Doubly- and Triply-bridging Ligands derived from 2-Pyridone and 2-Aminopyridine. Crystal and Molecular Structure of the 2-Pyridylamido Complex $[Os_3H(CO)_9\{\mu_3\text{-}NC_5H_4(NH)\}]$ * formed from 2-Aminopyridine and Dodecacarbonyltriosmium

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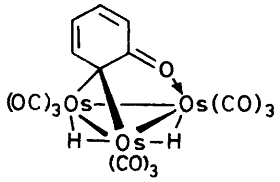
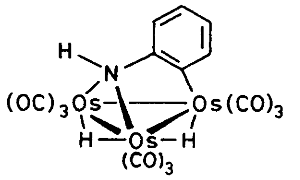
The bis(cyclo-octene) complex $[Os_3(CO)_{10}(C_8H_{14})_2]$ at room temperature or $[Os_3(CO)_{12}]$ at elevated temperatures reacts with 2-pyridone, 2-aminopyridine, and 2-(benzylamino)pyridine. The clusters $[Os_3H(CO)_{10}(\mu\text{-}NC_5H_4X)]$ (X = O, NH, or NCH_2Ph) were formed under the mildest conditions and adopt structures directly corresponding with that of the acetato-complex $[Os_3H(CO)_{10}(\mu\text{-}O_2CCH_3)]$. Unlike the μ-acetato-complex, however, these readily decarbonylate thermally to give $[Os_3H(CO)_9(\mu_3\text{-}NC_5H_4X)]$. The crystal and molecular structure of $[Os_3H(CO)_9\{\mu_3\text{-}NC_5H_4(NH)\}]$ has been determined by *X*-ray methods. The crystals are monoclinic, space group $P2_1/n$, $a = 8.497(2)$, $b = 15.019(2)$, $c = 15.649(7)$ Å, $\beta = 103.47(3)°$, and $Z = 4$. The structure was refined to $R = 0.0473$ for 2 735 observed reflections. The pyridine ring is co-ordinated at one osmium atom while the NH substituent bridges the other two equivalent osmium atoms. The hydride ligand lies on the molecular plane of symmetry and bridges these equivalent osmium atoms. Decarbonylation of the decacarbonyl complex $[Os_3H(CO)_{10}\{\mu\text{-}NC_5H_4(NCH_2Ph)\}]$ partly occurs in the same way but also gives the *ortho*-metallated complex $[Os_3H_2(CO)_9\{\mu\text{-}NC_5H_4(NCH_2C_6H_4)\}]$, isomeric with $[Os_3H(CO)_9\{\mu_3\text{-}NC_5H_4(NCH_2Ph)\}]$. Vigorous treatment of $[Os_3(CO)_{12}]$ with an excess of the 2-substituted pyridines gives the dinuclear species, $[Os_2(CO)_6(\mu\text{-}NC_5H_4X)_2]$ (X = O or NH), which exist as *cis* and *trans* isomers. Amphoteric behaviour is illustrated by the reversible addition of PMe_2Ph to the 2-aminopyridine derivative $[Os_3H(CO)_9(\mu_3\text{-}NC_5H_4X)]$ (X = NH) and by its single and double protonations at osmium.

PHENOL and aniline react with $[Os_3(CO)_{12}]$ to give double oxidative addition products with equivalent stoicheiometries, $[Os_3H_2(CO)_9(C_6H_4X)]$ (1; X = O) and (2; X = NH), but with different structures.[1-4] This was indicated by ^{13}C n.m.r. spectra and confirmed by *X*-ray structure determinations of the derivatives of 2-benzylphenol [2] and 4-fluoroaniline [4] which are the appropriately substituted versions of (1) and (2). While the carbon ring in (2) is aromatic, the phenol derivative (1) adopts the carbon-bridging dienone form of the ligand as shown. The structural difference could result from stronger Os–N than Os–O bonds favouring the nitrogen-bridging geometry, but also possibly from the keto-form being intrinsically more favourable than the imino-form as in the tautomeric equilibria (*a*) and (*b*). Although 2-hydroxypyridine exists predominantly as such in the gas phase,[5] the keto-tautomer pyridone exists exclusively in polar solvents (or the hydrogen-bonded dimer in non-polar solvents). 2-Aminopyridine has a lesser tendency to exist in the imine form. Since both 2-hydroxy- and 2-amino-pyridine have a much greater propensity than phenol or aniline to adopt keto or imine forms, we expected these molecules to form triosmium clusters related to (1) rather than (2). We now report clusters in which the replacement of the osmium-bonded carbon atom of (1) or (2) by a nitrogen atom leads to corresponding compounds which are, of course, mono- rather than di-hydrides to maintain even-electron molecules. A brief note on some of this work has appeared.[6] Unexpectedly the 2-substituted pyridine derivatives adopt structures related to (2) rather than (1), and we believe these are the first μ_3-ligands derived from these organic molecules.



