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SYNTHESES AND CHARACTERISATION OF $[Os_3(CO)_{11}(PRH_2)]$, $[(\mu_2\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}PRH)]$ (R = C_6H_5, $p\text{-}CH_3OC_6H_4$, C_6H_{11}) AND $[(\mu_2\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}PR)]$ (R = C_6H_5, C_6H_{11}). INTERCONVERSION OF CLUSTER-BOUND PHOSPHINE AND PHOSPHIDO LIGANDS. CRYSTAL AND MOLECULAR STRUCTURES OF $[(\mu_2\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}P(C_6H_5)H)]$ AND $[(\mu_2\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}PC_6H_5)]$

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Summary

Monoorganophosphines react with $Os_3(CO)_{12}$ in presence of trimethylamine oxide to give the phosphine-substituted cluster $[Os_3(CO)_{11}(PRH_2)]$ and the phosphido-bridged hydrido cluster $[(\mu_2\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}PRH)]$ (R = C_6H_5, $p\text{-}CH_3OC_6H_4$, C_6H_{11}). The thermolysis of $[Os_3(CO)_{11}(PRH)_2)]$ gave, under different conditions, $[(\mu_2\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}PRH)]$ and $[(\mu_2\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}PR)]$, and the thermolysis of $[(\mu_2\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}PRH)]$ gave $[(\mu_2\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}PR)]$ (R = C_6H_5, C_6H_{11}). All the compounds have been studied by IR, NMR (^{31}P and ^1H) and mass spectrometry. The structures of $[(\mu_2\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}P(C_6H_5)H)]$ and $[(\mu_2\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}PC_6H_5)]$ have been determined by X-ray crystallography.

The results obtained for the system $Os_3(CO)_{12}/PRH_2$ demonstrate a stepwise transformation of a terminally bonded PRH_2 ligand to a doubly bridging μ_2-PRH unit and finally to a triply bridging μ_3-PR group by successive hydrogen transfer and CO substitution processes.

Introduction

Primary phosphines (PRH_2) have been found to react with trinuclear carbonyl compounds $M_3(CO)_{12}$ (M = Fe, Ru) under rather mild conditions to give μ_3-PR-bridged dihydro clusters $[(\mu_2\text{-}H)_2M_3(CO)_9(\mu_3\text{-}PR]$ in fair yields [1—3].

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It is reasonable to assume that these reactions involve an initial substitution of a CO group in $M_3(CO)_{12}$ by the primary phosphines to give $M_3(CO)_{11}(PRH_2)$, with subsequent hydrogen migration and CO substitution processes giving $[(\mu_2\text{-H})M_3(CO)_{10}(\mu_2\text{-PRH})]$ and finally $[(\mu_2\text{-H})_2M_3(CO)_9(\mu_3\text{-PR})]$. None of the expected intermediates have, however, so far been observed and only the final product with a μ_3-bridging PR group could be obtained.

With the hope of substantiating the proposed scheme, we studied the reactions of primary phosphines with $Os_3(CO)_{12}$. Since the carbonyl groups of $Os_3(CO)_{12}$ are far less liable to substitution than those of its ruthenium and iron analogues [4], one might expect that in this case the intermediates might be stable enough to be isolated, so that the hypothesis of a stepwise formation of μ_3-PR bridged clusters might be checked. Although the thermal substitution of CO groups in $Os_3(CO)_{12}$ by tertiary phosphines or arsines is well documented [5—7], rather drastic conditions are necessary for such reactions. Other methods of substitution under mild conditions have been developed for mononuclear complexes; one such method is the use of Me_3NO which facilitates the removal of CO as CO_2 by oxidation [8]. Since this approach had already been sucessfully applied in the chemistry of $Os_3(CO)_{12}$ [9—11], we studied the reactions of PRH_2 with $Os_3(CO)_{12}$ in the presence of Me_3NO. The monosubstituted compounds $[Os_3(CO)_{11}(PRH_2)]$ and $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-PRH})]$ were indeed, obtained in this way, and their synthesis, as well as their stepwise transformation to $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-PRH})]$ and finally to $[(\mu_2\text{-H})_2Os_3(CO)_9(\mu_3\text{-PR})]$ are described below *.

Experimental

$Os_3(CO)_{12}$, $P(C_6H_5)H_2$ and $P(p\text{-}CH_3OC_6H_4)H_2$ were prepared by the literature methods [12—14]. $P(C_6H_{11})H_2$ and $P(C_6H_5)_2H$ were obtained from the Strem Chemical Corp. and Me_3NO from Fluka AG. The solvents used were dried over sodium/benzophenone and distilled under nitrogen. All operations were performed either under oxygen-free nitrogen or under vacuum.

Microanalyses were done at the Microanalytical Section of our department. Infrared spectra were recorded on a Zeiss IR spectrometer IMR-40. NMR (^{31}P and ^1H) were recorded on Bruker WP-80 FT and Bruker WM-250 FT spectrometers. Mass spectra were obtained with a Varian MAT 320 spectrometer at 70 eV. Melting points were determined in open capillaries using a Gallenkamp melting point apparatus, and are uncorrected.

(1) Reaction of $P(C_6H_5)H_2$ with $Os_3(CO)_{12}$

A solution of $Os_3(CO)_{12}$ (450 mg, 0.5 mmol), $P(C_6H_5)H_2$ (55 mg, 0.5 mmol) and $Me_3NO \cdot 2H_2O$ (55 mg, 0.5 mmol) in toluene (80 cm^3) was stirred at 60°C for 20 h. The yellow solution was cooled, whereupon 80 mg of $Os_3(CO)_{12}$ separated, and this was filtered off. The filtrate was concentrated under vacuum to a small volume (5 cm^3) and 5 g silica gel was added. The residue was taken to dryness under vacuum and transferred to a silica gel column made up with pentane at −30°C. The first, yellow fraction, eluted with 10/1 pentane/toluene gave $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-P(C_6H_5)H})]$ (50 mg, 12.5% based on

* *Note added in proof.* Results similar to the ones described here have meanwhile been obtained independently [33].

$Os_3(CO)_{12}$ reacted) and recrystallised from toluene to give yellow crystals. The second, yellow fraction, eluted with 5/1 pentane/toluene, gave [$Os_3(CO)_{11}$-($P(C_6H_5)H_2$) (150 mg, 37.5% based on $Os_3(CO)_{12}$ reacted) which was recrystallised from toluene. [(μ_2-H)$Os_3(CO)_{10}$(μ_2-$P(C_6H_5)H$)]: M.p. 157°C. Mass spec. *m/e* 960. Anal. Found: C, 20.14; H, 0.74; P, 3.45. Calcd. for $C_{16}H_7O_{10}POs_3$: C, 19.99; H, 0.73; P, 3.23%. [$Os_3(CO)_{11}(P(C_6H_5)H_2)$]: M.p. 106°C. Mass spec. *m/e* 988. Anal. Found: C, 21.07; H, 0.74; P, 2.80. Calcd. for $C_{17}H_7O_{11}POs_3$: C, 20.63; H, 0.70; P, 3.13%.

