Reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with Organic Azides: Structural Characterization of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}HN_3Ph)]$ † and $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ ‡

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The unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ reacts with azides N_3R [R = Ph (1), Bu^n (2), CH_2Ph (3), cyclo-C_6H_{11} (4), or $CPhCH_2$ (5)] to give complexes with the general formula $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$. The structure of complex (1) has been established by an *X*-ray analysis, and shown to contain an equilateral Os_3 triangle one edge of which is bridged by the HN_3Ph group. This complex crystallises in the monoclinic space group $P2_1/c$ with $a = 9.665(3)$, $b = 8.823(4)$, $c = 25.571(14)$ Å, $\beta = 100.17(4)°$, and $Z = 4$. This structure was solved by a combination of direct methods and Fourier-difference techniques and refined by blocked-cascade least squares to $R = 0.042$ for 3 155 observed intensities. At 85 °C in 1,2-dimethoxyethane the complexes (1)—(4) liberate a N_2 and a CO molecule to give complexes with the general formula $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NR)]$ [R = Ph (6), Bu^n (7), CH_2Ph (8), or cyclo-C_6H_{11} (9)]. The structure of complex (6) contains an isosceles triangle of Os atoms which is capped by the N atom of the NPh group. This complex also crystallises in space group $P2_1/c$ with $a = 11.630(4)$, $b = 9.217(4)$, $c = 18.527(7)$ Å, $\beta = 99.71(2)°$, and $Z = 4$. The structure was solved and refined, by the same techniques as for complex (1), to $R = 0.033$ for 2 861 observed intensities. Thermolysis of the azido-1-phenylethene adduct (5) under the same conditions, however, gave $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NCMePh)]$ (10) presumably by rapid tautomerism after loss of N_2. Azides with an electron-withdrawing substituent adjacent to the azido-function evolved N_2 when reacted with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give clusters of the type $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHR)]$ [R = $PO(OPh)_2$ (11) or 2-(6-$ClNC_5H_3$) (12)] or products which are, apparently, formed by rearrangement of this system, *i.e.* $[Os_3(\mu\text{-}H)(CO)_{10}(NHCOPh)]$ (14) (from phenacyl azide) and $[Os_3(\mu\text{-}H)(CO)_{10}(2\text{-}NHCN_2HC_6H_4)]$ (15) (from 2-azidobenzimidazole).

The recent suggestion that complexes of the type $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NR)]$ (R = Ph [1] or Me [2]) may be an entry into a dehydrogenation–hydrogenation cycle,[3] similar to that observed for $[Fe_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NEt)]$,[4] has caused increased interest in the reactions between triosmium clusters and nitrogen-containing organic molecules especially 1,3-dipolar compounds. For instance, the unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ has been reacted with diazoalkanes ($N_2CR^1R^2$) to give clusters in which the nitrogen is retained [5,6] $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCR^1R^2)]$ ($R^1 = R^2$ = Ph; R^1 = Ph, R^2 = Me; R^1 = Ph, R^2 = H; or $R^1 = R^2$ = Me) and clusters in which the nitrogen is lost $[Os_3(\mu\text{-}H)(CO)_{10}(CH_2R)]$ (R = H,[7] Me,[8] or CO_2Et [9]). Furthermore, addition of diazomethane to the unsaturated cluster $[Os_3(CO)_9(C_2Ph_2)]$ has led to the formation of $[Os_3(CO)_9(C_2Ph_2)(CH_2)]$ *via* an intermediate cluster in which nitrogen is retained.[10] Trimethylsilyl azide (Me_3SiN_3) adds to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to form a complex containing a bridging triazenido-ligand $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3H)]$.[11] Here we report that primary alkyl-, secondary alkyl-, and aryl-azides give cyclo-adducts $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$ with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$; thermolysis of these adducts causes extrusion of carbon monoxide and dinitrogen to give the face-capped complexes $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NR)]$. A preliminary report of this work has appeared.[12] Azido-1-phenylethene (N_3CPhCH_2) also forms an adduct $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3CPhCH_2)]$ but on thermolysis this liberates only dinitrogen to give $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NCMePh)]$. It has been shown [13] that toluene-*p*-sulphonyl azide ($4\text{-}MeC_6H_4SO_2N_3$) adds to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me\text{-}p)]$ presumably by loss of N_2 from an intermediate adduct. Here we present evidence that this type of reaction is general for azides bearing an electron-withdrawing substituent adjacent to the azido-function although the products obtained may not, in some cases, have an $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHR)]$ structure due to subsequent rearrangement.

Results and Discussion

Reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with the azides N_3R in hexane at *ca.* 20 °C for 24 h leads to the formation of the complexes $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$ [R = Ph (1), Bu^n (2), CH_2Ph (3), or cyclo-C_6H_{11} (4)]. The ^1H n.m.r. spectra of the cyclo-adducts (1)—(4) each contain a metal hydride and a broad N–*H* signal together with resonances characteristic of the substituent organic groups (Table 1). Analytical (Table 2) and mass spectroscopic (Table 1) data for the complexes are consistent with the formulation $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$. When the adducts (1)—(4) were maintained in refluxing 1,2-dimethoxyethane for *ca.* 24 h the clusters $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NR)]$ [R = Ph (6), Bu^n (7), CH_2Ph (8), or cyclo-C_6H_{11} (9)] could be isolated by thin-layer chromatography (t.l.c.) (Scheme 1, Tables 2 and 3). The methylene protons of the benzyl adduct (3) are magnetically inequivalent, and consequently an AB n.m.r. pattern is observed. This inequivalence does not occur in the more symmetrical capped compound (8). The phenyl substituted nitrogen-capped cluster (6) has been previously prepared from $[Os_3(CO)_{12}]$ and phenylamine.[3]

A substituted triazene ligand may be expected to co-ordinate to two metal atoms asymmetrically. The molecular structures of the phenyl derivatives (1) and (6) were determined in order to elucidate the bonding mode of the nitrogen-containing ligand and to confirm the overall molecular geometries.

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† 1,1,1,2,2,2,3,3,3,3-Decarbonyl-1,2-μ-hydrido-1,2-μ-1′-phenyltriazenido(N^1N^3)-*triangulo*-triosmium.

‡ 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2;1,3-di-μ-hydrido-μ_3-phenylimido-*triangulo*-triosmium.

