Reaction of $[Os_5H_2(CO)_{15}]$ with Pyridine: Crystal and Molecular Structures of $[Os_5H_3(CO)_{14}(C_5H_4N)]$ and $[Os_5H_2(CO)_{14}(C_5H_5N)]$†

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The reaction of the hydrido cluster $[Os_5H_2(CO)_{15}]$ with pyridine, in n-octane under reflux, affords three neutral products $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**), $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**), and $[Os_5H_2(CO)_{15}(C_5H_5N)]$ which exists in two isomeric forms (**3a**) and (**3b**), together with the monoanion $[Os_5H(CO)_{15}]^-$. The complexes were characterized by spectroscopic, and in the case of (**1**) and (**2**) by single-crystal *X*-ray crystallographic techniques. Within the series of neutral compounds the pyridine ligand occupies a variety of co-ordination sites and displays different bonding modes. In the case of complexes (**1**), (**3a**), and (**3b**) the reaction with pyridine also results in a change in metal framework geometry from that present in the starting material. The structure of (**1**) consists of an edge-bridged tetrahedron of Os atoms with an orthometallated pyridyl ligand linking the apex Os atom of the tetrahedron to the Os atom which bridges the tetrahedron. In (**2**) the five Os atoms define a trigonal bipyramid. The pyridine ligand bonds to the cluster *via* nitrogen, and occupies a pseudo-'axial' site on one of the equatorial Os atoms. The spectroscopic data for (**3a**) and (**3b**) are consistent with the presence of an edge-bridged tetrahedral metal geometry, with the pyridine terminally bound to a co-ordination site on the edge-bridging Os atom. In (**3a**) the pyridine occupies an equatorial site and in (**3b**) an axial site. A possible mechanism for the reaction is discussed.

Pyridine and its substituted derivatives have been shown to react with trinuclear osmium clusters in a variety of ways which depend on the nature of the cluster and upon the reaction conditions. The pyridine-derived ligand may bond to the cluster through the pyridine nitrogen, by orthometallation of the ring, *via* a substituent group only, or *via* the pyridine nitrogen and the substituent group.[1] The direct reaction of $[Os_3(CO)_{12}]$ with pyridine, 4-methylpyridine, or 4-benzylpyridine under harsh conditions leads to orthometallation of the organic group with a hydrogen being transferred to the cluster framework.[2] With unsaturated or labile clusters it is possible to carry out reactions under less forcing conditions and a wider variety of products have been obtained. The room temperature reaction of $[Os_3(CO)_{11}(NCMe)]$ with pyridine affords the simple substituted derivative $[Os_3(CO)_{11}(C_5H_5N)]$.[3] Treatment of the disubstituted complex $[Os_3(CO)_{10}(NCMe)_2]$ with a variety of 2-substituted pyridines, under mild conditions, affords a range of products dependent on the nature of the substituent group.[1] The unsaturated cluster $[Os_3H_2(CO)_{10}]$ reacts with 2-vinylpyridine in a similar manner to give $[Os_3H(CO)_{10}(NC_5H_4CH{=}CH)]$ in which the organic group is bound to the cluster *via* the pyridine nitrogen, vinyl CH, and the C=C double bond.[4] The labile cluster $[Os_3(CO)_{10}(C_8H_{14})_2]$ (C_8H_{14} = cyclo-octene) reacts with pyridine,[5] 2-alkyl- and -aryl-pyridines,[5] 2-pyridone,[6] 2-aminopyridine,[6] and 2-(benzylamino)pyridine[6] at room temperature to give complexes with the general formula $[Os_3H(CO)_{10}(\mu\text{-}L)]$ where L forms a 2-metallated heterocycle.

Despite this interest in the interaction of pyridines with trinuclear osmium clusters there have been few reports of their reactions with higher nuclearity carbonyls. The pyrolysis of $[Os_3(CO)_{11}(C_5H_5N)]$ leads to formation of the orthometallated cluster $[Os_5C(CO)_{14}H(C_5H_4N)]$ together with the $[Os_{10}C(CO)_{24}]^{2-}$ dianion.[7] In this pentanuclear cluster the 2-pyridyl ligand bridges two equatorially located Os atoms of an *arachno*-bipyramidal Os_5 arrangement which surrounds a semi-interstitial carbido atom.[7] Recently, $[Os_6(CO)_{18}]$ has been found to react with excess pyridine to give the anion $[Os_5(CO)_{15}]^{2-}$ together with small amounts of the neutral cluster $[Os_6(CO)_{17}(C_5H_5N)_2]$.[8] In the latter complex both pyridine ligands bond *via* nitrogen to the 'spike' Os atom of the 'spiked' trigonal-bipyramidal metal arrangement.[8] From these results it is apparent that two of the most common bonding modes found for pyridines co-ordinated to trinuclear clusters are also observed in high nuclearity clusters. Since the higher nuclearity complexes have a wider variety of metal framework geometries, and of co-ordination environments, it is of interest to see which types of co-ordination sites are favoured by which bonding modes of the pyridine ligands. It may also be possible to obtain new bonding modes for these ligands which are not available in the smaller clusters. We now report the reaction of pyridine with the hydrido pentanuclear cluster $[Os_5H_2(CO)_{15}]$, and show that both terminally bound and *ortho*-metallated pyridyl-containing products are obtained.

Results and Discussion

The complex $[Os_5H_2(CO)_{15}]$ reacts with pyridine in a 1 : 2 ratio, in n-octane under reflux, to give three neutral products $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**), $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**), and $[Os_5H_2(CO)_{15}(C_5H_5N)]$ which exists in two isomeric forms (**3a**) and (**3b**), together with the anion $[Os_5H(CO)_{15}]^-$. The reaction is carried out in non-polar solvents since bases such as pyridine tend to deprotonate $[Os_5H_2(CO)_{15}]$ and can convert

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† 1,1,2,2,2,3,3,3,4,4,4,5,5,5-Tetradecacarbonyl-1,2;1,3;1,4-tri-μ-hydrido-μ-[2-pyridyl-*C*(Os^1),*N*(Os^5)]-*cyclo*-pentaosmium(8 *Os–Os*) and 1,1,1,2,2,2,3,3,4,4,4,5,5,5-tetradecacarbonyl-1,3;2,3-di-μ-hydrido-3-pyridine-*cyclo*-pentaosmium(9 *Os–Os*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Spectroscopic data

