Metallation of 2-Ethenylpyridine at Triosmium Clusters: *X*-Ray Crystal Structures of the Open Trinuclear Clusters [$Os_3H(CO)_9L(NC_5H_4CH{=}CH)$] (L = CO or PMe_2Ph) †

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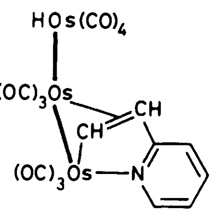
The compounds [$Os_3H_2(CO)_{10}$] and [$Os_3(CO)_{10}(MeCN)_2$] each react with 2-ethenylpyridine ($NC_5H_4CH{=}CH_2$) with C–H bond cleavage at the terminal carbon atom to give [$Os_3H(CO)_{10}$-($NC_5H_4CH{=}CH$)], (**1**). An analogous compound [$Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)$], (**2**), is formed similarly from [$Os_3H_2(CO)_9(PMe_2Ph)$]. Single-crystal *X*-ray structures of compounds (**1**) and (**2**) are reported. In these clusters the metal triangles have opened out with Os–Os–Os angles of 160.0(1) and 160.4(1)° in (**1**) and (**2**) respectively. Each of the compounds contains a terminal hydride ligand replaceable by Cl in carbon tetrachloride and has a five-electron donor $NC_5H_4CH{=}CH$ ligand chelating at a terminal Os atom of the Os_3 chain with a η^2-alkene co-ordination at the central Os atom. 2-Ethynylpyridine ($NC_5H_4C{\equiv}CH$) reacts with [$Os_3H_2(CO)_{10}$] to give compound (**1**) and an isomer in which the alkene is *trans* rather than *cis* and in which the 2-pyridyl group is non-co-ordinated.

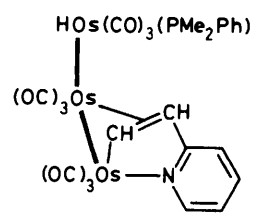
The triosmium cluster [$Os_3(CO)_{12}$] at high temperatures[1] and more reactive ones like [$Os_3(CO)_{10}L_2$] (L = cyclooctene[2,3] or MeCN[3]) at room temperature react with pyridine by *ortho*-metallation to give the μ-2-pyridyl cluster [$Os_3H(CO)_{10}(NC_5H_4)$]. Ethylene also oxidatively adds to give the μ-ethenyl complex [$Os_3H(CO)_{10}(CH{=}CH_2)$][4] on reaction with [$Os_3(CO)_{10}L_2$][3] or [$Os_3H_2(CO)_{10}$].[5,6] In this paper we have combined these two functionalities in 2-ethenylpyridine and have found that C–H bonds of the ethenyl function are cleaved rather than those at the heterocyclic ring. Co-ordination of the nitrogen atom and η^2-co-ordination of the alkene in the product [$Os_3H(CO)_{10}(NC_5H_4CH{=}CH)$] leads to opening of the metal triangle and an Os–Os–Os angle of about 160°.

Results and Discussion

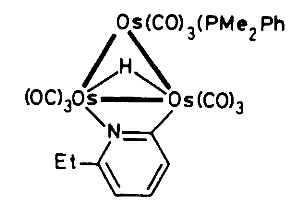
The reactions of [$Os_3H_2(CO)_{10}$] or of [$Os_3(CO)_{10}(MeCN)_2$] with 2-ethenylpyridine at room temperature or somewhat above give moderate to good yields of a single isolable product formulated as [$Os_3H(CO)_{10}(NC_5H_4CH{=}CH)$], compound (1), on the basis of elemental analysis, the observation of the parent molecular ion in the mass spectrum, and the ^1H n.m.r. spectrum (Table 1). The i.r. spectrum in the carbonyl region around 2 000 cm^{-1} (Table 1) is quite unlike those of [$Os_3H(CO)_{10}(\mu$-$CH{=}CH_2)$][4,5] and [$Os_3H(CO)_{10}(\mu$-2-$NC_5H_4)$][1] formed from ethylene and pyridine respectively and hence compound (1) is in no way similar structurally. The ^1H n.m.r. spectrum shows four signals for the heterocycle, which hence remains intact, and two coupled doublets (δ 5.75 and 9.20) for the 2-C_2H_2 group. The coupling of 7 Hz between these protons and their chemical



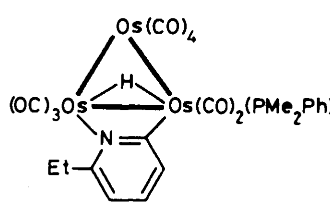
(1)



(2)



(3a)



(3b)

shifts imply a co-ordinated *cis*-CH=CH group and hence metallation at the terminal carbon atom has probably given a five-membered chelate ring as in [$RhCl_2(NC_5H_4CH{=}CH)(PBu_3)_2$][7] and [$Re(NC_5H_4CH{=}CH)(CO)_4$],[8] but with the C=C bond co-ordinated to an adjacent metal atom in the cluster. The $NC_5H_4CH{=}CH$ ligand thus acts as a five-electron donor and we would predict that there are only two Os–Os bonds in compound (1). Another unusual feature for a cluster is the hydride signal at δ −9.90, in the relatively low-field region normally associated with a terminal hydride ligand. Single-crystal *X*-ray structures of compound (1) and the PMe_2Ph-substituted analogue [$Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)$], (2), derived from [$Os_3H_2(CO)_9(PMe_2Ph)$] and 2-ethenylpyridine, confirm these features (see later).

