

# Complexation and metallation of $\text{Ph}_2\text{PC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CPh}_2$ in triosmium carbonyl clusters

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## Abstract

Reaction of  $\text{Ph}_2\text{PC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CPh}_2$  with  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  affords  $\text{Os}_3(\text{CO})_{10}(\mu, \eta^2\text{-(Ph}_2\text{P)}_2\text{C}_9\text{H}_{10})$  (**1**) and the double cluster  $[\text{Os}_3(\text{CO})_{10}]_2(\mu, \eta^2\text{-(Ph}_2\text{P)}_2\text{C}_9\text{H}_{10})_2$  (**2**), through coordination of the phosphine groups. Thermolysis of **1** in toluene generates  $\text{Os}_3(\text{CO})_7(\mu\text{-PPh}_2)(\mu_3, \eta^5\text{-Ph}_2\text{PC}_9\text{H}_{10})$  (**3**) and  $\text{Os}_3(\text{CO})_8(\mu\text{-PPh}_2)(\mu_3, \eta^6\text{-Ph}_2\text{P}(\text{C}_9\text{H}_{10})\text{CO})$  (**4**). The molecular structures of **1**, **3**, and **4** have been determined by an X-ray diffraction study. Both **3** and **4** contain a bridging phosphido group and a carbocycle connected to an osma-cyclopentadienyl ring, which are apparently derived from C–P bond activation and C–C bond rearrangement of the dpndy ligand governed by the triosmium clusters.

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**Keywords:** Triosmium; Cluster; Phosphine complex; Alkyne; Metallation

## 1. Introduction

The study of transition metal clusters has been an active area of current chemical research [1–8]. Discrete, soluble metal clusters often display catalytic activity and are studied as models for the surface of bulk metals [9,10]. In addition, the ability of a metal cluster to organize a flexible ligand around its coordination sphere has led to design of intramolecularly organized recognition sites [11]. Since the cluster-bonded ligand is capable of interacting with several metal centers, it frequently displays a reactivity different from that found in the monometallic systems [12]. For instance, the  $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{CH}=\text{N}(\text{CH}_2)_2(\text{C}_5\text{H}_4\text{N})$  molecule is a typical tridentate P–N–N ligand bound to a metal ion [13] or a  $\text{M}(\text{CO})_3$  species [14], while a sequence of the methylene and imine C–H bond activation occurs in coordination to a metal cluster [15].

We recently prepared the multifunctional molecule  $\text{Ph}_2\text{PC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CPh}_2$  (abbreviated as dpndy) and showed its reactions with tungsten carbonyls to yield a paddle-wheel complex  $[\text{W}(\text{CO})_3]_2(\mu, \eta^2\text{-dpndy})_3$  and a tripodal complex  $\text{W}(\text{CO})_3[(\mu, \eta^2\text{-dpndy})\text{W}(\text{CO})_3(\eta^2\text{-dpndy})]_3$  [16]. In these compounds, dpndy acts as a chelating/bridging ligand through coordination of the phosphorous atoms, while the nonadiynyl linkage remains intact. Our continuing interest in the cluster chemistry and alkyne-coupling reaction [17] prompted us to investigate the reaction of dpndy with  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ .

