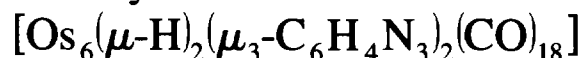


Studies of *N*-heterocyclic compounds with triosmium clusters: formation of the heterocyclic-linked dicluster compound



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Abstract

The cluster $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ reacts with indazole ($\text{C}_7\text{H}_6\text{N}_2$) to give two isomeric products $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_7\text{H}_5\text{N}_2)(\text{CO})_{10}]$ in which the five-membered ring has been metallated with N–H cleavage to give an *N,N*-bonded isomer or with C–H cleavage to give a *C,N*-bonded isomer. These two isomers have very similar X-ray structures but can be clearly distinguished by ¹H NMR methods. They are shown to correspond to related clusters derived from pyrazole. Benzotriazole ($\text{C}_6\text{H}_5\text{N}_3$) also reacts (as shown earlier by others) to give two isomers: an *N,N*-bonded species $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)(\text{CO})_{10}]$ coordinated only through the five-membered ring and a minor *C,N*-bonded isomer $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)(\text{CO})_{10}]$, metallated at the C_6 ring and coordinated through both rings. The former isomer reacts with Me_3NO in acetonitrile to give $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)(\text{CO})_9(\text{MeCN})]$ which thermally loses MeCN to produce the coupled product $[\text{Os}_6(\mu\text{-H})_2(\mu_3\text{-C}_6\text{H}_4\text{N}_3)_2(\text{CO})_{18}]$ which was shown by X-ray structure determination to have all six nitrogen atoms coordinated to osmium, a novel situation for coordinated benzotriazole. The two Os_3 units are linked together by an OsNNOsNN ring in a boat conformation with the whole cluster adopting C_2 symmetry. © 1997 Elsevier Science S.A.

Keywords: Osmium; Clusters; Indazole; Benzotriazole; Carbon–hydrogen bond activation

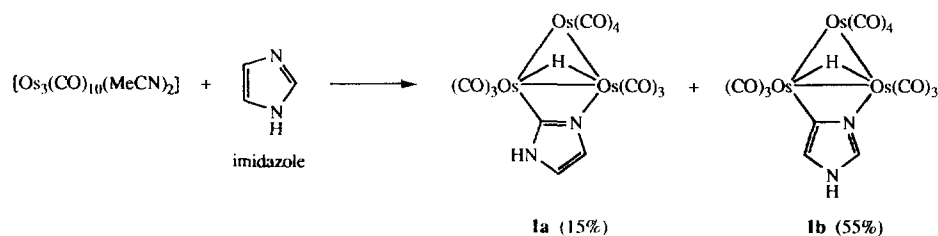
1. Introduction

The cluster $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ reacts readily with nitrogen heterocycles cleaving C–H or N–H bonds, whether or not they contain lone-pairs at nitrogen. Fundamental examples are provided by pyridine and pyrrole. Pyridine reacts rapidly with C–H cleavage to form the 2-pyridyl complex $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_5\text{H}_4\text{N})(\text{CO})_{10}]$ so that C–H cleavage competes very effectively with pyridine coordination because $[\text{Os}_3(\text{CO})_{10}(\text{py})_2]$ is not observed in this reaction [1–5]. Pyrrole having no lone-pair reacts more slowly but also metallates at the ring; *N*-methylpyrrole ($\text{C}_4\text{H}_4\text{NMe}$) gives $[\text{Os}_3(\mu\text{-H})(\mu,\eta^1\text{-C}_4\text{H}_3\text{NMe})(\text{CO})_{10}]$ by metallation at the 2-position [6,7]. However, for heterocyclic compounds containing nitrogen lone-pairs as well as pyrrole-type NH groups having no lone-pair, reaction

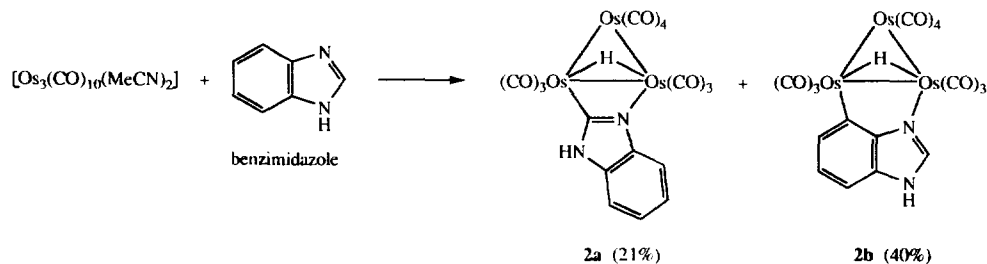
occurs preferentially at the more basic nitrogen centre. For example, imidazole reacts with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ to give two isomers **1a** and **1b** (Scheme 1) by initial coordination through the lone-pair, followed by metallation at either of the two adjacent non-equivalent CH groups [8,9]. There is some preference for one ortho site over the other. Benzimidazole (Scheme 2) has a nitrogen lone-pair with only one adjacent CH group and one might imagine there would be one product, **2a**. However, metallation at the C_6 ring can occur to give **2b** as an alternative, indeed major, product [7]. Metallation need not occur at a CH group. For example, pyrazole (Scheme 3) has a nitrogen lone-pair adjacent to CH and NH groups and metallation occurs competitively at both sites to give **3a** and **3b** with a preference for N–H bond cleavage [8].

We have now examined the reaction of indazole (Scheme 4) to compare with that of pyrazole (Scheme 3) and of 1,2,3-triazole (Scheme 5) to compare with the reported chemistry of benzotriazole (Scheme 6) [10]. In doing so we have found that, by a further CO displace-

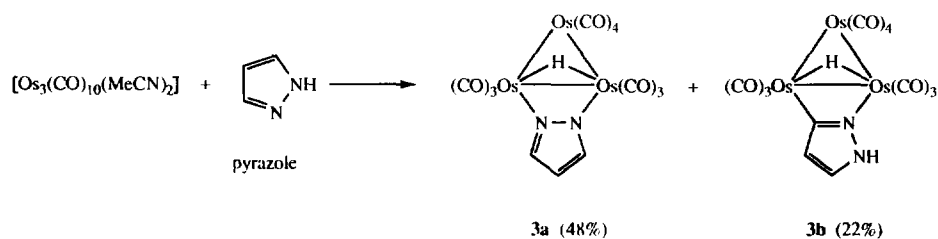
* Corresponding author.



