Ortho-Metallation Reactions of 2-Substituted Pyridines, 1,2-, 1,3-, and 1,4-Diazines, and 2,2′-Bipyridyl with Triosmium Clusters. Crystal and Molecular Structure of Nonacarbonyl-μ-(2,2′-bipyridyl-6-yl)-μ-hydrido-*triangulo*-triosmium(3*Os*–*Os*)

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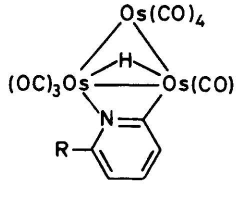
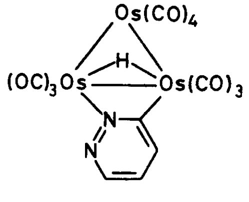
2-Methyl- or 2-benzyl-pyridine, and 1,2-, 1,3-, and 1,4-diazines all react like pyridine itself with $[Os_3(CO)_{10}(C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene) to give complexes of the type $[Os_3H(CO)_{10}(\mu\text{-}L)]$ where L is a 2-metallated heterocycle. The ^{1}H n.m.r. spectrum of the 2-benzylpyridine complex shows that μ-L is in a locked configuration on the n.m.r. time-scale and does not alternate its bonding between the two Os atoms it bridges. 2,2′-Bipyridyl reacts with $[Os_3(CO)_{12}]$ to give the related red complex $[Os_3H(CO)_9(C_{10}H_7N_2)]$ which contains the chelating bridging 6-metallated bipy ligand as established by a single-crystal *X*-ray structure determination. The crystals are monoclinic, space group $P2_1/c$, with a = 9.113(2), b = 13.157(2), c = 18.209(2) Å, β = 91.59(2)°, and Z = 4. The structure was refined to R = 0.0427 for 3 550 observed reflections. The structure of $[Os_3H(CO)_9(C_{10}H_7N_2)]$ is rather like those of compounds $[Os_3H(CO)_{10}X]$ and in particular where X = 2-pyridyl except that in the nonacarbonyl complex described here the *ortho*-metallated pyridine ring is part of a 2,2′-bipyridyl chelating ligand.

WE have previously described the *ortho*-metallation of pyridine (py) on reaction with $[Os_3(CO)_{12}]$. The direct thermal reaction gives a series of μ-2-pyridyl complexes,[1] and the *X*-ray structures of three of these have been determined: $[Os_3H_2(CO)_8(C_5H_4N)_2]$ and the 4-methylpyridine analogues of the two isomers of $[Os_2(CO)_6(C_5H_4N)_2]$.[2] The only known simple pyridine-substituted derivative of $[Os_3(CO)_{12}]$ is $[Os_3(CO)_{11}(py)]$ prepared by displacement of CH_3CN from $[Os_3(CO)_{11}(CH_3CN)]$,[3] and this is thought to be the precursor to the 2-metallated complexes shown in the Scheme although it is not observed in the direct thermal reaction. The difficulty of the direct reaction of pyridines with $[Os_3(CO)_{12}]$ is the number of products, and a simple alternative route to complexes such as $[Os_3H(CO)_{10}(C_5H_4N)]$ is the displacement of weakly bound ligands L from $[Os_3(CO)_{10}L_2]$.[3,4] We have now applied this method where L = cyclo-octene[4] to the synthesis of metallated pyridine and diazine cluster complexes. Our intention was to examine the chemistry of compounds with two nitrogen atoms, either in one ring as in diazines or in separate rings as in 2,2′-bipyridyl, to assess the consequences of using potentially bridging or chelating ligands. Initially, we studied some 2-substituted pyridines to establish that metallated derivatives could be formed as we expected using $[Os_3(CO)_{10}L_2]$.