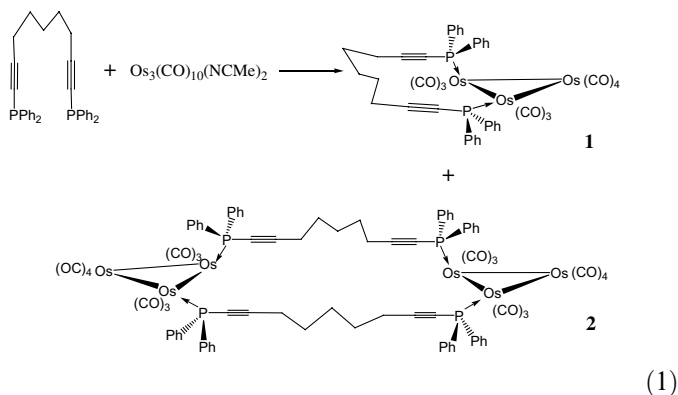
## 2. Results and discussion

Treatment of  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  with equimolar amounts of  $\text{Ph}_2\text{PC}\equiv\text{C}(\text{CH}_2)_5\text{C}\equiv\text{CPh}_2$  at ambient temperature results in facile substitution of the labile acetonitrile ligands by the phosphine groups to afford  $\text{Os}_3(\text{CO})_{10}(\mu, \eta^2\text{-(Ph}_2\text{P)}_2\text{C}_9\text{H}_{10})$  (**1**; 63%) and the double cluster  $[\text{Os}_3(\text{CO})_{10}]_2(\mu, \eta^2\text{-(Ph}_2\text{P)}_2\text{C}_9\text{H}_{10})_2$  (**2**; 4%) (Eq. (1)) as air-stable, yellow crystalline solids. Johnson and coworkers

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previously reported the reaction of  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  and  $\text{Ph}_2\text{P}=\text{C}(\text{CPh})=\text{CPh}_2$  (dppa) to yield the di-, tri-, and tetrameric clusters  $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_n$  ( $n = 2-4$ ) in moderate yields [18]. It has been argued that the rigidity of the linear  $-\text{C}=\text{C}-$  unit and the lone P–P distance (4.7 Å) prevents dppa to chelate one metal center or cross a metal–metal bond [19]. For the dpndy molecule, however, the flexible pentylene chain allows the two phosphine groups to span one Os–Os edge to yield **1** as the major product.



The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** presents two signals at  $-33.6$  and  $-35.8$  ppm, suggesting the presence of two inequivalent phosphorous atoms in the molecule. The  $^1\text{H}$  NMR spectrum shows the phenyl proton resonances in the range 7.80–7.20 ppm and three multiplets at 2.71 (4H), 1.86 (2H), and 1.77 (4H) ppm for the methylene protons. For structural characterization, an X-ray diffraction study was carried out on a single crystal obtained from *n*-hexane/toluene at  $-10$  °C. An ORTEP diagram of **1** is illustrated in Fig. 1. Compound **1** is a 48-electron cluster. The molecule is based on a trimetallic array of osmium atoms in which the individual bond lengths are Os1–Os2 2.9081(3), Os2–Os3 2.9025(3), and Os1–Os3 2.8792(3) Å.

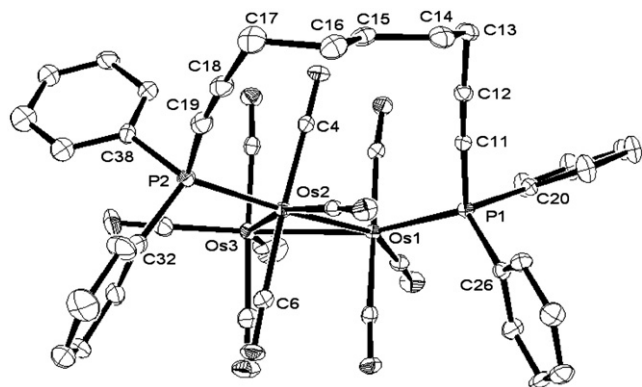
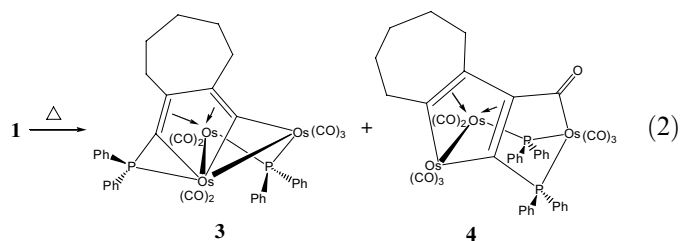


Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°): Os1–Os2 2.9081(3), Os1–Os3 2.8792(3), Os2–Os3 2.9025(3), Os1–P1 2.336(1), Os2–P2 2.345(1), C11–P1 1.767(6), C11–C12 1.202(7), C12–C13 1.462(7), C19–P2 1.761(6), C18–C19 1.195(8), C17–C18 1.468(8) and Os1–Os2–Os3 59.406(4), Os1–Os3–Os2 60.395(7), Os2–Os1–Os3 60.199(7), Os1–P1–C11 113.7(2), P1–C11–C12 175.5(5), C11–C12–C13 176.3(5), Os2–P2–C19 109.7(2), P2–C19–C18 171.4(6), C19–C18–C17 176.3(6), Os1–Os2–C4 80.3(2), Os1–Os2–C6 95.5(2), Os3–Os2–C4 91.3(1), Os3–Os2–C6 86.4(2).

The dpndy molecule bridges the Os1–Os2 edge with Os1–P1 2.336(1) and Os2–P2 2.345(1) Å. The two Os–P bonds are essentially equatorial with respect to the  $\text{Os}_3$  plane with the torsional angles P1–Os1–Os2–Os3 171.0(8)°, P2–Os2–Os3–Os1 171.6(1)°, and P1–Os1–Os2–P2 143.6(1)°. The P–C≡C–C backbones are slightly bowed as indicated by the P–C≡C angles (175.5(5)° to P1 and 171.4(6)° to P2) and the C≡C–C angles (176.3(6)°). The Os1, Os2, and Os3 atoms are each connected to 3, 3, and 4 terminal carbonyl ligands, respectively, with the Os–C–O angles in the range 174.4(5)–178.5(6)°. The axial carbonyls associated with the Os2 atom are no longer perpendicular to the triosmium plane, with the angles Os1–Os2–C4 80.3(2)°, Os1–Os2–C6 95.5(2)°, and Os3–Os2–C6 86.4(2)°, probably because of steric interactions with the hydrocarbon chain.

Compound **2** presents the same elementary analysis to **1**, while the FAB mass data indicate a dimeric cluster formula  $[\text{Os}_3(\text{CO})_{10}(\text{dpndy})]_2$  for **2**. It probably has a structure analogous to  $[\text{Os}_3(\text{CO})_{10}(\text{dppa})]_2$  [19] that the two triosmium clusters are linked by two dpndy ligands in a macro-ring fashion. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** at 23 °C shows a signal at  $\delta -35.8$ , suggesting that the four phosphine groups bridge the two  $\text{Os}_3$  clusters symmetrically, or they are equivalent through a dynamic process proposed for the  $\text{M}_3(\text{CO})_{10}(\text{PR}_3)_2$  complexes [20]. However, these cannot be verified by a variable-temperature NMR study due to the poor solubility of **2** at lower temperatures.

Compound **1** is stable at 80 °C, while in refluxing toluene it decomposes within 3 h to generate several products. After separation by TLC, two major compounds were purified for characterization, namely  $\text{Os}_3(\text{CO})_7(\mu\text{-PPh}_2)(\mu_3, \eta^5\text{-Ph}_2\text{PC}_9\text{H}_{10})$  (**3**; 35%) and  $\text{Os}_3(\text{CO})_8(\mu\text{-PPh}_2)(\mu_3, \eta^6\text{-Ph}_2\text{P}(\text{C}_9\text{H}_{10})\text{CO})$  (**4**; 21%) (Eq. (2)). Compounds **3** and **4** form air-stable, yellow crystalline solids which have been characterized by elemental analyses, mass, IR, and NMR.