Supplementary data available (No. SUP 23379, 42 pp.): observed and calculated structure factors, thermal parameters, least-squares planes, hydrogen atomic co-ordinates: for (1) and (6). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

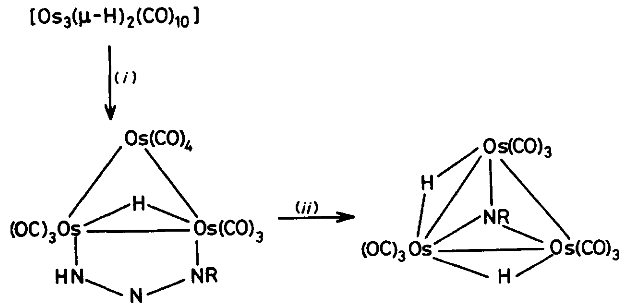
Table 1. Spectral data for the complexes $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$

Compound	R	m/e (M^+ ^{192}Os)	N.m.r. (δ/p.p.m.)				ν(CO)/cm^{-1} (hexane solution)
			Solvent	N–H (br s, 1 H)	Os–H (s, 1 H)	Other	
(1)	Ph	977	CD_2Cl_2	8.75	−12.41	7.55—7.04 (m, 5 H)	2 110w, 2 069s, 2 061s, 2 047w, 2 026s, 2 015s, 2 010 (sh), 2 001m, 1 990w, 1 975w
(2)	Bu^n	957	$CDCl_3$	8.01	−12.50	4.31—3.96 (m, 6 H) 2.01—1.04 (m, 6 H)	2 109w, 2 067s, 2 050s, 2 045w, 2 031m, 2 025s, 2 014s, 2 007m, 1 998m, 1 990m, 1 978w
(3)	CH_2Ph	991	CD_2Cl_2	8.13	−12.77	5.36 (d, J = 13 Hz, 1 H) 4.65 (d, J = 13 Hz, 1 H)	2 108w, 2 067s, 2 061s, 2 045w, 2 025m, 2 014s, 2 010s, 2 001m, 1 991w, 1 978w
(4)	cyclo-C_6H_{11}	983	$CDCl_3$	8.02	−12.52	3.96 (m, 1 H) 2 02—1.45 (m, 10 H)	2 109w, 2 065s, 2 059s, 2 045w, 2 024s, 2 015s, 2 006w, 1 997w, 1 988w, 1 976w
(5)	$CPhCH_2$	1 003	$(CD_3)_2CO$	10.40	−12.62	5.05 (s, 1 H) 4.80 (s, 1 H)	2 109w, 2 068s, 2 058s, 2 044w, 2 025s, 2 012s, 2 008 (sh), 2 001m, 1 989w, 1 978w

Table 2. Analytical and yield data for the new complexes [a]

Compound	Yield [b] (%)	Elemental analysis [c]						
		Found (%)				Required (%)		
		C	H	N	Formula	C	H	N
(1)	81	19.85	1.05	4.45	$C_{16}H_{17}N_3O_{10}Os_3$	19.75	0.70	4.30
(2)	67	17.90	1.50	4.70	$C_{14}H_{11}N_3O_{10}Os_3$	17.65	1.15	4.40
(3)	65	21.10	1.20	4.20	$C_{17}H_9N_3O_{10}Os_3$	20.70	0.90	4.25
(4)	43	19.75	1.45	4.25	$C_{16}H_{13}N_3O_{10}Os_3$	19.65	1.35	4.30
(5)	61	21.65	0.90	4.20	$C_{18}H_9N_3O_{10}Os_3$	21.45	0.90	4.05
(7)	42	17.45	1.30	1.50	$C_{13}H_{11}NO_9Os_3$	17.40	1.25	1.55
(8)	40	20.55	1.00	1.35	$C_{16}H_9NO_9Os_3$	20.65	1.00	1.50
(9)	38	19.75	1.55	1.40	$C_{15}H_{13}NO_9Os_3$	19.55	1.40	1.50
(10)	35	22.30	1.00	1.45	$C_{18}H_9NO_{10}Os_3$	22.30	0.95	1.45
(11)	46	24.15	1.15	1.55	$C_{22}H_{12}NO_{13}Os_3P$	24.00	1.10	1.25
(12)	96	18.10	0.45	2.90	$C_{15}H_5ClN_2O_{10}Os_3$	18.40	0.50	2.85
(14)	21	20.65	0.70	4.20	$C_{17}H_{17}N_3O_{10}Os_3$	20.75	0.70	4.25
(15)	25 [d]	17.95	0.70	3.05	$C_{14}H_5ClN_2O_9Os_3$	17.70	0.55	2.95

[a] Compounds (6) and (13) were identified by comparison of spectra with those previously reported [3,19] and were formed in 81 and 30% yields respectively. [b] Based on $[Os_3(\mu\text{-}H)_2(CO)_{10}]$. [c] Cambridge University analytical department. [d] Based on (12).



Scheme 1. Synthesis and thermolysis of azide adducts $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3R)]$: (*i*) N_3R, hexane, 20 °C, 24 h; (*ii*) 1,2-dimethoxyethane, 85 °C, 24 h

The molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}HN_3Ph)]$ (1) is shown in Figure 1 while the associated bond lengths and interbond angles are presented in Tables 4 and 5, respectively. The molecules are separated by normal van der Waals distances. The three Os atoms lie at the vertices of an approximately equilateral triangle. The triazenido-ligand bridges the Os(1)–Os(2) edge co-ordinating through N(1) and N(3) in two axial sites; the phenyl group is bonded to atom N(1) of the triazenido-ligand. The Os(1)Os(2)N(1)N(2)N(3) unit is planar, and this plane makes an angle of 82.9(1)° with the Os_3 triangle. Metal atoms Os(1) and Os(2) are each co-ordinated to two equatorial and one axial carbonyl groups in a terminal fashion. The Os(3) atom is co-ordinated to two axial and two equatorial carbonyls such that this metal atom exhibits distorted octahedral co-ordination geometry. The hydride ligand was not located directly in the analysis, however, the distribution of the carbonyl groups indicates that it lies in the plane of the Os_3 triangle and bridges the Os(1)–Os(2) edge. The

Table 3. Spectral data for the complexes $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NR)]$

			N.m.r. (δ/p.p.m.)			
Compound	R	*m/e* (M^+ ^{192}Os)	Solvent	Os–H (s, 2 H)	Other	ν(CO)/cm^{-1} (hexane solution)
(6)	Ph	921	CD_2Cl_2	−18.19	7.19 (m, 5 H)	2 115w, 2 083s, 2 056s, 2 034m, 2 010s, 1 988m, 1 977w
(7)	Bu^n	901	$CDCl_3$	−18.47	4.23—4.19 (m, 6 H) 1.99—1.08 (m, 3 H)	2 111w, 2 077s, 2 050s, 2 031m, 2 001s, 1 983m, 1 971w
(8)	CH_2Ph	935	CD_2Cl_2	−18.65	7.39 (m, 5 H) 5.08 (s, 2 H)	2 111w, 2 078w, 2 052s, 2 030s, 2 029m, 2 003m, 1 986m, 1 974w
(9)	cyclo-C_6H_{11}	927	$CDCl_3$	−18.53	3.01 (m, 1 H) 2.32—1.09 (m, 10 H)	2 111w, 2 078s, 2 051s, 2 031s, 1 985m, 1 973w

