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Journal of Organometallic Chemistry 690 (2005) 4206–4211
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Note

Addition of primary phosphines to the unsaturated triosmium cluster [(μ-H)$Os_3(CO)_8${$Ph_2PCH_2P(Ph)C_6H_4$}]: Synthesis of triosmium clusters bearing dppm, phosphide and phosphinidene ligands via P–H bond activation

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Received 21 May 2005; received in revised form 29 May 2005; accepted 3 June 2005

Abstract

Treatment of the electronically unsaturated cluster [(μ-H)$Os_3(CO)_8${$Ph_2PCH_2P(Ph)C_6H_4$}] (**1**) with primary phosphines $PPhH_2$ and $PCyH_2$ gives the phosphido bridged compounds [(μ-H)$Os_3(CO)_8$(μ-PPhH)(μ-dppm)] (**2**) and [(μ-H)$Os_3(CO)_8$(μ-PCyH)(μ-dppm)] (**3**), respectively, by P–H bond activation of the phosphines and demetallation of the phenyl ring of the diphosphine ligand. Thermolysis of **2** and **3** in refluxing octane at 128 °C results in the formation of the phosphinidene compounds [$(\mu\text{-H})_2Os_3(CO)_7(\mu_3$-PPh)(μ-dppm)] (**4**) and [$(\mu\text{-H})_2Os_3(CO)_7(\mu_3$-PCy)(μ-dppm)] (**5**), respectively, by further P–H bond cleavage of the phosphido groups. All the compounds have been characterized by infrared, ^1H NMR, $^{31}P\{^1H\}$ NMR and mass spectroscopic data together with single-crystal X-ray diffraction studies for **4**. Compound **4** consists of a triangular cluster of osmium atoms with a symmetrically capped phosphinidene ligand and a bridging dppm ligand.

Keywords: Triosmium clusters; Primary phosphine; Phosphide; Phosphinidene; X-ray structure

1. Introduction

The scission of a P–H bond of a secondary or primary phosphine within the coordination sphere of a transition metal di- and polynuclear compound either thermally or photochemically leading to the formation of bridging hydrido and phosphido ligands has been the subject of numerous studies [1]. The phosphide ligand (μ_2-PR_2) acts as a robust and flexible bridge and keeps the integrity of the metal framework in a great variety of reactions including decarbonylation [2], oxidation [3], and protonation [4] thus leading to many new metal–metal bonded substrates. In case of a primary phosphine, the μ_2-PRH ligand on thermolysis or photolysis can lead to further oxidative addition resulting in the formation of phosphinidene (μ_3-PR) moiety in the presence of more than two metal centers [5]. Trinuclear complexes of the type [(μ-H)$M_3(CO)_{10}$(μ-PR_2)] (M = Fe, Ru, Os; R = organic residue) have been extensively investigated by several groups [6–8].

During the past few years, we have been studying the reactions of the coordinatively unsaturated trios-

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0022-328X/$ - see front matter
doi:10.1016/j.jorganchem.2005.06.005

