Alkyl and Hydrido Derivatives of Tetrakis(trimethylphosphine)osmium(II). X-Ray Crystal Structure of the Metallacycle Os[(CH₂)₂SiMe₂](PMe₃)₄ †

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The interaction of the osmium acetato-complexes $trans$-$Os^{II}(O_2CMe)_2(PMe_3)_4$ and $Os^{III}_2Cl_2(\mu$-$O_2CMe)_4$ with alkylating agents in the presence of trimethylphosphine has led to the isolation of cis-$OsMe_2(PMe_3)_4$, $Os[(CH_2)_2SiMe_2](PMe_3)_4$, $OsCl(CH_2PMe_2)(PMe_3)_3$, and $Os(CH_2C_6H_4)(PMe_3)_4$. The hydride cis-$OsH_2(PMe_3)_4$ has been obtained from $K_2[OsO_2(OMe)_4]$ by interaction with PMe_3 and methanol. The ^1H, ^{13}C-$\{^1H\}$, and ^{31}P-$\{^1H\}$ n.m.r. spectra of the compounds are discussed. The X-ray crystal structure of the metallacycle $Os[(CH_2)_2SiMe_2](PMe_3)_4$ has been determined, and the $\overline{Os\text{-}C\text{-}Si\text{-}C}$ ring found to be flat. The Os–C distances are 2.24(1) Å, while the Os–P distances of 2.32 ($trans$ to C) and 2.35 Å ($trans$ to P) indicate the $trans$ influence of the metallacyclobutane is low compared to that of the σ alkyl groups.

The interaction of $Ru_2Cl(O_2CMe)_4$ with alkylating agents in the presence of trimethylphosphine has led to a variety of mononuclear Ru^{II} alkyl and aryl complexes.[1,2] During these studies, it was found that alkylation with $Mg(CH_2SiMe_3)_2$ or $Mg(CH_2CMe_3)_2$ gave not the expected dialkyls, but resulted in the formation of metallacyclobutane complexes and one equivalent of alkane. Similar behaviour was noted for rhodium. These reactions were the first examples of γ-activation of C–H bonds in alkyl ligands; since then similar reactions leading to metallacycles have been discovered, notably with compounds of iridium and platinum.[3]

We now report the synthesis and characterisation of some new alkyl, metallacyclic, and hydrido-compounds of osmium(II). Some related work has recently appeared[4] and osmium alkyls have been reviewed.[5]

Results

cis-Dimethyltetrakis(trimethylphosphine)osmium(II).—The acetato-complex $trans$-$Os(O_2CMe)_2(PMe_3)_4$[6] reacts with Mg-Me₂ in tetrahydrofuran (thf) over several hours to give colourless cis-$OsMe_2(PMe_3)_4$ in high yield. No evidence for $trans$-$OsMe_2(PMe_3)_4$ was noted; if this is a thermodynamic effect, then presumably the cis isomer is favoured because the good $trans$-directing methyl groups prefer not to compete with each other for bonding to the metal d orbitals. The ^1H n.m.r. spectrum of the complex (see Table 1) shows a doublet and a virtually coupled triplet due to the equatorial (mutually cis) and axial (mutually $trans$) PMe₃ groups, respectively. The Os–Me resonance appears to be a triplet of pseudo-quartets. The triplet splitting may be assigned to coupling to the two axial phosphines, $^3J_{PH}$(axial) = 8.3 Hz, while the pseudo-quartet pattern arises from coupling to the magnetically inequivalent equatorial phosphines. This sub-spectrum may be analysed in a fashion analogous to that for cis-$PtMe_2(PMe_3)_2$,[7] giving $^3J_{PH}(cis)$ = +7.0, $^3J_{PH}(trans)$ = −3.5 Hz, and a very small $^2J_{PP}$ coupling constant between the required phosphines of $ca.$ 5 Hz.

