

CLUSTER CHEMISTRY

IL *. FURTHER EXAMPLES OF RUTHENIUM AND OSMIUM CLUSTER CARBONYLS CONTAINING THE OLEFINIC TERTIARY PHOSPHINE $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2-2)$ (sp): X-RAY STRUCTURE OF $\text{Os}_3\text{H}(\mu\text{-H})(\text{CO})_{10}$ (sp)

MICHAEL I. BRUCE and MICHAEL L. WILLIAMS

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

(Received April 17th, 1986)

Summary

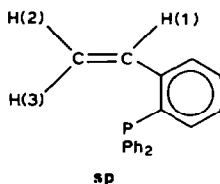
Reactions between $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ or $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and $\text{PPh}_2(\text{C}_6\text{H}_4\text{-CH}=\text{CH}_2-2)$ (sp) give the *P*-bonded complex $\text{Os}_3(\text{CO})_{11}(\text{sp})$ and the chelated complex $\text{Os}_3(\text{CO})_{10}(\text{sp})$, respectively. Between 100–120°C, both complexes form $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2, P\text{-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$. With $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$, sp affords *P*-bonded $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{sp})$, fully characterised by an X-ray structure. Crystals are triclinic, space group $P\bar{1}$, with *a* 10.546(4), *b* 11.272(2), *c* 15.214(4) Å, α 67.63(2), β 73.82(2), γ 74.04(2)° and *Z* = 2; 3383 data with $I \geq 2.5\sigma(I)$ were refined to *R* = 0.032, *R_w* = 0.032. The reaction between sp and $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ gave $\text{Ru}_3(\text{CO})_{10}(\text{sp})$ and $\text{Ru}_3(\text{CO})_9(\text{CNBu}^t)(\text{sp})$, both containing chelating sp ligands.

Introduction

We have previously described the radical anion-initiated reaction between $\text{Ru}_3(\text{CO})_{12}$ and the olefinic tertiary phosphine $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2-2)$ (sp), which afforded the chelate complex $\text{Ru}_3(\mu\text{-}\eta^2, P\text{-}2\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2)(\text{CO})_{10}$ (1). No evidence was obtained for the formation of either the *P*-bonded or η^2 -bonded isomers of a putative intermediate $\text{Ru}_3(\text{CO})_{11}(\text{sp})$ [1]. On heating, rapid dehydrogenation of 1 occurred at low temperatures (40°C) to give the hydrido-alkynyl complex $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2, P\text{-}2\text{-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$ (2), which above 135°C formed the Ru_4C_2 cluster $\text{Ru}_4(\mu_4\text{-}\eta^2, P\text{-}2\text{-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2)(\text{CO})_{11}$ (3) [2]. A binuclear complex, $\text{Ru}_2(\mu\text{-}\eta^1, \eta^3\text{-MeCC}_6\text{H}_4\text{PPh}_2)(\text{CO})_6$ (4) was obtained on heating 2 in a CO atmosphere [3]. This paper describes some related chemistry of osmium: earlier, others reported the thermal reactions between $\text{Os}_3(\text{CO})_{12}$ and sp in refluxing

* For Part XXXXVIII, see ref. 17.

TABLE 1

¹H NMR DATA FOR THE VINYL GROUP OF THE sp LIGAND (in CDCl₃)

Compound	Chemical shifts ^a			Coupling constants ^b		
	$\delta(\text{H}(1))$	$\delta(\text{H}(2))$ ^d	$\delta(\text{H}(3))$ ^d	$J(12)$	$J(13)$	$J(23)$
sp	^c	4.99dd	5.45dt	11.0	17.5	1.3
Ru ₃ (CO) ₁₀ (sp) (1)	4.90dd	2.51d	3.24d	8.5	12.5	–
Os ₃ (CO) ₁₀ (sp) (5)	4.71dd	2.21dd	2.87dd	8.0	19.5	2.5
Os ₃ (CO) ₁₁ (sp) (6)	6.76dd	5.11d	5.68d	11.0	17.0	–
Os ₃ (H) ₂ (CO) ₁₀ (sp) (7)	6.73dd	5.18d	5.67d	11.0	17.0	–
Ru ₃ (CO) ₉ (sp)(CNBu ^t) (9)	4.65dd	2.38d	3.07d	8.0	11.5	–

^a In ppm. ^b In Hz. ^c Obscured by aromatic resonances. ^d The assignment of H(2) and H(3) has been made on the basis of $J(13)$ (*trans*-olefinic coupling) being greater than $J(12)$ (*cis*-olefinic coupling).

octane, from which the osmium analogue of **2** was isolated in low yield [4]. We also describe the reaction between sp and Ru₃(CO)₁₁(CNBu^t).