mium cluster $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**1**) with a wide variety of small inorganic and organic molecules to afford many interesting and potentially useful compounds [9]. A few years ago, we reported that **1** reacts with PPh_2H at ambient temperature to give $[(\mu\text{-H})Os_3(CO)_8\{\mu_3\text{-}\eta^3\text{-}Ph_2PCH_2P(Ph)C_6H_4\}(PPh_2H)]$ and $[Os_3(CO)_8(\mu\text{-dppm})(PPh_2H)_2]$ [10]. We also found that $[Os_3(CO)_{10}(\mu\text{-dppm})]$, the precursor of **1**, gives completely different products, $[Os_3(CO)_9(\mu\text{-dppm})(Ph_2PH)]$ and $[H(\mu\text{-H})Os_3(CO)_7(\mu\text{-dppm})(\mu\text{-PPh}_2)_2]$ when treated with PPh_2H at 110 °C. Böttcher et al. reported that bulky phosphines, such as, $^tBu_2PH$ reacts with $[Os_3(CO)_{10}(\mu\text{-dppm})]$ and $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ to give exclusively the electron deficient compounds $[(\mu_3\text{-H})(\mu\text{-H})Os_3(CO)_5(\mu\text{-dppm})(\mu\text{-P}^tBu_2)_2]$ [11] and $[(\mu_3\text{-H})(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_4(\mu\text{-dppm})(\mu\text{-P}^tBu_2)_2]$ [12], respectively. Interestingly, the reaction of $[Ru_3(CO)_{10}((\mu\text{-dppm})]$ with less bulky phosphine Cy_2PH leads to the electronically saturated compound $[(\mu\text{-H})_2Ru_3(CO)_6(\mu\text{-dppm})(\mu\text{-PCy}_2)_2]$ [12]. Recently, we have reported that $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ reacts with PPh_2H in refluxing heptane to give four triruthenium compounds, $[Ru_3(CO)_6(\mu\text{-CO})(\mu_3\text{-CH}_2PPh)(\mu\text{-PPh}_2)_2]$, $[(\mu\text{-H})Ru_3(CO)_6(\mu_3\text{-}\eta^2\text{-PPh}_2CH_2PPh)(\mu\text{-PPh}_2)_2]$, $[(\mu\text{-H})_2Ru_3(CO)_5(\mu\text{-dppm})(\mu_3\text{-PPh})(\mu\text{-PPh}_2)_2]$, and $[(\mu\text{-H})_2Ru_3(CO)_6(\mu\text{-dppm})(\mu\text{-PPh}_2)_2]$ formed by the cleavage of P–C and P–H bonds of the ligands [13]. Herein, we report our findings on the synthesis and characterization of $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-PPhH})(\mu\text{-dppm})]$ (**2**) and $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-PCyH})(\mu\text{-dppm})]$ (**3**) along with the results of our experiments on the thermolysis of **2** and **3** to give $[(\mu\text{-H})_2Os_3(CO)_7(\mu_3\text{-PPh})(\mu\text{-dppm})]$ (**4**) and $[(\mu\text{-H})_2Os_3(CO)_7(\mu_3\text{-PCy})(\mu\text{-dppm})]$ (**5**), respectively.

2. Experimental

All reactions were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. Solvents were dried and distilled under nitrogen from appropriate drying agents and degassed prior to use. Phenylphosphine and cyclohexylphosphine were purchased as 10% hexane solution from Strem and used as received. The starting cluster $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (**1**) was prepared according to the literature method [14]. Infrared spectra were recorded on a Shimadzu FT-IR 8101 spectrophotometer. ^{1}H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer. Chemical shifts for the $^{31}P\{^1H\}$ NMR spectra are relative to 85% H_3PO_4. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Elemental analyses were carried out at the microanalytical Laboratories, University College London.

2.1. Reaction of $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (1) with $PPhH_2$

A 10% hexane solution of $PPhH_2$ (0.014 g, 0.127 mmol) was added to a CH_2Cl_2 solution (25 mL) of **1** (0.075 g, 0.064 mmol) and the reaction mixture was stirred at room temperature for 30 min during which time the color changed from green to yellow. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (2:1, v/v) developed one band which afforded $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-PPhH})(\mu\text{-dppm})]$ (**2**) (0.049 g, 60%) as orange crystals after recrystallization from CH_2Cl_2/hexane at −4 °C. Anal. Calc. for $C_{39}H_{29}O_8Os_3P_3$: C, 36.33; H, 2.27. Found: C, 36.55; H, 2.45%. IR (νCO, CH_2Cl_2): 2066 s, 2020 s, 1991 vs, 1933 m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.66–7.08 (m, 25H), 6.17 (d, 1H, $^1J_{P-H} = 413.5$), 5.56 (m, 1H), 4.67 (m, 1H), −18.24 (ddd, 1H, $^2J_{P-H} = 17.6$, 7.8, $^3J_{P-H} = 4.4$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −14.1 (dd, 1P, $^2J_{P-P} = 20.4$, $^3J_{P-P} = 3.6$ Hz), −20.4 (dd, 1P, $^2J_{P-P} = 41.3$, 20.6 Hz), −28.5 (dd, 1P, $^2J_{P-P} = 41.3$, $^3J_{P-P} = 3.6$ Hz); FAB MS: m/z 1288 (M^+).

