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Protonation and hydrogenation of triosmium clusters containing the bridging diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1 to 4)

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Abstract

Members of the series of bridging diphosphine clusters $[Os_3(CO)_{10}(diphos)]$ where diphos = $Ph_2P(CH_2)_nPPh_2$ [dppm (n = 1), dppe (n = 2), dppp (n = 3), or dppb (n = 4)] show interesting differences in their reactivity towards H^+ and H_2. Protonation leads to $[Os_3(\mu\text{-H})(CO)_{10}(diphos)]^+$ with the hydrides bridging the same osmium atoms as the diphos ligand when diphos is dppe, dppp, or dppb, whereas the hydride and dppm bridge different edges in $[Os_3(\mu\text{-H})(CO)_{10}(dppm)]^+$. Hydrogenation of the 1,2-diphos compounds leads to $[Os_3(\mu\text{-H})_2(CO)_8(diphos)]$ (diphos = dppm, dppe, dppp) in good to excellent yield but the dppb analogue could not be made. Geometric and electronic factors affecting the ability to incorporate hydride ligands in these clusters are discussed.

Introduction

Hydride ligands in triosmium clusters are generally doubly bridging [1] and clusters containing terminal hydride ligands are quite rare. One example is $[Os_3H_2(CO)_{10}L]$ [1–4], formed by addition of L (CO, PR_3, RCN, RNC etc.) to the di-μ-hydride $[Os_3H_2(CO)_{10}]$, and there just a few other examples of terminal hydrides [5,6]. Bridging hydride ligands are generally bonded to the most electron-rich osmium atoms, which are the ones most substituted by donor ligands. For example, the hydride ligands introduced by protonation of the monodentate tertiary phosphine complexes 1,2-$[Os_3(CO)_{10}L_2]$ seem invariably to bridge the two substituted metal atoms [7,8]. Here we will describe some work on the interestingly complete series of bridging diphosphine clusters (**1**) 1,2-$[Os_3(CO)_{10}(diphos)]$ where diphos = $Ph_2P(CH_2)_nPPh_2$ [dppm (n = 1), dppe (n = 2), dppp (n = 3), dppb (n = 4)] and 1,1-$[Os_3(CO)_{10}(diphos)]$ where diphos = dppe, dppp, or dppb [9]. In the 1,2-series the diphos ligands form 5- to 8-membered rings but apart from the difference in ring size these compounds are very similar. Protonation at the most electron-rich

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metal centres would incorporate the hydride into these rings and steric constraint might prevent the hydride entering the smaller ones. We have already described protonation of 1,2-[$Os_3(CO)_{10}$(dppe)] and have compared the crystal structures of this compound and the cation formed by protonation [10]. In this paper we consider the effects of the bridge ring size on the incorporation of hydride ligands by protonation. We also describe some hydrogenation products of the same series of the type [$Os_3H_2(CO)_8$(diphos)].

Results and discussion

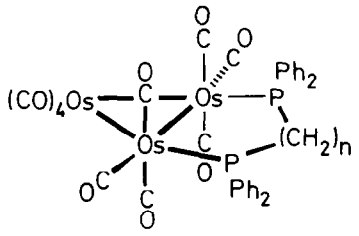
Protonation reactions

We examined the protonation of the compounds 1,2-[$Os_3(CO)_{10}$(diphos)] (**1**) initially by adding trifluoroacetic acid to $CDCl_3$ solutions and observing ^1H NMR signals in the hydride region. Addition to a 16-fold excess of CF_3CO_2H to a bright yellow solution of [$Os_3(CO)_{10}$(dppm)] (**1a**) gave an NMR spectrum consistent with the complete formation of the monoprotonated cation, 1,2-[$Os_3H(CO)_{10}$(dppm)]$^+$ (**2**). The hydride signal is a doublet (Table 1) and hence the hydride is not at the most electron-rich bridging site but rather at a side Os–Os bond. The observation of two doublets in the $^{31}P\{^1H\}$ NMR spectrum (Table 1) confirms the loss of two-fold symmetry on protonation.

