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Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 7-azaindole (L); molecular structures of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ and $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}L)]$

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The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 1 equivalent of 7-azaindole (HL) in CH_2Cl_2 at room temperature led to two structural isomers (**1a** and **1b**) of formula $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$; both in 25% yield. A minor product, $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}L)]$ **2** was also isolated in 10% yield. The compounds were characterised by IR, ^1H NMR, elemental analysis and structurally by single-crystal X-ray analyses. The co-ordinating 7-azaindole bridges along an edge of the triosmium triangle with both nitrogen atoms bound to two osmium atoms in complex **1a**. However, it was found to be orthometallated in complex **1b**. The pyridinic and pyrrolic nitrogen atoms co-ordinate to the osmium triangle in a μ_3-η^2 fashion in complex **2**. Formation of **2** from **1a** was achieved by thermal, chemical and photochemical means.

Reactions of nitrogen heterocycles with triosmium clusters have been intensively studied over the last two decades.[1–3] Examples of these include imidazoles,[4] 1,8-naphthyridine[5] and 7-azaindole[6] which act as bidentate ligands and afford structurally interesting complexes. Some of these are also potential catalysts for industrial applications.[7] In this paper, the reaction of the activated triosmium cluster $[Os_3(CO)_{10}(NCMe)_2]$ with 7-azaindole (HL) is described. This nitrogen heterocycle is of interest because it exhibits several co-ordination modes on the triosmium framework which may include bridging across metal–metal bonds or across two non-bonded metal atoms as manifested in dimolybdenum[8] and dirhodium[7] complexes as well as in a number of triruthenium clusters.[9]

Experimental

General procedures

All manipulations were carried out under a dinitrogen atmosphere using standard Schlenk techniques, unless stated otherwise. Solvents were purified and distilled from the appropriate drying agents and stored under dinitrogen prior to use. Products were separated by thin layer chromatography (TLC) on silica gel (type 60) GF_{254} Merck 7730 in air.

Instrumentation

Infrared spectra were recorded on a Bio-Rad FTS-7 IR spectrometer in CH_2Cl_2; ^1H NMR spectra were recorded in CD_2Cl_2 or $CDCl_3$ on a Bruker DPX 300 FT-NMR spectrometer with $SiMe_4$ as internal reference. Mass spectra were recorded on a Finnigan MAT 95 spectrometer with fast atom bombardment techniques. The photolysis experiment was conducted with an Oriel 68811 200 W mercury xenon arc lamp supply.

Reagents

The compound $[Os_3(CO)_{10}(NCMe)_2]$ was prepared according to a published procedure.[10] 7-Azaindole was used as purchased (Aldrich) and trimethylamine *N*-oxide (Me_3NO) was sublimed immediately prior to use.

Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 7-azaindole

A solution of $[Os_3(CO)_{10}(NCMe)_2]$ (100 mg, 0.11 mmol) in CH_2Cl_2 (25 cm^3) was stirred with 7-azaindole (12.6 mg, 0.11 mmol) at room temperature for 1.5 h. The solvent was then removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (*ca.* 2 cm^3) and separated by preparative TLC using the eluent CH_2Cl_2–*n*-hexane (1 : 2 v/v) to give four yellow bands. The first band ($R_f \approx 0.75$) was isolated as $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ **1a** in 25% yield while the second band ($R_f \approx 0.6$) was isolated as $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}L)]$ **2** in 10% yield. The third band was shown to be $[Os_3(CO)_{10}(NCMe)_2]$ ($R_f \approx 0.5$, 15%) by IR spectroscopy. The fourth product ($R_f \approx 0.4$) $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ **1b** was isolated in 25% yield. Complexes **1a**, **1b** and **2** crystallised overnight from CH_2Cl_2–*n*-hexane at room temperature to give yellow crystals (Found for **1a**: C, 21.15; H, 0.6; N, 2.8. Calc. for $C_{17}H_6N_2O_{10}Os_3$: C, 21.05; H, 0.5; N, 3.0. **1b**: C, 21.0; H, 0.65; N, 2.8. Calc. for $C_{17}H_6N_2O_{10}Os_3$: C, 21.05; H, 0.5; N, 3.0. **2**: C, 20.55; H, 0.7; N, 2.75. Calc. for $C_{16}H_6N_2O_9Os_3$: C, 20.5; H, 0.65; N, 2.8%).

