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Triosmium clusters containing diphosphine and triphosphine ligands

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Abstract

The isomeric butadiene compounds 1,1- and 1,2-[$Os_3(C_4H_6)(CO)_{10}$] and the acetonitrile compound 1,2-[$Os_3(CO)_{10}(MeCN)_2$] react with the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$, 3 or 4) to give separable isomers of [$Os_3(CO)_{10}$(diphosphine)] in which the diphosphine is either bridging or chelating, whereas dppm ($n = 1$) gives only the 1,2-isomer. The mono-acetonitrile compound [$Os_3(CO)_{11}(MeCN)$] reacts to give two series of compounds: [$Os_3(CO)_{11}$(diphosphine)], containing one coordinated and one free phosphorus atom, and [$Os_6(CO)_{22}$(diphosphine)] with two $Os_3(CO)_{11}$ groups bridged by the diphosphine. The triphosphine, $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$ (triphos), reacts similarly to give two separable isomers of [$Os_3(CO)_{11}$(triphos)] and two inseparable isomers of [$Os_6(CO)_{22}$(triphos)]. Whereas [$Os_3(CO)_{11}$(dppm)] readily undergoes decarbonylation to give 1,2-[$Os_3(CO)_{10}$(dppm)], other compounds of the type [$Os_3(CO)_{11}$(diphosphine)] are not decarbonylated under the same conditions, but react with Me_3NO to give the 1,2- but not the 1,1-isomers of [$Os_3(CO)_{10}$(diphosphine)].

Introduction

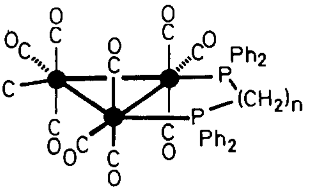
Clusters of the type [$Os_3(CO)_{11}L$], [$Os_3(CO)_{10}L_2$], and [$Os_3(CO)_9L_3$] (L = tertiary phoshine) and their reactions to give interesting decarbonylation products containing ligands formed by fragmentation of the ligands L have been known for a long time (see for examples refs. 1–7). Less is known about diphosphine-substituted derivatives of [$Os_3(CO)_{12}$]. Reactions of [$Ru_3(CO)_{12}$] with diphoshine ligands dppm [8,9] and dppe [10,11] have been described, however. During the course of this work the cluster 1,2-[$Os_3(CO)_{10}$(dppm)] (dppm = $Ph_2PCH_2PPh_2$) with bridging dppm was reported to be formed by reaction of [$Os_3(CO)_{12}$], dppm, and Me_3NO [12], or by decarbonylation of [$Os_3(CO)_{11}$(dppm)] [13]. We have recently reported that [$Os_3(CO)_{10}(PMe_2Ph)_2$] can be prepared as 1,1- and 1,2-isomers, the latter existing as two interconverting isomers in solution [14]. The occurrence of these isomers led us to consider the synthesis of the related 1,1- and 1,2-isomers of $[Os_3(CO)_{10}$(diphosphine)], since this would enable a direct comparison of bridging and chelating diphosphines in isomers. A preliminary account of some of this work has appeared [15]. We have also described the synthesis and X-ray structures of 1,2-$[Os_3(CO)_{10}$(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$) and its monoprotonated derivative [16] and some hydrido clusters derived from 1,1-$[Os_3(CO)_{10}$(dppe)] and 1,1-$[Os_3(CO)_{10}$(dppp)] where dppp = $Ph_2P(CH_2)_3PPh_2$ [17]. In this paper we describe the syntheses and characterisation of the full range of triosmium clusters from the diphosphines dppm, dppe, dppp and dppb, all with the general formula $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ to 4), and from the triphosphine $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$.

