Journal of Organometallic Chemistry, 368 (1989) 119–130
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09829

Trapping of an unstable tautomer of indole by *ortho*-metallation at triosmium clusters

Kenneth I. Hardcastle *, **Houri Minassian,**

Department of Chemistry, California State University Northridge, 18111 Nordhoff Street, Northridge, California 91330 (U.S.A.)

Alejandro J. Arce *, **Ysaura De Sanctis**

Chemistry Center, Instituto Venezolano de Investigaciones Cientificas, Apartado 21827,
Caracas 1020-A (Venezuela)

and Antony J. Deeming *

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)

(Received January 12th, 1989)

Abstract

Indole was reacted with $[Os_3(CO)_{12}]$ in an attempt to prepare the analogue of the C,C-bonded clusters $[Os_3H_2(\mu_3\text{-}\overline{C{=}CCH{=}CHNR})(CO)_9]$ (**1**; R = H or Me) formed by direct double oxidative additions of pyrrole or *N*-methylpyrrole at $[Os_3(CO)_{12}]$ but unexpected results were obtained. Only minor traces of $[Os_3H_2(\mu_3\text{-}\overline{C_6H_4NHC{=}C})(CO)_9]$ (**3**), the analogue of **1**, were obtained, the major product being $[Os_3H_2(\mu\text{-}\overline{C_6H_4CH_2C{=}N})_2(CO)_8]$ (**4**) (45%). Crystals of **4** are monoclinic, space group $C2/c$, $a = 40.007(7)$, $b = 9.059(1)$, $c = 14.072(2)$ Å, $\beta = 96.47(1)°$, $Z = 8$. The structure was refined to $R = 0.052$. The organic (indolyl) ligands each bridge two osmium atoms through the nitrogen and the 2-carbon atoms and are shown to be *ortho*-metallated forms of the unstable tautomer of indole, $\overline{C_6H_4CH_2CH{=}N}$ containing a non-aromatic heterocyclic ring. In a further attempt to make the C,C-bonded cluster (**3**), 3-formylindole was reacted with $[Os_3(CO)_{10}(MeCN)_2]$ to give the acyl complex $[Os_3H(\mu_2\text{-}\overline{C_6H_4NHCH{=}C}CO)(CO)_{10}]$ (**5**) (57%) and $[Os_3H(\mu_2\text{-}\overline{C_6H_4CH_2C{=}N})(CO)_{10}]$ (**6**) (15%) which contains the same type of ligand as those in **4**. Cluster **5** undergoes thermal decarbonylation to give $[Os_3H_2(\mu_3\text{-}\overline{C_6H_4NHC{=}C})(CO)_9]$ (**3**), which is analogous to the pyrrole derivatives **1**, except that, unlike (**1**, R = H), compound **3** does not isomerise from a C,C-bonded form to a C,N-bonded isomer when heated and the reasons for this thermal stability are discussed.

0022-328X/89/$03.50

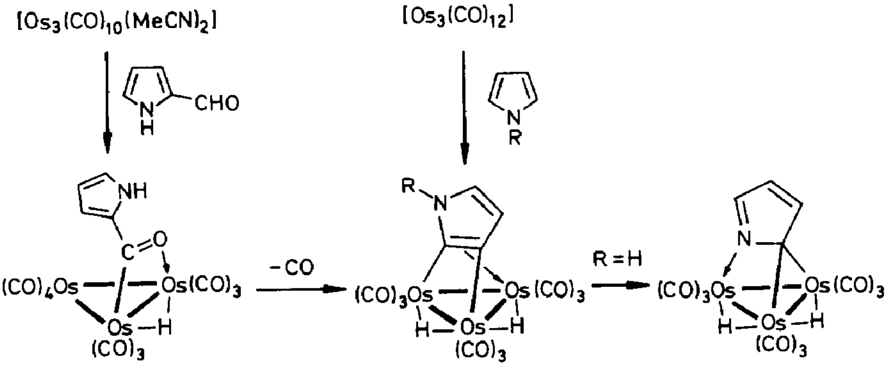
Introduction

We have described some triosmium clusters containing μ_2 and μ_3 ligands derived from pyrrole and *N*-methylpyrrole (Scheme 1) [1–3]. These were formed by direct high-temperature reaction of the pyrrole with $[Os_3(CO)_{12}]$ or under more gentle conditions from $[Os_3(CO)_{10}(MeCN)_2]$ and 2-formylpyrrole. Oxidative addition in the latter case gave the acyl cluster $[Os_3H(\overline{NHCH{=}CHCH{=}C}CO)(CO)_{10}]$, which was then decarbonylated thermally to give $[Os_3H_2(R\overline{NCH{=}CHC{=}C})(CO)_9]$ (**1**) (R = H) in which the pyrrole ligand is bonded to osmium through two adjacent carbon atoms and retains the N–H bond. The X-ray structure of the *N*-methyl analogue (**1**: R = Me) was determined [2]. A very interesting feature of this chemistry is that cluster **1** (R = H) isomerises thermally from the C,C-bonded form to the C,N-bonded isomer **2** by a process requiring the formal transfer of a hydrogen atom from a nitrogen to a carbon atom (Scheme 1). The mechanism involves transfer of a hydrogen atom from osmium to carbon and from nitrogen to osmium. Clearly this isomerisation cannot occur when there are substituents other than hydrogen at nitrogen; for example (**1**: R = Me) is thermally stable. The main objective of the present study was to synthesise the indole analogues of these compounds, in particular $[Os_3H_2(\mu_3\text{-}\overline{C_6H_4NHC{=}C})(CO)_9]$ (**3**), analogous to compounds **2**. We predicted that, although this compound contains an N–H bond necessary for the isomerisation, the C,N-bonded isomeric product would be of high energy if a structure entirely analogous to that of **2** were adopted, since the benzo group would need to span a single C–C bond of the five-membered ring. Alternatively, however, the presence of the benzo group might favour a different geometry for the C,N-bonded isomer, with the N-atom instead of a C-atom bridging two osmium atoms. We set out to synthesise cluster **3** to test these ideas.

