Hydrido-Nitrosyl Clusters $[M_3(CO)_{10}H(NO)]$ (M = Ru or Os) and the Molecular and Crystal Structure of $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$ †

By **Brian F. G. Johnson,* Paul R. Raithby,** and **Camillo Zuccaro,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The hydrido-nitrosyl cluster $[Ru_3(CO)_{10}H(NO)]$ has been prepared in high yield from the reaction of $Na[Ru_3(CO)_{11}H]$ with $[NO][PF_6]$. The corresponding osmium complex, $[Os_3(CO)_{10}H(NO)]$, has been prepared in lower yield from $Na[Os_3(CO)_{11}H]$. The complex $[Ru_3(CO)_{10}H(NO)]$ reacts with $P(OMe)_3$ to produce the tri-substituted complex $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$, which crystallises in the monoclinic space group $P2_1/c$ with cell dimensions $a = 14.666(4)$, $b = 12.743(4)$, $c = 18.384(7)$ Å, $\beta = 112.57(3)°$, and $Z = 4$. The structure has been solved by a combination of multisolution sigma-2 sign-expansion and Fourier techniques, and refined by full-matrix least squares to R 0.052 for 4 547 unique observed intensities. The three ruthenium atoms define an isosceles triangle, the shortest edge of which is symmetrically bridged by both a nitrosyl and a hydrido-ligand. The complex $[Ru_3(CO)_{10}H(NO)]$ reacts with PPh_3 to give the three related complexes $[Ru_3(CO)_{10-n}H(NO)(PPh_3)_n]$ (n = 1—3).

FEW nitrosyl clusters have been reported. In an earlier paper [1] we reported the synthesis and characterisation of the dinitrosyltriosmium cluster $[Os_3(CO)_9(NO)_2]$; we now report the preparation and characterisation of a new hydrido-cluster $[M_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NO)]$ (M = Ru or Os) which forms a member of the closely related series of compounds $[M_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CO)]^-$,[2] $[M_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NO)]$, and $[M_3(CO)_{10}(\mu\text{-}NO)_2]$.[3]

RESULTS AND DISCUSSION

Preparation and Characterisation.—We have previously reported [2] that triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$, reacts with sodium tetrahydroborate, $Na[BH_4]$, in tetrahydrofuran at room temperature to yield almost quantitatively the hydrido-species $Na[Ru_3(CO)_{11}H]$. After separation, this salt reacts with nitrosyl hexafluorophosphate in acetonitrile to produce the hydrido-nitrosyl cluster $[Ru_3(CO)_{10}H(NO)]$ according to reaction (1). The reaction solution also contains a

$$Na[Ru_3(CO)_{11}H] + [NO][PF_6] \longrightarrow [Ru_3(CO)_{10}H(NO)] + Na[PF_6] + CO \quad (1)$$

small amount of $[Ru_3(CO)_{12}]$. The complex $[Ru_3(CO)_{10}H(NO)]$ may also be obtained from the reaction of $[Ru_4(CO)_{13}H_2]$ and $[NO][PF_6]$ in MeCN. Yields of $[Ru_3(CO)_{10}H(NO)]$ from this reaction are comparatively low (15% as opposed to 60% by the above method). The other product of this reaction is also $[Ru_3(CO)_{12}]$.

TABLE 1

Infrared (cm^{-1}) [a] and ^{1}H n.m.r.[b] spectroscopic data for $[M_3(CO)_{10}H(NO)]$ and some substituted derivatives (M = Ru or Os)

Complex	ν(CO) and ν(NO)	τ(M–H) [c]
$[Ru_3(CO)_{10}H(NO)]$	2 109w, 2 070vs, 2 064s, 2 033vs, 2 027m, 2 019s, 1 998w ν(NO) 1 550w	21.85
$[Ru_3(CO)_9H(NO)(PPh_3)]$ [d]	2 091s, 2 054vs, 2 029vs, 2 018vs, 2 003 (sh), 2 000m, 1 985w, 1 976w	21.23
$[Ru_3(CO)_8H(NO)(PPh_3)_2]$ [d]	2 073m, 2 068m, 2 029vs, 2 019s, 2 007s, 2 001vs, 1 975m, 1 961w	20.25
$[Ru_3(CO)_7H(NO)(PPh_3)_3]$ [d]	2 031m, 2 000s, 1 987m, 1 973vs, 1 951m	19.63
$[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$	2 051m, 2 014s, 1 984vs, 1 960m ν(NO) 1 460 (KBr)	21.86
$[Os_3(CO)_{10}H(NO)]$	2 113w, 2 072vs, 2 065s, 2 029vs, 2 020m, 2 008s, 1 987m ν(NO) 1 586	
$[Os_3(CO)_9H(NO)\{P(OMe)_3\}]$	2 097s, 2 068w, 2 055vs, 2 034w, 2 019vs, 2 008vs, 1 986m, 1 978s, 1 971s, 1 956m ν(NO) 1 460 (KBr)	

[a] Solvent was cyclohexane unless otherwise stated. [b] Solvent was CD_2Cl_2. [c] Chemical shifts relative to $SiMe_4$ (τ 10) as standard. [d] ν(NO) not observed.