(1)



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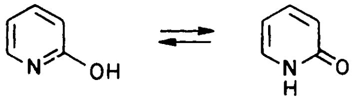
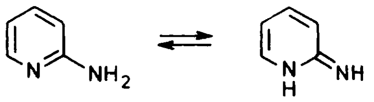


(*a*)



(*b*)

RESULTS AND DISCUSSION

Pyridone and 2-Aminopyridine Derivatives.—Synthetic details are given in the Experimental section. The organic molecules were reacted either directly with $[Os_3(CO)_{12}]$ at high temperatures or at roomtemperature (r.t.) with $[Os_3(CO)_{10}(C_8H_{14})_2]$ from which it is known that the cyclo-octene ligands are readily displaced.[7] The decacarbonyl complexes (3) † and (6a) readily decarbonylate in refluxing hydrocarbon solvents to give the corresponding nonacarbonyl complexes (4) and (7a) in

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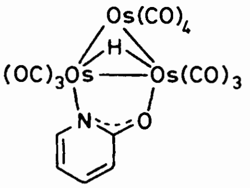
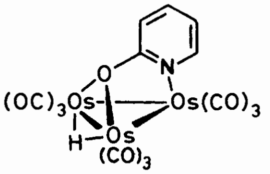
* Nonacarbonyl-μ-hydrido-(μ_3-2-pyridylamido)-*triangulo*-triosmium.

† Compound (3) has recently been reported by other workers (B. F. G. Johnson, J. Lewis, T. I. Odiaka, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **216**, C56).



(3)



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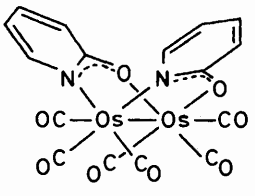
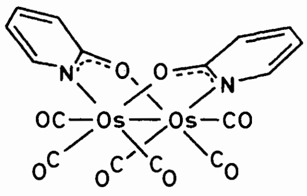


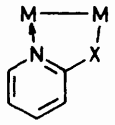
(5a)



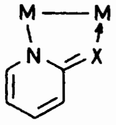
(5b)

good yield. Under the most vigorous conditions in the presence of an excess of ligand, breakdown of the clusters to the colourless dimeric complexes (5) and (9) is observed. The 2-(benzylamino)-substituted compound gave (6b) which decarbonylated to give the isomeric compounds (7b) and (8). Spectroscopic and analytical data are given in Tables 1 and 2.

The decacarbonyl complexes (3) and (6a) have the structures shown which relate closely to those of the corresponding carboxylato-complexes $[Os_3H(CO)_{10}(RCO_2)]$. Whereas the carboxylato-bridges are symmetrical, those in (3) and (6a) are not of course and (C) and (D) (X = O or NH) could be regarded as contributing forms.



(C)



(D)

In dinuclear complexes of type $[M_2\{NC_5H_3(Me\text{-}6)O\text{-}2\}_4]$ (M = Cr, Mo, or W) with related ligands from 2-hydroxy-6-methylpyridine there was judged to be approximately equal contributions of (C) and (D).[8] Without structural data we can make no comment for our compounds, except to say that there are quite significant ^1H n.m.r. chemical shift differences between the ring hydrogen signals of (3) and (6a) whereas for the nonacarbonyls (4) and (7a) the shifts for the corresponding protons are extremely similar. The signals for (3) are 0.21—0.39 p.p.m. lower than for (6a) which almost certainly indicates different contributions of (C) and (D) in the two cases.

TABLE 1

Analytical and selected infrared data

			Analysis [b]/%		
Compound		ν(CO) [a]/cm^{-1}	C	H	N
$[Os_3H(CO)_{10}(NC_5H_4O)]$	(3)	2 112m, 2 071s, 2 061s, 2 026s, 2 018s, 2 016 (sh), 2 002m, 1 991m, 1 984m, 1 981m	19.15 (19.05)	0.55 (0.55)	1.45 (1.50)
$[Os_3H(CO)_9(NC_5H_4O)]$	(4)	2 091m, 2 062s, 2 034s, 2 025w, 2 003s, 1 996m, 1 970m, 1 958m	19.60 (18.30)	0.95 (0.55)	1.35 (1.55)
$[Os_2(CO)_6(NC_5H_4O)_2]$	(5a)	2 092m, 2 056s, 2 004vs, 2 000 (sh), 1 975m, 1 971m	28.35 (26.10)	1.65 (1.10)	3.60 (3.80)
$[Os_2(CO)_6(NC_5H_4O)_2]$	(5b)	2 091m, 2 055m, 2 001vs, 1 980m, 1 969w	28.10 (26.10)	1.60 (1.10)	4.45 (3.80)
$[Os_3H(CO)_{10}\{NC_5H_4(NH)\}]$	(6a)	2 108m, 2 065s, 2 058s, 2 022s, 2 014s, 2 005m, 1 996m, 1 988m, 1 985m, 1 975m	19.55 (19.05)	0.80 (0.65)	2.60 (2.95)
$[Os_3H(CO)_{10}\{NC_5H_4(NCH_2Ph)\}]$	(6b)	2 107m, 2 064s, 2 057s, 2 022s, 2 012s, 2 004m, 1 995m, 1 986m, 1 975w	25.50 (25.55)	1.25 (1.15)	2.85 (2.70)
$[Os_3H(CO)_9\{NC_5H_4(NH)\}]$	(7a)	2 085m, 2 056s, 2 029s, 2 001s, 1 992w, 1 983m, 1 967m, 1 953m	18.60 (18.35)	0.85 (0.65)	3.05 (3.05)
$[Os_3H(CO)_9\{NC_5H_4(NCH_2Ph)\}]$	(7b)	2 085m, 2 056s, 2 029s, 2 000s, 1 990w, 1 984m, 1 977m, 1 965m, 1 953m	25.05 (25.05)	1.30 (1.20)	2.80 (2.80)
$[Os_3H_2(CO)_9\{NC_5H_4(NCH_2C_6H_4)\}]$	(8)	2 091m, 2 058s, 2 028s, 2 009s, 2 005 (sh), 1 988m, 1 984m, 1 964s, 1 933w	24.85 (25.05)	1.50 (1.20)	2.75 (2.80)
$[Os_2(CO)_6\{NC_5H_4(NH)\}_2]$	(9a)	2 082m, 2 043s, 1 998vs, 1 981m, 1 965s, 1 937w	27.10 (26.15)	2.00 (1.35)	6.90 (7.65)
$[Os_2(CO)_6\{NC_5H_4(NH)\}_2]$	(9b)	2 083m, 2 045s, 1 998vs, 1 981m, 1 966s, 1 939w	27.05 (26.10)	1.85 (1.50)	6.95 (7.60)
$[Os_3H(CO)_9(PMe_2Ph)\{NC_5H_4(NH)\}]$ [c]	(10)	2 092m, 2 049s, 2 012vs, 2 007 (sh), 1 994m, 1 975m, 1 966m, 1 941w	25.10 (25.05)	1.80 (1.60)	2.60 (2.65)
$[Os_3H(CO)_8(PMe_2Ph)\{NC_5H_4(NH)\}]$	(11)	2 065s, 2 027vs, 1 993s, 1 987s, 1 965m, 1 956s, 1 943m, 1 935m	24.80 (24.55)	1.95 (1.65)	2.75 (2.75)
$[Os_3H_2(CO)_9\{NC_5H_4(NH)\}][PF_6]$	(12)	2 138m, 2 105s, 2 079vs, 2 059 (sh), 2 028m, 2 013 (sh)	15.95 (15.80)	0.65 (0.65)	2.60 (2.65)