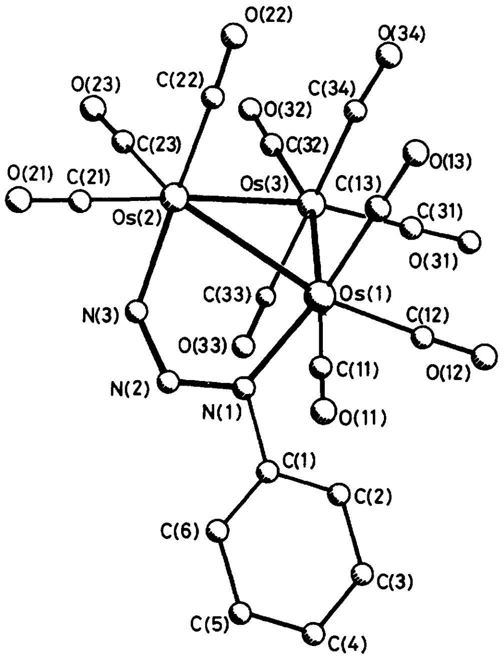


Figure 1. The molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}HN_3Ph)]$ showing the atom numbering scheme adopted

average *cis* Os–Os–C(carbonyl) angle for the two equatorial carbonyl groups adjacent to the Os(1)–Os(2) bond is 118(1)° which is considerably wider than the average angle of 90(2)° for the other equatorial carbonyl groups. The steric influence of hydride causes the carbonyl groups to bend away from the bridged edge.

Triazenido-ligands have been observed previously in a number of cluster complexes such as $[Cu(MeN_3Me)]_4$[14] and $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3H)]$.[11] The structure of the latter osmium complex is similar to that of (1). Both clusters are formally 48 electron species, with the triazenido-ligand acting as a three-electron donor. In $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3H)]$[11] the Os–Os bond bridged by the triazenido-ligand is *ca.* 0.03 Å longer than the mean value of 2.889(4) Å for the two unbridged Os–Os bonds. However, in (1) the bridged and unbridged Os–Os bonds show little variation but all are longer than the average value of 2.877(1) Å for the Os–Os distances in the parent car-

Table 4. Bond lengths (Å) for $[Os(\mu\text{-}H)(CO)_{10}(\mu\text{-}HN_3Ph)]$ (1)

Os(1)–Os(2)	2.900(2)	Os(1)–Os(3)	2.888(2)
Os(1)–N(1)	2.137(10)	Os(1)–C(11)	1.908(15)
Os(1)–C(12)	1.918(13)	Os(1)–C(13)	1.882(13)
Os(2)–Os(3)	2.900(2)	Os(2)–N(3)	2.110(10)
Os(2)–C(21)	1.897(13)	Os(2)–C(22)	1.898(13)
Os(2)–C(23)	1.929(14)	Os(3)–C(31)	1.899(11)
Os(3)–C(32)	1.876(15)	Os(3)–C(33)	1.972(15)
Os(3)–C(34)	1.929(15)	N(1)–N(2)	1.317(15)
N(1)–C(1)	1.445(14)	N(2)–N(3)	1.291(16)
C(11)–O(11)	1.134(20)	C(12)–O(12)	1.133(16)
C(13)–O(13)	1.165(17)	C(21)–O(21)	1.145(17)
C(22)–O(22)	1.131(16)	C(23)–O(23)	1.116(18)
C(31)–O(31)	1.127(15)	C(32)–O(32)	1.172(21)
C(33)–O(33)	1.120(19)	C(34)–O(34)	1.136(19)

Table 5. Bond angles (°) for $[Os(\mu\text{-}H)(CO)_{10}(\mu\text{-}HN_3Ph)]$ (1)

Os(2)–Os(1)–Os(3)	60.1(1)	Os(2)–Os(1)–N(1)	81.2(3)
Os(3)–Os(1)–N(1)	90.6(3)	Os(2)–Os(1)–C(11)	118.2(4)
Os(3)–Os(1)–C(11)	177.0(4)	N(1)–Os(1)–C(11)	86.6(5)
Os(2)–Os(1)–C(12)	146.2(4)	Os(3)–Os(1)–C(12)	86.3(4)
N(1)–Os(1)–C(12)	96.5(5)	C(11)–Os(1)–C(12)	95.1(6)
Os(2)–Os(1)–C(13)	93.9(4)	Os(3)–Os(1)–C(13)	91.1(5)
N(1)–Os(1)–C(13)	173.1(5)	C(11)–Os(1)–C(13)	91.5(6)
C(12)–Os(1)–C(13)	90.3(5)	Os(1)–Os(2)–Os(3)	59.7(1)
Os(1)–Os(2)–N(3)	80.7(3)	Os(3)–Os(2)–N(3)	90.5(3)
Os(1)–Os(2)–C(21)	117.7(5)	Os(3)–Os(2)–C(21)	176.2(4)
N(3)–Os(2)–C(21)	86.2(5)	Os(1)–Os(2)–C(22)	95.9(4)
Os(3)–Os(2)–C(22)	92.2(4)	N(3)–Os(2)–C(22)	173.8(6)
C(21)–Os(2)–C(22)	90.9(4)	Os(1)–Os(2)–C(23)	144.8(4)
Os(3)–Os(2)–C(23)	85.9(4)	N(3)–Os(2)–C(23)	93.6(5)
C(21)–Os(2)–C(23)	96.3(6)	C(22)–Os(2)–C(23)	92.2(6)
Os(1)–Os(3)–Os(2)	60.1(1)	Os(1)–Os(3)–C(31)	98.4(5)
Os(2)–Os(3)–C(31)	158.4(5)	Os(1)–Os(3)–C(32)	160.7(4)
Os(2)–Os(3)–C(32)	100.7(4)	C(31)–Os(3)–C(32)	100.9(6)
Os(1)–Os(3)–C(33)	88.8(4)	Os(2)–Os(3)–C(33)	90.6(4)
C(31)–Os(3)–C(33)	91.3(6)	C(32)–Os(3)–C(33)	89.0(6)
Os(1)–Os(3)–C(34)	90.7(5)	Os(2)–Os(3)–C(34)	88.3(4)
C(31)–Os(3)–C(34)	89.7(6)	C(32)–Os(3)–C(34)	91.2(6)
C(33)–Os(3)–C(34)	179.0(5)	Os(1)–N(1)–N(2)	128.6(8)
Os(1)–N(1)–C(1)	121.6(7)	N(2)–N(1)–C(1)	108.5(9)
N(1)–N(2)–N(3)	117.5(10)	Os(2)–N(3)–N(2)	131.3(8)
N(1)–C(1)–C(6)	119.2(5)	N(1)–C(1)–C(2)	120.7(5)
Os(1)–C(11)–O(11)	178.9(13)	Os(1)–C(12)–O(12)	175.6(12)
Os(1)–C(13)–O(13)	177.5(13)	Os(2)–C(21)–O(21)	177.4(13)
Os(2)–C(22)–O(22)	177.4(12)	Os(2)–C(23)–O(23)	177.9(11)
Os(3)–C(31)–O(31)	179.6(13)	Os(3)–C(32)–O(32)	178.5(12)
Os(3)–C(33)–O(33)	177.3(12)	Os(3)–C(34)–O(34)	174.7(13)

