* 2374 (M^+) corresponding to the formulation $[Os_6(CO)_{12}(\mu_3\text{-}S)_4(\mu\text{-}dppm)_2]$. Both **3** and its selenium analogue are dark green. The proposed structure of **3** gives a $96e^-$ count, two more than that required for a hexanuclear cluster with seven metal–metal bonds. The two extra electrons probably occupy an antibonding molecular orbital and one would expect to see elongated metal–metal bonds for **3** as reported for the selenium analog [8] where four elongated metal–metal bonds in the range of 2.982(4)–3.042(5) Å are observed for the osmium–osmium bonds around the periphery of the central cluster.

The reaction of **1** with $[Os_3(CO)_{10}(MeCN)_2]$ in refluxing benzene for 3 h followed by usual work up and



Scheme 1.

chromatographic separation has resulted in the isolation of a hexanuclear cluster $[Os_6(\mu_3\text{-}S)_2(CO)_{14}(\mu\text{-dppm})]$ (**4**) in 15% yield (Scheme 2). Cluster **4** has been characterized by elemental analysis, infrared, ^1H NMR, $^{31}P\{^1H\}$ NMR and FAB mass spectroscopic data and by single crystal X-ray diffraction analysis. The molecular structure of **4** is shown in Fig. 1, crystal data are given in Table 1 and the selected bond distances and angles are listed in Table 2. The molecule consists of an extended array of six osmium atoms and two triply bridging sulfido ligands. The metal core can be described as a central tetrahedral array capped on two faces with two additional osmium atoms. The triply bridging sulfido ligands face cap the two tetrahedral arrays formed by metal capping of the two faces of the central tetrahedron. The dppm ligand bridges one edge {Os(1)–Os(2)} of one of the external tetrahedral arrays. The compound contains fourteen linear terminal carbonyl ligands. The metal–metal bonding within the cluster is not uniform with the metal–metal bond distances between the apical–equatorial and equatorial–equatorial osmium atoms ranging from 2.701 (1) to 3.058 (1) Å. There are two metal–metal bonds which are significantly longer {Os(1)–Os(3) = 3.014(1) and Os(1)–Os(4) = 3.058(1) Å} than the average Os–Os bond distances in $[Os_3(CO)_{12}]$ {2.877(3) Å} [12]. Each hinge metal contains two linear terminal carbonyl ligands. The other metal atoms are ligated by three CO ligands. In cluster **1,** all the metal atoms contain 18-electron configurations; however, these configurations cannot be maintained in the $88e^-$ **4** if the newly formed bonds are of a two-centered two-electron type. Compound **4** has 88 electrons and the effective atomic number rule predicts 86 electrons for a hexanuclear cluster with eleven metal–metal bonds. As for **3** this cluster contains two extra electrons which occupy a low lying anti bonding orbital



Scheme 2.

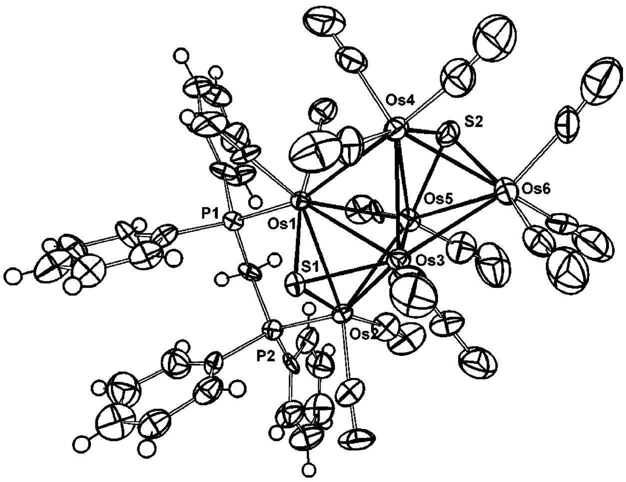


Fig. 1. Molecular structure of $[Os_6(CO)_{14}(\mu_3\text{-}S)_2(\mu\text{-dppm})]$ (**4**) showing the crystallographic labeling scheme. Thermal ellipsoids are at the 50% probability level.

of the central Os_4 core which correlates well with the lengthening of four Os–Os bonds. Electronically, the cluster $[Os_6(CO)_{17}(\mu_4\text{-}S)_2]$, also contains two electrons in excess of the requirements of the 18-electron rule and it was proposed that these electrons also occupy a low-lying antibonding orbital and also exhibits elongated metal–metal bonds [7]. The Os–S bond distances in **4** lie within the range {2.316(6)–2.410(5) Å} and are comparable to those observed for other capping sulfido bridges (2.35–2.45 Å) [13–16]. The details of the nature of the delocalized bonding in cluster **4** remain to be established. This bonding could have an important influence on the reactivity of compounds **3** and **4** and could lead to the development of new reaction pathways that are characteristic of the multinuclear metal centers containing more than the number of electrons required by the effective atomic number rule (vide infra).

