Complexation and metallation of Ph₂PC≡C(CH₂)₅C≡CPh₂ in triosmium carbonyl clusters

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Abstract

Reaction of Ph₂PC≡C(CH₂)₅C≡CPh₂ with Os₃(CO)₁₀(NCMe)₂ affords Os₃(CO)₁₀(μ,η²-(Ph₂P)₂C₉H₁₀)(1) and the double cluster [Os₃(CO)₁₀]₂(μ,η²-(Ph₂P)₂C₉H₁₀)₂ (2), through coordination of the phosphine groups. Thermolysis of 1 in toluene generates Os₃(CO)₁₀(μ-PPPh₂)(μ,η²-Ph₃PC₉H₁₀) (3) and Os₃(CO)₁₀(μ-PPPh₂)(μ,η⁶-Ph₃P(C₉H₁₀)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 osmacyclopentadienyl ring, which are apparently derived from C–P bond activation and C–C bond rearrangement of the dpndy ligand governed by the triosmium clusters.

Keywords: Triosium; 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 Ph₃P(C₆H₄)CH=NH(CH₂)₅(C₅H₄N) molecule is a typical tridentate P–N–N ligand bound to a metal ion [13] or a M(CO)₅ 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 Ph₂PC≡C(CH₂)₅C≡CPPh₂ (abbreviated as dpndy) and showed its reactions with tungsten carbonyls to yield a paddle-wheel complex [W(CO)₅]₂(μ,η²-dpndy) and a tripod complex W(CO)₅(μ,η²-dpndy)W(CO)₅(η³-dpndy) [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 Os₃(CO)₁₀(NCMe)₂.

2. Results and discussion

Treatment of Os₃(CO)₁₀(NCMe)₂ with equimolar amounts of Ph₂PC≡C(CH₂)₅C≡CPPh₂ at ambient temperature results in facile substitution of the labile acetonitrile ligands by the phosphine groups to afford Os₃(CO)₁₀⁻(μ,η²-(Ph₂P)₂C₉H₁₀) (1; 63%) and the double cluster [Os₃(CO)₁₀]₂(μ,η²-(Ph₂P)₂C₉H₁₀)₂ (2; 4%) (Eq. (1)) as air-stable, yellow crystalline solids. Johnson and coworkers
previously reported the reaction of \( \text{Os}_3(\text{CO})_{10}(\text{NCMe})_2 \) and \( \text{Ph}_2\text{PC} \equiv \text{CCPH}_2 \) (dppa) to yield the di-, tri-, and tetramer 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.

\[
\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2 + \text{Ph}_2\text{PC} \equiv \text{CCPH}_2 (\text{dppa}) \rightarrow \{\text{Os}_3(\text{CO})_{10}(\text{dppa})\}_2 (1)
\]

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 \( \text{n}-\text{hexane/toluene} \) at \(-10^\circ\text{C}\). 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 \( \text{Os}1–\text{Os}2 2.9081(3), \text{Os}2–\text{Os}3 2.9025(3), \) and \( \text{Os}1–\text{Os}3 2.8792(3) \) Å.

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 Os3 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–C–C 86.4(2), Os1–Os2–C–C 95.5(2), and Os3–Os2–C–C 86.4(2)°, probably because of steric interactions with the hydrocarbon chain.

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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 trisodium 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 Os3 clusters symmetrically, or they are equivalent through a dynamic process proposed for the \( \text{M}_3(\text{CO})_{10}(\text{PR})_x \) 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 \( \text{Os}_3(\text{CO})_{10}(\mu-\text{PPh}_2)(\mu_3,\eta^5-\text{Ph}_2\text{PC}_9\text{H}_{10}) (3; 35\%) \) and \( \text{Os}_3(\text{CO})_{10}(\mu-\text{PPh}_2)(\mu_3,\eta^5-\text{Ph}_2\text{P}(\text{C}_9\text{H}_{10})\text{CO}) (4; 21\%) \) (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 the range 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\(_2\) bond is cleaved and the two alkyne units are coupled to form a

![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 2.326(1), Os2–P2 2.345(1), C11–P1 1.767(6), C11–C12 1.202(7), C12–C13 1.462(7), C19–C29 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).](Image 39x143 to 277x286)

![Fig. 2. The dpndy ligand has undergone a tremendous change that one C–PPh\(_2\) bond is cleaved and the two alkyne units are coupled to form a macro-ring structure.](Image 143x143 to 277x286)
metallacycle. Compound 3 is a 50-electron cluster to contain two Os–Os bonds (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 2.384(3), Os2–P2 2.491(1), Os3–P1 2.395(1), 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 1.528(8), C13–C14 1.528(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).