The complex $[Ru_3(CO)_{10}H(NO)]$ is obtained as dark red crystals which are slightly air-sensitive and which decompose under nitrogen over prolonged periods to give some $[Ru_3(CO)_{12}]$ and other, as yet uncharacterised, substances. The i.r. and ^{1}H n.m.r. spectroscopic data are presented in Table 1. The i.r. spectrum (in cyclohexane) has seven bands in the ν(CO) region, four of which are strong or very strong. A single weak band at 1 550 cm^{-1} is assigned to the N–O stretching vibration of the edge-bridging nitrosyl group. The single high-field resonance at τ 21.85 in the ^{1}H n.m.r. spectrum is ascribed to a bridging hydride. Molecular-weight determination by mass spectroscopic analysis confirms the formula as $[Ru_3(CO)_{10}H(NO)]$.

The corresponding osmium complex is obtained similarly from the reaction of $Na[Os_3(CO)_{11}H]$ with $[NO][PF_6]$ and may be characterised also on the basis of the spectroscopic data presented in Table 1.

Reaction with $P(OMe)_3$ *or* PPh_3.—The complex $[Ru_3(CO)_{10}H(NO)]$ reacts with trimethyl phosphite, $P(OMe)_3$, in cyclohexane under reflux to produce the complex $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$, and with triphenylphosphine to produce the three substituted derivatives $[Ru_3(CO)_9H(NO)(PPh_3)]$, $[Ru_3(CO)_8H(NO)(PPh_3)_2]$, and

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† 1,1,1,2,2,3,3-Heptacarbonyl-2,3-μ-hydrido-2,3-μ-nitrosyl-1,2,3-tris(trimethyl phosphite)-*triangulo*-triruthenium.

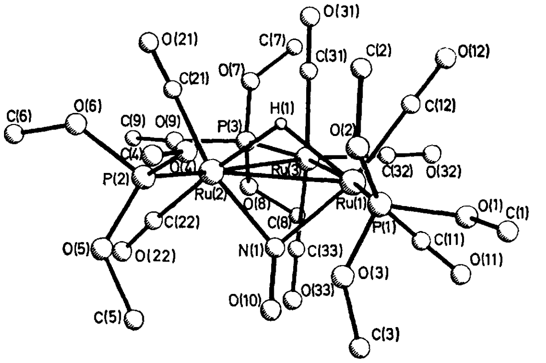


FIGURE 1 A molecule of $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$

$[Ru_3(CO)_7H(NO)(PPh_3)_3]$. It would appear that as with the parent carbonyl, $[Ru_3(CO)_{12}]$,[4] the rate of substitution increases across the series $[Ru_3(CO)_8H(NO)(PR_3)_2] > [Ru_3(CO)_9H(NO)(PR_3)] > [Ru_3(CO)_{10}H(NO)]$ and, as a consequence, the isolation of the mono- and di-substituted complexes is moderately difficult. The tertiary phosphine or phosphite complexes were characterised on the basis of their spectroscopic data (Table 1).

Crystal and Molecular Structure.—The crystal structure is built up from discrete molecules of $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$ held together only by van der Waals forces. Figure 1 is a PLUTO [5] plot of a single molecule, and includes the atom-labelling scheme adopted. The bond distances and interbond angles are presented in Tables 2 and 3, respectively.

The three ruthenium atoms define a slightly distorted isosceles triangle, the shortest edge [Ru(1)–Ru(2)] of which is symmetrically bridged by both the nitrosyl and the hydrido-ligand. The Ru(1)Ru(2)N(1)O(10) and Ru(1)Ru(2)H(1) planes make an angle of 24.7° with each other, and angles of 79.5 and 104.2°, respectively, with the Ru_3 plane. Each metal atom is also co-ordinated to a trimethyl phosphite ligand, the three phosphorus atoms being close to the Ru_3 plane. In addition, the Ru(1) and Ru(2) atoms are each bonded to two carbonyl groups, which lie in positions approximately *trans* to the bridging ligands; Ru(3) is co-ordinated to three carbonyls, two in axial and one in an equatorial site. Then, if metal–metal bonds are included, Ru(1) and Ru(2) are seven-co-ordinate and Ru(3) is six-co-ordinate. All the carbonyl groups are terminal and approximately linear with an average Ru–C–O angle of 177.9°.

