

hydrido-clusters derived by Protonation, Hydrogenation, or Photolytic Decarbonylation of the Chelating Diphosphine Compounds

1,1-[Os₃(CO)₁₀(diphosphine)] where diphosphine is Ph₂PCH₂CH₂PPh₂ or Ph₂PCH₂CH₂CH₂PPh₂, and Crystal Structure of [OsH₂{Ph₂P(CH₂)₃PC₆H₄}(CO)₈].0.5CH₂Cl₂ *

Antony J. Deeming, Kenneth I. Hardcastle, and Shariff E. Kabir

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

The hydrides 1,1-[Os₃H(CO)₁₀(diphosphine)]⁺ were formed by the addition of trifluoroacetic acid to the chelating diphosphine compounds 1,1-[Os₃(CO)₁₀(diphosphine)], where diphosphine = Ph₂PCH₂CH₂PPh₂ (dppe) or Ph₂PCH₂CH₂CH₂PPh₂ (dppp) and were isolated as hexafluorophosphate salts. Reactions of the parent diphosphine compounds with H₂ at atmospheric pressure in refluxing toluene do not lead to the simple dihydrides [Os₃H₂(CO)₈(diphosphine)] as found for the corresponding 1,2 isomers. Instead the clusters [Os₃H₂{Ph₂P(CH₂)_nPC₆H₄}(CO)₈] (*n* = 2 or 3) are obtained by loss of C₆H₆ and orthometallation. The X-ray structure when *n* = 3 establishes the presence of the six-electron donating ligand μ₃-Ph₂PCH₂CH₂CH₂PC₆H₄. Orthometallation of the clusters 1,1-[Os₃(CO)₁₀(diphosphine)] occurs on u.v. photolysis to give [Os₃H{Ph₂P(CH₂)_nPPhC₆H₄}(CO)₉] (*n* = 2 or 3) which can be hydrogenated to give the clusters [Os₃H₂{Ph₂P(CH₂)_nPC₆H₄}(CO)₈]. This is evidence that decarbonylation and orthometallation could occur before hydrogenation in the initial thermal reaction of the diphosphine compounds with H₂.

We have prepared a series of diphosphine compounds [Os₃(CO)₁₀(diphosphine)] in which the diphosphine ligands are bridging or chelating.^{1,2} The 1,2 isomers (mode of attachment at metal atoms) with bridging diphosphines have been made for Ph₂P(CH₂)_nPPh₂ where *n* = 1 (dppm), 2 (dppe), 3 (dppp), and 4 (dppb), but the 1,1 isomers have only been obtained with the chelating ligands dppe, dppp, and dppb. The compound 1,2-[Os₃(CO)₁₀(dppm)] has already been reported by others.³

Hydride clusters may be obtained from non-hydride clusters by protonation, hydrogenation, or oxidative addition involving C-H bond cleavage (or cleavage of other bonds to hydrogen) and we describe here all these ways of forming Os-H bond derivatives of 1,1-[Os₃(CO)₁₀(diphosphine)].

Hydrogenation of [Os₃(CO)₁₂] gives the well known dihydride [Os₃H₂(CO)₁₀]⁴ and we were interested in making related dihydrides by hydrogenation of this series of diphosphine compounds. The compound [Os₃H₂(CO)₈(dppm)] and its crystal structure are known.⁵ This was formed by hydrogenation of the orthometallated compound [Os₃H(Ph₂PCH₂PPhC₆H₄)(CO)₈]⁵ but we have found that direct reaction of H₂ with 1,2-[Os₃(CO)₁₀(diphosphine)] gives the series 1,2-[Os₃H₂(CO)₈(diphosphine)] where diphosphine = dppm (84), dppe (28), or dppp (63%).⁶ These have the hydrido and diphosphine ligands bridging the same pair of osmium atoms.^{5,6} This paper describes similar but unsuccessful attempts to prepare corresponding isomeric dihydrides of the 1,1 isomers. We have found that the compounds 1,1-[Os₃H₂(CO)₈(diphosphine)] are unavailable by this route; instead orthometallated compounds are obtained.

