2-Pyridyl Complexes derived Directly from Pyridine and Dodecacarbonyl-*triangulo*-triosmium

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Pyridine reacts with $Os_3(CO)_{12}$ to give a series of bridging 2-pyridyl complexes: $[HOs_3(NC_5H_4)(CO)_{10}]$; $[HOs_3(NC_5H_4)(CO)_9(py)]$, isomers (A) and (B); $[H_2Os_3(NC_5H_4)_2(CO)_8]$; and $[Os_2(NC_5H_4)_2(CO)_6]$, isomers (A) and (B). Several of the corresponding derivatives of 4-methyl- and 4-benzyl-pyridine are also described. Evidence is given for successive and reversible reactions in which loss of CO from the cluster is accompanied either by co-ordination of an extra py or by hydrogen transfer from co-ordinated py to the metal. Quinoline and isoquinoline with $Os_3(CO)_{12}$ give the isomers $[HOs_3(NC_9H_6)(CO)_{10}]$ in which quin has been metallated exclusively at the 2-position whereas iquin gives isomers metallated at the 1- and 3-positions respectively.

FIVE-MEMBERED ring formation is a dominating effect in the metallation of ligands in systems with single metal atoms, so that carbon–hydrogen bond fission normally occurs at a γ-carbon atom to the donor heteroatom.[1] In metal clusters on the other hand a ligand co-ordinated to one metal atom may be metallated by an adjacent metal atom, so that β-carbon–hydrogen cleavage produces a five-membered ring as in the formation of $[H_2Os_3(H_4C_6NH\text{-}o)(CO)_9]$ from aniline.[2] Surprisingly $[Os_3(CO)_{11}(PEt_3)]$ undergoes C–H fission at the α-carbon atom to give $[H_2Os_3(PEt_2CMe)(CO)_9]$ which contains four-membered rings,[3] even though five-membered rings could have been formed. This prompted us to examine the chemistry of pyridine (py) with $Os_3(CO)_{12}$ since its conversion into 2-pyridyl by direct reaction was previously unknown in spite of its extensive use as a ligand. We describe here reactions of py, 4-substituted pyridines, NC_5H_4X (X = Me or benzyl), quinoline (quin), and isoquinoline (iquin) with $Os_3(CO)_{12}$ confirming that metallation at the α position is the preferred mode of reaction in all these cases.

RESULTS AND DISCUSSION

Reactions between $Os_3(CO)_{12}$ *and Pyridine.*—We obtained six crystalline complexes by direct reaction of $Os_3(CO)_{12}$ with py either neat or in saturated hydrocarbon solvents, refluxing under nitrogen or in sealed evacuated glass tubes: $[HOs_3(NC_5H_4)(CO)_{10}]$; $[HOs_3(NC_5H_4)(CO)_9(py)]$, isomers (A) and (B); $[H_2Os_3(NC_5H_4)_2(CO)_8]$; and $[Os_2(NC_5H_4)_2(CO)_6]$, isomers (A) and (B). The separation and isolation of these species was by t.l.c. on silica eluting with chloroform–pentane and the yields quoted in Table 1 are after isolation and must be regarded as minimum values. Yields for various reaction conditions support their formation in the above order, with significant cluster breakdown to dimers only occurring after more extended reaction times. Some brown intractable material was always formed in these reactions but much less was formed in sealed evacuated tubes than in open vessels under nitrogen.

Studies to establish Reaction Paths.—The decacarbonyl $[HOs_3(NC_5H_4)(CO)_{10}]$ is the first complex seen to be formed in these reactions, presumably *via* the intermediacy of $[Os_3(CO)_{11}(py)]$ which was never observed to be formed. When CO was bubbled through a refluxing solution of $Os_3(CO)_{12}$ and py in octane no reaction occurred after 3.5 h, whereas when N_2 was used the reaction proceeded and $Os_3(CO)_{12}$ was almost completely converted into the deca- and octa-carbonyl complexes after 2.5 h. The inhibition by CO does not arise because $[HOs_3(NC_5H_4)(CO)_{10}]$ is formed reversibly since this complex is unreactive towards CO(1 atm) even in refluxing decalin (194 °C) for 3.5 h.† Either formation of $Os_3(CO)_{11}$ by a pre-equilibrium involving CO dissociation is suppressed or py is readily displaced from $[Os_3(CO)_{11}(py)]$ by CO. Once the hydrogen atom has been transferred to the metal the reaction is irreversible under conditions we have tried. The sequence is then repeated with CO substitution to give $[HOs_3(NC_5H_4)(CO)_9(py)]$ followed by

TABLE 1

Percentage yields of products from the reaction of $Os_3(CO)_{12}$ with pyridine in sealed glass tubes at 184 ± 4 °C

	Reaction time, *t*/h		
	1	4	6
$[HOs_3(NC_5H_4)(CO)_{10}]$	34	11	4
$[H_2Os_3(NC_5H_4)_2(CO)_8]$	17	12	4
$[Os_2(NC_5H_4)_2(CO)_6]$, Isomer (A)	8	22	31
Isomer (B)	11	11	16

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† 1 atm = 101 325 Pa.