Results and discussion

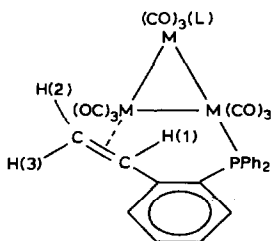
Radical anion-initiated reactions between tertiary phosphines and Os₃(CO)₁₂ are not particularly selective [5], and it is preferable to use the acetonitrile derivatives Os₃(CO)_{12-n}(NCMe)_n ($n = 1, 2$) as precursors [6]. The reaction between Os₃(CO)₁₀(NCMe)₂ with sp in heptane at 50°C afforded Os₃(CO)₁₀(sp) (**5**) in moderate yield. This complex showed similar spectroscopic properties [IR $\nu(\text{CO})$, ¹H NMR (Table 1 and Experimental)] to those of **1** and undoubtedly has a similar structure.

Treatment of Os₃(CO)₁₁(NCMe) with sp at room temperature afforded the *P*-bonded complex Os₃(CO)₁₁(sp) (**6**) in 72% yield. This yellow complex was identified by elemental analysis and by the similarity of its IR $\nu(\text{CO})$ spectrum to that of Os₃(CO)₁₁(PPh₃) [6]. The presence of the uncoordinated vinyl group was confirmed by the ¹H NMR spectrum (Table 1); the olefinic protons appear at lower field than those found for the complexes **1** and **5**.

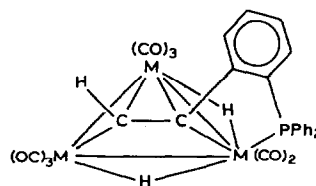
The unsaturated cluster hydride Os₃($\mu\text{-H}$)₂(CO)₁₀ readily adds ligands to give complexes containing one terminal and one bridging hydride ligand. The purple solution of Os₃($\mu\text{-H}$)₂(CO)₁₀ in CH₂Cl₂ rapidly turns yellow upon addition of sp. Thin-layer chromatographic separation afforded yellow Os₃($\mu\text{-H}$)(H)(CO)₁₀(sp) (**7**) in 66% yield together with a small amount of a second yellow product which has not presently been identified. The IR $\nu(\text{CO})$ spectrum of the major product closely resembles those found in other Os₃($\mu\text{-H}$)(H)(CO)₁₀(L) complexes (L = PPh₃ [7,8], PMe₂Ph [7,8] and P(OMe)₃ [9]). The ¹H NMR spectrum contains three characteristic signals at similar chemical shifts to those found in complex **6** (Table 1) for the uncoordinated vinyl group. The existence of the bridging and terminal hydride ligands, which are fluxional at room temperature, was revealed in a ¹H NMR spectrum obtained at 244 K which had resonances at $\delta -19.76\text{dd}$ ($J(\text{HH})$ 3.5,

$J(\text{HP})$ 11.0 Hz) and $\delta -10.10\text{d}$ respectively. The precise stereochemistry of **7** was confirmed by an X-ray diffraction study.