Results and Discussion

Protonation of 1,1-[Os₃(CO)₁₀(diphosphine)].—The compound [Os₃(CO)₁₂]⁷⁻⁹ and its tertiary phosphine derivatives^{8,10} are protonated by sulphuric acid or by weaker acids when tertiary phosphines have been introduced. We have described the protonation of 1,1- and 1,2-[Os₃(CO)₁₀(PMe₂Ph)₂] and the X-ray structures of the monohydrido-cations formed from each and as a confirmation of structure we have protonated the compounds 1,1-[Os₃(CO)₁₀(diphosphine)] with CF₃CO₂H and isolated the cationic products as PF₆⁻ salts. Proton and ³¹P n.m.r. and i.r. data for [Os₃H(CO)₁₀(dppe)] [PF₆] (1) and its dppp analogue (2) are given in Table 1. The hydride ligand in (1) is coupled equally (17.0 Hz) to the ³¹P nuclei which is rather unexpected because the edge-bonded hydride has *cis* and *trans* relations with the two ³¹P nuclei respectively. However, the phosphorus nuclei are non-equivalent (³¹P n.m.r. data, Table 1) so that the couplings to the hydride are equivalent accidentally. The isomeric compound 1,2-[Os₃H(CO)₁₀(dppe)]⁺ also gives a hydride triplet in the ¹H n.m.r. spectrum but in that case the phosphorus nuclei are equivalent.² For the dppp analogue of (1), cation (2), the ¹H n.m.r. hydride signal is a double doublet (*J* = 11.7, 8.3 Hz). Cations (1) and (2) are isostructural; see the similarity of their ν(CO) spectra (Table 1). These differences in *J*_{PH} values probably result from angular differences resulting from the different sizes of the chelate rings in these compounds.

Hydrogenation of 1,1-[Os₃(CO)₁₀(diphosphine)].—There was no evidence for the formation of the compounds [Os₃H₂(CO)₈(diphosphine)] in the thermal hydrogenation of the 1,1-dppe and -dppp compounds in refluxing toluene. The 1,2 isomers give dihydrides of this formula⁶ so that at 100 °C there is no interconversion of 1,1 and 1,2 isomers. The compound 1,1-[Os₃(CO)₁₀(dppp)] gave only one isolable hydrogenation product: [Os₃H₂(Ph₂PCH₂CH₂CH₂PC₆H₄)(CO)₈] (3) (39%).

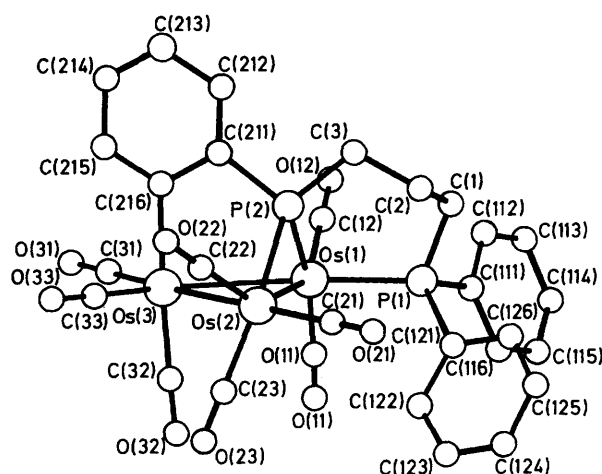
* 1,1,1,2,2,2,3,3-Octacarbonyl-μ₃-{*o*-(3-(diphenylphosphino)propylphosphido)phenyl-C¹(Os¹)P(Os^{2,3})}-1,3,2,3-di-μ-hydrido-triangulo-triosmium-dichloromethane (2/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. I.r., ^1H , and ^{31}P n.m.r. data for compounds (1)–(7)