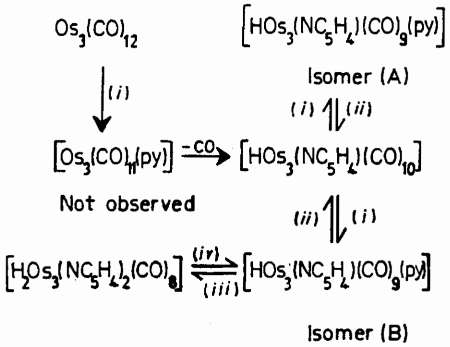
[1] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[2] C. Choo Yin and A. J. Deeming, *J.C.S. Dalton*, 1974, 1013.

[3] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1973, 2727.

hydrogen transfer to give $[H_2Os_3(NC_5H_4)_2(CO)_8]$. The nonacarbonyl complexes were not easy to prepare and isolate in good yield. The best method was to treat a solution containing mainly $[HOs_3(NC_5H_4)(CO)_{10}]$ prepared *in situ* (see Experimental section) with py. The isomer obtained depended on the conditions. Reaction in refluxing n-heptane (97 °C) showed rapid formation of isomer (A) and then over 82 h of refluxing there was a gradual build-up of the octacarbonyl in solution. When, however, the reaction was carried out in refluxing n-octane (125 °C) very little isomer (A) was observed while (B) was formed instead. Again, after more extended reaction times the octacarbonyl was formed. Isomers (A) and (B) were isolated from these respective solutions and each was shown to react quantitatively with CO in refluxing heptane to regenerate the complex $[HOs_3(NC_5H_4)(CO)_{10}]$ in agreement with the idea that co-ordinated py is readily displaced.

All the complexes described in this paper clearly showed parent molecular ions in their mass spectra, except the two isomeric nonacarbonyls. Isomer (A) showed only ions due to the decacarbonyl, whereas (B) showed the octacarbonyl in its spectrum. Source temperatures above 150 °C were required to obtain these spectra. To show that these species could have been formed by thermal decomposition in the spectrometer we heated each isomer in refluxing n-decane at 175 °C. Isomer (A) gave $[HOs_3(NC_5H_4)(CO)_{10}]$ with considerable decomposition but, as expected from the mass-spectrometry results, (B) gave $[H_2Os_3(NC_5H_4)_2(CO)_8]$ rapidly and quantitatively. From this it seems that only isomer (B) is on the direct reaction path to the octacarbonyl. These final steps are reversible and the action of CO on $[H_2Os_3(NC_5H_4)_2(CO)_8]$ is to displace one molecule of py to give $[HOs_3(NC_5H_4)(CO)_{10}]$. These reactions are summarised in the scheme below. The reaction proceeds further to give two isomeric dimers $[Os_2(NC_5H_4)_2(CO)_6]$ which are the main products from the $Os_3(CO)_{12}$–py reaction after 6 h at 184 °C in a sealed glass tube (see Table 1). In principle the reaction could continue beyond the octacarbonyl stage to give $[H_2Os_3(NC_5H_4)_2(CO)_7(py)]$ and $[H_3Os_3(NC_5H_4)_3(CO)_6]$, but although treatment of the octacarbonyl with py did give species in solution other than the dimers as indicated by new ν(CO) absorptions no other complexes were isolated. The proportion of the two dimers varied with time in the reaction by which they were formed (Table 1) and this may indicate initial formation of isomer (B) followed by isomerisation. Heating each of the isomers separately in refluxing n-decane for several hours gave approximately the same isomeric mixture; isomer (A): isomer (B) = 1.2 : 1. However, due to some decomposition under these conditions, which is reduced by using an atmosphere of CO, these isomers are not at equilibrium.



SCHEME

(*i*), −CO + py; (*ii*), −py + CO; (*iii*), −CO; (*iv*), +CO.

Reactions of $Os_3(CO)_{12}$ *with* 4-*Substituted Pyridines*.—Reactions of $Os_3(CO)_{12}$ with $4\text{-}XC_5H_4N$ (X = Me or CH_2Ph) are very similar to that of py and data for some of the isolated complexes are given in Table 2. We believe that a similar series of complexes are formed as with py but we only characterised the most easily isolated species. It is notable that in all cases the dimer exists in two isomeric forms which must be directly comparable in structure because of the correspondence of their i.r. spectra at *ca.* 2 000 cm^{-1}.