Compound	ν(CO) (CH_2Cl_2)/cm^{-1}	^1H N.m.r./p.p.m.[a]	m/e[b]
(**1**)	2 102w, 2 070s, 2 042vs, 2 009w, 1 994m, 1 975w	9.12 (d, 1 H), 8.16 (d, 1 H), 7.36 (t, 1 H), 6.84 (t, 1 H), −16.60 (s, 1 H), −19.10 (s, 2 H)	1 433
(**2**)	2 093w, 2 060vs, 2 039s, 2 017s, 1 985w, 1 941vw	8.83 (d, 2 H), 7.99 (t, 1 H), 7.42 (t, 2 H), −14.09 (s, 1 H), −19.39 (s, 1 H)	1 433
(**3a**)	2 098w, 2 071s, 2 050s, 2 035ms, 2 017w, 1 995mw, 1 987(sh)	—	[c]
(**3b**)	2 099w, 2 071vs, 2 048ms, 2 038ms, 2 012w, 1 998mw, 1 979w	—	[c]

[a] In CD_2Cl_2 at room temperature. [b] Based on ^{192}Os. [c] Highest mass observed at m/e 1 382 which corresponds to $[Os_5H_2(CO)_{15}]$.

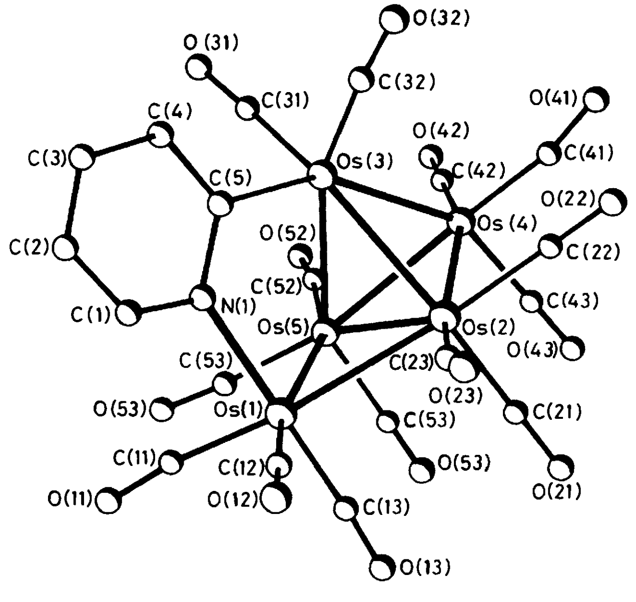


Figure 1. The molecular structure of $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**) showing the atom-numbering scheme

it into $[Os_5H(CO)_{15}]^-$ instead of giving the desired pyridine-containing products. When the reaction is carried out in dichloromethane solution, the yield of the anionic product is increased.

Spectroscopic data for (**1**)—(**3**) are given in Table 1. The ^1H n.m.r. of (**1**) shows the inequivalence of the four hydrogen atoms in the pyridine ring consistent with the presence of an *ortho*-metallated pyridyl ligand. Two signals in the ratio 2:1 in the hydride region can also be observed and (**1**) can thus be formulated as $[Os_5H_3(CO)_{14}(C_5H_4N)]$. In order to establish the overall molecular structure of the complex, a single-crystal *X*-ray structure analysis was undertaken. The molecular structure of (**1**) is shown in Figure 1 together with the atom-numbering scheme adopted. Bond lengths and interbond angles are listed in Table 2. The metal framework geometry is best described as an edge-bridged tetrahedron, similar to that observed in the adducts $[Os_5H_2(CO)_{15}Y]$ [Y = CO or $P(OMe)_3$].[9,10] The pyridyl ligand is bonded through the N atom to the bridging Os atom while the apex of the tetrahedron is bonded to the α-carbon of the ring. The hydrides were not located directly from the *X*-ray analysis but potential energy calculations[11] indicate that they bridge the three long apex–basal edges Os(2)–Os(3), Os(4)–Os(3), and Os(5)–Os(3), which is consistent with the ^1H n.m.r. data. The metal–metal distances in (**1**) are similar to those in $[Os_5H_2(CO)_{15}Y]$ although those which involve the edge-bridging metal atom are slightly shorter (mean 2.86 Å) than those observed in $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$[9] (mean 2.913 Å), $[Os_5H_2(CO)_{15}I]^-$ (mean 2.912 Å), or $[Os_5H_2(CO)_{16}]$[10] (mean 2.893 Å). This difference may be due to the constraint imposed by the bonding mode of the pyridyl ligand. The angle between the planes formed by Os(1)Os(2)Os(5) and Os(2)Os(4)Os(5) in (**1**) is 169.1°, with Os(1) displaced towards the apical Os(3) atom. This contrasts the essentially planar Os_4 systems observed in the other adducts. This feature may also be related to the bonding requirements of the pyridyl ligand. The atoms forming the pyridyl ring and Os(1) and Os(3) are effectively coplanar and this plane is perpendicular to the base of the tetrahedron. The Os atom at the apex of the tetrahedron is only bonded to two carbonyl groups while the remaining Os atoms are bonded to three terminal carbonyls each. All carbonyl groups are essentially linear with an average Os–C distance of 1.87 Å. The bond lengths between the pyridyl ligand and the metal atoms, Os(1)–N(1) and Os(3)–C(5), are not significantly different from those in $[Os_5H(CO)_{14}C(C_5H_4N)]$, a compound where *ortho*-metallation has also occurred, with Os–N and Os–C distances of 2.16(2) and 2.04(2) Å in the carbido cluster.[7]

The structure of (**1**) indicates that the reaction to give the *ortho*-metallated pyridyl product involves a rearrangement of the metal framework of the starting material $[Os_5H_2(CO)_{15}]$. Although the *X*-ray structure of this dihydride has never been determined it is assumed that the molecule consists of a trigonal bipyramid of Os atoms by analogy with the structure of $[Os_5H_2(CO)_{14}(PEt_3)]$ which is known.[12] The trigonal-bipyramidal structure is consistent with the formal electron count of 72 for the *closo* geometry. The reaction to form $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**) involves the loss of a carbonyl group, which acts as a two-electron donor, and the addition of a 2-pyridyl ligand and a hydride, which together donate four electrons to the cluster. Complex (**1**) has a formal electron count of 74, consistent with the opening up of the cluster to give the observed edge-bridged tetrahedral geometry, and with the loss of one 'formal' Os–Os bond.