(1; R = Me)
(2; R = CH$_2$Ph)



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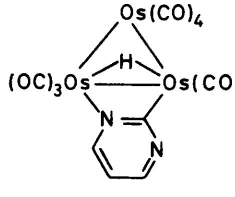

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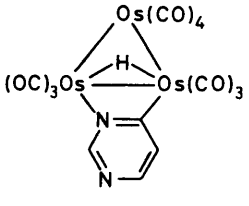

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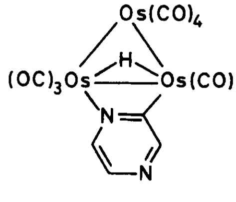

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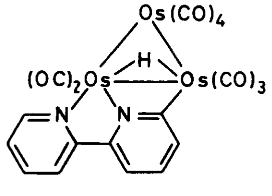


(7)

RESULTS AND DISCUSSION

2-*Substituted Pyridines*.—2-Alkyl-substituted pyridines RC_5H_4N react more slowly with $[Os_3(CO)_{10}L_2]$ (L = cyclo-octene) than does pyridine but to give the same type of product $[Os_3H(CO)_{10}(RC_5H_3N)]$ (1; R = Me) and complex (2; R = $PhCH_2$). The related complex $[Os_3H(CO)_{10}(C_2H_3)]$ undergoes a fast intramolecular process (Figure 1) leading to a time-average plane of symmetry,[5] but in contrast (2) is rigid. A sharp, well resolved AB quartet for the CH_2 group in the room-temperature ^{1}H n.m.r. spectrum indicates that the process in Figure 2 is either slow or does not occur. This process could not occur without exchange of sites between H^a and H^b. The interconversion of the two dimeric isomers shown in the Scheme requires an interchange of this sort but these isomers may be separated by chromatography at room temperature, and only slowly interconvert at 150 °C and above.[1]

Diazines.—Cyclo-octene is readily displaced from $[Os_3(CO)_{10}(C_8H_{14})_2]$ by 1,2-diazine ($N_2C_4H_4$) to give an almost black precipitate of $[Os_3(CO)_{10}(N_2C_4H_4)]$.[6] This solid is very insoluble but is partly dissolved when a suspension in xylene is kept under reflux for a few hours. However, it was shown to dissolve as its yellow *ortho*-metallated isomer $[Os_3H(CO)_{10}(C_4H_3N_2)]$ (3). In contrast, 1,3- and 1,4-diazines cannot form bridges without C–H fission and lead directly to the *ortho*-metallated complexes (4)—(6). Compounds (3)—(6) were characterised as isomers by mass spectroscopy and metallation positions were easily established from ^1H n.m.r. spectra (see Table 1).

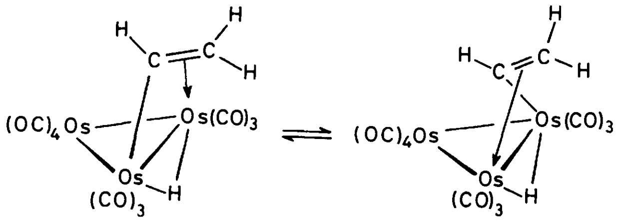


FIGURE 1 Rapid enantiomerisation as identified for $[Os_3H(CO)_{10}(C_2H_3)]$ from its ^{13}C n.m.r. spectrum (ref. 5)

2,2′-*Bipyridyl.*—The Scheme shows that Os complexes containing two 2-pyridyl ligands may be obtained from pyridine. This suggests the possibility of a reductive elimination with C–C coupling to give 2,2′-bipyridyl (bipy) or even the catalytic conversion of py into bipy. However, our treatment of the dimeric complexes with CO did not generate free or co-ordinated bipy. Indeed these dinuclear 2-pyridyl complexes are very unreactive, being formed at about 190 °C, and we have been unable to characterise any of their reactions except their slow interconversions at high temperatures. Furthermore, we have no evidence for bipy or its derivatives from the reaction of $[Os_3(CO)_{12}]$ with py. Since bipy is not formed in this way we attempted to establish whether the reverse formation of 2-pyridyl complexes from bipy by C–C bond cleavage occurs. Treatment of $[Os_3(CO)_{10}(C_8H_{14})_2]$ with bipy at room temperature gave a dark insoluble material which might be $[Os_3(CO)_{10}(bipy)]$, by analogy with the 1,2-diazine compound, but we did not attempt full characterisation. Instead, we reacted bipy with $[Os_3(CO)_{12}]$ in a sealed glass tube at 185 °C, the conditions under which the dinuclear 2-pyridyl complexes are formed from py. Apart from some almost black insoluble solid, we obtained a red complex with apparent formula $[Os_3(CO)_9(bipy)]$ (parent molecular ion in the mass spectrum) in 44% yield. The ^1H n.m.r. spectrum was complex but of rather poor quality because of problems of low solubility, but a hydride resonance suggested that C–H cleavage had occurred. A single-crystal *X*-ray structure determination was carried out. The molecular structure of (7) is shown in Figure 3.