Nature of Complexes.—The molecular formulae of the complexes were established by elemental analysis and mass spectra (except for the nonacarbonyls). For py the *ortho*-hydrogen signals occur at τ 1.9 in the n.m.r. spectrum and are clearly assigned. On simple co-ordination the chemical shift is normally lowered. In the decacarbonyl $[HOs_3(NC_5H_4)(CO)_{10}]$ integration of the signal at τ 1.87 corresponds to one proton. This was assigned to the remaining hydrogen *ortho* to nitrogen. There was no significant chemical-shift change from that for the free ligand. Transfer of an *ortho*-hydrogen atom to the metal was confirmed by n.m.r. spectra of the 4-substituted derivatives. The 4-Mepy complexes in particular gave very simple spectra, unambiguously assigned. Thus we believe that the 2-pyridyl ligand is bridging as a three-electron donor forming a four-membered ring as in (I). Similar decacarbonyls $[HOs_3X(CO)_{10}]$ (X = OPh,[4] SPh,[4] NHPh,[2] CH:CH$_2$,[5] OH,[6] *etc.*) are formed in reactions of HX with $Os_3(CO)_{12}$ where group X is a bridging three-electron donor. The 2-pyridyl and vinyl groups are different from the others in the series by being inherently asymmetric, formally donating 2e$^-$ to one metal atom but only 1e$^-$ to the other. Simple electron counting requires the hydrogen to be exclusively located on one osmium as in (II). Nevertheless, we prefer structure (I) since hydrides have only been found to be bridging in osmium clusters. All the complexes in the above series including the case where X = NC_5H_4 have a very similar pattern of absorptions

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[4] B. F. G. Johnson, P. A. Kilty, and J. Lewis, *Chem. Comm.*, 1968, 180; *J. Chem. Soc.* (*A*), 1968, 2859; B. F. G. Johnson, P. A. Kilty, J. Lewis, and I. G. Williams, *Chem. Comm.*, 1968, 861; G. R. Crooks, B. F. G. Johnson, J. Lewis, and I. G. Williams, *J. Chem. Soc.* (*A*), 1969, 797.

[5] A. J. Deeming and M. Underhill, *J.C.S. Dalton*, 1974, 1415; A. J. Demming, S. Hasso, and M. Underhill, *ibid.*, 1975, 1614 and refs. therein.

[6] C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1973, **57**, C84.

TABLE 2

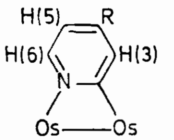
Analytical, i.r. and ^1H n.m.r. data for the complexes

