Reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with Diazo-compounds: Structural Characterization of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPh_2)]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPhMe)]$ †

By **Kevin Burgess, Brian F. G. Johnson, Jack Lewis,*** and **Paul R. Raithby,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The unsaturated cluster $[Os_3H_2(CO)_{10}]$ reacts with diazo-compounds $N_2CR^1R^2$ to give complexes of the form $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCR^1R^2)]$ [$R^1 = R^2 = Ph$(1); $R^1 = Ph$, $R^2 = Me$(2); $R^1 = Ph$, $R^2 = H$(3); and $R^1 = R^2 = Me$(4)]. Compound (4) reverts to $[Os_3H_2(CO)_{10}]$ in solution at 20 °C; a mechanism for the decomposition of complex (4) is proposed. Complexes (1)—(3) are stable in solution and the structures of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPh_2)]$ (1) and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPhMe)]$ (2) in the solid state have been confirmed by single-crystal *X*-ray analyses. Both complexes crystallise in the monoclinic space group $P2_1/c$ with $Z = 4$, and $a = 13.645(7)$, $b = 11.948(8)$, $c = 16.784(11)$ Å, $\beta = 101.36(3)°$ for (1) and $a = 17.020(8)$, $b = 9.181(3)$, $c = 16.594(7)$ Å, and $\beta = 113.70(2)°$ for (2). The structures have been solved by a combination of direct methods and Fourier techniques, and refined by blocked full-matrix least squares to $R = 0.079$ for 2 712 observed intensities (1) and $R = 0.050$ for 2 375 intensities (2). In both structures the Os atoms define an isosceles triangle the short edge of which is bridged by an N atom of the $NHNCR^1R^2$ ligand and by the hydride. Spectroscopic data for (2) indicate the presence of two isomers in solution.

THE unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ reacts with 1,3-dipolar compounds in two ways. With the diazo-compounds N_2CHR ($R = H$, Me, or CO_2Et) and with toluene-*p*-sulphonyl azide $4\text{-}MeC_6H_4SO_2N_3$ dinitrogen is evolved to give the bridged species $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CH_2R)]$ [1-3] and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me\text{-}p)]$,[4] respectively. Primary alkyl-, secondary alkyl-, and aryl-azides react with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give [2 + 3] cyclo-adducts which result in cluster species containing a chelating triazene ligand.[5,6] In this paper we report a third type of interaction in which diazoalkanes add to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$, with retention of dinitrogen, to give clusters of the type $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCR^1R^2)]$, where the diazo-ligand is co-ordinated to the metal triangle through its terminal nitrogen only.

RESULTS AND DISCUSSION

Reaction of $[Os_3H_2(CO)_{10}]$ with the diazo-compounds $N_2CR^1R^2$ leads to the formation of four diazo-adducts with the general formula $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCR^1R^2)]$ [$R^1 = R^2 = Ph$(1); $R^1 = Ph$, $R^2 = Me$(2); $R^1 = Ph$, $R^2 = H$(3); and $R^1 = R^2 = Me$(4)] (Figure 1). The reactions were carried out in hexane [(1) and (2)] or diethyl ether [(3) and (4)] under mild conditions [69 °C for (1), 20 °C for (2) and (3), and 0 °C for (4)]. Compounds (1)—(3) were separated by chromatographic techniques, while (4) was precipitated at −78 °C. The best yields of (2) and (3) were obtained by using a large excess of the diazoalkane.

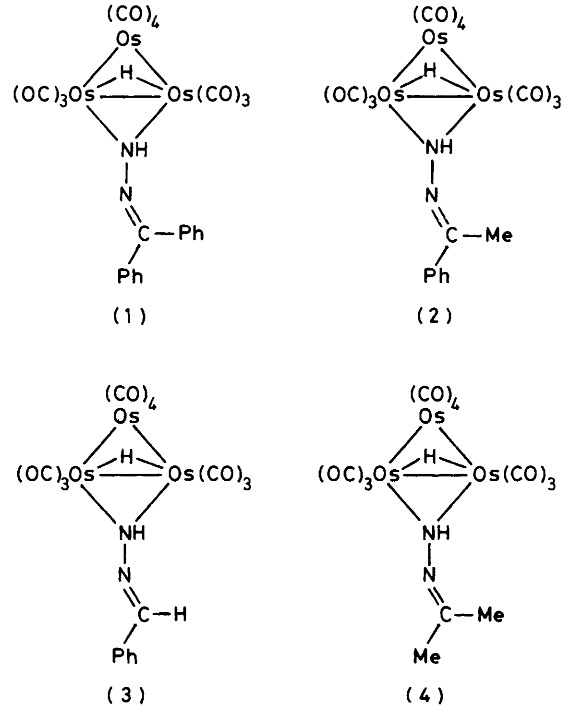

FIGURE 1 Structures of the $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCR^1R^2)]$ complexes

The 2-diazopropane adduct (4) was deposited as a yellow solid at −78 °C but darkened at 20 °C *in vacuo*. Freshly prepared solutions of (4) at 20 °C exhibited i.r. and ^1H n.m.r. signals characteristic of $[Os_3H_2(CO)_{10}]$ which became predominant after several hours. A possible mechanism for the decomposition of (4) is by initial conversion into a $NHNCMe_2$-chelating form followed by loss of dinitrogen and then β-hydrogen transfer with elimination of an alkene (Scheme). Intermediates (I) and (II) were not detected in the reaction mixture but the Scheme is supported by several criteria: (*i*) 1,3-sigmatropic shifts have many precedents in organic chemistry; (*ii*) intermediate (I) is analogous to the structures of the cyclo-adducts formed from the reaction of