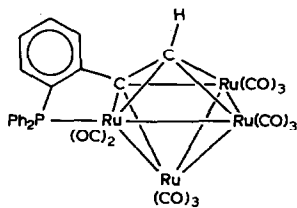
The crystal of **7** consists of discrete molecules, and there are no intermolecular contacts shorter than Van der Waals separations. The molecular structure, which is similar to that found in $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{PPh}_3)$ [10], is shown in Fig. 1 (see also Table 2). The three osmium atoms define a triangular cluster core with bond lengths $\text{Os}(1)\text{-Os}(2)$ 3.018(1), $\text{Os}(1)\text{-Os}(3)$ 2.911(1), and $\text{Os}(2)\text{-Os}(3)$ 2.854(1) Å. The sp ligand is located in an equatorial site bonded to $\text{Os}(1)$ (2.374(2) Å) as a monodentate phosphorus donor. The ten terminal CO groups are arranged such that $\text{Os}(3)$ is associated with four, while $\text{Os}(1)$ and $\text{Os}(3)$ have three each. Although the hydride ligands were not located in the structural study, their positions may be deduced by the Os-Os separations and the geometry of the sp and CO ligands. Thus, the edge-bridging hydride (H_B) is located in the equatorial plane displaced outward from the $\text{Os}(1)\text{-Os}(2)$ bond for the following reasons: the $\text{Os}(1)\text{-Os}(2)$ distance is significantly longer than the other two Os-Os distances, while the equatorial ligands P(1) and CO(21) are splayed out to form the usual cavity associated with bridging hydride ligands. The location of the terminal hydride (H_T) is the seemingly empty axial site on $\text{Os}(2)$ *trans* to CO(23). The C(1)-C(2) bond (1.23(4) Å) is, within the precision of the experiment, consistent with a C=C double bond. The large e.s.d. associated with this bond length is in part the result of very high thermal motion associated with the terminal vinyl carbon C(2).



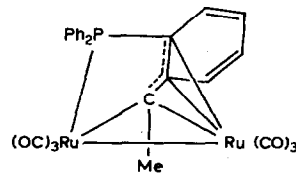
(1 , M = Ru , L = CO ;
5 , M = Os , L = CO ;
9 , M = Ru , L = CNBu^t)



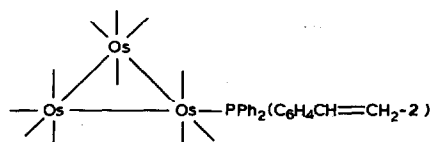
(2 , M = Ru ;
8 , M = Os)



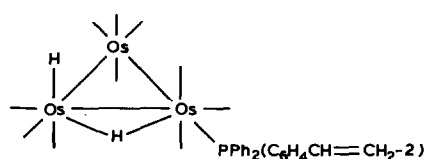
(3)



(4)



(6)



(7)

Thermolysis of $\text{Os}_3(\text{CO})_{10}(\text{sp})$ (**5**) (111°C, 5 h) or $\text{Os}_3(\text{CO})_{11}(\text{sp})$ (**6**) (98°C, 18 h) affords yellow $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2, P\text{-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$ (**8**) in moderate to high yield. This complex was readily identified by its spectral and microanalytical data, and by comparison with the analogous complex **2** and literature values.

Attempts to prepare the more highly substituted derivatives $\text{Ru}_3(\text{CO})_9(\text{sp})_2$ or $\text{Ru}_3(\text{CO})_8(\text{sp})_2$ by the sodium diphenylketyl-initiated reaction between $\text{Ru}_3(\text{CO})_{10}(\text{sp})$ (**1**) and sp met with no success. However, addition of the initiator to an equimolar mixture of $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ and sp afforded, after chromatography, the mixed ligand complex $\text{Ru}_3(\text{CO})_9(\text{CNBu}^t)(\text{sp})$ (**9**) in 18% yield, together with **1** and unreacted $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$. Complex **9**, which can also be prepared in low yield (ca. 1–5%) from the addition of sodium diphenyl ketyl to a mixture of **1** and CNBu^t , was identified by the usual combination of analytical and spectroscopic techniques (see Table 1 and Experimental). The formation of **9** from the former reaction is not an unexpected result when we recall that $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ reacts readily with donor ligands L by displacement of CO or CNBu^t to give $\text{Ru}_3(\text{CO})_{10}(\text{CNBu}^t)(\text{L})$ and $\text{Ru}_3(\text{CO})_{11}(\text{L})$, respectively (L = CNBu^t , PPh_3 , PCy_3 , AsPh_3 , and $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$) [11].