Compound	$\tilde{\nu}(\text{CO})^a/\text{cm}^{-1}$	^1H N.m.r. ^b	
(1) $1,1\text{-}[\text{Os}_3\text{H}(\text{CO})_{10}(\text{dppe})][\text{PF}_6]$	2 135m, 2 084s, 2 062m, 2 053vs, 2 046m, 2 005m, 1 970w	7.42 (m) Ph 3.12(m) CH_2 –18.40 (t) OsH (
(2) $1,1\text{-}[\text{Os}_3\text{H}(\text{CO})_{10}(\text{dppp})][\text{PF}_6]$	2 136m, 2 084s, 2 064m, 2 054vs, 2 044m, 2 003m, 1 955w	7.83 (m) Ph 3.61 (m) CH_2 3.31 (m) CH_2 3.10 (m) CH_2	
(3) $[\text{Os}_3\text{H}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PC}_6\text{H}_4\}(\text{CO})_8]\cdot 0.5\text{CH}_2\text{Cl}_2$	2 074s, 2 037vs, 1 995s, 1 984m, 1 959m	–19.60 (dd) OsH (11.7, 8.3) 7.83–6.88 Ph, C_6H_4 5.30 (s) CH_2Cl_2 3.28 (m) CH_2 2.68 (m) CH_2 1.78 (m) CH_2	–166.33 (d) (18.7) –135.10 (d) (18.7)
(4) $[\text{Os}_3\text{H}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PC}_6\text{H}_4\}(\text{CO})_8]$	2 075s, 2 038vs, 1 997s, 1 985m, 1 959m	–16.65 (dd) OsH (27.4, 5.9) –16.88 (dd) OsH (11.7, 9.4) 7.82–6.90 Ph, C_6H_4 2.72 (m) CH_2 2.50 (m) CH_2	
(5) $[\text{Os}_3\text{H}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPhC}_6\text{H}_4\}(\text{CO})_8]$	2 072s, 2 020s, 2 010s, 1 997m, 1 982w, 1 954m ^d	–17.18 (dd) OsH (28.3, 5.0) –18.04 (dd) OsH (12.0, 9.2) 7.78–6.80 Ph, C_6H_4 3.05 (m) CH_2 2.05 (m) CH_2	
(6) $[\text{Os}_3\text{H}\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPhC}_6\text{H}_4\}(\text{CO})_9]$	2 080m, 2 039s, 2 013vs, 2 007s, 1 986w, 1 977m, 1 963m ^d	–10.29 (dd) OsH (7.9, 1.9) –10.25 (dd) OsH (14.4, 12.8) –12.20 (d) OsH (10.8) 8.18–6.96 Ph, C_6H_4 2.60 (m) CH_2 2.20 (m) CH_2	–108.19 (d) (9.3) –100.56 (d) (9.3)
(7) $[\text{Os}_3\text{H}\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPhC}_6\text{H}_4\}(\text{CO})_9]$	2 064s, 2 026vs, 2 008vs, 1 987w, 1 970m, 1 957ms ^d	–16.82 (t) OsH (12.8) 8.23–6.51 Ph, C_6H_4 3.05 (m) CH_2 2.61 (m) CH_2 2.12 (m) CH_2 –17.64 (t) OsH (14.2)	–164.10 (d) (26.8) –148.00 (d) (26.8)

^a Recorded in CH_2Cl_2 unless stated otherwise. ^b Recorded in CDCl_3 at 200 MHz, coupling constants/Hz in parentheses. ^c Recorded at 80.984 MHz in CDCl_3 , chemical shift relative to $\text{P}(\text{OMe})_3$. ^d Recorded in cyclohexane.

**Figure.** Molecular structure of $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]\cdot 0.5\text{CH}_2\text{Cl}_2$ (3)

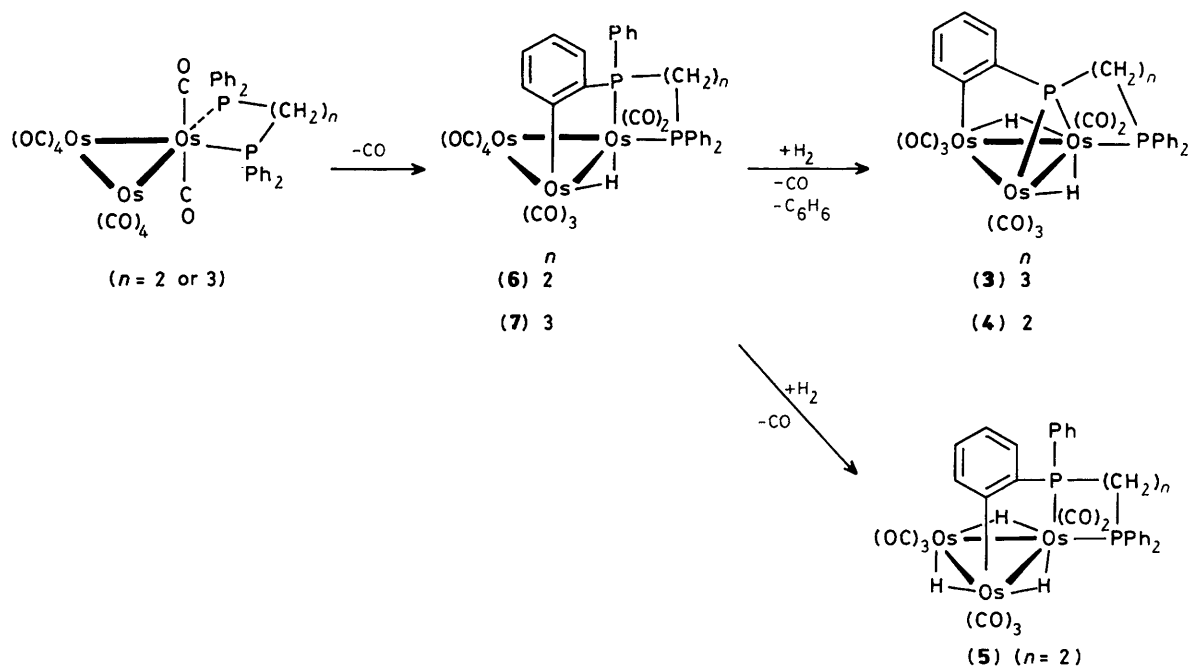
The corresponding dppe derivative (4) was only obtained in low yield (11%) under similar conditions along with an even lower yield (5%) of the trihydride $[\text{Os}_3\text{H}_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)(\text{CO})_8]$ (5). Characterising i.r. and n.m.r. data for hydrides (3)–(5) are in Table 1. Compound (3) gave a parent molecular