Results and discussion

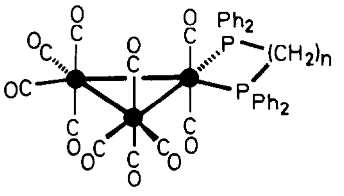
Diphosphine compounds

The chelating butadiene compound 1,1-$[Os_3(C_4H_6)(CO)_{10}]$ [18] reacts with the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 2$ to 4; dppe, dppp, dppb, respectively) to give two isomers each of $[Os_3(CO)_{10}$(diphosphine)], characterised as the 1,2-isomers (**1**) and the 1,1-isomers (**2**). The 1,1-isomers predominate for dppe and dppp while the 1,2-isomer is the major product in the case of dppb. Dppm behaves differently, giving only the recently reported cluster 1,2-$[Os_3(CO)_{10}$(dppm)] [12,13]. The expected 1,1-isomer is not formed, presumably because of the strain in the four-membered ring and the high steric favourability of the bridging 1,2-system. However, there are examples of chelating dppm in clusters, such as in $[Ru_5C(CO)_{12}$(dppm)] [19] and $[Ir_4(CO)_{10}$(dppm)] [18], but bridging dppm is rather more common, e.g. tetra- and hexa-nuclear rhodium clusters contain μ-dppm [20]. The non-occurrence of 1,1-$[Os_3(CO)_{10}$(dppm)] may reflect the wide angle between equatorial sites in triosmium clusters, e.g. 103.5(7)° in $[Os_3(CO)_{12}]$ [21]. Thus dppm is commonly found to chelate in octahedral compounds but chelation is less satisfactory in triosmium compounds, because the distortion from octahedral geometry disfavours chelation.

The isomeric compound 1,2-$[Os_3(C_4H_6)(CO)_{10}]$ reacts with dppm and dppb to give exclusively the 1,2-compounds **1a** and **1d** whereas with dppe and dppp the 1,2-compounds **1b** and **1c** are formed predominantly with small amounts of the



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



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

Table 1

IR and $^{31}P\{^{1}H\}$ NMR data for diphosphine and triphosphine compounds

Compound		ν(CO)[a] (cm^{-1})	δ(^{31}P)[b] [J (Hz)]
1,2-[$Os_3(CO)_{10}$(dppm)]	**(1a)**[c]	2091m, 2028m, 2015s, 2005vs, 1979m, 1961m, 1952m, 1940w.	−168.7(s)
1,2-[$Os_3(CO)_{10}$(dppe)]	**(1b)**[d]	2086m, 2023m, 2013vs, 1999vs, 1974m, 1958m, 1941w, 1932w.	−138.6(s)
1,2-[$Os_3(CO)_{10}$(dppp)]	**(1c)**	2085m, 2019m, 2010s, 1999vs, 1974w, 1957m, 1930w, 1922w.	−146.5(s)
1,2-[$Os_3(CO)_{10}$(dppb)]	**(1d)**	2084ms, 2017m, 2007vs, 2001vs, 1972w, 1957m, 1926w, 1915w.	−150.4(s)
1,1-[$Os_3(CO)_{10}$(dppe)]	**(2b)**	2092m, 2041s, 2012s, 2007vs, 1987s, 1974m, 1962m, 1929w.	−110.4(s)
1,1-[$Os_3(CO)_{10}$(dppp)]	**(2c)**	2091m, 2041s, 2015s, 2004vs, 1988m, 1979m, 1965m, 1909m.	−160.6(s)
1,1-[$Os_3(CO)_{10}$(dppb)]	**(2d)**	2090ms, 2041s, 2012sh, 2003vs, 1988sh, 1979sh, 1959m, 1902w.	[e]
[$Os_3(CO)_{11}$(η^1-dppm)]	**(3a)**[f]	2104w, 2051s, 2032m, 2016vs, 2000w, 1987m, 1976w.	
[$Os_3(CO)_{11}$(η^1-dppe)]	**(3b)**	2106w, 2052s, 2033s, 2017vs, 2000w, 1987m, 1976w, 1957w.	−154.0(d) −147.0(d) [39.1]
[$Os_3(CO)_{11}$(η^1-dppp)]	**(3c)**	2105w, 2052s, 2033m, 2016vs, 1999w, 1988m.	−159.0(s) −150.8(s)
[$Os_3(CO)_{11}$(η^1-dppb)]	**(3b)**	2105w, 2052s, 2032m, 2016vs, 2000w, 1999m, 1988w, 1975w.	−157.3(s) −150.3(s)
[$Os_6(CO)_{22}$(μ-dppe)]	**(4b)**	2105w, 2052s, 2033s, 2017vs, 2001w, 1989m, 1978w.	−150.0(s)
[$Os_6(CO)_{22}$(μ-dppp)]	**(4c)**	2105w, 2052s, 2033s, 2017vs, 2001w, 1989m, 1978w.	−151.0(s)
[$Os_6(CO)_{22}$(μ-dppb)]	**(4b)**	2105w, 2052s, 2033m, 2017vs, 2000w, 1989m, 1978w.	−150.3(s)
1,2-[$Os_3(CO)_{10}(dppe)_2$]	**(5b)**	2082w, 2025s, 2010sh, 1997vs, 1965m, 1953sh.	[e]
1,2-[$Os_3(CO)_{10}(dppp)_2$]	**(5c)**	2082w, 2024m, 2011m, 2000s, 1996m, 1953w.	−150.7(s), −152.2(s) −155.9(s), −160.2(s)

continued

Table 1 (continued)