Experimental

All reactions were carried out under nitrogen. Common organic solvents were dried and distilled in nitrogen before use. Light petroleum refers to a fraction of b.p. 62–65°C. The complexes $\text{Ru}_3(\text{CO})_{12}$ [12], $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ [12], $\text{Os}_3(\text{CO})_{12}$ [13] and $\text{Os}_3(\text{CO})_{12-n}(\text{NCMe})_n$ ($n = 1, 2$) [6] and sodium diphenyl ketyl solutions were prepared by the cited procedures. The ligand $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)_2$ was a gift from Dr M.A. Bennett, Canberra.

IR spectra were obtained with a Perkin–Elmer 683 double-beam spectrometer using NaCl cells, and calibrated using the CO absorption at 2147 cm^{-1} . ^1H NMR spectra were obtained in a Bruker WP80DS spectrometer (^1H , 80 MHz). Elemental microanalyses were determined by the Canadian Microanalytical Service, Vancouver. Thin layer chromatography (TLC) was carried out on preparative plates (20 × 20 cm) coated with Kieselgel 60 GF₂₅₄.

Preparation of $\text{Os}_3(\text{CO})_{10}(\text{sp})$ (**5**)

A mixture of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (150 mg, 0.161 mmol) and sp (47 mg, 0.163 mmol) was stirred in cyclohexane (50 ml) at 50°C for 4 h. Evaporation and recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ afforded yellow crystals of $\text{Os}_3(\text{CO})_{10}(\text{sp})$ (**5**) (101 mg, 55%), m.p. 169–172°C. (Found: C, 31.95; H, 1.29; $\text{C}_{30}\text{H}_{17}\text{O}_{10}\text{Os}_3\text{P}$ calcd.: C, 31.63; H, 1.50%). Infrared (cyclohexane): $\nu(\text{CO})$ 2104m, 2048m, 2032m, 2020vs, 2000w, 1987w, 1978m, 1969w cm^{-1} . ^1H NMR: δ (CDCl_3) 2.21 (dd, $J(12)$ 8.0, $J(32)$ 2.5 Hz, 1H, H(2)), 2.87 (dd, $J(13)$ 19.5 Hz, 1H, H(3)), 4.71 (dd, 1H, H(1)), 7.51 (m, 14H, Ph and C_6H_4).

Preparation of $\text{Os}_3(\text{CO})_{11}(\text{sp})$ (**6**)

A mixture of $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ (150 mg, 0.163 mmol) and sp (47 mg, 0.163 mmol) in dichloromethane (30 ml) was stirred at ambient temperature for 24 h. Evaporation and recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ afforded an orange-yellow powder of $\text{Os}_3(\text{CO})_{11}(\text{sp})$ (**6**) (137 mg, 72%), m.p. 68–72°C. (Found: C, 32.17; H, 1.32; $\text{C}_{31}\text{H}_{17}\text{O}_{11}\text{Os}_3\text{P}$ calcd.: C, 31.90; H, 1.47%). Infrared (cyclohexane): $\nu(\text{CO})$

2112m, 2059s, 2038s, 2023vs, 2004w, 1997m, 1985m, 1972vw, 1963w cm^{-1} . ^1H NMR: δ (CDCl_3) 5.11 (d, $J(12)$ 11.0 Hz, 1H, H(2)), 5.68 (d, $J(13)$ 17.0 Hz, 1H, H(3)), 6.76 (dd, 1H, H(1)), 7.50 (m, 14H, Ph and C_6H_4).

Preparation of $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{sp})$ (7)