The spectroscopic data for $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**) are consistent with the presence of a terminally bound pyridine ligand, and with the existence of two hydrides in two different environments. A single crystal of (**2**) was grown and the molecular structure determined. The structure of (**2**) is illustrated in Figure 2 and the bond parameters are listed in Table 3. The trigonal-bipyramidal metal arrangement of the dihydride is retained in (**2**), and the formal electron count of 72 for this complex is in agreement with the *closo* structure. The pyridine ligand is terminally bound *via* the N atom to one of the equatorial osmium atoms, Os(1), which is also co-ordinated to two terminal carbonyl groups. The other four Os atoms each have three terminally bound carbonyls. The site on Os(1) occupied by the pyridine may be described as pseudo-'axial' in that it lies out of the Os(1)Os(2)Os(3) plane in an orientation similar to that observed for the PEt_3 group in $[Os_5H_2(CO)_{14}(PEt_3)]$.[12] This contrasts the ligand arrangement in the related clusters $[Os_5(CO)_{16}]$[13] and $[Os_5I(CO)_{15}]^-$[14] where one equatorial Os atom is bound to four ligands, two of which lie close to the Os_3 equatorial plane. However, in the anion[14] the iodine ligand takes up an 'axial' position. The distribution of carbonyl and hydride ligands in (**2**) is also similar to that in $[Os_5H_2(CO)_{14}(PEt_3)]$.[12] Although the hydride ligands in (**2**)

Table 2. Bond lengths (Å) and angles (°) for $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**)

Os(2)–Os(1)	2.862(3)	Os(5)–Os(1)	2.859(3)	C(5)–Os(3)	2.036(31)	C(31)–Os(3)	1.847(26)
N(1)–Os(1)	2.213(25)	C(11)–Os(1)	1.874(29)	C(32)–Os(3)	1.863(28)	Os(5)–Os(4)	2.854(3)
C(12)–Os(1)	1.826(32)	C(13)–Os(1)	1.848(28)	C(41)–Os(4)	1.799(33)	C(42)–Os(4)	1.894(31)
Os(3)–Os(2)	2.938(3)	Os(4)–Os(2)	2.850(3)	C(43)–Os(4)	1.884(26)	C(51)–Os(5)	1.924(24)
Os(5)–Os(2)	2.827(3)	C(21)–Os(2)	1.896(27)	C(52)–Os(5)	1.873(28)	C(53)–Os(5)	1.887(29)
C(22)–Os(2)	1.911(28)	C(23)–Os(2)	1.844(28)	C(1)–N(1)	1.273(40)	C(5)–N(1)	1.468(38)
Os(4)–Os(3)	2.951(3)	Os(5)–Os(3)	2.923(3)	C(2)–C(1)	1.382(46)	C(3)–C(2)	1.278(47)
				C(4)–C(3)	1.514(50)	C(5)–C(4)	1.403(44)
Os(5)–Os(1)–Os(2)	59.2(1)	N(1)–Os(1)–Os(2)	94.6(7)	C(32)–Os(3)–C(31)	92.6(16)	Os(3)–Os(4)–Os(2)	60.8(1)
N(1)–Os(1)–Os(5)	95.4(7)	C(11)–Os(1)–Os(2)	159.7(13)	Os(5)–Os(4)–Os(2)	59.4(1)	Os(5)–Os(4)–Os(3)	60.5(1)
C(11)–Os(1)–Os(5)	100.5(13)	C(11)–Os(1)–N(1)	87.0(13)	C(41)–Os(4)–Os(2)	107.4(13)	C(41)–Os(4)–Os(3)	110.4(12)
C(12)–Os(1)–Os(2)	106.0(13)	C(12)–Os(1)–Os(5)	165.1(13)	C(41)–Os(4)–Os(5)	166.1(13)	C(42)–Os(4)–Os(2)	162.9(13)
C(12)–Os(1)–N(1)	86.8(15)	C(12)–Os(1)–C(11)	94.3(18)	C(42)–Os(4)–Os(3)	111.6(13)	C(42)–Os(4)–Os(5)	103.5(13)
C(13)–Os(1)–Os(2)	85.4(12)	C(13)–Os(1)–Os(5)	87.3(13)	C(42)–Os(4)–C(41)	89.5(18)	C(43)–Os(4)–Os(2)	89.3(12)
C(13)–Os(1)–N(1)	176.9(15)	C(13)–Os(1)–C(11)	94.1(16)	C(43)–Os(4)–Os(3)	147.5(12)	C(43)–Os(4)–Os(5)	94.4(11)
C(13)–Os(1)–C(12)	90.2(18)	Os(3)–Os(2)–Os(1)	81.9(1)	C(43)–Os(4)–C(41)	89.7(17)	C(43)–Os(4)–C(42)	93.3(17)
Os(4)–Os(2)–Os(1)	119.8(1)	Os(4)–Os(2)–Os(3)	61.3(1)	Os(2)–Os(5)–Os(1)	60.4(1)	Os(3)–Os(5)–Os(1)	82.2(1)
Os(5)–Os(2)–Os(1)	60.3(1)	Os(5)–Os(2)–Os(3)	60.9(1)	Os(3)–Os(5)–Os(2)	61.4(1)	Os(4)–Os(5)–Os(1)	119.8(1)
Os(5)–Os(2)–Os(4)	60.4(1)	C(21)–Os(2)–Os(1)	98.4(12)	Os(4)–Os(5)–Os(2)	60.2(1)	Os(4)–Os(5)–Os(3)	61.4(1)
C(21)–Os(2)–Os(3)	154.1(13)	C(21)–Os(2)–Os(4)	97.5(13)	C(51)–Os(5)–Os(1)	94.3(13)	C(51)–Os(5)–Os(2)	88.6(12)
C(21)–Os(2)–Os(5)	96.6(13)	C(22)–Os(2)–Os(1)	162.6(14)	C(51)–Os(5)–Os(3)	147.5(12)	C(51)–Os(5)–Os(4)	93.8(12)
C(22)–Os(2)–Os(3)	97.0(14)	C(22)–Os(2)–Os(4)	73.6(14)	C(52)–Os(5)–Os(1)	160.2(11)	C(52)–Os(5)–Os(2)	134.8(11)
C(22)–Os(2)–Os(5)	133.9(14)	C(22)–Os(2)–C(21)	90.1(18)	C(52)–Os(5)–Os(3)	95.0(11)	C(52)–Os(5)–Os(4)	74.7(11)
C(23)–Os(2)–Os(1)	73.4(13)	C(23)–Os(2)–Os(3)	113.5(13)	C(52)–Os(5)–C(51)	98.3(17)	C(53)–Os(5)–Os(1)	76.0(15)
C(23)–Os(2)–Os(4)	162.7(13)	C(23)–Os(2)–Os(5)	133.7(13)	C(53)–Os(5)–Os(2)	136.4(15)	C(53)–Os(5)–Os(3)	117.1(14)
C(23)–Os(2)–C(21)	91.0(19)	C(23)–Os(2)–C(22)	91.5(19)	C(53)–Os(5)–Os(4)	162.2(15)	C(53)–Os(5)–C(51)	93.0(18)
Os(4)–Os(3)–Os(2)	57.9(1)	Os(5)–Os(3)–Os(2)	57.7(1)	C(53)–Os(5)–C(52)	88.0(18)	C(1)–N(1)–Os(1)	118.1(23)
Os(5)–Os(3)–Os(4)	58.1(1)	C(5)–Os(3)–Os(2)	98.5(9)	C(5)–N(1)–Os(1)	125.3(19)	C(5)–N(1)–C(1)	116.4(27)
C(5)–Os(3)–Os(4)	153.0(8)	C(5)–Os(3)–Os(5)	99.5(8)	C(2)–C(1)–N(1)	128.7(34)	C(3)–C(2)–C(1)	120.1(40)
C(31)–Os(3)–Os(2)	162.1(12)	C(31)–Os(3)–Os(4)	109.7(12)	C(4)–C(3)–C(2)	116.8(37)	C(5)–C(4)–C(3)	120.0(33)
C(31)–Os(3)–Os(5)	105.4(12)	C(31)–Os(3)–C(5)	89.7(15)	N(1)–C(5)–Os(3)	121.1(20)	C(4)–C(5)–Os(3)	122.3(25)
C(32)–Os(3)–Os(2)	103.2(12)	C(32)–Os(3)–Os(4)	106.4(12)	C(4)–C(5)–N(1)	116.6(28)		
C(32)–Os(3)–Os(5)	159.3(12)	C(32)–Os(3)–C(5)	90.8(15)				