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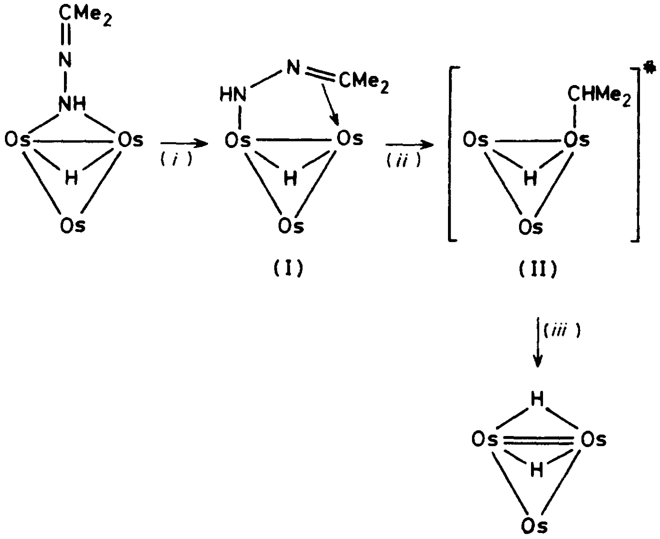
† 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-2-diphenylmethylenehydrazido(1−)- and 1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-μ-2-(1′-phenylethylidene)hydrazido(1−)-1,2-μ-hydrido-*triangulo*-triosmium.

$[Os_3H_2(CO)_{10}]$ with organic azides;[6] (*iii*) loss of N_2 from diazoalkane complexes of $[Os_3H_2(CO)_{10}]$ gives structures analogous to (II);[1,2] and (*iv*) the μ-CH_2 and μ-$CHCO_2Et$ analogues of (II) are stable at room temperature but the μ-$CHCH_3$ derivative rapidly decomposes to ethene and $[Os_3H_2(CO)_{10}]$;[3] only in the latter case and in the instance cited (see above) are β-hydrogens present. Steric factors may disfavour the 1,3-shift step in compounds (1)—(3) and enhance their stability; (1) was maintained in heptane solution, under a pressure of argon, at 170 °C for 1 h without decomposition. Propene was not detected, however, and the possibility of a simple equilibrium between $[Os_3H_2(CO)_{10}]$ and 2-diazopropane cannot be discounted.



(I) (II)

Scheme Proposed mechanism for the decomposition of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCMe_2)]$ (4)
(*i*) 1,3-sigmatropic shift; (*ii*) $-N_2$; (*iii*) β-elimination

For these diazoalkane complexes the four possible isomeric configurations, assuming that the N–H vector points away from the Os_3 plane, are shown in Figure 2. (Models indicate that if the N–N vector were to point away from the Os_3 plane there would be unacceptably short contacts between the diazoalkane ligand and carbonyl groups on the cluster.) The isomeric forms (a) and (c), and (b) and (d), are interconvertible by rotation about the N–C bond, but are indistinguishable when $R^1 = R^2$. Also (a) and (b), and of course (c) and (d), are related by a rotation about the N–N bond. In the ^1H n.m.r. spectrum (Table 1) of the methylphenyl derivative (2) two methyl and two sets of hydride signals are observed, consistent with the presence of two isomers. In the other three complexes it has not been possible to identify the presence of isomers, but in general the compounds (1)—(4) show ^1H n.m.r. signals for the N–*H* proton and for the metal hydride; the latter is split by coupling to the N–*H* proton. The large variation in the chemical shift of the ^1H n.m.r. signals for the N–*H* proton may be associated with the variation of the shielding effects of the R^1 and R^2 substituents. In the cases (1) and (3) where it is probable that there is a phenyl group close to the N-bound proton this atom would be subject to ring-current effects. For (2) and (4), where the adjacent groups are methyls, the chemical shifts are in the region typical of this class of N–*H* protons.

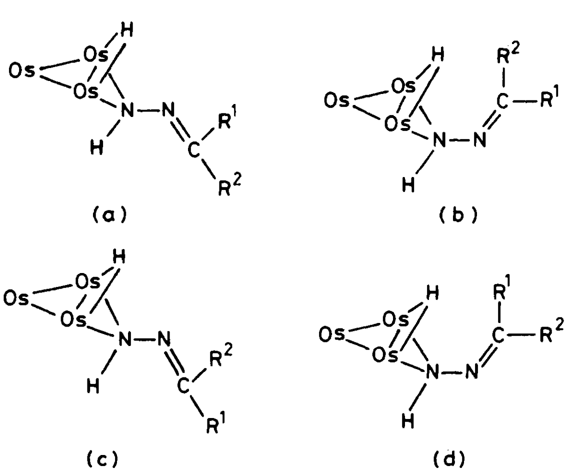


Figure 2 Possible isomeric structures for $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCR^1R^2)]$

Table 1

Spectral data for the complexes $[Os_3(\mu\text{-}H)(CO)_{10}(NHNCR^1R^2)]$

Compound	R^1 and R^2	m/e [a] (M^+ ^{192}Os)	P.m.r.[b] (δ/p.p.m.) N–*H* [c]	M–*H* (*J*/Hz) [d]	Other	$\tilde{\nu}(CO)$ [e]/cm^{-1}
(1)	Ph, Ph	1 052	4.24	−14.41 (1.6)	7.46—7.01 (m, 10 H)	2 104w, 2 067s, 2 054s, 2 017s 2 001s, 1 997s, 1 979w
(2)	Ph, Me	990	7.72	−14.45 (1.6)	7.47—6.98 (m) 2.03 (s)	2 106s, 2 071s, 2 057s, 2 022s
				−14.59 (2.1)	7.47—6.98 (m) 1.99 (s)	2 004s, 2 000s, 1 985w, 1 972w
(3)	Ph, H	976	4.29	−14.47 (2.4)	7.59—7.08 (m, 5 H) 5.09 (s, 1 H)	2 106w, 2 071s, 2 056s, 2 021s 2 006s, 2 000s, 1 984w, 1 974w
(4)	Me, Me	928	8.90 [f]	−14.59 [f] (2.4)	1.88 (s, 6 H) [f]	2 105w, 2 070s, 2 055s, 2 020s 2 003m, 1 998s, 1 983s, 1 970s

[a] A.E.I. MS12 spectrometer at 70 eV; 1 eV ≈ 1.60×10^{-19} J. [b] CFT 20 Varian spectrometer at 80 MHz using an internal deuterium lock, $CDCl_3$ solvent. [c] All broad resonances, relative intensity 1 H. [d] All doublets. [e] Perkin-Elmer 257 spectrometer, hexane solution, calibrated with CO. [f] CD_2Cl_2 solvent.

