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Synthesis and molecular structure of the triosmium carbonyl cluster $[Os_3(CO)_{10}\{\mu\text{-}N(H)(C_5H_3NBr)\}\{\mu\text{-}N(C_{10}H_{13}NO)\}]$, containing two types of amido ligands

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Abstract

Treatment of $[Os_3(CO)_{10}(NCMe)_2]$ with an equivalent amount of 2-(5-bromo-2-pyridyiazo)-5-(diethylamino)phenol (Br–PADAP) in CH_2Cl_2 at room temperature for 1 h afforded a major brown cluster $[Os_3(CO)_{10}\{\mu\text{-}N(H)(C_5H_3NBr)\}\{\mu\text{-}N(C_{10}H_{13}NO)\}]$; the compound contains two types of μ-bridging amido ligands across the same Os · · · Os edge. © 1997 Elsevier Science S.A.

The chemistry of carbonyl clusters of iron triad containing azo ligands has been extensively studied [1–7]. It has been shown that $Fe_3(CO)_{12}$ reacts with azoalkanes, R_2N_2 (R = Et, Pr) to give $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2R_2)]$. Subsequent thermolysis leads to N–N bond cleavage and the formation of nitrene-bridged clusters $[Fe_3(CO)_9(\mu_3\text{-}NR)_2]$ [8]. Similarly, $Ru_3(CO)_{12}$ reacts with azoarenes, N_2Ar_2 to give $[Ru_3(CO)_9(\mu_3\text{-}NAr)_2]$ in moderate yields [9]. However, the osmium carbonyl cluster, $Os_3(CO)_{12}$ would not undergo a similar reaction. It has been reported that $Os_3(CO)_{12}$ reacts with azoethane at 140°C to give hydrazone derivatives $[Os_3(\mu\text{-}H)(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN\text{–}N{=}C\text{–}HCH_3)]$ in low yield [1]. However, no products due to N–N cleavage have been isolated in this system. Recently, we have shown that the labilised triosmium cluster, $[Os_3(CO)_{10}(NCMe)_2]$ reacts with 2-phenylazopyridine (2-PAP) to afford $[Os_3(CO)_{10}(\mu\text{-}\eta^3\text{-}NC_5H_4N{=}NC_6H_5)]$ in which the azo moiety is coordinated to Os metal centers [10]. However, attempts to cleave the N=N bond of this compound by thermal and photochemical methods has met little success. Nevertheless, we believe that by careful choice of substituents in the aromatic system, one would be able to modify the electron density around the azo linkage so that cleavage reaction can be effected. Herein, we report in this communication the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (Br–PADAP) to give a brown cluster containing two types of amido moieties in which N–N cleavage of the azo ligand is observed.

Treatment of $[Os_3(CO)_{10}(NCMe)_2]$ with 1 equivalent of Br–PADAP in dichloromethane at room temperature gives a dark brown solid $[Os_3(CO)_{10}\{\mu\text{-}N(H)(C_5H_3NBr)\}\{\mu\text{-}N(C_{10}H_{13}NO)\}]$ I in 50% yield and two other uncharacterized products in low yields upon TLC separation on silica, see Scheme 1. The ^1H NMR spectrum of I in CD_2Cl_2 shows two sets of three signals that are attributable to the protons of two aromatic rings. The amido proton resonance appears as a board singlet at 3.59 ppm. The positive FAB mass spectrum of I exhibits an envelope centered at m/z 1200 with an isotopic distribution characteristic of three osmium and one bromine atom. To establish the molecular structure of I, an X-ray analysis has been carried out on a dark brown crystal obtained by slow evaporation of an ethanol solution at 0°C. This analysis revealed that cluster I contains an open triangular metal core with two types of amido fragment bridging across the same Os · · · Os edge. The molecular structure of I is shown in Fig. 1 together with selected bond parameters. The amido ligand containing pyridine ring is arranged in exo orientation, although both exo and endo forms have been

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Table 1
Atomic coordinates and B_{iso} / B_{eq}