Results and discussion

Reaction of indole with $[Os_3(CO)_{12}]$

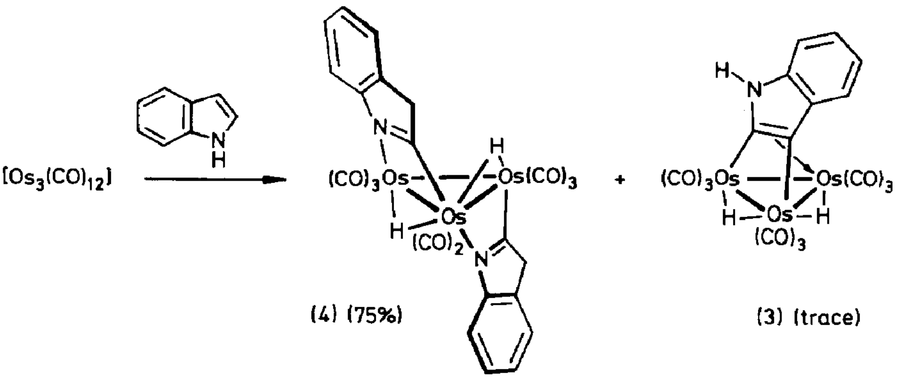
N-methylpyrrole reacts slowly with $[Os_3(CO)_{12}]$ in refluxing decane to give a 75% yield of $[Os_3H_2(C_4H_2NR)(CO)_9]$ (**1**, R = Me) (Scheme 1) [1]. The crystal structure



(1; R = H or Me)

(2)

Scheme 1



Scheme 2

is essentially consistent with its depiction in Scheme 1 except that the direction of the coordinated C–C bond is twisted somewhat out of parallel with an Os–Os bond [2]. We have interpreted this effect as a distortion towards the structure found for $[Os_3H_2(Et_2NC_2H)(CO)_9]$, in which the diethylaminoethyne is coordinated with the C–C bond perpendicular to one of the Os–Os bonds [4]. The difference in structure is because the Et_2N group is a much better π-donor than the NMe group in (**1**:R = Me). The pyrrole analogue (**1**: R = H) is not obtained in very good yield by direct reaction of pyrrole with $[Os_3(CO)_{12}]$ because of isomerisation to **2** under the reaction conditions: the other route in Scheme 1, via 2-formylpyrrole, is more effective in this case.

We initially thought that in the direct reaction with $[Os_3(CO)_{12}]$ indole would either give cluster **3** analogous to **1**, or that cluster **3** would isomerise to the C,N-bonded analogue of **2**. However, none of product **2** was obtained and only a minute amount of cluster **3**. The reaction in refluxing decane gave, apart from this trace of **3** and a trace of another nonacarbonyl cluster which we have been unable to characterise, only one major product in 45% yield, which we have characterised as $[Os_3H_2(C_8H_6N)_2(CO)_8]$ (**4**) (Scheme 2). For a triangular triosmium cluster with three Os–Os bonds, the 18-electron rule would require each C_8H_6N ligand to be a three-electron donor. The IR spectrum around 2000 cm^{-1} agrees well with that of the 2-pyridyl complex $[Os_3H_2(\mu\text{-}C_5H_4N)_2(CO)_8]$ that is formed in the direct reaction of pyridine with $[Os_3(CO)_{12}]$ [5]. This indicates that each C_8H_6N ligand is doubly-bridging and is bonded to osmium through a σ-Os–C bond adjacent to a coordinated nitrogen atom as in μ-2-pyridyl. The absence of signals that would be expected in the IR and ^1H NMR spectra of **4** for an NH group confirmed its absence. The ^1H NMR spectrum (Fig. 1 and Table 1) contains two hydride signals (δ −11.24s and −12.87s) and multiplets for the aromatic protons between δ 6.95 and 7.40. The only other resonances were an AB quartet {δ 3.47(d) and 3.58(d): $J = 23.6$ Hz} and a singlet (δ 3.59) at much higher field than found for indole itself consistent with two non-equivalent CH_2 groups, only one of which show diastereotopic protons. In C_6D_6 solution two AB quartets are clearly resolved but a singlet is observed in CD_3COCD_3 (Fig. 1 and Table 1); we assume that in this case there is accidental coincidence of signals, because no mechanism for exchange peculiar to acetone as solvent can be envisaged. On this basis we formulate these (non-equivalent) ligands as the indolyl ligands $\overline{C_6H_4CH_2C{=}N}$. The organic ligands and the

