

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 $\text{Os}_3(\text{CO})_{10}(\mu, \eta^2\text{-}(\text{Ph}_2\text{P})_2\text{C}_9\text{H}_{10})$ (**1**) and the double cluster $[\text{Os}_3(\text{CO})_{10}]_2(\mu, \eta^2\text{-}(\text{Ph}_2\text{P})_2\text{C}_9\text{H}_{10})_2$ (**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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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 $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$.

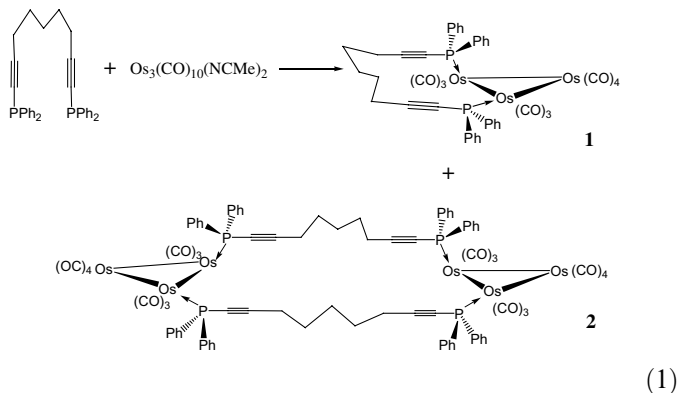
2. Results and discussion

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 $\text{Os}_3(\text{CO})_{10}(\mu, \eta^2\text{-}(\text{Ph}_2\text{P})_2\text{C}_9\text{H}_{10})$ (**1**; 63%) and the double cluster $[\text{Os}_3(\text{CO})_{10}]_2(\mu, \eta^2\text{-}(\text{Ph}_2\text{P})_2\text{C}_9\text{H}_{10})_2$ (**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 $\text{Ph}_2\text{P}=\text{C}(\text{CPh})\text{PPh}_2$ (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 $-\text{C}\equiv\text{C}-$ 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 ^1H 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.

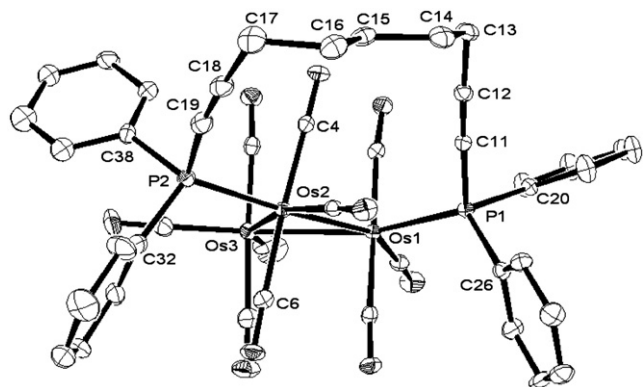
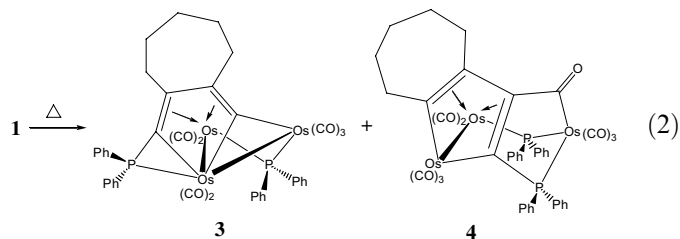


Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°): Os1–Os2 2.9081(3), Os1–Os3 2.8792(3), Os2–Os3 2.9025(3), Os1–P1 2.336(1), Os2–P2 2.345(1), C11–P1 1.767(6), C11–C12 1.202(7), C12–C13 1.462(7), C19–P2 1.761(6), C18–C19 1.195(8), C17–C18 1.468(8) and Os1–Os2–Os3 59.406(4), 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 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 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 ^1H 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–PPh₂ bond is cleaved and the two alkyne units are coupled to form a

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