(2) Reaction of $P(p\text{-}CH_3OC_6H_4)H_2$ with $Os_3(CO)_{12}$

The reaction was carried out as in (1) with $Os_3(CO)_{12}$ (450 mg, 0.5 mmol), $P(p\text{-}CH_3OC_6H_4)H_2$ (70 mg, 0.5 mmol) and $Me_3NO \cdot 2\,H_2O$ (55 mg, 0.5 mmol) in toluene (80 cm^3). In the chromatography, the first, yellow fraction, eluted with 10/1 pentane/toluene gave [(μ_2-H)$Os_3(CO)_{10}$(μ_2-$P(p\text{-}CH_3OC_6H_4)$)] (40 mg, 10.5% based on $Os_3(CO)_{12}$ reacted). The second, yellow fraction, collected using 5/1 pentane/toluene, gave [$Os_3(CO)_{11}(P(p\text{-}CH_3OC_6H_4)H_2)$] (100 mg, 26.3% based on $Os_3(CO)_{12}$ reacted), which was recrystallised from toluene. [(μ_2-H)$Os_3(CO)_{10}$(μ_2-$P(p\text{-}CH_3OC_6H_4)H$)]: M.p. 160°C. Mass spec. *m/e* 993. Anal. Found: C, 20.64; H, 0.96; P, 3.35. Calcd. for $C_{17}H_9O_{11}POs_3$: C, 20.59; H, 0.90; P, 3.13%. [$Os_3(CO)_{11}(P(p\text{-}CH_3OC_6H_4)H_2)$]: M.p. 99°C. Mass spec. *m/e* 1018. Anal. Found: C, 21.41; H, 0.94; P, 3.02. Calcd. for $C_{18}H_9O_{11}POs_3$: C, 21.20; H, 0.88; P, 3.04%.

(3) Reaction of $P(C_6H_{11})H_2$ with $Os_3(CO)_{12}$

(a) The reaction was carried out as in (1) with $Os_3(CO)_{12}$ (450 mg, 0.5 mmol), $P(C_6H_{11})H_2$ (58 mg, 0.5 mmol) and $Me_3NO \cdot 2\,H_2O$ (55 mg, 0.5 mmol) in toluene (80 cm^3) at 100°C for 20 h. In the chromatography, the first, yellow fraction, eluted with 10/1 pentane/toluene, gave [$Os_3(CO)_{11}(P(C_6H_{11})H_2)$] (150 mg, 37.5% based on $Os_3(CO)_{12}$ reacted) which was recrystallised from toluene. M.p. 93°C. Mass spec. *m/e* 996. Anal. Found: C, 20.63; H, 1.24; P, 3.18. Calcd. for $C_{17}H_{13}O_{11}POs_3$: C, 20.51; H, 1.30; P, 3.11%.

(b) The reaction was carried out as in (1) with $Os_3(CO)_{12}$ (300 mg, 0.33 mmol), $P(C_6H_{11})H_2$ (45 mg, 0.38 mmol) and $Me_3NO \cdot 2\,H_2O$ (75 mg, 0.67 mmol) in toluene (80 cm^3). In the chromatography, the first, yellow fraction, eluted with pentane alone, gave the yellow [(μ_2-H)$Os_3(CO)_{10}$(μ_2-$P(C_6H_{11})H$)] (52 mg, 16% based on $Os_3(CO)_{12}$ reacted). The second, yellow fraction, eluted with 10/1 pentane/toluene, gave [$Os_3(CO)_{11}(P(C_6H_{11})H_2)$] (95 mg, 27% based on $Os_3(CO)_{12}$ reacted). [(μ_2-H)$Os_3(CO)_{10}$(μ_2-$P(C_6H_{11})H$)]: M.p. 114°C. Mass spec. *m/e* 968. Anal. Found: C, 20.37; H, 1.35; P, 3.21. Calcd. for $C_{16}H_{13}O_{10}$-POs_3: C, 19.86; H, 1.34; P, 3.21%.

(4) Reaction of $P(C_6H_5)_2H$ with $Os_3(CO)_{12}$

The reaction was carried out as in (1) with $Os_3(CO)_{12}$ (450 mg, 0.5 mmol), $P(C_6H_5)_2H$ (93 mg, 0.5 mmol) and $Me_3NO \cdot 2\,H_2O$ (55 mg, 0.5 mmol) in toluene (80 cm^3) at 100°C for 20 h. In the chromatography, the first, yellow fraction, eluted with 10/1 pentane/toluene, gave small amount of $Os_3(CO)_{12}$ (50 mg). The second yellow fraction, eluted with 5/1 pentane/toluene, gave [$Os_3(CO)_{11}(P(C_6H_5)_2H)$] (100 mg, 22% based on $Os_3(CO)_{12}$ reacted) and was recrystallised from toluene. M.p. 89°C. Mass spec. *m/e* 1065. Anal. Found:

C, 25.81; H, 1.23; P, 2.82%. Calcd. for $C_{23}H_{11}O_{11}POs_3$: C, 25.92; H, 1.03; P, 2.91.

Thermal reactions of [$Os_3(CO)_{11}(PRH_2)$] and [(μ_2-H)$Os_3(CO)_{10}$(μ_2-PRH)] (R = C_6H_5, C_6H_{11})

(a) A solution of [$Os_3(CO)_{11}(PRH_2)$] (120 mg) in toluene (40 cm^3) was stirred at 100°C for 24 h.The resulting yellow solution was concentrated under vacuum to a small volume (5 cm^3) and silica gel (5 g) was added. The residue was dried under vacuum and chromatographed on silica gel. The first, yellow fraction, eluted with 5/1 pentane/toluene, gave [(μ_2-H)$Os_3(CO)_{10}$(μ_2-PRH)] (60 to 66%).

(b) A solution of [$Os_3(CO)_{11}(PRH_2)$] (120 mg) in nonane (40 cm^3) was refluxed for 3 h. The solution was worked up as under (a), and the product purified by chromatography on silica gel. The first, yellow fraction, eluted with 10/1 pentane/toluene gave pale yellow compound [(μ_2-H)$_2Os_3(CO)_9$(μ_3-PR)] (55 to 65%) which was recrystallised from toluene.

[(μ_2-H)$_2Os_3(CO)_9$(μ_3-PC_6H_5)]: M.p. 134°C. Mass spec. *m/e* 937. Anal. Found: C, 19.59; H, 0.66; P, 3.52. Calcd. for $C_{15}H_7O_9POs_3$: C, 19.32; H, 0.75; P, 3.32%.

[(μ_2-H)$_2Os_3(CO)_9$(μ_3-PC_6H_{11})]: M.p. 121°C. Mass spec. *m/e* 940. Anal. Found: C, 19.39; H, 1.42; P, 3.44. Calcd. for $C_{15}H_{13}O_9POs_3$: C, 19.19; H, 1.38; P, 3.30%.

(c) A solution of [(μ_2-H)$Os_3(CO)_{10}$(μ_2-PRH)] (100 mg) in nonane (40 cm^3) was refluxed for 2 h. After the usual work up, the compound was separated by chromatography. The pale yellow fraction eluted with 10/1 pentane/toluene gave the compound [(μ_2-H)$_2Os_3(CO)_9$(μ_3-PR)] (60 to 70%).