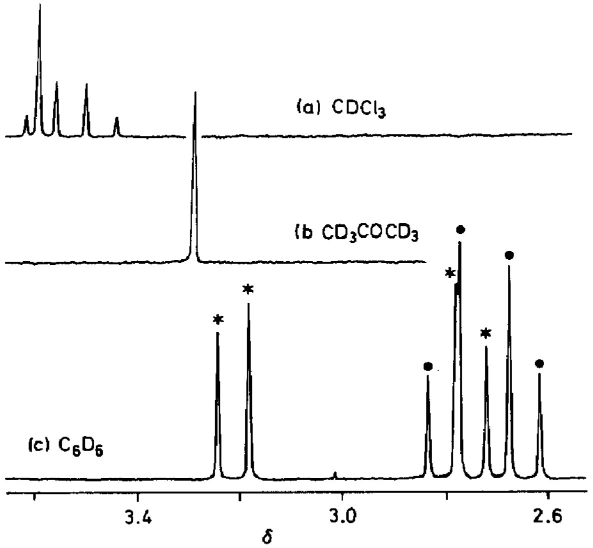


Fig. 1. 400 MHz ^{1}H NMR spectrum of $[Os_3H_2(\overline{C_6H_4\ CH_2C{=}N})_2(CO)_8]$ (Cluster 4) in the CH_2 region of the spectrum recorded in the solvents given. The two AB quartets in C_6D_6 are marked * and ● respectively.

hydrides must therefore bridge non-equivalent Os–Os edges. The X-ray structures of the 2-pyridyl cluster $[Os_3H_2(\mu\text{-}C_5H_4N)_2(CO)_8]$ and the related 4-benzylpyridine derivative have been determined [6], and non-equivalent Os–Os edges in these compounds are bridged by the 2-pyridyl ligands. These clusters are therefore directly analogous to cluster 4 as depicted in Scheme 2. Both $\overline{C_6H_4CH_2C{=}N}$ ligands in 4 should show diastereotopic CH_2 protons as found clearly in C_6D_6 solution (Figure 1).

Structure of the cluster $[Os_3H_2(C_8H_6N)_2(CO)_8]$ (4)

Overall geometry. Yellow-orange crystals of 4 suitable for an X-ray structure determination were obtained by slow evaporation of a heptane solution. The molecular structure is shown in Fig. 2 and Table 2 contains selected bond lengths and angles and some dihedral angles. The cluster contains a closed Os_3 triangle consistent with there being three Os–Os bonds as required by the 18-electron rule. The two edges accommodating the C_8H_6N bridges are longer than the non-bridged edge; Os(1)–Os(2) [2.950(1) Å] and Os(2)–Os(3) [2.956(1) Å] may be compared with Os(1)–Os(3) [2.861(1) Å]. It is likely that longer Os–Os bonds are required simply to fit the organic bridge; Os–Os bond lengths have been found in the range 2.918 to 2.961 Å for related clusters with RC=NR bridges between osmium atoms (Table IV in reference [7]). Atom Os(2) is bonded to both organic ligands, and carries only two CO ligands, while each of atoms Os(1) and Os(3) is bonded to one organic ligand and carries three CO ligands. A curious feature of this structure and that of the related 2-pyridyl structures [6] is that Os(2) is bonded to a carbon atom of one ligand, C(1b), and to a nitrogen atom of the other, N(a). It is this that makes the two organic ligands, A and B, different and the structure asymmetric. Reversal of the coordination of any one ligand, such as rotation of ligand A so that the N(a) and C(1a) coordination positions are interchanged, would generate a two-fold rotation

Table 1

IR and ^1H NMR data for new indole-derived clusters

Compound	ν(CO) [a] (cm^{-1})	^1H NMR [b]	
$[Os_3H_2(\overline{C_6H_4NHC{=}C})(CO)_9]$	2104m, 2076vs,	8.9(br,s)	N*H*
(3)	2052vs, 2028vs,	7.3(m)	C_6H_4
	2020s, 2004vs,	−16.7(s)	Os*H* [c]
	1987m, 1958w.	−20.9(s)	Os*H* [c]
$[Os_3H_2(\overline{C_6H_4CH_2C{=}N})_2(CO)_8]$	2082m, 2048s,	7.35(m)	4H
(4)	2032vs, 2004s,	7.19(d)	1H C_6H_4
	1991w, 1983m,	7.10(m)	2H
	1974m.	7.98(d)	1H
		3.47(d)	CH_2 [d] J 23.6 Hz
		3.58(d)	
		3.59(s)	CH_2 [d]
		−11.24(s)	Os*H*
		−12.87(s)	Os*H*
$[Os_3H(\overline{C_6H_4NHCH{=}C}CO)(CO)_{10}]$	2104w, 2064vs,	8.4(s)	N*H*
(5)	2052s, 2020s,	7.4(m)	C_6H_4, C*H*
	2013s, 2004m,	−13.6(s)	Os*H*
	1983m, 1968m. [e]		
$[Os_3H(\overline{C_6H_4CH_2{=}N})(CO)_{10}]$	2104w, 2063vs,	7.3(m)	C_6H_4
(6)	2052s, 2032sh,	3.6(s)	CH_2
	2021s, 2006s,	−15.0(s)	Os*H*
	1987m, 1972w.		