TABLE 2

Bond lengths (Å)

Ru(2)–Ru(1)	2.816(2)	N(1)–Ru(1)	1.989(8)
Ru(3)–Ru(1)	2.843(2)	P(1)–Ru(1)	2.283(2)
Ru(3)–Ru(2)	2.856(2)	N(1)–Ru(2)	1.973(5)
H(1)–Ru(1)	1.810(10)	P(2)–Ru(2)	2.284(2)
H(1)–Ru(2)	1.810(19)	P(3)–Ru(3)	2.267(2)
C(11)–Ru(1)	1.884(8)	O(1)–P(1)	1.576(6)
C(12)–Ru(1)	1.900(12)	O(2)–P(1)	1.573(7)
C(21)–Ru(2)	1.929(9)	O(3)–P(1)	1.600(8)
C(22)–Ru(2)	1.876(11)	O(4)–P(2)	1.559(9)
C(31)–Ru(3)	1.912(10)	O(5)–P(2)	1.565(10)
C(32)–Ru(3)	1.897(9)	O(6)–P(2)	1.607(6)
C(33)–Ru(3)	1.948(11)	O(7)–P(3)	1.579(13)
O(10)–N(1)	1.230(9)	O(8)–P(3)	1.570(11)
C(1)–O(1)	1.490(12)	O(9)–P(3)	1.572(8)
C(2)–O(2)	1.422(15)	O(11)–C(11)	1.135(10)
C(3)–O(3)	1.438(14)	O(12)–C(12)	1.138(16)
C(4)–O(4)	1.500(13)	O(21)–C(21)	1.129(11)
C(5)–O(5)	1.447(12)	O(22)–C(22)	1.137(14)
C(6)–O(6)	1.398(17)	O(31)–C(31)	1.137(13)
C(7)–O(7)	1.310(22)	O(32)–C(32)	1.125(11)
C(8)–O(8)	1.421(16)	O(33)–C(33)	1.115(13)
C(9)–O(9)	1.443(17)		

A comparison of the Ru–Ru distances in this complex with those in the parent carbonyl shows that the two unbridged distances are similar to the mean value of 2.854 Å in $[Ru_3(CO)_{12}]$,[6] while the dibridged bond is *ca.* 0.033 Å shorter. This is in contrast with the metal–metal distances in the doubly nitrosyl-bridged complex $[Ru_3(CO)_{10}(\mu\text{-}NO)_2]$,[3] where the two unbridged distances are longer (2.866 Å) and the doubly bridged edge is extended to 3.15 Å and is not considered to be a direct metal–metal bond. The small but significant difference of 0.013 Å between the Ru(1)–Ru(3) and Ru(2)–Ru(3) bond lengths is presumably due to the influence of the phosphite ligands. Since there is no severe steric con-

TABLE 3

Bond angles (°)