Crystallographic analysis. General data and solution and refinement of the structures

Single crystals for X-ray work were grown by cooling solutions of [(μ_2-H)$Os_3(CO)_{10}$(μ_2-P(C_6H_5)H)] and [(μ_2-H)$_2Os_3(CO)_9$(μ_3-PC_6H_5)] in toluene at −20°C for several days. All diffraction data were obtained using a Syntax-P3 four circle diffractometer. The space groups as determined by diffractometry were checked by examination of precession photographs for systematic absences. Cell parameters and X-ray diffraction intensities were obtained on the same instrument at 233 K with the parameters given in Table 1. One standard reflection was measured for every 100 reflections during data collection in order to check the crystal and instrument stability. No decrease in intensity was observed during the time of measurement. A total of 2659 reflections were collected for [(μ_2-H)$Os_3(CO)_{10}$(μ_2-P(C_6H_5)H)], of which 2076 reflections having $I > 4\sigma$ were used to solve and refine the structure. For [(μ_2-H)$_2Os_3(CO)_9$(μ_3-PC_6H_5)], a total of 2434 reflections were collected from which 1837 reflections having $I > 4\sigma$ were used to solve and refine the structure. The intensities were corrected for absorption by empirical methods [15]. The structures were solved by direct methods and refined by least squares refinements using the SHELXTL program [16]. The positions of the bridging hydrogens and other hydrogens were found by difference electron density

TABLE 1

EXPERIMENTAL DATA FOR THE DIFFRACTION STUDY OF $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-P}(C_6H_5)H)]$ AND $[(\mu_2\text{-H})_2Os_3(CO)_9(\mu_3\text{-PC}_6H_5)]$

Parameter or Expt. detail	$[HOs_3(CO)_{10}(P(C_6H_5)H)]$	$[H_2Os_3(CO)_9(PC_6H_5)]$
(A) Crystal parameters at —40°C		
a (Å)	17.71(4)	9.50(1)
b (Å)	8.71(1)	14.45(1)
c (Å)	18.72(5)	18.07(1)
α (deg.)	90.00(16)	90.00(5)
β (deg.)	134.66(12)	126.33(4)
γ (deg.)	90.00(15)	90.00(5)
V (Å^3)	2052.03	1998.6
Z	4	4
mol. wt.	960.63	932.63
ρ (calcd.) (g cm^{-3})	3.11	3.10
μ (calcd.) (cm^{-1})	197.5	202.8
Space group	$P\,2_1/c$	$P\,2_1/c$
$F(000)$	1700	1648
(B) Measurement of intensity data		
Monochromator	graphite	graphite
Radiation	Mo-K_α (λ = 0.71069 Å)	Mo-K_α (λ = 0.71069 Å)
Ω scan $\Delta\omega$ (deg)	1.2	1.1
$2\theta_{max}$ (deg)	40	42
Background/peak time	0.4	0.4
Reflections measured	$+h, +k, \pm l$	$+h, +k, \pm l$
Reflections collected	2659	2434
Reflections remaining	2076	1837
Significance test	$F_0 > 4\sigma(F_0)$	$F_0 > 4\sigma(F_0)$
Scan speed (variable) (deg. min^{-1})	1.1—29.3	1.1—29.3

syntheses and are not refined. The refinement converged at $R_1 = 0.028$ and $R_2 = 0.034$ for $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-P}(C_6H_5)H)]$ and $R_1 = 0.050$ and $R_2 = 0.059$ for $[(\mu_2\text{-H})Os_3(CO)_9(\mu_3\text{-PC}_6H_5)]$, respectively. For $[(\mu_2\text{-H})_2Os_3(CO)_9\text{-}(\mu_3\text{-PC}_6H_5)]$, the phenyl group was found to be disordered over the two positions given by $C_1...C_6$ (55%) and C(X1)...C(X6) (45%), respectively. Their parameters were refined by rigid group methods [16] (d_{C-C} = 1.395 Å, C—C—C = 120°).

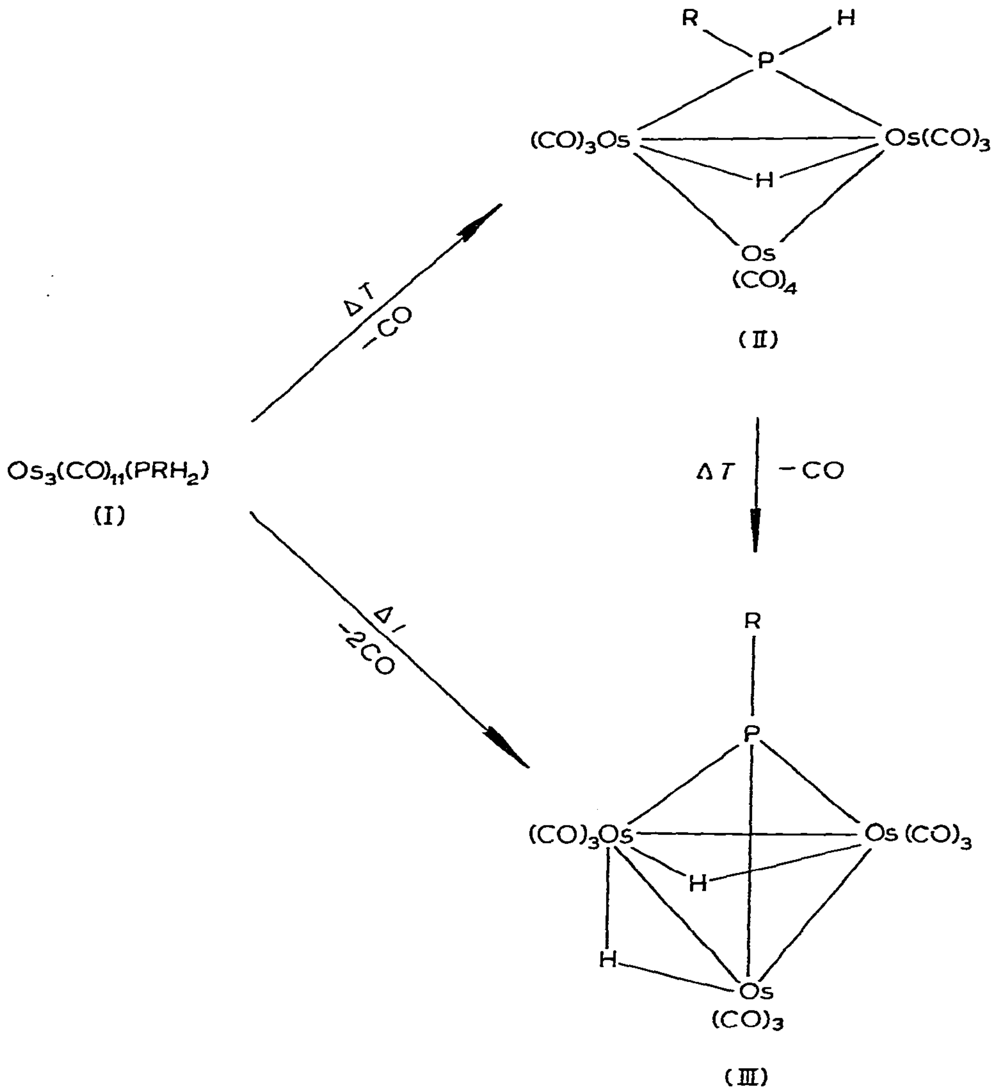
Results and discussion

In the presence of Me_3NO, primary phosphines react with $Os_3(CO)_{12}$ to give the monosubstituted cluster compounds I.

$$Os_3(CO)_{12} + PRH_2 \xrightarrow[\text{Toluene, } 60^\circ C, 20\,h]{Me_3NO} \underset{(I)}{[Os_3(CO)_{11}(PRH_2)]} + \underset{(II)}{[HOs_3(CO)_{10}(PRH)]}$$

($R = C_6H_5$, $p\text{-}CH_3OC_6H_4$, C_6H_{11})

In addition, depending on the conditions, the PRH-bridged cluster hydrides II are also obtained, in lower yields. The substitution products I, when heated to higher temperatures are transformed into clusters with doubly or triply bridging phosphorus ligands by stepwise loss of up to two CO ligands and concomitant hydrogen migrations accompanied by formation of additional Os—P bonds:



Thus, in the case of the formation of $[(\mu_2\text{-H})_2Os_3(CO)_9(\mu_3\text{-PR})]$ from PRH_2 and $Os_3(CO)_{12}$, all the expected intermediates are isolated in pure form. No intermediates of type I or II are found in the course of analogous reactions of $M_3(CO)_{12}$ (M = Fe, Ru) [1—3] with PRH_2, where only the μ_3-PR-bridged clusters of type III are obtained.