[a] Recorded in cyclohexane. [b] Recorded at 60 MHz in CD_2Cl_2 for 3, at 400 MHz in $CDCl_3$ for 4, at 60 MHz in CD_3COCD_3 for 5 and 6. [c] Signals recorded at 193 K. At 298 K the hydride signals have coalesced to a singlet at δ −18.7. [d] CH_2 protons give a singlet (δ 3.29) in CD_3COCD_3 and two AB quartets (δ 3.21 and 2.7, J 23.6 Hz and δ 2.80 and 2.64, J 24.4 Hz) in C_6D_6. [e] ν(CO) (acyl) 1430w cm^{-1}.

axis and molecular C_2 symmetry. The two hydrides, the two organic ligands, and Os(1) and Os(3) would then be symmetry related. The asymmetric structure persists in solution and is non-fluxional. It is not obvious why this asymmetric structure is adopted. The hydride ligands as shown in Fig. 2 are placed in positions calculated by use of the program HYDEX which places them so as to minimise interactions with adjacent ligands [8]. The organic ligands lie respectively above and below the metal plane, as do the hydride ligands, each opposite its corresponding organic ligand. The calculated hydride positions make good sense since these complete octahedral coordination geometries of the osmium atoms, if one ignores the Os(1)–Os(2) and Os(2)–Os(3) directions. The metal–metal directions define the coordination geometries of the metal atoms only when there are no hydride or other bridges.

Nature of the indolyl ligands C_8H_6N in cluster 4. The bicyclic ligands labelled **A** and **B** in Fig. 2 are closely planar, and are at 103.4(2) and 104.8(2)° respectively with respect to the Os_3 plane. Hydrogen atom positions on these ligands were not determined, and Fig. 2 shows the hydrogen atoms on the indole-derived ligands in calculated positions. It is clear that H-atoms have been transfered both from nitrogen and the 2-carbon atoms of the indole on complexation. One of these has been added to the metal atoms and the other to the 3-carbon atom, to create a CH_2

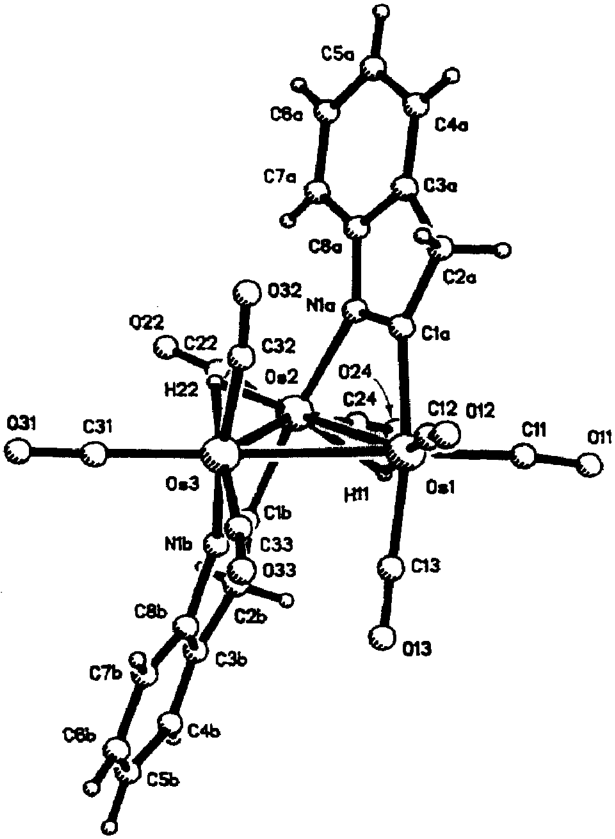


Fig. 2. Molecular structure of $[\mathrm{Os_3H_2(\overline{C_6H_4CH_2C{=}N})_2(CO)_8}]$ (cluster **4**).The hydrogen positions were not directly located from the diffraction data.

group at this site. Figure 3 shows a comparison of bond lengths in the 5-membered rings of 3-methylindole [9] and in ligands **A** and **B** of cluster **4**. A shortening of the N–C(1) distances (1.32 and 1.31 Å) from that in the free ligand (1.40 Å) is consistent with the localization of a N=C bond in these ligands. The long C–C distances associated with the 3-position in ligands **A** and **B** can only be reconciled with the presence of a CH_2 group at this position. These distances are therefore consistent with our interpretation of the ^1H NMR data.