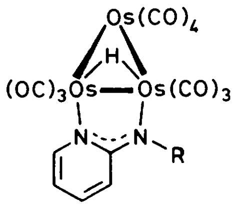
[a] Recorded in cyclohexane, except (12) which was in CH_2Cl_2. [b] Calculated figures in parentheses; certain compounds are high in carbon because of contamination with hydrocarbon. [c] P = 2.95 (2.95)%.

TABLE 2

Hydrogen-1 n.m.r. data [a]

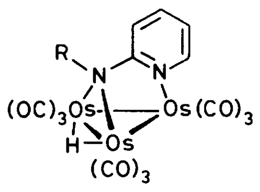
Compound	δ/p.p.m. Heterocyclic ligand 3-H [b]	4-H [c]	5-H [c]	6-H [b]	Others	Hydride
(3)	6.43	7.11	6.23	8.08		−10.73s
(4)	6.37	7.51	6.71	8.51		−9.73s
(5a)	6.30	7.31	6.56	8.16		
(5b)	6.51	7.31	6.38	8.31		
(6a)	6.12	6.72	5.85	7.87	3.85 N*H*	−12.24s
(6b)	6.24	6.89	5.95	8.18	5.02d, 4.54d C*H*$_2$ 7.0—7.4 Ph	−11.72s
(7a)	6.50	7.47	6.66	8.55	4.54 N*H*	−12.71s
(7b)	6.23	7.34	6.64	8.66	5.40d, 4.42d C*H*$_2$ 6.8—7.3 Ph	−11.22s
(8)	*d*	*d*	*d*	8.92	4.82d, 4.40d C*H*$_2$	−11.08s −12.31s
(9a)	6.07	6.84	5.81	7.99	4.98 N*H*	
(9b)	6.09	6.87	5.79	7.89	4.82 N*H*	
(10)	5.67	6.59	5.71	7.85	7.3—7.6 Ph 3.41s N*H* 2.15d PMe 2.24d PMe	−12.47d (*J* = 12 Hz)
(11)	5.05	*e*	6.43	8.46	7.0—7.4 Ph 2.21d PMe 2.36d PMe	−14.70d (*J* = 11 Hz)
(12)	7.09	7.74	6.94	8.36		−13.12d −14.70d
(13)	7.37	8.02	7.58	8.43		−14.8s (2 H) −16.0s (1 H)

[a] Recorded at 100 MHz at 27 °C in $CDCl_3$. [b] Double doublets; one *ortho* and one *meta* coupling of appropriate value. [c] Approximate double triplets; two *ortho* and one *meta* coupling of appropriate value. [d] Assignments not made for signals in the ' aromatic ' region. [e] Overlapping with the phenyl resonances.



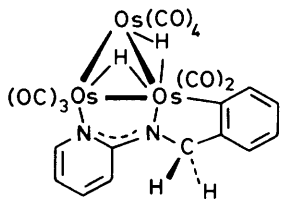
(6a) R = H

(6b) R = $PhCH_2$



(7a) R = H

(7b) R = $PhCH_2$



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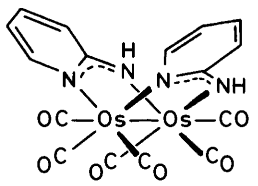
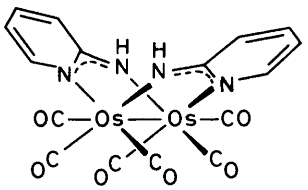


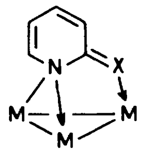
(9a)