It is unclear whether only one isomer is present in solution for complexes (1), (3), and (4) or whether the process is dynamic at room temperature. The i.r. spectra of the compounds are similar and the mass spectra show the appropriate molecular ion in each case.

In order to confirm the overall molecular geometry of the $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHNCR}^1R^2)]$ complexes and to investigate the possibility of isomeric forms in the solid state the molecular structures of the diphenyl and the phenylmethyl derivatives (1) and (2) were determined. The structures of (1) and (2) are shown in Figures 3 and 4, respectively, and the associated bond lengths and angles in Tables 2 and 3.

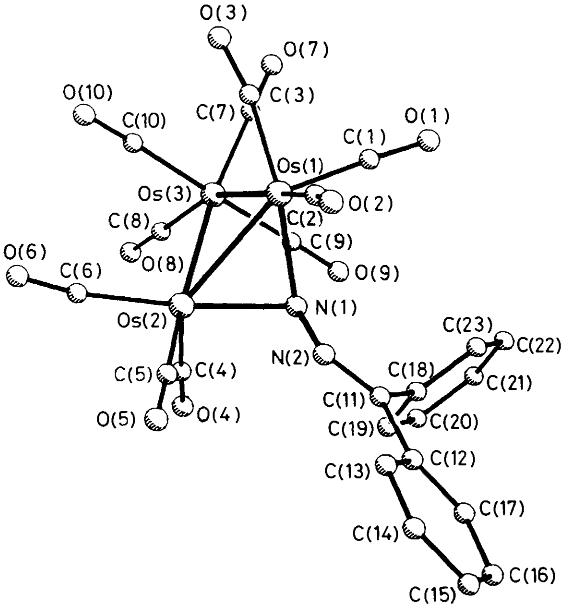


FIGURE 3 The molecular structure of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHNCPh}_2)]$ (1); hydrogen atoms have been omitted for clarity

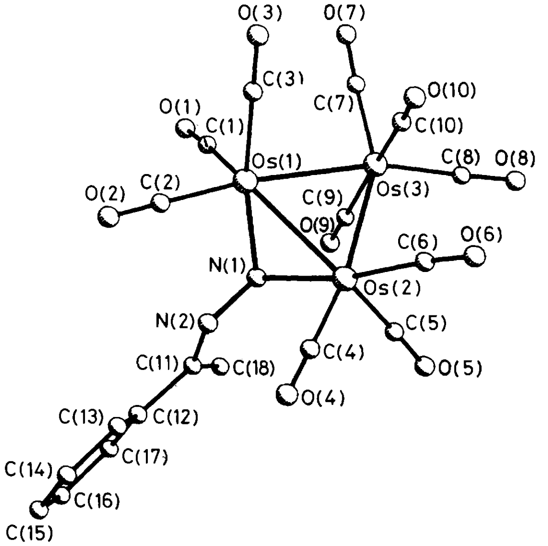


FIGURE 4 The molecular structure of $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHNCPhMe})]$ (2); hydrogen atoms have been omitted for clarity

TABLE 2

Bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHNCPh}_2)]$ (1)

Os(2)–Os(1)	2.778(3)	C(1)–Os(1)	1.874(34)
Os(3)–Os(1)	2.841(3)	C(2)–Os(1)	1.930(37)
Os(3)–Os(2)	2.836(3)	C(3)–Os(1)	1.972(36)
N(1)–Os(1)	2.149(24)	C(4)–Os(2)	1.830(33)
N(1)–Os(2)	2.082(22)	C(5)–Os(2)	1.868(33)
N(2)–N(1)	1.388(35)	C(6)–Os(2)	1.900(32)
C(11)–N(2)	1.269(35)	C(7)–Os(3)	1.852(32)
C(12)–C(11)	1.497(37)	C(8)–Os(3)	1.834(28)
C(18)–C(11)	1.511(31)	C(9)–Os(3)	1.914(30)
C(12)–C(13)	1.395(30)	C(10)–Os(3)	1.994(40)
C(14)–C(13)	1.395(34)	O(1)–C(1)	1.170(45)
C(15)–C(14)	1.395(29)	O(2)–C(2)	1.147(44)
C(16)–C(15)	1.395(30)	O(3)–C(3)	1.089(44)
C(17)–C(16)	1.395(34)	O(4)–C(4)	1.132(41)
C(12)–C(17)	1.395(29)	O(5)–C(5)	1.196(41)
C(18)–C(19)	1.395(26)	O(6)–C(6)	1.175(43)
C(18)–C(23)	1.395(24)	O(7)–C(7)	1.159(44)
C(20)–C(19)	1.395(26)	O(8)–C(8)	1.217(40)
C(21)–C(20)	1.395(24)	O(9)–C(9)	1.110(41)
C(22)–C(21)	1.395(26)	O(10)–C(10)	1.067(49)
C(23)–C(22)	1.395(26)		