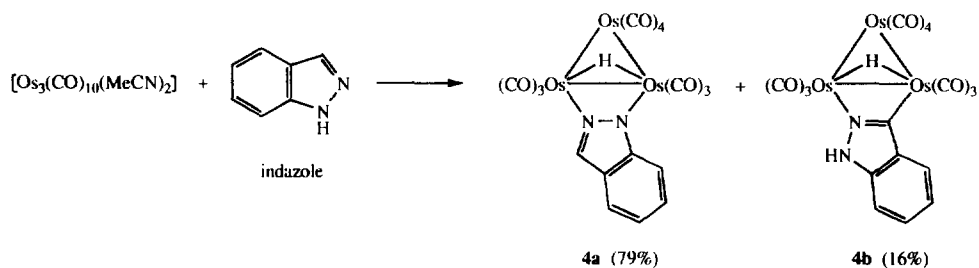
Scheme 1.



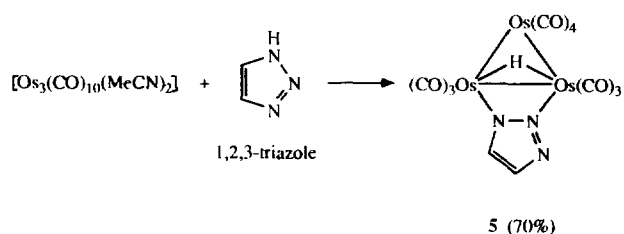
Scheme 2.



Scheme 3.



Scheme 4.

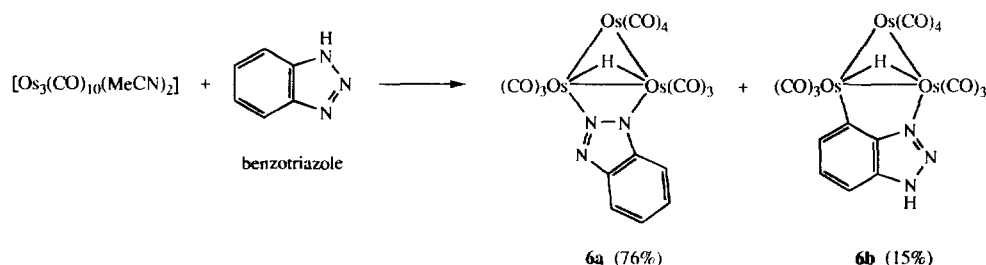


Scheme 5.

ment, clusters can be coupled by heterocyclic bridges to form Os_2N_4 rings.

2. Experimental section

The complex $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ was prepared as reported [11]. Indazole, 1,2,3-triazole and benzotriazole were used as purchased from Aldrich.



Scheme 6.

2.1. Reaction of indazole with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

A colourless solution of indazole ($\text{C}_7\text{H}_6\text{N}_2$) (0.027 g, 2.36×10^{-4} mol) in dichloromethane (10 cm^3) was added to a yellow solution of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.220 g, 2.36×10^{-4} mol) in dichloromethane (20 cm^3). The mixture was stirred at room temperature for 4 h and the solvent was removed under reduced pressure. The residue was separated by TLC (SiO_2 ; eluent: dichloromethane, petroleum ether (b.p. $< 40^\circ\text{C}$); 1:4 v/v) to give two yellow bands. These bands yielded the N,N -bonded isomer of $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_7\text{H}_5\text{N}_2)(\text{CO})_{10}]$ **4a** (79%) and the C,N -bonded isomer **4b** (16%) as yellow crystals from dichloromethane–hexane mixtures. **Compound 4a**. Anal. Found: C, 20.6; H, 0.8; N, 2.8%. $\text{C}_{17}\text{H}_6\text{N}_2\text{O}_{10}\text{Os}_3$. Calc.: C, 21.1; H, 0.6; N, 2.9%. ^1H NMR (CDCl_3 , 27°C): δ 7.90 (s, 1H, H^3), 7.54 (d, 1H, J 8.7, H^8), 7.33 (dd, 1H, J 7.7, 8.7, H^7), 7.10 (d, 1H, J 8.7, H^5), 6.98 (dd, 1H, J 7.7, 8.7, H^6), -13.22 (s, 1H, OsHOs). $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2106s, 2069vs, 2058vs, 2018vs, 1977s. **Compound 4b**. Anal. Found: C, 22.95; H, 0.9; N, 2.5%. $\text{C}_{17}\text{H}_6\text{N}_2\text{O}_{10}\text{Os}_3$. Calc.: C, 21.1; H, 0.6; N, 2.9%. ^1H NMR (CDCl_3 , 27°C): δ 9.72 (s, 1H, NH), 7.60 (d, 1H, J 9.0, H^8), 7.37 (dd, 1H, J 7.6, 9.0, H^7), 7.31 (d, 1H, J 8.2, H^5), 7.17 (dd, 1H, J 7.6, 8.2, H^6), -14.92 (s, 1H, OsHOs). $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2101m, 2059vs, 2049vs, 2013vs, 1991m, 1967s, 1947m. Crystals of **4a** and **4b** suitable for X-ray structure determination were obtained by slow evaporation of mixed dichloromethane–heptane solutions.

2.2. Reaction of 1,2,3-triazole with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

1,2,3-Triazole (0.0494 g, 7.16×10^{-4} mol) in dichloromethane (10 cm^3) was added to a solution of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.108 g, 1.16×10^{-4} mol) in dichloromethane (25 cm^3) and the mixture was stirred at room temperature for 5 h. Removal of solvent under reduced pressure and TLC separation as above gave one major yellow band which gave yellow crystals of $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_2\text{H}_2\text{N}_3)(\text{CO})_{10}]$ **5** (0.074 g, 70%) from dichloromethane–heptane. Anal. Found: C, 16.5; H, 0.35; N, 4.55%. $\text{C}_{12}\text{H}_3\text{N}_3\text{O}_{10}\text{Os}_3$. Calc.: C, 15.7; H,

0.35; N, 4.55%. ^1H NMR (CDCl_3 , 27°C): δ 7.51 (s, 1H, H^4) 7.35 (s, 1H, H^5 , $J\text{H}^4\text{H}^5$ unresolved), -13.37 (s, 1H, OsHOs). $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2110m, 2073vs, 2061vs, 2024vs, 2012s, 2002sh, 1978m.