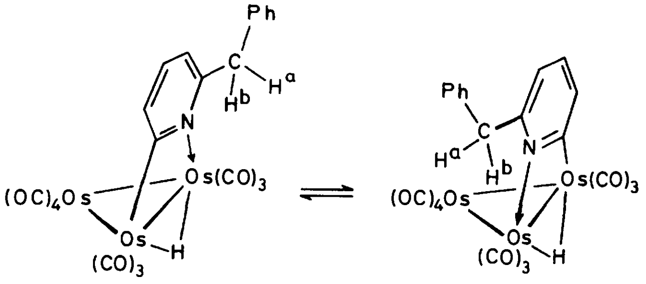
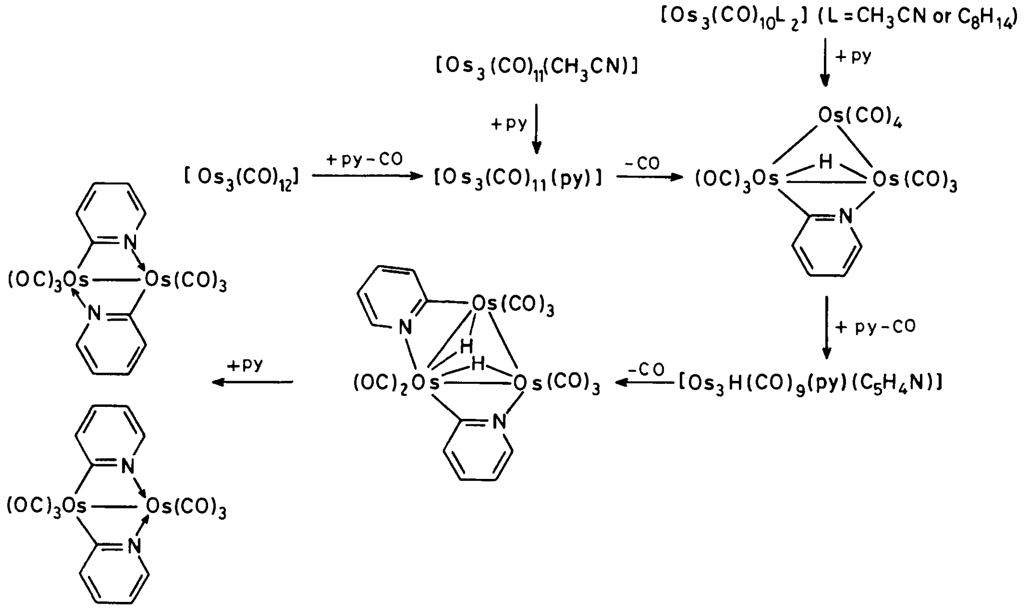


FIGURE 2 A possible enantiomerisation for $[Os_3H(CO)_{10}(PhCH_2C_5H_3N)]$



SCHEME

The formulation $[Os_3H(CO)_9(C_{10}H_7N_2)]$ for (7) is established and the compound is directly related to the well known class of compounds $[Os_3H(CO)_{10}X]$ where X is a bridging ligand (H, OR, SR, halogen, *etc.*). More immediately, it is related directly to $[Os_3H(CO)_{10}(C_5H_4N)]$ formed from $[Os_3(CO)_{12}]$ and pyridine.[1] One of the bipyridyl rings is 2-metallated and bridges Os(1) and Os(3) while the bipy ligand as a whole is chelating at Os(1). Consequently, the five-membered chelate ring at Os(1) is fused to a four-membered ring containing Os(1), Os(3), C(1), and N(2). The two non-bridged Os–Os bonds are the same length, 2.878(4) and 2.877(4) Å, while the bridged Os–Os bond is rather longer, 2.926(4) Å. The lengths of the bridged Os–Os bonds in complexes of type $[Os_3H(CO)_{10}X]$ and related compounds like it have been considered. When X is a single-atom bridge, the bridged Os–Os distance is close to or slightly shorter than the other Os–Os bonds if the bridging atom of X is a first-row element, but rather longer if it is heavier.[7] The size of X is most important and arguments of Os–Os bond order based on bond length are invalid. Where there is a double-atom bridge, as in (7), the bridged Os–Os bond is the longest of the three and again its length is controlled presumably by the geometric requirements of the pyridyl bridge.