A mixture of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (100 mg, 0.117 mmol) and sp (35 mg, 0.121 mmol) in dichloromethane (5 ml) was stirred at ambient temperature for 15 min, during which time the colour changed from purple to yellow. Evaporation and preparative TLC (light petroleum/acetone 90/10) gave two bands: Band 1, R_f 0.25, yellow, recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give yellow crystals of $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{sp})$ (7) (88 mg, 66%), m.p. 142–143°C. (Found: C, 31.88; H, 1.31; $\text{C}_{30}\text{H}_{19}\text{O}_{10}\text{Os}_3\text{P}$ calcd.: C, 31.58; H, 1.66%). Infrared (cyclohexane): $\nu(\text{CO})$ 2109m, 2071m, 2056m, 2019vs, 2012(sh), 2004w, 1992(sh), 1989m, 1977 cm^{-1} . ^1H NMR: δ (CDCl_3 , 224 K) –19.76 (dd, $J(\text{H}_\text{B}\text{H}_\text{T})$ 3.5, $J(\text{PH}_\text{B})$ 11.0 Hz, 1H, OsH_B), –10.10 (d, 1H, OsH_T), 5.18 (d, $J(12)$ 11.0 Hz, 1H, H(2)), 5.67 (d, $J(13)$ 17.0 Hz, 1H, H(3)), 6.73 (dd, 1H, H(1)), 7.49 (m, 14H, Ph and C_6H_4). Band 2, R_f 0.15, yellow, trace, uncharacterised.

Reaction of $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ with sp

A mixture of $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ (150 mg, 0.216 mmol) and sp (69 mg, 0.239 mmol) in thf (10 ml) at ambient temperature was treated dropwise with a solution of $\text{Na}[\text{Ph}_2\text{CO}]$ (ca. 0.025 mol dm^{-3} , ~1 ml) in the same solvent. Evaporation and preparative TLC (pentane/diethyl ether 90/10) gave four bands: Band 1, R_f 0.75, orange, $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$, (25 mg, 17%). Band 2, R_f 0.63, orange, $\text{Ru}_3(\text{CO})_{10}(\text{sp})$ (1), (21 mg, 11%). Band 3, R_f 0.50, red, crystallised from warm hexane to give deep red crystals of $\text{Ru}_3(\text{CO})_9(\text{sp})(\text{CNBu}^t) \cdot \text{C}_6\text{H}_{14}$ (9) (36 mg, 18%). m.p. > 200°C. (Found: C, 47.12; H, 3.86; N, 1.41; $\text{C}_{34}\text{H}_{26}\text{NO}_9\text{PRu}_3 \cdot \text{C}_6\text{H}_{14}$ calcd.: C, 47.43; H, 3.98; N, 1.38%). Infrared (cyclohexane): $\nu(\text{CN})$ 2165w, $\nu(\text{CO})$ 2074(sh), 2063m, 2051w, 2037w, 2024m, 2011vs, 1999vs, 1993m, 1985m, 1970s, 1961(sh) cm^{-1} . ^1H NMR: δ (CDCl_3) 1.43 (s, 9H, CMe_3), 2.38 (d, $J(12)$ 8.0 Hz, 1H, H(2)), 3.07 (d, $J(13)$ 11.5 Hz, 1H, H(3)), 4.65 (dd, 1H, H(1)), 7.46 (m, 14H, Ph and C_6H_4). Band 4, R_f 0.41 (trace), not identified. Bands 1 and 2 were identified by comparison of their IR $\nu(\text{CO})$ spectra with those of authentic samples.

Pyrolysis of $\text{Os}_3(\text{CO})_{10}(\text{sp})$ (5)

A solution of $\text{Os}_3(\text{CO})_{10}(\text{sp})$ (5) (100 mg, 0.088 mmol) in toluene (25 ml) was heated at reflux point for 5 h after which time the reaction was adjudged complete (TLC). Evaporation and preparative TLC (light petroleum/acetone 85/15) afforded one major pale yellow product, R_f 0.31, recrystallisation of which from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave yellow rosettes of $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-P-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2\text{-})(\text{CO})_8$ (8) (69 mg, 73%), m.p. 225–230°C (lit. [10] 230–235°C). (Found: C, 30.93; H, 1.43; $\text{C}_{28}\text{H}_{17}\text{O}_8\text{Os}_3\text{P}$ calcd.: C, 31.05, H, 1.58%). Infrared (cyclohexane): $\nu(\text{CO})$ 2099w, 2086s, 2053vs, 2037vs, 2022w, 2008vs, 1999m, 1991vs, 1987w, 1981w, 1964w cm^{-1} . ^1H NMR: δ (CDCl_3) –20.52 (d, $J(\text{PH})$ 27.5 Hz, 1H, OsH), –18.04 (s(br), 1H, OsH), 7.51 (m, 14H, Ph and C_6H_4), 10.78 (s, 1H, $\text{C}\equiv\text{CH}$). Three yellow products were present in trace amounts only and were not characterised.

Pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{sp})$ (6)

A solution of $\text{Os}_3(\text{CO})_{11}(\text{sp})$ (6) (30 mg, 0.026 mmol) in n-heptane (10 ml) was

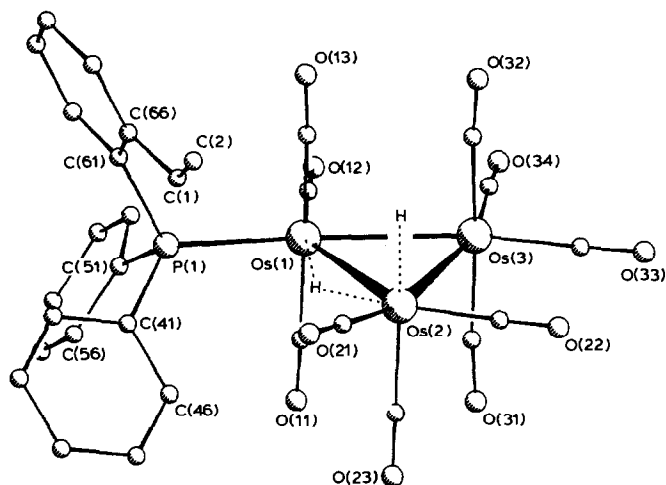


Fig. 1. A molecule of $\text{Os}(\mu\text{-H})(\text{H})(\text{CO})_{10}\{\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\text{-}2)\}$ (**7**) showing atom numbering scheme.

heated at reflux point for 18 h after which time the reaction was adjudged complete (the disappearance of the IR $\nu(\text{CO})$ band of **6** at 2112 cm^{-1} was monitored). Evaporation and recrystallisation from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ gave pale yellow crystals of $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2\text{-}P\text{-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$ (**8**) (19 mg, 67%), identified by comparison of its IR $\nu(\text{CO})$ spectrum with the product obtained from **5**.

Crystallography

Crystals of complex **7** suitable for the X-ray structure determination were obtained from a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture. A crystal was mounted on a glass fibre with cyanoacrylate superglue. Lattice parameters were determined from a least-squares fit to the setting angles of 25 high-angle reflections on an Enraf–Nonius

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR **7**

Os(1)–Os(2)	3.018(1)	P(1)–C(41)	1.828(5)
Os(1)–Os(3)	2.911(1)	P(1)–C(51)	1.834(8)
Os(2)–Os(3)	2.854(1)	P(1)–C(61)	1.843(6)
Os(1)–P(1)	2.374(2)	C(1)–C(2)	1.23(4)
Os(2)⋯C(1)	4.01(1)	C(1)–C(66)	1.49(1)
Os–CO range from 1.88(1)–1.96(1) (av. 1.92)			
C–O range from 1.13(2)–1.17(2) (av. 1.45)			
Os(1)–Os(2)–Os(3)	59.4(3)	Os(1)–P(1)–C(51)	110.7(2)
Os(2)–Os(1)–Os(3)	57.5(1)	Os(1)–P(1)–C(61)	116.3(2)
Os(1)–Os(3)–Os(2)	63.1(1)	C(66)–C(1)–C(2)	127.4(13)
Os(2)–Os(1)–P(1)	115.8(1)	C(66)–C(61)–P(1)	121.9(4)
Os(3)–Os(1)–P(1)	173.2(1)	C(61)–C(66)–C(1)	121.8(7)
Os(1)–P(1)–C(41)	117.2(2)		
Os–C–O range from 174.6(8)–178.7(13) (av. 176.6)			

CAD4F diffractometer using graphite-monochromated Mo- K_{α} radiation, λ 0.7107 Å. Intensity data were measured using an ω -(1/3) θ scan, with ω scan angle $(1.8 + 0.35\tan\theta)^{\circ}$, horizontal counter aperture $(2.4 + 0.5\tan\theta)$ mm. The intensities of three standard reflections, monitored after every 60 min X-ray exposure, showed that no decomposition had occurred during data collection.