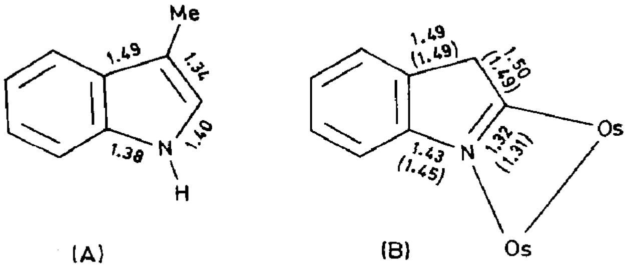


Fig. 3. Geometry of 3-methylindole [9] and the two ligands **A** and **B** in cluster **4**; data for the indolyl ligand **B** are in parentheses.

Table 2

Selected bond lengths (Å) and bond angles (°) in $[Os_3H_2(C_8H_6N)_2(CO)_8]$ (cluster **4**) (numbers in parentheses are the standard deviations of the distances or angles unless otherwise noted)

Os1–Os2	2.950(1)	Os1–Os2–Os3	57.94(3)
Os1–Os3	2.861(1)	Os2–Os1–Os3	61.13(3)
Os2–Os3	2.956(1)	Os1–Os3–Os2	60.93(3)

		A	**B**
Indole ring:	N–C1	1.32(3)	1.31(3)
	N–C8	1.43(3)	1.45(3)
	C1–C2	1.50(3)	1.49(3)
	C2–C3	1.49(4)	1.49(3)
Phenyl ring:	C3–C4	1.40(4)	1.37(4)
	C4–C5	1.38(4)	1.41(4)
	C5–C6	1.39(4)	1.37(4)
	C6–C7	1.41(4)	1.37(4)
	C7–C8	1.37(3)	1.37(4)
	C8–C3	1.38(3)	1.41(3)

Average distances and angles (errors listed are calculated standard deviations of the mean):

Os–C(carbonyl) = 1.89(2) Os–C–O = 175(2)

C–O(carbonyl) = 1.15(2)

Os–H (calcd., bridging) = 1.85(1)

Indole ring C–H (calcd., fixed) = 0.96

Dihedral angles between planes:

Os1–Os2–Os3	Indole **A**	103.4(2)
Os1–Os2–Os3	Indole **B**	104.8(2)
Indole **A**	Indole **B**	52.1(4)

We believe that in the reaction of indole with $[Os_3(CO)_{12}]$ a C_8H_6N ligand and a hydride are incorporated successively along the Os–Os edges, so that cluster **6** is an intermediate in the formation of **4**. Compound **6** was, however, not observed in this reaction. After incorporation of these ligands along two edges of the cluster, it is easy to see from the X-ray structure of **4** that there is no space for a similar incorporation along the third Os–Os edge, and there is no evidence for subsequent reaction of cluster **4** with indole.

Figure 4 shows pyrrole (**A**), indole (**D**), and their tautomers derived by transfering a H-atom from nitrogen to carbon. The tendency for indole to exist as a tautomer is greater than that for pyrrole. Thus tautomer **E** is more stable than tautomer **B** relative to their parent molecules (indole and pyrrole) since, as a result of the benzo-annelation, loss of resonance energy on forming the tautomer is less [8]. The introduction of π-electron donors (SEt, OEt, and especially NR_2) at the 2-position of indole greatly increases the proportion of **E** in equilibrium with **D**. In contrast, the tautomer **F** is very much less stable than the corresponding pyrrole tautomer **C** and apparently plays no role in the chemistry of indole. Since the organic ligands in cluster **4** are *ortho*-metallated forms of tautomer **E**, it is therefore reasonable that **4** is formed from indole, but the pyrrole analogue is not formed in the corresponding reaction of pyrrole with $[Os_3(CO)_{12}]$. We have not carried out experiments to establish whether **4** is formed by reaction of tautomer **E** with the