2.2. Reaction of $[(\mu\text{-H})Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ (1) with $PCyH_2$

A similar reaction between a 10% hexane solution of $PCyH_2$ (0.021 g, 0.181 mmol) and **1** (0.105 g, 0.089 mmol) followed by similar chromatographic separation afforded $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-PCyH})(\mu\text{-dppm})]$ (**3**) (0.052 g, 45%) as yellow crystals after recrystallization from CH_2Cl_2/hexane at −4 °C. Anal. Calc. for $C_{39}H_{35}O_8Os_3P_3$: C, 36.16; H, 2.73. Found: C, 36.29; H, 2.95%. IR (νCO, CH_2Cl_2): 2065 s, 2021 s, 1990 vs, 1933 m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.49–7.19 (m, 25H), 5.24 (ddt, 1H, $^1J_{P-H} = 381.7$, $^2J_{P-H} = 4.0$, $^3J_{P-H} = 2.0$ Hz), 5.18 (m, 1H), 5.14 (m, 1H), 2.06–0.45 (m, 11H), −18.61 (ddd, 1H, $^2J_{P-H} = 15.6$, 9.6, $^3J_{P-H} = 4.4$ Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −1.8 (dd, 1P, $^2J_{P-P} = 20.6$, $^3J_{P-P} = 4.0$ Hz), −26.2 (dd, 1P, $^2J_{P-P} = 40.0$, $^3J_{P-P} = 4.0$ Hz), −28.5 (dd, 1P, $^2J_{P-P} = 40.0$, 20.6 Hz); FAB MS: m/z 1294 (M^+).

2.3. Thermolysis of $[(\mu\text{-H})Os_3(CO)_8(\mu\text{-PPhH})(\mu\text{-dppm})]$ (2)

An octane solution (30 mL) of **2** (0.025 g, 0.019 mmol) was heated to reflux at 128 °C for 4 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (7:3, v/v) gave a single band which afforded $[(\mu\text{-H})_2Os_3(CO)_7(\mu_3\text{-PPh})(\mu\text{-dppm})]$ (**4**) (0.018 g, 75%) as pale yellow crystals from hexane/CH_2Cl_2. Anal. Calc. for $C_{38}H_{29}O_7Os_3P_3$: C, 36.19; H, 2.32. Found: C, 36.37; H, 2.49%. IR (νCO, CH_2Cl_2):

2053 vs, 2024 vs, 1985 vs, 1927 m cm^{-1}; ^{1}H NMR (CD_2Cl_2): δ 7.59–6.99 (m, 25H), 4.64 (m, 1H), 3.02 (m, 1H), −19.77 (dd, 1H, $^{2}J_{P–H}$ = 19.6, 10.8 Hz), −20.56 (dd, 1H, $^{2}J_{P–H}$ = 29.6, 10.8 Hz); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 124.0 (dd, 1P, $^{2}J_{P–P}$ = 14.3, 3.2 Hz), −14.3 (dd, 1P, $^{2}J_{P–P}$ = 48.9, 14.5 Hz), −25.0 (dd, 1P, $^{2}J_{P–P}$ = 48.9, 3.2 Hz); FAB MS: *m/z* 1260 (M^+).