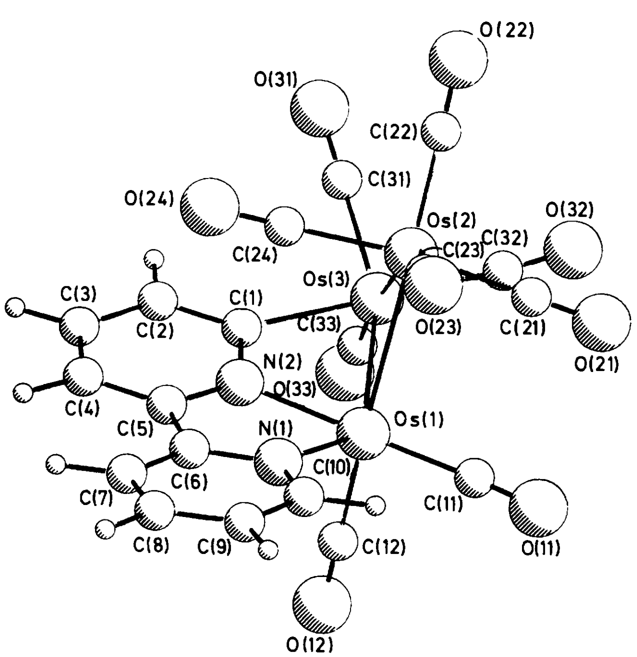


FIGURE 3 Molecular structure of $[Os_3H(CO)_9(C_{10}H_7N_2)]$ (7), showing the atom numbering

The bridging hydride H^b was located experimentally (but with a large uncertainty in its position) lying close to the intersection of the Os(1)N(1) and Os(3)C(31) directions.

Other 2-substituted pyridines give bridging/chelating ligands as identified here for cluster (7). Thus where the 2-substituent is CH_2OH or CO_2H, instead of the 2-pyridyl group as here, we obtained similarly structured clusters with five-membered chelate rings fused to 4-membered rings associated with the metal bridge. Indeed, whatever the substituents at pyridine, the tendency for 2-metallation is high. This chemistry will be described fully elsewhere.

EXPERIMENTAL

Syntheses.—The bis(cyclo-octene) complex $[Os_3(CO)_{10}(C_8H_{14})_2]$ was prepared by the method of Tachikawa and Shapley[4] and stored (−20 °C) and used as a cyclo-octene solution. All new complexes gave parent molecular ions in the mass spectra, but in a few cases contamination by cyclo-octene prevented accurate elemental analysis.

Reactions of $[Os_3(CO)_{10}(C_8H_{14})_2]$.—(*a*) *With 2-methylpyridine.* A solution of the cyclo-octene complex (0.30 g) in cyclo-octene (12 cm³) was stirred with 2-methylpyridine (0.1 cm³) for 17 h at room temperature under nitrogen. Only partial reaction had occurred so the temperature was raised to 76 °C for 2 h. Evaporation to dryness and separation of the residue by thin-layer chromatography (t.l.c.) on

TABLE 1

Selected i.r. and ¹H n.m.r. data for the new complexes

Complex	ν(CO) [a]/cm⁻¹	Chemical shifts [b] (δ/p.p.m.)					
		H^2	H^4	H^5	H^6	Os*H*	Others
(1) $[Os_3H(CO)_{10}(6\text{-}MeC_5H_3N)]$	2 106m, 2 062s, 2 053s, 2 023s, 2 012s, 2 003m, 1 990m, 1 976m, 1 951w	*c*	*c*	*c*	7.19	−14.34	CH_3 3.15
(2) $[Os_3H(CO)_{10}(6\text{-}PhCH_2C_5H_3N)]$	2 104m, 2 062s, 2 053s, 2 022s, 2 010s, 2 002m, 1 976m, 1 950w		6.23	6.90	*d*	−14.22	$PhCH_2$ 4.13 and 3.89, *J* = 17 Hz
(3) $[Os_3H(CO)_{10}(C_4H_3N_2)]$	2 107m, 2 070s, 2 056s, 2 026s, 2 010s, 1 995m, 1 980m, 1 966vw, 1 953w		8.23	6.93	6.93	−14.95	
(4) $[Os_3H(CO)_{10}(C_4H_3N_2)]$	2 107m, 2 069s, 2 057s, 2 027s, 2 010s, 2 000s, 1 991s, 1 981m, 1 965vw, 1 957vw	8.33	6.85	8.12		−14.88	
(5) $[Os_3H(CO)_{10}(C_4H_3N_2)]$	2 110m, 2 070s, 2 059s, 2 029s, 2 015s, 2 011 (sh), 1 999s, 1 984m, 1 972vw, 1 958vw	8.51		7.91	7.35	−14.95	
(6) $[Os_3H(CO)_{10}(C_4H_3N_2)]$	2 109m, 2 069s, 2 059s, 2 028s, 2 014s, 2 011 (sh), 1 998m, 1 983m, 1 970w, 1 959w	8.25	8.00		7.76	−14.98	
(7) $[Os_3H(CO)_9(C_{10}H_7N_2)]$	2 086m, 2 044m, 2 009s, 2 005 (sh), 1 988m, 1 980m, 1 963m, 1 942w						