In the reaction of [$Os_3H_2(CO)_9(PMe_2Ph)$][9] with 2-ethenylpyridine, compound (2) is the major product but there are also low yields of [$Os_3(CO)_{11}(PMe_2Ph)$][10] and two isomers of [$Os_3H(CO)_9(PMe_2Ph)(NC_5H_3Et)$], (3a) and (3b). Compounds

† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-3-hydrido-1,2-μ-[2-(2′-pyridyl)ethenyl-C^1,N(Os^1),C^1,C^2(Os^2)]triosmium(2 *Os–Os*) and 1,1,1,2,2,2,3,3,3-nonacarbonyl-3-dimethylphenylphosphine-3-hydrido-1,2-μ-[2-(2′-pyridyl-ethenyl-C^1,N(Os^1),C^1,C^2(Os^2)]triosmium(2-*Os–Os*).

Supplementary data available (No. SUP 56073, 10 pp.): thermal parameters, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Proton n.m.r. and i.r. data for compounds (**1**)—(**6**)

Compound	$\tilde{\nu}(CO)^a/cm^{-1}$	δ^b	
(**1**) $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$	2 111m, 2 073s, 2 048m,	6.81(t), 7.50(d),	NC_5H_4
(*cis*-vinyl)	2 022s, 2 014s, 2 003s,	7.75(t), 8.86(d)	
	1 985s, 1 975m	5.75(d), 9.20(d)	CH=CH (J = 7 Hz)
		−9.90(s)	OsH
(**2**) $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$	2 079s, 2 054s, 2 020w,	6.47(m), 7.12(d)	NC_5H_4
(*cis*-vinyl)	2 002(sh), 1 995vs, 1 982vs,	7.56(m),[d] 8.48(d)	
	1 974s, 1 962w	5.36(d), 9.09(d)	CH=CH (J = 6.8 Hz)
		2.20(d)	PCH_3[c] (J = 9.8 Hz)
		−9.64(d)	OsH (J = 19.7 Hz)
(**3a**) $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_3Et)]$	2 078s, 2 046vs, 2 019vs,	6.58(d,br), 6.96(t),	NC_5H_3
	1 997vs, 1 983vs, 1 967s,	7.08(d,br)	
	1 957m, 1 949(sh)	2.68(q,br), 1.22(t)	CH_2CH_3 (J = 7.0 Hz)
		2.17(d)	PCH_3[c] (J = 10.0 Hz)
		−13.89(s,br)	OsH
(**3b**) $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_3Et)]$	2 089s, 2 045vs, 2 011vs,	6.37(d), 6.51(d),	NC_5H_3
	2 007(sh), 1 992s, 1 987(sh),	6.76(t)	
	1 973s, 1 966s, 1 943m	2.57(q), 1.15(t)	CH_2CH_3 (J = 7.5 Hz)
		1.93(d), 1.95(d)	PCH_3[c] (J = 9.4 Hz)
		−14.20(d)	OsH (J = 12.2 Hz)
(**5**) $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$	2 106m, 2 065s, 2 056s,	7.14(d), 7.31(t),	NC_5H_4
(*trans*-vinyl)	2 023s, 2 018m, 2 001m,	7.62(t), 8.51(d)	
	1 996m, 1 986m, 1 980m	5.04(d), 8.43(d)	CH=CH (J = 13 Hz)
		−18.80(s)	OsH
(**6**) $[Os_3Cl(CO)_{10}(NC_5H_4CH{=}CH)]$	2 126m, 2 077vs, 2 044vs,	5.59(m), 7.34(d),	NC_5H_4
(*cis*-vinyl)	2 010vs, 2 005(sh), 1 985s	7.56(m), 8.49(d)	
		5.66(d), 9.19(d)	CH=CH (J = 6.8 Hz)
(**7**) $[Os_3Cl(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$	2 089m, 2 061s, 2 031m,	6.47(m), 7.12(d),	NC_5H_4
(*cis*-vinyl)	2 005vs, 1 983(sh)	*ca.* 7.4(m),[d] 8.45(d)	
		5.50(d), 9.13(d)	CH=CH (J = 6.7 Hz)
		2.15(d)	PCH_3[c] (J = 10.1 Hz)

[a] Measured in cyclohexane. [b] In $CDCl_3$ at 200 MHz. [c] PC_6H_5 resonances not listed. [d] Underlying PC_6H_5 resonances.