2.3. Reaction of benzotriazole with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$

By a method similar to that of Aime et al. [10], $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.259 g, 2.78×10^{-4} mol) in dichloromethane (25 cm^3) was treated with a solution of benzotriazole (0.0350 g, 2.78×10^{-4} mol) in dichloromethane (10 cm^3). The solution was diluted to 100 cm^3 and was stirred for 2 h at room temperature. The residue after removal of solvent under reduced pressure was separated by TLC (SiO_2 ; eluent: dichloromethane–petroleum ether (b.p. $< 40^\circ\text{C}$), 1:1 v/v) to give three yellow bands yielding traces of unreacted $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$, and two isomers of $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)(\text{CO})_{10}]$ **6a** (0.204 g, 76%) and **6b** (0.042 g, 15%), each giving yellow crystals from a dichloromethane–heptane mixture. Previously reported yields were **6a** (90%) and **6b** (5%) [9]. **Compound 6a**: ^1H NMR (CDCl_3 , 27°C): δ 7.82 (d, 1H, H^5), 7.42 (dd, 1H, H^7), 7.25 (d, 1H, H^6), 7.27 (dd, 1H, H^8), -13.28 (s, 1H, OsHOs). $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2109m, 2074vs, 2061s, 2025vs, 2016vs, 2011s, 1991m, 1980m. **Compound 6b**: ^1H NMR (CDCl_3 , 27°C): δ 9.45 (br, 1H, NH), 7.81 (d, 1H, J 7.3, H^5), 7.24 (dd, 1H, J 8.4, 7.3, H^6), 7.04 (d, 1H, J 8.4), -13.82 (s, 1H, OsHOs); $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2101m, 2061vs, 2048vs, 2017vs, 2003s, 1989m, 1980w, 1967w.

2.4. Substitution of CO by MeCN in $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)(\text{CO})_{10}]$ **6a**

A yellow solution of **6a** (0.139 g, 1.43×10^{-4} mol) in acetonitrile (20 cm^3) was prepared by stirring a suspension at room temperature for 15 min under N_2 . A solution of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (0.016 g, 1.45×10^{-4} mol) in acetonitrile (12 cm^3) was then added dropwise over 10 min to the stirred solution of **6a**. The progress of the reaction was monitored over 35 min by the IR spectrum. The solution was passed through a small SiO_2 column, eluting with acetonitrile to remove the excess of amine oxide. The solvent was removed under reduced pressure

to leave a yellow residue which was separated by TLC (SiO₂; acetonitrile–dichloromethane–petroleum ether (b.p. < 40 °C), 80:5:15 by volume) to give one major yellow band which was extracted with acetonitrile and the solvent was removed to give [Os₃(μ-H)(μ-C₆H₄N₃)(CO)₉(MeCN)] **7** as a yellow solid (0.084 g, 60%). $\nu(\text{CO})/\text{cm}^{-1}$ (acetonitrile): 2110s, 2073vs, 2063vs, 2026vs, 2014vs, 1999sh, 1980s.

2.5. Treatment of [Os₃(μ-H)(μ-C₆H₄N₃)(CO)₉ MeCN] **7** in cyclohexane

A suspension of compound **7** (0.084 g, 8.9 × 10⁻⁵ mol) in cyclohexane (80 cm³) was gently warmed to about 40 °C to give a solution which was stirred at room temperature for 30 min. The grey-brown solution was then refluxed for 30 min. Removal of solvent under reduced pressure and extraction of the residue with dichloromethane gave a yellow-brown solution which was separated by TLC (SiO₂; dichloromethane–petroleum ether (b.p. < 40 °C), 2:3 v/v) to give one major

yellow band. The CH₂Cl₂ extract was evaporated to a low volume and petroleum ether (b.p. < 40 °C) was added to give yellow crystals (0.067 g, 80%) of [Os₆(μ-H)₂(μ₃-C₆H₄N₃)₂(CO)₁₈] **8**. Most of the sample was microcrystalline, but a few crystals were found to be suitable for single-crystal X-ray analysis. ¹H NMR (CDCl₃, 27 °C): δ 7.89 (dd, 1H, H⁵), 7.44 (dt, 1H, H⁷), 7.34 (d, 1H, H⁶), 7.26 (d, 1H, H⁸), -13.82 (s, 1H, OsHOs); $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2101w, 2094m, 2060vs, 2021vs, 1999m, 1937w.

2.6. Crystal structure determinations for compounds **4a**, **4b** and **8**

Table 1 lists the crystal data for each compound, together with details of the intensity data collections and the structure solutions and refinements. All data were collected at 20 °C using a Nicolet R3V/m diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarisation effects and for absorption based on Ψ -scans. Instrument and

Table 1
Details of crystal data, data collection and refinement for compounds **4a**, **4b**, and **8**^a

Compound	4a	4b	8
Formula	C ₁₇ H ₆ N ₂ O ₁₀ Os ₃	C ₁₇ H ₆ N ₂ O ₁₀ Os ₃	C ₃₀ H ₁₀ N ₆ O ₁₈ Os ₆
<i>M</i> /g mol ⁻¹	968.85	968.85	1883.66
Colour	yellow	yellow	yellow
Size/mm ³	0.20 × 0.25 × 0.38	0.15 × 0.20 × 0.35	0.03 × 0.30 × 0.35
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	8.905(2)	8.841(4)	32.907(9)
<i>b</i> /Å	15.852(5)	15.740(9)	14.811(5)
<i>c</i> /Å	16.481(4)	16.630(7)	23.868(5)
α /deg	86.78(2)	86.02(4)	90
β /deg	79.19(2)	79.79(4)	128.20(2)
γ /deg	76.99(2)	77.57(4)	90
<i>V</i> /Å ³	2226(1)	2223(2)	9139(5)
<i>Z</i>	4	4	8
<i>D</i> _c /g cm ⁻³	2.89	2.90	2.74
μ (Mo Kα)/cm ⁻¹	171.6	171.8	167.0
<i>F</i> (000)	1720	1720	6656
No. of orientation reflections; 2θ range (eg)	28; 9 ≤ 2θ ≤ 24	25; 11 ≤ 2θ ≤ 20	35; 11 ≤ 2θ ≤ 25
Scan mode	ω -2θ	ω -2θ	ω
<i>hkl</i> range	0, -19, -20 to 11,19,20	0, -19, -20 to 11,19,20	0,0, -18 to 24,11,18
Total data	8289	8211	8291
Unique data	7758	7680	7818
Rejection criterion	<i>I</i> ₀ ≤ 3σ(<i>I</i> ₀)	<i>I</i> ₀ ≤ 3σ(<i>I</i> ₀)	<i>I</i> ₀ ≤ 4σ(<i>I</i> ₀)
Reflections used	4952	4511	3640
Parameters	577	317	271
<i>R</i> ^b	0.058	0.059	0.075
<i>R</i> _w ^c	0.059	0.061	0.071
<i>g</i> in weighting scheme $w = [\sigma^2(F) + gF^2]$	0.000974	0.00130	0.00050
Max. shift/e.s.d.	0.011	0.001	0.004
Max. peak in final diff. Fourier/e ⁻ Å ⁻³	3.45	3.05	3.08

^a Data collected on a Nicolet R3V/m diffractometer at 20 °C using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the range 5 ≤ 2θ ≤ 50°. Corrections for Lorentz and polarisation effects and for absorption (ψ -scan methods).

^b $R = \sum [F_o - F_c] / \sum F_o$.