Atom	x	y	z	B_{eq}
Os(1)	0.4684(1)	0.55150(7)	0.23301(7)	3.94(3)
Os(2)	0.5201(1)	0.74271(7)	0.16588(7)	3.17(2)
Os(3)	0.7202(1)	0.61556(7)	0.27467(7)	3.33(2)
Br(1)	1.2106(4)	0.9199(2)	0.0051(2)	5.50(9)
O(1)	0.305(3)	0.673(1)	0.412(1)	5.4(4)
O(2)	0.502(3)	0.356(2)	0.326(2)	7.8(6)
O(3)	0.201(4)	0.540(2)	0.168(2)	9.4(8)
O(4)	0.680(3)	0.478(2)	0.050(1)	6.1(5)
O(5)	0.573(2)	0.945(1)	0.098(1)	4.6(4)
O(6)	0.200(3)	0.809(1)	0.236(1)	5.7(5)
O(7)	0.483(3)	0.685(2)	−0.020(2)	6.5(5)
O(8)	0.901(3)	0.414(2)	0.203(2)	6.4(5)
O(9)	0.988(3)	0.689(1)	0.325(1)	5.9(5)
O(10)	0.649(3)	0.533(1)	0.463(1)	5.5(4)
O(11)	0.691(4)	0.729(2)	0.467(2)	4.2(7)
O(12)	0.385(5)	0.937(3)	0.286(2)	4.4(7)
O(13)	0.297(4)	0.119(2)	0.277(2)	10.9607
O(14)	0.155(4)	0.236(2)	0.428(2)	10.5961
N(1)	0.753(2)	0.673(1)	0.138(1)	3.4(4)
N(2)	0.858(2)	0.816(1)	0.152(1)	3.3(4)
N(3)	0.580(2)	0.754(1)	0.295(1)	3.4(4)
N(4)	0.293(3)	0.975(2)	0.614(1)	4.3(4)
C(1)	0.365(4)	0.625(2)	0.352(2)	5.4(7)
C(2)	0.499(4)	0.428(2)	0.293(2)	4.8(6)
C(3)	0.300(4)	0.547(2)	0.185(2)	5.7(7)
C(4)	0.593(4)	0.510(2)	0.116(2)	5.1(6)
C(5)	0.557(3)	0.866(2)	0.129(2)	3.7(5)
C(6)	0.332(4)	0.788(2)	0.211(2)	5.2(6)
C(7)	0.491(4)	0.707(2)	0.055(2)	4.6(6)
C(8)	0.839(5)	0.491(3)	0.224(3)	7.9(10)
C(9)	0.892(3)	0.665(2)	0.301(2)	3.4(5)
C(10)	0.679(4)	0.566(2)	0.395(2)	4.9(6)
C(11)	0.861(3)	0.727(2)	0.105(1)	2.6(4)
C(12)	0.966(3)	0.701(2)	0.028(2)	4.0(5)
C(13)	1.070(4)	0.748(2)	−0.001(2)	4.4(6)
C(14)	1.071(3)	0.837(2)	0.045(2)	3.9(5)
C(15)	0.961(3)	0.865(2)	0.120(2)	3.5(5)
C(16)	0.528(3)	0.810(2)	0.369(1)	2.6(4)
C(17)	0.565(3)	0.798(2)	0.456(2)	3.6(5)
C(18)	0.484(3)	0.853(2)	0.529(2)	4.3(5)
C(19)	0.370(3)	0.927(2)	0.533(2)	3.6(5)
C(20)	0.340(3)	0.951(2)	0.450(2)	4.4(6)
C(21)	0.415(3)	0.902(2)	0.368(2)	3.2(4)
C(22)	0.312(4)	0.942(2)	0.705(2)	5.9(7)
C(23)	0.251(5)	0.857(3)	0.736(3)	7.6(9)
C(24)	0.176(4)	1.049(2)	0.617(2)	4.6(6)
C(25)	0.025(6)	1.018(3)	0.618(3)	9(1)
C(26)	0.3242	0.1400	0.1808	10.0500
C(27)	0.221(7)	0.160(4)	0.156(3)	10.6070
H(1)	0.7641	0.6261	0.1014	4.0
H(2)	0.9616	0.6430	−0.0065	4.8
H(3)	1.1458	0.7230	−0.0531	5.2
H(4)	0.9596	0.9265	0.1508	4.2
H(5)	0.5108	0.8383	0.5869	5.1
H(6)	0.2635	1.0048	0.4483	5.2
H(8)	0.4132	0.9270	0.7024	7.0
H(9)	0.2685	0.9949	0.7486	7.0
H(10)	0.1490	0.8702	0.7399	9.0
H(11)	0.2935	0.8024	0.6933	9.0
H(12)	0.2695	0.8411	0.7953	9.0
H(13)	0.1652	1.0890	0.6714	5.5
H(14)	0.1989	1.0871	0.5638	5.5