Table 3

Fractional atomic coordinates for $[Os_3H_2(C_8H_6N)_2(CO)_8]$ (cluster 4) [a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Os1	0.35564(2)	0.3607(1)	0.32689(6)	2.31(2)
Os2	0.36344(2)	0.1433(1)	0.48391(7)	2.22(2)
Os3	0.40898(2)	0.3993(1)	0.47815(7)	2.38(2)
O11	0.3033(6)	0.257(3)	0.169(2)	5.3(5)*
O12	0.3583(5)	0.682(3)	0.270(2)	5.3(5)*
O13	0.4145(5)	0.289(2)	0.215(1)	4.6(4)*
O22	0.3743(6)	0.010(3)	0.681(2)	5.8(5)*
O32	0.3677(5)	0.657(2)	0.537(1)	4.5(4)*
C1a	0.3202(6)	0.387(3)	0.424(2)	2.6(4)*
N1b	0.4292(5)	0.193(2)	0.441(1)	2.4(3)*
N1a	0.3214(5)	0.284(2)	0.492(1)	2.2(3)*
C8a	0.2963(5)	0.311(2)	0.554(2)	2.2(4)*
C3a	0.2785(6)	0.436(3)	0.524(2)	2.7(4)*
C2a	0.2922(6)	0.494(3)	0.437(2)	2.9(5)*
C7a	0.2904(6)	0.232(3)	0.634(2)	2.9(5)*
C4a	0.2522(7)	0.482(3)	0.574(2)	3.6(5)*
C11	0.3215(7)	0.302(3)	0.229(2)	3.4(5)*
C12	0.3565(6)	0.563(3)	0.296(2)	2.5(4)*
C13	0.3929(6)	0.316(3)	0.256(2)	2.4(4)*
C1b	0.4091(6)	0.080(3)	0.448(2)	2.6(4)*
C22	0.3687(7)	0.059(3)	0.604(2)	3.7(5)*
C32	0.3828(6)	0.562(3)	0.510(2)	2.6(4)*
C6a	0.2642(7)	0.281(3)	0.685(2)	3.4(5)*
C5a	0.2461(7)	0.408(3)	0.656(2)	3.9(5)*
C2b	0.4270(6)	−0.057(2)	0.423(2)	2.3(4)*
C3b	0.4608(6)	−0.006(3)	0.401(2)	2.4(4)*
C8b	0.4610(6)	0.149(3)	0.409(2)	2.7(4)*
C31	0.4436(7)	0.410(3)	0.584(2)	4.0(5)*
O31	0.4640(6)	0.428(3)	0.647(2)	5.9(5)*
C4b	0.4887(6)	−0.074(3)	0.373(2)	3.5(5)*
C6b	0.5165(7)	0.164(3)	0.371(2)	3.8(5)*
O24	0.3249(5)	−0.128(2)	0.411(1)	5.0(4)*
C5b	0.5172(7)	0.014(3)	0.362(2)	4.0(6)*
C24	0.3402(6)	−0.023(3)	0.441(2)	2.8(4)*
C7b	0.4885(6)	0.234(3)	0.397(2)	3.2(5)*
C33	0.4304(8)	0.509(3)	0.391(2)	4.3(6)*
O33	0.4447(5)	0.595(3)	0.346(2)	5.5(5)*
H11	0.358	0.160	0.352	4.0*
H22	0.384	0.294	0.558	4.0*
H21a	0.276	0.492	0.382	4.9*
H22a	0.300	0.591	0.447	4.9*
H21b	0.429	−0.123	0.477	5.0*
H22b	0.415	−0.107	0.370	5.0*
H6b	0.535	0.222	0.356	5.0*
H4a	0.240	0.569	0.552	5.6*
H5a	0.228	0.439	0.689	5.2*
H6a	0.260	0.233	0.744	4.7*
H7a	0.303	0.143	0.652	3.7*
H4b	0.490	−0.177	0.371	5.0*
H5b	0.538	−0.029	0.339	5.0*
H7b	0.489	0.340	0.400	5.0*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

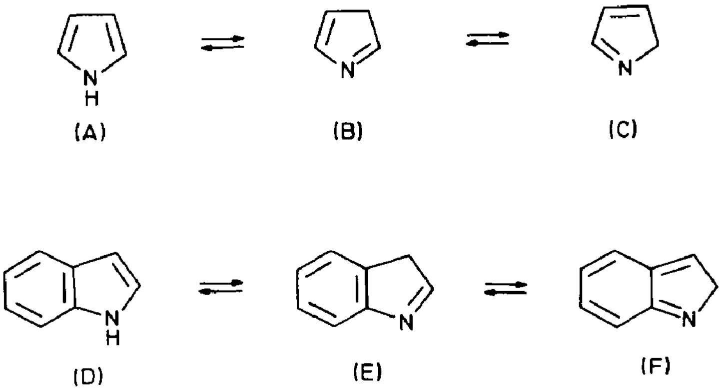
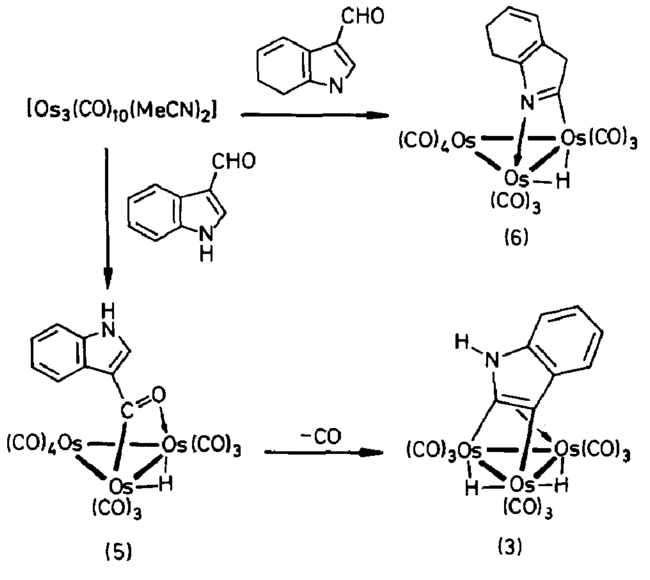


Fig. 4. Pyrrole (A), indole (D), and their tautomers.