The ^{13}C-$\{^1H\}$ n.m.r. spectrum shows a three-line pattern for

the equatorial phosphines (relative intensities, $ca.$ 5 : 1 : 5). The outer two lines give $^1J_{PC}$ = 22.0 Hz, while the small central line again reflects a small amount of coupling ($ca.$ 5 Hz) between the two equatorial phosphorus nuclei (see above). The axial phosphines appear as a normal virtually coupled 1 : 2 : 1 triplet. The Os–Me groups give a first-order spectrum at δ −17.4 p.p.m., consisting of a doublet of quartets, due to the phosphines $trans$ and cis to the ^{13}C nucleus respectively. Finally, the ^{31}P-$\{^1H\}$ n.m.r. spectrum re-confirms the cis geometry, consisting of an A_2B_2 pattern with a $^2J_{PP}$ coupling constant between the axial and equatorial phosphines of 15.5 Hz (see Table 2).

(2,2-Dimethyl-2-silapropane-1,3-diyl)tetrakis(trimethylphosphine)osmium(II).—The reaction of $Os(O_2CMe)_2(PMe_3)_4$ with $Mg(CH_2SiMe_3)_2$ in thf yields the colourless metallacycle $Os[(CH_2)_2SiMe_2](PMe_3)_4$. Its ^1H n.m.r. spectrum is similar to that of the dimethyl compound above; the CH₂ groups appear at δ −0.98 p.p.m. as a triplet of pseudo-triplets, with $^3J_{PH}$(axial) = 12.2, $^3J_{PH}(cis)$ = +4.6, $^3J_{PH}(trans)$ = −4.6 Hz, and a $^2J_{PP}$ coupling constant between the two equatorial phosphine nuclei of $ca.$ 5 Hz, as before. In the ^{13}C-$\{^1H\}$ n.m.r. spectrum, the CH₂ groups appear as a doublet of quartets at δ −41.8, while the ^{31}P-$\{^1H\}$ n.m.r. spectrum is an A_2B_2 pattern, as expected.

The X-ray crystal structure of this complex has been determined, and an ORTEP view of the molecule is shown in the Figure. The crystal structure contains two crystallographically independent molecules whose co-ordination geometries are equal, within the limits of experimental error, and can be described as octahedral with distortions due mainly to the restricted bite of the chelate.

Selected bond lengths and angles are given in Table 3. The chelate bonds symmetrically, with Os–C distances in the narrow range 2.236(9)—2.253(9) Å, and the four-membered ring is essentially planar in each molecule (Table 3).

The Os–P distances fall into two distinct groups, with those for phosphorus atoms $trans$ to other phosphorus atoms longer than those $trans$ to the carbons: 2.339(9)—2.361(4) and 2.309(5)—2.324(4) Å respectively, indicating a large phosphorus $trans$ influence compared to carbon.

Toluene-2,α-diyltetrakis(trimethylphosphine)osmium(II).—The alkylation of $Os(O_2CMe)_2(PMe_3)_4$ with benzylmagnesium chloride proceeds, as in the trimethylsilyl case, to give the colourless o-metallated species, $Os(CH_2C_6H_4)(PMe_3)_4$ (1).
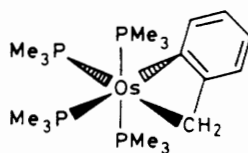

Table 1. Hydrogen-1 and ^{13}C-$\{^1H\}$ n.m.r. spectra of osmium compounds [a]