Ru(3)–Ru(1)–Ru(2)	60.6(1)	P(1)–Ru(1)–Ru(2)	112.0(1)
Ru(3)–Ru(2)–Ru(1)	60.2(1)	P(1)–Ru(1)–Ru(3)	172.6(1)
Ru(2)–Ru(3)–Ru(1)	59.2(1)	N(1)–Ru(1)–Ru(2)	44.5(2)
P(2)–Ru(2)–Ru(1)	108.9(1)	N(1)–Ru(1)–Ru(3)	76.7(2)
P(2)–Ru(2)–Ru(3)	168.2(1)	C(11)–Ru(1)–Ru(2)	133.7(3)
N(1)–Ru(2)–Ru(1)	44.9(2)	C(11)–Ru(1)–Ru(3)	91.8(3)
N(1)–Ru(2)–Ru(3)	76.6(2)	C(12)–Ru(1)–Ru(2)	120.8(2)
C(21)–Ru(2)–Ru(1)	121.8(3)	C(12)–Ru(1)–Ru(3)	90.9(3)
C(21)–Ru(2)–Ru(3)	90.1(3)	H(1)–Ru(1)–Ru(2)	38.9(6)
C(22)–Ru(2)–Ru(1)	134.9(2)	H(1)–Ru(1)–Ru(3)	75.6(15)
C(22)–Ru(2)–Ru(3)	95.1(2)	N(1)–Ru(1)–P(1)	98.1(2)
H(1)–Ru(2)–Ru(1)	38.9(2)	C(11)–Ru(1)–P(1)	94.0(3)
H(1)–Ru(2)–Ru(3)	75.3(13)	C(11)–Ru(1)–N(1)	96.2(4)
N(1)–Ru(2)–P(2)	98.9(2)	C(12)–Ru(1)–P(1)	93.3(3)
C(21)–Ru(2)–P(2)	92.7(3)	C(12)–Ru(1)–N(1)	164.3(3)
C(21)–Ru(2)–N(1)	164.9(4)	C(12)–Ru(1)–C(11)	93.7(4)
C(22)–Ru(2)–P(2)	96.2(3)	H(1)–Ru(1)–P(1)	98.5(15)
C(22)–Ru(2)–N(1)	95.6(3)	H(1)–Ru(1)–N(1)	80.9(4)
C(22)–Ru(2)–C(21)	92.8(4)	H(1)–Ru(1)–C(11)	167.5(15)
H(1)–Ru(2)–P(2)	93.3(13)	H(1)–Ru(1)–C(12)	86.8(5)
H(1)–Ru(2)–N(1)	81.4(6)	O(1)–P(1)–Ru(1)	110.4(2)
H(1)–Ru(2)–C(21)	88.3(9)	O(2)–P(1)–Ru(1)	122.1(2)
H(1)–Ru(2)–C(22)	170.4(12)	O(2)–P(1)–O(1)	104.3(4)
P(3)–Ru(3)–Ru(1)	161.3(1)	O(3)–P(1)–Ru(1)	119.4(3)
P(3)–Ru(3)–Ru(2)	102.1(1)	O(3)–P(1)–O(1)	103.4(4)
C(31)–Ru(3)–Ru(1)	84.7(2)	O(3)–P(1)–O(2)	94.6(4)
C(31)–Ru(3)–Ru(2)	84.3(3)	C(1)–O(1)–P(1)	121.8(6)
C(32)–Ru(3)–Ru(1)	97.9(3)	C(2)–O(2)–P(1)	122.5(7)
C(32)–Ru(3)–Ru(2)	157.1(3)	C(3)–O(3)–P(1)	118.6(7)
C(33)–Ru(3)–Ru(1)	88.4(2)	O(4)–P(2)–Ru(2)	112.0(3)
C(33)–Ru(3)–Ru(2)	85.0(2)	O(5)–P(2)–Ru(2)	121.3(3)
C(31)–Ru(3)–P(3)	92.9(3)	O(5)–P(2)–O(4)	106.4(4)
C(32)–Ru(3)–P(3)	100.8(3)	O(6)–P(2)–Ru(2)	117.6(3)
C(32)–Ru(3)–C(31)	94.2(4)	O(6)–P(2)–O(4)	98.6(4)
C(33)–Ru(3)–P(3)	91.0(3)	O(6)–P(2)–O(5)	97.8(4)
C(33)–Ru(3)–C(31)	169.2(4)	C(4)–O(4)–P(2)	122.9(9)
C(33)–Ru(3)–C(32)	95.0(4)	C(5)–O(5)–P(2)	123.9(7)
Ru(2)–N(1)–Ru(1)	90.6(3)	C(6)–O(6)–P(2)	124.2(8)
O(10)–N(1)–Ru(1)	134.1(5)	O(7)–P(3)–Ru(3)	120.4(5)
O(10)–N(1)–Ru(2)	135.2(6)	O(8)–P(3)–Ru(3)	118.1(4)
O(11)–C(11)–Ru(1)	179.6(6)	O(8)–P(3)–O(7)	102.1(6)
O(12)–C(12)–Ru(1)	176.8(8)	O(9)–P(3)–Ru(3)	116.2(3)
O(21)–C(21)–Ru(2)	178.8(9)	O(9)–P(3)–O(7)	97.0(5)
O(22)–C(22)–Ru(2)	176.4(7)	O(9)–P(3)–O(8)	98.9(6)
O(31)–C(31)–Ru(3)	178.1(8)	C(7)–O(7)–P(3)	132.0(9)
O(32)–C(32)–Ru(3)	178.2(9)	C(8)–O(8)–P(3)	129.3(12)
O(33)–C(33)–Ru(3)	177.4(8)	C(9)–O(9)–P(3)	124.1(7)
Ru(2)–H(1)–Ru(1)	102.1(4)		