^c $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$.

Table 2
Fractional atomic coordinates ($\times 10^4$) for the compound **4a**

	x	y	z
Os(1)	2097(1)	3627(1)	6228(1)
Os(2)	1393(1)	2197(1)	7364(1)
Os(3)	-612(1)	2933(1)	6213(1)
N(1)	3514(20)	2402(11)	5848(12)
N(2)	3211(23)	1736(12)	6368(12)
C(1)	4257(31)	1027(14)	6141(15)
C(71)	4854(33)	2100(15)	5258(16)
C(72)	5364(29)	1190(18)	5427(17)
C(73)	6755(31)	753(22)	4979(21)
C(74)	7546(46)	1114(27)	4383(21)
C(75)	7066(34)	2045(22)	4201(16)
C(76)	5735(28)	2509(18)	4636(14)
C(11)	818(28)	4363(16)	6719(14)
O(11)	150(24)	5325(11)	6983(12)
C(12)	3946(31)	4050(16)	6313(13)
O(12)	5042(22)	4314(13)	6338(15)
C(13)	1948(27)	4043(15)	5134(15)
O(13)	1843(28)	4293(14)	4472(12)
C(21)	-208(32)	2667(20)	8229(17)
O(21)	-1223(28)	3014(18)	8771(13)
C(22)	2878(35)	1776(18)	8095(14)
O(22)	3643(31)	1550(17)	8545(14)
C(23)	625(35)	1117(23)	7384(17)
O(23)	125(30)	537(15)	7404(18)
C(31)	676(45)	2014(13)	5469(18)
O(31)	1422(28)	1489(13)	5043(14)
C(32)	-1700(33)	3813(19)	7022(17)
O(32)	-2362(27)	4363(15)	7458(14)
C(33)	-1495(29)	3573(18)	5297(17)
O(33)	-1974(25)	3943(14)	4761(12)
C(34)	-2214(33)	2282(23)	6586(19)
O(34)	-3219(32)	1967(19)	6853(18)
Os(4)	5504(1)	1985(1)	624(1)
Os(5)	2446(1)	1559(1)	1249(1)
Os(6)	3719(1)	2598(1)	2204(1)
N(3)	3715(22)	2768(12)	81(12)
N(4)	2344(24)	2582(12)	382(12)
C(2)	1169(32)	3133(17)	37(14)
C(81)	3515(30)	3445(13)	-475(13)
C(82)	1855(31)	3713(19)	-509(17)
C(83)	1278(44)	4389(22)	-996(20)
C(84)	2372(36)	4782(17)	-1461(19)
C(85)	4054(36)	4508(20)	-1458(20)
C(86)	4562(29)	3847(16)	-963(16)
C(41)	6933(30)	1202(24)	1150(20)
O(41)	7912(29)	701(16)	1416(17)
C(42)	6548(27)	2913(18)	677(17)
O(42)	7194(26)	3441(15)	699(15)
C(43)	6536(30)	1585(21)	-485(16)
O(43)	7191(29)	1308(19)	-1068(15)
C(51)	2760(38)	627(22)	1995(17)
O(51)	3076(37)	33(15)	2442(18)
C(52)	1769(38)	877(23)	473(20)
O(52)	1351(36)	525(19)	59(15)
C(53)	378(60)	2039(24)	1836(19)
O(53)	-837(31)	2270(22)	2221(17)
C(61)	2815(45)	3629(22)	1598(15)
O(61)	2257(30)	4265(14)	1292(12)
C(62)	4858(39)	1501(16)	2684(15)
O(62)	5481(36)	924(16)	2962(15)
C(63)	4968(33)	3295(15)	2602(15)

Table 2 (continued)

	x	y	z
O(63)	5691(29)	3701(14)	2841(14)
C(64)	2037(39)	2710(18)	3147(15)
O(64)	950(31)	2789(16)	3644(13)

crystal stabilities were checked by measuring three standard reflections periodically; only minor variations of intensities were observed and corrections were made for these.

Structures were determined by direct methods in the space groups given. Structure **4a**: all non-H atoms were refined anisotropically and H-atoms were included in the model in idealised positions riding on the carbon atoms with C–H distances fixed at 0.96 Å and thermal parameters at 0.08 Å³. Structure **4b**: non-H atoms, except for those of the CO ligands and the C₆ rings, were refined anisotropically; H-atoms were treated as above. Structure **8**: only the metal atoms were refined anisotropically and H-atoms were treated as above. Hydride ligands were not included in any of the models.

All calculations were carried out using a MicroVax II computer running SHELXTL-PLUS [12]. Fractional atomic coordinates for **4a**, **4b** and **8** are given in Tables 2–4 respectively. Additional material is available from the Cambridge Crystallographic Data Centre, comprising thermal parameters and full tables of bond lengths and angles.

3. Results and discussion

3.1. Reaction of [Os₃(CO)₁₀(MeCN)₂] with indazole

Indazole reacts smoothly with [Os₃(CO)₁₀(MeCN)₂] (1 mol indazole/mol Os₃) in dichloromethane at room temperature over several hours to give two yellow air-stable products, **4a** (79%) and **4b** (16%), which were separated by TLC (Scheme 4). ¹H NMR resonances for four protons at the C₆ ring were observed for both isomers. Metallation at the C₆ ring as observed for benzimidazole (Scheme 2) has not occurred [8]. Note that this is possible for benzimidazole because there is a nitrogen lone-pair adjacent to the C₆ ring, whereas indazole has the lone-pair away from the six-membered ring. Indazole (**A**) could only react like benzimidazole through its unstable tautomer (**B**) in Fig. 1, but apparently reaction occurs as expected through (**A**). Preliminary coordination through the lone-pair of (**A**) would allow metallation at an adjacent CH or NH group and apparently both occur to give the isomers **4a** and **4b**. The structural assignments of **4a** and **4b** were primarily