(**3**) were formed in too low yield for full characterisation but 200-MHz ^1H n.m.r. spectra clearly confirm their identity as μ-2-pyridyl complexes related to $[Os_3H(CO)_{10}(\mu\text{-}NC_5H_4)]$ (see Table 1).[1] In the spectrum of compound (**3b**) the hydride signal shows ^{31}P coupling (J = 12.2 Hz) so that we deduce the PMe_2Ph is co-ordinated at one of the bridged osmium atoms, possibly that shown, while with (**3a**) there is no coupling so the structure is probably as illustrated. The formation of these compounds requires transfer of two H atoms from $[Os_3H_2(CO)_9(PMe_2Ph)]$ to give 2-ethylpyridine which then undergoes *ortho*-metallation.

The formation of compound (1) from $[Os_3(CO)_{10}(MeCN)_2]$ and 2-ethenylpyridine simply requires displacement of the acetonitrile ligands and an oxidative addition of the alkene function. Starting from $[Os_3H_2(CO)_{10}]$, however, the loss of two hydrogen atoms is required. When carried out in an n.m.r. tube, the reaction of $[Os_3H_2(CO)_{10}]$ with 1 mol equivalent of $NC_5H_4CH{=}CH_2$ gives a final solution containing equal concentrations of the parent dihydride, compound (**1**), and 2-ethylpyridine. Two mol equivalents of $NC_5H_4CH{=}CH_2$ give complete conversion into compound (**1**). The stoicheiometries of these reactions are given by equations (1) and (2). No intermediate was observed in reaction (2) and hence an insertion compound $[Os_3H(CO)_{10}(NC_5H_4C_2H_4)]$ must be formed in the rate-determining step but this readily eliminates NC_5H_4Et on reaction with a second mol of $NC_5H_4CH{=}CH_2$.

The cluster $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$, (**1**), gave yellow needles which were not ideal for single-crystal X-ray structure determination but even so this was carried out and the structure refined to R = 0.100. The PMe_2Ph-substituted derivative (**2**) gave rather better crystals, the structure of which was determined and refined to R = 0.038. Atomic co-ordinates and selected bond parameters for (1) are given in Tables 2 and 3, while those for (2) are given in Tables 4 and 5. Their molecular structures, which correspond directly, are shown in Figures 1 and 2.

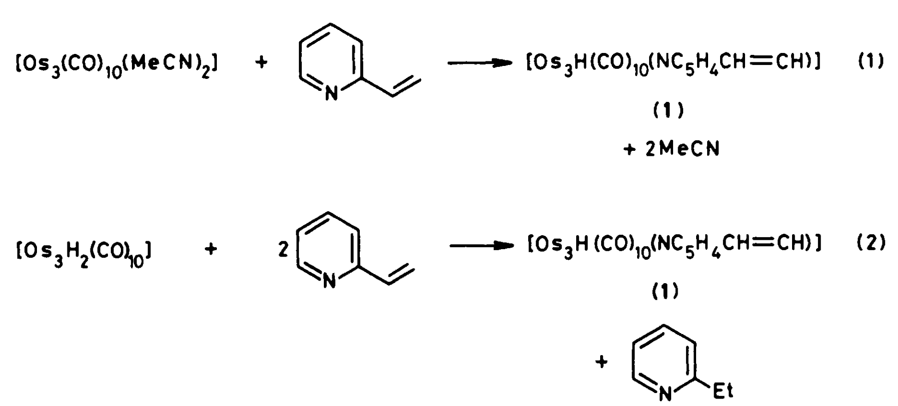


Table 2. Atom co-ordinates ($\times 10^4$) for $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$, (**1**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	9 503(3)	4 185(1)	2 480(1)	O(31)	3 842(62)	721(26)	4 528(30)
Os(2)	8 046(3)	2 867(1)	2 934(1)	C(32)	5 133(253)	2 629(110)	3 865(132)
Os(3)	5 985(3)	1 878(1)	3 732(2)	O(32)	4 884(64)	3 109(27)	4 687(32)
C(11)	11 079(79)	4 907(33)	2 602(38)	C(33)	7 578(123)	1 786(50)	4 353(60)
O(11)	12 235(67)	5 344(27)	2 700(32)	O(33)	9 226(77)	1 578(32)	5 060(39)
C(12)	10 571(77)	3 693(32)	1 763(38)	C(34)	4 733(116)	1 930(49)	2 660(58)
O(12)	11 259(61)	3 340(25)	1 169(30)	O(34)	3 419(60)	2 014(24)	1 973(30)
C(13)	7 907(106)	4 534(43)	1 652(52)	N(1)	8 428(55)	4 614(22)	3 476(27)
O(13)	6 688(60)	4 818(24)	1 020(29)	C(1)	7 591(87)	5 302(36)	3 438(43)
C(21)	7 393(93)	2 732(39)	1 868(47)	C(2)	6 987(87)	5 493(36)	4 175(44)
O(21)	7 043(64)	2 384(26)	1 075(32)	C(3)	7 165(77)	5 132(32)	4 974(38)
C(22)	9 569(99)	2 050(41)	3 084(48)	C(4)	7 977(74)	4 402(31)	4 960(36)
O(22)	10 710(73)	1 666(29)	3 365(35)	C(5)	8 674(63)	4 227(26)	4 258(31)
C(23)	5 832(82)	3 527(35)	2 741(39)	C(6)	9 509(75)	3 458(31)	4 268(37)
O(23)	4 768(58)	3 931(24)	2 609(28)	C(7)	10 573(77)	3 513(32)	3 503(37)
C(31)	4 584(88)	1 110(36)	4 257(42)				