It seems very probable that the reactions of $M_3(CO)_{12}$ (M = Fe, Ru) with PRH_2 generally involve intermediates analogous to I and II. Owing to the relative inertness of osmium carbonyl groups towards substitution [4,17], the intermediates I and II can be isolated in the case of $Os_3(CO)_{12}$, whereas with

$Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ with their more reactive metal carbonyl groups, the conditions necessary for the initial substitution process will at the same time promote the transformation of intermediates of types I and II into the final products of type III. The interconversion of I to II and III by hydrogen migration and substitution processes bears some resemblance to processes known for the transformation of organic ligands in a cluster environment. For example, it has been demonstrated that the interconversion of cluster-bound methyl and methylene ligands occurs in the case of $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-CH}_3)]$ to give $[(\mu_2\text{-H})_2Os_3(CO)_{10}(\mu_2\text{-CH}_2)]$ and finally to $[(\mu_2\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})]$ [18] and in the case of $(\mu_2\text{-H})Os_3(CO)_{10}(\mu\text{-C(O)CH}_3)$ [19] to give $[(\mu_2\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})]$. Similar stepwise hydrogen migration processes have been documented for $[HFe_3(CO)_9(CH_3C{=}NH)]$ [20].

Monosubstituted derivatives $[Os_3(CO)_{11}(PRH_2)]$ *(R =* C_6H_5*,* $p\text{-}CH_3OC_6H_4$*,* C_6H_{11}*) and* $[Os_3(CO)_{11}(P(C_6H_5)_2H)]$ *(I)*

The monosubstituted derivatives were all prepared by the reactions of primary and secondary phosphines with $Os_3(CO)_{12}$ in the presence of Me_3NO in toluene. All the compounds gave clear and unambiguous mass spectra, showing prominent molecular ions and stepwise loss of 11 carbonyl groups down to an Os_3L^+ core. IR and NMR (^{31}P and ^{1}H) data are given in Table 2. The solution IR $\nu(CO)$ spectra of all the compounds are essentially identical. The $\nu(CO)$ bands are due to terminal carbonyl groups, and the pattern of bands is similar to that observed for (equatorially) monosubstituted phosphine derivatives [10,21]. This evidence alone suggests that the phosphine ligand is equatorially bonded in all the derivatives. In general the substituting ligand L occupies an equatorial site [22,23] for simple substitution products of type $[Os_3(CO)_{11}(L)]$.

The ^{31}P NMR spectra of these compounds show low-field shifts relative to the signals of the free ligands as expected for coordinated phosphines. In the ^{1}H NMR spectra of these compounds, the resonances due to the R(C_6H_5, $p\text{-}CH_3OC_6H_4$, C_6H_{11}) groups are quite normal, and the signal for the proton

TABLE 2

IR, NMR (^{31}P AND ^{1}H) DATA FOR OSMIUM CLUSTERS

No.	Compound	^{31}P NMR ^{a}	^{1}H NMR ^{b}		IR ^{e} ($\nu(CO)$)
1	$Os_3(CO)_{11}(P(C_6H_5)H_2)$	−112.8	a) C_6H_5:	7.6(m)	2110s, 2082s, 2056s, 2036s, 2019s, 2000w, 1989s, 1976w
			b) PH:	6.66(d) (J(PH) = 396 Hz)	
2	$Os_3(CO)_{11}(P(C_6H_4OCH_3)H_2)$	−114.6	a) C_6H_4:	7.66(m), 7.20(m)	2110w, 2069w, 2057s, 2036s, 2019s, 2001w, 1989w, 1977w
			b) PH:	6.46(d) (J(PH) = 373 Hz)	
			c) OCH_3:	3.88(s)	
3	$Os_3(CO)_{11}(P(C_6H_{11})H_2)$ ^{c}	−96.41	a) C_6H_{11}:	0.86 to 2.25(m)	2100w, 2055s, 2034w, 2017s, 2001w, 1988m, 1974m
			b) PH:	5.11(dd) (J(HH) = 4.4 Hz) (J(PH) = 364 Hz)	

TABLE 2 (continued)

No.	Compound	^{31}P-NMR [a]	^{1}H-NMR [b]		IR [e] (ν(CO))
4	$Os_3(CO)_{11}(P(C_6H_5)_2H)$	—40.76	a) C_6H_5:	7.54(m)	2109s, 2079w, 2069w, 2053s, 2033w, 2013s, 1988m, 1975m
			b) PH:	7.42(d) (J(PH) = 343 Hz)	
5	$HOs_3(CO)_{10}(P(C_6H_5)H)$	—37.8	a) C_6H_5:	7.47(m)	2105s, 2061s, 2053s, 2021s, 2005s, 1992s, 1980w
			b) OsHOs:	—19.10(dd) J(HH) = 4.3 Hz) (J(PH) = 18 Hz)	
			c) PH:	7.35(dd) (J(HH) = 4.3 Hz) (J(PH) = 422 Hz)	
6	$HOs_3(CO)_{10}(P(C_6H_4OCH_3)H)$	—38.13	a) C_6H_4:	7.10(m), 7.50(m)	2106s, 2061s, 2053s, 2022s, 2007w, 1992w
			b) OsHOs:	—19.04(dd) (J(HH) = 4 Hz) (J(PH) = 18 Hz)	
			c) PH:	7.37(dd) (J(HH) = 4 Hz) (J(PH) = 421 Hz)	
			d) OCH_3:	3.85(s)	
7	$HOs_3(CO)_{10}(P(C_6H_{11})H)$ [c]	—14.08	a) C_6H_{11}:	0.55 to 2.45(m)	2105s, 2059s, 2052s, 2021m, 2003w, 1985w
			b) OsHOs:	—19.56(dd) (J(HH) = 4.3 Hz) (J(PH) = 14.9 Hz)	
			c) PH:	5.76m (J(HH) = 4.3 Hz) (J(H(C_6H_{11}—H) = 9.4 Hz) (J(PH) = 392 Hz)	
8	$H_2Os_3(CO)_9(PC_6H_5)$	119.13	a) C_6H_5:	8.05(m), 7.65(m)	2107s, 2074s, 2046s, 2034w, 2021w, 2005s, 1988m, 1973m
			b) OsHOs:	—21.05(d) (J(PH) = 10.4 Hz)	
9	$H_2Os_3(CO)_9(PC_6H_{11})$ [c]	155.03	a) C_6H_{11}:	2.90 to 1.09(m)	2106m, 2071s, 2042s, 2018w, 2002s, 1983m, 1967m
			b) OsHOs:	—21.45(d) (J(PH) = 9.8 Hz)	

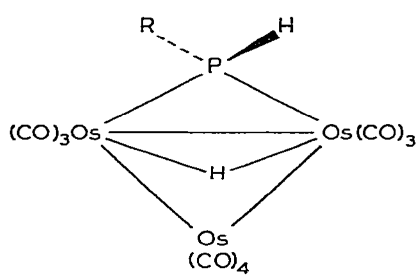
[a] δ Value in ppm rel. H_3PO_4 in toluene. [b] δ Value in ppm rel. ext. TMS (in acetone-d_6) (m = multiplet, d = doublet, s = singlet). [c] In $CDCl_3$. [e] cm^{-1} in toluene (s = strong, m = medium, w = weak).

attached to the phosphorus atom appears as a doublet with J(PH) coupling in the range from 342 to 396 Hz. In the case of the cyclohexylophosphine derivative, in addition to the phosphorus coupling, another coupling arises from the α-hydrogen atom of the cyclohexyl group (J(HH) = 4.4 Hz).