The spectroscopic data for **4** are in accord with the solid-state structure. The infrared spectrum of **4** in the CO region exhibits absorption bands characteristic of terminal carbonyl ligands. The ^1H NMR spectrum of **4** shows a series of well-separated multiplets centered at δ 7.31 and two equal intensity pseudo quartets at δ 4.37 and 3.99 for the methylene protons of the dppm ligand. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows two doublets at δ 5.52 ($J = 34.0$ Hz) and 4.37 ($J = 34.0$ Hz) indicating that the two ^{31}P nuclei are non-equivalent. The FAB mass spectrum exhibits the molecular ion peak at m/z 1980 (M^+).

The lability of the Os-amine bond of **2** may be exploited for the selective preparation of other substituted

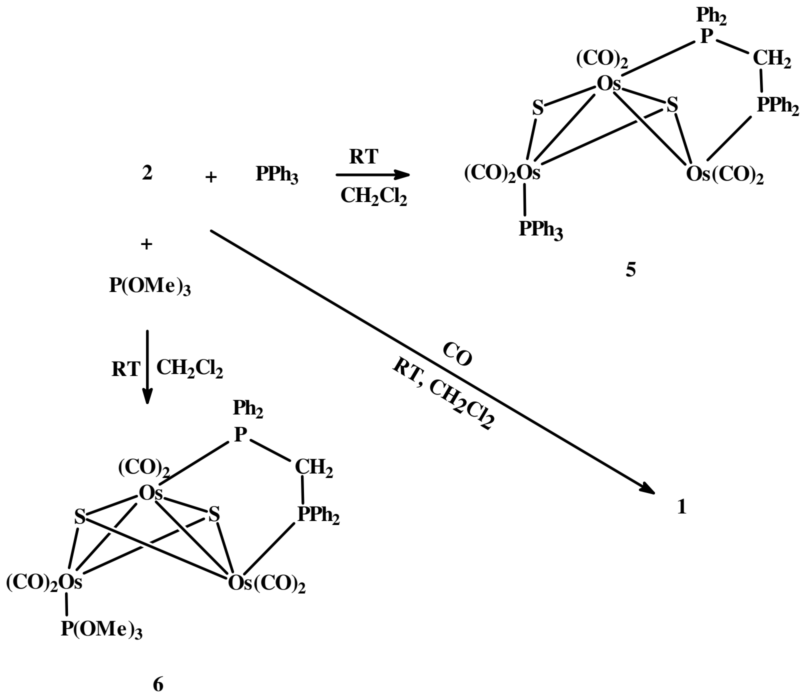
Table 1
Crystal data and structure refinement for **4** and **6**

	4	**6**
Empirical formula	$C_{39}H_{22}O_{14}Os_6P_2S_2$	$C_{34}H_{31}O_9Os_3P_3S_2$
Formula weight	1981.86	1311.22
Temperature	293 (2)	293(2)
Wavelength	0.71073	0.71069
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
Unit cell dimensions (Å)		
a (Å)	11.719(5)	16.767(5)
b (Å)	12.880(5)	17.812(5)
c (Å)	17.0481(5)	28.951(5)
α (°)	69.280(5)	90.00
β (°)	77.500(5)	90.00
γ (°)	70.460(5)	90.00
V (Å^3)	2254.1(15)	8646(4)
Z	2	8
D_{calc} (Mg m^{-3})	2.920	2.015
Absorption coefficient (mm^{-1})	17.071	9.049
F (000)	1772	4896
Crystal size (mm)	0.32×0.10×0.07	0.33×0.26×0.14
θ range for data collection (°)	2.11–20.02	2.18–20.00
Index ranges	$-10 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 16$	$0 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 27$
Reflections collected	4164	3967
Independent reflections	4164	3967
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4164/334/569	3967/224/461
Goodness-of-fit on F^2	1.163	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0504$, $wR_2 = 0.1181$	$R_1 = 0.0567$, $wR_2 = 0.1430$
R indices (all data)	$R_1 = 0.0567$, $wR_2 = 0.1233$	$R_1 = 0.0849$, $wR_2 = 0.1667$
Largest diff. peak and hole (e Å^{-3})	2.028 and −2.796	1.602 and −1.460