Table 3
Fractional atomic coordinates ($\times 10^4$) for the compound **4b**

	x	y	z
Os(1)	2955(1)	6344(1)	3755(1)
Os(2)	3646(1)	7797(1)	2588(1)
Os(3)	5710(1)	7073(1)	3733(1)
C(1)	1568(28)	7567(16)	4094(14)
N(1)	1879(25)	8196(14)	3594(14)
N(2)	806(29)	8987(17)	3778(13)
C(71)	128(32)	7944(19)	4712(17)
C(72)	-215(34)	8813(20)	4466(18)
C(73)	-1650(40)	9389(25)	4874(21)
C(74)	-2483(39)	8992(23)	5476(20)
C(75)	-2154(39)	8122(23)	5716(21)
C(76)	-830(35)	7586(21)	5363(18)
C(11)	4202(32)	5252(19)	3312(17)
O(11)	4864(24)	4623(15)	3021(13)
C(12)	1082(33)	5987(19)	3669(17)
O(12)	19(29)	5671(17)	3656(15)
C(13)	3035(33)	5983(22)	4835(20)
O(13)	3112(27)	5718(16)	5530(15)
C(21)	5298(35)	7297(20)	1733(19)
O(21)	6183(32)	7002(18)	1201(17)
C(22)	2118(38)	8199(22)	1850(20)
O(22)	1386(29)	8445(17)	1402(16)
C(23)	4485(37)	8774(22)	2537(19)
O(23)	4998(28)	9440(17)	2541(15)
C(31)	4475(35)	8010(21)	4437(19)
O(31)	3753(30)	8571(18)	4858(16)
C(32)	6741(36)	6133(21)	2989(19)
O(32)	7379(31)	5632(18)	2554(17)
C(33)	6437(36)	6458(22)	4658(20)
O(33)	6953(26)	6074(15)	5213(14)
C(34)	7328(36)	7748(21)	3375(19)
O(34)	8371(28)	8055(16)	3101(15)
Os(4)	9400(1)	8070(1)	-667(1)
Os(5)	12563(1)	8439(1)	-1277(1)
Os(6)	11149(2)	7470(1)	-2243(1)
C(2)	11202(34)	7209(17)	-168(16)
N(3)	12650(25)	7349(14)	-445(13)
N(4)	13766(29)	6823(18)	-64(14)
C(81)	11404(34)	6524(20)	468(18)
C(82)	13078(33)	6252(19)	454(17)
C(83)	13787(40)	5585(22)	929(20)
C(84)	12768(42)	5130(25)	1440(22)
C(85)	11042(39)	5388(23)	1462(21)
C(86)	10369(41)	6027(22)	977(20)
C(41)	8022(43)	9006(25)	-1182(22)
O(41)	7082(35)	9491(20)	-1465(18)
C(42)	8431(37)	8447(22)	370(20)
O(42)	7831(33)	8647(19)	1031(18)
C(43)	8242(37)	7243(22)	-658(19)
O(43)	7367(31)	6737(18)	-687(16)
C(51)	12152(36)	9423(22)	-1992(19)
O(51)	11833(35)	10035(21)	-2432(19)
C(52)	13416(42)	9028(25)	-510(23)
O(52)	13839(36)	9383(21)	-95(19)
C(53)	14593(43)	7964(25)	-1895(22)
O(53)	15837(34)	7699(19)	-2269(17)
C(61)	12157(33)	6413(20)	-1653(17)
O(61)	12758(30)	5787(18)	-1375(16)
C(62)	10083(38)	8532(23)	-2702(20)
O(62)	9398(31)	9183(18)	-2985(16)
C(63)	9836(41)	6836(24)	-2625(22)

Table 3 (continued)

	x	y	z
O(63)	8995(28)	6435(16)	-2834(15)
C(64)	12841(36)	7338(21)	-3168(19)
O(64)	13859(32)	7273(18)	-3702(17)

based on ^1H NMR data; the signals for the remaining H atoms at the five-membered rings are singlets at δ 7.90 for **4a** and δ 9.72 for **4b** which are best assigned to CH and NH respectively. Furthermore, **4a** and **4b** closely relate to pyrazole derivatives **3a** and **3b** and the ^1H NMR hydride shifts correspond closely: **4a** δ -13.22, **3a** δ -13.47 and **4b** δ -14.92, **3b** δ -15.05. Therefore the major product (79%) is the *N,N*-bonded isomer **4a** derived by N-H bond cleavage and the minor *C,N*-bonded isomer (16%) **4b** is the result of C-H cleavage. N-H bond cleavage is preferred and the product ratio **4a/4b** (4.94) compared with **3a/3b** (2.18) indicates that there is a greater preference for NH vs. CH activation for indazole than for pyrazole.

Since **4a** and **4b** only differ in the positions of carbon and nitrogen atoms we decided to determine the crystal structures of each to look for structural differences between the *N,N*- and the *C,N*-bonded isomers. In imidazole-derived clusters of this type it is understandable that there have been problems associated with disorder [8,9], but the benzo groups in **4a** and **4b** would make this less likely and this was found to be so. The molecular structures of **4a** and **4b** are shown in Figs. 2 and 3 respectively, and selected lengths and angles are in Table 5 Both crystals are triclinic with closely similar cell parameters and indistinguishable cell volumes (Table 1). Unfortunately, the quality of the crystals and the derived structural data are quite low and it was not possible to detect any significant differences between the two structures. While our conclusions from spectroscopy were confirmed, little other useful information was derived from these structures.

3.2. Reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with 1,2,3-triazole

A single product **5** (70%) was obtained from this reaction at room temperature. Traces of another cluster, possibly an isomer of **5**, were formed but in such low quantities that it could not be characterised. Two sharp ^1H NMR signals for **5** at δ 7.51 and 7.35 indicate that these correspond to CH rather than NH groups and that the structure of **5** is that shown in Scheme 5. It could be that initial coordination of 1,2,3-triazole through the central N atom is preferred and this would allow N-H but not C-H bond cleavage.