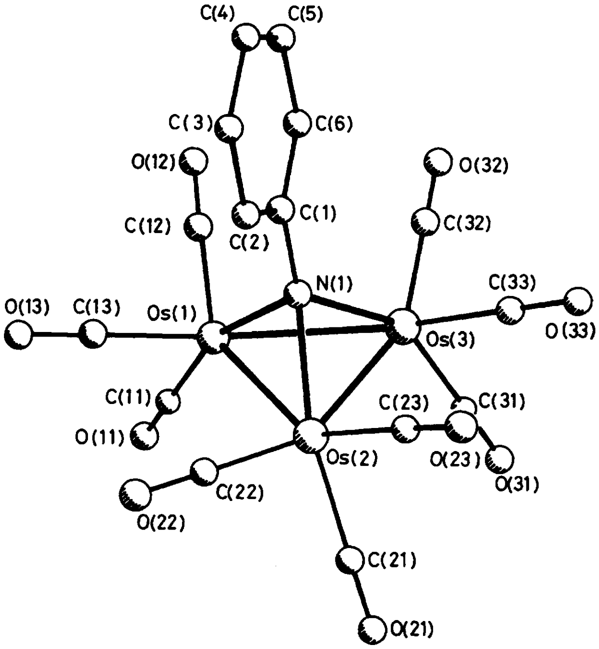


Figure 2. The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ showing the atom numbering scheme adopted

bonyl $[Os_3(CO)_{12}]$.[15] Adams and co-workers [16] obtained structural information on a number of triosmium clusters in which an Os–Os bond is bridged by a three atom unit in an η-fashion similar to that observed in (1). In the cases where the Os–Os bond is bridged by both the η-group and a hydride the bridged bond is generally slightly longer than the corresponding unbridged Os–Os bonds. In the cases where the η-bridged Os–Os bond does not have a hydride across it the bond length is shorter than for the unbridged bonds. It seems that in all these Os_3 clusters containing a three atom η-bridging unit the ligand exerts an Os–Os bond shortening effect which at least partially counterbalances the bond lengthening influence of the bridging hydride.

The dimensions of the triazenido N_3 unit in (1) are similar to the average values for the Os–N [2.13(2) Å] and N–N [1.32(2) Å] distances and the N–N–N angle [118(1)°] in $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3H)]$.[11] The triazenido-bridge unit in (1) bridges the Os(1)–Os(2) edge in a fairly symmetrical fashion and indicates electron delocalisation over the N–N–N unit. Any slight increase in asymmetry over the case of the unsubstituted HN_3H ligand may be ascribed to the presence of the phenyl ring bonded to N(1). This ring makes an angle of 55.7° with the Os(1)N(1)N(2)N(3)Os(2) plane.

All the carbonyl ligands are linear to within experimental error. The Os–C(carbonyl) bonds may be separated into three groups in terms of length. The longest Os–C distances [mean 1.95(2) Å] occur in *axial* carbonyl groups *trans* to another carbonyl ligand. Intermediate in length [mean 1.90(2) Å] are the equatorial Os–C bonds *trans* to an Os–Os bond. The average Os–C distance for the axial carbonyls *trans* to the N atoms of the triazenido-ligand [1.89(2) Å] is slightly shorter than, although probably not significantly different from, the Os–C distances of the equatorial carbonyls. These trends are in agreement with the proposal that *trans* axial groups compete for back donation of electron density from the same metal orbital, and that the carbonyl is a better π-acceptor than an Os atom or the N atom of the triazene.

Table 6. Bond lengths (Å) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ (6)

Os(1)–Os(2)	2.848(2)	Os(1)–Os(3)	2.846(2)
Os(1)–N(1)	2.099(8)	Os(1)–C(11)	1.942(12)
Os(1)–C(12)	1.914(11)	Os(1)–C(13)	1.912(12)
Os(2)–Os(3)	2.715(2)	Os(2)–N(1)	2.074(8)
Os(2)–C(21)	1.936(13)	Os(2)–C(22)	1.922(12)
Os(2)–C(23)	1.916(13)	Os(3)–N(1)	2.078(9)
Os(3)–C(31)	1.888(13)	Os(3)–C(32)	1.936(14)
Os(3)–C(33)	1.897(11)	N(1)–C(1)	1.448(12)
C(11)–O(11)	1.120(15)	C(12)–O(12)	1.148(14)
C(13)–O(13)	1.146(15)	C(21)–O(21)	1.122(19)
C(22)–O(22)	1.148(15)	C(23)–O(23)	1.126(17)
C(32)–O(32)	1.142(18)	C(33)–O(33)	1.126(14)

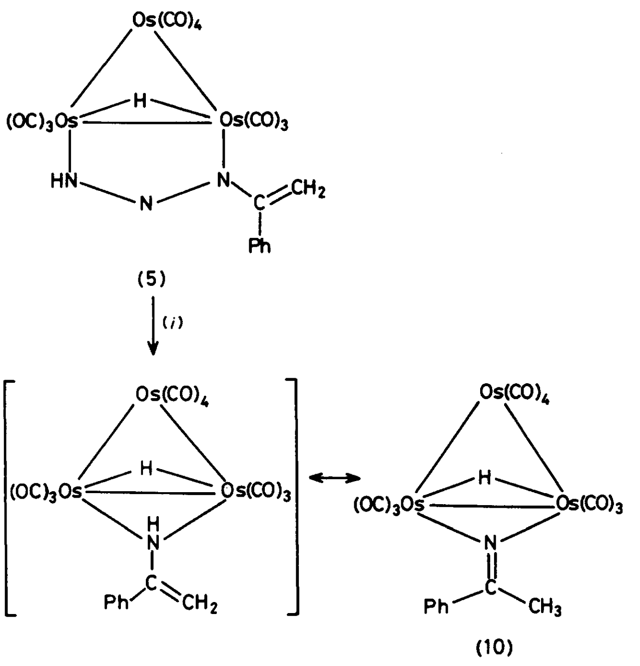
Table 7. Bond angles (°) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ (6)