Compound		ν(CO) [a] (cm^{-1})	δ(^{31}P) [b] [J (Hz)]
[$Os_3(CO)_{11}$(triphos)]	**(6a)**	2105w, 2051s, 2030m, 2015vs, 1999w, 1987m, 1973w, 1955w.	−153.8 AB$_2$ spectrum −154.6 [∼ 35]
[$Os_3(CO)_{11}$(triphos)]	**(6b)**	2105w, 2052s, 2033m, 2016vs, 1999w, 1989m, 1976w, 1956w.	−147.7(d) −153.9(d) [31.5] −158.4(t) [31.5]
[$Os_6(CO)_{22}$(μ-triphos)]	**(7)**	2105w, 2052s, 2033s, 2016vs, 2001w, 1989m, 1978w, 1959w.	−147.4(d) [33.5] −158.7(6) [33.5] [g] −149.5(d) [30.5] −153.1(d) [40.7] −155.4(dd) [30.5, 40.7] [h]
1,2-[$Os_3(CO)_{10}$(triphos)]	**(8)**	2086m, 2023m, 2009s, 1999vs, 1974m, 1961m, 1927w.	

[a] Recorded in cyclohexane. [b] Recorded in $CDCl_3$ relative to $P(OMe)_3$. [c] Ref. 12. [d] Ref. 16. [e] Not recorded. [f] Ref. 13. [g] Isomer a. [h] Isomer b.

1,1-isomers **2b** and **2c** also formed. Unlike PMe_2Ph [14], the diphosphines react with [$Os_3(CO)_{10}(MeCN)_2$] to form only the 1,2-isomers **1**. Thus significant quantities of the 1,1-isomers **2** for dppe, dppp, or dppb can only be obtained from the precurser 1,1-[$Os_3(C_4H_6)(CO)_{10}$].

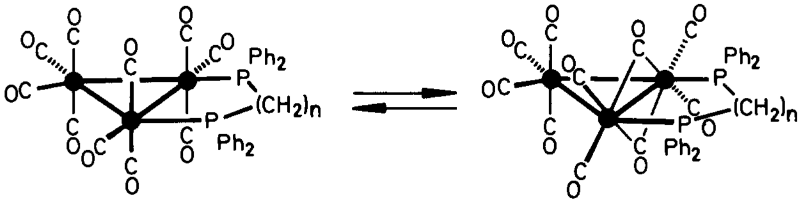
The IR and $^{13}C\{^1H\}$ NMR data in Tables 1 and 2 of the 1,1-isomers **2** are very similar to those of 1,1-[$Os_3(CO)_{10}(PMe_2Ph)_2$] [14] and totally consistent with the proposed structures. As expected $^{31}P\{^1H\}$ NMR spectra show equivalent phosphorus nuclei. Corresponding spectroscopic data for the 1,2-isomers **1** are also given in Tables 1 and 2. The X-ray structure of 1,2-[$Os_3(CO)_{10}$(dppe)] (**1b**) shows the dppe ligand is coordinated in equatorial sites in a bridging mode [16]. A comparison of IR and NMR data of dppm, dppp, and dppb compounds **1** with those of **1b** shows that the compounds **1a–d** are isostructural.

Table 2

^{13}C NMR data for the CO ligands of the clusters [$Os_3(CO)_{10}$(diphosphine)] and [$Os_3(CO)_{10}$(triphos)]

Compound		δ [a]	T (°C)
1,2-[$Os_3(CO)_{10}$(dppm)]	**(1a)**	194.2(4,s) 187.0(2,s), 180.9(2,s), 172.6(2,s)	−50
1,2-[$Os_3(CO)_{10}$(dppe)]	**(1b)**	194.1(4,s) [b], 185.9(2,s) 180.1(2,5), 174.5(2,s)	−20
1,2-[$Os_3(CO)_{10}$(dppp)]	**(1c)**	194.4(4,s), 184.6(2,s), 177.6(2,s), 173.8(2,s)	−50
1,2-[$Os_3(CO)_{10}$(dppb)]	**(1d)**	188.6(6,s) [c], 183.5(2,s), 173.3(2,s)	−50
1,1-[$Os_3(CO)_{10}$(dppe)]	**(2b)**	197.9(2,t) [d], 185.8(4,s), 178.2(2,s), 170.9(2,s)	−50
1,1-[$Os_3(CO)_{10}$(dppp)]	**(2c)**	201.7(2,t) [e], 187.1(4,s) 176.7(2,s), 170.1(2,s)	−50
1,2-[$Os_3(CO)_{10}$(triphos)]	**(8)**	194.0(4,s), 184.7(2,s), 179.1(2,s), 174.5(2,s)	−50