ion and elemental analysis corresponding to our formulation. Low symmetry is apparent from the spectroscopic data; there are non-equivalent hydrides and non-equivalent phosphorus nuclei. Although the loss of C_6H_6 and 2CO on addition of H_2 was apparent, it was only possible to establish the structure of (3) by a single-crystal X-ray structure determination.

Crystals of (3) came out of a dichloromethane–hexane mixture with the formula $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]\cdot 0.5\text{CH}_2\text{Cl}_2$. The molecular structure is shown in the Figure, fractional atomic co-ordinates are given in Table 2, and selected bond lengths and angles in Table 3. The hydride ligands were not detected but, by usual criteria such as the CO positions and the $\text{Os}(1)\text{--Os}(2)$ and $\text{Os}(1)\text{--Os}(3)$ distances [2.946(4) and 3.054(4) Å respectively] being longer than that of $\text{Os}(2)\text{--Os}(3)$ [2.862(4) Å], we prefer to position these along the longer edges of the Os_3 triangle. This arrangement is consistent with ^1H n.m.r. data which show each hydride to be coupled to each ^{31}P nucleus. The cluster is electron-precise with three Os–Os bonds and contains a six-electron donating $\mu_3\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{-PC}_6\text{H}_4$ ligand derived by loss of C_6H_6 from dppp. This ligand is linked as a RPC_6H_4 -type group to the three osmium atoms. We also found a μ_3 ligand of this type in $[\text{Os}_3(\mu_3\text{-MePC}_6\text{H}_4)(\text{CO})_{10}]$ which was likewise formed by loss of C_6H_6 and CO , in this case, from $[\text{Os}_3(\text{CO})_{11}(\text{PMePh}_2)]$.¹¹ The compound $[\text{Os}_3(\mu\text{-Ph})(\mu\text{-PPh}_2)(\mu_3\text{-PhPC}_6\text{H}_4)(\text{CO})_8]$ contains a similar μ_3 ligand.¹² In the conversion of $1,1\text{-}[\text{Os}_3(\text{CO})_{10}(\text{dppp})]$ into (3), the diphosphine ligand has remained chelated through the phosphorus atoms while becoming bridged through the

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]\cdot 0.5\text{CH}_2\text{Cl}_2$ (**3**)