Thermolysis of $[Os(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ 1a

A suspension of **1a** (0.1 g, 0.10 mmol) in freshly distilled *n*-heptane (98 °C) was refluxed under an inert atmosphere. The reaction was monitored by IR spectroscopy and was completed in 1 d. The solvent was removed *in vacuo* and the residue was redissolved in CH_2Cl_2 (*ca.* 2 cm^3). Purification by TLC using CH_2Cl_2–*n*-hexane (1:2 v/v) as eluent afforded $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}L)]$ **2** in 60% yield and $[Os(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ **1a** in 20% yield.

Chemical activation of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ 1a with trimethylamine *N*-oxide

A suspension of **1a** (0.1 g, 0.10 mmol) in CH_2Cl_2 (25 cm^3) was cooled to −78 °C. An acetonitrile solution (5 cm^3) of Me_3NO (4.1 mg, 0.10 mmol) was added dropwise over a period of 15 min. The mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was evaporated *in vacuo* and the residue was redissolved in CH_2Cl_2 (*ca.* 2 cm^3). Purification by TLC using CH_2Cl_2–*n*-hexane (1:2 v/v) as eluent afforded the intermediate $[Os_3(\mu\text{-}H)(CO)_9(NCMe)(\mu\text{-}L)]$ **3** ($R_f = 0.2$) which converted into **2** quantitatively in 20 min under ambient conditions.

Carbonylation of $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}L)]$ 2

Carbon monoxide gas at 1 atm (1 atm = 101 325 Pa) was bubbled through a yellow solution of complex **2** (0.05 g, 0.05 mmol) in refluxing *n*-hexane for 3 h. The solvent was then removed *in vacuo* and the residue was redissolved in CH_2Cl_2 (*ca.* 2 cm^3). Purification by TLC (CH_2Cl_2–*n*-hexane, 1:2 v/v) and IR spectroscopy indicated that **1a** was the only separable product (70%).

Photolysis of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ 1a

A solution of **1a** (0.1 g, 0.10 mmol) in deoxygenated cyclohexane (20 cm^3) was irradiated by UV/VIS light for 1 h. The solvent was then removed *in vacuo* and the residue was redissolved in CH_2Cl_2 (*ca.* 2 cm^3). Separation by TLC using CH_2Cl_2–*n*-hexane (1 : 2 v/v) as eluent afforded **2** as the only separable product (75%).