The FAB mass spectrum of **3** presents the molecular ion peak at  $m/z$  1254 corresponding to loss of three carbonyls from **1** upon thermolysis. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows two singlets at  $-49.0$  and  $-191.5$  ppm, with the latter resonance assigned to a bridging phosphide ligand [21]. The  $^1\text{H}$  NMR spectrum is complicated, showing six sets of multiplets in 3.38–1.92 ppm for the methylene protons. An X-ray diffraction study was carried out, and the ORTEP diagram is illustrated in Fig. 2. The dpndy ligand has undergone a tremendous change that one C–PPh<sub>2</sub> bond is cleaved and the two alkyne units are coupled to form a

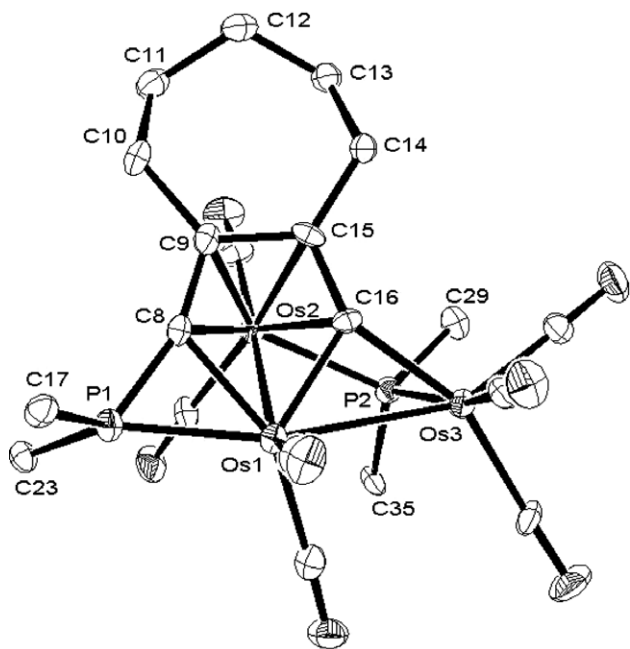


Fig. 2. Molecular structure of **3**. The  $C_6H_5$  groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Os1–Os2 2.7978(6), Os1–Os3 2.8656(6), Os1–P1 2.334(3), Os2–P2 2.364(3), Os3–P2 2.444(3), Os1–C8 2.09(1), Os1–C16 2.05(1), Os3–C16 2.07(1), Os2–C8 2.19(1), Os2–C9 2.27(1), Os2–C15 2.295(9), Os2–C16 2.29(1), C8–P1 1.74(1), C8–C9 1.39(1), C9–C10 1.54(1), C9–C15 1.47(1), C15–C14 1.51(1), C15–C16 1.38(1) and Os2–Os1–Os3 78.89(2), Os1–P1–C8 59.4(3), Os2–P2–Os3 96.9(1), P1–C8–C9 159.2(8), P1–C8–Os1 74.5(4), C8–C9–C10 122.1(9), C8–C9–C15 109.7(9), C9–C15–C14 125.0(9), C9–C15–C16 110.3(8), C14–C15–C16 124.6(9), C15–C16–Os1 124.6(8), C15–C16–Os3 146.5(8), Os1–C16–Os3 88.2(4).

metallacycle. Compound **3** is a 50-electron cluster to contain two Os–Os bonds (Os1–Os2 2.7978(6) and Os1–Os3 2.8656(6) Å) and one  $\mu$ -PPh<sub>2</sub> group across the noninteracting metals (Os2···Os3 3.599 Å) with the lengths Os2–P2 2.364(3) and Os3–P2 2.444(3) Å, and the angle Os2–P2–Os3 96.9(1) $^\circ$ . The dihedral angle between the plane (Os2, P2, Os3) and the Os<sub>3</sub> plane is 45.2(1) $^\circ$ . The Os1, C8, C9, C15, and C16 atoms form a osmacyclopentadienyl ring, where the carbon atoms are coplanar to within 0.01 Å and the Os1 atom is ca. 0.2 Å away from the plane. The C8–C9 unit can be described as a vinyl species which is  $\sigma$ -bonded to the Os1 atom with C8–Os1 2.09(1) Å and  $\pi$ -bonded to the Os2 atom with C8–Os2 2.19(1) and C9–Os2 2.27(1) Å. On the other hand, the C15–C16 unit is best considered as a vinylidene ligand which bridges the Os1–Os3 edge with C16–Os1 2.05(1) and C16–Os3 2.07(1) Å and forms a  $\pi$ -bond to the Os2 atom with C16–Os2 2.29(1) and C15–Os2 2.295(9) Å. The phosphine group occupies an equatorial site of the Os<sub>3</sub> frame with Os1–P1 2.334(3) Å. The triangular arrangement of the C8, P1, and Os1 atoms results in the angles P1–C8–C9 159.2(8) $^\circ$  and C8–P1–Os1 59.4(3) $^\circ$  being substantially distorted from the idealized values of 120 $^\circ$  and 109.5 $^\circ$ , respectively.