Os(2)–Os(1)–Os(3)	57.0(1)	Os(2)–Os(1)–N(1)	46.6(2)
Os(3)–Os(1)–N(1)	46.7(2)	Os(2)–Os(1)–C(11)	120.2(3)
Os(3)–Os(1)–C(11)	119.3(3)	N(1)–Os(1)–C(11)	163.1(4)
Os(2)–Os(1)–C(12)	143.5(3)	Os(3)–Os(1)–C(12)	96.6(3)
N(1)–Os(1)–C(12)	97.3(4)	C(11)–Os(1)–C(12)	93.8(4)
Os(2)–Os(1)–C(13)	97.5(3)	Os(3)–Os(1)–C(13)	146.1(3)
N(1)–Os(1)–C(13)	100.0(4)	C(11)–Os(1)–C(13)	92.0(5)
C(12)–Os(1)–C(13)	93.6(5)	Os(1)–Os(2)–Os(3)	61.5(1)
Os(1)–Os(2)–N(1)	47.3(2)	Os(3)–Os(2)–N(1)	49.2(2)
Os(1)–Os(2)–C(21)	116.6(4)	Os(3)–Os(2)–C(21)	104.2(4)
N(1)–Os(2)–C(21)	151.8(4)	Os(1)–Os(2)–C(22)	99.8(3)
Os(3)–Os(2)–C(22)	155.8(3)	N(1)–Os(2)–C(22)	107.2(4)
C(21)–Os(2)–C(22)	97.9(5)	Os(1)–Os(2)–C(23)	146.0(4)
Os(3)–Os(2)–C(23)	95.3(4)	N(1)–Os(2)–C(23)	98.9(4)
C(21)–Os(2)–C(23)	92.0(5)	C(22)–Os(2)–C(23)	93.6(5)
Os(1)–Os(3)–Os(2)	61.6(1)	Os(1)–Os(3)–N(1)	47.3(2)
Os(2)–Os(3)–N(1)	49.1(2)	Os(1)–Os(3)–C(31)	114.1(4)
Os(2)–Os(3)–C(31)	103.4(4)	N(1)–Os(3)–C(31)	150.2(5)
Os(1)–Os(3)–C(32)	100.5(3)	Os(2)–Os(3)–C(32)	155.3(4)
N(1)–Os(3)–C(32)	106.5(4)	C(31)–Os(3)–C(32)	99.5(5)
Os(1)–Os(3)–C(33)	148.1(4)	Os(2)–Os(3)–C(33)	94.6(4)
N(1)–Os(3)–C(33)	101.4(4)	C(31)–Os(3)–C(33)	90.7(5)
C(32)–Os(3)–C(33)	94.4(5)	Os(1)–N(1)–Os(2)	86.1(3)
Os(1)–N(1)–Os(3)	85.9(3)	Os(2)–N(1)–Os(3)	81.7(3)
Os(1)–N(1)–C(1)	125.2(5)	Os(2)–N(1)–C(1)	131.9(5)
Os(3)–N(1)–C(1)	130.0(6)	Os(1)–C(11)–O(11)	179.4(11)
N(1)–C(1)–C(2)	120.1(4)	N(1)–C(1)–C(6)	119.9(4)
Os(1)–C(12)–O(12)	177.7(9)	Os(1)–C(13)–O(13)	175.6(11)
Os(2)–C(21)–O(21)	177.0(11)	Os(2)–C(22)–O(22)	178.9(8)
Os(2)–C(23)–O(23)	177.7(11)	Os(3)–C(32)–O(32)	178.0(10)
Os(3)–C(33)–O(33)	178.5(11)		

The molecular structure of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ (6) is shown in Figure 2. The final bond lengths and angles are listed in Tables 6 and 7, respectively. There are no abnormally short intermolecular contacts between the molecules.

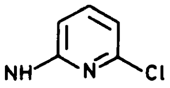
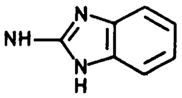
The molecular structure of (6) is very similar to that of the methyl derivative $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NMe)]$.[3] The three Os atoms lie at the vertices of an isosceles triangle. Each metal is co-ordinated to three terminal carbonyls, two of which occupy pseudo-equatorial positions close to the plane of the Os_3 triangle while the third occupies an axial site approximately *trans* to the N–Os bond from the μ_3-N atom. The NPh group caps the Os_3 triangle with the N atom lying 1.31 Å from the Os_3 plane. The phenyl ring makes an angle of 93.5° with the Os triangle. The two hydrides were not located directly in the *X*-ray analysis but the distribution of the carbonyl ligands indicates that they bridge the two longer sides of the triangle, Os(1)–Os(2) and Os(1)–Os(3), and lie on the opposite side of the Os_3 triangle to the capping N atom. The Os–Os–C(carbonyl) angles for the axial carbonyls adjacent to the longer Os–Os bonds average 118(2)° compared to the value of 104(2)° for the axial carbonyls adjacent to the shorter Os(2)–Os(3) bond.

All the Os–Os distances in (6) are shorter than the average



Scheme 2. A possible mechanism for formation of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NCMePh)]$ (10): (*i*) 1,2-dimethoxyethane, 85 °C, 24 h, $-N_2$

Table 8. Spectral data for the complexes $[Os_3(\mu\text{-}H)(CO)_{10}(X)]$

				N.m.r. (δ/p.p.m.)			
Compound	X	*m/e* (M^+ ^{192}Os)	Solvent	N-*H* (br, 1 H)	Os-*H* (1 H)	Other	ν(CO)/cm^{-1} (hexane solution)
(10)	NCMePh	963	CD_2Cl_2		−14.97 (s)	7.50—7.10 (m, 5 H) 2.82 (s, 3 H)	2 104w, 2 068s, 2 054s, 2 020s, 2 006m, 1 994s, 1 978w
(11)	$NHPO(OPh)_2$	1 105	$(CD_3)_2CO$	3.03	−14.82 (d, *J* = 1 Hz)	7.70—7.24 (m, 5 H)	2 111s, 2 078s, 2 061s, 2 025s, 2 014m, 2 004s, 1 989w, 1 970w
(12)		984, 986 (3 : 1)	$(CD_3)_2CO$	6.12	−14.18 (d, *J* = 2 Hz)	7.68 (dd, 1 H) 7.17 (d, *J* = 12 Hz, 1 H) 7.10 (d, *J* = 12 Hz, 1 H)	2 105w, 2 072s, 2 056s, 2 022s, 2 006m, 2 000s, 1 985w, 1 970w
(15)		989	$(CD_3)_2CO$	3.36 9.33	−15.04 (s)	6.89 (m, 4 H)	2 102w, 2 060s, 2 052s, 2 016s, 2 010s, 1 994 (sh), 1 988m

value of 2.877(1) Å in $[Os_3(CO)_{12}]$.[15] However, the hydride bridged and unbridged Os–Os bond lengths are similar to the values of 2.861 2(7) and 2.749 8(7) Å, respectively, in $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NMe)]$.[3] In a number of triosmium and triruthenium clusters of the general formula $[M_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}X)]$, where X is a sulphur or phosphorus donor ligand, the presence of the capping group has a bond shortening influence on the metal–metal bonds partially counterbalancing the bond lengthening influence of the hydrides.[17] In the case of these two osmium clusters the bond shortening influence of the capping NR group more than counterbalances the lengthening effect of the hydrides, and the unbridged Os(2)–Os(3) distance in (6) is one of the shortest observed in trinuclear Os clusters where multiple bond character for the bond has not been invoked. The complex (6) is formally a 48 electron system, and the Os(2)–Os(3) interaction may be described in terms of a two-centre two-electron bond.