*2.4. Thermolysis of [(μ-H)Os$_3$(CO)$_8$(μ-PCyH)-(μ-dppm)] (**3**)*

A similar thermolysis to that above of **3** (0.035 g, 0.027 mmol) in refluxing octane for 5 h followed by similar chromatographic separation developed two bands. The first band afforded unreacted **3** (0.004 g) while the second band gave [(μ-H)$_2$Os$_3$(CO)$_7$(μ$_3$-PCy)(μ-dppm)] (**5**) (0.017 g, 50%) as pale yellow crystals from hexane/CH_2Cl_2 at −4 °C. Anal. Calc. for $C_{38}H_{35}O_7Os_3P_3$: C, 36.01; H, 2.79. Found: C, 36.25; H, 2.93%. IR (CO, CH_2Cl_2): 2051 vs, 2023 vs, 1984 vs, 1925 m cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.56–7.19 (m, 20H), 4.34 (m, 1H), 3.53 (m, 1H), 2.04–1.24 (m, 11H), −19.59 (dd, 1H, $^{2}J_{P–H}$ = 18.0, 8.8 Hz), −20.84 (dd, 1H, $^{2}J_{P–H}$ = 31.2, 10.4 Hz); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 124.0 (dd, 1P, $^{2}J_{P–P}$ = 14.3, 3.2 Hz), −14.3 (dd, 1P, $^{2}J_{P–P}$ = 48.9, 14.5 Hz), −25.0 (dd, 1P, $^{2}J_{P–P}$ = 48.9, 3.2 Hz); FAB MS: *m/z* 1266 (M^+).

2.5. X-ray crystallography

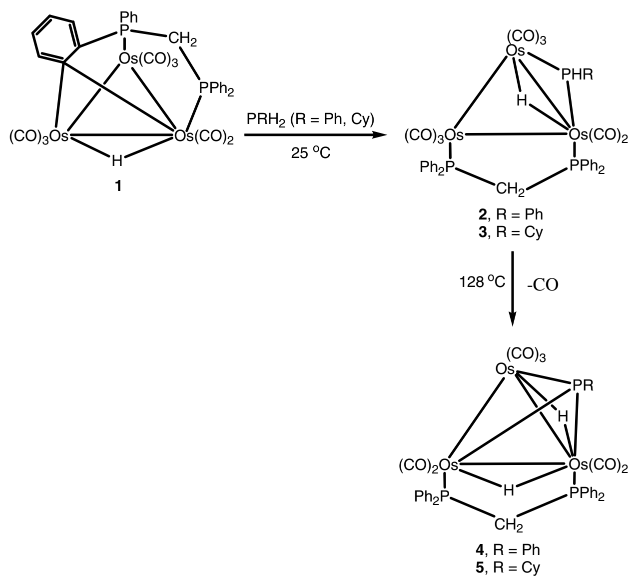
Single crystals of **4** suitable for X-ray diffraction were grown by slow diffusion of hexane into a dichloromethane solution at −4 °C. Crystallographic data were collected at 150 K, on a CAD4 diffractometer using graphite monochromatised Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were determined from all observed reflections in a θ-range of 3–10° and refined using the entire data set. The structures were solved by direct methods (SHELXS-97) [15] and refined on F^2 by full matrix least-squares (SHELXL-97) [16] using all unique data and corrected for absorption by using the semi empirical ψ-scan methods [17]. All nonhydrogen atoms were refined anisotropically. 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. Final difference maps did not show any residual electron density of stereochemical significance. The details of the data collection and structure refinement are given in Table 1.

Table 1
Crystal data and structure refinement for [(μ-H)$_2$Os$_3$(CO)$_7$(μ$_3$-PPh)-(μ-dppm)] · 1/2H_2O (**4**)