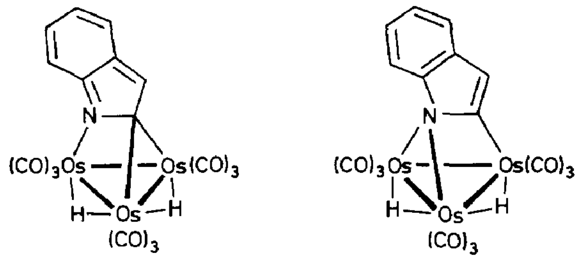
cluster or whether it is the stable tautomer of indole **D** which reacts followed by N–H cleavage and by subsequent rearrangement. Certainly cluster **4** is an expected product from the reaction of **E** since pyridine reacts in the same way [5].

Introduction of indole ligands into triosmium clusters using 3-formylindole

Our previous use of 2-formylpyrrole as in Scheme 1 suggested a similar application of a formylindole and, since 3-formylindole and not the 2-isomer is commercially available, we used this. The simple oxidative addition product (**5**) was formed readily, readily isolated, and characterised from the spectroscopic data in Table 1. Decarbonylation of **5** allows easy access to indole-derived ligands bonded only through carbon atoms to the cluster. Thus, **5** is converted into our target molecule **3** in satisfactory yield (Scheme 3). The IR and ^{1}H NMR spectra of **3** (Table 1) confirm that it is very closely related to clusters **1**. We have also confirmed that **3**



Scheme 3



(7a) (7b)

Fig. 5. Hypothetical C,N-bonded isomers **7a** and **7b** of the C,C-bonded cluster $[Os_3H_2(\overline{C_6H_4C{=}CNH})(CO)_9]$ (**3**).

contains a fairly acidic NH group. Treatment of **3** in CD_2Cl_2 with an excess of D_2O caused no change in the ^1H NMR spectrum during 8 h. However, addition of a catalytic amount of NEt_3 induced complete exchange to give $[Os_3H_2(\overline{C_6H_4C{=}CND})(CO)_9]$ within the time required to record a spectrum; the broad singlet at δ 8.9 disappeared without any change in the other signals. No other changes occurred during 24 h.

Whereas (**1**; R = H) isomerises to **2** on heating, thermal treatment of **3** in refluxing decane over 3 h led only to some decomposition. Figure 5 shows two hypothetical molecules. Cluster **7a** is analogous to **3**, and it can be seen that the benzo-annelation would destabilise this form of bonding, in the same way that **F** (Fig. 3) is unstable. Rotation of the ligand by 60° so that the N-atom bridges two osmium atoms, instead of a carbon atom doing so, would generate **7b**, in which the benzo group incorporates a double C=C bond of the five-membered ring. Form **7b** is therefore expected to the stabilized as a result of benzo-annelation. However, neither **7a** nor **7b** are producted as isomers of **3**, and it is not clear why **7b** is not formed and why cluster **3** is so much more thermally robust than its pyrrole analogue.

Experimental

$[Os_3(CO)_{10}(MeCN)_2]$ was prepared by a published method [11]. Indole and 3-formylindole was used as purchased from Aldrich plc.

Reaction of $[Os_3(CO)_{12}]$ with indole

A refluxing solution of $[Os_3(CO)_{12}]$ (0.200 g) in refluxing decane (40 cm^3) was treated with indole (0.52 g, 20 mol/mol Os_3) for 4 h. The solvent was removed under reduced pressure, and TLC [SiO_2; eluant, light petroleum (b.p. < 40 °C)] gave three significant bands. The top band gave a trace of a nonacarbonyl cluster characterised only by its IR spectrum [ν(CO) 2102m, 2075vs, 2050vs, 2026s, 2015m, 2006s, 1984ms cm^{-1}]. The main band was recovered from an orange-yellow band and characterised as $[Os_3H_2(C_8H_6N)_2(CO)_8]$ (**4**) (0.10 g, 45%) (Found: C, 28.0; H, 1.3; N, 2.8. $C_{24}H_{14}N_2O_8Os_3$ calc: C, 28.0; H, 1.35; N, 2.7%). Crystals suitable for an crystal structure determination were obtained by slow evaporation of a heptane solution. Another very minor band near the baseline gave traces of $[Os_3H_2(C_8H_5N)$-

$(CO)_9]$ (**3**) characterised only by its $\nu(CO)$ spectrum (see below for a better synthesis).

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ *with 3-formylindole*

A suspension of the bis-acetonitrile compound (0.150 g) in cyclohexane (60 cm^3) was heated with an excess of 3-formylindole (0.25 g, 10 mol/mol Os_3) and the mixture refluxed for 3 h. The IR spectrum indicated complete reaction in this time. The solvent was removed under reduced pressure and the residue separated by TLC [SiO_2; eluant: light petroleum (b.p. $< 40\,°C$)] to give two yellow bands. One gave the acyl derivative $[Os_3H(C_9H_6NO)(CO)_{10}]$ (**5**) (0.080 g, 57%) (Found: C, 22.95; H, 0.75; N, 1.4. $C_{19}H_7NO_{11}Os_3$ calc: C, 22.9; H, 0.7; N, 1.4%) as yellow crystals and the decarbonylated compound $[Os_3H(C_8H_6N)(CO)_{10}]$ (**6**) (0.025 g, 15%) as yellow crystals.