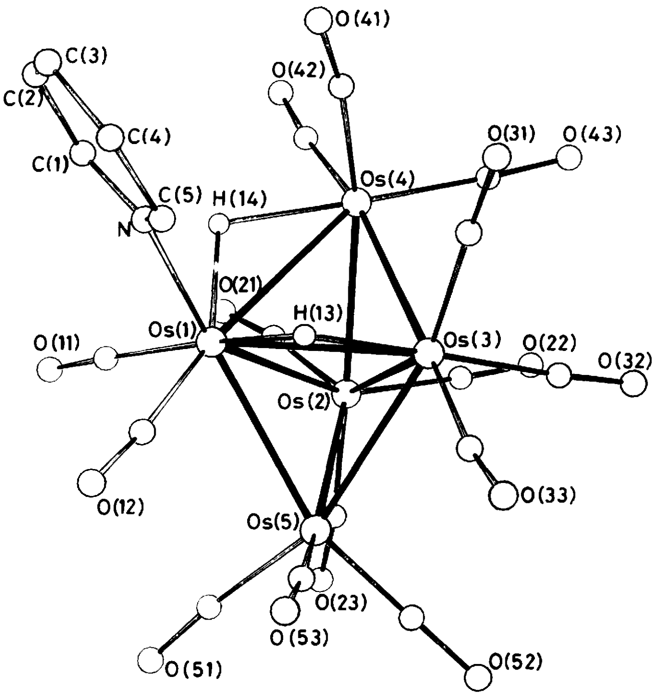


Figure 2. The molecular structure of the pyridine adduct $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**). The carbonyl carbon atoms have the same numbers as the corresponding oxygen atoms

were not located directly, potential energy calculations[11] confirm the ^1H n.m.r. evidence that the two hydride ligands are in different environments. One hydride bridges the longest of the three equatorial edges, Os(1)–Os(3), while the second hydride bridges the long Os(1)–Os(4) axial–equatorial edge, so that both hydrides are directly bonded to the pyridine-substituted Os atom. The Os–Os bond distances within the metal framework of (**2**) closely resemble those in $[Os_5H_2(CO)_{14}(PEt_3)]$.[12] The shortest Os–Os distances in (**2**) are the unbridged Os(equatorial)–Os(axial) edges [range 2.678(2)—2.880(2) Å] which compare well with 2.681(2)—2.943(3) Å in the phosphine complex. The two unbridged equatorial Os–Os edges in (**2**) are also similar to those in the phosphine complex [2.832(3) and 2.837(2) Å]. The two hydride-bridged edges in both structures are the longest, with the Os(axial)–Os(equatorial) distance being *ca.* 0.09 Å longer than the bridged Os(equatorial)–Os(equatorial) bond in (**2**), and *ca.* 0.15 Å longer in $[Os_5H_2(CO)_{14}(PEt_3)]$.[12] The Os(1)–N bond length in (**2**) is not significantly different from the equivalent Os–N distance for the *ortho*-metallated pyridyl in (**1**), but these two lengths are at the top of the range [2.04(2)—2.16(2) Å] found in other pyridine–osmium systems.[4–8] The carbonyl groups are all essentially linear except for C(23)O(23) which forms a weak incipient bridge to the apical Os(5) atom, presumably to partially redress the electron imbalance within the cluster framework; Os(5) is formally associated with only 17 electrons. The average Os–C(carbonyl) distance is 1.88 Å.