[a] Measured in cyclohexane, ±1 cm⁻¹. [b] 100 MHz at 27 °C in $CDCl_3$ solution. The Os-bound carbon is position 1 and the Os-bound nitrogen position 2, *etc.* [c] Signals overlapping in the region δ 7.45—7.77. [d] Obscured by resonances of Ph group.

silica gave two yellow bands giving $[Os_3H(CO)_{10}(OH)]$ (0.026 g) and $[Os_3H(CO)_{10}(6\text{-}MeC_5H_3N)]$ (1) (0.078 g, 29%) (Found: C, 20.75; H, 0.9; N, 1.45. $C_{16}H_7NO_{10}Os_3$ requires C, 20.35; H, 0.75; N, 1.5%), both as yellow crystals.

(*b*) *With 2-benzylpyridine.* A similar treatment to that above gave only very slow reaction at room temperature but at 120 °C for 6 h gave yellow crystals of $[Os_3H(CO)_{10}(6\text{-}PhCH_2C_5H_3N)]$ (2) (40%) (Found: C, 25.4; H, 1.1; N, 1.2. $C_{22}H_{11}NO_{10}Os_3$ requires C, 25.9; H, 1.1; N, 1.35%).

(*c*) *With* 1,2-*diazine.* A solution of the cyclo-octene complex (0.56 g) in cyclo-octene (20 cm³) was reacted with pyridazine (1,2-diazine) (0.2 cm³) at room temperature to give a black precipitate. The cyclo-octene solvent was removed under reduced pressure and replaced by *o*-xylene (50 cm³) and the suspension refluxed for 7.5 h. The black solid remaining was removed by filtration and the filtrate evaporated to dryness. T.l.c. (silica) separation of the residue gave $[Os_3H(CO)_{10}(C_4H_3N_2)]$ (3) as yellow crystals (0.033 g, 7%) (Found: C, 19.0; H, 0.7; N, 3.1. $C_{14}H_4N_2O_{10}Os_3$ requires C, 18.05; H, 0.45; N, 3.0%).

TABLE 2

Atomic co-ordinates (× 10^4) for compound (7) *

	x	*y*	*z*
Os(1)	2 391	3 140	1 187
Os(2)	3 498	2 232	2 529
Os(3)	547	1 774	2 031
N(1)	4 308(9)	3 034(6)	558(5)
N(2)	2 356(9)	1 685(6)	772(4)
C(1)	1 387(11)	1 056(7)	1 090(6)
C(2)	1 223(12)	109(8)	760(6)
C(3)	2 043(12)	−169(8)	172(6)
C(4)	3 117(12)	486(8)	−86(5)
C(5)	3 241(10)	1 432(8)	232(5)
C(6)	4 368(11)	2 201(8)	121(5)
C(7)	5 500(13)	2 103(10)	−369(6)
C(8)	6 565(15)	2 837(11)	−408(7)
C(9)	6 531(13)	3 672(11)	42(7)
C(10)	5 353(13)	3 730(10)	518(7)
C(11)	2 603(14)	4 471(8)	1 574(6)
C(12)	1 209(12)	3 618(8)	396(6)
C(21)	2 649(12)	3 425(8)	2 964(6)
C(22)	3 478(13)	1 445(9)	3 417(6)
C(23)	5 366(14)	2 863(10)	2 518(7)
C(24)	4 101(11)	1 063(8)	1 967(6)
C(31)	644(12)	507(8)	2 522(6)
C(32)	9 879(13)	2 454(9)	2 915(6)
C(33)	8 606(12)	1 648(8)	1 615(6)
O(11)	2 786(12)	5 287(6)	1 771(6)
O(12)	418(11)	3 874(8)	9 922(6)
O(21)	2 199(10)	4 140(6)	3 213(5)
O(22)	3 423(12)	972(7)	3 939(5)
O(23)	6 508(13)	3 233(9)	2 516(7)
O(24)	4 522(9)	364(6)	1 653(5)
O(31)	778(11)	9 748(7)	2 815(6)
O(32)	9 435(11)	2 779(7)	3 435(5)
O(33)	7 462(9)	1 561(8)	1 369(5)
H(2)	429(12)	−418(8)	971(6)
H(3)	1 860(12)	−895(8)	−92(6)
H(4)	3 833(12)	258(8)	−520(5)
H(7)	5 535(13)	1 446(10)	−724(6)
H(8)	7 441(15)	2 751(11)	−791(7)
H(9)	7 364(13)	4 255(11)	27(7)
H(10)	5 285(13)	4 382(10)	876(7)
H^b	892	3 045(78)	1 684(58)