Table 4
Fractional atomic coordinates ($\times 10^4$) for the compound **8**

	<i>x</i>	<i>y</i>	<i>z</i>
Os(1)	2004(1)	8556(1)	287(1)
Os(2)	1742(1)	9807(1)	983(1)
Os(3)	1300(1)	8044(1)	558(1)
N(1)	1471(13)	9510(18)	-435(19)
N(2)	1373(11)	10147(16)	-108(15)
N(3)	1076(13)	10863(18)	-620(18)
C(71)	1256(16)	9812(22)	-1099(22)
C(72)	1023(16)	10673(21)	-1170(22)
C(73)	775(15)	11163(21)	-1828(21)
C(74)	719(21)	10701(29)	-2374(30)
C(75)	986(20)	9904(29)	-2257(29)
C(76)	1256(18)	9372(27)	-1617(26)
C(11)	2515(18)	7771(25)	1040(26)
O(11)	2819(14)	7264(20)	1402(20)
C(12)	1693(16)	7658(22)	-421(22)
O(12)	1498(14)	7078(20)	-812(19)
C(13)	2461(22)	9096(28)	125(30)
O(13)	2748(15)	9321(21)	27(21)
C(21)	2181(23)	9374(31)	1924(33)
O(21)	2460(14)	9239(19)	2519(21)
C(22)	1311(22)	10113(31)	1148(31)
O(22)	991(17)	10175(24)	1275(23)
C(31)	757(20)	8702(28)	-288(28)
O(31)	388(16)	9012(21)	-835(22)
C(32)	1847(20)	7547(27)	1395(28)
O(32)	2198(14)	7212(18)	1932(19)
C(33)	1080(21)	6924(31)	85(29)
O(33)	963(13)	6212(18)	-202(18)
C(34)	928(22)	8036(31)	904(32)
O(34)	667(16)	7993(24)	1120(23)
Os(4)	1609(1)	13604(1)	82(1)
Os(5)	943(1)	12050(1)	-222(1)
Os(6)	899(1)	13650(1)	405(1)
N(4)	2029(12)	12605(16)	872(17)
N(5)	1740(13)	11812(17)	690(18)
N(6)	2047(15)	11117(19)	1114(20)
C(81)	2527(16)	12341(22)	1373(22)
C(82)	2529(18)	11408(26)	1494(25)
C(83)	3021(20)	10978(27)	2025(27)
C(84)	3442(29)	11504(38)	2276(37)
C(85)	3451(22)	12427(32)	2156(30)
C(86)	2995(17)	12898(25)	1690(24)
C(41)	2113(19)	13486(26)	-71(27)
O(41)	2425(17)	13554(23)	-194(22)
C(42)	1902(22)	14542(31)	697(31)
O(42)	2128(14)	15195(20)	1110(19)
C(43)	1175(21)	14388(29)	-734(30)
O(43)	970(16)	14817(22)	-1195(22)
C(51)	311(21)	12382(28)	-1089(30)
O(51)	-55(14)	12583(19)	-1668(20)
C(52)	529(20)	11469(28)	-55(27)
O(52)	259(16)	11150(21)	44(22)
C(61)	1394(16)	13009(23)	1278(23)
O(61)	1672(14)	12632(21)	1805(20)
C(62)	370(20)	14189(28)	-533(29)
O(62)	92(18)	14506(26)	-1070(26)
C(63)	376(24)	13282(32)	457(32)
C(64)	999(26)	14739(37)	844(36)
O(64)	1151(19)	15455(28)	1208(26)
O(63)	69(17)	13028(24)	483(23)

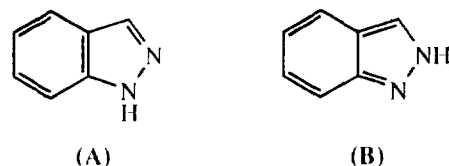


Fig. 1. Stable tautomer (A) and less stable tautomer (B) of indazole.

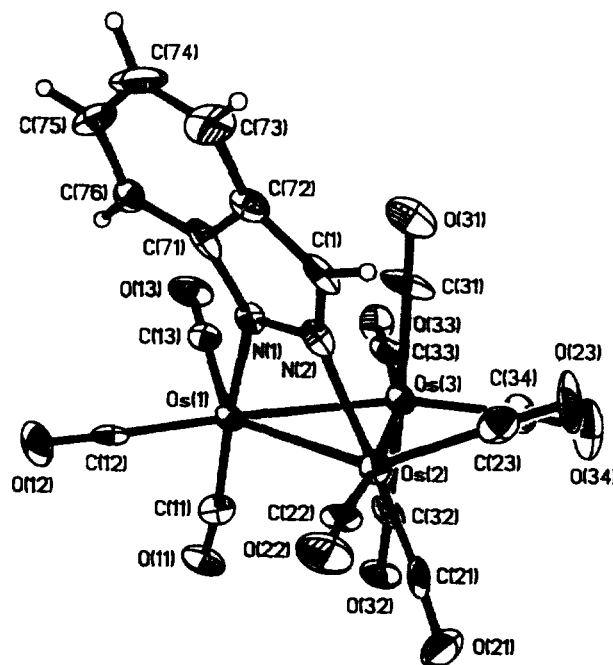


Fig. 2. Molecular structure of the *N,N*-bonded isomer $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_7\text{H}_5\text{N}_2)(\text{CO})_{10}]$ **4a** from indazole.

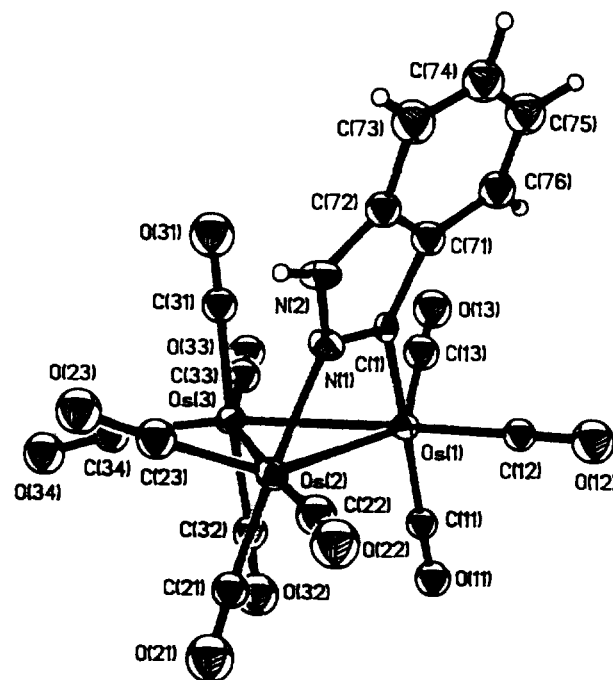


Fig. 3. Molecular structure of the *C,N*-bonded isomer $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_7\text{H}_5\text{N}_2)(\text{CO})_{10}]$ **4b** from indazole.

Table 5
Selected bond lengths (Å) and angles (deg) for compounds **4a** and **4b**

Compound 4a (<i>N,N</i> -bonded isomer)		Compound 4b (<i>N,C</i> -bonded isomer)	
Os(1)–Os(2)	2.959(2)	Os(1)–Os(2)	2.989(2)
Os(1)–Os(3)	2.873(2)	Os(1)–Os(3)	2.902(2)
Os(2)–Os(3)	2.867(2)	Os(2)–Os(3)	2.878(2)
Os(1)–N(1)	2.12(2)	Os(1)–C(1)	2.10(2)
Os(2)–N(2)	2.11(2)	Os(2)–N(1)	2.10(2)
N(1)–C(71)	1.40(3)	C(1)–C(71)	1.53(3)
N(1)–N(2)	1.36(3)	N(1)–C(1)	1.29(3)
N(2)–C(1)	1.31(3)	N(1)–N(2)	1.41(3)
C(1)–C(72)	1.44(4)	N(2)–C(72)	1.38(4)
Os(2)–Os(1)–Os(3)	58.9(1)	Os(2)–Os(1)–Os(3)	58.5(1)
Os(1)–Os(3)–Os(2)	62.1(1)	Os(1)–Os(3)–Os(2)	62.3(1)
Os(1)–Os(2)–Os(3)	59.1(1)	Os(1)–Os(2)–Os(3)	59.3(1)
Os(3)–Os(1)–N(1)	88.4(5)	Os(3)–Os(1)–C(1)	88.1(7)
Os(3)–Os(2)–N(2)	89.7(6)	Os(3)–Os(2)–N(1)	89.0(6)