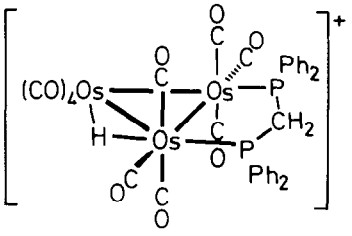
Thus the structure of **2** is different from that of the compound 1,2-[$Os_3H(CO)_{10}$(dppe)]$^-$ (**3**) which is formed similarly by protonation of **1b** [10]. The crystal structure of **3** confirms the ^1H NMR evidence (a hydride 1/2/1 triplet) that the hydride bridges the same metal atoms as the dppe ligand. On protonation of **1b** to give **3** the OsOsP angles in the bridge ring increase from 101.2 to 103.0° and the bridged Os–Os distance from 2.891 to 3.056 Å (average values). A much larger expansion of OsOsP angles is found on protonating the monophosphine analogue to give [$Os_3H(CO)_{10}(PMe_2Ph)_2$][$PF_6$] for which the average OsOsP angle is 117.5° [7]. Very similar increases in the corresponding angles and distances are found on protonating related systems such as [$Os_3(CO)_{10}(MeCN)_2$] [11] and this has been a useful criterion in deciding where a hydride ligand is positioned when it has not been detected in an X-ray structure. This increase in angle is not to make room for the hydride but rather to maintain as far as possible octahedral geometries at the bridged metal atoms (see Fig. 1). An increase in the OsOsP angle of this kind is not possible for protonation of **1a** on the bridged Os–Os edge: the distance between the P atoms does not allow it. The small span of the dppm ligand is already causing these adjacent ligand sites at osmium to be pinched in and an expansion of angles and distances as in Fig. 1 is hardly possible. Hence in **2** the proton has not entered the most electron-rich site between the phosphorus atoms but at a side Os–Os edge.

Compound **2** readily deprotonates. Addition of NH_4PF_6 to a methanolic solution of **2** and precipitation with water gives the neutral starting material **1a**, whereas a similar treatment of **3** gives a precipitate of the salt [$Os_3H(CO)_{10}$(dppe)][PF_6]. This is consistent with the more substituted Os–Os edge being the more basic.

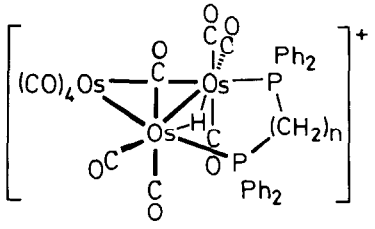
Protonation of 1,2-[$Os_3(CO)_{10}$(dppe)] (**1b**) in $CDCl_3$ with CF_3CO_2H at −50 °C gave a mixture of two hydride species [weaker signal: δ −19.48(d), J(PH) 14.3 Hz and stronger signal: δ −21.32(t) J(PH) 17.0 Hz]. After 48 h the doublet had disappeared and the triplet corresponding with **3** was correspondingly more intense. Thus even in the dppe case, an isomer corresponding with **2** is present initially but



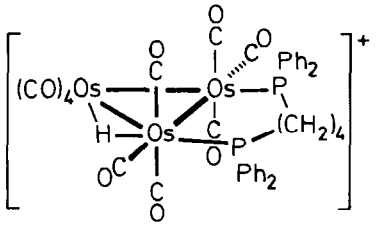
(1a) (n = 1)
(1b) (n = 2)
(1c) (n = 3)
(1d) (n = 4)



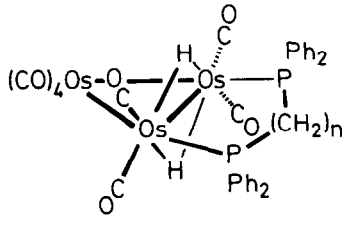
(2)



(3) (n = 2)
(4) (n = 3)
(5) (n = 4)



(6)



(8) (n = 1)
(9) (n = 2)
(10) (n = 3)

the thermodynamically more stable isomer **3** predominates eventually. We believe that the least substituted Os–Os edge is more easily accessed by acid than the more basic edge, which is that crowded by the bridging dppe ligand. Slow isomerisation then gives the more stable form.

