A Convenient Route to Binuclear Osmium(I) Complexes containing Diphosphine and Arsinophosphine Ligands. *X*-Ray Crystal Structure of $[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$†

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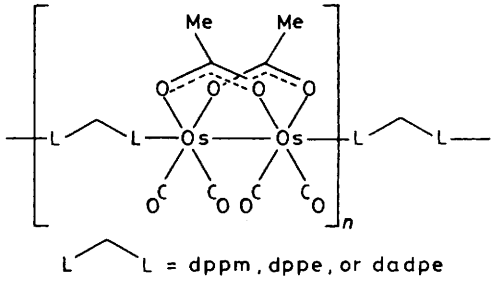
Reaction of the binuclear osmium(I) compound $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$ with 1 equivalent of the bidentate groups L–L (L–L = dppm, dppe, or dadpe) [dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, and dadpe = 1-diphenylarsino-2-diphenylphosphinoethane] yields the osmium(I) polymers $[\{Os_2(MeCO_2)_2(CO)_4(L{-}L)\}_n]$ in which two metals are bridged by two carboxylate groups and the binuclear units are linked by diphosphine ligands. Reaction of $[Os_2(MeCO_2)_2(CO)_6]$ in refluxing tetrahydrofuran (thf) with 2 equivalents of dppm yields the neutral diaxially substituted compound $[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$, the *X*-ray structure of which confirms axial substitution. No evidence for equatorial substitution was found for dppm using alcohols or excess of ligand. Treatment of $[Os_2(MeCO_2)_2(CO)_6]$ in refluxing ethanol with 2 equivalents of dppe or dadpe yields two different types of cationic compounds of formula $[Os_2(MeCO_2)(CO)_4(L{-}L)_2]^+$ (L–L = dppe or dadpe) in which an acetate group has been displaced. An edge-sharing bioctahedral structure having two bridging carbonyls and one bridging acetate group with one dppe chelating each metal is suggested in the first case, while either of two possible structures having no bridging carbonyls and one bridging acetate with one dadpe chelating each metal in two possible orientations is suggested for the second.

The analogy between the chemisorbed state of organic molecules on metal surfaces and the multiply co-ordinated state of organic fragments covalently bonded to metal atom polyhedra has been widely cited.[1,2] Since metal–metal bonds are generally more robust for third-series transition metals, binuclear osmium(I) complexes may be useful models for studying the chemical reactivity of the metal–metal bonded core of these metal clusters. Up to recently the preferred routes to osmium(I) dimers were *via* the complexes $[Os_3(CO)_{12}]$ and $[Os_2H_2(CO)_8]$.[3,4] Substitution reactions[5,6] on the carboxylato-bridged dimer $[Os_2(MeCO_2)_2(CO)_6]$ with a range of monodentate ligands have shown the usefulness of this complex as a precursor for binuclear osmium(I) complexes. Our work with bidentate and tridentate groups extends the studies of Deeming *et al.*[6] and shows the versatility of this compound and its acetonitrile derivative, $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$, as precursors for the synthesis of a series of new osmium(I) dimers. These include neutral and cationic dimers containing mono- and bi-dentate tertiary phosphorus groups, diamines,[7] and polypyrazolylborato[7] ligands. These investigations parallel our studies on the corresponding ruthenium(I) complex *catena*-$[Ru(MeCO_2)(CO)_2]$ and its acetonitrile derivative.[8–11] In this paper we describe the interaction of $[Os_2(MeCO_2)_2(CO)_6]$ and $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$ with diphosphine and arsinophosphine ligands affording products in which the co-ordination modes of the ligands are monodentate, bidentate, or bridging.

Results and Discussion

Stirring a solution of the carboxylate-bridged dimer $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$ in acetone with 1 molar equivalent of the diphosphines, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), or 1-diphenylarsino-2-diphenylphosphinoethane (dadpe), at room temperature for 24 h yields the creamy white air-stable sparingly soluble polymers $[\{Os_2(MeCO_2)_2(CO)_4(L{-}L)\}_n]$ (L–L = dppm, dppe, or dadpe) in moderate to good yields. The i.r. spectra (see Table 1) of these complexes contain four sharp bands in the terminal carbonyl region at 2 012—1 905 cm^{-1}. In addition, unsymmetrical and symmetrical bridging carboxylate stretching frequencies are observed at 1 575—1 440 cm^{-1}. These correspond to the spectra observed previously for cisoid bis(μ-acetato)-dimetal tetracarbonyls[5,6,9,12] with carbonyl groups in a C_{2v} sawhorse arrangement. Such a core structure eliminates the possibility of an Os–Os dimer bridged by diphosphine or dadpe ligands. The ^{31}P-{^1H} n.m.r. spectra (Table 1) for L–L = dppm or dppe contain singlet resonances at 16.96 and 20.24 p.p.m. respectively. For L–L = $Ph_2AsCH_2CH_2PPh_2$ (dadpe) two bands of unstructured singlets at 20.31 and 16.55