Complex	M.p. (θ_c/°C)	Analyses [a]/%			$\nu(CO)$ [b]/cm^{-1}	^1H N.m.r. data [c]			
		C	H	N		τ	Assignment [d]	Rel. intensity	J/Hz
$[HOs_3(NC_5H_4)(CO)_{10}]$	141—143	19.4	0.6	1.5	2 105m, 2 064s,	1.87 (dd)	H(6)	1	$J(H^5H^6)$ 5.2
		(19.4)	(0.55)	(1.5)	2 054s, 2 023s,	2.74 (m)	H(3), H(4)	2	$J(H^4H^6)$ } 1.6
					2 011s, 2 004s,	3.32 (td)	H(5)	1	J (H^3H^5) }
					1 991s, 1 976s	24.86 (s)	OsH	1	$J(H^4H^5)$ 7.2
									$J(H^3H^4)$ 7.7
$[HOs_3(NC_5H_4)(CO)_9(py)]$,	116—118	23.2	1.1	2.9	2 092s, 2 048s,	1.29 (dd)	} NC_5H_4		
Isomer (A)		(23.3)	(1.05)	(2.85)	2 014s, 2 006s,	1.47	} NC_5H_5	[e]	
					1 995s, 1 976m,	1.8—3.3			
					1 967s, 1 935s	24.22 (s)	OsH		
Isomer (B) [f]	144—148	23.25	1.0	3.15	2 086s, 2 047s,	1.11 (dd)	H(2′), H(6′)	2	
		(23.3)	(1.05)	(2.85)	2 004s, 1 996s,	1.99 (d)	H(6)	1	
					1 973m, 1 967m,	2.34 (td)	} Other ring protons	1	
					1 934m	2.86 (m)		[e]	
						3.53 (td)		1	
						20.80 (s)	OsH	1	
$[H_2Os_3(NC_5H_4)_2(CO)_8]$	Decomp.	22.8	1.2	2.8	2 083s, 2 048s,	1.80 (dd)	} H(6), H(6′)	1	$J(H^5H^6)$
	ca. 210	(22.7)	(1.05)	(2.95)	2 031s, 2 003s,	1.91 (dd)		1	$J(H^{5'}H^{6'})$ 5.6
					1 994m, 1 986m,	2.81 (m)	H(4), H(4′),	4	
					1 979s, 1 965s	3.38 (m)	H(3), H(3′)	2	
							H(5), H(5′)		
						20.80 (s)	} OsH, OsH′	1	
						22.47 (s)		1	
$[Os_2(NC_5H_4)_2(CO)_6]$	decomp.	27.25	1.25	3.95	2 076s, 2 036s,	1.88 (d)	H(6)	1	$J(H^4H^6)$ } 1.6
Isomer (A)	>158	(27.25)	(1.15)	(4.00)	2 001s,	2.69 (m)	H(3), H(4)	2	$J(H^3H^5)$ }
					1 992w (sh),	3.29 (td)	H(5′)	1	$J(H^5H^6)$ 5.2
					1 974s, 1 958s				$J(H^5H^4)$ 7.2
									$J(H^3H^4)$ 7.7
Isomer (B)	>220	27.25	1.25	3.95	2 075s, 2 037s,	1.91 (d)	H(6)	1	$J(H^4H^6)$ } 1.6
		(27.25)	(1.15)	(4.00)	2 001s,	2.67 (m)	H(3), H(4)	2	$J(H^3H^5)$ }
					1 993w (sh),	3.26 (td)	H(5)	1	$J(H^5H^6)$ 5.5
					1 976w, 1 969s,				$J(H^5H^4)$ 7.2
					1 958s				$J(H^3H^4)$ 7.7
$[H_2Os_3(NC_5H_3Me\text{-}4)_2(CO)_8]$	188—192	24.7	1.6	3.05	2 082s, 2 048s,	1.97 (d)	} H(6), H(6′)	1	$J(H^5H^6)$ 5.5
		(24.45)	(1.65)	(2.85)	2 029s, 2 002s,	2.09 (d)		1	$J(H^{5'}H^{6'})$ 5.8
					1 992w (sh),	2.86 (d)	} H(3), H(3′)	1	
					1 985m, 1 978s	2.94 (d)		1	
					1 963s	3.52 (dd)	} H(5), H(5′)	1	$J(H^3H^5)$ } 2.0
						3.62 (dd)		1	$J(H^{3'}H^{5'})$ }
						7.86 (s)	2Me	6	
						20.93 (s)	} OsH, OsH′	1	
						22.59 (s)		1	
$[Os_2(NC_5H_3Me\text{-}4)_2(CO)_6]$	203—205	29.4	1.85	3.75	2 075s, 2 035s,	2.06 (d)	H(6)	1	$J(H^5H^6)$ 5.8
Isomer (A)	(decomp.)	(29.45)	(1.90)	(3.80)	2 001s, 1 974s,	2.73 (s)	H(3)	1	$J(H^3H^5)$ 2.1
					1 957s	3.47 (dd)	H(5)	1	
						7.83 (s)	Me	3	
Isomer (B)	Sublimes	29.6	1.65	3.7	2 074s, 2 036s,	2.08 (d)	H(6)	1	$J(H^5H^6)$ 5.8
	204—206	(29.45)	(1.9)	(3.8)	2 001s,	2.69 (s)	H(3)	1	$J(H^3H^5)$ 2.0
					1 993 (sh),	3.45 (dd)	H(5)	1	
					1 976m, 1 968s,	7.82 (s)	Me	3	
					1 957s				
$[HOs_3\{NC_5H_3(CH_2Ph\text{-}4\}(CO)_{10}]$	147—148	26.15	1.1	1.25	2 104m, 2 063s,	2.06 (d)	H(6)	1	$J(H^5H^6)$ 6.0
		(25.9)	(1.1)	(1.35)	2 053s, 2 023s,	2.63—	H(3) + Ph	*ca.* 6	
					2 011s, 2 003s,	3.03 (m)			
					1 993 (sh),	3.60 (dd)	H(5)	1	$J(H^3H^5)$ 2.2
					1 990s, 1 976m	6.24 (s)	CH_2	2	
						24.89 (s)	OsH	1	
$[H_2Os_3\{NC_5H_3(CH_2Ph\text{-}4)_2\}(CO)_8]$	167—169	34.1	2.0	2.4	2 081s, 2 047s,	2.05 (d)	} H(6), H(6′)	2	$J(H^5H^6)$ } 5.8
		(33.9)	(1.95)	(2.45)	2 029s, 2 001s,	2.18 (d)			$J(H^{5'}H^{6'})$ }
					1 993m, 1 985m,	2.74—	H(3), H(3′),	*ca.* 10 [e]	
					1 977s, 1 963s	3.08 (m)	Ph_2		
						3.63 (dd)	} H(5), H(5′)	2	$J(H^3H^5)$ } 2.0
						3.78 (dd)			$J(H^{3'}H^{5'})$ }
						6.33 (s)	} CH_2, CH'_2	4	
						6.36 (s)			
						20.93 (s)	} OsH, OsH′		
						22.57 (s)			
$[Os_2\{NC_5H_3(CH_2Ph\text{-}4\}_2(CO)_6]$,	123—124	40.95	2.45	3.3	2 074s, 2 034s,	2.09 (d)	H(6)	1	$J(H^5H^6)$ 5.9
Isomer (A)		(40.7)	(2.3)	(3.15)	1 999s, 1 973s,	2.65—	H(3), Ph	6 [e]	
					1 955s	2.98 (m)			
						3.58 (dd)	H(5)	1	$J(H^3H^5)$ 2.0
						6.25 (s)	CH_2	2	