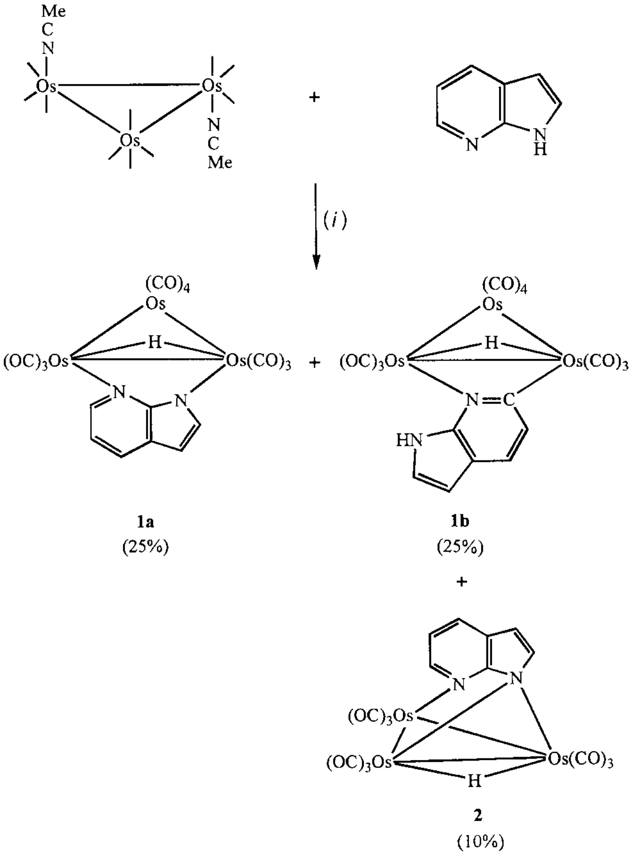
X-Ray analyses of 1a, 1b and 2

Single crystals of complexes **1a**, **1b** and **2** suitable for X-ray analyses were obtained by slow evaporation from a *n*-hexane–CH_2Cl_2 solution at room temperature. Crystals for all the complexes were mounted in air on a glass fibre with epoxy resin. X-Ray diffraction data of **1a**, **1b** and **2** were collected on a Rigaku AFC7R diffractometer, with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) using the ω–2θ scan method. All intensity data were corrected for Lorentz and polarisation effects and absorption corrections by the ψ-scan method were also applied. All structures were solved by direct methods (SIR 92)[11] and Fourier-difference techniques and refined by full-matrix least-squares analysis on *F*. Hydrogen atoms were generated in their ideal positions while hydride atoms were estimated from potential energy calculations.[12] All calculations were performed using the TEXSAN[13] crystallographic software package on a Silicon-Graphics computer.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/405.

Results and Discussion

The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with a stoichiometric amount of 7-azaindole at room temperature in CH_2Cl_2 afforded a pair of isomers $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}L)]$ **1a** and **1b** and $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}L)]$ **2** in moderate yields and is summarised in Scheme 1. The ^1H NMR, IR and FAB mass spectroscopic data of **1a**, **1b** and **2** all indicate that the organic fragment has co-ordinated to the triosmium framework but in different bonding modes (Table 1). The ^1H NMR spectra showed a hydride resonance at δ −11.89, −14.69 and −11.65 for **1a**, **1b** and **2** respectively. To establish their molecular structures, single-crystal X-ray analyses were carried out (Table 2). 7-Azaindole acts as a three-electron donor thus allowing the cluster to comply with



Scheme 1 Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 7-azaindole at 25 °C. (*i*) CH_2Cl_2, 1.5 h

Table 1 Spectroscopic data for complexes **1a**, **1b**, **2** and **3**

Cluster	IR, ν(CO)/cm^{-1}	^1H NMR/δ (*J*/Hz)	FAB mass spectrometry (*m/z*) $M^{+\,a}$
1a	2109w, 2067s, 2060s, 2021m[b]	8.22 (d, *J* = 7.5, 1 H, aryl H), 7.72 (d, *J* = 7.4, 1 H, aryl H), 7.31 (d, *J* = 3.1, 1 H, aryl H), 6.67 (dd, *J* = 7.5 and 7.4, 1 H, aryl H), 6.38 (d, *J* = 3.1, 1 H, aryl H), −11.89 (s, 1 H, OsH)[c]	970 (970)
1b	2103m, 2059vs, 2052vs, 2015s, 1997m, 1986m[b]	8.12 (br, 1 H, aryl H), 7.40 (d, *J* = 8.0, 1 H, aryl H), 7.00 (m, 2 H, aryl H), 6.44 (d, *J* = 3.1, 1 H, aryl H), −14.69 (s, 1 H, OsH)[d]	970 (970)
2	2085m, 2056s, 2027s, 1997s[b]	8.21 (d, *J* = 7.5, 1 H, aryl H), 7.81 (d, *J* = 8.3, 1 H, aryl H), 6.90 (dd, *J* = 8.3 and 7.5, 1 H, aryl H), 6.54 (d, *J* = 3.3, 1 H, aryl H), 6.40 (d, *J* = 3.3, 1 H, aryl H), −11.65 (s, 1 H, OsH)[d]	940 (940)
3	2243s, 2095w, 2066s, 2026s, 2015vs, 1985m[b]	8.28 (d, *J* = 7.5, 1 H, aryl H), 7.78 (d, *J* = 7.5, 1 H, aryl H), 7.37 (d, *J* = 3.5, 1 H, aryl H), 6.60 (dd, *J* = 7.5 and 7.5, 1 H, aryl H), 6.44 (d, *J* = 3.5, 1 H, aryl H), 2.00 (s, 3 H, MeCN), −11.07 (s, 1 H, OsH)[d]	987 (987)

[a] M^+ = parent molecular ion based on ^{192}Os and calculated values in parentheses. [b] Recorded in CH_2Cl_2 at 298 K. [c] Recorded in CD_2Cl_2 at 298 K. [d] Recorded in $CDCl_3$ at 298 K.