Fig. 2. Molecular structure of 3. The C6H5 groups have been artificially omitted, except the ipso carbon atoms, for clarity. Selected bond lengths (Å) and bond angles (°): 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 2.384(3), Os2–P2 2.491(1), Os3–P1 2.395(1), 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 1.528(8), C13–C14 1.528(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).

The molecular ion peak at m/z 1310 for 4 corresponds to loss of one carbonyl ligand from 1. The IR spectrum 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 31P{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–C8–C9–C10 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).
likely derived from $1/C_{176}$ 2.491(1) Å. The bond angles C10–P1–Os3 103.4(2) ˚A, and a phosphido species with P2–Os3 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 an 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 decarboxylation 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 Os3 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 Ph2P–C

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. Os3(CO)10(NCMe)2 [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). $^1$H and $^{31}$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 Os3(CO)10(NCMe)2

Os3(CO)10(NCMe)2 (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 Os3(CO)10($\mu$,$\eta^2$–(Ph2P)2C9H10) (1; 54 mg, 63%), and the second yellow band afforded [Os3(CO)10]$\mu$($\mu$,$\eta^2$–(Ph2P)2C9H10)2 (2; 8 mg, 4%).

3.2.1. Compound 1


Found: C, 38.62; H, 2.33%. IR (CH2Cl2, νCO): 2084w, 2016m, 1992s, 1960m cm$^{-1}$. MS (FAB): m/z 1338 (M$^+$, 199Os). $^1$H NMR (CD2Cl2, 23 °C): 7.80–7.14 (m, 20H, Ph), 2.71 (m, 4H), 1.86 (m, 2H), 1.77 (m, 4H, CH2) ppm. $^{31}$P($^1$H) NMR (CD2Cl2, 23 °C): –33.6 (s), –35.8 (s) ppm.

3.2.2. Compound 2


Found: C, 38.74; H, 2.19%. IR (CH2Cl2, νCO): 2020m, 1990s, 1966cm$^{-1}$. MS (FAB): m/z 2660 (M$^+$–O, 199Os). $^1$H NMR (CD2Cl2, 23 °C): 7.76 (m, 16H), 7.45 (m, 24H, Ph), 2.64 (m, 8H), 1.74 (m, 4H, CH2), 1.63 (m, 8H, CH2) ppm. $^{31}$P($^1$H) NMR (CD2Cl2, 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 Os3(CO)$\mu$–(μ–PPh2)($\mu$,$\eta^5$–Ph2P)C9H10 (3; 20 mg, 35%), and the second yellow band afforded Os3(CO)$\mu$–(μ–PPh2)($\mu$,$\eta^5$–Ph2P)C9H10CO (4; 13 mg, 21%).

3.3.1. Compound 3


Found: C, 39.64; H, 2.15%. IR (CH2Cl2, νCO): 2060m, 1992s, 1982vs, 1940m, 1926m cm$^{-1}$. MS (FAB): m/z 1254 (M$^+$, 199Os). $^1$H NMR (CD2Cl2, 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, CH2) ppm. 31P{1H} NMR (CD2Cl2, 23 °C): -49.0 (s), -191.5 (s, µ-PPh2) ppm.

3.3.2. Compound 4

Anal. Calc. for C42H30O9P2Os3: C, 38.47; H, 2.29. Found: C, 39.22; H, 2.13%. IR (CH2Cl2, νCO): 2092m, 2056s, 2012s, 1985vs, 1976vs, 1958s, 1942s, 1618br cm⁻¹. MS (FAB): m/z 1310 (M⁺, 192Os). 1H NMR (CD2Cl2, 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, CH2) ppm. 31P{1H} NMR (CD2Cl2, 23 °C): 55.1 (s), -87.3 (s, µ-PPh2) 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 1.25–27.50° 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

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Acknowledgement

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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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