The Os(1)–N(1) distance is slightly longer than the distances from the capping N atom to the other two metal atoms. Similar trends are observed in $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NMe)]$,[3] where the distance from the nitrogen cap to the unique Os atom, the one co-ordinated to both bridging hydrides, is 2.081(14) Å compared to the value of 2.070(8) Å for the other two Os–N bonds. The N(1)–C(1) bond length suggests that there is little multiple bond character in this bond.

None of the carbonyl groups deviates significantly from linearity. There is no significant difference between the average bond lengths of the axial and equatorial Os–C(carbonyl) bonds [1.92(3) Å].

The azido-1-phenylethene adduct $[Os_3(\mu\text{-}H)(CO)_{10}(HN_3CPhCH_2)]$ (5) was formed in the same way as clusters (1)—(4) although a longer reaction time (3 weeks) was required (Tables 1 and 2). Thermolysis of (5) under the same conditions as were used for adducts (1)—(4) gives $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NCMePh)]$ (10); this was clearly shown by the physical and spectral data (Tables 2 and 8), notably by the NC*H*$_3$ ^1H n.m.r. resonance. It seems reasonable that the cluster (5) loses dinitrogen on heating and then rapid tautomerism prevents subsequent decarbonylation (see Scheme 2).

Spectral and physical data (Tables 8 and 2) show that reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ under various conditions (see Experimental section) with azides bearing an electron-withdrawing substituent results in loss of dinitrogen to give clusters of the type $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHR)]$ [R = $PO(OPh)_2$ (11) or 2-(6-$ClNC_5H_3$) (12)]; a similar reaction has been reported elsewhere to give an analogous cluster (R = 4-$MeC_6H_4SO_2$).[13] We propose that the electron-withdrawing substituent stabilizes the transition state involved in the loss of dinitrogen from a cyclo-adduct which consequently is not observed (Scheme 3); this is a simple analogy to the decomposition of triazoles to aziridines which is more facile with an electron-withdrawing substituent on the retained nitrogen than without such a substituent.[18,*] Clusters formed in this case are less likely to decarbonylate to a N-capped system than

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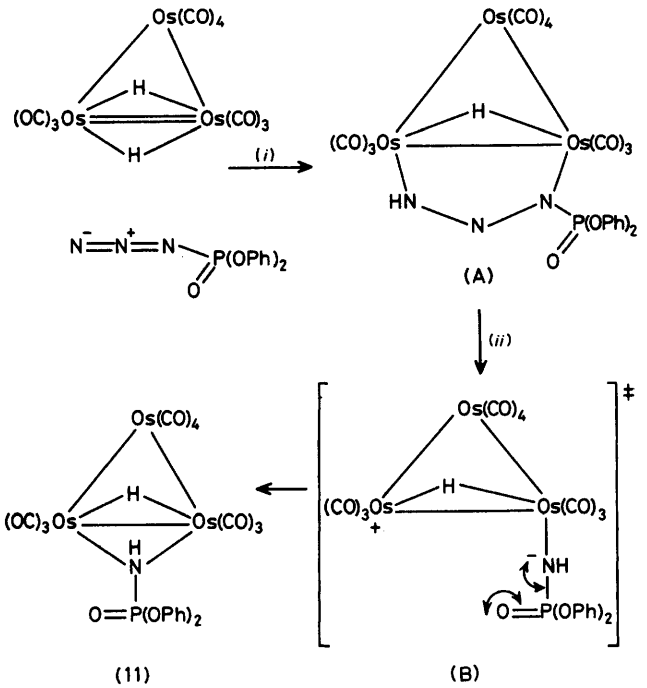
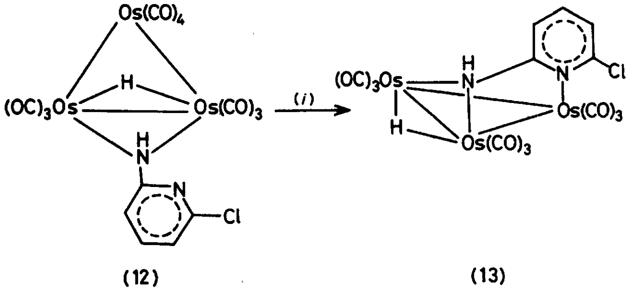
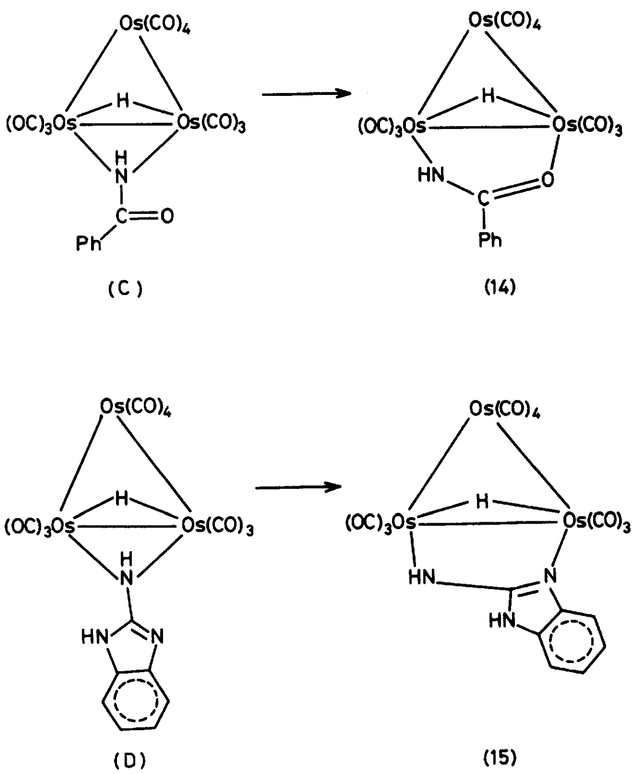
[*] Although in some of the examples loss of dinitrogen could be a consequence of the higher temperatures necessary to cause reaction, see Experimental section.



Scheme 3. A possible mechanism for the reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with azide bearing an electron-withdrawing substituent [here $PO(OPh)_2$]: (*i*) addition to give the triazenido-complex (A) which was not observed; (*ii*) H transfer, $-N_2$, to give (B), a stabilized transition state



Scheme 4. Decarbonylation of $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}NH\text{-}2\text{-}(6\text{-}ClNC_5H_3)\}]$ (12): (*i*) 130 °C, $-CO$



Scheme 5. Possible rearrangements to form $[Os_3(\mu\text{-}H)(CO)_{10}(NHCOPh)]$ (14) and $[Os_3(\mu\text{-}H)(CO)_{10}(NHCN_2HC_6H_4)]$ (15). (C) and (D) not observed

similar clusters with alkyl nitrogen substituents because the electron-withdrawing group reduces the availability of the nitrogen lone pair for further co-ordination. The presence of another functional group within the ligand may facilitate further reaction, thus the cluster $[Os_3(\mu\text{-}H)(CO)_{10}\{\mu\text{-}NH\text{-}2\text{-}(6\text{-}ClNC_5H_3)\}]$ was decarbonylated to yield the complex $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}NH\text{-}2\text{-}(6\text{-}ClNC_5H_3)\}]$ (13) (see Scheme 4) in which the pyridine nitrogen is co-ordinated; cluster (13) is virtually identical to $[Os_3(\mu\text{-}H)(CO)_9\{\mu\text{-}NH\text{-}2\text{-}(NC_5H_4)\}]$, synthesized recently by a different route,[19] and spectral data for the two compounds are compatable with this.