Table 2 Crystallographic data for complexes **1a**, **1b** and **2**[a]

	1a	**1b**	**2**
Empirical formula	$C_{17}H_6N_2O_{10}Os_3$	$C_{17}H_6N_2O_{10}Os_3$	$C_{16}H_6N_2O_9Os_3$
M	968.84	968.84	940.83
Colour, habit	Yellow, plate	Yellow, block	Yellow, needle
Crystal size/mm	0.21 × 0.28 × 0.15	0.22 × 0.19 × 0.27	0.14 × 0.19 × 0.28
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\ 2_1/n$ (no. 14)	$P\ 2_1/a$ (no. 14)
a/Å	9.227(9)	12.491(3)	14.618(2)
b/Å	16.48(1)	11.320(2)	16.259(3)
c/Å	7.873(5)	15.637(4)	8.610(5)
α/°	99.19(7)		
β/°	113.81(5)	102.26(2)	97.43(2)
γ/°	76.95(7)		
U/Å^3	1063(1)	2161(1)	2029(1)
Z	2	4	4
D_c/g cm^{-3}	3.025	2.978	3.079
F(000)	860.00	1720	1664
μ(Mo-Kα)/cm^{-1}	179.21	176.44	187.78
Scan range (ω)/°	(1.68 + 0.35 tan θ)	(0.73 + 0.35 tan θ)	(1.57 + 0.35 tan θ)
Reflections collected	3012	3166	5561
Independent reflections	2803	3046	5438
Observed reflections	2128	2443	2105
R; R'[b]	0.052; 0.052	0.047; 0.041	0.056; 0.072
Goodness of fit	2.57	3.44	3.08
Largest Δ/σ	0.06	0.07	0.10
No. parameters	144	144	136
Residual extrema in final difference map/e Å^{-3}	2.28, −3.01 close to Os	3.01, −2.12 close to Os	2.85, −3.70 close to Os

[a] Data in common: radiation Mo-Kα (λ = 0.710 73 Å), scan type ω–2θ, diffractometer Rigaku AFC7R, temperature 298 K, 2θ range 4–45°, scan speed 16° min^{-1}. [b] Weighting scheme: $1/\sigma^2(F_o)$. $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