TABLE 2 (*Continued*)

Complex		Analyses [a]/%				^{1}H N.m.r. data [c]			
	(θ_c/°C)	C	H	N	ν(CO) [b]/cm^{-1}	τ	Assignment [d]	Rel. intensity	J/Hz
Isomer (B)	120—122	40.7	2.2	2.95	2 074s, 2 036s,	2.10 (d)	H(6)	1	$J(H^5H^6)$ 5.7
		(40.7)	(2.3)	(3.15)	1 999s, 1 976m,	2.60—	H(3), Ph	6 [e]	
					1 969s, 1 957s	2.97 (m)			
						3.55 (dd)	H(5)	1	$J(H^3H^5)$ 2.0
						6.22 (s)	CH_2	2	
[$HOs_3(NC_9H_6)(CO)_{10}$],	147—149	23.3	0.6	1.25	2 104s, 2 061s,	1.9—	H(3)—H(8)	6 [e]	
Structure (IX; R = H)		(23.3)	(0.7)	(1.45)	2 053s, 2 023s,	2.7(m)			
					2 012s, 2 003s,	24.37 (s)	OsH	1	
					1 990s, 1 975w				
[$HOs_3(NC_{10}H_8)(CO)_{10}$],	155—156	24.35	0.9	1.3	2 103m, 2 060s,	2.47 (s) (br)	H(8)	*e*	
Structure (IX; R = Me)		(24.15)	(0.9)	(1.4)	2 053s, 2 021s,	2.47 (d)	A } Two AB quartets for H(3)—H(6)		
					2 012s, 2 002s,	2.49 (d)	A		
					1 989s, 1 975w	2.67 (d)	B		J(AB) 8
						2.77 (d) (br)	B		
						7.44 (s)	CH_3		
						24.40 (s)	OsH		
[$HOs_3(NC_9H_6)(CO)_{10}$],	164—166	23.3	0.6	1.4	2 104m, 2 062s,	1.89 (m)	} H(5)—H(8)	1	
Structure (VIII)		(23.3)	(0.7)	(1.45)	2 053s, 2 023s,	2.31 (m)		3	
					2 012s, 2 003s,	2.16 (d)	H(3)	1	$J(H^3H^4)$ 7
					1 989s, 1 974w	2.99 (d)	H(4)	1	
						24.48 (s)	OsH	1	
Structure (VII)	188 (decomp.)	23.3	1.45	1.4	2 103m, 2 062s,	1.16 (s)	H(1)	1	
		(23.3)	(0.7)	(1.45)	2 052s, 2 021s,	2.0—	H(4)—H(8)	5	
					2 009s, 2 002s,	3.0(m)			
					1 989s, 1 974w	25.02(s)	OsH	1	

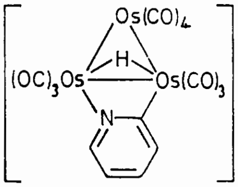
[a] Calculated figures are given in parentheses. [b] Recorded in cyclohexane solution; error ±1 cm^{-1}. [c] Recorded at 100 MHz at 27 °C in $CDCl_3$ solution. [d] Figures in parentheses refer to the usual system, *e.g.*



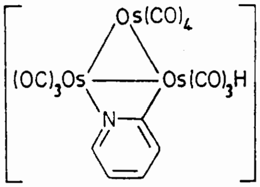
R = H(4), Me, or CH_2Ph

[e] Accurate integration of the peaks was not carried out. [f] O 14.75 (14.7%).

at *ca.* 2 000 cm^{-1} and almost certainly have corresponding structures.