* Estimated standard deviations are in parentheses in Tables 2—4.

TABLE 3

Bond lengths (Å) for compound (7)

Os(2)–Os(1)	2.878(4)	C(1)–N(2)	1.352(14)
Os(3)–Os(1)	2.926(4)	C(5)–N(2)	1.331(13)
N(1)–Os(1)	2.120(11)	C(2)–C(1)	1.390(15)
N(2)–Os(1)	2.058(9)	C(3)–C(2)	1.373(16)
C(1)–Os(1)	2.894(13)	C(4)–C(3)	1.395(16)
C(11)–Os(1)	1.895(13)	C(5)–C(4)	1.377(15)
C(12)–Os(1)	1.882(13)	C(6)–C(5)	1.460(15)
H^b–Os(1)	1.7(1)	C(7)–C(6)	1.388(17)
Os(3)–Os(2)	2.877(4)	C(8)–C(7)	1.373(20)
C(21)–Os(2)	1.930(12)	C(9)–C(8)	1.371(21)
C(22)–Os(2)	1.920(14)	C(10)–C(9)	1.400(18)
C(23)–Os(2)	1.895(15)	O(11)–C(11)	1.143(15)
C(24)–Os(2)	1.936(12)	O(12)–C(12a)	1.160(16)
N(2)–Os(3)	2.863(11)	O(21)–C(21)	1.126(14)
C(1)–Os(3)	2.118(12)	O(22)–C(22)	1.139(15)
C(31)–Os(3)	1.891(12)	O(23)–C(23)	1.149(18)
C(32)–Os(3b)	1.952(13)	O(24)–C(24)	1.154(14)
C(33)–Os(3b)	1.913(13)	O(31)–C(31c)	1.137(15)
H^b–Os(3)	1.8(1)	O(32)–C(32)	1.125(16)
C(6)–N(1)	1.356(14)	O(33)–C(33)	1.129(14)
C(10)–N(1)	1.325(16)		

Key to symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (a) *x*, *y*, 1 + *z*; (b) 1 + *x*, *y*, *z*; (c) *x*, 1 + *y*, *z*.

TABLE 4

Bond angles (°) for compound (7)