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† Di-μ-(acetato-*O,O'*)-bis{[1,2-bis(diphenylphosphino)methane-*P*]dicarbonylosmium}(*Os–Os*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Infrared, ^{1}H, and ^{31}P-{^{1}H} n.m.r. data for the complexes [{$Os_2(MeCO_2)_2(CO)_4$(L–L)}$_n$]

L–L	ν(CO)^a/cm^{-1}	ν(CO$_2$)^a/cm^{-1}	^{1}H N.m.r.^{b} (δ)	^{31}P-{^{1}H} N.m.r.^{c} (p.p.m.)
dppm	2 003vs, 1 970s, 1 933vs, 1 909(sh)	1 573vs, 1 440vs	7.33—7.10 (m, Ph), 4.14 (br s, CH$_2$), 1.64 (s, MeCO$_2$)	16.96
dppe	2 010vs, 1 964m, 1 931vs, 1 908(sh)	1 575s, 1 448s	7.45—7.15 (br s, Ph), 2.49 (br s, CH$_2$), 1.36 (s, MeCO$_2$)	20.24
dadpe	2 012vs, 1 963s, 1 933vs, 1 905(sh)	1 575s, 1 445s	7.20—7.45 (m, Ph), 2.68, 2.42 (br s, CH$_2$), 1.40 (m, MeCO$_2$)	20.31m 16.55m

^{a} In Nujol. ^{b} In CDCl$_3$ at 300 MHz. ^{c} In CDCl$_3$ at 121 MHz.

Table 2. Infrared and proton n.m.r. data for the complexes [$Os_2(MeCO_2)_2(CO)_4(dppm)_2$] and [$Os_2(MeCO_2)(CO)_4$(L–L)$_2$]PF$_6$

Compound	ν(CO)^a/cm^{-1}	ν(CO$_2$)^a/cm^{-1}	^{1}H N.m.r. (δ)
[$Os_2(MeCO_2)_2(CO)_4(dppm)_2$]	2 011vs, 1 966m, 1 934vs, 1 905(sh)	1 577s, 1 445m	^{b}7.48—7.10 (m, Ph), 3.35 (m, CH$_2$), 1.41 (s, MeCO$_2$)
[$Os_2(MeCO_2)(CO)_4(dppe)_2$]PF$_6$	2 017(sh), 1 994s, 1 955s, 1 708m	1 545w, 1 436m	^{c}7.59—7.27 (m, Ph), 2.72 (m, CH$_2$), 0.97 (s, MeCO$_2$)
[$Os_2(MeCO_2)(CO)_4(dadpe)_2$]PF$_6$	2 016s, 1 986s, 1 937s	1 539w, 1 436m	^{c}7.46—7.09 (m, Ph), 2.66, 2.52, 2.25 (m, CH$_2$), 0.61 (s, MeCO$_2$)

^{a} In CH$_2$Cl$_2$. ^{b} In CDCl$_3$ at 300 MHz. ^{c} In (CD$_3$)$_2$CO at 300 MHz.

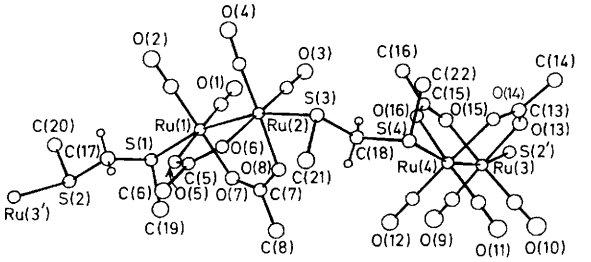


Figure 1. Molecular structure of the ruthenium(I) polymer [{$Ru_2(MeCO_2)_2(CO)_4(MeSCH_2SMe)$}$_n$]

p.p.m. are observed which are invariant with temperature indicating that the phosphorus nuclei are in a variety of different magnetic environments.