The molecular ion peak at  $m/z$  1310 for **4** corresponds to loss of one carbonyl ligand from **1**. The IR spectrum

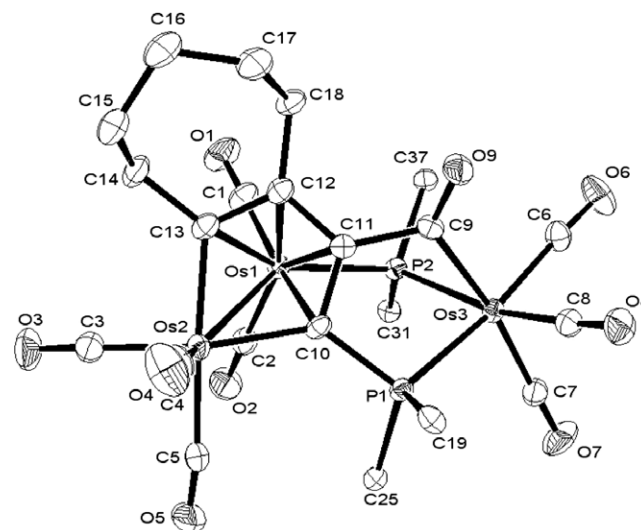
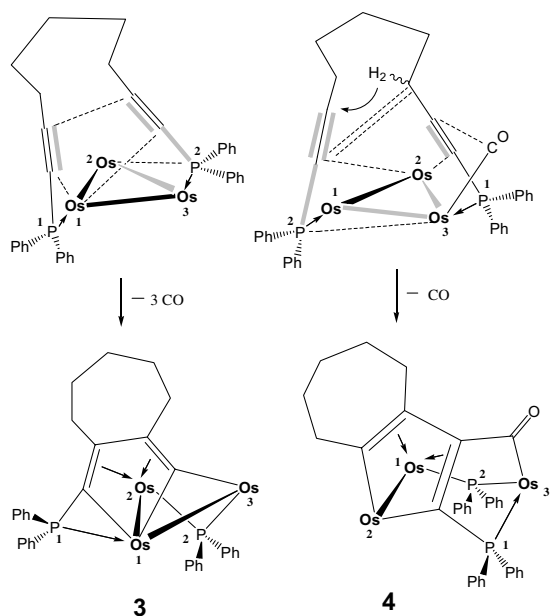


Fig. 3. Molecular structure of **4**. The  $C_6H_5$  groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Os1–Os2 2.7748(3), Os1–P2 2.383(1), Os3–P2 2.491(1), Os3–P1 2.395(1), Os1–C10 2.212(5), Os1–C11 2.215(5), Os1–C12 2.307(5), Os1–C13 2.292(5), Os2–C10 2.090(5), Os2–C13 2.081(6), Os3–C9 2.167(5), C9–O9 1.200(6), C9–C11 1.541(7), C10–P1 1.794(5), C10–C11 1.445(7), C11–C12 1.434(7), C12–C13 1.423(8), C12–C18 1.520(8), C13–C14 1.526(8) and Os3–P1–C10 103.4(2), Os1–P2–Os3 108.13(5), P1–Os3–P2 90.68(5), Os2–C10–P1 133.4(3), Os2–C10–C11 116.1(3), C11–C10–P1 110.3(4), C11–C9–Os3 114.3(3), C11–C9–O9 120.0(5), C9–C11–C12 126.1(5), C10–C11–C12 114.7(5), C11–C12–C13 113.0(5), C11–C12–C18 124.7(5), C12–C13–C14 116.4(5), C12–C13–Os2 118.0(4), C14–C13–Os2 125.1(4).