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Os(1)–Os(5)	2.8797(14)	Os(1)–Os(2)	2.9747(13)
Os(1)–Os(3)	3.0137(12)	Os(1)–Os(4)	3.0577(17)
Os(2)–Os(3)	2.7569(16)	Os(2)–Os(5)	2.8864(13)
Os(3)–Os(5)	2.7009(11)	Os(3)–Os(4)	2.8456(12)
Os(3)–Os(6)	2.8795(14)	Os(4)–Os(6)	2.8561(16)
Os(5)–Os(6)	2.9326(16)	Os(1)–S(1)	2.379(4)
Os(2)–S(1)	2.369(4)	Os(3)–S(1)	2.342(5)
Os(4)–S(2)	2.410(5)	Os(5)–S(2)	2.316(6)
Os(6)–S(2)	2.363(5)	Os(1)–P(1)	2.326(5)
Os(2)–P(2)	2.289(6)	Os–C (average)	1.87(3)
C–O (average)	1.14(2)		
Bond angles			
P(1)–Os(1)–Os(5)	118.94(10)	P(1)–Os(1)–S(1)	100.46(17)
S(1)–Os(1)–Os(5)	98.85(10)	P(1)–Os(1)–Os(2)	88.37(12)
S(1)–Os(1)–Os(2)	51.06(10)	Os(5)–Os(1)–Os(2)	59.06(3)
P(1)–Os(1)–Os(3)	141.62(12)	Os(5)–Os(1)–Os(3)	54.50(3)
Os(2)–Os(1)–Os(3)	54.82(3)	P(1)–Os(1)–Os(4)	162.34(12)
S(1)–Os(1)–Os(4)	95.52(13)	Os(5)–Os(1)–Os(4)	66.30(3)
Os(2)–Os(1)–Os(4)	107.68(3)	Os(3)–Os(1)–Os(4)	55.89(3)
P(2)–Os(2)–S(1)	100.78(16)	P(2)–Os(2)–Os(3)	152.32(11)
S(1)–Os(2)–Os(3)	53.73(12)	P(2)–Os(2)–Os(5)	124.52(12)
S(1)–Os(2)–Os(5)	95.89(12)	Os(3)–Os(2)–Os(5)	57.13(3)
P(2)–Os(2)–Os(1)	93.11(12)	S(1)–Os(2)–Os(1)	51.35(11)
Os(3)–Os(2)–Os(1)	63.31(3)	Os(5)–Os(2)–Os(1)	58.83(3)
S(1)–Os(3)–Os(5)	101.70(10)	S(1)–Os(3)–Os(2)	54.64(11)
Os(5)–Os(3)–Os(2)	63.85(3)	S(1)–Os(3)–Os(4)	102.24(12)
Os(5)–Os(3)–Os(4)	71.69(3)	Os(2)–Os(3)–Os(4)	120.76(4)
S(1)–Os(3)–Os(6)	158.74(11)	Os(5)–Os(3)–Os(6)	63.31(3)
Os(2)–Os(3)–Os(6)	122.13(4)	Os(4)–Os(3)–Os(6)	59.85(4)
S(1)–Os(3)–Os(1)	50.87(10)	Os(5)–Os(3)–Os(1)	60.22(3)
Os(2)–Os(3)–Os(1)	61.87(3)	Os(4)–Os(3)–Os(1)	62.84(4)
Os(6)–Os(3)–Os(1)	108.05(4)	S(2)–Os(4)–Os(3)	91.35(13)
Os(3)–Os(4)–Os(6)	60.67(3)	S(2)–Os(4)–Os(6)	52.49(12)
S(2)–Os(4)–Os(1)	90.54(14)	Os(3)–Os(4)–Os(1)	61.27(3)
Os(6)–Os(4)–Os(1)	107.47(3)	S(2)–Os(5)–Os(3)	97.20(12)
S(2)–Os(5)–Os(1)	97.05(12)	Os(3)–Os(5)–Os(1)	65.28(2)
S(2)–Os(5)–Os(2)	152.65(11)	Os(3)–Os(5)–Os(2)	59.02(3)
Os(1)–Os(5)–Os(2)	62.11(3)	S(2)–Os(5)–Os(6)	51.90(13)
Os(3)–Os(5)–Os(6)	59.02(3)	Os(1)–Os(5)–Os(6)	110.30(3)
Os(2)–Os(5)–Os(6)	115.94(4)	S(2)–Os(6)–Os(4)	54.00(11)
S(2)–Os(6)–Os(3)	91.49(14)	Os(4)–Os(6)–Os(3)	59.49(3)
S(2)–Os(6)–Os(5)	50.48(14)	Os(4)–Os(6)–Os(5)	68.30(3)
Os(3)–Os(6)–Os(5)	55.37(3)	Os(3)–S(1)–Os(2)	71.63(12)
Os(3)–S(1)–Os(1)	79.33(14)	Os(2)–S(1)–Os(1)	77.59(12)
Os(5)–S(2)–Os(6)	77.61(15)	Os(5)–S(2)–Os(4)	86.88(16)
Os(6)–S(2)–Os(4)	73.51(13)		