Thermal treatment of the acyl compound 5

A solution of compound **5** (0.060 g) in n-octane (40 cm^3) was heated under reflux under nitrogen for 8 h. The IR spectrum showed extensive conversion into a nonacarbonyl species. Removal of the solvent and TLC of the residue [SiO_2; eluant: light petroleum (b.p. $< 40\,°C$)] gave one main colourless band, from which the cluster $[Os_3H_2(\mu_3\text{-}C_8H_5N)(CO)_9]$ (**3**) was isolated as colourless crystals (0.035 g, 58%). The ^1H NMR spectrum (Table 1) contained a broad singlet at δ 8.9 assigned to N*H*. Treatment of a CD_2Cl_2 solution of **3** with D_2O caused no change in the spectrum during 8 h, but addition of triethylamine (0.5×10^{-3} cm^3) resulted in complete exchange to give the N*D* compound within the time needed to record the NMR spectrum. No further exchange or isomerisation occurred during 24 h.

Thermal treatment of compound 3

This compound is indefinitely stable at room temperature in solution, and a temperature as high as that of refluxing decane was required to produce any change. During 3 h in this solvent at 174 °C there was no change in the IR spectrum. No new carbonyl products were obtained, but some decomposition was apparent from the darkening of the solution.

Crystal structure determination for $[Os_3H_2(C_8H_6N)_2(CO)_8]$ *(4)*

Data were collected from a dark yellow crystals of dimensions $0.18 \times 0.15 \times 0.34$ mm^3 on an Enraf–Nonius CAD4 diffractometer with Mo-K_α radiation. Crystal data are summarized as follows: $M = 1028.99$, monoclinic, space group $C2/c$, $a =$ 40.007(7), $b = 9.059(1)$, $c = 14.072(2)$ Å, $\beta = 96.47(1)°$, $V = 5067.6$ Å^3, $D_{calc} = 2.70$ g cm^{-3} for $Z = 8$, $\lambda(\text{Mo-}K_\alpha) = 0.71073$ Å, $\mu(\text{Mo-}K_\alpha) = 150.8$ cm^{-1}.

The total number of reflections measured was 4659 of which 4452 were unique. Data were collected using the ω-scan technique. The scan rate varied from 3.7 to 8.3 deg min^{-1} and the maximum 2θ angle was 50°. A linear decay correction and an empirical absorption correction based on a number of psi-scans were applied to the data. Lorentz and polarization corrections were also made.

The three osmium atoms were located with SHELXS-86 [12] using the Patterson method. Successive difference Fourier maps revealed the positions of all non-hydrogen atoms. The molecular structure was refined by full matrix least-squares and the function minimised was $\Sigma w(|F_0| - |F_c|)^2$ where $w = 4F_0^2/[\sigma(F_0)^2]$. Hydrogen atom positions on the indole ring were calculated, while the two hydridic hydrogens were positioned with HYDEX [8].

The final cycle of refinement, which used 165 variables and 2767 reflections with $I > 3\sigma(I)$, showed a maximum parameter shift of 0.01 times its esd, $R = 0.052$ and $R_w = 0.059$. Only heavy atoms were refined anisotropically. All calculations were carried out on a MicroVAX II computer using SDP/VAX [13].

Additional information about bond distances, bond angles, observed and calculated structure factors can be obtained from the authors.

Acknowledgements

We thank the SERC and the NSF for support and NATO for support of collaborative research.

References

1 A.J. Arce, Y. De Sanctis, and A.J. Deeming, J. Organomet. Chem., 311 (1986) 371.
2 M.W. Day, K.I. Hardcastle, A.J. Deeming, A.J. Arce, and Y. De Sanctis, Organometallics, in press.
3 A.J. Deeming, A.J. Arce, Y. De Sanctis, M.W. Day, and K.I. Hardcastle, Organometallics, submitted for publication.
4 A.J. Deeming, D. Nuel, and N.I. Powell, Organometallics, in press; R.D. Adams and J.T. Tanner, ibid., 7 (1988) 2241.
5 C. Choo Yin and A.J. Deeming, J. Chem. Soc., Dalton Trans., (1975) 2091.
6 C. Choo Yin, A.J. Deeming, M.B. Hursthouse, and N.P.C. Walker, unpublished results.
7 A.J. Deeming, Adv. Organomet. Chem., 26 (1986) 1.
8 A.G. Orpen, J. Chem. Soc., Dalton Trans., (1980) 2509.
9 A.W. Hanson, Acta Crystallogr., 17 (1964) 59.
10 A.R. Katritzky, Handbook of Heterocyclic Chemistry, Pergamon Press, Oxford, 1985.
11 B.F.G. Johnson, J. Lewis, and D.A. Pippard, J.Chem. Soc., Dalton Trans., (1981) 407.
12 G.M. Sheldrick, SHELX-86, Program for Crystal Structure Solution, University of Göttingen, 1986.
13 B.A. Frenz, Computing in Crystallography, Delft University Press, Delft, Holland, 1978, pp. 64–71.