Atom	x	y	z	Atom	x	y	z
Os(1)	2 876(1)	7 409(1)	1 226(1)	O(33)	2 832(13)	3 576(8)	2 003(5)
Os(2)	685(1)	6 041(1)	1 460(1)	C(111)	2 220(15)	9 711(9)	858(5)
Os(3)	3 738(1)	5 505(1)	1 677(1)	C(112)	2 986(16)	9 884(10)	453(5)
P(1)	1 282(4)	8 607(2)	895(1)	C(113)	3 695(17)	10 758(11)	431(6)
P(2)	1 571(4)	6 297(2)	680(1)	C(114)	3 631(18)	11 431(11)	813(7)
C(1)	422(16)	8 408(9)	219(5)	C(115)	2 863(22)	11 235(11)	1 198(6)
C(2)	-554(15)	7 532(10)	145(5)	C(116)	2 129(19)	10 382(11)	1 241(6)
C(3)	385(15)	6 659(9)	81(5)	C(121)	-264(16)	8 885(9)	1 236(5)
C(11)	3 762(15)	8 139(9)	1 798(5)	C(122)	-68(17)	8 747(10)	1 775(5)
O(11)	4 317(13)	8 551(8)	2 135(4)	C(123)	-1 239(18)	9 006(11)	2 026(6)
C(12)	4 209(14)	7 752(9)	792(5)	C(124)	-2 528(19)	9 426(12)	1 761(8)
O(12)	5 005(12)	7 941(7)	515(4)	C(125)	-2 676(19)	9 560(13)	1 237(8)
C(21)	-1 248(16)	6 617(10)	1 323(5)	C(126)	-1 591(18)	9 297(11)	976(6)
O(21)	-2 407(11)	6 922(8)	1 254(4)	C(211)	2 666(14)	5 349(9)	500(5)
C(22)	108(17)	4 806(12)	1 292(6)	C(212)	2 612(15)	5 039(11)	12(5)
O(22)	-207(16)	4 046(8)	1 182(4)	C(213)	3 497(18)	4 246(11)	-94(7)
C(23)	540(15)	5 889(10)	2 170(5)	C(214)	4 384(18)	3 827(10)	300(6)
O(23)	437(12)	5 787(9)	2 593(4)	C(215)	4 397(17)	4 149(10)	807(6)
C(31)	5 766(16)	5 249(11)	1 771(6)	C(216)	3 609(15)	4 934(9)	914(5)
O(31)	7 027(12)	5 064(8)	1 845(5)				
C(32)	3 821(15)	6 081(11)	2 339(5)	C(S)	-3 269(27)	7 093(19)	3 555(15)
O(32)	3 864(12)	6 450(8)	2 727(4)	Cl(1)(S)	-2 577(8)	7 109(6)	4 083(3)
C(33)	3 147(16)	4 307(11)	1 885(5)	Cl(2)(S)	-2 095(12)	7 217(7)	3 076(3)

**Scheme.**

orthometallated phenyl group and a phosphido bridge between Os(1) and Os(2).

Mechanism of Formation of Complex (3) from 1,1-[Os₃(CO)₁₀(dppp)].—Hydrogenation to give [Os₃H₂(CO)₈(dppp)] followed by rapid loss of C₆H₆ and orthometallation could lead to cluster (3). Alternatively the orthometallation could occur before hydrogenation. While we have not unequivocally decided between these two, we favour the latter because we have been able to show that this route is viable.

Thus u.v. photolysis of 1,1-[Os₃(CO)₁₀(diphosphine)] (di-

phosphine = dppe or dppp) leads to decarbonylation and the orthometallated clusters [Os₃H{Ph₂P(CH₂)_nPPhC₆H₄}(CO)₉], (6) (42) and (7) (56%), with *n* = 2 and 3 respectively, can be isolated from the reaction mixture. These were characterised by data in Table 1. Although the ³¹P nuclei are clearly different, the ¹H n.m.r. hydride signals are 1:2:1 triplets in each case. We cannot be sure that (6) and (7) are isostructural; indeed their rather different i.r. ν(CO) spectra indicate that they are not. While in most respects clusters (6) and (7) appear to be analogous, the co-ordination positions of the PPh₂ and of the chelate could be different. The Scheme shows the probable

Table 3. Selected bond lengths (Å) and angles (°) for $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{-CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]\cdot 0.5\text{CH}_2\text{Cl}_2$ (3)