The above data are consistent with the following structure in which two osmium atoms are bridged by two carboxylate groups and the dinuclear units are linked by diphosphine ligands in the preferred[6] axial positions to form chains. Further evidence for this structure is provided by the *X*-ray structural determination of the related ruthenium(I) polymer [{$Ru_2(MeCO_2)_2(CO)_4(MeSCH_2SMe)$}$_n$],[9,13] which has been shown to consist of chains of dimeric ruthenium(I) units bridged by acetate and linked by dithioether units (Figure 1) The compound was similarly prepared from the corresponding ruthenium(I) acetonitrile dimer and has identical solubility properties and spectroscopic data.

Treatment of [$Os_2(MeCO_2)_2(CO)_6$] with 2 molar equivalents of dppm in refluxing tetrahydrofuran (thf) yields the white air-stable crystalline complex [$Os_2(MeCO_2)_2(CO)_4(dppm)_2$]. The i.r. spectrum (see Table 2) of this compound closely resembles that of the analogous axially substituted [$Os_2(MeCO_2)_2(CO)_4(L_2)$] (L = PPh$_3$, AsPh$_3$, PMe$_2$Ph, PMePh$_2$, C$_5H_5$N, or MeCN),[5,6] as well as that of the polymeric [{$Os_2(MeCO_2)_2(CO)_4$(L–L)}$_n$], in the carbonyl and carboxylate regions suggesting a similar core structure with two axial carbonyls displaced by monodentate dppm groups. N.m.r. data are given in Tables 2 and 3. The ^{31}P-{^{1}H} n.m.r. appears as two sets of multiplets at 17.77 and −26.36 p.p.m. characteristic of an AA′XX′ spin system for two different phosphorus environments. The low-field chemical shift at 17.77 p.p.m. is assigned to the axially co-ordinated phosphorus atom, P$_A$, while the value at −26.36 p.p.m. is assigned to the pendant phosphorus atom, P$_X$. Analysis of this spectrum has resulted in coupling constants ^2J(AX) = 71 and ^3J(AA′) = 62 Hz [^5J(AX′) and ^7J(XX′) were taken as zero from the resonance pattern]. The ^{13}C-{^{1}H} n.m.r. shows a single carbon resonance for carbonyl at 188.81 p.p.m., split into a 1:2:1 triplet from P–C couplings. The methylene carbon of the dppm ligand appears as a doublet of triplets. This arises from the coupling of carbon to the pendant phosphorus on which is superimposed the coupling of the two chemically equivalent phosphorus atoms co-ordinated *trans* to the metal–metal bond. The structure of this compound has been confirmed by an *X*-ray crystal structure analysis.

The molecular structure of [$Os_2(MeCO_2)_2(CO)_4(dppm)_2$] is given in Figure 2, corresponding parameters in Tables 4 and 5. The core structure '$Os_2(MeCO_2)_2(CO)_4$' compares closely with that of the parent compound [$Os_2(MeCO_2)_2(CO)_6$].[14] Both structures have osmium–osmium bonded cores [with osmium atoms at a distance of 2.740(1) in this complex and 2.731(2) Å for the parent hexacarbonyl[14]] which are doubly bridged by cisoid acetate ligands, *trans* to which are situated the carbonyls. In this compound each osmium atom is octahedrally surrounded by two carbon atoms from terminal carbonyls, two oxygen atoms from acetate ligands, the other osmium atom, and one phosphorus atom from dppm. Octahedral angles range from 82.2(3) to 98.3(5)°. Slight distortions from the ideal are caused by unsymmetrical ligand–ligand repulsive forces around the binuclear core due to acetate displaying ligation with minimum repulsion, thus pinching the molecule in on one side. The bridging acetate groups are planar and impose an eclipsed rotational conformation of substituents around the Os–Os bond. The dppm ligands are co-ordinated in the axial position *trans* to the metal–metal bond in a monohapto fashion, bending toward the acetate groups with a mean Os–Os–P of 162.6(1)°.

Attempts to displace equatorial carbonyls or acetate in

Table 3. $^{31}P-\{^1H\}$ and $^{13}C-\{^1H\}$ n.m.r. data for the complexes $[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$ and $[Os_2(MeCO_2)(CO)_4(L\text{–}L)_2]PF_6$