Table 6
Selected bond lengths (Å) and angles (deg) for compound **8**

Os(1)–Os(2)	2.951(3)	Os(4)–Os(5)	2.944(3)
Os(1)–Os(3)	2.866(4)	Os(4)–Os(6)	2.880(4)
Os(2)–Os(3)	2.852(2)	Os(5)–Os(6)	2.854(3)
Os(1)–N(1)	2.07(3)	Os(4)–N(4)	2.10(3)
Os(2)–N(2)	2.15(3)	Os(5)–N(5)	2.16(3)
Os(2)–N(6)	2.12(3)	Os(5)–N(3)	2.17(4)
N(1)–N(2)	1.38(6)	N(4)–N(5)	1.40(4)
N(2)–N(3)	1.45(4)	N(5)–N(6)	1.36(4)
Os(3)–Os(1)–N(1)	89(1)	Os(6)–Os(4)–N(4)	88(1)
Os(3)–Os(2)–N(2)	90.1(6)	Os(6)–Os(5)–N(5)	91.8(9)
N(2)–Os(2)–N(6)	80(1)	N(3)–Os(5)–N(5)	82(1)
Os(2)–N(2)–N(3)	141(3)	Os(5)–N(5)–N(6)	139(2)
Os(2)–N(6)–N(5)	121(2)	Os(5)–N(3)–N(2)	116(3)

3.3. Reactions of benzotriazole

We confirm the earlier results of Aime et al. [10] that benzotriazole reacts with $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ to give the isomeric products **6a** and **6b** and, although our yields are somewhat different, we confirm that **6a** is the major product. Cluster **6a** is derived by initial coordination through the central nitrogen atom, followed by N–H bond activation; cluster **6b** by coordination through the nitrogen lone-pair next to the benzo ring, allowing C–H activation in that ring to follow.

Having coordinated benzotriazole in **6a** and **6b** we examined ways to exploit the remaining nitrogen lone-pair for further coordination. Treatment of **6a** with $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ in acetonitrile gave a product in which CO has been substituted by MeCN: $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)(\text{CO})_9(\text{MeCN})]$ **7**. This synthesis corresponds to the formation of other compounds of the type $[\text{Os}_3(\mu\text{-H})(\mu\text{-X})(\text{CO})_9(\text{MeCN})]$ [13]. Compound **7** is moderately stable at room temperature, but on refluxing in cyclohexane for 30 min acetonitrile is displaced and the product $[\text{Os}_6(\mu\text{-H})_2(\mu\text{-C}_6\text{H}_4\text{N}_3)_2(\text{CO})_{18}]$ **8** is formed. There is very little change in the ^1H NMR spectrum of **8** compared with that of **6a**: signals at

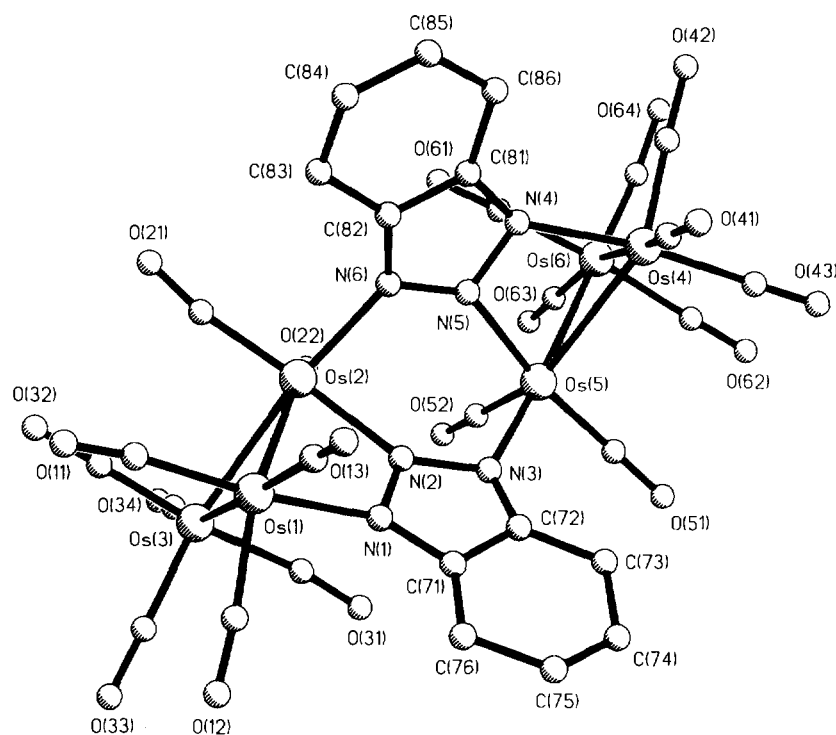


Fig. 4. Molecular structure of $[\text{Os}_6(\mu\text{-H})(\mu\text{-C}_6\text{H}_4\text{N}_3)_2(\text{CO})_{18}]$ **8**.

δ 7.82, 7.42, 7.27, 7.25, -13.28 for **6a** are replaced by ones at δ 7.89, 7.44, 7.34, 7.26 and -13.82 for **8**. Although **8** does not contain an acetonitrile ligand, little seems to have happened to the metallated benzotriazole ligand. The dimeric nature and structure of **8** were established by X-ray diffraction; the molecular structure is shown in Fig. 4 and selected bond lengths and angles in Table 6. The course of the reaction is shown in Scheme 7. By analogy with earlier reports on related MeCN complexes [13], we assume a CO ligand of one of the $\text{Os}(\text{CO})_3$ units has been replaced. This would be consistent with the structure of **8** in which an N atom of one $\mu\text{-C}_6\text{H}_4\text{N}_3$ ligand coordinates to the other cluster in the site from which CO has been displaced. The six-membered OsNNOsNN ring holding the two Os_3 clusters together adopts a boat configuration. The ring is folded along the $\text{Os}(2)\text{Os}(5)$ axis such that the dihedral angle between the $\text{Os}(2)\text{Os}(5)\text{N}(5)\text{N}(6)$ and the $\text{Os}(2)\text{Os}(5)\text{N}(2)\text{N}(3)$ planes is 113.8° . The pictures of **8** in Scheme 7 and in Fig. 4 do not show the boat arrangement of this ring; this is best depicted in Fig. 5 which gives two views of the cluster core. The two Os_3 triangles are closely parallel with a 4.7° dihedral angle between them. However, there is a 99.1° dihedral angle between the two ligand planes. Although the two cluster moieties are crystallographically independent, the molecule has C_2 symmetry and hence the cluster is chiral. The two Os_3 sets of atoms with their associated CO ligands do not approach very closely; the nearest contact except through the benzotriazole bridges is