presents a broad peak at 1618  $cm^{-1}$  for a C–O stretching, suggesting insertion (or migration) of a carbonyl group into the dpndy link. The  $^{31}P\{^1H\}$  NMR spectrum shows two singlets at 55.1 and  $-87.3$  ppm for the phosphine and phosphide resonances, respectively. For structural characterization of **4**, an X-ray diffraction study was carried out and the ORTEP diagram is illustrated in Fig. 3. Compound **4** is a 52-electron cluster to exhibit only one Os–Os bond (Os1–Os2 2.7748(3) Å). The noninteracting metal–metal distances are Os1···Os3 3.947 Å and Os2···Os3 5.350 Å. One C–PPh<sub>2</sub> bond of the dpndy molecule has been cleaved to generate a  $\mu$ -PPh<sub>2</sub> group and the two alkyne units are coupled to form a metallacycle, together with migration of one carbonyl group to give an acyl species. We note that the carbocycle (C14–C18) is connected to the  $\alpha,\beta$ -carbons of the metallacycle, while it is in the  $\beta,\beta'$ -position for **3**. The Os2, C10, C11, C12, and C13 atoms form a osmacyclopentadienyl ring, and the coordination about the Os1 atom can be viewed as a three-legged piano stool by considering the metallacycle as an  $\eta^5$ -ligand. Thus, the Os–Os interaction is best described as a dative bond by donating two nonbonding electrons from Os1 to Os2 to satisfy the 18-electron rule [22] for both osmium atoms. The coordination about the Os3 atom is a distorted octahedron, which is linked to three terminal carbonyls in a *facial*-fashion, an acyl group with C9–Os3 2.167(5) Å, a phosphine group with P1–Os3



Scheme 1.

2.395(1) Å, and a phosphido species with P2–Os3 2.491(1) Å. The bond angles C10–P1–Os3 103.4(2)° and Os1–P1–Os3 108.13(5)° are normal, due to a unstrained five-membered ring formed by the Os3, P1, C10, Os1, and P2 atoms.

Compounds **3** and **4** are not interconvertible, so they are likely derived from **1** via separate routes. *scheme 1* illustrates the plausible bond reformation for the dpndy ligand, where the gray and dash lines represent the chemical bonds broken and generated, respectively. Since this reaction is inhibited under a CO atmosphere, it is probable that thermal decarbonylation of **1** induces C–P bond activation and alkyne–alkyne coupling to generate **3**, while the formation of **4** is much complicated which also involves a C–C bond rearrangement and a CO migration.

In summary, we have prepared the mono- and dimeric Os<sub>3</sub> clusters containing the dpndy ligand. Activation of dpndy by the cluster to form a metallacycle and a carbocycle presented herein is unique because this feature is not available in the chemistry of the related Ph<sub>2</sub>P–C≡C–PPh<sub>2</sub> [18,23] and Ph<sub>2</sub>P–C≡C–C≡C–PPh<sub>2</sub> [24] molecules.