Compound	$^{31}P-\{^1H\}$ N.m.r. (p.p.m.)	$^{13}C-\{^1H\}$ N.m.r. (p.p.m.)					
		μ-CO	CO	CO_2	Ph	CH_2	Me
$[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$	17.77, −26.36 [AA′XX′; $^2J(AX)$ = 71, $^3J(AA')$ = 62 Hz][a]		188.81 [t, $\lvert\Sigma J(PC)\rvert$ = 18.1 Hz][b]	187.92 (s)	139.19—127.80	24.91 [dt, J = 31.9, $\lvert\Sigma J(PC)\rvert$ = 17.3 Hz]	22.13 (s)
$[Os_2(MeCO_2)(CO)_4(dppe)_2]PF_6$	27.06 (s)[c]	224.62 (m)	180.00 [qnt, $\lvert\Sigma J(PC)\rvert$ = 6.9 Hz][d]	184.82 (s)	132.85—128.77	29.79 [qnt, $\lvert\Sigma J(PC)\rvert$ = 22.7 Hz]	21.62 (s)
$[Os_2(MeCO_2)(CO)_4(dadpe)_2]PF_6$	40.58 (s)[c]		194.36 [t, $\lvert\Sigma J(PC)\rvert$ = 15.6 Hz] 193.47 (s)[e]	184.76	133.79—129.50	32.41 [t, $\lvert\Sigma J(PC)\rvert$ = 16.4], 28.04 [qnt, $\lvert\Sigma J(PC)\rvert$ = 29.8 Hz]	24.07 (s)

[a] In $CDCl_3$. [b] In $CDCl_3$ at 75 MHz. [c] In $(CD_3)_2CO$. [d] In CD_2Cl_2 at 75 MHz. [e] In $(CD_3)_2CO$ at 125 MHz.

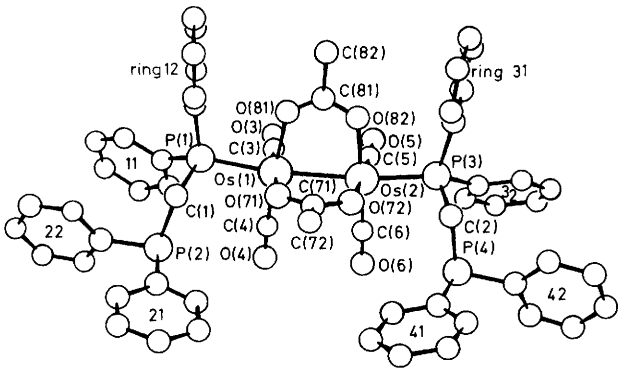
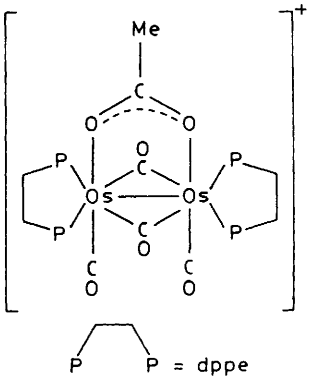


Figure 2. A perspective view of the osmium(I) dimer $[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$ showing the numbering scheme. Hydrogen atoms are omitted for clarity

$[Os_2(MeCO_2)_2(CO)_6]$ by excess of dppm in refluxing high boiling alcohols to give either neutral or cationic products have been unsuccessful. However, treatment of $[Os_2(MeCO_2)_2(CO)_6]$ with 2 molar equivalents of dppe or dadpe in refluxing ethanol affords the brightly coloured crystalline cationic complexes $[Os_2(MeCO_2)(CO)_4(L\text{–}L)_2]^+$ (L–L = dppe or dadpe), by acetate displacement. Infrared and n.m.r. data for the complexes are given in Tables 2 and 3. Spectral data indicate different structures for the two cationic products. The i.r. spectra show both terminal and bridging carbonyls for the dppe derivative, but only terminal carbonyls for the dadpe compound. The $^{31}P-\{^1H\}$ n.m.r. spectra exhibit singlets at 27.1 and 40.6 p.p.m. for the dppe and dadpe compounds, respectively. The $^{13}C-\{^1H\}$ n.m.r. for the dppe compound exhibits two carbonyl resonances *i.e.*, an unresolved multiplet at 224.6 p.p.m. for the bridging carbonyl and a quintet at 180.0 p.p.m. for the terminal carbonyl. The latter is consistent with the X part of an AA′BB′X spin system. Methylene carbons are observed as a 2:3:4:3:2 quintet representing the X part of an ABCDX spin system. This spectrum corresponds to that of $[Ru_2(MeCO_2)(\mu\text{-}CO)_2(CO)_2(dppe)_2]PF_6$[7,9] which has been structurally characterized. The following dioctahedral-type structure sharing an edge at the bridging carbonyl groups is therefore proposed for the new cationic complex.