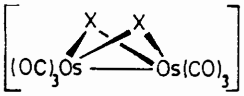
(I)



(II)

The complexes [$HOs_3(NC_5H_4)(CO)_9(py)$] are presumably simple substitution derivatives of the decacarbonyl with isomerism resulting from different substitution positions. The very different reactivity of these isomers probably means that the py is located on different metal atoms so that only one isomer is readily converted into the octacarbonyl. Preliminary results of an *X*-ray study [7] on [$H_2Os_3(NC_5H_4)_2(CO)_8$] show that the 2-pyridyl ligands bridge separate edges of the metal triangle and that the manner of bridging is as in the figures. The n.m.r. spectrum showed that both 2-pyridyl and both hydride ligands are different but the hydride positions are unknown. The molecule is apparently non-fluxional with sharp separate signals for each hydrogen atom. This is more clearly seen for the 4-Mepy derivative (see Table 2).

The origin of the isomerism found for [$Os_2(NC_5H_3R)_2(CO)_6$] (R = H, Me, or CH_2Ph) is an interesting structural problem. By analogy with other dimers of type [$M_2X_2(CO)_6$], particularly common for iron, they probably have structure (III) where X = NC_5H_4. Perhaps isomerism results from the Os_2X_2 framework being bent as in (III) or planar. However, the striking similarity in their spectra at *ca.* 2 000 cm^{-1} suggests that they are both bent. Both 2-pyridyl ligands are equivalent in each isomer and structures (IV) and (V) are possibilities; (IV) has equivalent metal atoms whereas (V) does not. Structure (V) is somewhat precedented by the complex [$Fe_2(OCPh)_2(CO)_6$], (VI).[8]



(III)

There was no evidence for formation of 2,2′-bipyridyl or derivatives of it in these reactions and indeed the dimeric complexes are extremely stable. They were unreactive towards H_2,CO, or acetylene when these gases were bubbled through refluxing decalin solutions. Even after heating at 175 °C under CO (130 atm) for

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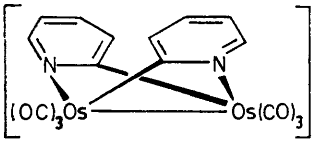
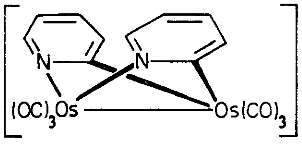
[7] M. B. Hursthouse and L. New, personal communication.

[8] E. O. Fischer and V. Kiener, *J. Organometallic Chem.*, 1970, **23**, 215.

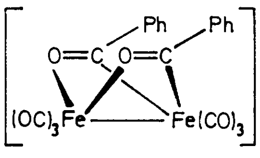
ca. 2 h the dimers were recovered quantitatively. It is possible that, under more forcing conditions or with systems containing weaker metal–carbon bonds, direct formation of bipy from py will be possible.



(IV)

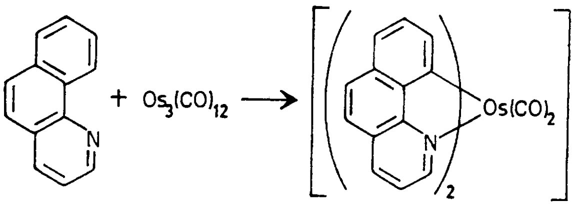


(V)



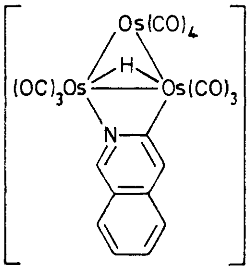
(VI)

Reaction of $Os_3(CO)_{12}$ *with Quinoline and Isoquinoline.*—Recently it has been shown that benzo[*h*]quinoline reacts with $Os_3(CO)_{12}$ to give the monomeric complex shown in equation (1) together with $[H_4Os_4(CO)_{12}]$.[9]

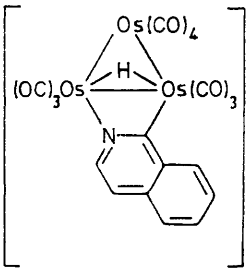


(1)

Since this ligand metallates to give five-membered chelate rings, cluster breakdown to monomers occurs. We have studied quinoline and isoquinoline to establish sites of metallation and whether bridges or chelates and of what size are formed. Not unexpectedly iquin behaves very much like py and forms two isomers of $[HOs_3(NC_9H_6)(CO)_{10}]$ both the result of metallation *ortho* to nitrogen. On the basis of their n.m.r. spectra these have structures (VII) and (VIII) and their yields (16 and 41% respectively) suggest that there are electronic reasons for favoured metallation at the 1-position.