[a] Natural abundance in $CDCl_3$ at 50.3 MHz with [$Cr(acac)_3$] (ca. 0.05 mol dm^{-3}); figures in parentheses indicate the number of CO ligands and multiplicity. [b] δ 194.1 signal splits into two at δ 196.5 and 192.0 at −50 °C. [c] 4 axial and 2 equatorial CO ligands exchanging rapidly at −50 °C. [d] ^2J(PC) 8.3 Hz. [e] ^2J(PC) 7.8 Hz.

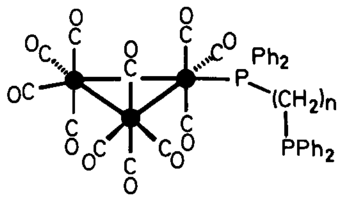


Scheme 1

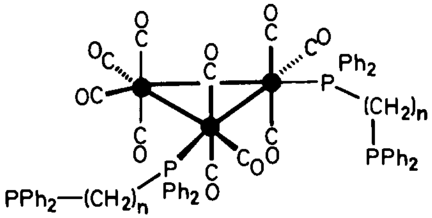
There are differences in the intramolecular behaviour in the series of compounds **1a–d** which are apparent from $^{13}C\{^1H\}$ NMR spectra (Table 2). Only for **1b** could the rate of inversion of the bridging ring be slowed sufficiently at $-50\,°C$ to give five CO signals (1/1/1/1/1) consistent with C_2 symmetry as found in the crystal [16]. Rapid ring inversion in the others (assuming that these rings are non-planar) leads to apparent C_{2v} symmetry at this temperature. Furthermore the process shown in Scheme 1 has very different rates within this series. This process leads to the exchange of all six CO ligands at the two equivalent Os atoms and is the fastest for compound **1d** (dppb) with T_c at ca. $-60\,°C$ and slowest for compound **1a** (dppm) with $T_c \gg 50\,°C$. Compounds **1b** and **1c** have intermediate behaviour with $T_c > 24\,°C$ (dppe) and ca. 15 °C (dppp). Increased flexibility within the diphosphine bridge allows access to the CO-bridged intermediate with the least expenditure of energy and therefore this process is fastest for dppb and unobserved for dppm.

The displacement of MeCN from $[Os_3(CO)_{11}(MeCN)]$ by dppe, dppp, or dppb proceeds smoothly but yields of products vary with the mol ratio of reagents. Using 1 mol diphosphine per mol cluster, two series of compounds were obtained; the main product is $[Os_3(CO)_{11}(\text{diphosphine})]$ (**3**) and a minor product is $[Os_6(CO)_{22}(\text{diphosphine})]$ (**4**). The compounds **4** can be made the only isolable product (76–90%) by using 0.5 mol diphosphine per mol cluster in the synthesis.

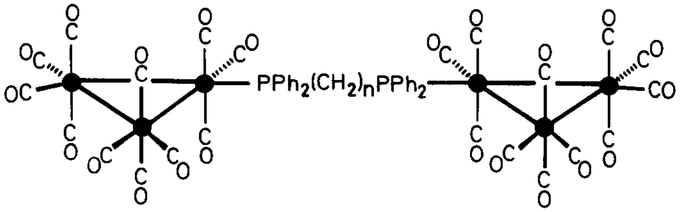
Both compounds **3** and **4** have very similar $\nu(CO)$ spectra to those of $[Os_3(CO)_{11}L]$ where L is a monophosphine or monodentate dppm [4,13,22]. The $^{31}P\{^1H\}$ NMR spectra (Table 1) of **3** clearly indicate that one phosphorus atoms is coordinated, the other free. For example, the spectrum of $[Os_3(CO)_{11}(\text{dppe})]$ (**3a**) contains doublets at δ -154.0 and -147.0 (J 39.1 Hz), the lowfield signal being unshifted from that of the free ligand. This is a similar situation to that found for $[Os_5(CO)_{15}(\eta^1\text{-dppe})]$



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



(5b) (n = 2)
(5c) (n = 3)



(4b) (n = 2)

(4c) (n = 3)

(4d) (n = 4)

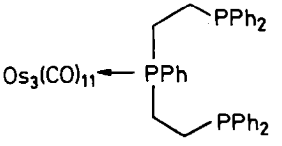
in which the pendant mode of the dppe ligand has been established by X-ray analysis [23]. Consistent with the proposed structure for compounds $[Os_6(CO)_{22}$(diphosphine)] (**4**) with a diphosphine ligand linking two Os_3 clusters, a single $^{31}P\{^1H\}$ NMR singlet is observed in each case. The corresponding ruthenium compounds $[Ru_3(CO)_{11}$(dppe)] and $[Ru_6(CO)_{22}$(dppe)] are known [10,22].