Os(3)–Os(1)–Os(2)	59.4	C(33)–Os(3)–Os(2)	171.5(3)
N(1)–Os(1)–Os(2)	99.0(3)	H^b–Os(3)–Os(2)	75.4(35)
N(2)–Os(1)–Os(2)	85.8(3)	C(1)–Os(3)–N(2)	26.5(3)
C(1)–Os(1)–Os(2)	76.2(3)	N(2)–Os(3)–C(31)	108.7(5)
C(11)–Os(1)–Os(2)	92.2(4)	C(1)–Os(3)–C(31)	88.6(5)
C(12)–Os(1)–Os(2)	165.5(3)	C(32)–Os(3)–C(31)	91.6(6)
H^b–Os(1)–Os(2)	77.3(37)	C(33)–Os(3)–C(31)	98.1(6)
N(1)–Os(1)–Os(3)	137.5(2)	H^b–Os(3)–C(31)	165.5(34)
N(2)–Os(1)–Os(3)	67.5(3)	N(2)–Os(3)–C(32)	151.4(4)
C(1)–Os(1)–Os(3)	42.7(2)	C(1)–Os(3)–C(32)	177.0(4)
C(11)–Os(1)–Os(3)	115.2(5)	C(33)–Os(3)–C(32)	93.5(6)
C(12)–Os(1)–Os(3)	106.4(4)	H^b–Os(3)–C(32)	85.7(35)
H^b–Os(1)–Os(3)	34.5(35)	N(2)–Os(3)–C(33)	103.0(5)
N(2)–Os(1)–N(1)	75.2(4)	C(1)–Os(3)–C(33)	89.5(5)
C(1)–Os(1)–N(1)	99.7(4)	H^b–Os(3)–C(33)	96.2(36)
C(1)–Os(1)–N(2)	25.1(3)	N(2)–Os(3)–H^b	69.5(35)
N(1)–Os(1)–C(11)	100.7(5)	C(1)–Os(3)–H^b	93.3(35)
N(2)–Os(1)–C(11)	175.0(4)	C(6)–N(1)–Os(1)	114.7(8)
C(1)–Os(1)–C(11)	157.9(4)	C(10)–N(1)–Os(1)	126.1(8)
C(12)–Os(1)–C(11)	91.5(6)	C(10)–N(1)–C(6)	119.0(10)
H^b–Os(1)–C(11)	86.8(37)	Os(3)–N(2)–Os(1)	70.8(3)
N(1)–Os(1)–C(12)	94.1(5)	C(1)–N(2)–Os(1)	114.6(7)
N(2)–Os(1)–C(12)	91.6(5)	C(5)–N(2)–Os(1)	120.0(8)
C(1)–Os(1)–C(12)	95.5(5)	C(1)–N(2)–Os(3)	44.3(5)
H^b–Os(1)–C(12)	88.9(38)	C(5)–N(2)–Os(3)	167.4(6)
N(1)–Os(1)–H^b	171.9(35)	C(5)–N(2)–C(1)	125.5(9)
N(2)–Os(1)–H^b	97.2(36)	Os(3)–C(1)–Os(1)	69.5(4)
C(1)–Os(1)–H^b	72.5(36)	N(2)–C(1)–Os(1)	40.3(4)
Os(3)–Os(2)–Os(1)	61.1	C(2)–C(1)–Os(1)	154.9(7)
C(21)–Os(2)–Os(1)	82.9(4)	N(2)–C(1)–Os(3)	109.2(7)
C(22)–Os(2)–Os(1)	158.1(3)	C(2)–C(1)–Os(3)	135.4(8)
C(23)–Os(2)–Os(1)	95.9(5)	C(2)–C(1)–N(2)	115.3(10)
C(24)–Os(2)–Os(1)	88.8(4)	C(3)–C(2)–C(1)	121.5(11)
C(21)–Os(2)–Os(3)	85.3(4)	C(4)–C(3)–C(2)	120.0(11)
C(22)–Os(2)–Os(3)	97.0(4)	C(5)–C(4)–C(3)	117.8(10)
C(23)–Os(2)–Os(3)	157.0(4)	C(4)–C(5)–N(2)	119.5(10)
C(24)–Os(2)–Os(3)	86.8(4)	C(6)–C(5)–N(2)	111.9(10)
C(22)–Os(2)–C(21)	94.6(6)	C(6)–C(5)–C(4)	128.2(10)
C(23)–Os(2)–C(21)	91.1(6)	C(5)–C(6)–N(1)	116.0(10)
C(24)–Os(2)–C(21)	170.5(4)	C(7)–C(6)–N(1)	119.7(11)
C(23)–Os(2)–C(22)	105.9(6)	C(7)–C(6)–C(5)	124.2(11)
C(24)–Os(2)–C(22)	91.5(6)	C(8)–C(7)–C(6)	120.4(13)
C(24)–Os(2)–C(23)	94.2(6)	C(9)–C(8)–C(7)	120.4(13)
Os(2)–Os(3)–Os(1)	59.4	C(10)–C(9)–C(8)	116.3(13)
N(2)–Os(3)–Os(1)	41.6(1)	C(9)–C(10)–N(1)	124.1(12)
C(1)–Os(3)–Os(1)	67.9(4)	O(11)–C(11)–Os(1)	175.6(11)
C(31)–Os(3)–Os(1)	140.3(3)	O(12)–C(12)–Os(1)	176.0(10)
C(32)–Os(3)–Os(1)	110.3(4)	O(21)–C(21)–Os(2)	177.5(10)
C(33)–Os(3)–Os(1)	112.5(4)	O(22)–C(22)–Os(2)	178.0(11)
H^b–Os(3)–Os(1)	31.2(35)	O(23)–C(23)–Os(2)	179.0(12)
N(2)–Os(3)–Os(2)	73.0(3)	O(24)–C(24)–Os(3)	176.7(9)
C(1)–Os(3)–Os(2)	89.6(4)	O(31)–C(31)–Os(3)	176.5(10)
C(31)–Os(3)–Os(2)	90.3(4)	O(32)–C(32)–Os(3)	174.6(10)
C(32)–Os(3)–Os(2)	87.4(5)	O(33)–C(33)–Os(3)	179.2(10)
Os(3)–H^b–Os(1)	114.2(60)		