Table 3. Selected bond parameters (lengths in Å, angles in °) for $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$, (**1**)

Os(1)–Os(2)	2.841(4)	Os(1)–Os(2)–Os(3)	160.0(1)	C(11)–Os(1)–N(1)	91.9(24)
Os(2)–Os(3)	2.895(5)	Os(2)–Os(1)–C(11)	156.3(7)	C(12)–Os(1)–N(1)	169.9(21)
Os(1)–N(1)	2.073(45)	Os(2)–Os(1)–C(12)	89.7(20)	C(13)–Os(1)–N(1)	92.9(31)
Os(1)–C(7)	2.016(55)	Os(2)–Os(1)–C(13)	104.0(28)	C(11)–Os(1)–C(7)	103.1(24)
Os(2)–C(6)	2.357(52)	Os(2)–Os(1)–N(1)	83.4(12)	C(12)–Os(1)–C(7)	90.0(25)
Os(2)–C(7)	2.295(56)	Os(2)–Os(1)–C(7)	53.2(16)	C(13)–Os(1)–C(7)	156.5(34)
N(1)–C(1)	1.421(79)	Os(1)–Os(2)–C(21)	86.0(26)	N(1)–Os(1)–C(7)	80.0(21)
N(1)–C(5)	1.368(62)	Os(1)–Os(2)–C(22)	115.3(25)	C(6)–Os(2)–C(7)	40.2(22)
C(1)–C(2)	1.373(103)	Os(1)–Os(2)–C(23)	80.6(18)	Os(1)–N(1)–C(1)	125.1(88)
C(2)–C(3)	1.372(89)	Os(1)–Os(2)–C(6)	71.2(15)	Os(1)–N(1)–C(5)	116.9(83)
C(3)–C(4)	1.490(83)	Os(1)–Os(2)–C(7)	44.7(14)	N(1)–C(5)–C(6)	116.9(45)
C(4)–C(5)	1.360(81)	Os(3)–Os(2)–C(21)	105.1(27)	C(4)–C(5)–C(6)	117.1(45)
C(5)–C(6)	1.559(75)	Os(3)–Os(2)–C(22)	81.4(25)	Os(2)–C(6)–C(5)	107.2(29)
C(6)–C(7)	1.600(91)	Os(3)–Os(2)–C(23)	84.0(18)	Os(2)–C(6)–C(7)	67.9(27)
		Os(3)–Os(2)–C(6)	97.3(16)	C(5)–C(6)–C(7)	103.1(44)
Averages:		Os(3)–Os(2)–C(7)	133.2(15)	Os(1)–C(7)–Os(2)	82.2(18)
Os–C (carbonyl)	1.76 ± 0.22	Os(2)–Os(3)–C(31)	175.8(19)	Os(1)–C(7)–C(6)	114.7(38)
C–O (carbonyl)	1.29 ± 0.17	Os(2)–Os(3)–C(32)	78.6(80)	Os(2)–C(7)–C(6)	71.9(29)
		Os(2)–Os(3)–C(33)	82.3(42)		
		Os(2)–Os(3)–C(34)	78.9(32)		

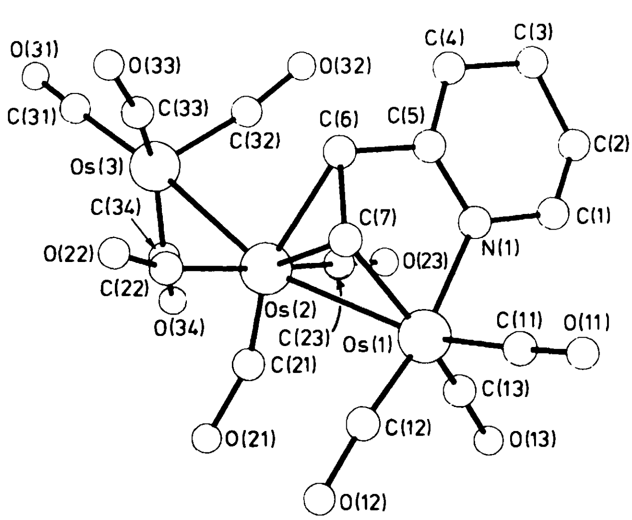


Figure 1. Molecular structure of $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$, compound (**1**)