In two cases the electron-withdrawing substituent of the azide becomes involved in direct bonding to the triosmium cluster skeleton. The initial product of addition of phenacyl azide rearranges yielding the known cluster $[Os_3(\mu\text{-}H)(CO)_{10}(NHCOPh)]$[20] in 30% yield; in the case of 2-azidobenzimidazole rearrangement is proposed, on the basis of dissimilarity of the carbonyl i.r. pattern observed and that for the compounds $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHR)]$ [$R = PO(OPh)_2$ (11), 2-(6-$ClNC_5H_3$) (12), and 4-$MeC_6H_4SO_2$[13]], the basic nitrogen of the heterocycle becomes co-ordinated (Scheme 5) and a μ-NHR system is not observed.

Experimental

Infrared spectra were recorded as solutions in 0.5 mm NaCl cells on a Perkin-Elmer 257 spectrometer with CO calibrant. Mass spectra were obtained using an A.E.I. M.S. 12 instrument at 70 eV ionizing potential. Hydrogen-1 n.m.r. were recorded at 20 °C on a Varian Associates CFT (80 MHz) spectrometer using an internal deuterium lock. Thin layer chromatography (t.l.c.) was carried out on commercial Merck plates coated with a 0.25 mm layer of silica. Solvents were dried and distilled before use. Phenyl-,[21] n-butyl-,[22] benzyl-,[22] benzoyl-,[23] cyclohexyl-,[24] 1-phenylethenyl-,[25] 2-(6-chloropyridyl)-,[26] and 2-benzimidazolyl-azide[27] were prepared by known methods; diphenylphosphoryl azide was purchased from Aldrich Chemical Company Limited.

Preparation of the Azide Adducts (1)—(5).—*The complex* $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (*ca.* 0.100 g) and the azide (2 equivalents) were stirred in hexane (20 cm³) at 20 °C for 24 h. Removal of the solvent under reduced pressure and t.l.c. (3 : 2 hexane–dichloromethane eluant) gave the azide adducts (1)—(4). A reaction time of 3 weeks was required to form the azido-1-phenylethene adduct (5), however. Samples were recrystallized for analysis and *X*-ray studies (where appropriate) from boiling hexane except for the n-butyl cluster (2) which was crystallized from aqueous ethanol at 0 °C.

Thermolysis of the Azide Adducts.—The adduct (*ca.* 0.100 g) was maintained in refluxing 1,2-dimethoxyethane for 24 h.

Removal of the solvent under reduced pressure and t.l.c. (3% ethyl acetate in hexane eluant) afforded the complexes (6)—(10) as the most intense (u.v.) bands. Purification and formation of single crystals was as for the azide adducts.

Other Preparations.—[$Os_3(\mu$-H)(CO)$_{10}$(NHR)] [R = PO(OPh)$_2$ (11), COPh (14), *or* 2-$CN_2HC_6H_4$ (15)]. The complex [$Os_3(\mu$-H)(CO)$_{10}$] (*ca.* 0.100 g) and the azide (3 equivalents) were maintained in refluxing hexane (30 cm^3) for 20 h. Removal of the solvent and t.l.c. (1 : 1 hexane–dichloromethane eluant) gave the appropriate product which was then recrystallized by slow evaporation of a hexane–dichloromethane solution at 0 °C under N_2.

[$Os_3(\mu$-H)(CO)$_{10}${μ-NH-2-(6-ClNC$_5$H$_3$)}] (12). The same method was employed as for compounds (11), (14), and (15) but using reaction conditions of 20 °C/3 d.

[$Os_3(\mu$-H)(CO)$_9${μ-NH-2-(6-ClNC$_5$H$_3$)}] (13). Cluster (12) (0.137 g) was maintained in hexane (30 cm^3) under argon (5 atm) at 130 °C for 14 h. The reaction mixture was then dealt with in the same way as for compounds (11), (14), and (15). *m/e* ^{192}Os: 956, 958 (3 : 1). ^{1}H N.m.r. [δ/p.p.m., $(CD_3)_2CO$]: 7.84 (m, 1 H), 7.44 (d, *J* = 8 Hz, 1 H), 6.82 (d, *J* = 8 Hz, 1 H), 3.31 (br s, 1 H), −13.00 (s, 1 H). I.r. (hexane solution): 2 086w, 2 057s, 2 031s, 2 002s, 1 983m, 1 968w, and 1 958w.

Molecular Structure Determination of [$Os_3(\mu$-H)(CO)$_{10}(\mu$-HN$_3$Ph)] (1).—A single crystal (*ca.* 0.36 × 0.27 × 0.25 mm) was mounted on a glass fibre with epoxy-resin adhesive, and unit-cell dimensions and space group determined *via* Weissenberg (Cu) *X*-ray photography.

The crystal was transferred to a Syntex $P2_1$ four-circle diffractometer and 4 135 reflections measured in the range $3.0 < 2\theta < 50.0°$ using graphite monochromated Mo-K_α radiation and a 96-step $\omega/2\theta$ scan technique. The scan width was set from 1° below λ(Mo-$K_{\alpha1}$) (0.709 26 Å) to 1° above λ(Mo-$K_{\alpha2}$) (0.713 54 Å), and the scan speed varied from 2.0° min^{-1} to 29.3° min^{-1} depending on the intensity from a 1 s prescan; reflections with intensities of <9 counts s^{-1} were not remeasured. Backgrounds were measured for half the scan time. Two check reflections were monitored periodically throughout data collection and showed no significant variation. Accurate cell dimensions were obtained from the centring of 15 strong reflections in the range $20 < 2\theta < 30°$.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 439 azimuthal scan data from 15 independent reflections were applied. Transmission factors ranged from 0.464 to 0.998 for the full data set. Lorentz polarisation corrections were also applied and equivalent reflections averaged to give 3 155 unique observed data [$F > 3\sigma(F)$].

Crystal data. $C_{16}H_7N_3O_{10}Os_3$, $M = 971.85$, Monoclinic, $a = 9.665(3)$, $b = 8.823(4)$, $c = 25.571(14)$ Å, $\beta = 100.17(4)°$, $U = 2\,146.3$ Å^3, D_m not measured, $Z = 4$, $D_c = 3.01$ g cm^{-3}, $F(000) = 1\,727$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 177.63 cm^{-1}, space group $P2_1/c$ from systematic absences.