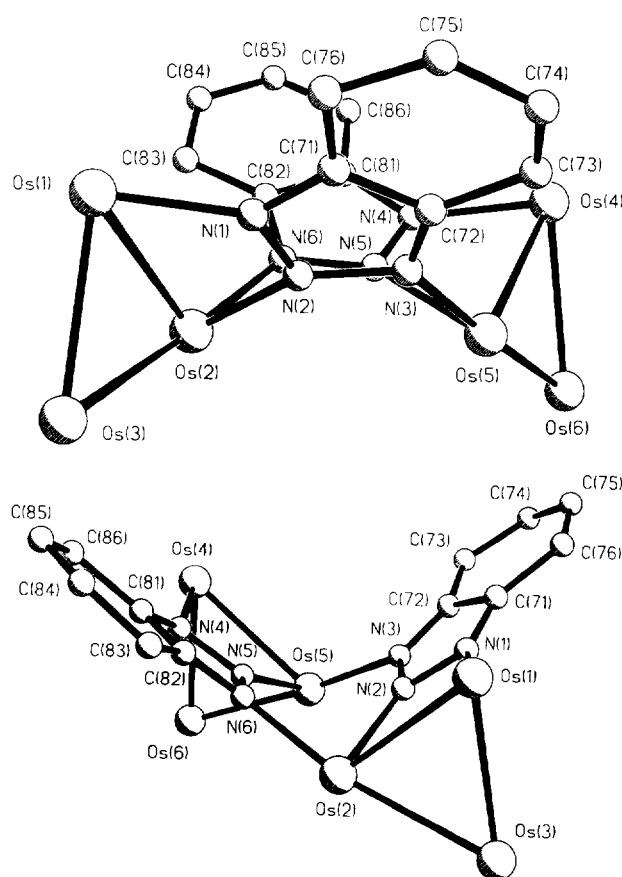
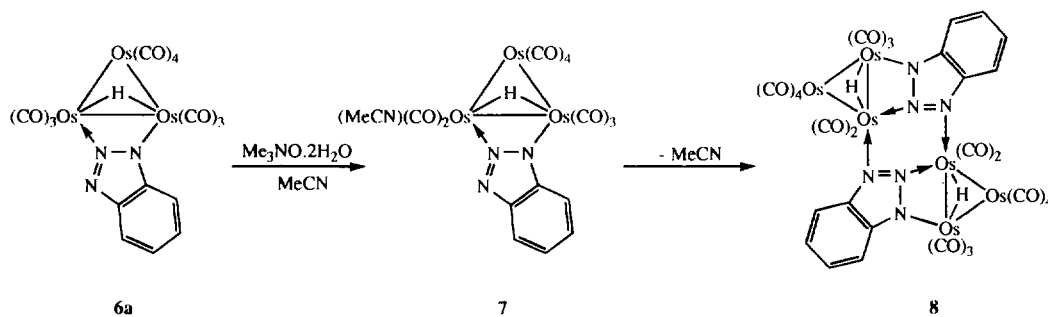
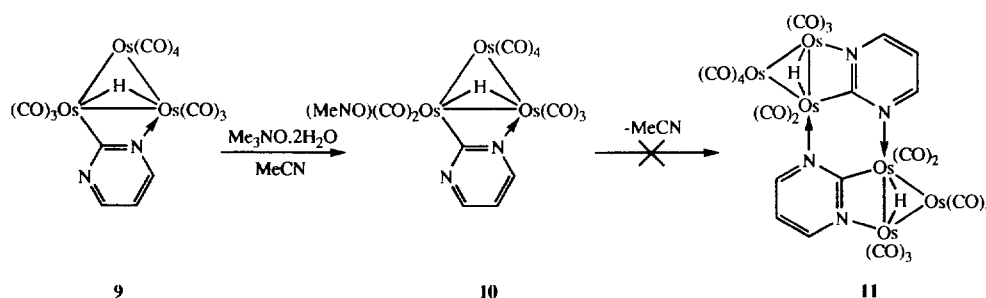


Fig. 5. Two views of the central core of the dinuclear cluster system $[\text{Os}_6(\mu\text{-H})(\mu_3\text{-C}_6\text{H}_4\text{N}_3)_2(\text{CO})_{18}]$ **8**.



Scheme 7.



Scheme 8.

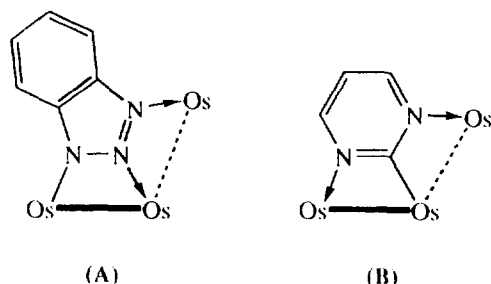


Fig. 6. A possible reason for the formation of $[\text{Os}_6(\mu\text{-H})(\mu_3\text{-C}_6\text{H}_4\text{N}_3)_2(\text{CO})_{18}]$ **8** but not $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-C}_4\text{H}_3\text{N}_2)(\text{CO})_{18}]$ **11**. The six-membered heterocyclic ring requires a closer approach between the Os atoms (and their associated CO ligands) of the different Os_3 subunits, indicated by the broken line.

$\text{O}(22) \cdots \text{O}(52)$ (2.787 \AA) and the shortest $\text{Os} \cdots \text{Os}$ distance between clusters is $\text{Os}(2) \cdots \text{Os}(5)$ (4.107 \AA). This distant relationship between the component clusters is largely the result of the large angles at the five-membered heterocycle: $\text{Os}(2)\text{-N}(2)\text{-N}(3)$, $141(3)^\circ$ and $\text{Os}(5)\text{-N}(5)\text{-N}(6)$, $139(2)^\circ$.

We have tried to make dimeric clusters of the type **8** with other heterocyclic ligand systems. For example, we synthesised the cluster $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{N}_2)(\text{CO})_{10}]$ **9** from 1,3-diazine (pyrimidine) and from this the acetonitrile derivative $[\text{Os}_3(\mu\text{-H})(\mu\text{-C}_4\text{H}_3\text{N}_2)(\text{CO})_9(\text{MeCN})]$ **10** was prepared (Scheme 8). However, treatment of **10** in refluxing cyclohexane led only to **9** with some decomposition. No evidence for a dimeric cluster **11** was found. We believe that the likely reason is that the coordination angles in the six-membered ring make the formation of the OsNNOsNN ring less favourable. In Fig. 6 we have shown how the formation of **11** would produce a rather closer approach

of the two Os_3 subunits than in **8**. We believe this makes the formation of **8** unfavourable.

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