The main structural conclusions from their spectra are confirmed: the presence of the terminal hydride ligand, the chelating $NC_5H_4CH{=}CH$ ligand, and the η^2-CH=CH bonding. The most obvious feature is the large Os–Os–Os angle, 160.0(1)° for (**1**) and 160.4(1)° for (**2**). The metal–metal distances are closely similar: non-bridged Os–Os distances of 2.895(5) and 2.897(4) Å and bridged Os–Os distances of 2.841(4) and 2.818(4) Å for compounds (**1**) and (**2**) respectively. The $NC_5H_4CH{=}CH$ ligand is a five-electron donor so that only two Os–Os bonds are required for co-ordinative saturation. Each Os atom is six-co-ordinate with an octahedral environment, distorted to a greater or less extent. Compounds (**1**) and (**2**) could be regarded as structurally derived from compounds of type $XOs(CO)_4Os(CO)_4Os(CO)_4X$ where X is halide or hydride. The bending of the Os_3 chain away from linearity results from the nature of the $NC_5H_4CH{=}CH$ bridge with the η^2-bonding at the central Os atom distorting its octahedral environment. The geometry of this bridging ligand is not unexpected. The unlikely C(6)–C(7) distance of 1.6(1) Å in compound (**1**) reflects the relatively poor quality of this structure and the corresponding distance of 1.42(2) Å in (**2**) is more reliable.

Table 4. Atom co-ordinates ($\times 10^4$) for $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$, (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	7 610(1)	4 073(1)	577(1)	C(14)	6 196(18)	2 861(8)	1 845(9)
Os(2)	5 836(1)	2 974(1)	774(1)	C(15)	7 349(22)	2 732(11)	−2 160(13)
Os(3)	3 975(1)	1 783(1)	338(1)	C(16)	8 593(17)	3 009(9)	−1 708(11)
C(1)	7 375(18)	4 484(11)	1 629(14)	C(17)	8 686(15)	3 402(9)	−968(11)
O(1)	7 124(17)	4 739(10)	2 241(11)	N(1)	7 596(12)	3 531(6)	−617(8)
C(2)	8 203(17)	4 917(10)	167(13)	P(1)	2 351(4)	892(2)	114(3)
O(2)	8 566(15)	5 444(7)	−49(11)	C(21)	1 817(15)	626(8)	1 097(10)
C(3)	9 401(17)	3 692(9)	1 214(11)	C(22)	607(18)	862(9)	1 250(11)
O(3)	10 400(14)	3 445(10)	1 559(11)	C(23)	318(20)	660(11)	2 029(12)
C(4)	7 085(17)	2 346(10)	396(11)	C(24)	1 117(23)	234(11)	2 633(13)
O(4)	7 836(13)	1 962(7)	233(10)	C(25)	2 292(23)	−29(12)	2 468(15)
C(5)	4 392(19)	3 358(9)	1 181(11)	C(26)	2 674(18)	179(12)	1 715(13)
O(5)	3 534(15)	3 573(8)	1 494(11)	C(27)	705(18)	1 090(10)	−737(11)
C(6)	6 758(19)	2 771(10)	1 954(11)	C(28)	2 864(19)	66(8)	−306(13)
O(6)	7 329(18)	2 659(10)	2 686(8)	H(1)	3 748(143)	2 002(78)	1 305(94)
C(7)	2 687(17)	2 488(8)	−256(10)	H(14)	5 200(18)	2 662(8)	−2 209(9)
O(7)	1 915(13)	2 917(7)	−579(10)	H(15)	7 269(22)	2 404(11)	−2 741(13)
C(8)	4 595(16)	1 506(8)	−668(10)	H(16)	9 495(17)	2 920(9)	−1 939(11)
O(8)	4 963(14)	1 304(7)	−1 274(8)	H(17)	9 669(15)	3 632(9)	−633(11)
C(9)	5 329(15)	1 285(9)	1 249(11)	H(22)	−90(18)	1 196(9)	770(11)
O(9)	6 108(15)	1 030(7)	1 820(9)	H(23)	−611(20)	858(11)	2 159(12)
C(11)	5 553(14)	3 970(7)	3(10)	H(24)	848(23)	98(11)	3 240(13)
C(12)	5 211(14)	3 446(8)	−679(9)	H(25)	2 921(23)	−399(12)	2 931(15)
C(13)	6 340(14)	3 268(8)	1 072(9)	H(26)	3 626(18)	−7(12)	1 607(13)

Table 5. Selected bond parameters (lengths in Å, angles in °) for $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$, (**2**)