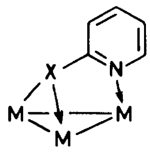
(9b)

The ^1H n.m.r. spectra of complexes (1) and (2) are very different reflecting their non-aromatic and aromatic structures respectively, whereas, in contrast, the 3-H—6-H signals of (4) and (7a) are within 0.13, 0.04, 0.05, and 0.04 p.p.m. of each other respectively. Thus there is no doubt that (4) and (7a) are isostructural, unlike (1) and (2). Unfortunately we could not be sure on spectroscopic grounds alone whether a structure analogous to (1) or (2) is adopted by these compounds, *i.e.* whether the structure is of type (E) or (F) (X = O or NH). The great accessibility of the dienone form of free pyridone [equation (*a*)] compared with the accessibility of the cyclohexadienone form of phenol leads us to expect that if compound (1) adopts the non-aromatic structure shown then compound (4) is even more likely to take up the non-aromatic form. Before obtaining a single-crystal *X*-ray structure of (7a) we strongly favoured a structure of type (E), but a structure of type (F) was found.

The molecule has an approximate mirror plane through



(E)



(F)

the pyridine ring and the atoms N(2) and Os(3) and there is a close correspondence of the bond lengths and angles related by this approximate mirror plane. The organic ligand is bound through the pyridine nitrogen atom N(1) to Os(3) and the exocyclic nitrogen atom N(2) bridges Os(1) and Os(2). The pyridine ring appears aromatic so that the exocyclic nitrogen atom is part of a bridging amido-group. Overall the ligand is a five-electron donor closely related to the four-electron-donating bridge in compound (2). Bond lengths in the organic ring range from 1.317 to 1.393 Å and not as expected for the bond description (E). The C(5)–N(2) bond length is 1.392 Å, rather shorter than the corresponding bond in $[Os_3H_2(CO)_9(NHC_6H_3F)]$ (1.459 Å),[4] but although this bond might have some multiple bond character the corresponding bond C(5)–N(1) is even shorter (1.317 Å).

The metal hydride ligand was not located in the *X*-ray study but from the positions of the carbonyl ligands one can deduce that it is bridging Os(1) and Os(2). The CO groups are opened out away from the Os(1)–Os(2) bond as expected if there is a hydride bridge. The OC–Os–Os angles for this metal pair are 111.7, 111.2° (equatorial) and 116.3, 116.6° (axial). Since both axial and equatorial groups experience this widening effect, the hydride ligand probably lies between these four CO groups, presumably close to the intersection of the C(23)–Os(2) and C(32)–Os(1) directions so that all three metal atoms are close to octahedral co-ordination [if the Os(1)–Os(2) contact is ignored]. Furthermore, the Os(1)–Os(3) (2.773 Å) and Os(2)–Os(3) (2.785 Å) bonds have similar lengths and are too short to be bridged by a hydride.

Before the *X*-ray crystal structure of (7a) was known we prepared the 2-(benzylamino)-derivatives (6b) and (7b) to examine whether the organic rings coincided with the planes of symmetry since, in the absence of such a plane of symmetry, the CH_2 atoms would be diastereotopic. Compound (6b) was readily formed on reacting $[Os_3(CO)_{10}(C_8H_{14})_2]$ with 2-(benzylamino)pyridine. A ^1H n.m.r. AB quartet was obtained for the CH_2 groups of (6b) since the molecule is chiral having the amidopyridine ligand lying below the triosmium plane. Also there is no rapid enantiomerisation leading to coalescence, *i.e.* the nitrogen atoms do not rapidly interchange positions. Whereas the decarbonylation of (6a) gave (7a) exclusively, the decarbonylation of (6b) in refluxing heptane gave two isomeric products, compound (7b) [analogous to (7a)] and compound (8). At higher temperatures, or on refluxing for longer in heptane, only compound (8) was obtained and in a separate experiment (7b) was shown to isomerise to (8) under these conditions. It seems likely that (7b) is the primary product. Compound (7b) has a similar ^1H n.m.r. spectrum to that of (7a) and a very similar spectrum around 2 000 cm^{-1} so that they must be isostructural in solution. Curiously the CH_2 group of (7b) gives a well defined AB quartet at −36 °C; there is no plane of symmetry through the organic ring as for (7a) in the crystal. If the μ_3-ligand is still attached to the triosmium cluster as in the crystals of (7a), the hydride ligand must bridge one of the side Os–Os bonds. The AB quartet broadens on raising the temperature, coalesces at around 25 °C, and gives a sharp singlet at >40 °C. The simplest process to give this effect is a rapid hydride migration across the cluster between the two corresponding edges of the triosmium triangle. Such migrations are known for many clusters, for example $[Os_3H_2(CO)_9(C{=}CH_2)]$.[9] Both (7a) and (7b) must be asymmetric in solution rather than as illustrated, as their i.r. and ^1H n.m.r. spectra correspond so well.