products. Thus as expected compound **2** reacts with CO, PPh_3 and $P(OMe)_3$ at room temperature to give **1**, $[Os_3(\mu_3\text{-}S)_2(CO)_6(PPh_3)(\mu\text{-dppm})]$ (**5**) and $[Os_3(CO)_6(\mu_3\text{-}S)_2(\mu\text{-dppm})\{P(MeO)_3\}]$ (**6**) in 90%, 77% and 81% yields, respectively (Scheme 3). Clusters **5** and **6** have been characterized on the basis of elemental analysis, IR, ^1H NMR, ^{31}P NMR and mass spectroscopic data together with a single crystal X-ray diffraction study for **6**. The solid-state structure of **6** is depicted in the Fig. 2, crystal data are provided in Table 1 and selected bond distances and angles are collected in Table 3. Compound **6** consists of an open triangular cluster having two almost equal metal–metal bonds Os(1)–Os(2) = 2.8106(14), Os(1)–Os(3) = 2.8122(13) Å, a bridging dppm ligand, two triply bridging sulfido ligands, a trimethylphosphite ligand and six linear terminal carbonyl ligands two bonded to each osmium atom. The Os–S bond distances to the triply bridging sulfido ligands {Os(1)/Os(2)/Os(3)–S(1) = 2.438(6)/2.426(5)/2.419(6) and Os(1)/Os(2)/Os(3)–S(2) = 2.404(6)/2.363(5)/2.354(6) Å} are comparable to the Os–S distances in **1** [15] and $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ [16]. The Os–P bond distances of the dppm ligand



Scheme 3.

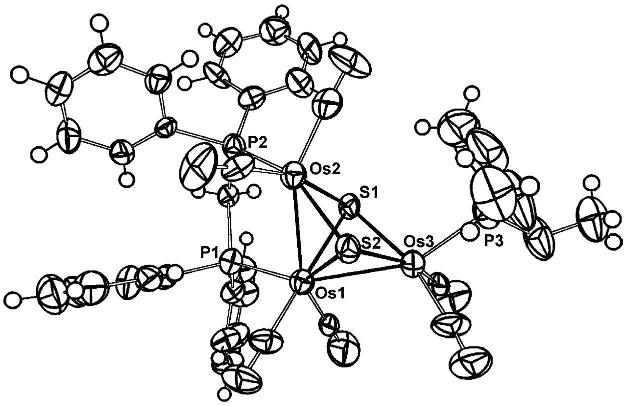


Fig. 2. Molecular structure of [$Os_3(CO)_6(\mu_3\text{-}S)_2(\mu\text{-dppm})\{P(OMe)_3\}$] (**6**) showing the crystallographic labeling scheme. Thermal ellipsoids are at the 50% probability level.

{Os(1)–P(1) = 2.332(6) and Os(2)–P(2) = 2.323(6) Å} are similar to those observed in **1** [15] and the parent compound [$Os_3(CO)_{10}(\mu\text{-dppm})$] [17]. Overall the structure of **6** is similar to that of **1** except that a $P(OMe)_3$ has been substituted for an equatorially positioned carbonyl ligand. Both complexes **5** and **6** contain 50-valence electrons and are electron precise with two metal–metal bonds.