Os(1)–Os(2)	2.818(4)	Os(1)–Os(2)–Os(3)	160.4(1)	C(1)–Os(1)–N(1)	171.5(6)
Os(2)–Os(3)	2.897(4)	Os(2)–Os(1)–C(1)	88.7(6)	C(2)–Os(1)–N(1)	92.4(7)
Os(1)–C(11)	2.037(16)	Os(2)–Os(1)–C(2)	159.5(5)	C(3)–Os(1)–N(1)	92.8(7)
Os(1)–N(1)	2.115(14)	Os(2)–Os(1)–C(3)	101.7(6)	C(1)–Os(1)–C(11)	93.7(8)
Os(2)–C(11)	2.212(15)	Os(2)–Os(1)–N(1)	83.3(4)	C(2)–Os(1)–C(11)	108.3(8)
Os(2)–C(12)	2.347(14)	Os(2)–Os(1)–C(11)	51.2(5)	C(3)–Os(1)–C(11)	152.1(6)
Os(3)–H(1)	1.63(16)	Os(1)–Os(2)–C(4)	86.2(6)	N(1)–Os(1)–C(11)	78.9(6)
Os(3)–P(1)	2.315(6)	Os(1)–Os(2)–C(5)	109.0(6)	C(11)–Os(2)–C(12)	36.2(5)
P(1)–C(27)	1.860(20)	Os(1)–Os(2)–C(6)	95.5(6)	Os(1)–N(1)–C(17)	128.1(11)
P(1)–C(28)	1.825(19)	Os(1)–Os(2)–C(11)	45.9(4)	Os(1)–N(1)–C(13)	114.4(10)
P(1)–C(21)	1.823(18)	Os(1)–Os(2)–C(12)	68.2(5)	N(1)–C(13)–C(12)	114.7(14)
N(1)–C(13)	1.369(18)	Os(3)–Os(2)–C(4)	83.5(6)	C(12)–C(13)–C(14)	124.7(14)
C(13)–C(14)	1.401(20)	Os(3)–Os(2)–C(5)	82.3(6)	Os(2)–C(12)–C(13)	106.0(13)
C(14)–C(15)	1.403(26)	Os(3)–Os(2)–C(6)	100.9(7)	Os(2)–C(12)–C(11)	66.7(8)
C(15)–C(16)	1.368(26)	Os(3)–Os(2)–C(11)	123.9(5)	C(11)–C(12)–C(13)	114.1(13)
C(16)–C(17)	1.350(23)	Os(3)–Os(2)–C(12)	94.8(5)	Os(1)–C(11)–Os(2)	83.0(6)
N(1)–C(17)	1.379(18)	Os(2)–Os(3)–C(7)	83.3(5)	Os(1)–C(11)–C(12)	113.9(11)
C(11)–C(12)	1.424(22)	Os(2)–Os(3)–C(8)	93.9(5)	Os(2)–C(11)–C(12)	77.0(9)
C(12)–C(13)	1.473(21)	Os(2)–Os(3)–C(9)	85.6(6)	Os(3)–P(1)–C(21)	115.8(6)
C(21)–C(22)	1.383(22)	Os(2)–Os(3)–P(1)	172.8(1)	Os(3)–P(1)–C(27)	114.9(7)
C(22)–C(23)	1.374(24)	P(1)–Os(3)–H(1)	93.0(51)	Os(3)–P(1)–C(28)	114.9(7)
C(23)–C(24)	1.331(29)	Os(2)–Os(3)–H(1)	80.3(52)	P(1)–Os(3)–C(7)	94.2(6)
C(24)–C(25)	1.375(31)	C(7)–Os(3)–H(1)	91.1(51)	P(1)–Os(3)–C(8)	93.1(5)
C(25)–C(26)	1.384(27)	C(8)–Os(3)–H(1)	169.1(49)	P(1)–Os(3)–C(9)	95.0(6)
C(26)–C(21)	1.391(24)	C(9)–Os(3)–H(1)	72.5(51)		

Os–C (carbonyl) 1.905 ± 0.031 C–O (carbonyl) 1.144 ± 0.021

From the arrangement of ligands around Os(3) in compound (**1**) the co-ordination site of the hydride is clear, even though the atom was not located. The hydride ligand in (**2**), however, was located as shown in Figure 2. The coupling of 19.7 Hz between the hydride and ^{31}P nuclei is consistent with this *cis* arrangement persisting in solution. Of the reported structures of Os_3 clusters that of $[Os_3H(CO)_{10}(PEt_3)(\mu\text{-}\eta^2\text{-}CF_3C{=}CHCF_3)]$, (**4**), is the closest to that of (**1**) and (**2**).[11] In compound (**4**) the co-ordinated 2-pyridyl group is replaced by a PEt_3 ligand and the Os–Os–Os angle is 162.3(1)°.

Compound (**1**) is also obtained (22%) from the reaction of $[Os_3H_2(CO)_{10}]$ with the alkyne 2-ethynylpyridine but the major product is the isomer $[Os_3H(CO)_{10}(\mu\text{-}\eta^2\text{-}trans\text{-}NC_5H_4CH{=}CH)]$, (**5**) (57%). Infrared and ^1H n.m.r. spectra for (**5**) are quite analogous to those of the well characterised vinyl complex $[Os_3H(CO)_{10}(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$.[4–6] In the *trans* form it is difficult for the pyridine to approach the metal atoms and so the nitrogen atom remains unco-ordinated. Compound (**5**) seems to be formed by direct addition of Os–H across the C≡C bond of $NC_5H_4C{\equiv}CH$ but compound (**1**) cannot be formed like this. There was no evidence for the other orientation of addition which would give $[Os_3H(CO)_{10}(NC_5H_4C{=}CH_2)]$ but perhaps this is formed but readily reductively eliminates to give the ethenylpyridine complex $[Os_3(CO)_{10}(NC_5H_4CH{=}CH_2)]$. We