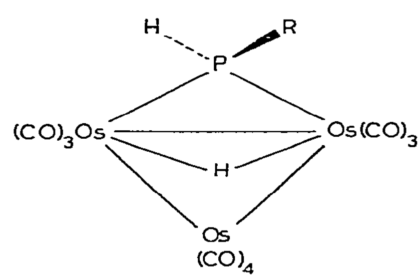
[(μ_2-H)$Os_3(CO)_{10}$(μ_2-PRH)] (R = C_6H_5, p-$CH_3OC_6H_4$, C_6H_{11}) (II)

These compounds were obtained either by the reactions of primary phosphines with $Os_3(CO)_{12}$ in presence of Me_3NO or by the thermolysis of [$Os_3(CO)_{11}(PRH_2)$] in toluene. They all show the parent molecular ions in their mass spectra, with additional peaks indicating the successive loss of up to 10 carbonyl groups. IR and NMR (^{31}P and ^{1}H) data are given in Table 2. These compounds are structurally comparable to [(μ_2-H)$Os_3(CO)_{10}$(μ-NC_5H_4)] [24] and [(μ_2-H)$Os_3(CO)_{10}$(μ-PhC=NMe)] [25], as evidenced by the strong similarity of the IR bands in the ν(CO) region, although in these compounds the bridging units are diatomic in contrast to the monoatomic μ_2-ligand in II. The ^{31}P NMR signals of compounds II are observed at lower fields than those of [$Os_3(CO)_{11}(PRH_2)$] (I), as expected for doubly bridging phosphido groups.

There is a possibility of *syn* and *anti* isomers for these compounds as shown below, in which case complicated ^{1}H NMR spectra are expected. The spectra



and



observed for II are quite simple, however, and indicate that only one of the possible isomers is present in solution. That the observed multiplicity of the signals arising from the bridging and the phosphorus-bonded hydrogens is due to coupling phenomena from just one isomer and not to the presence of an isomeric mixture has been demonstrated by measuring the spectra at 80 MHz and 250 MHz. It is probable then that the structure observed for [(μ_2-H)$Os_3(CO)_{10}$(μ_2-P(C_6H_5)H)] in the solid state (see later) also corresponds to the structures adopted by compounds II in solution.

Thus, in the ^{1}H NMR spectra (Table 2) of compounds II, a doublet of doublets appears around −19 ppm (J(PH) = 15 to 18 Hz; J(HH) = 4 to 4.3 Hz) for the bridging hydride, which is the result of the coupling by both the phosphorus and the hydrogen bonded to the phosphorus atom. The signal due to the phosphorus-bonded hydrogen again appears as a doublet of doublets (coupled to both phosphorus and the bridging hydrogen). In the case of the cyclohexyl compound, this signal is further split by the α-hydrogen atom of the cyclohexyl group (cf. Table 2). The resonances due to the R (C_6H_5, p-$CH_3OC_6H_4$, C_6H_{11}) group are as expected.

[(μ_2-H)$_2$Os$_3$(CO)$_9$(μ_3-PR)] (R = C_6H_5, C_6H_{11}) (III)

These compounds were obtained from the thermolysis of either [$Os_3(CO)_{11}$-(PRH_2)] or [(μ_2-H)$Os_3(CO)_{10}$(μ_2-PRH)] in refluxing nonane. The mass spectra of these compounds show the molecular ion peaks with successive loss of up to 9 carbonyl groups. The IR and NMR (^{31}P and ^{1}H) data are given in Table 2. The IR spectra of these compounds are very similar to those of the known iron and ruthenium analogues [(μ_2-H)$_2M_3(CO)_9$(μ_3-PR)] (M = Fe, Ru) [1—3], indicating that the structures are quite similar. This has been further established by the X-ray structure determination of [(μ_2-H)$_2Os_3(CO)_9$(μ_3-PC_6H_5)] (see later). The expected low field shifts in the ^{31}P NMR spectra of these compounds for the μ_3-bridged PR group relative to [$Os_3(CO)_{11}(PRH_2)$] and [(μ_2-H)$Os_3(CO)_{10}$-(μ_2-PRH)] are observed, but the magnitude of the shift is unusually small compared with that of the analogous compounds [(μ_2-H)$_2M_3(CO)_9$(μ_3-PR)] (M = Fe, Ru) [1—3]. However, there is a consistent shift of around 100 ppm towards higher fields on going from iron to analogous ruthenium compounds (Table 3). A similar feature is found for the osmium compounds, where there is a change of around 160 ppm towards higher fields with respect to the corresponding ruthenium compounds (Table 3).

It appears that the paramagnetic contribution of the metal—metal bonding system to the ^{31}P chemical shift decreases with increasing stability of M—M bonds [17] in the order Fe > Ru > Os, as predicted by H. Schäfer [26].

The ^{1}H NMR spectra of the compounds III show signals due to bridging hydrides as doublets around —21 ppm (*J*(PH) = 10 Hz), indicating chemically equivalent hydrogen ligands (Table 2).

Structure of [(μ_2-H)$Os_3(CO)_{10}$(μ_2-P(C_6H_5)H)]

The molecular structure of the compound is shown in Fig. 1, and the structural parameters are given in Tables 4—7. The molecule consists of a triangular cluster of mutually bonded osmium atoms, ten terminally bonded carbonyl ligands, a μ_2-hydride and a μ_2-P(C_6H_6)H ligand. The osmium triangle is slightly distorted and has one short bond, Os(1)—Os(2) = 2.842(1) Å and two longer bonds Os(2)—Os(3) = 2.888(1) Å and Os(1)—Os(3) = 2.876(1) Å. The longer distances agree satisfactorily with the distance of 2.877(3) Å which is the average Os—Os length in $Os_3(CO)_{12}$ [27]. In contrast to the expected net shortening of the dibridged linkage characteristic of Os(μ-H) (μ-X)Os systems containing relatively small X atoms (X = C, N) [28—30], there is no shortening of the dibridged bond (Os(2)—Os(3) = 2.888(1) Å) compared with the non-bridged bonds (Os(1)—Os(2) = 2.842(1) Å, Os(1)—Os(3) = 2.876(1) Å). The

TABLE 3

^{31}P NMR (ppm) DATA FOR [(μ_2-H)$_2M_3(CO)_9$(μ_3-PR)] (M = Fe, Ru, Os) [1—3] IN TOLUENE RELATIVE TO H_3PO_4

R	Fe	Ru	Os
C_6H_5	380	279	119
C_6H_{11}	432	328	155
p-$CH_3OC_6H_4$	382	281	

larger covalent radius of P (1.10 Å) than of C (0.77 Å) or N (0.70 Å) [31] may be responsible for this effect.