gestion between the ligands the effect is largely an electronic one. There are two phosphite ligands which are approximately collinear with the Ru(1)–Ru(3) bond, while the Ru(2)–Ru(3) bond is collinear with one phosphite and a carbonyl group. The carbonyl is a stronger π acceptor than the phosphite, so that the C(32)–O(32) group competes more strongly with Ru(2) for the appropriate set of *d*-orbital electrons on Ru(3), causing a lengthening of the metal–metal bond. The Ru(1)–P(1) and Ru(2)–P(2) distances are indicative of sigma bonds, while the Ru(3)–P(3) bond is 0.016 Å shorter and may indicate the presence of d_π–d_π bonding. The dimensions of the phosphite ligands are similar to those reported in a number of cluster structures.[7,8]

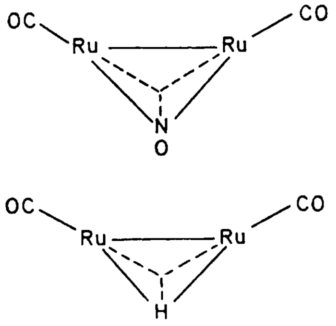


FIGURE 2 Planes containing the nitrosyl and hydride ligands

As in $[Ru_3(CO)_{12}]$,[6] the axial Ru–CO distances (mean 1.930 Å) on Ru(3) are lengthened in comparison to the equatorial bonds. This result is in accord with the accepted model for M–CO bonding, and occurs as a result of competition for d_π electron density between the mutually *trans* axial carbonyl ligands. An examination of the Ru–C distances for the carbonyl groups coordinated to Ru(1) and Ru(2) shows that those *trans* to the bridging hydride are short (mean 1.880 Å), while those *trans* to the nitrosyl are intermediate in length (mean 1.915 Å) between those of the axial and equatorial carbonyls on Ru(3). This can also be explained in terms of competition for π-electron density. The hydride has no orbitals available for π bonding so there is no competition between it and the *trans* carbonyl, which results in formation of a short Ru–C bond. A similar trend has been observed for the carbonyls *trans* to the hydride in $[Ru_3(CO)_{10}(C{=}NMe_2)H]$.[9] The nitrosyl ligand does have suitable π orbitals available, but the π-bonding properties of this group are not as strong as the $C{=}NMe_2$ species in $[Ru_3(CO)_{10}(C{=}NMe_2)H]$,[9] as evidenced by the longer *trans* Ru–CO bonds (mean 1.967 Å) in the latter compound.

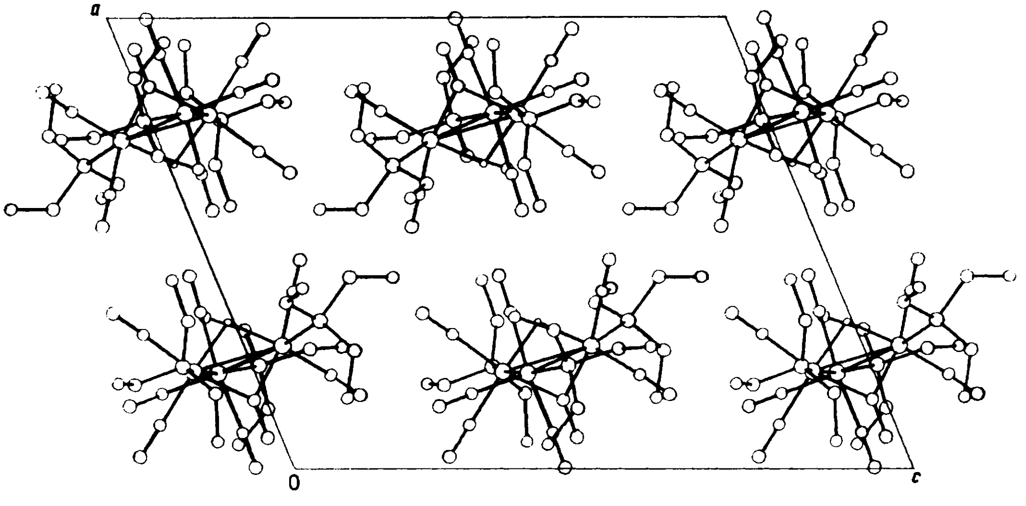
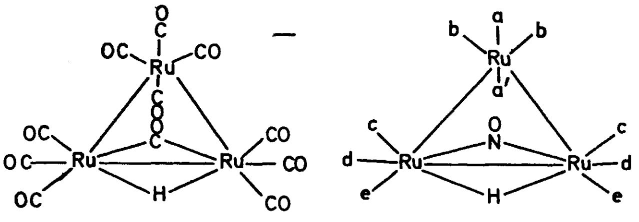