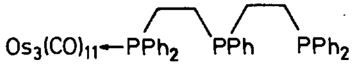
In contrast to the other diphosphines, dppm reacts with $[Os_3(CO)_{11}(MeCN)]$ to give 1,2-$[Os_3(CO)_{10}$(dppm)] (**1a**) [12,13] as the major product with only a small amount of $[Os_3(CO)_{11}(\eta^1$-dppm)] (**3a**) and no $[Os_6(CO)_{22}$(dppm)] (**4a**). The compound $[Os_3(CO)_{11}(\eta^1$-dppm)] (**3a**) undergoes decarbonylation, to form 1,2-$[Os_3(CO)_{10}$(dppm)] (**1a**) [13], at a much faster rate than to displace acetonitrile from another molecule of $[Os_3(CO)_{11}(MeCN)]$ to form the linked-cluster compound. Steric effects seem to limit the ability of dppm to bridge two $Os_3(CO)_{11}$ fragments. Similar behaviour has been observed in $[Fe(C_5H_5)(CO)_2(\eta^1$-diphosphine)$]^+$, which is a good ligand for cobalt(II) through the free phosphorus atom when the diphosphine is dppe or dppp but not when it is dppm [24].

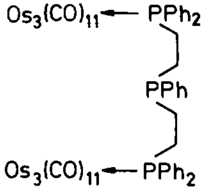
Triphosphine compounds

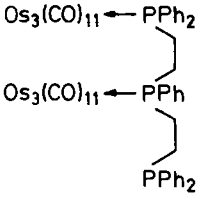
Using the same synthetic methods as above, we treated $[Os_3(CO)_{11}(MeCN)]$ with an equimolar quantity of the ligand triphos ($Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$) to give three separable compounds, all with very similar ν(CO) spectra quite characteristic of $[Os_3(CO)_{11}L]$. These products are readily characterised from their $^{31}P\{^1H\}$ NMR spectra. The first two are isomers of $[Os_3(CO)_{11}$(triphos)] (**6a** and **6b**). Compound **6a** gives an AB_2 $^{31}P\{^1H\}$ NMR spectrum which requires that the central phosphorus atom be coordinated. On the other hand compound **6b** gives an AMX spectrum with doublets at δ −147.7 and −153.9 and a triplet at δ −158.4 ($J_{AM} = J_{AX} = 31.5$ Hz). The low-field doublet at δ −147.7 is assigned to a coordinated terminal phosphorus atom; the other two signals remain more or less unshifted from those of the free ligand.

The $^{31}P\{^1H\}$ NMR spectrum of the third isolated species $[Os_6(CO)_{22}$(triphos)] (**7**) has five resonances which we interpret in terms of two isomers, (**7a** and **7b**), in solution. Isomer **7a** gives a doublet at δ −147.4 and a triplet at δ −158.7 (J 33.5 Hz) while **7b** gives doublets at δ −149.5 (J 30.5 Hz) and δ −153.1 (J 40.7 Hz) and a double doublet at δ −155.4 (J 30.5 and 40.7 Hz). These data are consistent with the structures illustrated for these isomers.


(6a)


(6b)


(7a)


(7b)

None of the isomers described in this paper was observed to undergo isomerisation at room temperature. They are easily separated by TLC except for **7a** and **7b**. Whereas CO ligands can rapidly transfer between metal atoms in clusters, there appears to be no evidence for intramolecular transfer of tertiary phosphine ligands between metal atoms in clusters. Furthermore these Os_3 systems are very inert, and the rates of opening of diphosphine chelates or bridges must be negligible as this would lead to isomerisation, which is not observed.

Experimental

The compounds $[Os_3(\eta^4\text{-}cis\text{-}C_4H_6)(CO)_{10}]$ [18], $[Os_3(\mu\text{-}trans\text{-}C_4H_6)(CO)_{10}]$ [25], and $[Os_3(CO)_{10}(MeCN)_2]$ [25] were prepared by published methods. The diphosphines and triphosphines were purchased from Strem Chemicals Inc. NMR spectra were recorded on a Varian XL200 spectrometer and IR spectra on a Perkin-Elmer PE983 spectrometer. Separation of the products in all cases was by TLC on silica, the eluant being a mixture of light petroleum (b.p. 30–40 ° C) with 10–40% dichloromethane or diethyl ether (by volume).