The spectroscopic data of **6** are consistent with the solid-state structure and the spectroscopic data for **5** are consistent with the structure proposed in Scheme 3. The patterns of their ν(CO) absorption bands are similar, indicating that they have a similar distribution of the carbonyl ligands. The $^{31}P\ \{^1H\}$ NMR spectra of **5** and **6** display three sets of equally intense resonances, indicating three different phosphorus atoms in the molecule. For **5**, the doublet of doublets at δ −9.7 ($J = 23.0$ and $J = 11.8$ Hz) and the doublet at δ −16.2 ($J = 23.0$ Hz) are due to the two non-equivalent phosphorous atoms of the dppm ligand while the doublet at δ 15.4 ($J = 11.8$ Hz) is due to the PPh_3 ligand. Similarly for **6**, the doublet at δ −16.0 ($J = 23.5$ Hz) and the doublet of doublets at δ −9.2 ($J = 23$, 9.2 Hz) are assigned to the non-equivalent ^{31}P nuclei of the dppm ligand while the doublet at 110.5 ($J = 9.2$ Hz) is due to the trimethylphosphite ligand. In addition to the usual phenyl resonances, the ^1H NMR spectrum of **5** and **6** shows two AB multiplets (δ 4.83 and 3.72 for **5** and δ 4.84 and 3.66 for **6**) due to the methylene protons of the dppm ligand and a doublet at δ 3.82 for **6** due to the methyl protons of the $P(OMe)_3$ ligand. The FAB mass spectra of **5** and **6** show the molecular ion peaks at *m/z* 1449 and 1310, respectively, and ions due to the sequential loss of six carbonyl groups.

We have studied the substitution reaction of the *nido* cluster **1** to see if the substitution occurs at apical or basal metal atoms. The reaction of **1** with PPh_3 in the presence of Me_3NO, results in the isolation of the PPh_3 substituted compound **5** in 53% yield in addition to **2** and **3** in 6 and 18% yields respectively. In contrast $P(OMe)_3$ reacts with **1** in presence of Me_3NO to give **6** as the only product in 81% yield. The formation of only **6** in the presence

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

Bond lengths			
Os(3)–C(6)	1.90(3)	Os(3)–C(7)	1.92(3)
Os(3)–P(3)	2.237(7)	Os(3)–S(2)	2.354(6)
Os(3)–S(1)	2.419(6)	Os(3)–Os(1)	2.8122(13)
Os(1)–C(1)	1.86(2)	Os(1)–C(2)	1.890(3)
Os(1)–P(1)	2.332(6)	Os(1)–S(2)	2.404(6)
Os(1)–S(1)	2.438(6)	Os(1)–Os(2)	2.8106(14)
Os(2)–C(34)	1.90(3)	Os(2)–C(33)	1.90(3)
Os(2)–P(2)	2.323(6)	Os(2)–S(2)	2.363(5)
Os(2)–S(1)	2.426(5)	Os–C(CO) (average)	1.89(7)
C–O (average)	1.19 (8)		
Bond angles			
P(3)–Os(3)–S(2)	106.1(2)	P(3)–Os(3)–S(1)	105.5(2)
S(2)–Os(3)–S(1)	77.75(18)	P(3)–Os(3)–Os(1)	152.7(2)
S(2)–Os(3)–Os(1)	54.61(15)	S(1)–Os(3)–Os(1)	54.94(13)
P(1)–Os(1)–S(2)	137.0(2)	P(1)–Os(1)–S(1)	94.1(2)
S(2)–Os(1)–S(1)	76.43(19)	P(1)–Os(1)–Os(2)	86.91(16)
S(2)–Os(1)–Os(2)	53.20(13)	S(1)–Os(1)–Os(2)	54.51(13)
P(1)–Os(1)–Os(3)	146.68(15)	S(2)–Os(1)–Os(3)	52.95(13)
S(1)–Os(1)–Os(3)	54.30(13)	Os(2)–Os(1)–Os(3)	82.32(4)
P(2)–Os(2)–S(2)	153.2(2)	P(2)–Os(2)–S(1)	90.86(19)
S(2)–Os(2)–S(1)	77.43(19)	P(2)–Os(2)–Os(1)	98.95(16)
S(2)–Os(2)–Os(1)	54.56(15)	S(1)–Os(2)–Os(1)	54.90(14)
Os(3)–S(1)–Os(2)	103.3(2)	Os(3)–S(1)–Os(1)	70.76(15)
Os(2)–S(1)–Os(1)	70.59(14)	Os(3)–S(2)–Os(2)	103.3(2)
Os(3)–S(2)–Os(1)	72.44(17)	Os(2)–S(2)–Os(1)	72.24(16)

of trimethyl phosphite but not in the presence of triphenylphosphine is probably due to the lower nucleophilicity of the phosphite relative to the phosphine.