Compound	^1H	Assignment	^{13}C-$\{^1H\}$
cis-OsMe₂(PMe₃)₄	−0.05 [b]	Os–Me	−17.4 (dq, 54.9, 6.6)
	1.21 (' t', 5.9)	PMe₃	17.9 (' t ', 30.8)
	1.28 (d, 5.6)	PMe₃	24.9 (d, 22.0) [b]
Os[(CH₂)₂SiMe₂](PMe₃)₄	−0.98 [b]	Os–CH₂	−41.8 (dq, 40.6, 18.0)
	0.38 (s)	SiMe₂	11.4 (s)
	1.15 (d, 5.8)	PMe₃	25.1 (d, 23.2)
	1.43 (' t ', 5.6)	PMe₃	20.7 (' t ', 29.6)
Os(CH₂C₆H₄)(PMe₃)₄	c	Os–CH₂	−16.5 (dq, 45.4, 6.9)
		C	168.3 (d, 9.0)
	6.63 (d, 6.8)	CH	119.9 (s)
	7.17 (t, 6.6)	CH	124.3 (s)
	7.29 (t, 6.9)	CH	125.4 (s)
	7.51 (s)	CH	136.2 (s)
	1.18 (' t ', 5.7)	PMe₃	19.0 (' t ', 30.3)
	1.30 (d, 6.1)	PMe₃	27.3 (d, 20.6)
	1.38 (d, 6.1)	PMe₃	−17.4 (m)
cis-OsH₂(PMe₃)₄	−10.86 [b]	Os–H	
	1.44 (d, 5.9)	PMe₃	25.6 (d, 23.5)
	1.56 (' t ', 5.8)	PMe₃	22.4 (' t ', 30.9)

[a] Virtually coupled triplets are identified by ' t ', and the number following is the separation between the outer lines in Hz (as in other cases); dq = doublet of quartets. [b] See text. [c] Not located.
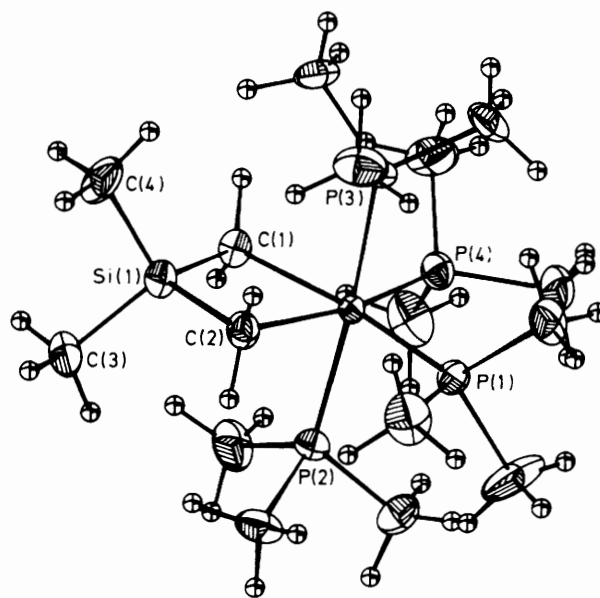
Table 2. ^{31}P-$\{^1H\}$ N.m.r. spectra of osmium compounds

Compound	Spin system	Chemical shifts (p.p.m.)	Coupling constants (Hz)
cis-OsMe₂(PMe₃)₄	A₂B₂	$\delta_A = -48.4$	$J_{AB} = 15.5$
		$\delta_B = -58.9$	
Os[(CH₂)₂SiMe₂](PMe₃)₄	A₂B₂	$\delta_A = -53.2$	$J_{AB} = 18.4$
		$\delta_B = -63.1$	
Os(CH₂C₆H₄)(PMe₃)₄	A₂BC	$\delta_A = -48.8$	$J_{AB} = 16.4$
		$\delta_B = -56.7$	$J_{AC} = 18.4$
		$\delta_C = -57\,1$	$J_{BC} = 4.6$
OsCl(CH₂PMe₂)(PMe₃)₃	ABCD	$\delta_A = -41.2$	$J_{AB} = 16.1$
		$\delta_B = -42.0$	$J_{AC} = 9.4$
		$\delta_C = -42.6$	$J_{AD} = 217.3$
		$\delta_D = -72.0$	$J_{BC} = 13.0$
			$J_{BD} = -18.7$
			$J_{CD} = -38.3$

(1)

Figure. Structure of Os[(CH₂)₂SiMe₂](PMe₃)₄ (molecule 1)