For the dadpe compound two terminal carbonyl resonances are observed in the $^{13}C-\{^1H\}$ n.m.r. spectrum as a 1:2:1 triplet (ABX spin system) at 194.4 p.p.m. and a singlet at 193.5 p.p.m. The observed coupling constant, $|\Sigma J(CP)|$ = 16 Hz, for the triplet is consistent with a *trans* carbonyl to phosphorus arrangement. The methylene carbons of the dadpe ligand appear as a triplet at 32.4 and a pseudo-quintet at 28.0 p.p.m., both consistent with an ABX spin system. The first resonance pattern represents the carbon [$|\Sigma J(CP)|$ = 16 Hz] adjacent to arsenic and the second pattern the carbon [$|\Sigma J(CP)|$ = 30 Hz] adjacent to phosphorus. Based upon these spectral data we propose either of the following structures for $[Os_2(MeCO_2)(CO)_4(dadpe)_2]^+$ differing only in the way in which the chelating dadpe ligand bonds to each osmium.

Experimental

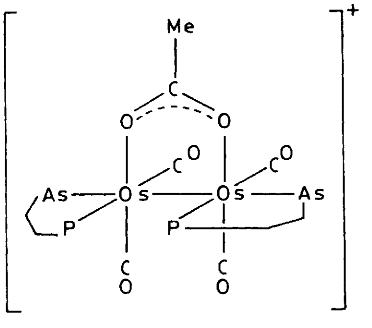
Physical Measurements.—Infrared spectra were recorded on a Bruker IFS85 FTIR spectrometer, ^1H, $^{13}C-\{^1H\}$, and $^{31}P-\{^1H\}$ spectra on a Bruker WM500 or AM300 n.m.r. spectrometer. For $^{31}P-\{^1H\}$ spectra 85% H_3PO_4 was used as an external standard, positive chemical shift being downfield from H_3PO_4. Microanalyses were performed by Mr. H. Lachman of the National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria.

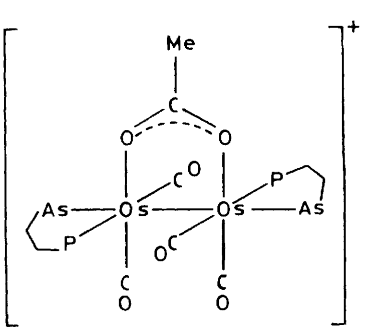
Starting Materials.—The acetato compounds $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$ and $[Os_2(MeCO_2)_2(CO)_6]$ were synthesized by the reported methods.[5,6]

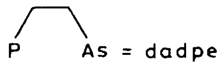
Syntheses.—$[\{Os_2(MeCO_2)_2(CO)_4(L\text{–}L)\}_n]$ (L–L = dppm, dppe, *or* dadpe). A mixture of $[Os_2(MeCO_2)_2(CO)_4(MeCN)_2]$ (0.35 g, 0.50 mmol) and L–L (dppm, 0.19 g; dppe, 0.20 g; dadpe, 0.22 g; 0.50 mmol) in acetone (40 cm^3) was stirred at room temperature for 24 h during which time creamy white precipitates formed. The precipitates were filtered off and washed with acetone to give the required products (dppm, 0.31 g, 61%; dppe, 0.11 g, 44%; dadpe, 0.11 g, 42%) [Found (L–L =