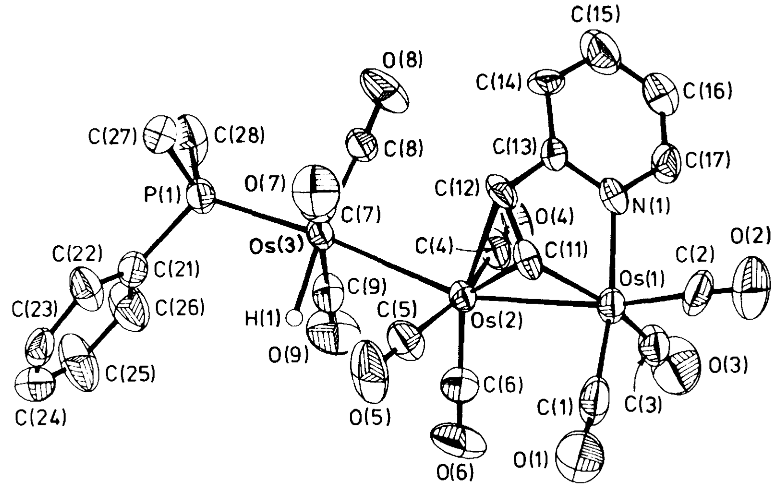
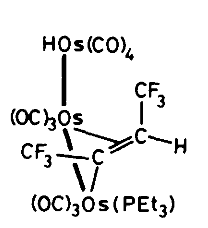
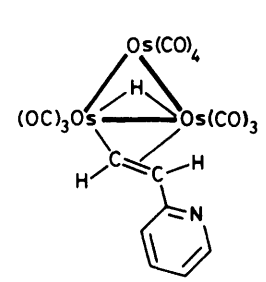


Figure 2. Molecular structure of $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$, compound **(2)**



(4)



(5)

would expect this to add oxidatively to give compound **(1)** as in the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2-ethenylpyridine. We can be sure that **(1)** is not formed from **(5)**, nor *vice versa*, since these do not interconvert under the reaction conditions.

Compounds **(1)** and **(2)** show the expected reaction of terminal hydrido-species with carbon tetrachloride, the replacement of H by Cl.[12] Thus, periodical recording of the ^1H n.m.r. spectra of CCl_4 solutions of these complexes over 2 d shows the gradual replacement of the hydride signal by that of $CHCl_3$. The sets of signals due to the $NC_5H_4CH{=}CH$ ligands of **(1)** and **(2)** are similarly replaced by very similar but new sets which we assign to complexes $[Os_3Cl(CO)_9L(NC_5H_4CH{=}CH)]$ (L = CO or PMe_2Ph), **(6)** and **(7)** respectively, which adopt structures like those of **(1)** and **(2)**. Spectra are given in Table 1.

Experimental

2-Ethenylpyridine was purchased from Aldrich Ltd. and used as supplied. Bromination to give 2-(1′,2′-dibromoethyl)pyridine and dehydrobromination with base gave 2-ethynylpyridine which was purified before use by precipitation of the silver acetylide and regeneration of the alkyne by treatment with aqueous cyanide ion.[13]

Reactions of 2-Ethenylpyridine.—With $[Os_3H_2(CO)_{10}]$. A solution of $[Os_3H_2(CO)_{10}]$ (0.34 g) and 2-ethenylpyridine (0.5 cm^3) in hexane (10 cm^3) was warmed to 50 °C and the yellow solution formed allowed to cool. Removal of the solvent and chromatography on silica (t.l.c.; eluant, pentane) gave a yellow band which gave $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$, compound **(1)** (0.20 g, 51%), as long thin yellow needles from a hexane–dichloromethane solution on cooling to 0 °C (Found: C, 21.4; H, 0.75; N, 1.4. $C_{17}H_7NO_{10}Os_3$ requires C, 21.35; H, 0.75; N, 1.45%).

With $[Os_3(CO)_{10}(MeCN)_2]$. Reaction of these reagents in toluene solution at room temperature for 3 h followed by a similar work-up to that above gave compound **(1)** as yellow needles (44%).

With $[Os_3H_2(CO)_9(PMe_2Ph)]$. The nonacarbonyl dihydride was generated *in situ* by refluxing a solution of $[Os_3H_2(CO)_{10}(PMe_2Ph)]$ (0.073 g) {itself formed by addition of PMe_2Ph to $[Os_3H_2(CO)_{10}]$} in heptane (60 cm^3) for 5 min. On adding 2-ethenylpyridine (0.02 cm^3) the refluxing brown solution became orange and the solution was cooled to room temperature after 4 min. Removal of the solvent and t.l.c. [silica; eluant, light petroleum (b.p. < 40 °C)–dichloromethane (7:3)] gave in order of elution: $[Os_3(CO)_{11}(PMe_2Ph)]$ (0.006 g, 8%), two compounds which are probably the isomers **(3a)** (0.009 g, 11%) and **(3b)** (0.014 g, 17%) of the 2-pyridyl compound $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_3Et)]$ which were characterised only by ^1H n.m.r. and i.r. spectroscopy, and finally $[Os_3H(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$, **(2)** (0.026 g, 32%). Compound **(2)** gave orange crystals (used for the *X*-ray structure determination) from methanol upon slow evaporation (Found: C, 27.2; H, 1.9; N, 1.3. $C_{24}H_{18}NO_9Os_3P$ requires C, 27.1; H, 1.6; N, 1.3%).