Treatment of **3** with CO at 98 °C results in the formation of **1** in 83% yield indicating that compound **3** is unusually reactive. The relatively mild conditions observed here for the cleavage of the hexanuclear **3** are most likely due to the occupation of the antibonding orbital by the extra two electrons.

3. Conclusions

In contrast to the Me_3NO initiated self condensation of $[Os_6(CO)_{12}(\mu_3\text{-}Se)_4(\mu\text{-}dppm)_2]$ and $[Ru_3(CO)_7(\mu_3\text{-}S)_2(\mu\text{-}dppm)]$ which afforded only the hexanuclear compounds $[Os_6(CO)_{12}(\mu_3\text{-}Se)_4(\mu\text{-}dppm)_2]$ and $[Ru_6(CO)_{12}(\mu_3\text{-}S)_4(\mu\text{-}dppm)_2]$ respectively, the reaction of **1** with Me_3NO at 80 °C gives the labile trinuclear compound **2** and as well as the hexanuclear compound **3.** The lability of the NMe_3 ligand in **2** has been demonstrated by its reaction with CO, PPh_3 and $P(OMe)_3$ which yielded compounds **1**, **5** and **6** respectively. Interestingly, **1** has been found to combine with $[Os_3(CO)_{10}(MeCN)_2]$ at 80 °C to give the hexanuclear compound **4** containing a bridging dppm and two triply bridging sulfide ligands. Compound **4** has a different structure from that of $[Os_6(CO)_{17}(\mu_4\text{-}S)_2]$ which was obtained from the reaction of $[Os_3(CO)_9(\mu_3\text{-}S)_2]$ with $[Os_3(CO)_{10}(MeCN)_2]$ at 128 °C. This complex has a square pyramidal core of osmium atoms with a sixth osmium bridging one basal edge and has a total of ten metal–metal bonds. Interestingly, the presence of the dppm ligand results in a structure with eleven metal–metal bonds but with two μ_3-sulfido ligands instead of two μ_4-sulfido ligands. Thus the bulky dppm ligand blocks additional closure of the sulfido caps. In addition, it should be noted that the reaction of **1** with $[Os_3(CO)_{10}(MeCN)_2]$ results in a structure with many more metal–metal bonds than the self condensation of **1** after treatment with one equivalent Me_3NO. This difference is undoubtedly due to the availability of two labile sites in the case of $[Os_3(CO)_{10}(MeCN)_2]$ rather than one as in **2** and underlines the general concept that the formation of higher nuclearity clusters is very sensitive to reaction pathway and therefore under kinetic control.

4. Experimental

All reactions were routinely performed under a nitrogen atmosphere using standard Schlenk techniques although no special precautions were taken to exclude air during work-up. The solvents were dried and distilled prior to use by standard methods (CH_2Cl_2 over CaH_2, toluene and benzene from sodium benzophenone). All other solvents were of reagent grade and used as received. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. ^{1}H and ^{31}P {^{1}H} NMR spectra were recorded on a Varian Unity Plus 400 and a Bruker DPX 400 spectrometers. Chemical shifts for the ^{31}P {^{1}H} NMR spectra are relative to 85% H_3PO_4. Mass spectra were recorded on Varian Mat 312 mass spectrometer. The cluster $[Os_3(\mu_3\text{-}S)_2(CO)_7(\mu\text{-dppm})]$ (**1**) was prepared by the literature procedure [15]. Triphenylphosphine and trimethyl phosphite were purchased from Aldrich and used as received.