Table 4. Fractional co-ordinates (× 10^4, 10^5 for Os) for $[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	28 021(6)	9 904(3)	63 772(2)	C(211)	1 076(15)	2 840(7)	5 327(7)
Os(2)	28 454(6)	8 682(3)	74 869(3)	C(212)	1 124(15)	3 265(8)	4 965(7)
C(3)	2 663(20)	299(9)	6 217(8)	C(213)	1 075(20)	3 804(8)	5 113(10)
C(4)	967(18)	1 087(9)	6 336(6)	C(214)	963(21)	3 923(9)	5 639(12)
C(5)	2 703(24)	160(8)	7 483(9)	C(215)	846(22)	3 524(10)	6 007(10)
C(6)	1 085(21)	948(11)	7 563(7)	C(216)	918(17)	2 985(8)	5 858(9)
C(71)	3 221(17)	1 999(7)	7 047(7)	C(221)	1 170(17)	2 112(7)	4 424(7)
C(72)	3 575(18)	2 598(7)	7 093(7)	C(222)	22(18)	1 949(7)	4 155(8)
C(81)	5 427(12)	879(8)	6 921(7)	C(223)	−11(20)	1 923(10)	3 591(9)
C(82)	6 944(12)	836(8)	6 912(7)	C(224)	989(24)	2 060(10)	3 290(9)
O(3)	2 527(19)	−189(5)	6 131(6)	C(225)	2 157(21)	2 221(9)	3 545(9)
O(4)	−126(12)	1 126(9)	6 338(6)	C(226)	2 211(17)	2 250(8)	4 100(7)
O(5)	2 673(22)	−335(6)	7 467(7)	C(311)	5 190(15)	854(8)	8 557(6)
O(6)	−90(13)	963(9)	7 588(5)	C(312)	6 093(17)	1 302(8)	8 522(7)
O(71)	3 157(12)	1 820(5)	6 570(5)	C(313)	7 362(19)	1 206(10)	8 546(8)
O(72)	3 152(11)	1 727(4)	7 471(5)	C(314)	7 802(21)	692(11)	8 627(8)
O(81)	4 864(9)	921(6)	6 481(4)	C(315)	7 034(21)	242(9)	8 649(8)
O(82)	4 898(10)	849(6)	7 364(5)	C(316)	5 691(19)	326(8)	8 592(6)
P(1)	3 330(4)	1 276(2)	5 475(2)	C(321)	2 669(16)	516(6)	8 941(7)
P(2)	1 178(4)	2 110(2)	5 157(2)	C(322)	1 648(18)	149(7)	8 799(8)
C(1)	2 919(13)	2 001(6)	5 343(6)	C(323)	1 095(19)	−165(8)	9 198(9)
P(3)	3 402(4)	955(2)	8 429(2)	C(324)	1 491(22)	−154(8)	9 723(9)
P(4)	1 308(4)	1 727(2)	8 841(2)	C(325)	2 472(22)	207(8)	9 864(7)
C(2)	3 048(14)	1 632(7)	8 693(6)	C(326)	3 077(19)	520(7)	9 482(8)
C(111)	2 589(15)	937(6)	4 892(6)	C(411)	1 174(16)	2 457(7)	8 683(7)
C(112)	1 328(15)	685(6)	4 917(6)	C(412)	846(18)	2 571(9)	8 148(8)
C(113)	706(16)	483(7)	4 473(8)	C(413)	773(22)	3 138(10)	7 981(9)
C(114)	1 340(21)	478(8)	3 989(8)	C(414)	1 049(22)	3 539(10)	8 360(12)
C(115)	2 581(20)	680(8)	3 929(8)	C(415)	1 362(18)	3 428(8)	8 877(10)
C(116)	3 155(17)	919(7)	4 380(7)	C(416)	1 415(14)	2 884(8)	9 047(8)
C(121)	5 098(13)	1 251(6)	5 360(5)	C(421)	1 177(17)	1 739(6)	9 569(6)
C(122)	5 680(17)	740(6)	5 258(6)	C(422)	−13(17)	1 626(7)	9 808(7)
C(123)	7 047(18)	695(8)	5 223(7)	C(423)	−281(18)	1 603(7)	10 344(9)
C(124)	7 820(18)	1 134(10)	5 307(8)	C(424)	802(18)	1 705(8)	10 697(8)
C(125)	7 260(17)	1 629(9)	5 425(7)	C(425)	2 023(20)	1 820(9)	10 484(9)
C(126)	5 918(17)	1 689(6)	5 462(6)	C(426)	2 264(19)	1 843(8)	9 923(8)







dppm): C, 39.85; H, 2.55. $C_{33}H_{28}O_8Os_2P_2$ requires C, 39.85; H, 2.85. Found (L–L = dppe): C, 40.50; H, 2.60. $C_{34}H_{30}O_8Os_2P_2$ requires C, 40.45; H, 3.00. Found (L–L =dadpe): C, 38.70; H, 2.70. $C_{34}H_{30}AsO_8Os_2P$ requires C, 38.80; H, 2.85%].

$[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$. A solution of $[Os_2(MeCO_2)_2(CO)_6]$ (0.33 g, 0.50 mmol) and dppm (0.38 g, 1.00 mmol) in thf (35 cm^3) was heated under reflux for 2 h. The solution was evaporated to dryness and the solid formed was recrystallized from dichloromethane–methanol as a cream crystalline solid (0.53 g, 78%) (Found: C, 50.10; H, 3.40. $C_{58}H_{50}O_8Os_2P_4$ requires C, 50.50; H, 3.65%).