The phosphorus atom of the phosphide ligand symmetrically bridges the Os(2)—Os(3) edge with Os(2)—P = 2.348(4) Å and Os(3)—P = 2.341(6) Å,

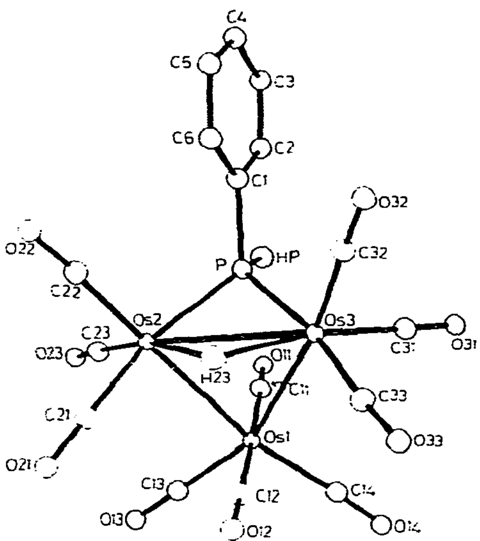


Fig. 1. The molecular structure of $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-P}(C_6H_5)H)]$.

the average of which (2.345 Å) is comparable to that observed (2.367 Å) for $[Os_5(CO)_{15}(\mu_4\text{-POMe})]$ [32]. The phosphorus atom lies 1.771 Å below the triosmium plane, with a dihedral angle of 73.4° between the planes Os(1)—Os(2)—Os(3) and Os(2)—P—Os(3). The hydride ligand bridges the same edge, with Os(2)—H(23) = 1.8 Å and Os(3)—H(23) = 1.9 Å, and is 1.1 Å above the triosmium plane, with a dihedral angle of 103° between the planes Os(1)—Os(2)—Os(3) and Os(2)—H(23)—Os(3).

Two of the three osmium atoms have three terminal carbonyl groups, whereas the third one has four. The Os—C distances range from 1.89 Å to 1.98 Å (average 1.92 Å) and C—O distances ranging from 1.09 Å to 1.13 Å, the average being 1.12 Å. The Os—C—O angles have values from 174.0(1.7)° to 178.9(1.9)°, indicating almost linear carbonyl groups. The ten Os—C_{CO} bonds fall into the following different chemical environments: the shortest pairs are Os(2)—C(23) = 1.91(2) Å and Os(3)—C(31) = 1.89(2) Å (*trans* to H) and Os(2)—C(21) = 1.94(2) Å and Os(3)—C(33) = 1.90(2) Å (*trans* to P); the pair Os(1)—C(11) = 1.91(2) Å and Os(1)—C(12) = 1.98(2) Å involve mutually *trans* axial carbonyl groups on Os(1), the remaining two pairs (Os(1)—C(13) = 1.93(2) Å and Os(1)—C(14) = 1.92(2) Å, Os(2)—C(22) = 1.90(2) Å and Os(3)—C(32) = 1.91(2) Å) are *trans* to osmium atoms (see Fig. 1 and angles in Table 7). The angles between Os—C_{CO} bonds which are mutually *cis* to one another range from 89.6 to 97.9°.

An approximate C_s symmetry is observed for the $(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-P})$ portion of the molecule. The equatorial carbonyl ligands, instead of lying

TABLE 4

FRACTIONAL COORDINATES (WITH E.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS [Å^2] FOR [$HOs_3(CO)_{10}(P(C_6H_5)H)$] [a]

Atom	x/a	y/b	z/c	U
Os(1)	0.7110(1)	0.1822(1)	0.3480(1)	
Os(2)	0.7732(1)	0.1858(1)	0.2435(1)	
Os(3)	0.6311(1)	−0.0504(1)	0.1999(1)	
P	0.8105(3)	−0.0748(5)	0.2887(3)	
C(11)	0.8362(11)	0.0690(18)	0.4525(10)	0.031(4)
O(11)	0.9136(9)	0.0101(14)	0.5199(8)	
C(12)	0.5809(13)	0.2896(20)	0.2306(12)	0.043(4)
O(12)	0.5096(9)	0.3526(13)	0.1677(9)	
C(13)	0.7814(13)	0.3693(20)	0.4201(13)	0.047(4)
O(13)	0.8215(9)	0.4812(13)	0.4614(9)	
C(14)	0.6501(13)	0.1359(20)	0.3993(12)	0.042(4)
O(14)	0.6152(10)	0.1192(16)	0.4307(10)	
C(21)	0.7084(12)	0.3854(19)	0.1963(12)	0.039(4)
O(21)	0.6735(11)	0.5055(14)	0.1699(11)	
C(22)	0.7990(12)	0.1858(18)	0.1606(11)	0.034(4)
O(22)	0.8128(10)	0.1915(16)	0.1113(9)	
C(23)	0.9100(13)	0.2613(19)	0.3633(12)	0.042(4)
O(23)	0.9865(8)	0.3031(14)	0.4326(8)	
C(31)	0.6351(13)	−0.2040(21)	0.2729(13)	0.045(4)
O(31)	0.6398(10)	−0.2974(16)	0.3174(10)	
C(32)	0.5821(12)	−0.1793(20)	0.0917(12)	0.037(4)
O(32)	0.5494(9)	−0.2556(13)	0.0268(8)	
C(33)	0.4884(12)	0.0081(17)	0.1252(10)	0.030(4)
O(33)	0.4029(8)	0.0309(15)	0.0801(8)	
C(1)	0.8518(10)	−0.2058(16)	0.2478(10)	0.022(3)
C(2)	0.9274(12)	−0.3174(19)	0.3142(11)	0.036(4)
C(3)	0.9595(13)	−0.4228(20)	0.2849(12)	0.043(4)
C(4)	0.9168(13)	−0.4137(21)	0.1883(13)	0.047(4)
C(5)	0.8409(14)	−0.3047(23)	0.1197(14)	0.056(5)
C(6)	0.8088(12)	−0.1989(20)	0.1495(12)	0.041(4)
H(P)	0.900	−0.154	0.391	0.08
H(23)	0.633	0.133	0.150	0.08

[a] H(P) stands for the hydrogen atom bonded to phosphorus. Hydrogen positions of the phenyl group correspond to the expected ones.

TABLE 5

ANISOTROPIC THERMAL PARAMETERS FOR [$HOs_3(CO)_9(P(C_6H_5)H)$] [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	0.032	0.030	0.031	−0.002	0.023	0.001
Os(2)	0.030	0.027	0.029	0.006	0.021	0.003
Os(3)	0.027	0.025	0.026	0.003	0.018	0.003
P	0.034(2)	0.031(2)	0.026(2)	0.005(2)	0.021(2)	0.005(2)
O(11)	0.054(7)	0.066(8)	0.031(6)	0.010(6)	0.028(6)	0.016(6)
O(12)	0.052(7)	0.041(8)	0.064(8)	0.009(6)	0.034(7)	0.016(6)
O(13)	0.057(8)	0.042(7)	0.057(8)	−0.009(6)	0.031(7)	−0.016(6)
O(14)	0.079(9)	0.079(10)	0.081(9)	−0.032(8)	0.069(8)	−0.037(8)
O(21)	0.072(9)	0.033(8)	0.112(11)	0.028(7)	0.064(9)	0.023(7)
O(22)	0.083(9)	0.081(10)	0.053(8)	0.010(7)	0.058(8)	0.011(8)
O(23)	0.040(7)	0.062(8)	0.041(7)	0.001(6)	0.020(6)	−0.012(6)
O(31)	0.072(9)	0.075(10)	0.089(10)	0.053(9)	0.064(9)	0.027(8)
O(32)	0.062(8)	0.043(7)	0.032(6)	0.001(6)	0.027(6)	0.007(6)
O(33)	0.034(7)	0.066(9)	0.046(7)	−0.003(6)	0.028(6)	0.003(6)

[a] Anisotropic thermal parameters in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^*)]$. E.s.d.'s for Os are less than 0.001.