(*d*) *With* 1,3-*diazine*. A solution of the cyclo-octene complex (0.358 g) in cyclo-octene (8 cm^3) was heated with pyrimidine (1,3-diazine) (0.02 cm^3) at 50 °C for 30 min under nitrogen. Removal of solvent gave an orange solid which was separated by t.l.c. (silica) eluting with toluene to give [$Os_3H(CO)_{10}(C_4H_3N_2)$] (4), as yellow crystals (0.023 g, 7%) and the isomeric complex (5) also as yellow crystals (0.096 g, 31%).

(*e*) *With* 1,4-*diazine*. A treatment very similar to that above using pyrazine (1,4-diazine) gave [$Os_3H(CO)_{10}$-($C_4H_3N_2$)] (6) as yellow crystals (31%).*

Reaction of 2,2′-*Bipyridyl with* [$Os_3(CO)_{12}$].—The osmium carbonyl (0.53 g) and 2,2′-bipyridyl (0.11 g) in n-decane (10 cm^3) were sealed under vacuum in a Pyrex tube and heated at 185 ± 2 °C for 3 h. A black, totally insoluble residue (0.067 g), possibly [$Os_3(CO)_{10}$(bipy)] (but not studied further), was removed by filtration and the solvent removed from the filtrate. Chromatography gave [$Os_3H(CO)_9$-($C_{10}H_7N_2$)] (7), as red crystals (0.26 g, 44%) (Found: C, 23.8; H, 1.3; N, 2.5. $C_{19}H_8N_2O_9Os_3$ requires C, 23.25; H, 1.05; N, 2.85%).

X-*Ray Structure Determination of* [$Os_3H(CO)_9(C_{10}H_7N_2)$] (7).—*Crystal data*. $C_{19}H_8N_2O_9Os_3$, $M = 978.88$, Monoclinic, $a = 9.113(2)$, $b = 13.157(2)$, $c = 18.209(2)$ Å, $\beta = 91.59(2)°$, $U = 2\,182.49$ Å^3, space group $P2_1/c$, $D_m = 2.85$ g cm^{-3}, $Z = 4$, $D_c = 2.98$ g cm^{-3}, $F(000) = 1\,743.74$, μ(Mo-K_α) = 167.65 cm^{-1}.

Data collection. CAD4 Diffractometer, $\omega/2\theta$ scan width = 0.8 + 0.15tanθ, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), $1.50 \leqslant \theta \leqslant 26.0°$, $\pm h,k,l$, $T_{\text{max.}} = 60$ s, crystal size 0.2373 $\{102\} \times 0.1095$ $\{012\} \times 0.475$ mm $\{0\bar{1}2\}$, total data measured = 4 861, unique = 3 551, observed = 3550 [$I > 3\sigma(I)$], absorption correction applied.

Structure solution and refinement. 'Best' EEES map (SHELX 76), all non-H atoms anisotropic, H atoms AFIX on rings, weighting scheme $w = 1/\{\sigma^2(F_o) + 0.0004F_o^2\}$, $R = 0.0427$, $R' = 0.0355$; computers: ICL1900 and CDC-7600, programs and scattering factors as in ref. 8.

Atomic co-ordinates are in Table 2 and bond lengths and angles are in Tables 3 and 4; anisotropic temperature factors and observed and calculated structure factors are in Supplementary Publication No. SUP 23237 (19 pp.).†

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[*] The analytical data for (4), (5), and (6) indicate contamination by a hydrocarbon impurity.

[†] For details see Notice to Authors No. 7, *J. Chem. Soc., Dalton*, 1981, Index Issue.

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