$[Os_2(MeCO_2)(CO)_4(dppe)_2]PF_6$. A suspension of $[Os_2(MeCO_2)_2(CO)_6]$ (0.33 g, 0.50 mmol) and dppe (0.40 g, 1.00 mmol) in ethanol (25 cm^3) was heated under reflux for 24 h. The resulting pink suspension was filtered to remove $[\{Os_2(MeCO_2)_2(CO)_4(dppe)\}_n]$ (0.35 g). To the filtrate was added NH_4PF_6 (0.16 g, 1.0 mmol) which precipitated the product (0.22 g, 30%) as crimson prisms (Found: C, 46.90; H, 3.40. $C_{58}H_{51}F_6O_6Os_2P_5$ requires C, 46.65; H, 3.45%).

$[Os_2(MeCO_2)(CO)_4(dadpe)_2]PF_6$. This compound was prepared by the previous method using dadpe (0.44 g, 1.00 mmol) and a reflux time of 48 h, affording $[\{Os_2(MeCO_2)_2(CO)_4(dadpe)\}_n]$ (0.28 g) and the required orange crystalline product (0.29 g, 37%) on addition of NH_4PF_6 (Found: C, 43.25; H, 2.80. $C_{58}H_{51}As_2F_6O_6Os_2P_3$ requires C, 44.00; H, 3.15%).

Single-crystal Structure Determination for $[Os_2(MeCO_2)_2(CO)_4(dppm)_2]$.—A colourless needle-shaped crystal

Table 5. Principal bond lengths (Å) and angles (°) for [$Os_2(MeCO_2)_2(CO)_4(dppm)_2$]

Os(1)–Os(2)	2.740(1)	Os(1)–C(3)	1.73(2)
Os(1)–C(4)	1.87(2)	Os(1)–O(71)	2.105(11)
Os(1)–O(81)	2.106(10)	Os(1)–P(1)	2.388(4)
Os(2)–C(5)	1.73(2)	Os(2)–C(6)	1.80(2)
Os(2)–O(72)	2.113(11)	Os(2)–O(82)	2.103(10)
Os(2)–P(3)	2.384(4)	C(3)–O(3)	1.21(3)
C(4)–O(4)	1.11(2)	C(5)–O(5)	1.21(2)
C(6)–O(6)	1.19(3)	C(71)–C(72)	1.51(2)
C(71)–O(71)	1.25(2)	C(71)–O(72)	1.24(2)
C(81)–C(82)	1.54(2)	C(81)–O(81)	1.22(2)
C(81)–O(82)	1.22(2)	P(1)–C(1)	1.843(14)
P(1)–C(111)	1.81(2)	P(1)–C(121)	1.815(14)
P(2)–C(1)	1.835(14)	P(2)–C(211)	1.83(2)
P(2)–C(221)	1.80(2)	P(3)–C(2)	1.81(2)
P(3)–C(311)	1.85(2)	P(3)–C(321)	1.81(2)
P(4)–C(2)	1.82(2)	P(4)–C(411)	1.82(2)
P(4)–C(421)	1.79(2)		