Os(3)–Os(1)–Os(2)	60.6(1)	C(1)–Os(1)–Os(2)	136.3(10)
Os(3)–Os(2)–Os(1)	60.8(1)	C(1)–Os(1)–Os(3)	95.5(10)
Os(2)–Os(3)–Os(1)	58.6(1)	C(2)–Os(1)–Os(2)	109.9(11)
N(1)–Os(1)–Os(2)	47.9(6)	C(2)–Os(1)–Os(3)	169.2(10)
N(1)–Os(1)–Os(3)	82.1(6)	C(3)–Os(1)–Os(2)	119.6(9)
N(1)–Os(2)–Os(1)	50.0(7)	C(3)–Os(1)–Os(3)	88.4(10)
N(1)–Os(2)–Os(3)	83.3(7)	C(4)–Os(2)–Os(1)	135.2(11)
N(1)–Os(1)–C(1)	96.2(12)	C(4)–Os(2)–Os(3)	91.2(12)
N(1)–Os(1)–C(2)	95.1(12)	C(5)–Os(2)–Os(1)	108.2(8)
N(1)–Os(1)–C(3)	167.2(11)	C(5)–Os(2)–Os(3)	169.0(8)
N(1)–Os(2)–C(4)	96.0(13)	C(6)–Os(2)–Os(1)	123.5(9)
N(1)–Os(2)–C(5)	89.9(11)	C(7)–Os(3)–Os(1)	102.9(9)
N(1)–Os(2)–C(6)	173.5(11)	C(7)–Os(3)–Os(2)	161.4(9)
Os(2)–N(1)–Os(1)	82.1(9)	C(8)–Os(3)–Os(1)	156.3(10)
N(2)–N(1)–Os(1)	117.2(15)	C(8)–Os(3)–Os(2)	98.0(10)
N(2)–N(1)–Os(2)	115.5(17)	C(9)–Os(3)–Os(1)	87.3(9)
C(11)–N(2)–N(1)	117.8(23)	C(9)–Os(3)–Os(2)	90.8(10)
C(12)–C(11)–N(2)	118.9(22)	C(10)–Os(3)–Os(1)	85.4(11)
C(18)–C(11)–N(2)	123.0(24)	C(10)–Os(3)–Os(2)	85.2(13)
O(1)–C(1)–Os(1)	176.7(27)	C(2)–Os(1)–C(1)	95.2(14)
O(2)–C(2)–Os(1)	177.6(30)	C(3)–Os(1)–C(1)	93.2(15)
O(3)–C(3)–Os(1)	176.2(29)	C(3)–Os(1)–C(2)	92.7(15)
O(4)–C(4)–Os(2)	177.5(33)	C(5)–Os(2)–C(4)	98.2(15)
O(5)–C(5)–Os(2)	174.8(26)	C(6)–Os(2)–Os(3)	93.0(10)
O(6)–C(6)–Os(2)	172.9(28)	C(6)–Os(2)–C(4)	89.5(14)
O(7)–C(7)–Os(3)	177.1(26)	C(6)–Os(2)–C(5)	92.8(14)
O(8)–C(8)–Os(3)	176.2(27)	C(8)–Os(3)–C(7)	100.6(13)
O(9)–C(9)–Os(3)	177.4(27)	C(9)–Os(3)–C(7)	89.7(13)
O(10)–C(10)–Os(3)	177.9(35)	C(9)–Os(3)–C(8)	89.6(12)
C(18)–C(11)–C(12)	118.1(20)	C(10)–Os(3)–C(7)	92.1(15)
C(13)–C(12)–C(11)	120.4(19)	C(10)–Os(3)–C(8)	97.1(14)
C(17)–C(12)–C(11)	119.6(20)	C(10)–Os(3)–C(9)	172.6(14)
C(19)–C(18)–C(11)	120.0(16)	C(23)–C(18)–C(11)	120.0(17)
C(23)–C(18)–C(19)	120.0(17)	C(18)–C(19)–C(20)	120.0(16)
C(17)–C(12)–C(13)	120.0(22)	C(21)–C(20)–C(19)	120.0(17)
C(12)–C(13)–C(14)	120.0(19)	C(22)–C(21)–C(20)	120.0(17)
C(15)–C(14)–C(13)	120.0(19)	C(23)–C(22)–C(21)	120.0(16)
C(16)–C(15)–C(14)	120.0(22)	C(18)–C(23)–C(22)	120.0(17)
C(17)–C(16)–C(15)	120.0(19)	C(12)–C(17)–C(16)	120.0(19)

In both complexes the Os atoms occupy the vertices of an isosceles triangle the shortest edge of which is bridged by both the $-NHN{=}CR^1R^2$ ligand and a hydride. All the Os–Os bonds are shorter than the average value of 2.877 Å in the parent binary carbonyl $[Os_3(CO)_{12}]$.[7] The two unbridged Os–Os lengths [mean 2.839(3) Å for (1) and 2.848(3) Å for (2)] are similar to the values reported for unbridged distances in a number of $[Os_3(\mu\text{-H})(CO)_{10}L]$ [L = $CHCH_2PMe_2Ph$,[8] $CHCH{=}NEt_2$,[9] $C{=}N(H)Bu^t$,[10] $N{=}NC_6H_4Me$,[11] and $NHSO_2C_6H_4Me$ [4]] type complexes

TABLE 3

Bond lengths (Å) and angles (°) for $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHNCPhMe})]$ (2)