Three phosphine environments are seen in the ^1H n.m.r. spectrum, in the ratio of 1 : 1 : 2; the first two are doublets due to the inequivalent equatorial phosphines, while the third resonance is a virtually coupled triplet due to the axial groups. The CH₂ protons could not be located, and presumably are obscured by the PMe₃ resonances; the aromatic protons, however, are nicely resolved into four equal-intensity features. The ^{13}C-$\{^1H\}$ spectrum reflects the proton data, with the CH₂ group appearing at δ −16.5 p.p.m. The ^{31}P-$\{^1H\}$ n.m.r. spectrum is an example of an A₂BC spin system, with small second-order effects due to the proximity of the B and C chemical shifts. The directly observable $^2J_{PP}$ coupling constant of 4.6 Hz between the equatorial phosphine nuclei is consistent with the value of ca. 5 Hz deduced from the ^1H and ^{13}C-$\{^1H\}$ n.m.r. spectra of OsMe₂(PMe₃)₄ and Os[(CH₂)₂-SiMe₂](PMe₃)₄.

Chloro(dimethylphosphinomethyl)tris(trimethylphosphine)-osmium(II).—The interaction of a suspension of Os₂Cl₂-(O₂CMe)₄ with Mg(CH₂CMe₃)₂ in thf did not yield the expected metallacycle Os[(CH₂)₂CMe₂](PMe₃)₄, but instead gave white needles of a compound which, from analytical and spectroscopic data, proved to be OsCl(CH₂PMe₂)(PMe₃)₃. The analogous OsX(CH₂PMe₂)(PMe₃)₃ (X = H or I) have recently been made [4] and the ruthenium analogue is also known.[8] The spectroscopic data indeed show very similar properties, with the ^1H n.m.r. spectrum showing a complex pattern comprising two multiplets for the Os–CH₂ protons of the o-metallated phosphine, two doublets of doublets for the PMe₂ protons. The other three phosphines give rise to a further two doublet of doublets and a simple doublet. The ^{31}P-$\{^1H\}$ n.m.r. spectrum shows the expected ABCD pattern.

Table 3. Selected molecular geometry parameters for $Os[(CH_2)_2$-$SiMe_2](PMe_3)_4$

	Molecule 1		Molecule 2
(a) Bond lengths (Å)			
Os(1)–P(1)	2.324(4)	Os(2)–P(5)	2.339(9)
Os(1)–P(2)	2.346(4)	Os(2)–P(6)	2.309(5)
Os(1)–P(3)	2.347(4)	Os(2)–P(7)	2.361(4)
Os(1)–P(4)	2.317(4)	Os(2)–P(8)	2.319(4)
Os(1)–C(1)	2.241(9)	Os(2)–C(5)	2.236(9)
Os(1)–C(2)	2.253(9)	Os(2)–C(6)	2.243(9)
Si(1)–C(1)	1.855(10)	Si(2)–C(5)	1.844(10)
Si(1)–C(2)	1.827(10)	Si(2)–C(6)	1.836(10)
Si(1)–C(3)	1.905(11)	Si(2)–C(7)	1.899(11)
Si(1)–C(4)	1.904(12)	Si(2)–C(8)	1.907(13)
P–C(Me)	1.821—1.862(15)		1.788—1.861(16)
(b) Bond angles (°)			
C(1)–Os(1)–C(2)	77.0(4)	C(5)–Os(2)–C(6)	77.0(4)
C(1)–Si(1)–C(2)	98.9(4)	C(5)–Si(2)–C(6)	98.5(4)
C(3)–Si(1)–C(4)	102.4(5)	C(7)–Si(2)–C(8)	101.9(5)
P(1)–Os(1)–P(4)	103.6(2)	P(6)–Os(2)–P(8)	103.0(2)
P(2)–Os(1)–P(1)	91.8(2)	P(5)–Os(2)–P(6)	92.2(2)
P(2)–Os(1)–P(4)	92.3(2)	P(5)–Os(2)–P(8)	91.5(2)
P(2)–Os(1)–C(1)	88.1(3)	P(5)–Os(2)–C(5)	88.1(3)
P(2)–Os(1)–C(2)	87.2(3)	P(5)–Os(2)–C(6)	88.2(3)
P(3)–Os(1)–P(1)	90.6(2)	P(7)–Os(2)–P(6)	91.9(2)
P(3)–Os(1)–P(4)	92.1(2)	P(7)–Os(2)–P(8)	91.2(2)
P(3)–Os(1)–C(1)	88.5(3)	P(7)–Os(2)–C(5)	88.3(3)
P(3)–Os(1)–C(2)	87.7(3)	P(7)–Os(2)–C(6)	87.0(3)