Compound (8) is isomeric with (7b) but is a dihydride, the second hydride ligand being derived by *ortho*-metallation of the benzyl group. Consistent with this, the ^1H n.m.r. aromatic region shows a complex set of signals which we have not analysed and the CH_2 group gives an AB quartet which is sharp over a range of temperatures. Metallation of benzyl alcohols,[10] 1-naphthol[1] with $[Os_3(CO)_{12}]$, or reaction of PhCH=NMe with $[Os_3H_2(CO)_{10}]$[11] (with *ortho*-metallation of the phenyl group) gives complexes of type $[Os_3H_2(CO)_9X]$ where there is a 4 : 3 : 2 distribution of the terminal carbonyl ligands at the three metal atoms and the ligand X chelates at one osmium atom while bridging this and another osmium atom. In the case of $[Os_3H_2(CO)_9(MeNCH_2C_6H_4)]$ formed from PhCH=NMe, the *X*-ray structure has been established.[11] We believe compound (8) is of the same type and has the structure shown.

The dinuclear complexes (5) and (9) of general formula $[Os_2(CO)_6(NC_5H_4X)_2]$ (X = O or NH) are formed under extreme conditions and relate to the dimer $[Os_2(CO)_6(O_2CCH_3)_2]$ formed from acetic acid and $[Os_3(CO)_{12}]$.[12] In the case of (5) and (9), careful thin layer chromatography (t.l.c.) on silica has given two isomers for each. The isomers give very similar ν(CO) and ^1H n.m.r. spectra and behave very similarly on chromatography indicating that structural differences are small. We propose that these are the *cis* and *trans* isomeric pairs (5a), (5b), (9a), and (9b), as shown. There is no indication that they interconvert at low temperatures, which is at least consistent with the non-dynamic nature of complex (6b). In many ways these isomers relate to the isomers we have already reported for the 2-pyridyl complexes $[Os_2(CO)_6(\mu\text{-}C_5H_4N)_2]$;[13] *X*-ray structure determinations for the 4-methylpyridine derivatives have confirmed the *cis–trans* nature of the isomerism.[14]

The only trinuclear complex observed in the reaction of acetic acid with $[Os_3(CO)_{12}]$ to give $[Os_2(CO)_6(O_2CCH_3)_2]$ is $[Os_3H(CO)_{10}(O_2CCH_3)]$, the analogue of clusters (3) and (6). We have tried unsuccessfully to obtain evidence for μ_3-acetato clusters related to (4) and (7), and it seems that 2-aminopyridinato and 2-pyridonato ligands show a greater tendency than acetate to form triple rather than double bridges and have a consequential lower tendency to cause cluster breakdown into dinuclear species.

Some reactions of $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (7a).—Since this is one of the easier compounds described in this paper to synthesise, we have been able to examine some of its reactions. Complex (7a) rapidly forms the adduct $[Os_3H(CO)_9(PMe_2Ph)\{NC_5H_4(NH)\}]$, compound (10,) with PMe_2Ph in refluxing cyclohexane. The shape of a cluster, that is the extent of metal–metal bonding, may be modified by direct addition of a donor ligand. Alternatively, as in this case, the way a ligand is bound to the cluster may change. Compound (10) may be regarded as a PMe_2Ph substitution derivative of (6a), so that there is a μ_3 to μ conversion on PMe_2Ph addition. The μ-2-aminopyridinato-ligand readily reverts to μ_3-co-ordination, since the PMe_2Ph addition is readily and totally reversed in refluxing octane. It is rather unusual for there to be such a marked preference for loss of tertiary phosphine rather than of CO in such a case. However, on vigorously passing nitrogen through a refluxing octane solution of (10), competitive loss of CO and PMe_2Ph occurs to give a mixture of compounds (7a) and (11) (see Scheme).

$$[Os_3H(CO)_9\{\mu_3\text{-}NC_5H_4(NH)\}] + PMe_2Ph$$

(7a)

$$\upharpoonleft\!\downharpoonright$$

$$[Os_3H(CO)_9(PMe_2Ph)\{\mu\text{-}NC_5H_4(NH)\}]$$

(10)

$$\upharpoonleft\!\downharpoonright$$

$$[Os_3H(CO)_8(PMe_2Ph)\{\mu_3\text{-}NC_5H_4(NH)\}] + CO$$

(11)

SCHEME

An increase in the proportion of (11) on thermolysis with N_2 passing through the solution implies the equilibrium involving free CO shown in the Scheme.

The co-ordination positions of PMe_2Ph in (10) and (11) are unknown except that PMe_2Ph and the hydride in each are bound to the same osmium atom.

Compound (7a) can be mono-protonated in neat trifluoroacetic acid or doubly protonated in concentrated sulphuric acid. The complex $[Os_3H_2(CO)_9\{NC_5H_4(NH)\}][PF_6]$ (12) was isolated and shown to contain non-equivalent hydride ligands. All Os–Os bonds carry hydride ligands in the dication $[Os_3H_3(CO)_9\{NC_5H_4(NH)\}]^{2+}$ (13), since there are two ^1H n.m.r. hydride singlets with intensities 1 : 2.

EXPERIMENTAL

Action of Pyridone on $[Os_3(CO)_{12}]$.—(*a*). The metal carbonyl (0.55 g), pyridone (0.19 g), and toluene (12 cm^3) were sealed in a degassed glass tube under vacuum and heated at 145 °C for 80 h. After cooling, the contents were extracted with dichloromethane and chromatographed on SiO_2 eluting with a pentane–toluene mixture (1 : 1 v/v) to give $[Os_3H(CO)_{10}(NC_5H_4O)]$ (3) (0.058 g, 10%) as a yellow solid, which gave crystals from hexane at 0 °C.