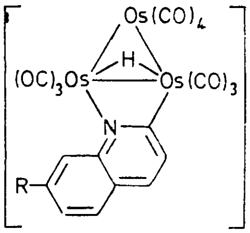


(VII)

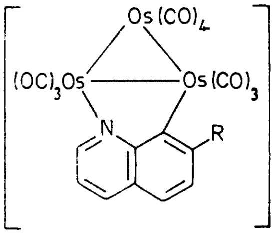


(VIII)

Reaction of $Os_3(CO)_{12}$ with a large excess of quin, containing *ca.* 1% iquin as impurity, gave significant amounts of the isomer of structure (VIII) derived from iquin. We found only one derivative of quin itself, also formulated as $[HOs_3(NC_9H_6)(CO)_{10}]$. Quinoline might be metallated at the 2-position to give structure (IX; R = H) or at the 8-position to give structure (X; R = H). The lack of a ^1H n.m.r. signal due to hydrogen *ortho* to nitrogen indicates structure (IX) and this was confirmed by the spectrum of the analogous 7-Mequin complex which unambiguously supports structure (IX; R = Me). The spectrum of $[HOs_3(NC_9H_5Me\text{-}7)(CO)_{10}]$ was comparatively simple showing two AB quartets, a singlet due to H^8, and no signal due to H^2.



(IX) R= H or Me



(X) R= H or Me

The isolation of only decacarbonyl complexes from quin and iquin is due to reaction conditions suited to their formation (see Experimental section). We have spectroscopic evidence that extended reaction in absence of CO gives $[H_2Os_3(NC_9H_6)_2(CO)_8]$ and dimeric species similar to those from py. The close similarity of quin to py in its reaction with $Os_3(CO)_{12}$ indicates that C-H cleavage α to the donor atom is dominant in these reactions as with alkylphosphines even where there are β-C-H bonds suitable for attack.

EXPERIMENTAL

All reactions except those carried out in sealed glass tubes were followed by changes in the i.r. spectrum in the range 2 150—1 900 cm^{-1}. On the scale at which we worked the yields of complexes isolated after t.l.c. must be regarded as minimum values, since there is evidence for significant losses in this separation method.

Whereas all trimeric complexes gave yellow crystals, white or off-white crystals were obtained for the dimers. All species except the nonacarbonyl complexes (see Discussion section) gave parent molecular ions in their mass spectra and fragmentation patterns consistent with their formulations.

*Reactions of Dodecacarbonyl-*triangulo*-triosmium.*—*With pyridine.* (a) Three glass tubes each containing $Os_3(CO)_{12}$ (0.20 g) and pyridine (AnalaR, 10 cm^3) were degassed, sealed *in vacuo*, and heated at 184 ± 4 °C for 1, 4, and 6 h respectively. The tubes were opened and the contents rinsed out with chloroform. After removal of solvent *in vacuo*, the residues were chromatographed (t.l.c. on silica) using pentane–chloroform as eluant. Yields of the complexes are given in Table 1 and their data in Table 2.

(b) A solution of $Os_3(CO)_{12}$ (0.16 g) in py (10 cm^3) and n-octane (70 cm^3) was heated under reflux for 3 h under an

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[9] M. I. Bruce, B. L. Goodall, and F. G. A. Stone, *J. Organometallic Chem.*, 1973, **60**, 343.

atmosphere of CO (not bubbled through) and 8 h under N_2. Removal of excess of ligand and solvent and separation by preparative-layer chromatography with chloroform–pentane as eluant gave two main bands, one containing a mixture of $[HOs_3(NC_5H_4)(CO)_{10}]$ (6) and $[H_2Os_3(NC_5H_4)_2(CO)_8]$ (32%) separated by further chromatography and crystallisation. The other main band gave $[HOs_3(NC_5H_4)(CO)_9(NC_5H_5)]$, isomer (B) (9%). Trace amounts only of isomer (A) and dimeric species were obtained.

(c) A solution of $Os_3(CO)_{12}$ (0.22 g) in py (5 cm^3) and octane (60 cm^3) was treated as above (under CO) for 3 h. The solvent was replaced by py (5 cm^3) and heptane (60 cm^3) and the mixture heated under reflux for 82 h. Following the reaction by i.r. spectra showed an increase in concentration of the octacarbonyl but an essentially constant concentration of $[HOs_3(NC_5H_4)(py)(CO)_9]$, isomer (A), over this period. Separation as above gave $[HOs_3(NC_5H_4)(CO)_{10}]$ (11), $[H_2Os_3(NC_5H_4)_2(CO)_8]$ (44), and $[HOs_3(NC_5H_4)(py)(CO)_9]$, isomer (A) (7%). Trace amounts of isomer (B) were also obtained.