(c) Least squares planes for chelate rings *

Molecule 1: $3.500X + 6.413Y + 19.442Z = 11.915$
  [Os(1) -0.008, Si(1) -0.011, C(1) 0.010, C(2) 0.010, P(1)
  -0.006, P(4) -0.026]
Molecule 2: $-1.653X - 0.696Y + 27.464Z = 1.241$
  [Os(2) 0.002, Si(2) 0.004, C(5) -0.003, C(6) -0.003, P(6)
  -0.025, P(8) 0.010]

* In each case the planes are defined by the metal, silicon, and two carbon atoms. The equations of the planes are of the form $AX + BY + CZ = D$, where X, Y, Z are fractional co-ordinates. Deviations (Å) of atoms from the planes are in square brackets.

cis-Dihydridotetrakis(trimethylphosphine)osmium(II).—Our attempted reduction of $Os(O_2CMe)(PMe_3)_4$,[6] Os_2Cl_2-$(O_2CMe)_4$,[6] or $OsCl_2(PMe_3)_4$[9] with sodium amalgam or Na/K, carried out in thf under varying pressures of hydrogen, failed. However, reduction using $Na(C_{10}H_8)$[4] has recently been found to be effective. We had, however, earlier made this hydride by a simpler route from $K_2[OsO_2(OMe)_4]$.[10] On the treatment of this salt in dichloromethane with trimethylphosphine, followed by addition of methanol, a solution containing the hydride is obtained. The i.r. spectrum of this complex shows a strong hydride stretch at 1 900 cm⁻¹. The ¹H n.m.r. spectrum shows a hydride resonance at δ -10.86 p.p.m. which is best described as a triplet of ten-line patterns, in addition to the usual axial and equatorial phosphine environments. Subtracting out the triplet coupling, $^2J_{PH}$ (axial) $= 27.0$ Hz, leaves the second-order sub-spectrum which corresponds to the X part of an AA'XX' spin system. Analysis gives an equatorial phosphine coupling of $^2J_{PP} = 14.0$ Hz, with $^2J_{PH}(cis) = -21.4$, $^2J_{PH}(trans) = 56.8$, and $^2J_{HH} = 6.0$ Hz.[11] The sub-spectrum may also be simulated with the values of $^2J_{PP}$ and $^2J_{HH}$ interchanged. We prefer the values given above, since $^2J_{HH}$ couplings between cis hydride ligands are usually ca. 5 Hz.[12] Here, the $^2J_{PP}$ coupling constant is larger than in the alkyl complexes, presumably because the equatorial P–Os–P angle increases as the anionic ligands become smaller.

pattern. A spectrum with only the phosphine protons decoupled shows that the downfield triplet becomes a first-order triplet of triplets, and therefore must be assigned to the axial phosphorus nuclei. By contrast, the upfield triplet becomes a triplet of second-order patterns due to a coupling with the hydride ligands, and must arise from the equatorial phosphine groups. The relative chemical shifts of the two types of phosphines (trans to H versus trans to P) reflects the higher position of hydrides relative to phosphines on a trans-influence series.

This osmium complex completes the $MH_2(PMe_3)_4$ triad, the iron and ruthenium analogues having been described previously.[13]

Discussion

Alkylation of $Os(O_2CMe)_2(PMe_3)_4$ with $MgMe_2$ gives the simple dialkyl complex, whereas $Mg(CH_2SiMe_3)_2$ and $Mg(CH_2Ph)Cl$ give metallacycles via a γ-elimination step. These results parallel those previously observed for ruthenium(II).[1] At least two alternative mechanisms exist for the formation of the metallacycles: (i) oxidative addition[1-3] of an alkyl ligand to give a metallacyclic Os^{IV} hydride intermediate, or (ii) intermolecular deprotonation[14] of a metal-bound alkyl hydrogen atom by a second alkyl group. Although Os^{IV} is an accessible oxidation state,[15] we have no direct evidence for its intermediacy; alkyls of osmium in even the $+6$ oxidation state are, however, known.[9] In any case, it seems reasonable to propose that osmium behaves in a fashion analogous to other platinum metals,[3] and that an oxidative addition step is involved in metallacycle formation.