Table 1 (continued)

Atom	x	y	z	B_{eq}
H(15)	−0.0457	1.0761	0.6195	11.2
H(16)	0.0322	0.9791	0.5632	11.2
H(17)	−0.0015	0.9810	0.6709	11.2
H(18)	0.3762	0.1937	0.1715	12.0
H(19)	0.3808	0.0831	0.1459	12.0
H(20)	0.1639	0.2171	0.1909	12.7
H(21)	0.2424	0.1742	0.0924	12.7
H(22)	0.1687	0.1065	0.1651	12.7
H(23)	0.3965	0.9263	0.3108	3.8

$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

reported in a related system $[Os_3(\mu\text{-}N(H)Ph)(\mu\text{-}Cl)(CO)_{10}]$ [11]. We did not detect the presence of an endo isomer in this system. The other amido moiety contains a C=N double bond (1.29(3) Å) which is marginally shorter than the C–N(H) distance (1.38(3) Å) in the other amido group. The N(3) atom is sp^2 hybridized as evident from the short N(3)–C(16) bond distance and the planarity of Os(2)–Os(3)–N(3)–C(16) moiety (max. deviation 0.10 Å). Osmium clusters con-

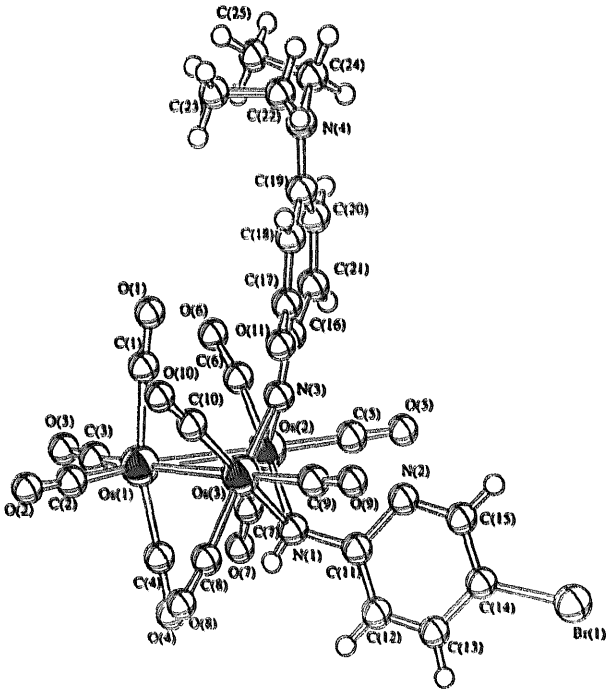
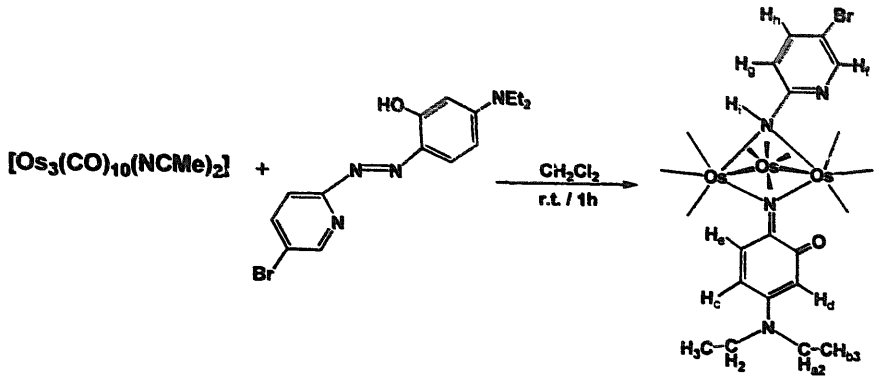