Empirical formula	$C_{38}H_{30}O_{7.5}Os_3P_3$
Formula weight	1270.13
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	11.210 (4)
b (Å)	21.454(6)
c (Å)	18.523(6)
α (°)	90
β (°)	104.08(2)
γ (°)	90
Volume (Å^3)	4321(2)
Z	4
Density (calculated) (mg/m^3)	1.952
Absorption coefficient (mm^{-1})	8.954
F(000)	2364
Crystal size (mm^3)	0.45 × 0.15 × 0.15
θ Range for data collection (°)	2.41–25.35
Index ranges	$-13 \leqslant h \leqslant 13$, $-25 \leqslant k \leqslant 6$, $0 \leqslant 1 \leqslant 22$
Absorption correction	ψ scan
Reflections collected	8201
Independent reflections	7831 [*R*(int) = 0.0341]
Completeness to theta = 25.35	98.9%
Maximum and minimum transmission	0.3469 and 0.1074
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7831/0/469
Goodness-of-fit on F^2	1.086
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0558$, $wR_2 = 0.1719$
R indices (all data)	$R_1 = 0.0874$, $wR_2 = 0.1989$
Largest difference in peak and hole (e A^{-3})	3.704 and −3.574

3. Results and discussion

The reactions of the unsaturated cluster [(μ-H)Os$_3$(CO)$_8${$Ph_2PCH_2P(Ph)C_6H_4$}] (**1**) with two equivalents of $PPhH_2$ and $PCyH_2$ at ambient temperature followed by usual workup and chromatographic separation gave exclusively the phosphido bridged compounds [(μ-H)Os$_3$(CO)$_8$(μ-PPhH)(μ-dppm)] and [(μ-H)Os$_3$(CO)$_8$(μ-PCyH)(μ-dppm)] (**3**) in 60% and 45% yields, respectively (Scheme 1). Compounds **2** and **3** have been characterized by mass spectrometry, elemental analysis and by ^{1}H, $^{31}P\{^{1}H\}$ NMR and IR spectroscopy. A partial determination of the molecular structure of compound **2** was made [18], but the poor quality of the data precludes discussion of the structural details. The X-ray analysis is, however, consistent with the proposed structure with two short Os–Os bonds one of which is bridged by the dppm ligand and a longer Os–Os bond, bridged by the hydride and the phosphide group. Furthermore, the spectroscopic properties of **2** are in agreement with the solid state structure being maintained in solution. Unfortunately, suitable single crystals could not be grown for compound **3** also. The infrared spectra of **2** and **3** are very similar and show bands characteristics of terminal carbonyl ligands. The close similarity of the IR spectra in the carbonyl region of **2** and **3** indicate that they are isostructural. The mass spectra exhibit



Scheme 1.

molecular ion peaks (*m/z* 1288 for **2**; 1294 for **3**) corresponding to their proposed formulations and fragmentation peaks due to the sequential loss of eight carbonyl ligands. The ^{1}H NMR spectra confirm the formation of a bridging hydrido and phosphido ligands by activation of a P–H bond by showing characteristic P–H (a doublet at δ 6.17, $^{1}J_{P-H} = 413.5$ Hz for **2** and a doublet of doublets of triplets at δ 5.24, $^{1}J_{P-H} = 381.7$, $^{2}J_{P-H} = 4.0$, $^{3}J_{P-H} = 2.0$ Hz for **3**) and hydride resonances {δ −18.24 (ddd, 1H, $^{2}J_{P-H} = 17.6$, 7.8, $^{3}J_{P-H} = 4.4$ Hz for **2** and δ −18.61 (ddd, 1H, $^{2}J_{P-H} = 15.6$, 9.6, $^{3}J_{P-H} = 4.4$ Hz) for **3**}. In the case of the cyclohexylphosphine compound **3**, in addition to the P–H coupling, another coupling arises from α-hydrogen atom of the cyclohexyl group ($J_{H-H} = 4.0$ Hz). The chemical shifts and coupling constants of these resonances in **2** and **3** are in agreement with the proposed structures and the data reported for the related phosphido bridged triosmium compounds [(μ-H)$Os_3(CO)_{10}$(μ-PPhH)] and [(μ-H)$Os_3(CO)_{10}$(μ-PCyH)] which were synthesized from the Me_3NO initiated reactions of [$Os_3(CO)_{12}$] with $PPhH_2$ and $PCyH_2$, respectively [18]. In addition to phenyl resonances, the multiplets at δ 5.56 and 4.67 for **2** and δ 5.18 and 5.14 for **3** are due to the methylene protons of the dppm ligands. In the $^{31}P\{^{1}H\}$ NMR spectra of **2** and **3**, there are three doublet of doublets, one due to μ-PRH ligand (δ-14.1, $^{2}J_{P-P} = 20.4$, $^{3}J_{P-P}$ 3.6 Hz for **2** and δ-1.8, $^{2}J_{P-P} = 20.6$, $^{3}J_{P-P}$ 4.0 Hz for **3**) and two due to the dppm ligand (δ-20.4, $^{2}J_{P-P} = 41.3$, 20.6 Hz, −28.5, $^{2}J_{P-P} = 41.3$, $^{3}J_{P-P} = 3.6$ Hz for **2**; δ-26.2, $^{2}J_{P-P} = 40.0$, $^{3}J_{P-P} = 4.0$ Hz, −28.5, $^{2}J_{P-P} = 40.0$, 20.6 Hz for **3**), indicating that all the ^{31}P nuclei are nonequivalent and coupled to each other.