Several X-ray crystal structures of metallacyclobutane complexes have now been reported, most of them involving platinum.* A point of continuing interest is the degree (if any) of puckering of the four-membered ring.[16] The present osmium complex extends the observation that flat rings are the rule for metals other than platinum. It is an interesting but unexplained observation that all the Pt^{II} metallacyclobutanes with phosphine ligands are puckered,* (f)—(i), whereas those with amine ligands are flat (j).* Doubtless, subtle electronic effects are involved, although steric factors cannot be ruled out completely.

An additional interesting feature of the osmium complexes reported here are the unusually high-field chemical shifts of the carbon and phosphorus nuclei directly bound to the metal. Thus, the α-carbon atom of the metallacycle in $Os[(CH_2)_2$-$SiMe_2](PMe_3)_4$ resonates at δ -41.8 p.p.m.,† while the

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† Only four diamagnetic compounds possess ¹³C resonances further upfield: see (a) S. Braun, P. Dahler, and P. Eilbracht, J. Organomet. Chem., 1978, 146, 135; (b) H. C. Clark and A. Shaver, Can. J. Chem., 1976, 54, 2068.

Table 4. Atomic co-ordinates ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Os(1)	4 037	6 006	3 417	Os(2)	6 715	2 372	917
Si(1)	2 566(1)	6 313(3)	3 578(1)	Si(2)	7 817(1)	4 484(3)	1 037(1)
C(1)	3 133(4)	7 284(8)	3 167(3)	C(5)	7 847(4)	2 531(8)	987(3)
C(2)	3 194(3)	5 132(8)	3 866(3)	C(6)	6 892(4)	4 718(8)	985(3)
C(3)	1 835(4)	5 309(11)	3 269(3)	C(7)	8 207(5)	5 226(10)	1 621(3)
C(4)	2 109(5)	7 501(10)	4 023(4)	C(8)	8 300(5)	5 499(11)	558(4)
P(1)	4 812(1)	4 463(2)	3 787(1)	P(5)	6 688(1)	2 261(3)	1 764(1)
C(11)	5 545(5)	5 065(11)	4 153(4)	C(51)	6 156(6)	896(13)	2 052(4)
C(12)	4 465(6)	3 259(11)	4 248(4)	C(52)	7 480(5)	1 921(12)	2 115(3)
C(13)	5 277(7)	3 123(12)	3 441(5)	C(53)	6 415(6)	3 842(12)	2 099(4)
P(2)	3 730(1)	4 305(2)	2 829(1)	P(6)	6 820(1)	−64(3)	852(1)
C(21)	3 323(5)	2 667(9)	3 033(4)	C(61)	7 352(8)	−749(12)	356(5)
C(22)	4 394(5)	3 532(11)	2 443(4)	C(62)	7 283(7)	−1 057(11)	1 320(5)
C(23)	3 117(5)	4 786(12)	2 330(3)	C(63)	6 093(6)	−1 238(11)	775(6)
P(3)	4 235(1)	7 692(2)	4 031(1)	P(7)	6 812(1)	2 676(3)	72(1)
C(31)	4 085(6)	7 126(11)	4 656(3)	C(71)	6 540(7)	4 407(12)	−185(4)
C(32)	3 756(5)	9 365(9)	4 031(4)	C(72)	7 662(6)	2 607(13)	−196(4)
C(33)	5 084(5)	8 480(11)	4 133(4)	C(73)	6 350(6)	1 493(13)	−360(4)
P(4)	4 687(1)	7 264(2)	2 876(1)	P(8)	5 550(1)	2 718(3)	859(1)
C(41)	5 609(4)	7 104(11)	2 856(4)	C(81)	5 249(5)	4 478(12)	969(6)
C(42)	4 483(6)	7 147(12)	2 221(3)	C(82)	5 049(6)	2 399(14)	313(4)
C(43)	4 640(6)	9 195(9)	2 899(4)	C(83)	4 972(5)	1 817(15)	1 261(5)