Os(2)–Os(1)	2.802(2)	C(1)–Os(1)	1.932(25)
Os(3)–Os(1)	2.844(2)	C(2)–Os(1)	1.903(27)
Os(3)–Os(2)	2.853(2)	C(3)–Os(1)	1.929(25)
N(1)–Os(1)	2.109(17)	C(4)–Os(2)	1.908(26)
N(1)–Os(2)	2.140(11)	C(5)–Os(2)	1.862(27)
N(2)–N(1)	1.418(23)	C(6)–Os(2)	1.886(20)
C(11)–N(2)	1.284(27)	C(7)–Os(3)	1.939(26)
C(12)–C(11)	1.490(28)	C(8)–Os(3)	1.921(22)
C(18)–C(11)	1.491(39)	C(9)–Os(3)	1.974(24)
C(12)–C(17)	1.395(22)	C(10)–Os(3)	1.928(28)
C(14)–C(13)	1.395(26)	O(1)–C(1)	1.112(32)
C(12)–C(13)	1.395(30)	O(2)–C(2)	1.134(32)
C(15)–C(14)	1.395(22)	O(3)–C(3)	1.126(32)
C(16)–C(15)	1.395(30)	O(4)–C(4)	1.161(33)
C(17)–C(16)	1.395(26)	O(5)–C(5)	1.153(33)
O(6)–C(6)	1.150(24)	O(9)–C(9)	1.101(31)
O(7)–C(7)	1.128(32)	O(10)–C(10)	1.150(35)
O(8)–C(8)	1.121(27)		

Os(3)–Os(1)–Os(2)	60.7(1)	C(1)–Os(1)–Os(2)	136.8(8)
Os(3)–Os(2)–Os(1)	60.4(1)	C(1)–Os(1)–Os(3)	93.7(7)
Os(2)–Os(3)–Os(1)	58.9(1)	C(2)–Os(1)–Os(2)	109.8(7)
N(1)–Os(1)–Os(2)	49.2(3)	C(2)–Os(1)–Os(3)	169.6(7)
N(1)–Os(1)–Os(3)	84.2(4)	C(3)–Os(1)–Os(2)	119.0(6)
N(1)–Os(2)–Os(1)	48.3(4)	C(3)–Os(1)–Os(3)	88.3(7)
N(1)–Os(2)–Os(3)	83.4(4)	C(4)–Os(2)–Os(1)	109.5(6)
C(9)–Os(3)–C(7)	96.7(10)	C(4)–Os(2)–Os(3)	169.1(7)
C(9)–Os(3)–C(8)	90.9(10)	C(5)–Os(2)–Os(1)	134.8(8)
C(10)–Os(3)–C(7)	92.0(11)	C(5)–Os(2)–Os(3)	93.4(8)
C(10)–Os(3)–C(8)	94.0(10)	C(6)–Os(2)–Os(1)	122.7(7)
C(10)–Os(3)–C(9)	168.8(11)	C(6)–Os(2)–Os(3)	90.6(8)
N(1)–Os(1)–C(1)	97.7(8)	C(7)–Os(3)–Os(1)	94.0(7)
N(1)–Os(1)–C(2)	92.4(8)	C(7)–Os(3)–Os(2)	152.8(8)
N(1)–Os(1)–C(3)	168.2(6)	C(8)–Os(3)–Os(1)	164.3(8)
N(1)–Os(2)–C(4)	92.5(7)	C(8)–Os(3)–Os(2)	105.4(8)
N(1)–Os(2)–C(5)	96.3(8)	C(9)–Os(3)–Os(1)	87.1(7)
N(1)–Os(2)–C(6)	170.9(8)	C(9)–Os(3)–Os(2)	85.2(7)
Os(2)–N(1)–Os(1)	82.5(6)	C(10)–Os(3)–Os(1)	85.4(7)
N(2)–N(1)–Os(1)	116.8(12)	C(10)–Os(3)–Os(2)	83.9(8)
N(2)–N(1)–Os(2)	113.9(11)	C(2)–Os(1)–C(1)	96.5(10)
C(11)–N(2)–N(1)	118.3(19)	C(3)–Os(1)–C(1)	91.8(10)
C(12)–C(11)–N(2)	116.1(21)	C(3)–Os(1)–C(2)	93.5(11)
C(18)–C(11)–N(2)	123.2(20)	C(5)–Os(2)–C(4)	97.1(11)
C(18)–C(11)–C(12)	120.7(18)	C(6)–Os(2)–C(4)	92.2(10)
C(13)–C(12)–C(11)	120.5(15)	C(6)–Os(2)–C(5)	90.8(10)
C(17)–C(12)–C(11)	119.4(19)	C(8)–Os(3)–C(7)	101.7(11)
C(17)–C(12)–C(13)	120.0(17)	O(1)–C(1)–Os(1)	175.2(23)
C(12)–C(13)–C(14)	120.0(15)	O(2)–C(2)–Os(1)	176.9(22)
C(15)–C(14)–C(13)	120.0(19)	O(3)–C(3)–Os(1)	179.9(4)
C(16)–C(15)–C(14)	120.0(17)	O(4)–C(4)–Os(2)	176.7(20)
C(17)–C(16)–C(15)	120.0(15)	O(5)–C(5)–Os(2)	177.5(22)
C(12)–C(17)–C(16)	120.0(19)	O(6)–C(6)–Os(2)	177.9(21)
O(7)–C(7)–Os(3)	176.6(22)	O(9)–C(9)–Os(3)	178.4(24)
O(8)–C(8)–Os(3)	176.2(22)	O(10)–C(10)–Os(3)	179.7(11)

[range 2.834(1)—2.873(6) Å]. The bridged Os–Os bonds in (1) and (2) are 0.061 Å and 0.047 Å shorter than the unbridged edges respectively. This is a feature of all triosmium clusters where an edge is bridged by both a ligand co-ordinated to the metals *via* a first-row main-group element and a hydride.[11] It is well established [12] that when a single hydride bridges an otherwise unsupported metal–metal edge the M–M distance is significantly longer than in the absence of such a bridging species. The presence of a ligand containing a first row main group bridgehead atom bridging the same edge appears to have a stronger bond-shortening effect which more than counterbalances the influence of the hydride.