Thermolysis of compounds **2** and **3** was carried out to ascertain whether further P–H bond cleavage of the μ-PRH ligand could be achieved. On heating either **2** or **3** at 128 °C in octane, compounds [(μ-H)$_2Os_3(CO)_7$-(μ$_3$-PPh)(μ-dppm)] (**4**) and [(μ-H)$_2Os_3(CO)_7$(μ$_3$-PCy)-(μ-dppm)] (**5**) were obtained in 75% and 50% yields, respectively. Compounds **4** and **5** have been characterized by elemental analysis, mass spectrometry and by IR, ^{1}H, $^{31}P\{^{1}H\}$ NMR spectroscopy. In addition, compound **4** has been the subject of a single crystal X-ray structure determination.

The solid-state structure of **4** is depicted in Fig. 1, crystal data and structure refinement parameters are given in Table 1, and selected bond distance and angles are listed in the caption. The structure is based on the previously reported compound [(μ-H)$_2Os_3(CO)_9$(μ$_3$-PPh)] which was synthesized by the thermolysis of either [$Os_3(CO)_{11}(PPhH_2)$] or [(μ-H)$Os_3(CO)_9$(μ$_2$-PPhH)] in refluxing nonane [19]. The molecular structure of **4** consists of a triangular core of osmium atoms with two similar but significantly elongated Os–Os bond distances, Os(1)–Os(2) = 2.9617(10), Os(1)–Os(3) = 2.9714(10) Å, and one shorter Os–Os bond, Os(2)–Os(3) = 2.8498(12) Å. The seven terminal carbonyl ligands are distributed so that two are bonded to each of Os(1) and Os(2) and three bonded to Os(3). The Os(1)–Os(2) edge is simultaneously bridged by a hydride and the dppm ligand. The other hydride ligand spans the Os(1)–Os(3) edge. The position of the hydride ligands were located but not refined. The elongation of the Os(1)–Os(2) and Os(1)–Os(3) edges are also consistent with the hydrides being bridged on these edges while