equatorial phosphine resonance (δ −63.1 p.p.m.) is actually upfield of free PMe₃.[17] The ruthenium analogues did not show such dramatic shifts.[1] This phenomenon has been rationalised on the basis of ' paramagnetic shielding ' by the transition metal atom, and is related to the upfield ¹H chemical shifts characteristic of hydride ligands.[18] Curiously however, in OsH₂(PMe₃)₄, the ¹H n.m.r. chemical shift (δ −10.86 p.p.m.) is quite normal for hydride ligands, which have been observed in some cases as far upfield as δ −50 p.p.m.[19]

Experimental

Microanalyses were performed by Pascher, Bonn.

Instruments.—The following instruments were used: Perkin-Elmer 683 (i.r.), Perkin-Elmer R32 (¹H n.m.r., 90 MHz), Bruker WM 250 (¹H, ¹³C, and ³¹P n.m.r.), JEOL FX90 (¹H, ¹³C, and ³¹P n.m.r.); data (δ/p.p.m.) are referenced to SiMe₄ in C₆D₆ for ¹H and ¹³C-{¹H} n.m.r. spectra, and to 85% H₃PO₄ for ³¹P-{¹H} n.m.r. spectra.

Syntheses.—The osmium starting material *trans*-Os(O₂CMe)₂(PMe₃)₄ was prepared as before.[6] All manipulations were performed under oxygen-free nitrogen or *in vacuo*. The light petroleum used had b.p. 40—60 °C, and this and other solvents were deoxygenated and distilled before use. Dialkylmagnesium compounds were prepared as before.[20]

cis-*Dimethyltetrakis*(*trimethylphosphine*)*osmium*(II).—Dimethylmagnesium (1.5 mmol in Et₂O) was added to a solution of Os(O₂CMe)₂(PMe₃)₄ (0.9 g, 1.47 mmol) in thf (40 cm³) at −78 °C. The mixture was then allowed to warm to room temperature and stirred for 18 h. The solution was evaporated and the residue extracted with toluene (3 × 20 cm³). After filtration the solution was reduced to *ca.* 10 cm³ and cooled to −78 °C to give colourless crystals of the complex which appear white when pumped dry. Yield 0.66 g, 85%; m.p. 128—132 °C (Found: C, 32.1; H, 7.8; P, 23.4. C₁₄H₄₂OsP₄ requires C, 32.0; H, 8.0; P, 23.7%).

(2,2-*Dimethyl-2-silapropane*-1,3-*diyl*)*tetrakis*(*trimethylphosphine*)*osmium*(II).—To a suspension of Os(O₂CMe)₂-(PMe₃)₄ (1.25 g, 2.04 mmol) in thf (50 cm³) was added Mg(CH₂SiMe₃)₂ (4.0 cm³ of a 0.52 mol dm⁻³ solution in Et₂O, 2.04 mmol). After 12 h the pale yellow solution was evaporated, and the residue extracted with light petroleum (50 cm³). The filtered extract was concentrated to *ca.* 10 cm³ and cooled to −20 °C to give colourless prisms of the complex. Yield 0.80 g, 68%; m.p. 172—175 °C (Found: C, 33.1; H, 8.0; P, 21.2. C₁₆H₄₆OsP₄Si requires C, 33.1; H, 8.0; P, 21.2%).

This complex may also be made from the dimer Os₂Cl₂-(O₂CMe)₄ and Mg(CH₂SiMe₃)₂ in thf in the presence of PMe₃ in similar yield.