Fig. 1. Molecular structure of cluster 1 showing the atom-numbering scheme, with selected bond distances (Å) and angles (°). Os(1)–Os(2) 2.884(1), Os(1)–Os(3) 2.879(2), Os(2)–N(1) 2.22(2), Os(2)–N(3) 2.11(2), Os(3)–N(1) 2.14(2), Os(3)–N(3) 2.11(2), Os(2)···Os(3) 3.075(2), N(1)···N(3) 2.65(2), C(17)–O(11)[a] 1.44(4), C(21)–O(12)[a] 1.37(4), C(16)–N(3) 1.29(3), C(11)–N(1) 1.38(3), Os(2)–Os(1)–Os(3) 64.5(1), Os(2)–N(1)–Os(3) 89.6(8), Os(2)–N(3)–Os(3) 93.6(7). [a] Occupancy factor 0.5.



Scheme 1.

taining this kind of μ-amido group is relatively rare, even though structurally characterized examples such as $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-N=C(H)CF}_3)]$ [12] and $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-N=C(H)Et}\}]$ [13] are known. It has been shown that $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-N=C(H)CF}_3\}]$ undergoes hydrogenation to give $[Os_3(\mu\text{-H})(CO)_{10}\{\mu\text{-N(H)CH}_2\text{CF}_3\}]$ at forcing condition [14]. However, cluster I is unreacted towards hydrogen at both room temperature and temperature of refluxing hexane.

Although the mechanistic details for the formation of I are unclear, it is tempting to propose some intermediates with similar bonding mode for the azo functionality bound to the osmium metal core as observed in $[Os_3(CO)_{10}(\mu\text{-}\eta^3\text{-C}_5\text{H}_4\text{N=NC}_6\text{H}_5)]$ may be present.

Acknowledgements

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Appendix A. Spectroscopic data for I

IR $[CH_2Cl_2, \nu(CO)]$ 2093 m, 2064 s, 2043 s, 2012 s, 1973 s and 1952 m cm^{-1}; IR [KBr, ν(C=O, ketone) 1626 cm^{-1}, ν(C=N) 1607 cm^{-1}; ^{1}H NMR(CD_2Cl_2, ppm): δ 8.21 (d, 1H, J_{HH} = 2.4, H_h), 7.65 (dd, 1H, J_{HH} = 2.4 and 8.6, H_f), 6.81 (m, 2H, H_c and H_d), 6.01 (d, 1H, J_{HH} = 8.6, H_g), 5.55 (s, br, 1H, H_e), 3.59 (s, br, 1H, H_i), 3.50 (q, 4H, J_{HH} = 7.0, H_a), 1.29 (t, 6H,

Table 3
Bond lengths (Å)

Atom	Atom	Distance	Atom	Atom	Distance
Os(1)	Os(2)	2.884(1)	Os(1)	Os(3)	2.879(2)
Os(1)	C(1)	2.00(3)	Os(1)	C(2)	1.92(3)
Os(1)	C(3)	1.90(4)	Os(1)	C(4)	1.90(3)
Os(2)	N(1)	2.22(2)	Os(2)	N(3)	2.11(2)
Os(2)	C(5)	1.84(3)	Os(2)	C(6)	1.79(4)
Os(2)	C(7)	1.80(3)	Os(3)	N(1)	2.14(2)
Os(3)	N(3)	2.11(2)	Os(3)	C(8)	1.93(4)
Os(3)	C(9)	1.99(3)	Os(3)	C(10)	1.89(3)
Br(1)	C(14)	1.90(3)	O(1)	C(1)	1.09(3)
O(2)	C(2)	1.10(3)	O(3)	C(3)	1.05(5)
O(4)	C(4)	1.17(3)	O(5)	C(5)	1.19(3)
O(6)	C(6)	1.22(4)	O(7)	C(7)	1.16(3)
O(8)	C(8)	1.13(4)	O(9)	C(9)	1.14(3)
O(10)	C(10)	1.11(3)	O(11)	C(17)	1.44(4)
O(12)	C(21)	1.37(4)	N(1)	C(11)	1.38(3)
N(2)	C(11)	1.39(3)	N(2)	C(15)	1.29(3)
N(3)	C(16)	1.29(3)	N(4)	C(19)	1.37(3)
N(4)	C(22)	1.44(4)	N(4)	C(24)	1.37(4)
C(11)	C(12)	1.35(3)	C(12)	C(13)	1.28(4)
C(13)	C(14)	1.39(3)	C(14)	C(15)	1.36(4)
C(16)	C(17)	1.40(3)	C(16)	C(21)	1.52(3)
C(17)	C(18)	1.34(3)	C(18)	C(19)	1.36(4)
C(19)	C(20)	1.34(4)	C(20)	C(21)	1.38(3)
C(22)	C(23)	1.42(5)	C(24)	C(25)	1.56(6)