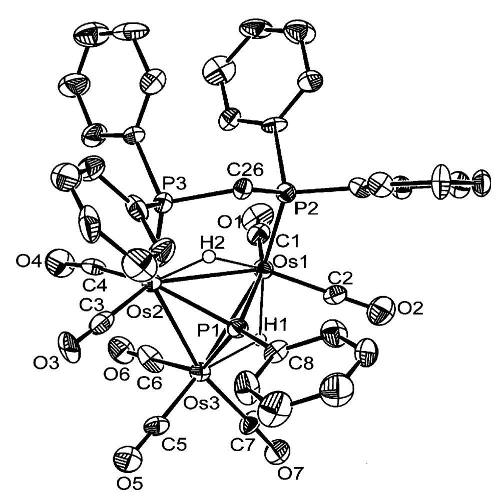


Fig. 1. ORTEP drawing of [(μ-H)$_2Os_3(CO)_7$(μ$_3$-PPh)(μ-dppm)] (**4**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angles (°): Os(1)–Os(3) = 2.9714(10), Os(2)–Os(3) = 2.8498(12), Os(1)–Os(2) = 2.9617(10), Os(2)–P(3) = 2.332(4), Os(3)–P(1) = 2.341(4), Os(1)–P(1) = 2.354(4), Os(2)–P(1) = 2.333(4), Os(1)–P(2) = 2.332(4), Os(2)–Os(1)–Os(3) = 57.41 (3), Os(2)–Os(3)–Os(1) = 61.12(2), Os(3)–Os(2)–Os(1) = 61.464(18), P(2)–Os(1)–Os(2) = 91.35(9), P(1)–Os(2)–Os(3) = 52.55(4), P(1)–Os(2)–Os(1) = 51.12(9), Os(3)–P(1)–Os(1) = 78.54(11), P(2)–C(26)–P(3) = 116.1(7), P(1)–Os(1)–Os(3) = 50.54(9), P(3)–Os(2)–Os(1) = 92.88(9), P(1)–Os(3)–Os(1) = 50.93(9), Os(2)–P(1)–Os(1) = 78.39(11).

the short Os(2)–Os(3) edge carries no hydride. An interesting feature of the structure is that the phosphinidene ligand, PPh, almost symmetrically caps the Os_3 triangle {Os(1)–P(1) = 2.354(4), Os(2)–P(1) = 2.333(4) and Os(3)–P(1) = 2.341(4) Å}. This observation is in contrast to that reported for [(μ-H)$_2$Os$_3$(CO)$_9$(μ$_3$-PPh)] in which the phosphinidene ligand asymmetrically caps the Os_3 triangle {2.309(8)–2.358(10) Å} [18]. The dppm ligand bridges in equatorial sites at Os(1) and Os(2) with both the phosphorus nuclei on the same side of the Os_3 plane. The Os–P bond distances involving the dppm ligand {Os(1)–P(2) = 2.332(4), Os(2)–P(3) = 2.332(4) Å} are also symmetric and very similar to the Os–P distances involving the phosphinidene ligand. All other features of the molecular geometry are within the expected range. Individual Os–CO distances range from 1.859(15) to 1.928(17) Å, C–O bond lengths range from 1.116(18) to 1.172(18) Å and Os–C–O angles are in the range 172.4(12)–178.1(13) Å. The cluster is electron precise with 48 electrons as expected for a closed triangular cluster.

The spectroscopic data of **4** are consistent with the solid state structure being maintained in solution. Furthermore, on the basis of close similarity of the spectroscopic data between **4** and **5**, a similar structure may be ascribed for **5**. Both compounds **4** and **5** exhibit carbonyl stretching bands in the region 2053–1921 cm^{-1}, indicating that all the carbonyl groups are terminal. The mass spectra exhibit molecular ion peaks (*m*/*z* 1260 for **4**; 1266 for **5**) and fragmentation peaks due to the sequential loss of seven carbonyl ligands. In addition to phenyl and cyclohexyl proton resonances, the ^{1}H NMR spectra of **4** and **5** in the aliphatic region shows two equally intense multiplets (δ 4.64 and 3.02 for **4**; 4.34 and 3.53 for **5**) for the diastereotopic methylene protons of the dppm ligand. The hydride region of the spectra contain two double doublets (δ −19.77, $^2J_{P-H}$ = 19.6, 10.8 Hz and −20.56, $^2J_{P-H}$ = 29.6, 10.8 Hz for **4**; δ −19.59, $^2J_{P-H}$ = 18.0, 8.8 Hz and −20.84, $^2J_{P-H}$ = 31.2, 10.4 Hz for **5**), indicating the presence of two nonequivalent hydride ligands each coupled to two nonequivalent phosphorus nuclei. Consistent with this the ^{31}P{^{1}H} NMR spectrum of **4** contains three equal intensity doublet of doublets at δ 124.0 ($^2J_{P-P}$ = 14.3, 3.2 Hz), −14.3 ($^2J_{P-P}$ = 48.9, 14.5 Hz), and −25.0 ($^2J_{P-P}$ = 48.9, 3.2 Hz) for the three magnetically non-equivalent phosphorus atoms. The deshielded resonance at δ 124.4 is readily assigned to the phosphinidene moiety while the two remaining resonances at δ 51.4 and 19.30 are due to the bridging dppm ligand. A similar ^{31}P{^{1}H} NMR is found for **5** with resonances appearing at δ 124.0 (dd, $^2J_{P-P}$ = 14.3, 3.2 Hz), −14.3 (dd, $^2J_{P-P}$ = 48.9, 14.5 Hz), and −25.0 (dd, $^2J_{P-P}$ = 48.9, 3.2 Hz). The ^{31}P nuclei of the dppm ligand both lie equatorially (*cis* to the PPh ligand) and it is the hydride locations that make the dppm ligand unsymmetrical.