Os(1)–Os(2)	2.946(4)	P(1)–Os(1)	2.342(5)
Os(1)–Os(3)	3.054(4)	P(2)–Os(1)	2.359(5)
Os(2)–Os(3)	2.862(4)	P(2)–Os(2)	2.369(6)
Os(3)–C(216)	2.175(15)	P(1)–C(1)	1.866(14)
		C(1)–C(2)	1.543(22)
		C(2)–C(3)	1.549(22)
		P(2)–C(3)	1.855(15)
Average distances:			
C–C (C_6H_4 ring)	1.403(22)		
C–C (phenyl ring 1)	1.403(24)		
C–C (phenyl ring 2)	1.400(25)	P(1)–C(11)	1.821(16)
		P(1)–C(121)	1.836(18)
Os–C (carbonyl)	1.908(16)	P(2)–C(211)	1.804(16)
C–O (carbonyl)	1.149(19)		
Os(3)–Os(1)–Os(2)	56.9(1)	Os(2)–P(2)–Os(1)	77.1(2)
Os(3)–Os(2)–Os(1)	63.4(1)	Os(2)–Os(1)–P(1)	99.9(2)
Os(2)–Os(3)–Os(1)	59.6(1)		
Os(2)–Os(3)–C(216)	90.3(5)		
C(216)–Os(3)–C(32)	176.7(6)		
C(3)–P(2)–C(211)	105.0(7)		
P(2)–C(211)–C(216)	114.0(11)		

structure of these compounds. Hydrogenation of (6) and (7) leads to the same products as from the direct hydrogenation of 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{diphosphine})]$ (diphosphine = dppe or dppp). Thus cluster (6) leads to (4) and (5) while (7) gives cluster (3) as the only isolable product (see Experimental section). There was no evidence for (6) and (7) from the i.r. spectra of solutions measured during the course of the hydrogenation of the two initial 1,1-diphosphine compounds. However, this is not surprising because (6) and (7) hydrogenate faster than the initial dppe and dppp compounds (in refluxing cyclohexane rather than refluxing toluene).

We have established therefore that the reactions in the Scheme do occur and could account for the formation of (3)–(5) in the direct hydrogenations of 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{diphosphine})]$. Presumably the loss of CO from (6) under H_2 leads either to P–C cleavage and the expulsion of C_6H_6 to give (4) or to oxidative addition of H_2 to give (5). In the case of (7) no compound corresponding to (5) was obtained.

The difference in the hydrogenation of 1,1- versus 1,2- $[\text{Os}_3(\text{CO})_{10}(\text{diphosphine})]$ may relate more to their relative ease of decarbonylation and orthometallation than to any intrinsic stability differences between 1,1- and 1,2- $[\text{Os}_3\text{H}_2(\text{CO})_8(\text{diphosphine})]$. We have previously shown that 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ orthometallates in refluxing toluene (110 °C) to form $[\text{Os}_3\text{H}(\text{Me}_2\text{PC}_6\text{H}_4)(\text{PMe}_2\text{Ph})(\text{CO})_9]$ ¹³ much more readily than does 1,2- $[\text{Os}_3(\text{CO})_{10}(\text{PMe}_2\text{Ph})_2]$ which only reacts at higher temperatures (125 °C) and then to give $[\text{Os}_3(\text{C}_6\text{H}_4)(\text{PMe}_2)_2(\text{CO})_7]$ as the predominant product.¹⁴ The greater reactivity of the 1,1 isomer towards orthometallation seems to be the cause of the different chemistries of the isomeric diphosphine compounds towards dihydrogen.

Experimental

The compounds 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppe})]$ and 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppp})]$ were prepared according to published methods.^{1,2}

Protonation Reactions.—1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppe})]$. Trifluoroacetic acid (0.048 cm³, 16 mol per mol Os_3) was added to a solution of the dppe compound (0.049 g) in CDCl_3 (0.5 cm³). The ¹H n.m.r. spectrum indicated the presence of a single hydrido-compound. The residue after removal of the solvent under reduced pressure was dissolved in methanol (5 cm³) and a methanolic solution of NH_4PF_6 (0.010 g) was added, followed by a few drops of water to give a yellow precipitate. This was extracted with dichloromethane and recrystallised from a CH_2Cl_2 –diethyl ether mixture to give 1,1- $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{dppe})][\text{PF}_6]$ (1) as pale yellow crystals (0.042 g, 76%) (Found: C, 30.7; H, 1.8; P, 6.45. $\text{C}_{36}\text{H}_{25}\text{F}_6\text{O}_{10}\text{Os}_3\text{P}_3$ requires C, 31.0; H, 1.8; P, 6.65%).

1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppp})]$. A very similar treatment of the dppp compound (0.029 g) gave 1,1- $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{dppp})][\text{PF}_6]$ (2) as pale yellow crystals (0.021 g, 66%) (Found: C, 31.3; H, 2.0; P, 6.4. $\text{C}_{37}\text{H}_{27}\text{F}_6\text{O}_{10}\text{Os}_3\text{P}_3$ requires C, 31.55; H, 1.95; P, 6.85%).