In both (1) and (2) the N(1) atom of the $-NHN{=}CR^1R^2$ group bridges the Os(1)–Os(2) bond fairly symmetrically, with the larger deviation occurring in the diphenyl derivative (1). The Os–N(1) bond lengths are similar to the values of 2.145(7) and 2.162(7) Å found in $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me\text{-}p)]$,[4] and slightly longer than the values of 2.036(11) and 2.056(11) Å for $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-N=NC}_6H_4Me)]$ [11] where the bridgehead N atom does not have a proton bonded to it. Although the bridging hydrides were not located directly in these two structure determinations their approximate positions can be ascertained from a hole in the ligand polyhedron caused by the presence of the hydride. The carbonyl groups *cis* to the Os(1)–Os(2) edge bend away from it with average Os–Os–C angles of 115.3° for both (1) and (2). The average *cis* Os–Os–C angles for the other two Os–Os bonds are 94.8 (1) and 94.2° (2). Similar trends have been observed in many μ-H bridged carbonyl clusters and in a number of cases the presence of the hydrides in the proposed positions has been confirmed by neutron-diffraction studies.[13] Thus in (1) and (2) the hydrides bridge the Os(1)–Os(2) bond and lie on the opposite side of the Os_3 triangle to the diazoalkane group.

The orientation of the $-NHN{=}CR^1R^2$ ligands in the two complexes is of interest with regard to the formation and isolation of different isomeric forms. In both crystal structures the isomer isolated is of the type (a) or (c) (Figure 2), and it appears, by the use of models, that in an isomer of type (b) or (d) there would be a very short contact (*ca.* 1 Å) between the hydride ligand and an R group on the diazoalkane ligand. It is probable that there is a high barrier to rotation about the N–N bond and that isomers (b) and (d) do not exist even in solution.

The lengths of the N–N bonds in the $\mu\text{-NHNCR}^1R^2$ ligands in complexes (1) and (2) indicate that there is some multiple-bond character in these bonds, being slightly shorter than the expected single-bond value of 1.44 Å. The N(2)–C(11) distances in (1) and (2) are indicative of localised C–N double bonds. However, the atoms N(1)–N(2), C(11), C(12)–C(17), and C(18) are effectively coplanar which is consistent with electron delocalisation over the system. This is in agreement with the description of the ligand as a 1,3-dipolar unit with a net positive charge on N(1) and a negative charge on C(11), with an N–N multiple bond.

The bond parameters in the substituent phenyl and methyl groups in the two complexes do not deviate significantly from the idealised values. In neither complex are there any short contacts between the phenyl or methyl groups of the diazoalkane ligands and the carbonyl groups co-ordinated to the metal triangle. In the structure of (2) the relative positions of the methyl and phenyl substituents would not appear to be influenced by steric factors. However, rotation about the N–C bond would bring the methyl and phenyl substituents into contact with the equatorial carbonyl groups on Os(1) and Os(2) when the N(1), N(2), C(11), C(12), C(18) unit becomes parallel to the Os_3 plane. The hindered rotation about the N–C bond is consistent with the existence of two isomers with the methyl and phenyl positions reversed, in keeping with the ^{1}H n.m.r. data for the complex which exhibits two methyl signals (2.03 and 1.99 p.p.m.) and two hydride signals (−14.45 and −14.59 p.p.m.) in a ratio of *ca.* 6 : 1. Only one metal hydride doublet is seen for the phenyldiazomethane complex (3); apparently the relatively large difference between the size of hydrogen and a phenyl ring results in almost complete predominance of the isomer with the phenyl group pointing away from the Os_3 plane.

The ten carbonyl groups in each of the structures (1) and (2) are terminal and the Os–C–O angles do not deviate significantly from linearity. In each complex Os(3) displays distorted octahedral co-ordination geometry. The average Os(3)–C(axial) bond lengths 1.95 Å for (1) and (2) are significantly longer than the equatorial ones [1.84 (1) and 1.93 Å (2)]. This results from the greater competition between the two axial carbonyl groups for back donation from the same set of metal orbitals. The equatorial carbonyls are ***trans*** to Os–Os bonds which do not exhibit strong π-acceptor properties so that the back donation is to the Os–C bonds, shortening them.

The high standard deviations of the bond parameters of the carbonyl groups bonded to the Os(1) and Os(2) atoms makes an assessment of the bonding in these fragments of the molecules difficult. Although there are differences between equivalent Os–C bonds in the same structure, and the variations between inequivalent bonds may not be significant at the 2.5σ level, there appears to be a trend in average Os–C (carbonyl) distances which is more marked in the structure of (1) than in (2). The Os–C bond length [mean 1.94 (1) and 1.91 Å (2)] for the carbonyls ***trans*** to the diazoalkane nitrogen is longer than those ***trans*** to the Os–Os bonds [mean 1.90 Å for (1) and (2)], which are in turn longer than those ***trans*** to the bridging hydride [mean 1.85 (1) and 1.89 Å (2)]. These differences may be explained in the same way as the differences in bond lengths between the equatorial and axial carbonyls on Os(3). The diazoalkane ligands appear to be good π-acceptors competing strongly with the ***trans*** carbonyls for back donation from the metal. The hydride ligands have no orbitals available for π-back donation and the electron density is transferred to the Os–C bond of the ***trans*** carbonyl, which results in the shorter Os–C distances.

EXPERIMENTAL

Preparations.—[$Os_3(\mu$-H)$(CO)_{10}(\mu$-NHNCPh_2)] (1). The complex [$Os_3H_2(CO)_{10}$] (0.295 g) and diphenyldiazomethane (0.240 g, 3.6 equivalents) were dissolved in hexane (20 cm^3) and the mixture refluxed for 4 h. Column chromatography (silica 60—120 mesh, hexane eluant) gave (1) (0.261 g, 72%) [Found: C, 26.1; H, 1.30; N, 2.95. Calc. for $C_{23}H_{12}N_2O_{10}Os_3$; C, 26.4; H, 1.15; N, 2.70%].