FIGURE 3 Molecular packing diagram of $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$

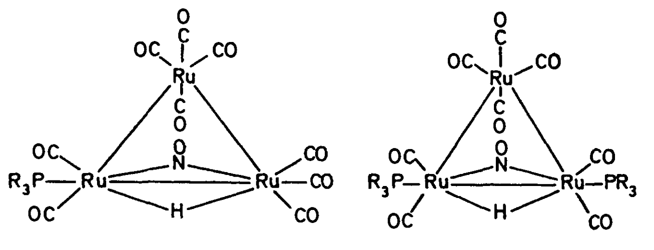
The bridging nitrosyl ligand acts as a three-electron donor and should formally be considered as a $[NO]^+$ species. The Ru–NO distances are equivalent (mean 1.981 Å), and are shorter than the mean bond length of 2.03 Å in the dinitrosyl complex $[Ru_3(CO)_{10}(NO)_2]$.[3] The N–O distance, however, is similar to the mean value of 1.22(2) Å in the dinitrosyl,[3] and to that reported for the μ-NO ligands [1.212(6) Å] in $[Mn_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}NO)(\mu\text{-}NO)_3]$.[10] All these distances are significantly longer than the N–O bond lengths (mean 1.16 Å) in the cluster $[Co_4(NO)_4\{\mu_3\text{-}NC(CH_3)_3\}_4]$[11] where the nitrosyls are terminal and linear. The C(12)Ru(1)Ru(2)N(1)C(21) system is planar. The two *trans* C(carbonyl)–Ru–N(nitrosyl) angles average 164.6° so that the extension of these O–C–Ru vectors would intersect near the centre of the Ru(1)N(1)Ru(2) triangle (Figure 2). This suggests that this system is best described as a 'closed' three-centre bond with appreciable metal–metal bonding present. Similarly the *trans* C(carbonyl)–Ru–H angles average 169.0°, also indicating the presence of a 'closed' three-centre bond. This is in agreement with a simple electron-counting scheme; with the hydride acting as a one-electron donor, the complex is an 'electron-precise' 48-electron system and requires three two-electron two-centre metal–metal bonds. The dinitrosyl complex,[3] where the two μ-NO ligands both act as three-electron donors, is a 50-electron system. The inclusion of an additional electron pair requires the breaking of a metal–metal bond.

The positions of hydrides in metal clusters are not located accurately by means of *X*-ray diffraction because the scattering is dominated by the metal contribution. In order to aid the refinement of this structure, although the hydride position was located in the Fourier difference map, a weak constraint was applied in the form of extra observational equations to make the Ru–H distances equal to 1.81 Å. This value was found from a combination of *X*-ray diffraction and nematic-phase ^1H n.m.r. techniques in $[Ru_3(CO)_9(CCH_3)H_3]$.[12] The resulting Ru–H–Ru angle is in close agreement with the value of 101.3° in $[Ru_3(CO)_{10}(C{=}NMe_2)H]$.[9]



$[Ru_3(CO)_{11}H]^-$ $[Ru_3(CO)_{10}H(NO)]$

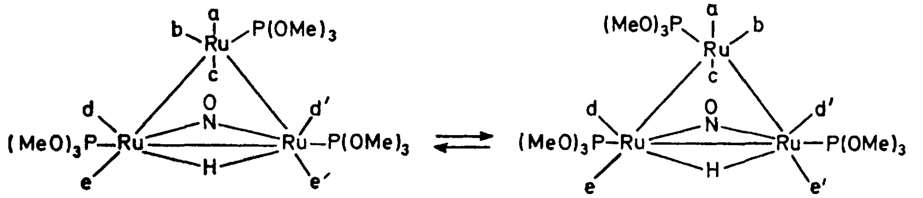
FIGURE 4 Structure of the anion $[Ru_3(CO)_{11}H]^-$ and $[Ru_3(CO)_{10}H(NO)]$



$[Ru_3(CO)_9H(NO)(PR_3)]$ $[Ru_3(CO)_8H(NO)(PR_3)_2]$

FIGURE 5 Probable structures of $[Ru_3(CO)_9H(NO)(PR_3)]$ and $[Ru_3(CO)_8H(NO)(PR_3)_2]$

A molecular packing diagram viewed down the *b* axis is shown in Figure 3. There are no short intermolecular contacts.