Hydrogenation Reactions.—1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppp})]$. Hydrogen at atmospheric pressure was bubbled for 3 h through a refluxing solution of the dppp compound (0.100 g) in toluene (100 cm³). Removal of the solvent and t.l.c. on silica [eluant: light petroleum (b.p. 30–40 °C)–dichloromethane, 10:4 v/v] gave unreacted 1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppp})]$ (0.005 g) as the fastest moving band. The second band gave $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]\cdot 0.5\text{CH}_2\text{Cl}_2$ (3) as pale yellow crystals (0.036 g, 39%) from a dichloromethane–hexane mixture (Found: C, 29.65; H, 2.0; O, 10.65; P, 5.3. $\text{C}_{29.5}\text{H}_{23}\text{ClO}_8\text{Os}_3\text{P}_2$ requires C, 30.2; H, 2.0; O, 10.9; P, 5.3%). Two other minor bands which moved more slowly were not characterised.

1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppe})]$. A similar treatment of this compound (0.200 g) in toluene (50 cm³) for 4 h gave only low yields of products separated by t.l.c. Apart from the starting dppe compound (0.010 g, 5%), the compound $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]$ (4), analogous to (3), was obtained as yellow crystals (0.020, 11%) from a dichloromethane–hexane mixture, together with a compound isolated in even lower yield (0.010 g, 5%) and tentatively characterised on the basis of i.r. and n.m.r. data as $[\text{Os}_3\text{H}_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)(\text{CO})_8]$, (5).

Compound (7). Hydrogen at atmospheric pressure was bubbled through a refluxing solution of compound (7) (0.125 g) in cyclohexane (50 cm³) for 4 h. T.l.c. separation of the reaction mixture [SiO_2 ; eluant, light petroleum (b.p. 30–40 °C)–dichloromethane–diethyl ether, 10:1:1 by volume] gave several bands of which only $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]$ (3) (0.050 g, 44%) was characterised.

Compound (6). A similar treatment of compound (6) (0.050 g) for 7 h with a similar t.l.c. work-up gave $[\text{Os}_3\text{H}_3(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)(\text{CO})_8]$ (5) (0.005 g, 10%), $[\text{Os}_3\text{H}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PC}_6\text{H}_4)(\text{CO})_8]$ (4) (0.005 g, 11%), and 1,2- $[\text{Os}_3\text{H}_2(\text{CO})_8(\text{dppe})]$ (0.015 g, 31%). The latter compound could also be obtained by hydrogenation of 1,2- $[\text{Os}_3(\text{CO})_{10}(\text{dppe})]$.

Photolysis Reactions.—1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppe})]$. A solution of the dppe compound (0.300 g) in cyclohexane (100 cm³) was irradiated in Pyrex apparatus with a medium-pressure mercury u.v. lamp for 1.5 h. Removal of the solvent and t.l.c. of the residue [SiO_2 ; eluant, light petroleum (b.p. 30–40 °C)–dichloromethane, 10:4 v/v] gave two bands of which only the main one was characterised: $[\text{Os}_3\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)(\text{CO})_9]$ (6) as yellow crystals (0.123 g, 42%) from a dichloromethane–hexane mixture (Found: C, 34.5; H, 2.0; P, 4.95. $\text{C}_{35}\text{H}_{24}\text{O}_9\text{Os}_3\text{P}_2$ requires C, 34.4; H, 2.0; P, 5.05%).

1,1- $[\text{Os}_3(\text{CO})_{10}(\text{dppp})]$. A similar photolysis of the dppp compound (0.309 g) for 4 h gave three t.l.c. bands. The main yellow band gave $[\text{Os}_3\text{H}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPhC}_6\text{H}_4)(\text{CO})_9]$

(7) as yellow crystals (0.173 g, 56%) from a dichloromethane-hexane mixture (Found: C, 34.9; H, 2.15; P, 4.75. $C_{36}H_{26}O_9Os_3P_2$ requires C, 35.0; H, 2.15; P, 5.0%). The other two bands gave starting material (0.010 g, 3%) and a small amount of an uncharacterised compound.