(*b*). A solution of the parent carbonyl (0.41 g) and pyridone (0.20 g) in nonane (15 cm^3) was heated in a degassed tube, sealed under vacuum, at 210 °C for 3 h. The tube was opened, the solvent removed, and the residue chromatographed on SiO_2 (t.l.c.) eluting with toluene. Two colourless bands gave the two isomers of $[Os_2(CO)_6(NC_5H_4O)_2]$ as white microcrystals [(5a) faster band (0.29 g, 55%); (5b) slower band (0.14 g, 27%)].

Thermolysis of Compound (3).—A solution of $[Os_3H(CO)_{10}(NC_5H_4O)]$ (0.045 g) in toluene (25 cm^3) was heated under reflux under nitrogen for 4 h. Chromatographic work-up (t.l.c., SiO_2) gave $[Os_3H(CO)_9(NC_5H_4O)]$ (4), as a yellow solid (0.034 g, 78%).

Action of 2-Aminopyridine on $[Os_3(CO)_{10}(C_8H_{14})_2]$.—A solution of the bis(cyclo-octene) complex (0.52 g) in cyclo-octene (10 cm^3) and freshly sublimed 2-aminopyridine (0.20 g) was stirred for 88 h at r.t. T.l.c. work-up (SiO_2) gave $[Os_3H(CO)_{10}\{NC_5H_4(NH)\}]$ (6a), as yellow crystals (0.30 g, 65%).

Action of 2-(Benzylamino)pyridine on $[Os_3(CO)_{10}(C_8H_{14})_2]$.—A solution of the bis(cyclo-octene) complex (0.39 g) in cyclo-octene (25 cm^3) was mixed with a solution of the pyridine (0.46 g) in dichloromethane (10 cm^3) and stirred for 20 h at r.t. The solvent was removed under vacuum keeping the temperature below 50 °C and the yellow solid residue chromatographed (t.l.c.) to give $[Os_3H(CO)_{10}\{NC_5H_4(NCH_2Ph)\}]$ (6b), as yellow crystals from hexane (0.124 g, 33%).

Action of 2-Aminopyridine on $[Os_3(CO)_{12}]$.—A solution of $[Os_3(CO)_{12}]$ (0.46 g) and freshly sublimed 2-aminopyridine (0.19 g) in octane was heated in a sealed evacuated glass tube at 183 °C for 69 h. Chromatographic work-up eluting with a pentane–diethyl ether mixture (1 : 1 v/v) gave two colourless isomers of $[Os_2(CO)_6\{NC_5H_4(NH)\}_2]$ as white microcrystals [(9a) faster band (0.016 g, 4%); (9b) slower band (0.033 g, 8%)].

Thermolysis of Compound (6a).—A solution of the decacarbonyl compound (6a) (0.065 g) in cyclohexane (25 cm^3) was refluxed for 8 h under nitrogen. Chromatography (t.l.c.) gave $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (7a), as yellow crystals (0.054 g, 86%).

Thermolysis of Compound (6b).—A solution of the decacarbonyl complex (6b) (0.060 g) in heptane (25 cm^3) was refluxed under nitrogen for 45 min. Chromatography (t.l.c.) gave two main bonds giving the isomers $[Os_3H(CO)_9\{NC_5H_4(NCH_2Ph)\}]$ (7b), as yellow crystals (0.021 g, 36%) and $[Os_3H_2(CO)_9\{NC_5H_4(NCH_2C_6H_4)\}]$ (8), as colourless crystals (0.022 g, 38%), both products crystallizing from hexane.

A yellow solution of (7b) (0.008 g) in heptane (25 cm^3) on refluxing for 100 min became colourless and was shown from its i.r. spectrum to contain only complex (8).

Addition of PMe_2Ph *to* $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (7a).—Dimethylphenylphosphine (0.22 g) was added to a refluxing solution of (7a) (0.29 g) in cyclohexane and refluxing was continued for 2 min. The yellow solution became orange and chromatographic work-up gave $[Os_3H(CO)_9(PMe_2Ph)\{NC_5H_4(NH)\}]$ (10) (0.26 g, 84%) which was crystallized from pentane at −20 °C.

Thermolysis of $[Os_3H(CO)_9(PMe_2Ph)\{NC_5H_4(NH)\}]$ (10).—A stream of nitrogen was passed through a refluxing octane solution (20 cm^3) of compound (10) (0.040 g) for 2 h. Chromatographic work-up gave $[Os_3H(CO)_8(PMe_2Ph)\{NC_5H_4(NH)\}]$ (11) as yellow crystals (0.019 g, 49%), and a similar amount of $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (7a).

Protonation Reactions.—(*a*). Compound (7a) $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (0.094 g) slowly dissolved over 1 h in trifluoroacetic acid (0.5 cm^3) to give a pale yellow solution. ^1H N.m.r. spectra indicated the formation of a cationic dihydride which was isolated as $[Os_3H_2(CO)_9\{NC_5H_4(NH)\}][PF_6]$ by adding excess of a saturated aqueous solution of KPF_6 to the trifluoroacetic acid solution to give a white solid, compound (12).

(*b*). Compound (7a) (0.063 g) was dissolved in concentrated sulphuric acid (0.5 cm^3) over 30 min to give a pale brown solution. ^1H N.m.r. spectra indicated the formation of $[Os_3H_3(CO)_9\{NC_5H_4(NH)\}]^{2+}$.