TABLE 6

BOND LENGTHS WITH E.s.d.'s (Å) FOR [$HOs_3(CO)_{10}(P(C_6H_5)H)$]

Atoms	Length	Atoms	Length
Os(1)—Os(2)	2.842(5)	C(11)—O(11)	1.14(2)
Os(1)—Os(3)	2.876(5)	C(12)—O(12)	1.09(2)
Os(2)—Os(3)	2.888(5)	C(13)—O(13)	1.13(2)
Os(2)—P	2.348(6)	C(14)—O(14)	1.12(4)
Os(3)—P	2.342(6)	C(21)—O(21)	1.14(2)
Os(2)—H(23)	1.82	C(22)—O(22)	1.11(3)
Os(3)—H(23)	1.87	C(23)—O(23)	1.09(2)
Os(1)—C(11)	1.90(1)	C(31)—O(31)	1.13(3)
Os(1)—C(12)	1.97(1)	C(32)—O(32)	1.13(2)
Os(1)—C(13)	1.91(2)	C(33)—O(33)	1.12(2)
Os(1)—C(14)	1.92(3)	C(1)—C(2)	1.40(2)
Os(2)—C(21)	1.92(2)	C(2)—C(3)	1.38(3)
Os(2)—C(22)	1.90(3)	C(3)—C(4)	1.39(3)
Os(2)—C(23)	1.92(1)	C(4)—C(5)	1.39(2)
Os(3)—C(31)	1.88(2)	C(5)—C(6)	1.39(4)
Os(3)—C(32)	1.91(2)	C(6)—C(1)	1.40(3)
Os(3)—C(33)	1.91(2)	P—H(P)	1.5
		P—C(1)	1.80(2)

strictly in the triosmium plane, are somewhat displaced in the direction of the bridging hydride ligand (individual displacements of carbonyl oxygen atoms from the Os(1)—Os(2)—Os(3) plane are: 0.26 Å for O(13), 0.03 Å for O(14), 0.29 Å for O(22) and 0.25 Å for O(32)).

TABLE 7

BOND ANGLES WITHIN THE [$HOs_3(CO)_{10}(P(C_6H_5)H)$] CLUSTER

Atoms	Angle (deg.)	Atoms	Angle (deg.)
Os(3)—Os(1)—Os(2)	60.7(1)	Os(2)—C(21)—O(21)	177.5(1.9)
Os(2)—Os(3)—Os(1)	59.1(1)	Os(2)—C(22)—O(22)	177.3(1.5)
Os(1)—Os(2)—Os(3)	60.3(1)	Os(2)—C(23)—O(23)	177.8(2.4)
Os(3)—P—Os(2)	76.0(2)	Os(3)—C(31)—O(31)	178.3(2.0)
P—Os(3)—Os(2)	52.1(1)	Os(3)—C(32)—O(32)	177.2(2.1)
P—Os(2)—Os(3)	51.9(2)	Os(3)—C(33)—O(33)	174.8(1.4)
P—Os(2)—Os(1)	83.6(2)	Os(2)—P—C(1)	123.6(6)
P—Os(3)—Os(1)	83.0(2)	Os(3)—P—C(1)	120.8(4)
Os(1)—C(11)—O(11)	174.8(1.6)	Os(2)—H(23)—Os(3)	103
Os(1)—C(12)—O(12)	177.7(2.0)	H(23)—Os(3)—Os(2)	38
Os(1)—C(13)—O(13)	178.8(1.4)	H(23)—Os(2)—Os(3)	39
Os(1)—C(14)—O(14)	175.3(1.6)		
CO groups trans to P		*CO group trans to Os(2)*	
P—Os(2)—C(21)	165.0(6)	Os(2)—Os(1)—C(14)	166.0(6)
P—Os(3)—C(33)	169.5(6)	*CO group trans to Os(3)*	
CO groups trans to H		Os(3)—Os(1)—C(13)	156.0(9)
H(23)—Os(3)—C(31)	167.0	*CO groups trans to Os(1)*	
H(23)—Os(2)—C(23)	163.0	Os(1)—Os(2)—C(22)	173.8(4)
CO groups trans on Os(1)		Os(1)—Os(3)—C(32)	170.1(6)
C(11)—Os(1)—C(12)	174.9		

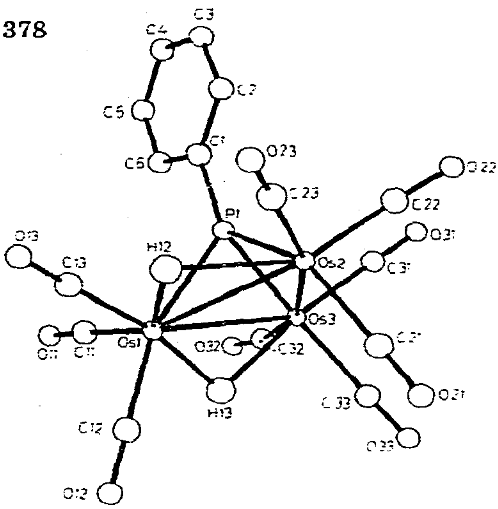


Fig. 2. The molecular structure of $[(\mu_2\text{-H})_2Os_3(CO)_9(\mu_3\text{-}PC_6H_5)]$.

TABLE 8

FRACTIONAL COORDINATES (WITH E.s.d.'s) AND ISOTROPIC THERMAL PARAMETERS ($Å^2$) FOR $[H_2Os_3(CO)_9(PC_6H_5)]$ [a]

Atoms	x/a	y/b	z/c	U
Os(1)	0.3657(1)	0.2222(1)	0.4375(1)	
Os(2)	0.2683(2)	0.3324(1)	0.5398(1)	
Os(3)	0.0684(2)	0.3539(1)	0.3459(1)	
P(1)	0.1063(10)	0.2212(5)	0.4271(5)	
O(11)	0.2419(32)	0.0947(18)	0.2747(17)	0.059(7)
O(12)	0.6899(29)	0.2925(17)	0.4511(16)	
O(13)	0.5651(28)	0.0692(14)	0.5776(14)	
O(21)	0.4481(33)	0.5216(15)	0.5768(21)	
O(22)	−0.0142(28)	0.4138(14)	0.5513(16)	
O(23)	0.4616(56)	0.2382(27)	0.7293(18)	
O(31)	−0.2618(25)	0.4232(14)	0.3196(15)	
O(32)	−0.1084(46)	0.2939(29)	0.1476(18)	
O(33)	0.1972(39)	0.5532(16)	0.3558(26)	
C(11)	0.2879(40)	0.1393(22)	0.3359(21)	0.033(9)
C(12)	0.5688(37)	0.2660(21)	0.4475(19)	0.030(7)
C(13)	0.4887(34)	0.1237(19)	0.5222(18)	0.022(7)
C(21)	0.3934(39)	0.4542(21)	0.5708(20)	0.034(8)
C(22)	0.0927(32)	0.3801(18)	0.5475(17)	0.016(6)
C(23)	0.3940(61)	0.2708(34)	0.6644(34)	0.079(13)
C(31)	−0.1467(40)	0.3970(20)	0.3260(19)	0.026(7)
C(32)	−0.0514(44)	0.3272(24)	0.2178(24)	0.046(9)
C(33)	0.1562(53)	0.4839(31)	0.3536(27)	0.061(11)
H(12)	0.4513	0.2114	0.5710	0.08
H(13)	0.3040	0.3278	0.3645	0.08
C(2)	−0.0942(43)	0.1196(22)	0.4670(18)	0.020(12)
C(3)	−0.2181(43)	0.0524(22)	0.4462(18)	0.050(17)
C(4)	−0.2988(43)	0.0015(22)	0.3651(18)	0.041(16)
C(5)	−0.2556(43)	0.0179(22)	0.3047(18)	0.037(14)
C(6)	−0.1317(43)	0.0850(22)	0.3255(18)	0.053(18)
C(1)	−0.0510(43)	0.1359(22)	0.4066(18)	0.013(12)
CX(2)	0.0402(34)	0.0244(25)	0.4123(27)	0.023(14)
CX(3)	−0.0703(34)	−0.0509(25)	0.3896(27)	0.020(14)
CX(4)	−0.2467(34)	−0.0364(25)	0.3503(27)	0.033(18)
CX(5)	−0.3124(34)	0.0536(25)	0.3336(27)	0.025(15)
CX(6)	−0.2019(34)	0.1289(25)	0.3563(27)	0.022(15)
CX(1)	−0.0256(34)	0.1143(25)	0.3956(27)	0.018(17)