Crystallographic Studies on $[Os_3H_2(Ph_2PCH_2CH_2CH_2PC_6H_4)(CO)_8] \cdot 0.5CH_2Cl_2$, (3).—Crystal data. $C_{29}H_{22}O_8Os_3P_2 \cdot 0.5CH_2Cl_2$, $M = 1173.6$, monoclinic, $a = 9.124(2)$, $b = 14.444(4)$, $c = 26.581(5)$ Å, $\beta = 98.98(2)^\circ$, $U = 3460.1$ Å³, space group $P2_1/n$, $D_c = 2.25$ g cm⁻³, $F(000) = 2156$, $\lambda = 0.71069$ Å, $\mu(Mo-K\alpha) = 112.3$ cm⁻¹.

Data collection. Unit-cell parameter and intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo- $K\alpha$ radiation and ω - 2θ scan procedure.¹⁵ Of the 6073 unique reflections measured ($1.5 \leq \theta \leq 25^\circ$), 4482 were considered observed [$I_o > 1.5\sigma(I_o)$]. A semi-empirical absorption correction using normalised and averaged ψ -scan measurements¹⁶ from three reflections was applied to the data; the maximum and minimum transmissions were 99.93 and 62.84% respectively.

Structure solution and refinement. The positions of the three Os atoms were determined by direct methods using SHELX 84.¹⁷ Least-squares refinement and difference Fourier synthesis revealed all other non-H atoms. Two fairly large peaks in a final difference map (5 and 7 e Å⁻³) not associated with the cluster were attributed to solvent (CH_2Cl_2) incorporated in the crystal lattice. This was verified by ¹H n.m.r. and chemical analysis, and a partial CH_2Cl_2 molecule was included in the final cycles of full-matrix, least-squares refinement with all non-H atoms anisotropic and weights, $w = 1/[\sigma^2(F_o)]$. The final values of R and R' were 0.0379 and 0.0312 respectively. All calculations were carried out using the programs SHELX 76¹⁸ and SNOOPI¹⁹ on a DEC VAX-11/750 computer. Atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Association of Commonwealth Universities for a studentship (for S. E. K.), the State University of California for leave (for K. I. H.), M.B. Hursthouse and R. Short for their

assistance, and G. M. Sheldrick for the use of SHELX 84 prior to publication.

References

- 1 A. J. Deeming, S. Donovan-Mtunzi, and S. E. Kabir, *J. Organomet. Chem.*, 1984, **276**, C65; 1987, **333**, 253.
- 2 A. J. Deeming, S. Donovan Mtunzi, K. I. Hardcastle, S. E. Kabir, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1988, 579.
- 3 J. A. Clucas, D. F. Foster, M. M. Harding, and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 949.
- 4 S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942; M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2697; A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *J. Chem. Soc., Chem. Commun.*, 1978, 723; R. W. Broach and J. M. Williams, *Inorg. Chem.*, 1979, **18**, 314.
- 5 J. A. Clucas, M. M. Harding, and A. K. Smith, *J. Chem. Soc., Chem. Commun.*, 1985, 1280.
- 6 A. J. Deeming, and S. E. Kabir, unpublished work.
- 7 J. Knight and M. J. Mays, *J. Chem. Soc. A*, 1970, 711.
- 8 A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 1970, 2967.
- 9 A. A. Koridze, O. A. Kizas, N. M. Astakhova, P. V. Petrovskii, and Yu. K. Grishin, *J. Chem. Soc., Chem. Commun.*, 1981, 853.
- 10 A. J. Deeming, S. Donovan-Mtunzi, S. E. Kabir, M. B. Hursthouse, K. M. A. Malik, and N. P. C. Walker, *J. Chem. Soc., Dalton Trans.*, 1987, 1869.
- 11 A. J. Deeming, S. E. Kabir, N. I. Powell, P. A. Bates, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1987, 1529.
- 12 C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 1973, 529 and refs. therein.
- 13 A. J. Deeming, S. Donovan-Mtunzi, S. E. Kabir, and P. J. Manning, *J. Chem. Soc., Dalton Trans.*, 1985, 1037.
- 14 A. J. Deeming, R. E. Kimber, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1973, 2589.
- 15 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
- 16 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- 17 G. M. Sheldrick, SHELX 84, Program for crystal structure solution, University of Göttingen, 1984.
- 18 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
- 19 E. K. Davies, SNOOPI, Program for drawing crystal structures, University of Oxford, 1983.

Received 11th March 1987; Paper 7/450