Reactions of Terminal Hydride Compounds with Carbon Tetrachloride.—The compound $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$, **(1)**, was dissolved in CCl_4 in an n.m.r. tube and the ^1H n.m.r. spectrum recorded periodically. Quantitative conversion into $[Os_3Cl(CO)_{10}(NC_5H_4CH{=}CH)]$, **(6)**, had occurred after 48 h. Compound **(2)** similarly gave $[Os_3Cl(CO)_9(PMe_2Ph)(NC_5H_4CH{=}CH)]$, **(7)**, but the conversion was less complete and a pure sample of **(7)** was obtained by t.l.c.

Reaction of $[Os_3H_2(CO)_{10}]$ *with 2-Ethynylpyridine.*—A solution of $[Os_3H_2(CO)_{10}]$ (0.22 g) and 2-ethynylpyridine (0.2 cm^3) in dichloromethane (25 cm^3) was allowed to stand at room temperature under nitrogen for 26 h. Removal of solvent and chromatographic separation [t.l.c., SiO_2; eluant, pentane–toluene (1:1 v/v)] gave two yellow bands yielding compound **(1)** (*cis*-vinyl) (0.054 g, 22%) and $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$ (*trans*-vinyl), **(5)** (0.140 g, 57%) (Found: C, 21.8; H, 0.9; N, 1.4. $C_{17}H_7NO_{10}Os_3$ requires C, 21.35; H, 0.75; N, 1.45%).

X-Ray Structure Determinations.—Crystal data for compound **(1)**. $C_{17}H_7NO_{10}Os_3$, M = 955.84, monoclinic, a = 17.289(11), b = 10.115(4), c = 17.719(5) Å, β = 104.15(4)°, U = 3 004.6(23) Å^3, space group $P2_1/n$, Z = 4, D_c = 2.11 g cm^{-3}, μ(Mo-K_α) = 121.9 cm^{-1}, $F(000)$ = 1 696.0.

Data collection. A Syntex $P2_1$ automatic four-circle diffractometer was used with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) and the ω—2θ scan mode; 2 030 unique reflections were measured (3 $\leqslant 2\theta \leqslant$ 50°) with $F_o \geqslant 3\sigma(F_o)$ and these were used in the structure solution and refinement. Empirical absorption and Lorentz polarisation corrections were applied to the data.

Structure solution. The structure was solved and refined using the SHELX 76 program system.[14] After suitable positions for the Os atoms had been found from the best E map, the ensuing difference syntheses and blocked-cascade least-squares refinements found all other non-hydrogen atoms. Final $R (= \Sigma\Delta/\Sigma F_o$, $\Delta = |F_o - F_c|)$ and R' $[= (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ values were 0.1001 and 0.1116. Unit weights were employed throughout. No positional parameters for hydrogen atoms were included during the calculations.

Crystal data for compound (**2**). $C_{24}H_{18}NO_9Os_3P$, M = 1 065.6, monoclinic, a = 10.113(3), b = 18.944(3), c = 15.525(4) Å, β = 105.77(2)°, U = 2 862.3 Å^3, space group $P2_1/n$, Z = 4, D_c = 2.47 g cm^{-3}, $F(000)$ = 1 936, λ = 0.710 69 Å, μ(Mo-K_α) = 128.6 cm^{-1}.

Data collection. Unit-cell parameters were determined, and intensity data collected, at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω—2θ scan procedure.[15] 6 647 Data (3 $\leqslant 2\theta \leqslant$ 54°) were measured of which 6 227 were unique and 4 242 were considered observed [$F_o \geqslant 3\sigma(F_o)$]. A semiempirical absorption correction[16] using normalised and averaged ψ scan measurements from three reflections was applied to the data; the maximum and minimum transmission of intensity was 99.8 and 70.2%, respectively.

Structure, solution, and refinement. The positions of the three Os atoms were solved by direct methods (SHELXS 84) and Fourier-difference syntheses were used to locate the remaining non-hydrogen atoms. After isotropic refinement of all non-hydrogen atoms, the DIFABS method of absorption correction[17] was applied. Following refinement using anisotropic thermal parameters for all atoms, Fourier-difference maps revealed the location of H(1) attached to Os(3) and some of the hydrogen atoms on the phenyl and pyridine rings.

Final refinement included H(1) and all hydrogens on the two rings with geometric constraints for the latter; no hydrogens were included for the two methyl groups on the phosphine group. The full-matrix least-squares refinement was carried out with unit weights and the final R-factor values were R = 0.038 and R' = 0.046 (see above for definitions).

All computations were made using SHELX 76 (apart from SHELXS 84 for direct methods) on a VAX-11/750 computer.

Acknowledgements

We thank Professor G. M. Sheldrick for providing us with a copy of SHELXS 84 prior to publication, the S.E.R.C. for financial support, and Johnson Matthey Ltd. for a loan of osmium tetraoxide.

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Received 6th April 1984; Paper 4/570