X-Ray Crystal Structure Determination for $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (7a).—*Crystal data.* $C_{14}H_6N_2O_9Os$, M = 916.807, Monoclinic, a = 8.497(2), b = 15.019(2), c = 15.649(7) Å, β = 103.47(3)°, U = 1 942.05 Å^3, space group $P2_1/n$, Z = 4, D_c = 3.13 g cm^{-3}, $F(000)$ = 1 615.74, $\mu(\text{Mo-}K_\alpha)$ = 188.60 cm^{-1}.

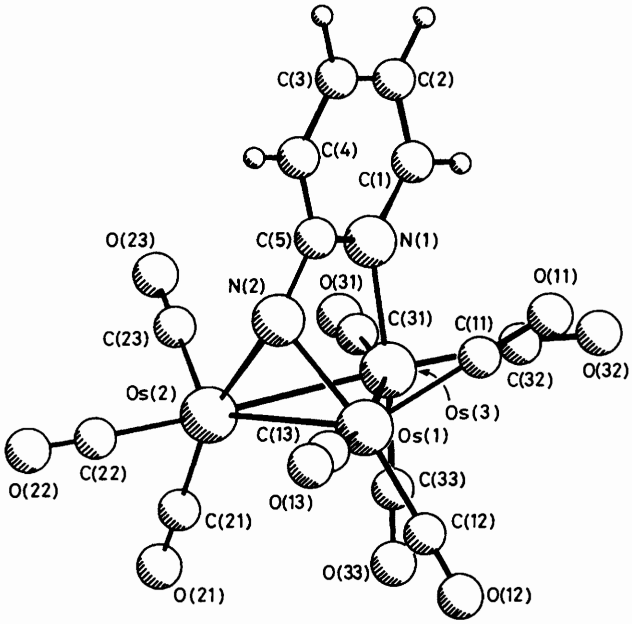


FIGURE The *X*-ray molecular structure of $[Os_3H(CO)_9\{NC_5H_4(NH)\}]$ (7a)

TABLE 3

Atomic co-ordinates (× 10^4) for (7a) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Os(1)	3 186(1)	1 414	631
Os(2)	1 787(1)	2 047	1 963
Os(3)	1 314(1)	2 945	366
N(1)	3 581(13)	3 568(8)	1 005(7)
N(2)	4 229(13)	2 243(8)	1 751(7)
C(1)	3 964(17)	4 422(10)	815(10)
C(2)	5 379(19)	4 826(12)	1 285(10)
C(3)	6 440(18)	4 341(11)	1 910(10)
C(4)	6 072(16)	3 485(11)	2 067(10)
C(5)	4 623(15)	3 122(10)	1 608(9)
C(11)	4 253(19)	1 936(11)	−193(11)
C(12)	1 814(19)	726(11)	−272(11)
C(13)	4 670(17)	453(11)	1 048(10)
C(21)	−427(19)	1 781(12)	1 853(10)
C(22)	2 488(18)	1 372(12)	3 036(10)
C(23)	1 602(18)	3 192(12)	2 452(9)
C(31)	20(18)	3 921(11)	611(9)
C(32)	1 516(15)	3 301(11)	−780(9)
C(33)	−495(18)	2 242(12)	−81(9)
O(11)	4 832(17)	2 260(10)	−699(11)
O(12)	993(15)	322(9)	−801(8)
O(13)	5 562(16)	−112(9)	1 258(8)
O(21)	−1 796(14)	1 644(11)	1 792(10)
O(22)	2 871(18)	999(11)	3 675(9)
O(23)	1 492(22)	3 868(9)	2 730(9)
O(31)	−784(14)	4 477(8)	745(7)
O(32)	1 545(14)	3 475(9)	−1 477(7)
O(33)	−1 597(14)	1 782(10)	−343(9)
H(1)	3 159(17)	4 784(10)	296(10)
H(2)	5 640(19)	5 510(12)	1 159(10)
H(3)	7 553(18)	4 638(11)	2 274(10)
H(4)	6 903(16)	3 092(11)	2 548(10)

TABLE 4

Bond lengths (Å) in (7a) with estimated standard deviations in parentheses

Os(2)–Os(1)	2.796(4)	C(5)–N(1)	1.317(18)
Os(3)–Os(1)	2.773(4)	C(5)–N(2)	1.392(19)
N(2)–Os(1)	2.164(13)	C(2)–C(1)	1.393(21)
C(11)–Os(1)	1.909(19)	C(3)–C(2)	1.375(24)
C(12)–Os(1)	1.911(19)	C(4)–C(3)	1.359(23)
C(13)–Os(1)	1.927(17)	C(5)–C(4)	1.385(20)
Os(3)–Os(2)	2.785(4)	O(11)–C(11)	1.135(21)
N(2)–Os(2)	2.196(13)	O(12)–C(12)	1.128(20)
C(21)–Os(2)	1.891(18)	O(13)–C(13)	1.135(19)
C(22)–Os(2)	1.933(17)	O(21)–C(21)	1.163(19)
C(23)–Os(2)	1.904(20)	O(22)–C(22)	1.126(19)
N(1)–Os(3)	2.164(13)	O(23)–C(23)	1.116(20)
C(31)–Os(3)	1.924(18)	O(31)–C(31)	1.129(19)
C(32)–Os(3)	1.917(16)	O(32)–C(32)	1.128(17)
C(33)–Os(3)	1.862(18)	O(33)–C(33)	1.158(20)
C(1)–N(1)	1.372(10)		