Reaction of 1,1-$[Os_3(cis\text{-}C_4H_6)(CO)_{10}]$ with dppm. A solution of the 1,1-butadiene compound (0.440 g) and dppm (0.280 g, 1.5 mol/mol Os_3) in chloroform (80 cm^3) was refluxed under nitrogen for 10.5 h. Removal of the solvent under vacuum followed by TLC gave the isomer 1,2-$[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ (0.035 g, 8%) and 1,2-$[Os_3(CO)_{10}(dppm)]$ (**1a**) (0.277 g, 46%) characterised by comparison of spectroscopic data with those reported [12].

Reaction of 1,2-$[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ with dppm. A similar reaction of the 1,2-butadiene isomer (0.037 g) with dppm (0.024 g, 1.5 mol/mol Os_3) in chloroform (15 cm^3) for 23 h gave unchanged butadiene complex (0.005 g) and 1,2-$[Os_3(CO)_{10}(dppm)]$ (**1a**) (0.010 g, 20%).

Reaction of $[Os_3(CO)_{11}(MeCN)]$ with dppm. A solution of the monoacetonitrile compound (0.243 g) and dppm (0.102 g, 1.0 mol/mol Os_3) in dichloromethane (60 cm^3) was kept at room temperature in the dark for 96 h. Work-up by TLC as above gave $[Os_3(CO)_{11}(dppm)]$ (**3a**) as yellow crystals from hexane (0.035 g, 10%) (Found: C, 33.85; H, 2.0; P, 4.7 $C_{36}H_{22}O_{11}Os_3P_2$ calc: C, 34.25; H, 1.75; P, 4.9%) and the compound 1,2-$[Os_3(CO)_{10}(dppm)]$ (**1a**) (0.211 g, 65%).

Reaction of 1,1-$[Os_3(cis\text{-}C_4H_6)(CO)_{10}]$ with dppe. A solution of the C_4H_6 complex (0.422 g) and dppe (0.278 g, 1.5 mol/mol Os_3) in chloroform (80 cm^3) was refluxed for 9 h. Removal of the solvent followed by TLC gave (i) unchanged $[Os_3(cis\text{-}C_4H_6)(CO)_{10}]$ (0.005 g); (ii) $[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ (0.022 g, 5%); (iii) 1,1-$[Os_3(CO)_{10}(dppe)]$ (**2b**), as orange crystals (0.250 g, 43%) from methanol (Found: C, 34.35; H, 2.0; P, 5.35. $C_{36}H_{24}O_{10}Os_3P_2$ calc: C, 34.6; H, 1.95; P, 4.95%); and (iv) 1,2-$[Os_3(CO)_{10}(dppe)]$ (**1b**) as yellow crystals (0.050 g, 9%).

Reaction of 1,2-$[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ with dppe. A similar reaction of the *trans*-C_4H_6 complex (0.042 g) and dppe (0.028 g, 1.5 mol/mol Os_3) for 22 h gave recovered starting material (0.004 g), 1,1-$[Os_3(CO)_{10}(dppe)]$ (**2b**) (0.005 g, 9%), and 1,2-$[Os_3(CO)_{10}(dppe)]$ (**1b**) (0.010 g, 17%).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with dppe. A solution of the bis-acetonitrile compound (0.288 g) and dppe (0.185 g, 1.5 mol/mol Os_3) in $CHCl_3$ (40 cm^3) was refluxed for 3 h. TLC gave $[Os_3(CO)_{11}(dppe)]$ (**3b**) as yellow crystals (0.040 g, 10%) from hexane, 1,2-$[Os_3(CO)_{10}(dppe)]$ (**1b**) (0.172 g, 45%), and 1,2-$[Os_3(CO)_{10}(dppe)_2]$ (**5b**) as red crystals (0.027 g, 5%) from n-hexane (Found: C, 44.75; H, 3.05; P, 7.5. $C_{62}H_{48}O_{10}Os_3P_4$ calc: C, 45.2; H, 2.95; P, 7.5%).