Table 2
Anisotropic displacement parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os(1)	0.0510(9)	0.0429(6)	0.0538(6)	−0.0161(5)	−0.0013(5)	−0.0051(5)
Os(2)	0.0401(7)	0.0414(6)	0.0376(5)	−0.0104(5)	−0.0032(4)	−0.0043(4)
Os(3)	0.0398(7)	0.0378(6)	0.0441(6)	−0.0030(4)	−0.0013(4)	−0.0036(4)
Br(1)	0.058(3)	0.073(2)	0.079(2)	−0.029(2)	−0.005(2)	0.014(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$.

Table 4
Bond lengths (Å)

Atom	Atom	Distance	Atom	Atom	Distance
O(12)	H(23)	0.41	N(1)	H(1)	0.82
C(12)	H(2)	0.95	C(13)	H(3)	0.95
C(15)	H(4)	0.95	C(18)	H(5)	0.96
C(20)	H(6)	0.95	C(21)	H(23)	0.97
C(22)	H(8)	0.95	C(22)	H(9)	0.95
C(23)	H(10)	0.95	C(23)	H(11)	0.95
C(23)	H(12)	0.95	C(24)	H(13)	0.95
C(24)	H(14)	0.95	C(25)	H(15)	0.95
C(25)	H(16)	0.94	C(25)	H(17)	0.95
C(27)	H(20)	0.94	C(27)	H(21)	0.94
C(27)	H(22)	0.96			