Table 1

^{1}H NMR data for the hydride complexes

Compound	δ [a]	Assignment	J(PH) (Hz)
1,2-[$Os_3H(CO)_{10}$(dppm)]$^+$ (**2**) [b]	5.39(t)	CH_2	
	7.42(m)	C_6H_5	
	−19.45(d)	OsH	13.6
1,2-[$Os_3H(CO)_{10}$(dppe)][PF_6] (**3**)	2.23(m)	CH_2	
	4.60(m)	CH_2	
	7.49(m)	C_6H_5	
	−21.32(t)	OsH	17.0
1,2-[$Os_3H(CO)_{10}$(dppp)][PF_6] (**4**)	1.96(m)	CH_2	
	3.12(m)	CH_2	
	7.45(m)	C_6H_5	
	−20.75(t)	OsH	10.8
1,2-[$Os_3H(CO)_{10}$(dppb)][PF_6] (**5**)	2.64(m)	CH_2	
	3.46(m)	CH_2	
	7.56(m)	C_6H_5	
	−19.95(t)	OsH	8.5
[$Os_3H_2(CO)_8$(dppm)] (**8**)	4.15(t)	CH_2	
	7.30(m)	C_6H_5	
	−10.31(t)	OsH	10.1
[$Os_3H_2(CO)_8$(dppe)] (**9**)	2.76(m)	CH_2	
	7.47(m)	C_6H_5	
	−10.74(t)	OsH	9.6
[$Os_3H_2(CO)_8$(dppp)] (**10**)	1.90(m)	CH_2	
	2.70(m)	CH_2	
	7.39(m)	C_6H_5	
	−10.15(t)	OsH	8.2

[a] Recorded at 200 MHz in $CDCl_3$ except **3** which was recorded in CD_2Cl_2 at −79 °C. [b] Generated in situ by adding CF_3CO_2H to a solution of **1a**. $^{31}P\{^1H\}$ NMR in $CDCl_3$ at 80.984 MHz: δ −180.27(d) and −170.14(d) [J(PP) 27.6 Hz] relative to $P(OMe)_3$.

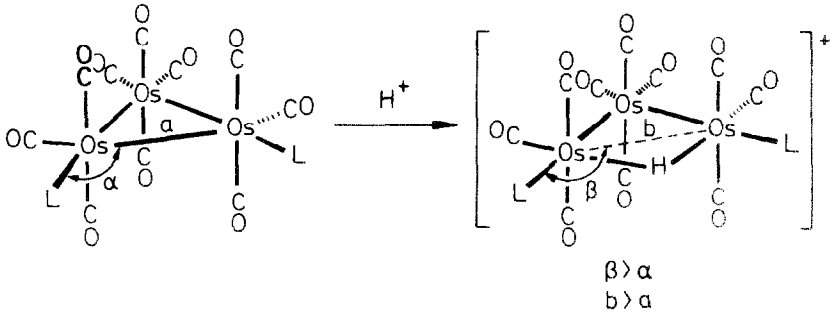


Fig. 1. The geometric consequences of protonation showing the increase in distance a and angle α. The maintenance of octahedral geometry at osmium seems to be dominant, the hydride occupying a coordination position.