Reactions of $[Os_3(CO)_{11}(MeCN)]$ with dppe. (a) A solution of the MeCN compound (0.150 g) and dppe (0.065 g, 1.0 mol/mol Os_3) in chloroform (30 cm^3) was refluxed under N_2 for 15 min. TLC gave $[Os_3(CO)_{11}(dppe)]$ (**3b**) as yellow crystals, (0.105 g, 51%) from hexane (Found: C, 35.25; H, 2.15; P, 4.8. $C_{37}H_{24}O_{11}Os_3P_2$ calc: C, 34.8; H, 1.9; P, 4.85%) and $[Os_6(CO)_{22}(\mu\text{-dppe})]$ (**4b**) as yellow crystals, (0.036 g, 20%) from hexane (Found: C, 26.75; H, 1.25; P, 2.9. $C_{48}H_{24}O_{22}Os_6P_2$ calc: C, 26.75; H, 1.1; P, 2.85%).

(b) A similar reaction between the MeCN compound (0.125 g) and dppe (0.027 g, 0.5 mol/mol Os_3) in refluxing chloroform (25 cm^3) gave $[Os_6(CO)_{22}(\mu\text{-dppe})]$ (**4b**) (0.132 g, 90%).

Reactions of 1,1-$[Os_3(cis\text{-}C_4H_6)(CO)_{10}]$ with dppp. A solution of dppp (0.417 g, 1.5 mol/mol Os_3) and the C_4H_6 compound (0.610 g) in dichloromethane (50 cm^3) was kept in the dark at room temperature under nitrogen for 30 d. TLC gave two products: 1,1-$[Os_3(CO)_{10}(dppp)]$ (**2c**) as orange crystals (0.330 g, 39%) from hexane (Found: C, 35.75; H, 2.1; P, 5.1. $C_{37}H_{26}O_{10}Os_3P_2$ calc: C, 35.2; H, 2.1; P, 4.9%) and 1,2-$[Os_3(CO)_{10}(dppp)]$ (**1c**) as yellow crystals (0.025 g, 3%) from methanol (Found: C, 35.65; H, 2.1; P, 4.9. $C_{37}H_{26}O_{10}Os_3P_2$ calc: C, 35.2; H, 2.1; P, 4.9%).

Reaction of 1,2-$[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ with dppp. A similar treatment of this C_4H_6 complex (0.050 g) with dppp (0.034 g, 1.5 mol/mol Os_3) for 24 h gave unchanged C_4H_6 complex (0.008 g), 1,1-$[Os_3(CO)_{10}(dppp)]$ (**2c**) (0.005 g, 7%), and 1,2-$[Os_3(CO)_{10}(dppp)]$ (**1c**) (0.010 g, 14%).

Reactions of $[Os_3(CO)_{11}(MeCN)]$ with dppp. (a) A solution of the MeCN compound (0.170 g) and dppp (0.076 g, 1.0 mol/mol Os_3) in chloroform (30 cm^3) was refluxed under N_2 for 15 min. TLC work-up gave $[Os_3(CO)_{11}(dppp)]$ (**3c**) as orange crystals (0.107 g, 45%) from hexane (Found: C, 35.75; H, 2.1; P, 4.8. $C_{38}H_{26}O_{11}Os_3P_2$ calc: C, 35.35; H, 2.05; P, 4.8%) and $[Os_6(CO)_{22}(\mu\text{-dppp})]$ (**4c**) as yellow crystals (0.083 g, 41%) from hexane (Found: C, 28.35; H, 1.5; P, 2.75. $C_{49}H_{26}O_{22}Os_6P_2$ calc: C, 27.1; H, 1.2; P, 2.85%).

(b) A similar reaction using $[Os_3(CO)_{11}(MeCN)]$ (0.130 g) and dppp (0.029 g) for 1 h gave $[Os_6(CO)_{22}(\mu\text{-dppp})]$ (**4c**) (0.127 g, 83%).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with dppp. A similar treatment of the bis-acetonitrile compound (0.769 g) and dppp (0.510 g, 1.5 mol/mol Os_3) for 3 h followed by a similar TLC work-up gave $[Os_3(CO)_{11}(dppp)]$ (**3c**) (0.080 g, 8%) and 1,2-$[Os_3(CO)_{10}(dppp)_2]$ (**5c**) as red crystals (0.076 g, 6%) from methanol (Found: C, 46.25; H, 3.45; P, 7.1. $C_{64}H_{52}O_{10}Os_3P_4$ calc: C, 45.85; H, 3.15; P, 7.4%) and 1,2-$[Os_3(CO)_{10}(dppp)]$ (**1c**) (0.312 g, 30%).