It is interesting to note that on heating the 72-electron system $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**), in octane, it converts to the more open 74-electron cluster $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**), with the loss of a metal–metal edge. In this process *ortho*-metallation

Table 3. Bond lengths (Å) and angles (°) for $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**)

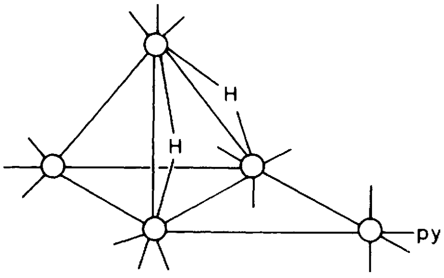
Os(1)–Os(2)	2.830(2)	Os(1)–Os(3)	2.908(1)	Os(3)–C(32)	1.91(3)	Os(3)–C(33)	1.93(3)
Os(1)–Os(4)	2.995(1)	Os(1)–Os(5)	2.880(2)	Os(4)–C(41)	1.92(3)	Os(4)–C(42)	1.88(3)
Os(1)–N	2.214(22)	Os(1)–C(11)	1.913(25)	Os(4)–C(43)	1.90(3)	Os(5)–C(23)	2.65(3)
Os(1)–C(12)	1.84(4)	Os(2)–Os(3)	2.838(2)	Os(5)–C(51)	1.90(4)	Os(5)–C(52)	1.78(4)
Os(2)–Os(4)	2.750(2)	Os(2)–Os(5)	2.678(2)	Os(5)–C(53)	1.84(3)	N–C(1)	1.32(4)
Os(2)–C(21)	1.93(3)	Os(2)–C(22)	1.86(3)	N–C(5)	1.39(3)	C(1)–C(2)	1.39(4)
Os(2)–C(23)	1.87(4)	Os(3)–Os(4)	2.873(1)	C(2)–C(3)	1.33(5)	C(3)–C(4)	1.43(4)
Os(3)–Os(5)	2.866(2)	Os(3)–C(31)	1.87(3)	C(4)–C(5)	1.44(4)		

Os(3)–Os(1)–Os(2)	59.3(1)	Os(4)–Os(1)–Os(2)	56.2(1)	C(32)–Os(3)–Os(4)	100.1(8)	C(32)–Os(3)–Os(5)	105.2(8)
Os(4)–Os(1)–Os(3)	58.2(1)	Os(5)–Os(1)–Os(2)	55.9(1)	C(32)–Os(3)–C(31)	94(1)	C(33)–Os(3)–Os(1)	114.0(9)
Os(5)–Os(1)–Os(3)	59.4(1)	Os(5)–Os(1)–Os(4)	103.3(1)	C(33)–Os(3)–Os(2)	128.7(9)	C(33)–Os(3)–Os(4)	171.2(9)
N–Os(1)–Os(2)	148.1(6)	N–Os(1)–Os(3)	107.8(5)	C(33)–Os(3)–Os(5)	76.2(9)	C(33)–Os(3)–C(31)	97(1)
N–Os(1)–Os(4)	91.9(6)	N–Os(1)–Os(5)	146.7(6)	C(33)–Os(3)–C(32)	87(1)	Os(2)–Os(4)–Os(1)	58.8(1)
C(11)–Os(1)–Os(2)	89.1(8)	C(11)–Os(1)–Os(3)	148.3(8)	Os(3)–Os(4)–Os(1)	59.4(1)	Os(3)–Os(4)–Os(2)	60.6(1)
C(11)–Os(1)–Os(4)	106.9(8)	C(11)–Os(1)–Os(5)	103.5(8)	C(41)–Os(4)–Os(1)	100.2(9)	C(41)–Os(4)–Os(2)	157.7(9)
C(11)–Os(1)–N	100(1)	C(12)–Os(1)–Os(2)	125(1)	C(41)–Os(4)–Os(3)	103.4(9)	C(42)–Os(4)–Os(1)	115(1)
C(12)–Os(1)–Os(3)	109(1)	C(12)–Os(1)–Os(4)	165(1)	C(42)–Os(4)–Os(2)	104(1)	C(42)–Os(4)–Os(3)	165(1)
C(12)–Os(1)–Os(5)	72(1)	C(12)–Os(1)–N	86(1)	C(42)–Os(4)–C(41)	91(1)	C(43)–Os(4)–Os(1)	146.9(9)
C(12)–Os(1)–C(11)	88(1)	Os(3)–Os(2)–Os(1)	61.7(1)	C(43)–Os(4)–Os(2)	99.2(9)	C(43)–Os(4)–Os(3)	88.8(9)
Os(4)–Os(2)–Os(1)	64.9(1)	Os(4)–Os(2)–Os(3)	61.8(1)	C(43)–Os(4)–C(41)	96(1)	C(43)–Os(4)–C(42)	94(1)
Os(5)–Os(2)–Os(1)	63.0(1)	Os(5)–Os(2)–Os(3)	62.5(1)	Os(2)–Os(5)–Os(1)	61.1(1)	Os(3)–Os(5)–Os(1)	60.8(1)
Os(5)–Os(2)–Os(4)	116.2(1)	C(21)–Os(2)–Os(1)	96(1)	Os(3)–Os(5)–Os(2)	61.5(1)	C(23)–Os(5)–Os(1)	93.7(8)
C(21)–Os(2)–Os(3)	142(1)	C(21)–Os(2)–Os(4)	81(1)	C(23)–Os(5)–Os(2)	41.0(8)	C(23)–Os(5)–Os(3)	98.3(8)
C(21)–Os(2)–Os(5)	137(1)	C(22)–Os(2)–Os(1)	151(1)	C(51)–Os(5)–Os(1)	99(1)	C(51)–Os(5)–Os(2)	105(1)
C(22)–Os(2)–Os(3)	96(1)	C(22)–Os(2)–Os(4)	89(1)	C(51)–Os(5)–Os(3)	159(1)	C(51)–Os(5)–C(23)	76(1)
C(22)–Os(2)–Os(5)	125(1)	C(22)–Os(2)–C(21)	92(1)	C(52)–Os(5)–Os(1)	161(1)	C(52)–Os(5)–Os(2)	103(1)
C(23)–Os(2)–Os(1)	117(1)	C(23)–Os(2)–Os(3)	124(1)	C(52)–Os(5)–Os(3)	103(1)	C(52)–Os(5)–C(23)	78(1)
C(23)–Os(2)–Os(4)	174(1)	C(23)–Os(2)–Os(5)	69(1)	C(52)–Os(5)–C(51)	96(2)	C(53)–Os(5)–Os(1)	100(1)
C(23)–Os(2)–C(21)	93(1)	C(23)–Os(2)–C(22)	90(1)	C(53)–Os(5)–Os(2)	155(1)	C(53)–Os(5)–Os(3)	95.2(9)
Os(2)–Os(3)–Os(1)	59.0(1)	Os(4)–Os(3)–Os(1)	62.4(1)	C(53)–Os(5)–C(23)	164(1)	C(53)–Os(5)–C(51)	94(2)
Os(4)–Os(3)–Os(2)	57.6(1)	Os(5)–Os(3)–Os(1)	59.8(1)	C(53)–Os(5)–C(52)	91(1)	C(1)–N–Os(1)	119(2)
Os(5)–Os(3)–Os(2)	56.0(1)	Os(5)–Os(3)–Os(4)	106.8(1)	C(5)–N–Os(1)	119(2)	C(5)–N–C(1)	121(2)
C(31)–Os(3)–Os(1)	107.2(9)	C(31)–Os(3)–Os(2)	134.4(9)	C(2)–C(1)–N	121(3)	C(3)–C(2)–C(1)	121(3)
C(31)–Os(3)–Os(4)	77.2(9)	C(31)–Os(3)–Os(5)	159.0(9)	C(4)–C(3)–C(2)	120(3)	C(5)–C(4)–C(3)	117(3)
C(32)–Os(3)–Os(1)	147.4(8)	C(32)–Os(3)–Os(2)	88.4(8)			C(4)–C(5)–N	119(2)