[a] The phenyl group has been found to be disordered, C(1)—C(6) corresponds to one orientation (55%) and CX(1)—CX(6) to the other (45%).

Structure of $[(\mu_2\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}PC_6H_5)]$

The molecular structure is shown in Fig. 2 and the structural parameters are given in Tables 8—11. The overall geometry of the cluster framework is that of a trigonal pyramid with an osmium triangle at the base and the phosphorus atom at the apex. Two of the three Os—Os bonds are bridged by hydrogens. The atoms Os(2) and Os(3) each are bonded to only one bridging hydrogen, whereas Os(1) bears two hydride bridges. The bonds which are bridged by hydrides (Os(1)—Os(2) = 2.972(3) Å and Os(1)—Os(3) = 2.967(2) Å are longer than the unbridged one (Os(2)—Os(3) = 2.845(2) Å). The positions of the hydrogen atoms were inferred from difference electron density syntheses but have not been refined; they may be in error to an uncertain extent, and so detailed discussion is not justified.

TABLE 9

ANISOTROPIC THERMAL PARAMETERS FOR $[H_2Os_3(CO)_9(P(C_6H_5)]$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	0.024(1)	0.010(1)	0.023(1)	—0.002(1)	0.014(1)	0.000(1)
Os(2)	0.027(1)	0.009(1)	0.022(1)	—0.003(1)	0.014(1)	0.000(1)
Os(2)	0.027(1)	0.016(1)	0.023(1)	0.005(1)	0.015(1)	0.005(1)
P(1)	0.029(4)	0.014(4)	0.023(4)	—0.002(3)	0.015(4)	—0.008(3)
O(12)	0.045(14)	0.058(16)	0.059(16)	—0.009(13)	0.028(13)	—0.005(13)
O(13)	0.051(14)	0.026(12)	0.034(12)	0.021(10)	0.014(11)	0.016(11)
O(21)	0.069(18)	0.014(12)	0.142(26)	—0.029(14)	0.070(19)	—0.027(12)
O(22)	0.050(14)	0.025(12)	0.060(15)	—0.011(11)	0.032(13)	—0.002(11)
O(23)	0.205(42)	0.116(30)	0.022(16)	0.037(18)	0.029(22)	0.045(30)
O(31)	0.024(12)	0.029(12)	0.064(15)	0.013(11)	0.027(11)	0.021(10)
O(32)	0.137(38)	0.188(38)	0.021(15)	—0.010(19)	0.017(17)	0.077(27)
O(33)	0.104(23)	0.011(14)	0.214(37)	0.006(17)	0.127(26)	—0.004(14)

[a] Anisotropic thermal parameters in the from $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^*)]$

TABLE 10

BOND LENGTHS (Å) WITH E.s.d.'s FOR $[H_2Os_3(CO)_9(PC_6H_5)]$

Atoms	Length	Atoms	Length
Os(1)—Os(2)	2.972(3)	Os(1)—P(1)	2.358(10)
Os(1)—Os(3)	2.967(2)	Os(2)—P(1)	2.320(7)
Os(2)—Os(3)	2.845(2)	Os(3)—P(1)	2.309(8)
Os(1)—H(12)	2.04	Os(2)—H(12)	2.29
Os(1)—H(13)	1.87	Os(3)—H(13)	2.09
Os(1)—C(11)	1.94(4)	C(11)—O(11)	1.12(5)
Os(1)—C(12)	1.94(4)	C(12)—O(12)	1.18(5)
Os(1)—C(13)	1.90(3)	C(13)—O(13)	1.14(3)
Os(2)—C(21)	2.01(3)	C(21)—O(21)	1.08(4)
Os(2)—C(22)	1.89(4)	C(22)—O(22)	1.17(5)
Os(2)—C(23)	2.03(5)	C(23)—O(23)	1.06(6)
Os(3)—C(31)	1.96(4)	C(31)—O(31)	1.10(5)
Os(3)—C(32)	1.92(4)	C(32)—O(32)	1.15(5)
Os(3)—C(33)	2.03(5)	C(33)—O(33)	1.07(5)
P(1)—C(1)	1.80(4)	P(1)—CX(1)	1.85(3)

TABLE 11

BOND ANGLES (deg.) WITHIN $[H_2Os_3(CO)_9(PC_6H_5)]$

Atoms	Angle	Atoms	Angle
Os(1)—Os(2)—Os(3)	61.3(1)	Os(1)—Os(3)—P(1)	51.3(2)
Os(1)—Os(3)—Os(2)	61.5(1)	Os(2)—Os(3)—P(1)	52.2(2)
Os(2)—Os(1)—Os(3)	57.2(1)	Os(1)—P(1)—Os(2)	78.9(2)
Os(2)—Os(1)—P(1)	50.0(2)	Os(1)—P(1)—Os(3)	79.0(3)
Os(3)—Os(1)—P(1)	49.8(2)	Os(2)—P(1)—Os(3)	75.9(2)
Os(1)—Os(2)—P(1)	51.1(3)	Os(1)—H(12)—Os(2)	86.0
Os(3)—Os(2)—P(1)	51.9(2)	Os(2)—H(13)—Os(3)	97.0
Os—C—O angles range from 166(3) to 179(6)			

The $(\mu_2\text{-H})_2Os_3P$ core of the cluster shows an idealised C_s symmetry with a mirror plane passing through Os(1), P(1) and the midpoint between Os(2) and Os(3). The Os—Os distances as well as the Os—P distances, which are related by this approximate symmetry, are almost identical, but distinctly different from the third independent Os—Os or Os—P distances, respectively (Os(2)—P(1) = 2.320(7) Å; Os(3)—P(1) = 2.309(8) Å as compared with Os(1)—P(1) = 2.358(10) Å). The same type of symmetry is observed for the analogous iron and ruthenium clusters [1—3]. The same kind of deviation is also observed in the Os—C_{CO} distances. The average Os(2)—C_{CO} distance (1.973 Å) and Os(3)—C_{CO} distance (1.967 Å) are almost equivalent, but a slightly shorter Os(1)—C_{CO} distance (1.923 Å) is observed. The phosphorus atom lies 1.602 Å below the plane of the three osmium atoms.

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