Reaction of 1,1-$[Os_3(cis\text{-}C_4H_6)(CO)_{10}]$ with dppb. A solution of the C_4H_6 complex (0.051 g) and dppb (0.035 g, 1.5 mol/mol Os_3) in chloroform (20 cm^3) was refluxed for 5.5 h. TLC work-up gave 1,2-$[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ (0.005 g, 10%), 1,1-$[Os_3(CO)_{10}(dppb)]$ (**2d**) (0.004 g, 6%), and 1,2-$[Os_3(CO)_{10}(dppb)]$ (**1d**) as red crystals (0.023 g, 24%) from hexane (Found: C, 36.05; H, 2.1; P, 4.85. $C_{38}H_{28}O_{10}Os_3P_2$ calc: C, 35.75; H, 2.2; P, 4.85%).

Reaction of 1,2-$[Os_3(trans\text{-}C_4H_6)(CO)_{10}]$ with dppb. A similar reaction to that above using the 1,2-C_4H_6 complex (0.041 g) and dppb (0.032 g, 1.5 mol/mol Os_3) for 29 h gave unchanged C_4H_6 compound (0.007 g) and 1,2-$[Os_3(CO)_{10}(dppb)]$ (0.015 g, 26%).

Reactions of $[Os_3(CO)_{11}(MeCN)]$ with dppb. (a) A solution of the MeCN compound (0.111 g) and dppb (0.052 g, 1.0 mol/mol Os_3) in chloroform (25 cm^3) was refluxed for 15 min. TLC gave $[Os_3(CO)_{11}(dppb)]$ (**3d**) as orange crystals (0.060 g, 40%) from hexane (Found: C, 36.35; H, 2.35; P, 4.75. $C_{39}H_{28}O_{11}Os_3P_2$ calc: C, 35.9; H, 2.15; P, 4.75%) and $[Os_6(CO)_{22}(dppb)]$ (**4d**) as yellow crystals (0.021 g, 16%) from hexane (Found: C, 27.8; H, 1.35; P, 2.9. $C_{50}H_{28}O_{22}Os_6P_2$ calc: C, 27.5; H, 1.3; P, 2.85%).

(b) A similar reaction using the MeCN compound (0.167 g) and dppb (0.039 g, 0.5 mol/mol Os_3) for 1 h gave $[Os_6(CO)_{22}(dppb)]$ (**4d**) (0.150 g, 76%).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with dppb. A similar treatment of the bis-acetonitrile compound (0.496 g) and dppb (0.345 g, 1.5 mol/mol Os_3) for 4 h followed by TLC gave $[Os_3(CO)_{11}(dppb)]$ (**3d**) (0.048 g, 7%) and 1,2-$[Os_3(CO)_{10}(dppb)]$ (**1d**) (0.173 g, 28%).

Reaction of $[Os_3(CO)_{11}(MeCN)]$ with triphos. A solution of the MeCN compound (0.188 g) and triphos (0.109 g, 1.0 mol/mol Os_3) in chloroform (30 cm^3) was refluxed for 45 min. TLC gave two isomers of $[Os_3(CO)_{11}(triphos)]$ (**6a**) (0.025 g, 9%) and (**6b**) (0.057 g, 20%) and $[Os_6(CO)_{22}(triphos)]$ (**7**) as yellow crystals (0.095 g, 41%) from hexane (Found: C, 29.45; H, 1.55; P, 4.0. $C_{56}H_{33}O_{22}Os_6P_3$ calc: C, 29.35; H, 1.45; P, 4.0%).

Reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with triphos. A similar treatment of the bis-MeCN complex (0.500 g) and triphos (0.287 g) in refluxing chloroform (60 cm^3) for 3 h gave the two isomers: **6a** (0.020 g, 3%) and **6b** (0.030 g, 4%) and the compound 1,2-$[Os_3(CO)_{10}(triphos)]$ (**8**) as yellow crystals (0.093 g, 13%) from methanol (Found: C, 38.3; H, 2.3. $C_{44}H_{33}O_{10}Os_3P_3$ calc: C, 38.15; H, 2.4%).

Decarbonylation of $[Os_3(CO)_{11}(diphosphine)]$

(a) Thermally. Solutions of the complexes where diphosphine = dppe, dppp, or dppb in refluxing cyclohexane showed no change in the IR spectra after 3 h under nitrogen.

(b) With Me_3NO. $Me_3NO \cdot 2H_2O$ (0.007 g) was added to a solution of

$[Os_3(CO)_{11}(dppe)]$ (**3b**) (0.039 g) in dichloromethane. The solution immediately changed from yellow to orange. It was filtered through silica to remove the excess of amine oxide. TLC gave 1,2-$[Os_3(CO)_{10}(dppe)]$ (**1b**) (0.027 g, 71%). Similar reactions with **3c** and **3d** gave **1c** (69%) and **1d** (65%), respectively.

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