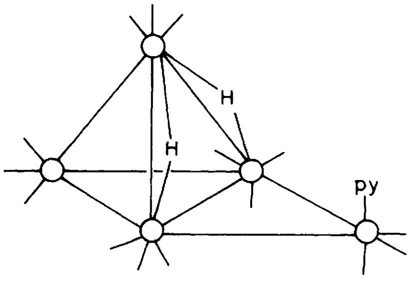
occurs with associated oxidative cleavage of an Os–Os bond rather than loss of CO which has previously been observed on *ortho*-metallation. However, oxidative cleavage of a metal–metal bond is well known in triosmium chemistry; for example, halogens react with $[Os_3(CO)_{12}]$ to give the linear $[Os_3(CO)_{12}X_2]$.[15]

The remaining neutral isomeric products of the reaction, (**3a**) and (**3b**), have tentatively been formulated as $[Os_5H_2(CO)_{15}(C_5H_5N)]$ on the basis of their i.r. spectra which are similar to that of the known species $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$.[9] The closest similarity is observed between complex (**3a**) and $[Os_5H_2(CO)_{15}\{P(OMe)_3\}]$ and this is therefore believed to have the same structural characteristics, that is, an edge-bridged tetrahedral metal framework with the ligand co-ordinated in an equatorial position of the edge-bridging Os atom. The other isomer (**3b**) is proposed to have the pyridine ligand in an axial position (Figure 3). On standing in dichloromethane (**3a**) and (**3b**) do not interconvert but both dissociate to the monoanion $[Os_5H(CO)_{15}]^-$. The counter ion for the cluster anion is presumably pyridinium, $[Hpy]^+$, but it has not been identified. This dissociation in polar solvents might be associated with the large quantity of the anion $[Os_5H(CO)_{15}]^-$ (40% yield) isolated in the reaction. This is because, before the reaction mixture was separated by t.l.c., the residue was taken up in CH_2Cl_2 and dissociation of (**3a**) and (**3b**) could have occurred at this stage and continued through the whole purification procedure. This may also explain why poor quality ^1H n.m.r. spectra were obtained for these two isomers since these were run in CD_2Cl_2.

In this reaction a possible mechanistic pathway would appear to involve the initial attack of pyridine at an axial Os atom of



(**3a**)



(**3b**)

Figure 3. Proposed structures for compounds (**3a**) and (**3b**)

the trigonal bipyramid. This process would be associated with the opening of an Os–Os edge to give either (**3a**) or (**3b**). This is a facile process which has been demonstrated in the reactions of pentanuclear Os clusters with iodine or phosphite.[9] However, in these examples only one isomer was observed.

Three different reaction pathways are then available to the isomers of $[Os_5H_2(CO)_{15}(C_5H_5N)]$ (**3a**) and (**3b**) apart from the loss of the pyridine ligand which does not yield any new product and is reversible.

Deprotonation of $[Os_5H_2(CO)_{15}(C_5H_5N)]$ to give the anion $[Os_5H(CO)_{15}]^-$ and $[Hpy]^+$ could occur, but as indicated above it is probably only significant in polar solvents. Secondly, the closure of an Os–Os edge with the loss of a carbonyl group to give $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**) could occur. This reaction has been observed in the chemistry of $[Os_5H_2(CO)_{15}Y]$ [Y = CO or $P(OMe)_3$] systems.[9] Then (**2**) may convert to $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**) by *ortho*-metallation, this being associated with the reopening of a metal–metal edge. Thirdly, the *ortho*-metallation of the pyridine adduct with the associated loss of a carbonyl to give (**1**) directly is also possible.

A requirement of some of these reaction steps is that pyridine is free to move about the metal framework, for example, from an axial to an equatorial Os atom. Such a process has been observed in the reaction of $[Os_5H_2(CO)_{14}(PEt_3)]$ with phosphite.[12]

Experimental

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer using an internal calibrant. Mass spectra were obtained using an AEI MS12 instrument at 70 eV ($\sim 112 \times 10^{-19}$ J) ionizing potential. ^{1}H N.m.r. spectra were recorded on a Bruker WH250 spectrometer using CD_2Cl_2 as solvent. Thin-layer chromatography plates were purchased from Merck and consisted of 20 × 20 cm glass plates coated with a 0.25-mm layer of silica gel. Reactions were routinely performed under a nitrogen atmosphere with purified solvents.

Preparation of $[Os_5H_2(CO)_{15}]$.—Potassium hydroxide (360 mg) was dissolved in dry, degassed methanol (5 cm^3), and $[Os_6(CO)_{18}]$ (100 mg) added. The brown solution was stirred at room temperature for 0.5 h. $[N(PPh_3)_2]Cl$ (220 mg) was then added and $[N(PPh_3)_2]_2[Os_5(CO)_{15}]$ (121 mg, 80% yield from Os_6) precipitated as a brown powder, which was filtered off and washed with dry methanol. The dianion was dissolved in the minimum quantity of MeCN, the solution filtered to eliminate any residual $[N(PPh_3)_2]Cl$, and concentrated H_2SO_4 (1 cm^3) added dropwise with stirring. The mixture was allowed to stand at −20 °C for 5 h and $[Os_5H_2(CO)_{15}]$ (36 mg, 55% yield from dianion) precipitated as a brown powder.