Os(2)–Os(1)C(3)	96.9(6)	Os(2)–Os(1)–C(4)	94.2(4)
C(3)–Os(1)–C(4)	91.8(9)	Os(2)–Os(1)–O(71)	83.1(3)
C(3)–Os(1)–O(71)	174.8(7)	C(4)–Os(1)–O(71)	93.4(7)
Os(2)–Os(1)–O(81)	82.2(3)	C(3)–Os(1)–O(81)	91.6(8)
C(4)–Os(1)–O(81)	175.3(6)	O(71)–Os(1)–O(81)	83.3(5)
Os(2)–Os(1)–P(1)	162.3(1)	C(3)–Os(1)–P(1)	95.2(6)
C(4)–Os(1)–P(1)	98.3(5)	O(71)–Os(1)–P(1)	83.7(3)
O(81)–Os(1)–P(1)	84.6(3)	Os(1)–Os(2)–C(5)	95.9(7)
Os(1)–Os(2)–C(6)	94.9(6)	C(5)–Os(2)–C(6)	91.5(12)
Os(1)–Os(2)–O(72)	82.9(3)	C(5)–Os(2)–O(72)	176.1(9)
C(6)–Os(2)–O(72)	92.3(9)	Os(1)–Os(2)–O(82)	82.3(3)
C(5)–Os(2)–O(82)	93.4(9)	C(6)–Os(2)–O(82)	174.6(9)
O(72)–Os(2)–O(82)	82.8(5)	Os(1)–Os(2)–P(3)	162.9(1)
C(5)–Os(2)–P(3)	96.4(7)	C(6)–Os(2)–P(3)	96.5(6)
O(72)–Os(2)–P(3)	84.0(3)	O(82)–Os(2)–P(3)	85.2(3)
Os(1)–C(3)–O(3)	176(2)	Os(1)–C(4)–O(4)	176(2)
Os(2)–C(5)–O(5)	176(2)	Os(2)–C(6)–O(6)	175(2)
C(72)–C(71)–O(71)	115(2)	C(72)–C(71)–O(72)	118(2)
O(71)–C(71)–O(72)	127(2)	C(82)–C(81)–O(81)	116.8(14)
C(82)–C(81)–O(82)	117.1(14)	O(81)–C(81)–O(82)	126.1(12)
Os(1)–O(71)–C(71)	123.6(11)	Os(2)–O(72)–C(71)	123.7(11)
Os(1)–O(81)–C(81)	124.6(9)	Os(2)–O(82)–C(81)	124.7(10)
Os(1)–P(1)–C(1)	112.9(5)	Os(1)–P(1)–C(111)	120.5(5)
C(1)–P(1)–C(111)	102.0(7)	Os(1)–P(1)–C(121)	111.4(4)
C(1)–P(1)–C(121)	103.1(6)	C(111)–P(1)–C(121)	105.3(7)
C(1)–P(2)–C(211)	98.0(7)	C(1)–P(2)–C(221)	104.1(7)
C(211)–P(2)–C(221)	103.0(8)	P(1)–C(1)–P(2)	113.3(7)
Os(2)–P(3)–C(2)	112.5(5)	Os(2)–P(3)–C(311)	112.0(5)
C(2)–P(3)–C(311)	104.9(7)	Os(2)–P(3)–C(321)	121.7(6)
C(2)–P(3)–C(321)	101.8(7)	C(311)–P(3)–C(321)	102.1(7)
C(2)–P(4)–C(411)	98.6(7)	C(2)–P(4)–C(421)	106.5(7)
C(411)–P(4)–C(421)	101.0(7)	P(3)–C(2)–P(4)	112.6(8)

(0.25 × 0.10 × 0.10 mm) deposited from dichloromethane–methanol mounted on the tip of a glass fibre was used. Crystallographic measurements were made on an Enraf–Nonius CAD4F diffractometer operating in the ω—2θ scan mode with graphite crystal monochromated Mo-K_α radiation (λ = 0.710 73 Å). Cell dimensions and their estimated (e.s.d.s) were obtained by least-squares refinement of 24 reflections. Orientation controls (every 300 reflections) and intensity controls (every 5 000 s) were performed by means of three standard reflections ($2\,0\,\bar{8}$, $2\,3\,\overline{10}$, and 0 0 18) indicating a 0.7% loss in intensity during data collection. The data were corrected for Lorentz and polarization effects and for absorption using the empirical absorption correction method (minimum, maximum correction factors: 0.9655, 0.9999). The structure was solved by heavy-atom methods and Fourier difference synthesis and refined by blocked-matrix least-squares methods. All non-hydrogen atoms except C(82) [isotropic thermal parameter 98(6) × 10^3 Å^2; anisotropic refinement resulted in non-positive definite thermal parameters] were refined anisotropically; hydrogen atoms were included at calculated positions with common isotropic thermal parameters for methyl [0.14(3) Å^2], methylene [0.04(2) Å^2], and phenyl hydrogens [0.10(1) Å^2]. The weighting scheme $w = 1.0174/\sigma^2(F_o)$ was applied in the final refinement.

Crystal data. $C_{58}H_{50}O_8Os_2P_4$, M = 1 379.34, monoclinic, a = 10 122(2), b = 24.345(6), c = 24.549(5) Å, β = 90.56(2)°, U = 6 049.27 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.514 g cm^{-3}, $F(000)$ = 2 696, μ(Mo-K_α) = 41.57 cm^{-1}.

Data collection. ω (scan angle) (0.62 + 0.34 tan θ)°, scan speed 0.76—3.30° min^{-1}, $3 \leqslant \theta \leqslant 23°$, 8 008 data measured, 6 424 unique, 4 910 observed [$I \geqslant 2\sigma(I)$].

Structure refinement. Number of parameters 697, R = 0.061, R' = 0.041, with maximum shift/e.s.d. for positional parameters in the last cycles = 0.5 and maximum residual electron density 0.9 e Å^{-3}, showing no distinct features. Atomic scattering factors were from ref. 15; computations were performed with SHELX 76[16] and the figure drawn with ORTEP.[17] Final atomic co-ordinates are listed in Table 4 and principal bond lengths and angles in Table 5. A perspective view of [$Os_2(MeCO_2)_2(CO)_4(dppm)_2$] with the numbering scheme is shown in Figure 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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