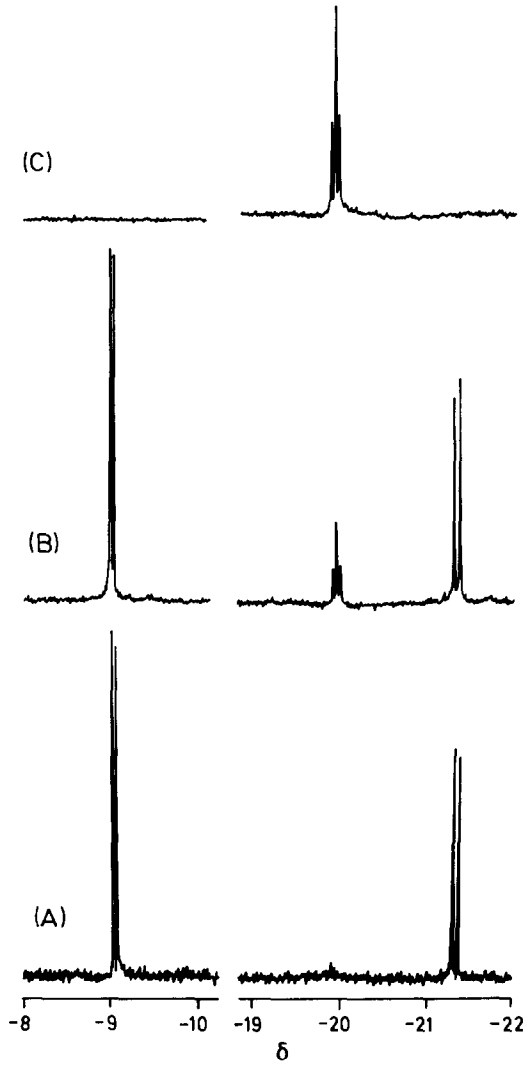


Fig. 2. 200 MHz ^{1}H NMR spectra for 1,2-[$Os_3(CO)_{10}$(dppb)] (**1d**) in $CDCl_3$ with a 16-fold excess of CF_3CO_2H added at −49 °C (A). Spectrum (B) was obtained on warming to 22 °C and (C) after keeping for 24 h at room temperature.

Protonation of 1,2-[$Os_3(CO)_{10}$(dppp)] (**1c**) gave only one protonated product in solution, compound **4**, showing a ^{1}H NMR hydride triplet. We initially assumed that the increase in diphosphine chain length had allowed greater flexibility and easier movement of the hydride into the more basic site. However, this simple picture was marred by our protonation of the dppb compound **1d** which gave hydride intermediates which only slowly converted to the thermodynamically stable product **5**. Figure 2 shows the changes in the hydride region of the ^{1}H NMR spectrum on adding CF_3CO_2H to **1d** in $CDCl_3$ at −49 °C and allowing the stable isolable product **5** to be formed at 22 °C over 24 h. One of the two initial doublets

[that at δ −21.33(d), J(PH) 13.6 Hz] is due to cation **6** having a structure corresponding to that of **2** but we cannot assign a structure to the other species present **7** [δ −9.07, J(PH) 9.0 Hz]. This hydride signal is in a region normally associated with terminal hydride. None of these species has coordinated trifluoroacetate because [$HOEt_2$][BF_4] (2 mol/Os_3) gave the same intermediates and final product. The hydride complexes **3** to **5** were easily isolated and fully characterised but **2**, **6**, and **7** were only identified by their spectra in solution, either because of ready deprotonation or easy isomerisation.

Hydrogenation reactions

The dihydride 1,2-[$Os_3H_2(CO)_8$(dppm)] (**8**) is formally a hydrogenation product of 1,2-[$Os_3(CO)_{10}$(dppm)] (**1a**) although it has apparently not been synthesised by direct hydrogenation of **1a** previously. The cyclometallated derivative [$Os_3H(CO)_8(Ph_2PCH_2PPhC_6H_4)$] has been synthesised from **1a** by decarbonylation and internal oxidative addition. Hydrogenation of this product at 80 °C in toluene gives a good yield (75%) of dihydride **8** [12]. We now report a more simple synthesis by the treatment of **1a** with H_2 in refluxing toluene which gives **8** in good yield [84%: 90% if recovered **1a** is allowed for] together with recovered **1a** (7%). Thus there are excellent routes to this dihydride but not by treatment of [$Os_3H_2(CO)_{10}$] with dppm [12]. The structure of **8** relates closely to that of [$Os_3H_2(CO)_{10}$] [13]. Notably the short bridged Os–Os distances are 2.681 Å in each. Whereas the hydride in [$Os_3H(CO)_{10}$(dppm)]$^+$ cannot fit into the ring formed by the dppm bridge, the hydride ligands in **8** are presumably well outside the Os_3 plane (above and below it) and there is no steric problem in getting the two hydrides and the dppm ligand to bridge the same pair of osmium atoms.