Table 5
Bond angles (°)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Os(2)	Os(1)	Os(3)	64.59(4)	Os(2)	Os(1)	C(1)	85.6(9)
Os(2)	Os(1)	C(2)	158(1)	Os(2)	Os(1)	C(3)	97.3(10)
Os(2)	Os(1)	C(4)	81.1(9)	Os(3)	Os(1)	C(1)	83(1)
Os(3)	Os(1)	C(2)	93(1)	Os(3)	Os(1)	C(3)	161.8(10)
Os(3)	Os(1)	C(4)	84(1)	C(1)	Os(1)	C(2)	92(1)
C(1)	Os(1)	C(3)	96(1)	C(1)	Os(1)	C(4)	165(1)
C(2)	Os(1)	C(3)	104(1)	C(2)	Os(1)	C(4)	97(1)
C(3)	Os(1)	C(4)	91(1)	Os(1)	Os(2)	N(1)	84.6(5)
Os(1)	Os(2)	N(3)	82.0(5)	Os(1)	Os(2)	C(5)	176.9(8)
Os(1)	Os(2)	C(6)	87.6(10)	Os(1)	Os(2)	C(7)	89.4(9)
N(1)	Os(2)	N(3)	75.5(8)	N(1)	Os(2)	C(5)	94.4(10)
N(1)	Os(2)	C(6)	168(1)	N(1)	Os(2)	C(7)	95(1)
N(3)	Os(2)	C(5)	95.0(10)	N(3)	Os(2)	C(6)	94(1)
N(3)	Os(2)	C(7)	167(1)	C(5)	Os(2)	C(6)	93(1)
C(5)	Os(2)	C(7)	93(1)	C(6)	Os(2)	C(7)	93(1)
Os(1)	Os(3)	N(1)	86.2(6)	Os(1)	Os(3)	N(3)	82.0(6)
Os(1)	Os(3)	C(8)	90(1)	Os(1)	Os(3)	C(9)	177.6(7)
Os(1)	Os(3)	C(10)	90(1)	N(1)	Os(3)	N(3)	77.2(7)
N(1)	Os(3)	C(8)	89(1)	N(1)	Os(3)	C(9)	92.2(9)
N(1)	Os(3)	C(10)	176(1)	N(3)	Os(3)	C(8)	164(1)
N(3)	Os(3)	C(9)	95.9(9)	N(3)	Os(3)	C(10)	100(1)
C(8)	Os(3)	C(9)	91(1)	C(8)	Os(3)	C(10)	92(1)
C(9)	Os(3)	C(10)	90(1)	Os(2)	N(1)	Os(3)	89.6(8)
Os(2)	N(1)	C(11)	120(1)	Os(3)	N(1)	C(11)	122(1)
C(11)	N(2)	C(15)	116(2)	Os(2)	N(3)	Os(3)	93.6(7)
Os(2)	N(3)	C(16)	134(1)	Os(3)	N(3)	C(16)	130(1)
C(19)	N(4)	C(22)	123(2)	C(19)	N(4)	C(24)	121(2)
C(22)	N(4)	C(24)	114(2)	Os(1)	C(1)	O(1)	173(2)
Os(1)	C(2)	O(2)	172(3)	Os(1)	C(3)	O(3)	171(3)
Os(1)	C(4)	O(4)	172(3)	Os(2)	C(5)	O(5)	173(2)
Os(2)	C(6)	O(6)	172(2)	Os(2)	C(7)	O(7)	174(3)
Os(3)	C(8)	O(8)	172(3)	Os(3)	C(9)	O(9)	173(2)
Os(3)	C(10)	O(10)	175(2)	N(1)	C(11)	N(2)	118(1)
N(1)	C(11)	C(12)	123(2)	N(2)	C(11)	C(12)	118(2)
C(11)	C(12)	C(13)	124(2)	C(12)	C(13)	C(14)	118(2)
Br(1)	C(14)	C(13)	123(2)	Br(1)	C(14)	C(15)	119(1)
C(13)	C(14)	C(15)	116(2)	N(2)	C(15)	C(14)	125(2)
N(3)	C(16)	C(17)	127(2)	N(3)	C(16)	C(21)	120(2)
C(17)	C(16)	C(21)	112(1)	O(11)	C(17)	C(16)	121(2)
O(11)	C(17)	C(18)	119(2)	C(16)	C(17)	C(18)	119(2)
C(17)	C(18)	C(19)	128(2)	N(4)	C(19)	C(18)	122(2)
N(4)	C(19)	C(20)	122(2)	C(18)	C(19)	C(20)	114(2)
C(19)	C(20)	C(21)	123(2)	O(12)	C(21)	C(16)	120(2)
O(12)	C(21)	C(20)	118(2)	C(16)	C(21)	C(20)	120(2)
N(4)	C(22)	C(23)	115(3)	N(4)	C(24)	C(25)	117(2)

Table 6
Bond angles (°)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C(21)	O(12)	H(23)	4.0	Os(2)	N(1)	H(1)	107.4
Os(3)	N(1)	H(1)	106.9	C(11)	N(1)	H(1)	107.2
C(11)	C(12)	H(2)	117.5	C(13)	C(12)	H(2)	118.3
C(12)	C(13)	H(3)	120.9	C(14)	C(13)	H(3)	120.9
N(2)	C(15)	H(4)	117.4	C(14)	C(15)	H(4)	117.4
C(17)	C(18)	H(5)	115.5	C(19)	C(18)	H(5)	115.8
C(19)	C(20)	H(6)	118.0	C(21)	C(20)	H(6)	118.9
O(12)	C(21)	H(23)	1.7	C(16)	C(21)	H(23)	120.0
C(20)	C(21)	H(23)	119.8	N(4)	C(22)	H(8)	107.9
N(4)	C(22)	H(9)	107.7	C(23)	C(22)	H(8)	108.1
C(23)	C(22)	H(9)	108.1	H(8)	C(22)	H(9)	109.1
C(22)	C(23)	H(10)	109.3	C(22)	C(23)	H(11)	109.5
C(22)	C(23)	H(12)	109.6	H(10)	C(23)	H(11)	109.4
H(10)	C(23)	H(12)	109.3	H(11)	C(23)	H(12)	109.7
N(4)	C(24)	H(13)	106.9	N(4)	C(24)	H(14)	107.0
C(25)	C(24)	H(13)	108.4	C(25)	C(24)	H(14)	107.8
H(13)	C(24)	H(14)	108.8	C(24)	C(25)	H(15)	109.0
C(24)	C(25)	H(16)	109.5	C(24)	C(25)	H(17)	108.6
H(15)	C(25)	H(16)	110.4	H(15)	C(25)	H(17)	109.3
H(16)	C(25)	H(17)	110.0	H(20)	C(27)	H(21)	111.4
H(20)	C(27)	H(22)	109.1	H(21)	C(27)	H(22)	109.7