(A) (B)

Attempts to establish the molecular structure of $[Ru_3(CO)_{10}H(NO)]$ were thwarted by disorder problems and $[Ru_3(CO)_9H(NO)(PPh_3)]$ decomposed on *X*-ray irradiation. However, given the geometry established for $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$, we suggest that the structure of $[M_3(CO)_{10}H(NO)]$ (M = Ru or Os) is related to that established [2] for $[Ru_3(CO)_{11}H]^-$ with the μ-CO replaced by a μ-NO group (Figure 4). The spectroscopic data discussed above and given in Table 1 support this conclusion. It follows that the structures of $[Ru_3(CO)_9H(NO)(PR_3)]$ and $[Ru_3(CO)_8H(NO)(PR_3)_2]$ are as shown in Figure 5. In all cases we believe that the PR_3 ligands occupy equatorial sites about the Ru_3 triangle.

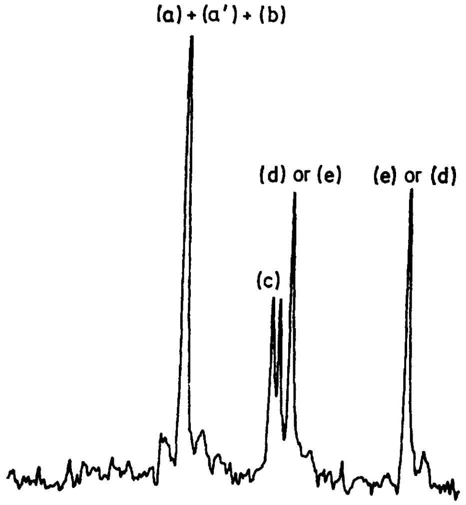


FIGURE 6 The ^{13}C Fourier-transform n.m.r. spectrum of $[Ru_3(CO)_{10}H(NO)]$

Study of ^{13}*CO Fourier-transform N.M.R. Structure in Solution*.—The ^{13}C Fourier-transform n.m.r. spectrum of $[Ru_3(CO)_{10}H(NO)]$ (*ca.* 70% enriched in ^{13}CO) was recorded over the temperature range −80 to +50°C. There are three singlets at 202.8, 194.2, and 184.8 p.p.m. and a doublet at 195.4 p.p.m. (Figure 6) of relative intensity 4 : 2 : 2 : 2. In the ^1H-decoupled spectrum four singlets at 202.9, 195.5, 194.3, and 184.8 p.p.m. are observed. On these grounds the signal at 195.5 p.p.m. may be assigned unambiguously to carbonyl groups (c). The further assignment of (a), (a'), (b), (d), and (e) is not unequivocal but we suggest that the signal at 202.8 p.p.m. of intensity 4 corresponds to (a) + (a') + 2(b), *i.e.* carbonyl scrambling is occurring rapidly about the unique ruthenium atom Ru. The ^{13}C Fourier-transform n.m.r. spectrum of $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$ at 30°C is in agreement with the structure established in the solid. Three signals at 210.7, 209.1, and 201.9 p.p.m. of relative intensity 2 : 3 : 2 are observed. All signals are broad indicating coupling with the ^{31}P nuclei. This spectrum is unchanged down to −80 °C and we suggest that interconversion of the two forms (A) and (B) is occurring *via* CO scrambling about the unique Ru atom. By this process carbonyls a, b, and c are equilibrated as are carbonyls d, e, d′, and e′.