Reaction of $[Os_5H_2(CO)_{15}]$ *with Pyridine*.—The dihydride $[Os_5H_2(CO)_{15}]$ (10 mg) was suspended in dry, degassed n-octane (50 cm^3) and two molar equivalents of pyridine in octane added. The solution was heated under reflux for 1 h during which time the colour changed from light brown to yellow-orange. The solvent was removed under vacuum and the mixture separated by t.l.c. using dichloromethane–hexane (2:3) as eluant. Four solid products were obtained, and were characterized as $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**) (orange-yellow, 2 mg, 25% yield from the dihydride), $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**) (orange-red, 1 mg, 10% yield), and the two isomers of $[Os_5H_2(CO)_{15}(C_5H_5N)]$ (**3a**) and (**3b**) [(**3a**), orange, 1.5 mg, 15% yield; (**3b**), orange-brown, 1 mg, 10% yield]. A heavy baseline was also present on the t.l.c. plates which was characterized as the known anion[16] $[Os_5H(CO)_{15}]^-$ from its i.r. spectrum {brown, 5 mg, 40% yield as $[N(PPh_3)_2]^+$ salt}. Neither (**3a**) nor (**3b**) showed parent peaks in their mass spectra, instead the highest mass observed was at 1 382 which corresponds to the parent cluster $[Os_5H_2(CO)_{15}]$. This behaviour is typical of cluster compounds containing labile ligands such as pyridine or MeCN.[3]

Table 4. Atomic co-ordinates (× 10^4) for $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	4 529(2)	2 830(1)	4 599(1)
Os(2)	4 107(2)	1 404(1)	3 782(1)
Os(3)	3 483(2)	2 462(1)	2 480(1)
Os(4)	1 444(2)	1 170(1)	2 872(1)
Os(5)	1 678(2)	2 458(1)	3 904(1)
N(1)	5 416(31)	3 458(15)	3 574(15)
C(1)	6 288(39)	4 032(19)	3 693(20)
C(2)	7 051(47)	4 478(23)	3 154(22)
C(3)	6 900(44)	4 341(20)	2 426(22)
C(4)	5 680(42)	3 771(20)	2 193(22)
C(5)	4 992(36)	3 307(17)	2 760(18)
C(11)	4 091(47)	3 800(18)	5 028(21)
O(11)	3 895(37)	4 371(17)	5 367(18)
C(12)	6 472(37)	2 814(24)	4 963(23)
O(12)	7 721(36)	2 826(17)	5 171(18)
C(13)	3 897(46)	2 291(21)	5 468(18)
O(13)	3 497(35)	1 982(17)	6 031(17)
C(21)	3 556(48)	776(20)	4 640(20)
O(21)	3 294(33)	372(17)	5 162(16)
C(22)	4 457(52)	500(20)	3 168(25)
O(22)	4 862(32)	−24(16)	2 803(16)
C(23)	6 094(31)	1 420(24)	4 111(25)
O(23)	7 392(31)	1 339(14)	4 164(15)
C(31)	2 512(42)	3 137(19)	1 812(19)
O(31)	2 019(31)	3 593(15)	1 385(15)
C(32)	4 754(43)	2 101(22)	1 697(20)
O(32)	5 538(33)	1 818(16)	1 237(17)
C(41)	1 788(45)	360(21)	2 240(21)
O(41)	2 078(42)	−70(21)	1 744(20)
C(42)	−487(38)	1 297(24)	2 408(24)
O(42)	−1 659(34)	1 379(17)	2 114(17)
C(43)	716(42)	491(19)	3 642(19)
O(43)	233(33)	78(15)	4 111(16)
C(51)	970(45)	1 886(21)	4 792(19)
O(51)	370(28)	1 556(14)	5 291(14)
C(52)	−178(34)	2 582(21)	3 389(21)
O(52)	−1 361(31)	2 730(15)	3 136(15)
C(53)	1 339(54)	3 421(19)	4 389(26)
O(53)	1 022(35)	4 025(17)	4 632(17)

Conversion of $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**) *into* $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**).—Compound (**2**) (5 mg) was heated under reflux in octane (10 cm^3) for 1 h with the solution slowly changing from orange-red to yellow. The product (**1**) was formed in quantitative yield.

Crystal-structure Determination of $[Os_5H_3(CO)_{14}(C_5H_4N)]$ (**1**).—Crystals of (**1**) were grown by slow evaporation of an ethyl acetate solution and mounted on glass fibres.

Crystal data. $C_{19}H_7NO_{14}Os_5$, M = 1 424.11, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$, no. 14), a = 8.844(4), b = 17.306(9), c = 17.157(9) Å, β = 90.23(4)°, U = 2 626(2) Å^3 (by least-squares refinement on diffractometer angles from 15 automatically-centred reflections in range $15 < 2\theta < 25°$, λ = 0.710 69 Å), Z = 4, D_c = 3.60 g cm^{-3}, D_m not measured, $F(000)$ = 2 480. Yellow tablets. Crystal dimensions 0.37 × 0.15 × 0.18 mm, $\mu(\text{Mo-}K_\alpha)$ = 241.67 cm^{-1}.