Compound **8** is considerably less reactive that its congener [$Os_3H_2(CO)_{10}$]. Whereas the latter forms adducts readily with CO, PR_3 etc. [2–4], catalyses double bond shifts in alkenes [14], inserts alkynes into the Os–H bonds [15], all at room temperature, compound **8** does not react in this way. We presume that the four phenyl groups protect the reactive, or rather would-be reactive, metal atoms from direct attack. Furthermore, in the adduct formed by the addition of a neutral ligand L, [$Os_3H(\mu$-H)$(CO)_8$(dppm)L], the bridging hydride would need to be in the plane of the Os_3 ring and inside the ring formed by the dppm bridge. We have already shown above that this geometry is unobtainable in the protonation of [$Os_3(CO)_{10}$(dppm)].

We have also been able to synthesise by direct hydrogenation the corresponding dihydrides [$Os_3H_2(CO)_8$(diphos)] where diphos is dppe (**9**) or dppp (**10**). Compounds **8**–**10** all give hydride triplets in their ^{1}H NMR spectra and have very similar ν(CO) infrared spectra and are presumed to be isostructural. Whereas **8** is red, **9** and **10** are a very similar purple to the unsubstituted compound [$Os_3H_2(CO)_{10}$]. Curiously, in spite of the reasonable to excellent yields of compounds **8** to **10**, we were unable to isolate any [$Os_3H_2(CO)_8$(dppb)] by direct hydrogenation of compound **1d**. Low yields of various uncharacterised compounds were obtained. Note also that the direct hydrogenation of 1,1-[$Os_3(CO)_{10}$(diphos)] (diphos = dppe or dppp) does not give any [$Os_3H_2(CO)_8$(diphos)] either [8]. We have not yet examined the reactivity of the dihydrides.

Experimental

The compounds 1,2-$[Os_3(CO)_{10}(diphos)]$, where diphos = dppm, dppe, dppp, dppb, were prepared as described earlier [9,10,16]. NMR spectra were recorded on a Varian XL200 spectrometer in $CDCl_3$.

*Protonation of 1,2-$[Os_3(CO)_{10}(dppm)]$ (**1a**)*

A pale yellow solution was formed on addition of trifluoroacetic acid (0.057 cm^3, 16 mol/mol Os_3) to a bright yellow solution of 1,2-$[Os_3(CO)_{10}(dppm)]$ (0.057 g) in $CDCl_3$ (0.5 cm^3). The ^1H and ^{31}P NMR spectra indicated complete protonation to give **2**, as did the IR spectrum [ν(CO) (CH_2Cl_2): 2136s, 2086m, 2056vs, 2048vs, 2004s, 1985s, 1975 cm^{-1}]. The residue after the removal of solvent was dissolved in methanol. Addition of methanolic NH_4PF_6 and precipitation with water gave a quantitative yield of the starting material **1a**.

*Protonation of 1,2-$[Os_3(CO)_{10}(dppe)]$ (**1b**)*

This gave the salt $[Os_3H(CO)_{10}(dppe)][PF_6]$ (**3**) by a procedure described previously [10]. [ν(CO) (CH_2Cl_2): 2121m, 2078vs, 2068ms, 2038vs, 2020vs cm^{-1}].

*Protonation of 1,2-$[Os_3(CO)_{10}(dppp)]$ (**1c**)*

Trifluoroacetic acid (0.048 cm^3, 16 mol/mol Os_3) was added to a solution of the dppp-compound (0.048 g) in $CDCl_3$ (0.5 cm^3). Removal of the solvent and addition of a methanolic solution of NH_4PF_6 to a methanolic solution of the residue gave a yellow solution, which gave yellow crystals on addition of water. These were recrystallised from dichloromethane/ether mixtures to give $[Os_3H(CO)_{10}(dppp)][PF_6]$ (**4**) (0.033 g, 61%) (Found: C, 31.8; H, 1.95; P, 6.85; $C_{37}H_{27}F_6O_{10}Os_3P_3$ calc.: C, 31.55; H, 1.95; P, 6.85%). [ν(CO) (CH_2Cl_2): 2120m, 2078m, 2068ms, 2037vs, 2021ms, 1971w, 1954w cm^{-1}].