4.1. Reaction of $[Os_3(\mu_3\text{-}S)_2(CO)_7(\mu\text{-dppm})]$ (1) with Me_3NO

A toluene solution (30 ml) of **1** (0.105 g, 0.086 mmol) and Me_3NO (0.009 g, 0.120 mmol) was heated to 80 °C for 15 min, during this time the color changed from orange to green. The reaction mixture was filtered through a short silica column to remove excess Me_3NO. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (1:1, v/v) developed four bands. The first band gave unconsumed starting material **1** (0.004 g). The second band gave $[Os_3(CO)_6(\mu_3\text{-}S)_2(\mu\text{-dppm})(NMe_3)]$ (**2**) (0.032 g, 30%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C (Anal. Calc. for $C_{34}H_{31}NO_6Os_3P_2S_2$: C, 32.76; H, 2.51; N, 1.12. Found: C, 32.98; H, 2.82; N, 1.25%). IR (νCO, CH_2Cl_2): 2006 vw, 1983 vs, 1975 vs, 1927 s; ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 20H) 4.61(m, 1H), 3.48 (m, 1H), 2.81 (s, 9H); ^{31}P {^{1}H} NMR ($CDCl_3$): δ −13.6 (d, $J = 92.4$ Hz), −14.8 ($J = 92.4$ Hz); mass spectrum: *m*/*z* 1245 (M^+). The third band was too small for complete characterization. The fourth band gave $[Os_6(CO)_{12}(\mu_3\text{-}S)_4(\mu\text{-dppm})_2]$ (**3**) (0.053 g, 51%) as green crystals after recrystallization from heptane/CH_2Cl_2 at 25 °C (Anal. Calc. for $C_{62}H_{44}O_{12}Os_6P_4S_4$: C, 31.36; H, 1.87. Found: C, 31.60; H, 2.02%). IR (νCO, CH_2Cl_2): 2035 vw, 2020 vs, 1985s, 1954 m, 1898 vw cm^{-1}; ^{1}H NMR ($CDCl_3$): 7.49 (m, 40H), 3.80 (m, 2H), 3.56 (m, 2H); ^{31}P {^{1}H} NMR ($CDCl_3$): δ −9.8 ($J = 17.2$ Hz), −6.4 ($J = 17.\ 2$ Hz); mass spectrum: *m*/*z* 2374 (M^+).

4.2. Reaction of 1 with $[Os_3(CO)_{10}(MeCN)_2]$

A benzene solution (100 ml) of **1** (0.075 g, 0.062 mmol) and $[Os_3(CO)_{10}(MeCN)_2]$ **4** (0.230 g, 0.246 mmol) was refluxed for 4 h, during this time the color changed from yellow to red. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (7:3, v/v) developed one major and two very minor bands. The slower moving major band gave $[Os_6(CO)_{14}(\mu_3\text{-}S)_2(\mu\text{-dppm})]$ **4** (0.018 g, 15%) as red crystals after recrystallization from hexane/CH_2Cl_2 at −20 °C (Anal. Calc. for $C_{39}H_{22}O_{14}Os_6P_2S_2$: C, 23.63; H, 1.12. Found: C, 23.75; H, 1.28%). IR (νCO, CH_2Cl_2): 2256 w, 2127 w, 2081 s, 2052 s, 2019 s, 2008 vs, cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 7.31 (m, 20H), 4.37(m, 1H), 3.99 (m, 1H); ^{31}P {^{1}H} NMR (CD_2Cl_2): δ 5.5 (d, $J = 34.0$ Hz), 4.4 (d, $J = 34.0$ Hz); mass spectrum: *m*/*z* 1982 (M^+). The minor bands were too small for complete characterization.

4.3. Reaction of $[Os_3(CO)_6(\mu_3\text{-}S)_2(\mu\text{-dppm})(NMe_3)]$ (2) with PPh_3

A dichloromethane solution (20 ml) of **2** (0.020 g, 0.016 mmol) and PPh_3 (0.005 g, 0.019 mmol) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was separated by TLC on silica gel. Elution with hexane/CH_2Cl_2 developed a single band which afforded $[Os_3(CO)_6(\mu_3\text{-}S)_2(PPh_3)(\mu\text{-dppm})]$ (**5**) (0.017 g, 77%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C (Anal. Calc. for $C_{49}H_{37}O_6Os_3P_3S_2$: C, 41.49; H, 2.63. Found: C, 41.68.; H, 2.75%). IR (νCO, CH_2Cl_2): 2016 s, 1991 vs, 1943 vs, 1935 m cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 7.67 (m, 35 H), 4.83 (m, 1H), 3.72 (m, 1H); ^{31}P {^{1}H} NMR (CD_2Cl_2): δ 15.4 ($J = 11.8$), −16.2 ($J = 23.0$) and δ −9.7 (dd, $J = 23.0$ and $J = 11.8$); mass spectrum: *m*/*z* 1417 (M^+).