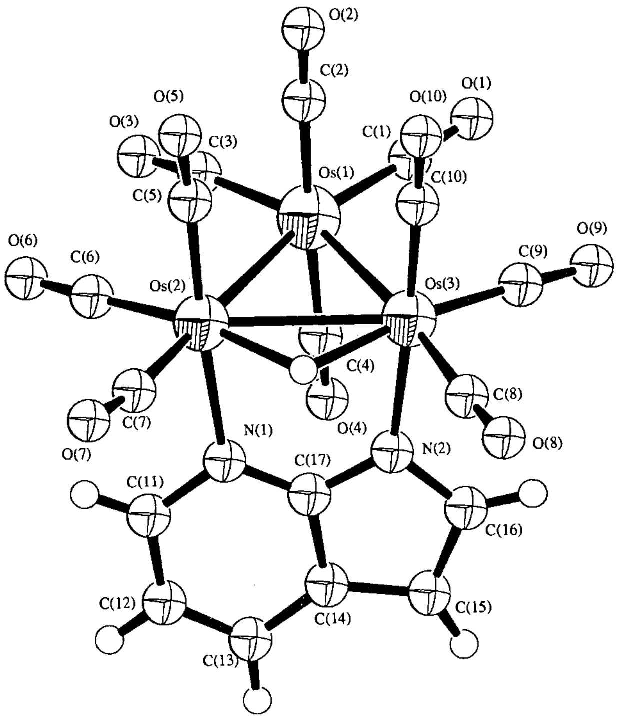


Fig. 1 An ORTEP drawing of the molecular structure of complex **1a**

the 18-electron rule with a total electron count of 48. This is consistent with the observed triangular cluster geometry for **1a**. An ORTEP[14] drawing of complex **1a** is shown in Fig. 1, selected bond lengths and angles are listed in Table 3. The hydride ligand originating from the pyrrolic N–H bond cleavage of 7-azaindole is coplanar to the plane of the triosmium triangle. The co-ordinated azaindole remains essentially coplanar with a maximum deviation of 0.03(3) Å and is almost perpendicular to the triosmium plane (dihedral angles 83.23°). The Os(2)–Os(3) edge is doubly-bridged by L and hydride ligands and is slightly longer than the two other Os–Os bonds. In addition, L is chelated to Os(2) and Os(3) *via* N(1) and N(2) by donating two and one electrons respectively. The Os(2)–C(5) [1.91(3) Å] and Os(3)–C(10) [1.88(3) Å] distances are slightly shorter than that of Os(1)–C(2) [1.95(3) Å]. This observation is attributed to the *trans* influence of the co-ordinating nitrogen atoms of L which increase the electron densities of Os(2) and Os(3), thereby increasing the π back bonding of the metals to the *trans* carbon atoms of the associated carbonyl ligands.

Table 3 Selected bond distances (Å) and angles (°) for complex **1a**

Os(1)–Os(2)	2.902(2)	Os(2)–C(5)	1.91(3)
Os(2)–Os(3)	2.923(3)	Os(2)–C(6)	1.86(2)
Os(1)–Os(3)	2.880(2)	Os(2)–C(7)	1.92(3)
Os(2)–N(1)	2.19(2)	Os(3)–C(8)	1.86(3)
Os(3)–N(2)	2.14(2)	Os(3)–C(9)	1.86(4)
Os(1)–C(2)	1.95(3)	N(1)–C(11)	1.37(3)
Os(3)–C(10)	1.88(3)	N(1)–C(17)	1.31(3)
C(15)–C(16)	1.44(4)		
Os(2)–Os(1)–Os(3)	60.72(6)	Os(1)–Os(3)–N(2)	90.1(5)
Os(1)–Os(3)–Os(2)	60.01(4)	Os(1)–Os(2)–N(1)	92.5(6)
Os(1)–Os(2)–Os(3)	59.26(5)	Os(3)–Os(2)–N(1)	83.3(5)
Os(2)–Os(3)–N(2)	81.7(5)	N(1)–Os(2)–C(5)	176.1(9)

An ORTEP drawing of complex **1b** is shown in Fig. 2 and selected bonding parameters are listed in Table 4. In contrast to observations made for **1a**, the C(1)–H bond of L is activated by the triosmium framework and lead to orthometallation. The pendant pyrrolic N–H is also manifested by a broad singlet at δ 8.12 in the ^{1}H NMR spectrum of **1b**. The co-ordinated L again acts as a three-electron donor and the three osmium atoms define an isosceles triangle [Os(1)–Os(2) 2.877(1), Os(1)–Os(3) 2.871(1), Os(2)–Os(3) 2.914(1) Å] and have ten terminal carbonyl ligands. The dihedral angle between the best planes of L and the Os triangle is 109.0°. The Os(2)–C(5) bond [1.90(3) Å] is slightly shorter than that of Os(3)–C(10) [1.94(2) Å] and is attributed to the *trans* influence of N-co-ordination of the orthometallated pyridine moiety. Other triosmium carbonyl clusters containing similar orthometallated ligands include