[$Os_3(\mu$-H)$(CO)_{10}(\mu$-NHNCPhMe)] (2). The complex [$Os_3H_2(CO)_{10}$] (0.046 g) and methylphenyldiazomethane (*ca.* 100 equivalents) were stirred in hexane (10 cm^3) at 20 °C for 48 h. Removal of solvent and thin-layer chromatography (t.l.c.) (silica, hexane eluant) gave (2) (0.013 g, 24%). Complete analysis was not obtained due to organic impurities (see text) [Found: N, 2.85. Calc. for $C_{23}H_{12}N_2O_{10}Os_3$: N, 2.70%].

[$Os_3(\mu$-H)$(CO)_{10}(\mu$-NHNCHPh)] (3). The compound [$Os_3H_2(CO)_{10}$] (0.032 g) and phenyldiazomethane (*ca.* 100 equivalents) were stirred in diethyl ether (10 cm^3) at 20 °C for 1 h. Removal of solvent and t.l.c. (silica, hexane eluant) gave (3) (0.002 g, 5%).

[$Os_3(\mu$-H)$(CO)_{10}(\mu$-NHNCMe_2)] (4). The compound [$Os_3H_2(CO)_{10}$] (0.118 g) was dissolved in diethyl ether (20 cm^3) and the solution cooled to 0 °C. 2-Diazopropane (*ca.* 100 equivalents) in diethyl ether (10 cm^3) was added to the solution. The volume of solvent was reduced to *ca.* 10 cm^3, the solution being maintained at 0 °C throughout. Further cooling to −78 °C precipitated (4) (*ca.* 0.049 g, 36%).

Molecular-structure Determination of [$Os_3(\mu$-H)$(CO)_{10}(\mu$-NHNCPh_2)] (1).—Crystals of (1) were obtained as yellow blocks from hexane. A single crystal (*ca.* 0.24 × 0.21 × 0.48 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 placed on an automated Stoe STADI-2 two-circle diffractometer with the crystallographic b axis aligned to be collinear with the diffractometer spindle axis. The a and c cell lengths and the β angle were obtained by a least-squares fit to diffractometer zero-layer ω-angle measurements. The b cell length was determined from accurate μ angle measurements of several axial reflections. 3 815 Intensities (layers 0—h, 13, l) were recorded using graphite-monochromated Mo-K_α radiation. Lorentz polarisation and empirical absorption corrections were applied (based on an azimuthal scan of the 020 reflection). Equivalent reflections were merged to yield 2 712 unique observed data [$F > 5\sigma(F)$].

Crystal data. $C_{23}H_{12}N_2O_{10}Os_3$, M = 1 046.95, Monoclinic, a = 13.645(7), b = 11.948(8), c = 16.784(11) Å, β = 101.36(3)°, U = 2 682.69 Å^3, D_m = not measured, Z = 4, D_c = 2.59 g cm^{-3}, F(000) = 1 887.41, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 142.15 cm^{-1}, space group $P2_1/c$ from systematic absences.

The three Os atom positions were located by multisolution Σ_2 sign expansion. These atoms were assigned isotropic thermal parameters, and subjected to three cycles of least-squares refinement. The refined parameters of these atoms were used for calculating a difference electron-density synthesis from which all the non-hydrogen atoms were located. Refinement continued, and after several cycles the Os, N, and O atoms were assigned anisotropic thermal parameters. The phenyl rings were refined as rigid bodies with the phenyl H atoms constrained to be in idealised positions (C–H 1.08 Å, C–C–H 120.0°); these atoms were assigned a common isotropic thermal parameter. Interlayer scale factors were also refined, and the constraint $U_{22} = \frac{1}{2}(U_{11} + U_{33})$ was applied to reduce correlation involving interlayer scale factors. A weighting scheme of the form $w = 14.8768/[\sigma^2(F_o) + 0.0007|F_o|^2]$ was introduced and blocked full-matrix least squares refinement continued until convergence was reached. The final residuals were R = 0.079 and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ = 0.082. A difference map calculated at this stage showed no regions of significant electron density. The hydride atom was not located. The atomic fractional co-ordinates are listed in Table 4.

Molecular-structure Determination of [$Os_3(\mu$-H)$(CO)_{10}(\mu$-NHNCPhMe)] (2).—Crystals of (2) (hexagonal plates) were

TABLE 4

Atom co-ordinates (× 10^4) for $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPh_2)]$ (1)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	3 017(1)	4 731(1)	3 585(1)
Os(2)	2 354(1)	3 346(1)	2 259(1)
Os(3)	932(1)	4 414(1)	3 027(1)
C(1)	2 926(25)	6 257(28)	3 820(20)
O(1)	2 908(21)	7 203(25)	3 998(16)
C(2)	4 456(28)	4 666(29)	3 887(21)
O(2)	5 308(18)	4 587(21)	4 069(17)
C(3)	2 842(26)	4 263(28)	4 676(21)
O(3)	2 708(19)	3 966(19)	5 258(14)
C(4)	1 542(27)	3 519(30)	1 260(22)
O(4)	1 048(28)	3 666(26)	644(14)
C(5)	3 471(23)	2 763(24)	1 916(17)
O(5)	4 157(18)	2 306(21)	1 703(16)
C(6)	1 795(24)	1 905(26)	2 345(18)
O(6)	1 477(21)	1 029(24)	2 485(18)
C(7)	378(22)	5 251(25)	3 756(18)
O(7)	58(22)	5 751(23)	4 239(17)
C(8)	−203(23)	3 940(24)	2 333(17)
O(8)	−951(22)	3 566(28)	1 897(20)
C(9)	955(23)	5 720(25)	2 370(18)
O(9)	932(18)	6 471(22)	1 978(17)
C(10)	1 096(30)	3 083(33)	3 758(24)
O(10)	1 178(21)	2 352(25)	4 130(17)
N(1)	2 982(16)	4 939(19)	2 308(14)
N(2)	3 895(17)	5 009(20)	2 064(14)
C(11)	4 015(19)	5 801(21)	1 588(15)
C(12)	4 946(17)	5 824(17)	1 243(11)
C(13)	5 734(17)	5 096(17)	1 536(11)
C(14)	6 604(17)	5 132(17)	1 217(11)
C(15)	6 685(17)	5 897(17)	605(11)
C(16)	5 897(17)	6 624(17)	312(11)
C(17)	5 028(17)	6 588(17)	631(11)
C(18)	3 249(16)	6 712(14)	1 337(12)
C(19)	2 479(16)	6 555(14)	664(12)
C(20)	1 763(16)	7 389(14)	438(12)
C(21)	1 816(16)	8 379(14)	885(12)
C(22)	2 586(16)	8 535(14)	1 558(12)
C(23)	3 302(16)	7 702(14)	1 784(12)