### 3. Experimental

#### 3.1. General methods

All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub> [25] and bis(diphenylphosphino)-1,9-nonadiyne (dpndy) [16] were prepared by literature method. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). <sup>1</sup>H and <sup>31</sup>P NMR spectra

were obtained on a Varian Unity INOVA-500 spectrometer. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

#### 3.2. Reaction of dpndy with Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>

Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub> (60 mg, 0.064 mmol) and dpndy (35 mg, 0.071 mmol) were placed in an oven-dried 50 ml Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. Dichloromethane (10 ml) was introduced into the flask and the solution was stirred at room temperature for 24 h. The solution was concentrated to ca. 2 ml on a rotary evaporator and then subjected to TLC, eluting with dichloromethane/*n*-hexane (1:1, v/v). Isolation of the material forming the first yellow band afforded Os<sub>3</sub>(CO)<sub>10</sub>(μ,η<sup>2</sup>-(Ph<sub>2</sub>P)<sub>2</sub>C<sub>9</sub>H<sub>10</sub>) (**1**; 54 mg, 63%), and the second yellow band afforded [Os<sub>3</sub>(CO)<sub>10</sub>]<sub>2</sub>(μ,η<sup>2</sup>-(Ph<sub>2</sub>P)<sub>2</sub>C<sub>9</sub>H<sub>10</sub>)<sub>2</sub> (**2**; 8 mg, 4%).

##### 3.2.1. Compound 1

Anal. Calc. for C<sub>43</sub>H<sub>30</sub>O<sub>10</sub>P<sub>2</sub>Os<sub>3</sub>: C, 38.57; H, 2.24. Found: C, 38.62; H, 2.33%. IR (CH<sub>2</sub>Cl<sub>2</sub>, ν<sub>CO</sub>): 2084w, 2016m, 1992s, 1960m cm<sup>-1</sup>. MS (FAB): *m/z* 1338 (M<sup>+</sup>, <sup>192</sup>Os). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): 7.80–7.14 (m, 20H, Ph), 2.71 (m, 4H), 1.86 (m, 2H), 1.77 (m, 4H, CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): –33.6 (s), –35.8 (s) ppm.

##### 3.2.2. Compound 2

Anal. Calc. for C<sub>86</sub>H<sub>60</sub>O<sub>20</sub>P<sub>4</sub>Os<sub>6</sub>: C, 38.57; H, 2.24. Found: C, 38.74; H, 2.19%. IR (CH<sub>2</sub>Cl<sub>2</sub>, ν<sub>CO</sub>): 2020m, 1990s, 1966m cm<sup>-1</sup>. MS (FAB): *m/z* 2660 (M<sup>+</sup>–O, <sup>192</sup>Os). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): 7.76 (m, 16H), 7.45 (m, 24H, Ph), 2.64 (m, 8H), 1.74 (m, 4H, CH<sub>2</sub>), 1.63 (m, 8H, CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): –35.8 (s) ppm.

#### 3.3. Thermal reaction of 1

Compound **1** (60 mg, 0.045 mmol) and toluene (5 ml) was placed in Schlenk tube and the solution was heated to reflux for 3 h under dinitrogen. The solvent was removed under vacuum and the residue was subjected to TLC with dichloromethane/*n*-hexane (1:1, v/v) as eluant. Isolation of the material forming the first yellow band afforded Os<sub>3</sub>(CO)<sub>7</sub>(μ-PPh<sub>2</sub>)(μ<sub>3</sub>,η<sup>5</sup>-Ph<sub>2</sub>PC<sub>9</sub>H<sub>10</sub>) (**3**; 20 mg, 35%), and the second yellow band afforded Os<sub>3</sub>(CO)<sub>8</sub>(μ-PPh<sub>2</sub>)(μ<sub>3</sub>,η<sup>6</sup>-Ph<sub>2</sub>P(C<sub>9</sub>H<sub>10</sub>)CO) (**4**; 13 mg, 21%).