4. Conclusion

In this paper, we have demonstrated that the electronically unsaturated cluster [(μ-H)Os$_3$(CO)$_8${Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$}] (**1**) reacts with two equivalents of PPhH$_2$ and PCyH$_2$ at room temperature to give the phosphido bridged compounds [(μ-H)Os$_3$(CO)$_8$(μ-PPhH)(μ-dppm)] (**2**) and [(μ-H)Os$_3$(CO)$_8$(μ-PCyH)(μ-dppm)] (**3**), respectively. The formation of **2** and **3** from **1** involves oxidative addition of PRH$_2$ followed by demetallation of the phenyl ring of the diphosphine ligand. These results are in sharp contrast to those obtained from the reaction of PPh$_2$H with **1** which afforded two phosphine-substituted compounds, [(μ-H)Os$_3$(CO)$_8${μ$_3$-η^3-Ph$_2$PCH$_2$P(Ph)C$_6$H$_4$}(PPh$_2$H)] and [Os$_3$(CO)$_8$(μ-dppm)(PPh$_2$H)$_2$] [10]. It leads one to think of the P–H bond activation in terms of acid/base chemistry rather than an enhanced oxidative cleavage (or addition) due to rapid kinetics, whose origin undoubtedly lies in the greater accessibility of 1° versus 2° P–H bonds towards cleavage at a metal center(s). When refluxed in octane at 128 °C, a further P–H bond activation in both **2** and **3** occurs resulting in the formation of the dihydrido phosphinidene compounds [(μ-H)$_2$Os$_3$(CO)$_7$(μ$_3$-PPh)(μ-dppm)] (**4**) and [(μ-H)$_2$Os$_3$(CO)$_7$(μ$_3$-PCy)(μ-dppm)] (**5**), respectively.

Acknowledgement

The support of this research by the Ministry of Science and Technology, Government of the Peoples Republic of Bangladesh is gratefully acknowledged.

Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 271515 for the compound **4**. 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; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.06.005.

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[18] Crystals of **2** were triclinic, space group $P\bar{1}$, with $a = 11.669$ Å, $b = 12.393$ Å, $c = 15.401$ Å, $\alpha = 112.69°$, $\beta = 101.33°$, $\gamma = 106.26°$, Os(1)–Os(2) = 2.8758, Os(1)–Os(3) = 2.8787, Os(2)–Os(3) = 2.9358, Os(2)–P(3) = 2.353, Os(2)–P(3) = 2.353, Os(3)–P(3) = 2.365, Os(1)–P(1) = 2.333, Os(2)–P(2) = 2.304 Å. They were thin needles giving weak, poor quality diffraction data (despite repeated recrystallization and data collection), and the structure could not be satisfactorily refined giving a high R_1 value.

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