deposited from hexane. A suitable single crystal with dimensions 0.23 × 0.21 × 0.08 mm was mounted on a glass fibre, and cell dimensions and space group determined photographically.

The crystal was transferred to a Stoe four-circle diffractometer and 3 873 reflections measured in the range $3.0 < 2\theta < 55.0°$ using Mo-K_α radiation and a 70-step ω/θ scan technique. The step width was 0.02° with a counting time of 0.5 s per step; backgrounds were measured for 8.75 s at each end of the scan. Reflections with intensities of <8 counts s^{-1} for an initial 1-s peak count were not remeasured. Two check reflections were monitored periodically throughout data collection and showed no significant variation. Accurate cell dimensions were obtained from the centring of 20 strong reflections in the range $15 < 2\theta < 25°$.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 458 azimuthal scan data from 22 independent reflections were applied. Transmission factors ranged from 0.384 to 0.990 for the full data set. Lorentz polarisation corrections were also applied and equivalent reflections averaged to give 2 375 unique observed data $[F > 5\sigma(F)]$.

Crystal data. $C_{18}H_{10}N_2O_{10}Os_3$, $M = 984.88$, Monoclinic, $a = 17.020(8)$, $b = 9.181(3)$, $c = 16.594(7)$ Å, $\beta = 113.70(2)°$, $U = 2\,374.30$ Å^3, D_m = not measured, $Z = 4$, $D_c = 2.75$ g cm^{-3}, $F(000) = 1\,759.41$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 160.57$ 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 phenyl and methyl groups were refined as rigid bodies with the hydrogen atoms constrained to lie in idealised positions (phenyl: C-H 1.08 Å and C-C-H 120.0°; methyl: C-H 1.08 Å and C-C-H 109.5°). Each type of H atom was assigned a common isotropic thermal parameter. The Os, N, and O atoms were assigned anisotropic thermal parameters, and in the final cycles of refinement a weighting scheme of the form $w = 0.9001/[\sigma^2(F_o)]$ was introduced. Blocked full-matrix least-squares refinement continued until convergence was reached. The final residuals were $R = 0.050$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0.044$. A difference map calculated at this stage showed no regions of significant electron density. The hydride ligand was not located directly. The atomic fractional co-ordinates are listed in Table 5.

TABLE 5

Atom co-ordinates (× 10^4) for $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPhMe)]$ (2)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	2 161(1)	2 473(1)	−115(1)
Os(2)	3 097(1)	397(1)	1 142(1)
Os(3)	3 977(1)	2 728(1)	725(1)
C(1)	2 111(16)	3 155(25)	−1 236(14)
O(1)	2 133(13)	3 499(21)	−1 869(10)
C(2)	965(17)	2 111(26)	−490(14)
O(2)	251(11)	1 885(21)	−751(10)
C(3)	2 080(16)	4 431(27)	265(14)
O(3)	2 033(13)	5 575(20)	487(11)
C(4)	2 324(15)	−920(24)	1 338(13)
O(4)	1 855(11)	−1 679(18)	1 491(10)
C(5)	3 940(17)	−962(26)	1 232(14)
O(5)	4 463(12)	−1 818(20)	1 317(11)
C(6)	3 654(16)	831(25)	2 352(14)
O(6)	3 994(11)	1 052(19)	3 095(9)
C(7)	4 010(16)	4 534(29)	134(14)
O(7)	4 072(12)	5 584(18)	−189(11)
C(8)	5 173(16)	2 409(27)	1 439(13)
O(8)	5 868(12)	2 284(20)	1 883(10)
C(9)	4 030(15)	1 406(25)	−190(13)
O(9)	4 075(12)	687(22)	−700(11)
C(10)	3 772(17)	3 744(27)	1 639(15)
O(10)	3 650(13)	4 344(19)	2 186(11)
N(1)	2 422(9)	264(18)	−257(8)
N(2)	1 714(11)	−705(19)	−535(10)
C(11)	1 704(13)	−1 764(22)	−1 045(11)
C(12)	942(12)	−2 741(18)	−1 324(9)
C(13)	400(12)	−2 726(18)	−879(9)
C(14)	−296(12)	−3 681(18)	−1 128(9)
C(15)	−448(12)	−4 651(18)	−1 822(9)
C(16)	94(12)	−4 667(18)	−2 266(9)
C(17)	790(12)	−3 712(18)	−2 018(9)
C(18)	2 398(16)	−2 018(26)	−1 361(14)

Complex neutral-atom scattering factors [14] were employed throughout both structure solutions and refinements. All the computations were performed on the University of Cambridge IBM 370/165 computer, using SHELX 76.[15] The molecular plots were drawn using the PLUTO package written by Dr. W. D. S. Motherwell. Details of hydrogen atomic co-ordinates, bond angles, least-square planes, isotropic and anisotropic thermal parameters, and observed and calculated structure factors for (1) and (2) may be found in Supplementary Publication No. SUP 23198 (39 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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