J_{HH} = 7.0 Hz, H_b); FAB mass spectrum: m/z 1200 (calc. 1200), M^+; elemental analysis (Found: C, 25.70; H, 1.70; N, 4.60%. $C_{25}H_{17}N_4O_{11}BrOs_3$ requires C, 25.70; H, 2.00; N, 4.40%).

Table 7
Summary of crystal data and data collection parameters for $[Os_3(CO)_{10}\{\mu\text{-}N(H)C_5H_3NBr\}\{\mu\text{-}NC_{10}H_{11}NO\}]$

Empirical Formula	$C_{25}H_{17}N_4O_{11}BrOs_3$
M	1199.93
Crystal color, habit	dark brown, blocks
Crystal size (mm)	0.23 × 0.25 × 0.33
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	a = 9.565(1) α = 90.15(2)
	b = 13.692(1) β = 77.69(2)
	c = 14.756(1) γ = 80.35(2)
U (Å^3)	1859.9(4)
Z	2
D_{calc} (g cm^{-3})	2.257
F(000)	1164
Diffractometer	MAR research image-plate
Radiation	Mo – K α (λ = 0.71073 Å)
μ(Mo – K α) (cm^{-1})	113.55
Temperature (K)	295
Reflections collected	14035
Unique reflections	3119
Observed reflections $I > 3\sigma(I)$	2212
Refinement method	full matrix least-squares
Weighing scheme	$w = [\sigma^2(F_o)]^{-1}$
R	0.058
R_w	0.064
Goodness of fit	2.75
Largest Δ/σ	0.09
No. of Parameter	210
Residual electron density (e Å^{-3})	0.68 to −0.74

Appendix B. Crystal Data for I (Tables 1–7)

$[Os_3(CO)_{10}\{\mu\text{-}N(H)(C_5H_3NBr)\}\{\mu\text{-}N(C_{10}H_{13}NO)\}] \cdot EtOH \cdot H_2O$; $C_{25}H_{17}N_4O_{11}BrOs_3$, $M = 1199.93$ (1264.02 with solvent), Triclinic, Space group $P\bar{1}$ (No. 2), $a = 9.565(1)$, $b = 13.692(1)$, $c = 14.756(1)$ Å, $\alpha = 90.15(2)$, $\beta = 77.69(2)$, $\gamma = 80.35(2)°$, $U = 1859.9(4)$ Å^3, $Z = 2$, $D_{calc} = 2.257$ g cm^{-3}, $F(000) = 1164$, Mo $-$ Kα radiation ($\lambda = 0.71073$ Å), $\mu(Mo - K\alpha) = 113.55$ cm^{-1}, crystal dimensions $0.23 \times 0.25 \times 0.33$ mm, 3119 unique data measured on a MAR research image-plate Scanner. 65 3° frames with an exposure time of 8 min per frame. 2213 observed reflections [$I > 3\sigma(I)$]. structure solved by direct methods (SIR88) [15] and Fourier difference techniques. We encountered a 2-fold positional disorder problem associated with the $N{=}CC_5H_3(O)(NEt_2)$ moiety. There are two orientations of this ring with the oxygen atom on the left hand side as shown in Fig. 1 or on the right hand side. Therefore, both possible sites for oxygen atom, O(11) and O(12), were assigned occupancy factors of 0.5. With this model, full-matrix least-squares refinement on F was employed with Os refined anisotropically. The amido-H was located from a difference Fourier synthesis based on low angle data [$2\theta < 30°$] while other hydrogen atoms on the organic moieties were generated in their ideal positions. They were included in the structure factors calculations but not refined. The refinement was converged to $R = 0.058$, $R' = 0.064$ with weighing scheme $w = [\sigma^2(F_o)]^{-1}$. All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN [16]. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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