TABLE 3

ATOMIC COORDINATES ($\times 10^5$ for Os, all others $\times 10^4$) FOR NON-HYDROGEN ATOMS IN Os₃(μ -H)(H)(CO)₁₀(sp) (7)

Atom	x	y	z
Os(1)	29266(4)	47667(4)	71867(3)
Os(2)	1920(4)	51222(4)	67604(3)
Os(3)	17296(4)	71477(4)	58191(3)
P	3690(2)	2716(2)	8306(2)
O(11)	1637(9)	5764(8)	8911(6)
O(12)	5223(8)	6151(8)	6818(6)
O(13)	4279(8)	3682(8)	5491(5)
O(21)	-866(9)	2620(8)	7398(7)
O(22)	-1910(9)	6751(9)	5536(7)
O(23)	-1366(9)	5981(11)	8525(8)
O(31)	264(9)	8210(8)	7493(6)
O(32)	2885(8)	5992(8)	4155(6)
O(33)	-170(10)	9108(8)	4518(7)
O(34)	3949(9)	8703(9)	5310(6)
C(1)	2912(11)	1197(10)	7216(7)
C(2)	2409(18)	783(26)	6781(20)
C(11)	2085(10)	5402(11)	8257(8)
C(12)	4379(12)	5580(10)	6941(8)
C(13)	3753(10)	4108(11)	6099(8)
C(21)	-468(11)	3565(12)	7177(8)
C(22)	-1130(11)	6151(11)	6001(8)
C(23)	-766(10)	5680(12)	7873(9)
C(31)	818(10)	7753(10)	6901(8)
C(32)	2474(11)	6358(11)	4798(8)
C(33)	537(13)	8385(11)	5017(9)
C(34)	3153(13)	8108(10)	5480(8)
C(41)	2411(5)	1829(5)	9193(4)
C(42)	2770(5)	486(5)	9644(4)
C(43)	1848(5)	-193(5)	10386(4)
C(44)	567(5)	471(5)	10677(4)
C(45)	207(5)	1815(5)	10226(4)
C(46)	1130(5)	2494(5)	9484(4)
C(51)	4611(6)	2917(6)	9085(4)
C(52)	5736(6)	3506(6)	8663(4)
C(53)	6405(6)	3725(6)	9243(4)
C(54)	5949(6)	3355(6)	10245(4)
C(55)	4824(6)	2766(6)	10667(4)
C(56)	4155(6)	2546(6)	10087(4)
C(61)	4810(5)	1476(5)	7782(4)
C(62)	6163(5)	1160(5)	7850(4)
C(63)	7052(5)	247(5)	7446(4)
C(64)	6589(5)	-349(5)	6975(4)
C(65)	5236(5)	-33(5)	6907(4)
C(66)	4347(5)	880(5)	7311(4)

Crystal data. $C_{30}H_{12}O_{10}Os_3P$, M 1141.0, crystal size $0.10 \times 0.14 \times 0.45$ mm, triclinic, space group $P1$, a 10.546(4), b 11.272(2), c 15.214(4) Å, α 67.63(2), β 73.82(2), γ 74.04(2)°, U 1576.9 Å³, D_m 2.40, D_c 2.40 g cm⁻³ for $Z = 2$, $F(000)$ 1042, $\lambda(Mo-K_\alpha)$ 0.7107 Å, $\mu(Mo-K_\alpha)$ 121.47 cm⁻¹. A total of 3731 unique reflections were collected in the range $2.4 \leq 2\theta \leq 44^\circ$, of which 3383 having $I \geq 2.5\sigma(I)$ were used in the refinement. Data reduction and application of Lorentz and polarisation corrections were performed with program SUSCAD [14]; absorption corrections were applied using programme ABSORB [14].