With 4-*methylpyridine*.—The complex (0.20 g), 4-methylpyridine (5 cm^3), and n-octane (5 cm^3) were degassed and sealed into an evacuated glass tube. Two such tubes were heated at 184 ± 4 °C for 4 and 35 h respectively. The contents were then treated as in the corresponding reaction with py to give $[H_2Os_3(NC_5H_3Me\text{-}4)_2(CO)_8]$ (38% after 4 h, 0% after 35 h), $[Os_2(NC_5H_3Me\text{-}4)_2(CO)_6]$, isomer (A) (17% after 4 h, 33% after 35 h), and $[Os_2(NC_5H_3Me\text{-}4)_2(CO)_6]$, isomer (B) (9% after 4 h, 24% after 35 h).

With 4-*benzylpyridine*.—The complex (0.20 g), 4-benzylpyridine $NC_5H_4(CH_2Ph\text{-}4)$ (5 cm^3), and n-octane (5 cm^3) were treated as in the 4-Mepy reaction (heating for 4 h) to give $[HOs_3\{NC_5H_3(CH_2Ph\text{-}4)\}(CO)_{10}]$ (26), $[H_2Os_3\{NC_5H_3(CH_2Ph\text{-}4)\}_2(CO)_8]$ (6), $[Os_2\{NC_5H_3(CH_2Ph\text{-}4)\}_2(CO)_6]$, isomer (A) (15), and $[Os_2\{NC_5H_3(CH_2Ph\text{-}4)\}_2(CO)_6]$, isomer (B) (14%).

With isoquinoline. A solution of $Os_3(CO)_{12}$ (0.109 g) and isoquinoline (recrystallised from light petroleum, 1.5 cm^3) in n-nonane (25 cm^3) was heated under reflux for 1.5 h in an atmosphere of CO. The solvent and the excess of ligand were removed under reduced pressure and decalin (60 cm^3) was added to the residue. Carbon monoxide was bubbled through this solution under reflux for 2.5 h. The residue after removal of solvent under reduced pressure was chromatographed (t.l.c. on silica) using light petroleum (b.p. <40 °C) as eluant. Two isomers of $[HOs_3(NC_9H_6)(CO)_{10}]$ were obtained, that with structure (VII) (0.019 g, 16%) and that with (VIII) (0.048 g, 41%), both as yellow crystals.

With quinoline. A solution of $Os_3(CO)_{12}$ (0.20 g) and quinoline (8 cm^3; shown by t.l.c. to contain a small proportion of iquin) in n-nonane (52 cm^3) was heated for 2.5 h under reflux in an atmosphere of carbon monoxide. The solvent and excess of ligand were removed under reduced pressure and decalin (60 cm^3) added to the residue. Carbon monoxide was bubbled through this solution under reflux for 4 h. Work-up as in the iquin reaction gave $[HOs_3(NC_9H_6)(CO)_{10}]$ isomers of structure (IX) (34) and (VIII) (24%), both as yellow crystals. The latter isomer was the same as the major isomer derived from iquin and assumed to be formed from the iquin impurity.

With 7-*methylquinoline*. A solution of $Os_3(CO_{12}$ (0.20 g) and 7-methylquinoline (1.5 g, purified by recrystallisation at low temperatures from light petroleum) in n-nonane (25 cm^3) was heated under reflux under an atmosphere of CO. Further treatment as with quin gave $[HOs_3(NC_9H_5Me\text{-}7)(CO)_{10}]$ (60%) as yellow crystals.

Some Reactions on Products.—(a) *Action of carbon monoxide on* $[H_2Os_3(NC_5H_4)_2(CO)_8]$. Carbon monoxide was passed through a refluxing solution of $[H_2Os_3(NC_5H_4)_2(CO)_8]$ (0.056 g) in n-nonane (40 cm^3). After 23 h the i.r. spectrum indicated *ca.* 40% conversion into $[HOs_3(NC_5H_4)(CO)_{10}]$. After removal of solvent *in vacuo* and separation by t.l.c. (silica) using chloroform–pentane as eluant, the complexes $[HOs_3(NC_5H_4)(CO)_{10}]$ (0.015 g) and $[H_2Os_3(NC_5H_4)_2(CO)_8]$ (0.013 g) were obtained. Using refluxing decalin as the solvent complete conversion into the decacarbonyl complex was observed after 1.5 h as judged by the i.r. spectrum.

(b) *Action of carbon monoxide on* $[HOs_3(NC_5H_4)(py)(CO)_9]$, *isomer* (A).—Carbon monoxide was bubbled through a solution of isomer (A) (0.016 g) in n-heptane (5 cm^3). After 1 h there was *ca.* 50% conversion into the decacarbonyl $[HOs_3(NC_5H_4)(CO)_{10}]$ as judged by changes in the i.r. spectrum.

Similar treatment of isomer (B) (0.010 g) in n-heptane (5 cm^3) gave complete conversion into $[HOs_3(NC_5H_4)(CO)_{10}]$ within 10 min.

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