##### 3.3.1. Compound 3

Anal. Calc. for C<sub>40</sub>H<sub>30</sub>O<sub>7</sub>P<sub>2</sub>Os<sub>3</sub>: C, 38.28; H, 2.39. Found: C, 39.64; H, 2.15%. IR (CH<sub>2</sub>Cl<sub>2</sub>, ν<sub>CO</sub>): 2060m, 1992s, 1982vs, 1940m, 1926m cm<sup>-1</sup>. MS (FAB): *m/z* 1254 (M<sup>+</sup>, <sup>192</sup>Os). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): 7.84 (m, 2H), 7.30 (m, 18H, Ph), 3.38 (m, 1H), 3.23 (m, 1H), 2.90 (m,



1H), 2.77 (m, 1H), 2.28 (m, 1H), 1.92 (m, 5H, CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): –49.0 (s), –191.5 (s, μ-PPh<sub>2</sub>) ppm.

### 3.3.2. Compound 4

Anal. Calc. for C<sub>42</sub>H<sub>30</sub>O<sub>9</sub>P<sub>2</sub>Os<sub>3</sub>: C, 38.47; H, 2.29. Found: C, 39.22; H, 2.13%. IR (CH<sub>2</sub>Cl<sub>2</sub>, ν<sub>CO</sub>): 2092m, 2056s, 2012s, 1988vs, 1976vs, 1958s, 1942s, 1618br cm<sup>-1</sup>. MS (FAB): *m/z* 1310 (M<sup>+</sup>, <sup>192</sup>Os). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): 7.95 (m, 2H), 7.48 (m, 13H), 7.08 (m, 5H, Ph), 3.85 (dd, 1H), 3.23 (dd, 1H), 2.88 (t, 1H), 2.56 (t, 1H), 2.17 (m, 1H), 2.11 (m, 1H), 2.01 (m, 1H), 1.69–1.50 (m, 3H, CH<sub>2</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 23 °C): 55.1 (s), –87.3 (s, μ-PPh<sub>2</sub>) ppm.

### 3.4. Structure determination for 1, 3, and 4

The crystals of **1**, **3**, and **4** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Nonius KappaCCD (for **1**) and Bruker Smart ApexCCD (for **3** and **4**) diffractometers, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The θ range for data collection is 1.23–27.50° for **1**, 1.43–25.00° for **3**, and 1.22–27.50° for **4**. Of the 38136, 29867, and 27524 reflections collected for **1**, **3**, and **4**, 10830, 7057, and 9535 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package [26]. The data collection and refinement parameters are presented in Table 1.

Table 1  
Crystallographic data for **1**, **3**, and **4**

	<b>1</b>	<b>3</b>	<b>4</b>
Formula	C <sub>50</sub> H <sub>38</sub> O <sub>10</sub> Os <sub>3</sub> P <sub>2</sub>	C <sub>43.5</sub> H <sub>33</sub> O <sub>7</sub> Os <sub>3</sub> P <sub>2</sub>	C <sub>43</sub> H <sub>34</sub> O <sub>10</sub> Os <sub>3</sub> P <sub>2</sub>
Crystal system	Triclinic	Monoclinic	Triclinic
Formula weight	1431.34	1300.24	1343.24
<i>T</i> (K)	150(1)	150(1)	295(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.1243(1)	9.9588(2)	11.0436(5)
<i>b</i> (Å)	12.8273(1)	20.2106(5)	12.1385(6)
<i>c</i> (Å)	17.3882(2)	20.0447(5)	17.5392(8)
α (°)	73.0486(6)	90	73.471(1)
β (°)	82.8708(7)	93.766(1)	88.316(1)
γ (°)	89.0696(8)	90	68.049(1)
<i>V</i> (Å <sup>3</sup> )	2354.53(4)	4025.8(2)	2082.8(2)
<i>Z</i>	2	4	2
<i>D</i> <sub>calc</sub> (Mg/m <sup>3</sup> )	2.019	2.145	2.142
μ (mm <sup>-1</sup> )	8.201	9.575	9.263
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub>	0.0299/0.0564	0.0422/0.0973	0.0327/0.0719
GOF on <i>F</i> <sup>2</sup>	1.029	1.102	1.028

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### Appendix A. Supplementary material

CCDC 640119, 640120, and 64121 contain the supplementary crystallographic data for **1**, **3**, and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.003.

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