TABLE 5

Bond angles (°) in (7a) with estimated standard deviations in parentheses

Os(3)–Os(1)–Os(2)	60.0	C(33)–Os(3)–Os(1)	88.9(6)
N(2)–Os(1)–Os(2)	50.6(4)	N(1)–Os(3)–Os(2)	82.4(4)
C(11)–Os(1)–Os(2)	135.6(4)	C(31)–Os(3)–Os(2)	99.2(5)
C(12)–Os(1)–Os(2)	116.3(6)	C(32)–Os(3)–Os(2)	161.6(4)
C(13)–Os(1)–Os(2)	111.2(5)	C(33)–Os(3)–Os(2)	89.8(6)
N(2)–Os(1)–Os(3)	75.9(4)	C(31)–Os(3)–N(1)	93.9(6)
C(11)–Os(1)–Os(3)	84.5(5)	C(32)–Os(3)–N(1)	92.8(6)
C(12)–Os(1)–Os(3)	96.2(6)	C(13)–Os(1)–Os(3)	168.3(5)
C(33)–Os(3)–N(1)	170.5(6)	C(32)–Os(3)–C(31)	98.9(7)
C(11)–Os(1)–N(2)	98.1(7)	C(33)–Os(3)–C(31)	92.7(7)
C(12)–Os(1)–N(2)	166.8(5)	C(33)–Os(3)–C(32)	93.0(7)
C(13)–Os(1)–N(2)	92.6(6)	C(1)–N(1)–Os(3)	122.3(10)
C(12)–Os(1)–C(11)	91.5(8)	C(5)–N(1)–Os(3)	119.3(10)
C(13)–Os(1)–C(11)	99.2(7)	C(5)–N(1)–C(1)	118.5(13)
C(13)–Os(1)–C(12)	94.8(8)	Os(2)–N(2)–Os(1)	79.8(5)
Os(3)–Os(2)–Os(1)	59.6	C(5)–N(2)–Os(1)	118.9(10)
N(2)–Os(2)–Os(1)	49.6(3)	C(5)–N(2)–Os(2)	114.9(9)
C(21)–Os(2)–Os(1)	116.6(6)	C(2)–C(1)–N(1)	120.8(15)
C(22)–Os(2)–Os(1)	111.7(6)	C(3)–C(2)–C(1)	119.2(16)
C(23)–Os(2)–Os(1)	134.2(4)	C(4)–C(3)–C(2)	119.3(15)
N(2)–Os(2)–Os(3)	75.1(4)	C(5)–C(4)–C(3)	119.5(15)
C(21)–Os(2)–Os(3)	95.1(6)	N(2)–C(5)–N(1)	116.8(12)
C(22)–Os(2)–Os(3)	169.8(5)	C(4)–C(5)–N(1)	122.7(15)
C(23)–Os(2)–Os(3)	85.1(5)	C(4)–C(5)–N(2)	120.5(14)
C(21)–Os(2)–N(2)	165.8(5)	O(11)–C(11)–Os(1)	177.3(15)
C(22)–Os(2)–N(2)	95.2(6)	O(12)–C(12)–Os(1)	179.3(14)
C(23)–Os(2)–N(2)	96.3(6)	O(13)–C(13)–Os(1)	176.9(13)
C(22)–Os(2)–C(21)	93.9(8)	O(21)–C(21)–Os(2)	177.9(16)
C(23)–Os(2)–C(21)	93.1(8)	O(22)–C(22)–Os(2)	177.6(18)
C(23)–Os(2)–C(22)	99.3(8)	O(23)–C(23)–Os(2)	179.3(14)
Os(2)–Os(3)–Os(1)	60.4	O(31)–C(31)–Os(3)	177.7(13)
N(1)–Os(3)–Os(1)	82.6(4)	O(32)–C(32)–Os(3)	175.3(13)
C(31)–Os(3)–Os(1)	159.6(4)	O(33)–C(33)–Os(3)	177.9(15)
C(32)–Os(3)–Os(1)	101.4(6)		

Data collection. CAD4 Diffractometer, ω—2θ scan, ω scan width = 0.18 + 1.5 tanθ, Mo-K_α radiation (λ = 0.710 69 Å), 1.50 ⩽ θ ⩽ 25.0°, ±h, k, l, $T_{max.}$ = 60 s, crystal size and morphology 0.095 {010}, 0.575 {011}, 0.1875 mm {10$\bar{1}$}. Total data measured = 3 764, unique = 3 377, observed = 2 735 [$I < 3\sigma(I)$], absorption correction applied.

Structure solution and refinement. Heavy-atom method, all non-hydrogen atoms anisotropic, H atoms on rings fixed in idealised positions, weighting scheme $w = 1/\{\sigma(F) + 0.0012_9(F_o)^2\}$, R = 0.0473, R' = 0.0432. Computers, programs, and scattering factors are as in ref. 15.

The molecular structure of compound (7a) is shown in the Figure and the atomic co-ordinates given in Table 3. Bond lengths and angles are given in Tables 4 and 5 respectively.

Tables of observed and calculated structure factors and anisotropic thermal parameters are available as Supplementary Publication No. SUP 23273 (15 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

We thank the S.R.C. for support, Johnson Matthey Ltd. for a loan of OsO_4, and University College London for a research studentship (to R. P.).

[1/1772 *Received*, 16*th November*, 1981]

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