Data collection and processing.[17] Intensity data were recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha 1}$ = 0.709 26, $\lambda_{\alpha 2}$ = 0.713 54 Å) and a 96-step (from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$) ω–2θ scan procedure,

Table 5. Fractional atomic co-ordinates for $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	−0.033 80(7)	0.184 89(8)	0.346 00(9)	O(23)	0.0156(17)	0.1318(22)	−0.0485(25)
Os(2)	−0.071 37(7)	0.239 09(8)	0.127 17(9)	C(31)	−0.0637(18)	0.4790(21)	0.3716(25)
Os(3)	−0.014 16(7)	0.394 17(8)	0.273 40(9)	O(31)	−0.0898(13)	0.5364(16)	0.4372(18)
Os(4)	−0.177 16(6)	0.314 03(8)	0.270 60(9)	C(32)	−0.0270(16)	0.4901(20)	0.1570(22)
Os(5)	0.086 76(7)	0.235 02(9)	0.196 27(10)	O(32)	−0.0372(14)	0.5476(17)	0.0914(20)
N	−0.0682(13)	0.1900(15)	0.5156(18)	C(33)	0.0950(19)	0.4467(22)	0.2992(25)
C(1)	−0.1293(19)	0.1330(23)	0.5448(27)	O(33)	0.1549(18)	0.4894(21)	0.3223(24)
C(2)	−0.1514(19)	0.1327(24)	0.6509(27)	C(41)	−0.2140(19)	0.3567(21)	0.4072(26)
C(3)	−0.1100(22)	0.1873(26)	0.7275(30)	O(41)	−0.2288(14)	0.3715(17)	0.4969(20)
C(4)	−0.0400(18)	0.2447(22)	0.7016(25)	C(42)	−0.2746(21)	0.2411(24)	0.2379(28)
C(5)	−0.0203(17)	0.2464(20)	0.5906(23)	O(42)	−0.3396(17)	0.2032(19)	0.2203(22)
C(11)	−0.0620(16)	0.0465(19)	0.3106(22)	C(43)	−0.2146(18)	0.4319(23)	0.1931(25)
O(11)	−0.0783(14)	−0.0330(17)	0.2850(20)	O(43)	−0.2375(13)	0.5090(17)	0.1538(18)
C(12)	0.0656(22)	0.1370(27)	0.4019(31)	C(51)	0.1219(26)	0.1009(33)	0.1649(38)
O(12)	0.1276(16)	0.1078(18)	0.4515(22)	O(51)	0.1483(16)	0.0226(19)	0.1405(21)
C(21)	−0.1591(21)	0.1423(26)	0.1014(28)	C(52)	0.1355(22)	0.2958(26)	0.0895(31)
O(21)	−0.2023(17)	0.0773(20)	0.0938(22)	O(52)	0.1686(18)	0.3384(20)	0.0155(25)
C(22)	−0.1168(20)	0.3280(24)	0.0224(28)	C(53)	0.1747(19)	0.2623(23)	0.2915(26)
O(22)	−0.1489(14)	0.3837(17)	−0.0449(20)	O(53)	0.2317(17)	0.2747(21)	0.3575(24)
C(23)	−0.0078(21)	0.1801(25)	0.0245(29)				

variable scan speed from 3° $\min^{-1}$ to 29° $\min^{-1}$, $5 < 2\theta < 50°$, off-line profile fitted. Two check reflections were monitored every 50 measurements throughout the data collection and showed no significant variation. 4 409 Reflections measured. Empirical absorption correction based on 321 measurements from 11 unique reflections. Maximum and minimum transmission factors of 0.99 and 0.19 respectively. 1 995 Unique reflections with $F_o > 3\sigma(F_o)$.

Structure analysis and refinement. The five Os atom positions were determined by direct methods followed by Fourier-difference syntheses to locate remaining non-hydrogen atoms. Refinement by full-matrix least squares with the Os atoms assigned anisotropic thermal parameters and the C, N, and O atoms individual isotropic thermal parameters. C–O (carbonyl) distances were constrained to 1.16(1) Å. Pyridyl H atoms were placed in idealized positions and allowed to ride 1.08 Å from the relevant carbon; these H atoms were assigned a common isotropic thermal parameter. The weighting scheme $w = 1.8/[\sigma^2(F_o) + 0.0012\ F_o{}^2]$ gave satisfactory analysis of variance. Prior to the final stage of refinement, a least-squares job was run with the scattering factors for N(1) and C(5) reversed to check if the 2-pyridyl nitrogen was co-ordinated to Os(3) rather than Os(1). Two equivalent refinements, differing only in the assignments of the scattering factors for the C(5) and N(1) atoms, were compared, and the refinement with N(1) bonded to Os(1) gave more realistic thermal parameters for both C(5) and N(1) and a slightly lower *R* factor than the refinement with the alternative orientation of the 2-pyridyl ligand. It was assumed that the original assignment of the orientation of the 2-pyridyl ligand was correct. Refinement of the structure continued until convergence was reached, $R = 0.048$, $R' = 0.048$. Complex neutral scattering factors[18] were employed throughout the structure solution and refinement. All computations were performed on the University of Cambridge IBM 370/165 computer using SHELX 76.[19] The final atomic co-ordinates are listed in Table 4.

Crystal-structure Determination of $[Os_5H_2(CO)_{14}(C_5H_5N)]$ (**2**).—Crystals of (**2**) were grown by slow evaporation of a hexane solution and mounted on glass fibres.

Crystal data. $C_{19}H_7NO_{14}Os_5$, $M = 1\,424.11$, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$, no. 14), $a = 16.418(3)$, $b = 13.090(3)$, $c = 12.394(2)$ Å, $\beta = 93.92(2)°$, $U = 2\,657(1)$ Å^3 (by least-squares refinement on diffractometer angles from 25 automatically-centred reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 3.56$ g cm^{-3}, D_m not measured, $F(000) = 2\,480$. Red rectangular block. Crystal dimensions 0.28 × 0.22 × 0.18 mm, $\mu(\text{Mo-}K_\alpha) = 229.59$ cm^{-1}.

Data collection and processing.[7] Philips PW1100 diffractometer, ω–2θ scan mode using parameters given in ref. 7, scan width = 0.8°; data collected in range $6 < 2\theta < 50°$, empirical absorption correction based on 372 azimuthal scan data (max., min. transmission factors = 1.000, 0.608), giving 2 308 reflections with $I > 3\sigma(I)$. Three standard reflections showed no significant decay over the data collection period.

Structure analysis and refinement. Patterson techniques for Os followed by Fourier-difference techniques. Refinement by full-matrix least squares with Os assigned anisotropic thermal parameters and N, C, and O individual isotropic thermal parameters. The weighting scheme $w = 1/[\sigma^2(F_o)]$, with $\sigma(F_o)$ from counting statistics,[7] gave satisfactory agreement analyses. Final *R* and *R'* values were 0.045 and 0.047 respectively. Programs and computers used and sources of scattering factors are given in ref. 7. Final atomic co-ordinates are presented in Table 5.

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