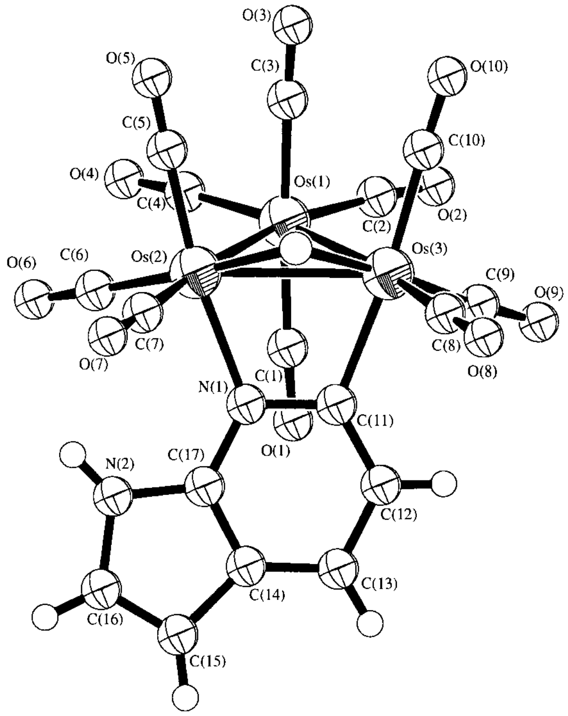


Fig. 2 An ORTEP drawing of the molecular structure of complex **1b**

Table 4 Selected bond distances (Å) and angles (°) for complex **1b**

Os(1)–Os(2)	2.877(1)	Os(2)–C(5)	1.90(3)
Os(2)–Os(3)	2.914(1)	Os(2)–C(6)	1.91(2)
Os(1)–Os(3)	2.871(1)	Os(2)–C(7)	1.91(2)
Os(2)–N(1)	2.13(2)	Os(3)–C(8)	1.88(2)
Os(3)–C(11)	2.12(2)	Os(3)–C(9)	1.88(2)
Os(1)–C(3)	1.92(3)	N(1)–C(11)	1.37(2)
Os(3)–C(10)	1.94(2)	N(1)–C(17)	1.39(2)
C(15)–C(16)	1.34(3)		
Os(2)–Os(1)–Os(3)	60.91(3)	Os(1)–Os(3)–C(11)	88.5(5)
Os(1)–Os(3)–Os(2)	59.64(3)	Os(1)–Os(2)–N(1)	88.2(4)
Os(1)–Os(2)–Os(3)	59.45(3)	Os(3)–Os(2)–N(1)	68.3(3)
Os(2)–Os(3)–C(11)	69.0(5)	Os(3)–C(11)–N(1)	111(1)

$[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-bzim})]$[15] (Hbzim = benzimidazole) and $[Os_3H(CO)_{10}(C_5H_4)]$.[16]

The molecular structure of complex **2** is shown in Fig. 3. Related bond lengths and angles are listed in Table 5. The molecular geometry consists of a nearly equilateral array of three Os atoms, each bonded to three terminal carbonyl groups with azaindole ligand bridging the osmium atoms in a μ_3-η^2 fashion. The Os(2)–Os(3) edge of the cluster is also bridged by a hydride. 7-Azaindole co-ordinates to Os(1) through its pyridinic nitrogen N(1) [Os(1)–N(1) 2.18(2) Å] and asymmetrically to the other two osmium atoms [Os(2)–N(2) 2.28(2), Os(3)–N(2) 2.19(3) Å]; L is essentially planar and almost perpendicular to the triosmium plane (dihedral angle 91.7°). A similar cluster–ligand disposition has been reported for $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-apy})]$[1] (apy = 2-aminopyridine) and $[Ru_3(\mu\text{-}H)(CO)_9(\mu_3\text{-btt})]$[17] (Hbtt = benzothiazole-2-thiol), but the edge of the metal triangle is bridged by a sulfur instead of a nitrogen atom in the latter case.

Chemical, thermal and photochemical activations of complex **1a** afforded **2** as the sole product. The pyrrolic nitrogen in **1a** substitutes for one of the carbonyls on the adjacent $Os(CO)_4$ unit, followed by hydride migration to give complex **2**. Furthermore, the conversion of **1a** into **2** (Scheme 2) is found to be reversible by bubbling carbon monoxide gas to a *n*-hexane solution of **2**. The organic fragments in **1a** and **2** can be considered as undergoing the 'windshield wiper' motion:[1,17] L is parallel and perpendicular to an edge of the metal triangle respectively. This situation is similar to the reversible interconversion between the parallel and perpendicular conformations of the triruthenium cluster $[Ru_3(\mu\text{-PhCCPh})(CO)_8(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$).[18] The formation of the intermediate **3** is observed during the chemical activation of **1a** by trimethylamine *N*-oxide (Scheme 2). Based on spectroscopic evidence, complex **3** is formulated as $[Os_3(\mu\text{-}H)(CO)_9(NCMe)(\mu\text{-}L)]$, its IR spectrum shows a strong absorption at 2243 cm^{-1} which is attributed to the co-ordinated MeCN group. Also, a resonance at δ 2 is observed in the ^1H NMR spectrum and can be assigned to MeCN. However, we are unable to obtain single crystals of **3** for detailed structural analysis due to its rapid conversion into **2**.