The three Os atom positions were located by multisolution Σ_2 sign expansion and all the remaining non-hydrogen atoms from a subsequent electron-density difference synthesis. The Os and N atoms were assigned anisotropic thermal parameters, and in the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F_o) + 0.0005|F_o|^2]$ was introduced. Blocked-cascade least-squares refinement continued until convergence was reached. The final residuals were $R = 0.042$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0.042$. A difference map calculated at this stage showed ripples of *ca.* 1.5 e Å^{-3} close to the Os atom positions but no other regions of significant electron density.

Table 9. Atom co-ordinates (×10^4) for [$Os_3(\mu$-H)(CO)$_{10}(\mu$-HN$_3$-Ph)] (1)

Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	8 409(1)	2 248(1)	3 571(1)
Os(2)	7 189(1)	−153(1)	4 117(1)
Os(3)	5 799(1)	2 764(1)	3 945(1)
N(1)	7 316(12)	1 059(11)	2 894(4)
N(2)	6 631(13)	−235(12)	2 879(5)
N(3)	6 401(12)	−781(11)	3 324(4)
C(1)	7 511(11)	1 428(9)	2 361(4)
C(2)	7 215(11)	2 880(9)	2 155(4)
C(3)	7 474(11)	3 239(9)	1 650(4)
C(4)	8 028(11)	2 147(9)	1 351(4)
C(5)	8 324(11)	696(9)	1 556(4)
C(6)	8 066(11)	336(9)	2 062(4)
C(11)	10 088(15)	1 820(15)	3 302(6)
O(11)	11 091(12)	1 591(14)	3 142(6)
C(12)	8 161(14)	4 238(14)	3 267(5)
O(12)	8 065(12)	5 447(10)	3 116(4)
C(13)	9 445(16)	3 065(15)	4 200(5)
O(13)	10 128(13)	3 540(13)	4 586(5)
C(21)	8 110(16)	−2 060(15)	4 181(6)
O(21)	8 659(13)	−3 214(11)	4 240(5)
C(22)	8 094(16)	400(15)	4 811(6)
O(22)	8 639(11)	672(12)	5 229(4)
C(23)	5 523(14)	−815(15)	4 370(5)
O(23)	4 582(12)	−1 230(12)	4 526(4)
C(31)	5 531(15)	4 828(13)	3 742(6)
O(31)	5 366(12)	6 054(10)	3 623(5)
C(32)	4 174(15)	2 397(15)	4 233(6)
O(32)	3 148(13)	2 199(15)	4 408(6)
C(33)	4 780(15)	2 085(15)	3 248(7)
O(33)	4 182(12)	1 756(13)	2 848(5)
C(34)	6 812(15)	3 392(16)	4 629(6)
O(34)	7 388(14)	3 874(13)	5 020(5)

The hydrogen atoms were not located. The atomic fractional co-ordinates are listed in Table 9.

Molecular Structure Determination of [$Os_3(\mu$-H)$_2$(CO)$_9(\mu_3$-NPh)] (6).—A single crystal (*ca.* 0.39 × 0.31 × 0.23 mm) was mounted on a glass fibre with epoxy-resin adhesive, and unit-cell dimensions and space group determined *via* Weissenberg (Cu) *X*-ray photography.

The crystal was transferred to a Syntex $P2_1$ diffractometer. 3 852 Reflections were collected using the same techniques and data collection parameters as for (1). Accurate cell parameters were determined in the same way.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 487 azimuthal scan data from 11 independent reflections were applied. Transmission factors ranged from 0.202 to 0.858 for the full data set. Lorentz polarisation corrections were applied and equivalent reflections averaged to give 2 861 unique observed data [$F > 4\sigma(F)$].

Crystal data. $C_{15}H_7NO_9Os_3$, $M = 915.82$, Monoclinic, $a = 11.630(4)$, $b = 9.217(4)$, $c = 18.527(7)$ Å, $\beta = 99.71(2)°$, $U = 1\,957.5$ Å^3, D_m not measured, $Z = 4$, $D_c = 3.11$ g cm^{-3}, $F(000) = 1\,611$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 194.64 cm^{-1}, space group $P2_1/c$ from systematic absences.

The structure was solved and refined using the same techniques as for (1). In this structure all the non-hydrogen atoms were assigned anisotropic thermal parameters. The phenyl group was refined as a rigid body with the associated hydrogen atoms constrained to lie in idealised positions (C–H, 1.08 Å and C–C–H, 120.0°); these H atoms were assigned a common isotropic temperature factor. In the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F) + 0.0005|F_o|^2]$ was

Table 10. Atom co-ordinates ($\times 10^4$) for $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$ (6)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	2 160(1)	2 094(1)	−52(1)
Os(2)	4 140(1)	2 281(1)	1 082(1)
Os(3)	2 340(1)	4 144(1)	1 111(1)
N(1)	2 386(7)	1 891(10)	1 092(4)
C(1)	1 798(5)	842(8)	1 483(4)
C(2)	2 404(6)	−357(8)	1 812(4)
C(3)	1 832(5)	−1 375(8)	2 182(4)
C(4)	654(5)	−1 193(8)	2 223(4)
C(5)	48(5)	6(8)	1 894(4)
C(6)	620(5)	1 024(8)	1 524(4)
C(11)	2 259(10)	2 763(11)	−1 034(6)
O(11)	2 325(9)	3 153(11)	−1 598(5)
C(12)	493(10)	1 980(12)	−238(5)
O(12)	−507(8)	1 922(10)	−325(5)
C(13)	2 356(10)	115(13)	−316(6)
O(13)	2 473(8)	−1 042(9)	−519(5)
C(21)	5 405(11)	3 511(14)	894(7)
O(21)	6 105(10)	4 261(14)	767(7)
C(22)	4 856(9)	439(13)	957(6)
O(22)	5 275(8)	−661(10)	870(5)
C(23)	4 683(10)	2 326(14)	2 117(8)
O(23)	5 032(10)	2 322(13)	2 723(6)
C(31)	2 961(12)	5 955(14)	895(7)
O(31)	3 355(10)	−2 952(11)	760(5)
C(32)	718(12)	4 684(13)	1 053(6)
O(32)	−238(9)	4 984(13)	1 038(6)
C(33)	2 731(10)	4 523(13)	2 129(6)
O(33)	2 961(9)	4 779(11)	2 730(5)

introduced. The final residuals were $R = 0.033$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0.034$. A difference map calculated at this stage showed no remaining regions of significant electron density; the two hydride atoms were not located directly. The atomic fractional co-ordinates are listed in Table 10.

Complex neutral-atom scattering factors[28] were employed throughout both structure solutions and refinements. All the computations were performed on the University of Cambridge IBM 370/165 computer, using programs written by Professor G. M. Sheldrick.[29] The molecular plots were drawn using the PLUTO package written by Dr. W. D. S. Motherwell.

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Received 2*nd April* 1982; *Paper* 2/570