Solution and refinement. The structure was solved by the direct methods routine in SHELX [14] to give the metal atom positions; all other non-hydrogen atoms were revealed in Fourier difference maps of successive blocked-matrix least-squares refinements. Phenyl rings were refined as rigid hexagonal groups (C–C 1.395 Å) with isotropic thermal parameters. Hydrogen atoms were placed in calculated positions (C–H 1.08 Å). In the final refinement cycles, with all non-hydrogen atoms and non-phenyl carbons anisotropic, the weighting scheme was $w = 12.3742 [\sigma^2(F) + 0.000046F^2]^{-1}$. The final R , R_w values were 0.032 and 0.032, respectively. Neutral Os atom scattering factors were taken from reference [15], while those for the remaining atoms were those incorporated in SHELX [14]. Six peaks of ca. 2 e Å⁻³ near the metal atoms were found in the final difference map and may indicate the presence of a small proportion of a second orientation of the Os₃ core within the same ligand polyhedron, as found for Ru₃(CO)₁₁(CNBu') [12,16]. However, further refinement on the basis of such a model did not lead to any significant improvement in the final R value.

The molecular structure and atom numbering scheme are shown in Fig. 1; atomic coordinates for non-hydrogen atoms are given in Table 3 and selected bond parameters are listed in Table 2. Supplementary material has been deposited and includes thermal parameters for non-hydrogen atoms, atomic coordinates and thermal parameters for hydrogen atoms, complete bond distance and bond angle tables, and observed and calculated structure factors.

Acknowledgements

This work was partially supported by the Australian Research Grants Scheme. M.L.W. was a Commonwealth Post-graduate Research Awardee. We thank Dr. M.R. Snow for use of X-ray facilities, and Dr M.A. Bennett (Research School of Chemistry, Australian National University) for a generous gift of sp.

References

- 1 M.I. Bruce, B.K. Nicholson and M.L. Williams, *J. Organomet. Chem.*, 243 (1983) 69.
- 2 M.I. Bruce, E. Horn, M.R. Snow and M.L. Williams, *J. Organomet. Chem.*, 255 (1983) 255.
- 3 M.I. Bruce, M.L. Williams and B.K. Nicholson, *J. Organomet. Chem.*, 258 (1983) 63.
- 4 A.J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, (1974) 1415.
- 5 M.I. Bruce, D.C. Kehoe, J.G. Matison, B.K. Nicholson, P.H. Rieger and M.L. Williams, *J. Chem. Soc., Chem. Commun.*, (1982) 442.
- 6 B.F.G. Johnson, J. Lewis and D. Pippard, *J. Chem. Soc., Dalton Trans.*, (1981) 407.
- 7 A.J. Deeming and S. Hasso, *J. Organomet. Chem.*, 88 (1975) C21.
- 8 J.R. Shapley, J.B. Keister, M.R. Churchill and B.G. DeBoer, *J. Am. Chem. Soc.*, 97 (1975) 4145.
- 9 J.B. Keister and J.R. Shapley, *Inorg. Chem.*, 21 (1982) 3304.

- 10 M.R. Churchill and B.G. DeBoer, *Inorg. Chem.*, 16 (1977) 2397.
- 11 M.I. Bruce, J.G. Matison and R.C. Wallis, *Aust. J. Chem.*, 35 (1982) 935.
- 12 M.I. Bruce, J.G. Matison, R.C. Wallis, J.M. Patrick, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1983) 2365.
- 13 B.F.G. Johnson and J. Lewis, *Inorg. Synth.*, 8 (1972) 92.
- 14 Programmes used in this structure determination included: SUSCAD and ABSORB, Data reduction and absorption correction programs for CAD4 diffractometer, J.M. Guss, University of Sydney (1976); SHELX, Programme for crystal structure determination, G.M. Sheldrick, University of Cambridge (1976).
- 15 W.C. Hamilton and J.A. Ibers, (Eds.), *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, Vol. 4.
- 16 M.I. Bruce, G.N. Pain, C. Hughes, J.M. Patrick, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, 307 (1986) 343.
- 17 M.I. Bruce, M.G. Humphrey, M.R. Snow, E.R.T. Tiekink and R.C. Wallis, *J. Organomet. Chem.*, 314 (1986) 311.