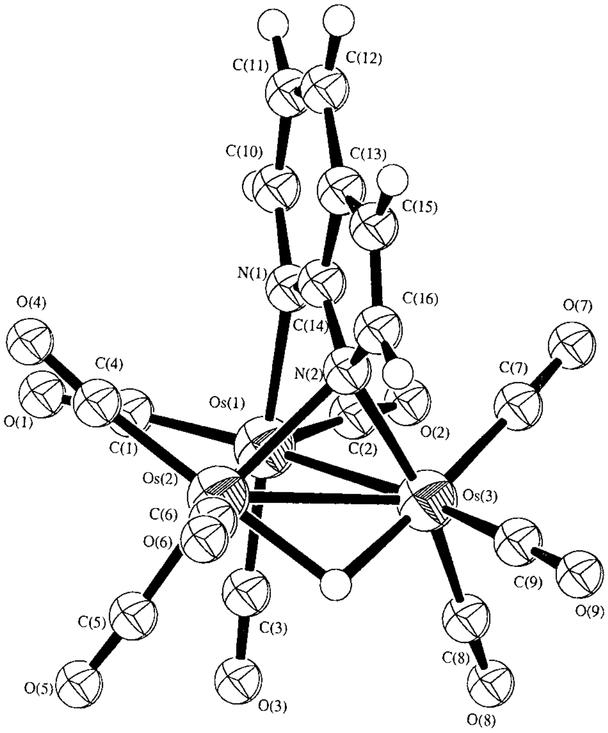


Fig. 3 An ORTEP drawing of the molecular structure of complex **2**

Table 5 Selected bond distances (Å) and angles (°) for complex **2**

Os(1)–Os(2)	2.793(2)	N(1)–C(14)	1.31(3)
Os(2)–Os(3)	2.794(2)	N(2)–C(16)	1.45(4)
Os(1)–Os(3)	2.794(2)	N(1)–C(10)	1.42(4)
Os(1)–N(1)	2.18(2)	N(2)–C(14)	1.37(3)
Os(3)–N(2)	2.19(3)	C(15)–C(16)	1.30(4)
Os(2)–N(2)	2.28(2)	C(13)–C(15)	1.39(4)
Os(2)–Os(1)–Os(3)	60.03(4)	Os(2)–N(2)–Os(3)	77.4(8)
Os(1)–Os(3)–Os(2)	59.96(4)	Os(2)–Os(3)–N(2)	52.8(6)
Os(1)–Os(2)–Os(3)	59.45(3)	Os(3)–Os(2)–N(2)	49.9(7)
Os(2)–Os(3)–C(11)	60.01(4)	Os(3)–C(11)–N(1)	111(1)

Acknowledgements

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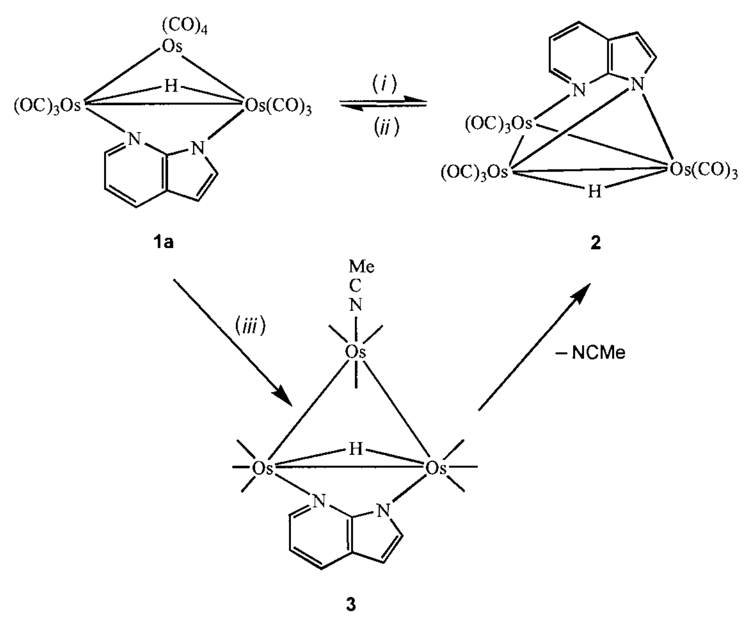

Scheme 2 Relationship between complexes **1a** and **2**. (*i*) *n*-Hepane, 98 °C, 1 d; (*ii*) CO, *n*-hexane, reflux, 3 h; (*iii*) Me_3NO, CH_2Cl_2, −78 °C

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