4.4. Reaction of 2 with $P(OMe)_3$

A similar reaction of **2** (0.025 g, 0.020 mmol) with $P(OMe)_3$ (0.008 g, 0.064 mmol) for 1 h followed by similar workup and chromatographic separation gave **6** (0.021 g, 81%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C (Anal. Calc. for $C_{34}H_{31}O_9Os_3P_3S_2$: C, 31.09; H, 2.53. Found: C, 31.32.; H, 2.63%). IR (νCO, CH_2Cl_2): 2026 vs, 1993 vs, 1950 vs, 1931, 1869 vw cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 7.41 (m, 20H), 4.84 (m, 1H), 3.89 (s, 9H), 3.66 (m, 1H); ^{31}P {^{1}H} NMR (CD_2Cl_2): δ 110.5 (d, $J = 9.2$ Hz), −9.2 (t, $J = 23.5$ and 9.2 Hz) and −16.0 (d. $J = 23.5$ Hz); mass spectrum: *m*/*z* 1312 (M^+).

4.5. Reaction of 2 with CO

Carbon monoxide gas was bubbled through a CH_2Cl_2 solution (20 ml) of **2** (0.025 g, 0.020 mmol) for 5 min. IR spectrum indicated quantitative formation of compound **1**.

4.6. Reaction of 1 with PPh_3

To a dichloromethane solution (20 ml) of **1** (0.050 g, 0.041 mmol) and PPh_3 (0.011 g, 0.042 mmol) was added dropwise a solution of Me_3NO (0.005 g, 0.066 mmol) in the same solvent (10 ml) over a period of 20 min. The resulting mixture was stirred at room temperature for 3 h during which time analytical TLC indicated complete consumption of **1**. The solvent was removed under reduced pressure and the resulting residue was separated by TLC on silica gel. Elution with hexane/CH_2Cl_2 (1:1, v/v) developed three bands which afforded the following compounds in order of elution: **5** (0.031 g, 53%) **2**, (0.003 g, 6%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C **3** (0.009 g, 18%).

*4.7. Reaction of **1** with $P(OMe)_3$*

To a dichloromethane solution (20 ml) of **1** (0.040 g, 0.033 mmol) and $P(OMe)_3$ (0.009 g, 0.073 mmol) was added dropwise a solution of Me_3NO (0.006 g, 0.080 mmol) in a methanolic solution (2 ml) of CH_2Cl_2 (10 ml) over a period of 10 min. The resulting mixture was stirred at room temperature for 3 h, during which time analytical TLC indicated complete consumption of **1**. The solvent was removed under reduced pressure and the resulting residue was separated by TLC on silica gel. Elution with hexane/CH_2Cl_2 (3:2, v/v) developed a single band, which afforded **6** (0.036 g, 84%).

*4.8. Reaction of **3** with CO*

Carbon monoxide gas was bubbled through a refluxing heptane solution (25 ml) of **3** (0.018 g, 0.007 mmol) for 3 h during which time the color changed from green to yellow. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/CH_2Cl_2 (3:1, v/v) gave a single band, which afforded **1** (0.014 g, 83%).

4.9. X-ray structure determination

Crystals of **4** and **6** for X-ray examination were obtained from saturated solutions of each in hexane/dichloromethane solvent at −20 °C. Crystallographic data for **4** and **6** were collected at 296 K, using Bruker P4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection and processing were carried out using XSCANS [18]. The unit cells were indexed on low angle reflections and refined from 25 reflections in a θ range of 12–13°. The structures were solved by direct methods (SHELXS-97) [19] and refined on F^2 by full matrix lest squares (SHELXL-97) [20], utilized as incorporated in the WINGX [21] program package using all unique data. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (riding model) with U_{iso} set at 1.2 times the U_{eq} of the parent atom. Selected bond lengths and angles for **4** and **6** are given in Tables 2 and 3, respectively. Crystallographic and other experimental data are summarized in Table 1.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 226811 for compound **4**, and 226812 for compound **6**. 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).

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