Toluene-2,α-*diyltetrakis*(*trimethylphosphine*)*osmium*(II).— Benzylmagnesium chloride (1.65 mmol in Et₂O) was added to a solution of Os(O₂CMe)₂(PMe₃)₄ (0.5 g, 0.82 mmol) in thf (40 cm³) at −78 °C and the mixture stirred for 18 h. After removal of solvent the residue was extracted with light petroleum (3 × 20 cm³). The extract was reduced to *ca.* 10 cm³ and cooled to −20 °C to yield colourless crystals. Yield 0.36 g, 75%; m.p. 184 °C (Found: C, 39.2; H, 7.0; P, 21.1. C₁₇H₄₂OsP₄ requires C, 39.1; H, 7.0; P, 21.3%).

Chloro(*dimethylphosphinomethyl*)*tris*(*trimethylphosphine*)-*osmium*(II).—To a suspension of Os₂Cl₂(O₂CMe)₄ (0.75 g, 1.09 mmol) in thf (50 cm³) was added PMe₃ (1 cm³, 9.87 mmol) and Mg(CH₂CMe₃)₂ (7.6 cm³ of a 0.43 mol dm⁻³ solution in Et₂O, 3.27 mmol). After 12 h the red-orange solution was evaporated, and the residue extracted with light petroleum (50 cm³). The filtered pale orange extract was concentrated to *ca.* 10 cm³ and cooled to −20 °C to give pale tan needles which were recrystallised from light petroleum to give off-white needles of the complex. Yield 0.54 g, 47%; m.p. 228—231 °C (Found: C, 27.2; H, 6.7; Cl, 6.7; P, 23.5. C₁₂H₃₅ClOsP₄ requires C, 27.1; H, 6.7; Cl, 6.7; P, 23.5%).

cis-*Dihydridotetrakis*(*trimethylphosphine*)*osmium*(II).—Trimethylphosphine (0.015 mol) was added to a suspension of K₂[OsO₂(OMe)₄] (0.8 g) in dichloromethane (40 cm³) at

−78 °C and stirred for 15 min. Methanol (*ca.* 10 cm^3) was then added, the mixture allowed to warm to room temperature, and stirred for 12 h. The solution was evaporated and the residue extracted with light petroleum (5 × 10 cm^3). The filtered extract was reduced to *ca.* 10 cm^3 and cooled to −78 °C, the resulting solid was then recrystallised from CH_2Cl_2 to yield colourless crystals of the complex. Yield *ca.* 0.46 g, 57%; m.p. 168 °C (Found: C, 28.9; H, 7.7; P, 24.7. $C_{12}H_{38}OsP_4$ requires C, 29.0; H, 7.7; P, 25.0%).

Crystallographic Studies.—Crystals used for *X*-ray work were sealed under argon in Lindemann capillaries. Unit-cell and intensity data were obtained at 295 K using a Nonius CAD4 diffractometer, operating in the ω/2θ scan mode and using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) in a manner previously described in detail.[21] The structure was solved and refined *via* routine procedures. The refinement used two blocks, each containing parameters for one of the two crystallographically independent molecules. Non-hydrogen atoms were refined with anisotropic thermal parameters whilst methyl hydrogen atoms were placed in idealised positions, and the CH_3 groups treated as rigid bodies. Methylene hydrogens were located on difference maps and freely refined with isotropic thermal parameters.

Crystal data. $C_{16}H_{46}OsP_4Si$, M = 580.1, monoclinic, a = 19.690(4), b = 9.411(1), c = 27.584(4) Å, β = 91.55(2)°, U = 5 109.5 Å^3, space group $P2_1/n$, Z = 8, D_c = 1.508 g cm^{-3}, μ(Mo-K_α) = 40.2 cm^{-1}. Data recorded over 1.5 ≤ θ ≤ 25°, giving 8 967 unique and 6 572 observed [I > 1.5σ(I)] data. R = 0.0388, R' = 0.0376 for 524 parameters and with least-squares weights of w = 1/[σ^2(F_o) + 0.0005$|F_o|^2$]. Final atomic fractional co-ordinates are given in Table 4.

Acknowledgements

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