*Protonation of 1,2-$[Os_3(CO)_{10}(dppb)]$ (**1d**)*

Trifluoroacetic acid (0.056 g, 16 mol/mol Os_3) was added to a solution of the dppb cluster (0.057 g) in CD_2Cl_2 (0.5 cm^3) at $-49°C$. The ^1H NMR spectrum was recorded at this temperature and then periodically during 24 h at room temperature. Removal of the solvent and treatment with NH_4PF_6 as above gave 1,2-$[Os_3H(CO)_{10}(dppb)][PF_6]$ (**5**) as pale yellow crystals (0.032 g, 50%) (Found: C, 32.15; H, 2.0; P, 6.45. $C_{38}H_{29}F_6O_{10}Os_3P_3$ calc: C, 32.05; H, 2.05; P, 6.55%). [ν(CO) (CH_2Cl_2): 2120m, 2078m, 2067ms, 2037vs, 2023ms, 2000w cm^{-1}].

Reactions of hydrogen with 1,2-$[Os_3(CO)_{10}(diphos)]$ clusters

*Dppm cluster (**1a**).* Hydrogen was bubbled through a refluxing solution of 1,2-$[Os_3(CO)_{10}(dppm)]$ (0.210 g) in toluene (100 cm^3) for 3 h. Removal of the solvent under vacuum and separation by TLC [SiO_2; eluant: light petroleum (b.p. 30–40 °C)/dichloromethane (10/3 V/V)] gave three bands, which yielded respectively starting material (0.015 g, 7%), 1,2-$[Os_3H_2(CO)_8(dppm)]$ (**8**) as red crystals (0.178 g, 84%) from a CH_2Cl_2/Et_2O mixture (Found: C, 15.45; H, 1.5; P, 7.3. $C_{33}H_{24}O_8Os_3P_2$ calc: C, 15.45; H, 1.55; P, 7.45%), and a small quantity of unidentified material. The dihydride product was spectroscopically identical to that reported previously [12]. [ν(CO) (CH_2Cl_2): 2066s, 2004vs, 1982s, 1954m, 1943m cm^{-1}].

*Dppe cluster (**Ib**).* A similar treatment of 1,2-$[Os_3(CO)_{10}(dppe)]$ (0.095 g) in refluxing toluene with hydrogen for 17 h and similar separation gave 1,2-$[Os_3H_2(CO)_8(dppe)]$ (**9**) (0.025 g, 28%) as purple crystals from a CH_2Cl_2/hexane mixture. The sample could not be obtained analytically pure but was characterised spectroscopically. [ν(CO) (CH_2Cl_2): 2063s, 2007vs, 1981vs, 1949m cm^{-1}].

*Dppp cluster (**Ic**).* A similar treatment of 1,2-$[Os_3(CO)_{10}(dppp)]$ (0.130 g) for 6 h gave starting material (0.008 g, 6%) and 1,2-$[Os_3H_2(CO)_8(dppp)]$ (**10**) as purple crystals (0.078 g, 63%) from diethyl ether (Found: C, 35.15; H, 2.4; P, 5.35. $C_{35}H_{28}O_8Os_3P_2$ calc: C, 34.75; H, 2.35; P, 5.1%). [ν(CO) (CH_2Cl_2): 2066s, 2007vs, 1980vs, 1948sh, 1943m cm^{-1}].

*Dppb cluster (**Id**).* A similar treatment of 1,2-$[Os_3(CO)_{10}(dppb)]$ (0.150 g) for 17 h gave a number of low yield products none of which was the expected dihydride and none was identified.

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