TABLE 4

Atom co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Ru(1)	7 849(1)	1 024(1)	5 990(1)
Ru(2)	7 279(1)	1 613(1)	4 400(1)
Ru(3)	7 889(1)	3 179(1)	5 603(1)
P(1)	7 744(2)	−747(2)	6 131(1)
O(1)	8 145(5)	−1 051(4)	7 030(4)
C(1)	8 119(11)	−2 153(8)	7 293(8)
O(2)	6 737(5)	−1 357(5)	5 757(4)
C(2)	5 826(8)	−926(10)	5 718(9)
O(3)	8.332(5)	−1 518(4)	5 778(4)
C(3)	9 390(8)	−1 439(9)	6 068(8)
P(2)	6 720(2)	163(2)	3 626(1)
O(4)	6 322(6)	−691(5)	4 035(4)
C(4)	6 001(11)	−1 759(8)	3 688(8)
O(5)	7 384(6)	−423(6)	3 262(5)
C(5)	8 426(8)	−624(9)	3 683(7)
O(6)	5 755(6)	294(6)	2 830(4)
C(6)	5 753(11)	770(13)	2 145(7)
P(3)	7 715(2)	4 574(2)	4 893(2)
O(7)	6 936(10)	5 531(7)	4 889(6)
C(7)	6 644(10)	5 863(11)	5 439(8)
O(8)	8 660(8)	5 354(7)	5 035(7)
C(8)	9 458(11)	5 594(11)	5 753(8)
O(9)	7 349(8)	4 538(5)	3 975(5)
C(9)	7 306(15)	5 379(11)	3 437(8)
N(1)	8 479(4)	1 005(4)	5 206(4)
O(10)	9 302(4)	757(5)	5 233(3)
C(11)	9 028(7)	1 157(6)	6 886(5)
O(11)	9 738(6)	1 245(6)	7 426(4)
C(12)	7 031(7)	1 331(7)	6 553(5)
O(12)	6 567(6)	1 557(6)	6 902(5)
C(21)	6 077(7)	2 382(7)	3 850(5)
O(21)	5 371(5)	2 821(6)	3 516(4)
C(22)	7 925(6)	2 220(6)	3 799(5)
O(22)	8 362(5)	2 568(5)	3 463(4)
C(31)	6 532(7)	3 174(6)	5 474(5)
O(31)	5 729(5)	3 197(5)	5 408(5)
C(32)	8 342(7)	3 727(7)	6 641(5)
O(32)	8 617(6)	4 076(6)	7 249(4)
C(33)	9 203(7)	2 953(6)	5 604(5)
O(33)	9 969(5)	2 849(5)	5 628(5)
H(1)	6 758(3)	1 197(39)	5 100(8)

EXPERIMENTAL

Molecular-structure Determination.—Crystals of $[Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3]$ were obtained as deep red blocks from hexane solution. A single crystal (*ca.* 0.188 × 0.169 × 0.338 mm) was mounted on a glass fibre with epoxy-resin adhesive, and the unit-cell dimensions and space group determined *via* Weissenberg (Cu) *X*-ray photography.

This crystal was transferred to a Syntex $P2_1$ four-circle diffractometer, and accurate cell dimensions obtained by centring 15 strong reflections ($20.0 < 2\theta < 30.0°$). 6 123 Intensities were measured in the range $3.0 < 2\theta < 60.0°$, using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha 1}$ 0.709 26, $\lambda_{\alpha 2}$ 0.713 54 Å) and a 96-step ω-2θ scan procedure; peaks were scanned from 1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$ at rates between 0.025 0 and 0.488 3° s^{-1}, dependent on an initial 2-s peak count; reflections with intensities of $\leqslant 7$ counts s^{-1} were not remeasured. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 140 azimuthal scan data from five independent reflections was applied. Transmission factors ranged from 0.932 to 1.000 for the full data set. Lorentz polarization corrections were also applied and equivalent reflections averaged to give 4 554 unique observed intensities [$I > 1.5\sigma(I)$].

Crystal Data.—$C_{16}H_{28}NO_{17}P_3Ru_3$, $M = 902.51$, Monoclinic, $a = 14.666(4)$, $b = 12.743(4)$, $c = 18.384(7)$ Å, $\beta = 112.57(3)°$, $U = 3\ 172.6$ Å^3, $Z = 4$, $D_c = 1.888$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 15.61 cm^{-1}, space group $P2_1/c$ from systematic absences.

The three ruthenium-atom positions were located by multisolution Σ_2 sign expansion. These atoms were assigned anisotropic thermal parameters, and subjected to two 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. Anisotropic refinement of all these atoms gave an R of 0.053 2. A difference map calculated at this stage, on the full data set, revealed the position of the bridging hydride ligand. This atom was included in further cycles of full-matrix least squares, with the two Ru–H distances constrained to equal 1.810(1) Å, and with the assignment of an isotropic temperature factor. At this stage seven strong low-angle reflections, which were considered to be suffering severely from extinction, were zero weighted and a weighting scheme of the form $w = 1.186\ 7/[\sigma^2(F_o) + 0.001|F_o|^2]$ introduced; this minimised the dependence of $w\Delta^2$ on $|F_o|$ and sin θ. Refinement continued until the maximum shift/e.s.d. for any parameter did not exceed 0.01. The final residuals for the 4 547 reflections were $R = 0.052$ and $R' = (\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|) = 0.053$, and a difference map calculated at this stage showed no regions of significant electron density. The methyl hydrogen atoms were not located.

Complex neutral-atom scattering factors were employed, and were modified for anomalous dispersion.[13] All the computations were performed on the University of Cambridge IBM 370/165 computer, using programs written by Dr. G. M. Sheldrick.[14] The atomic fractional co-ordinates are given in Table 4, while lists of thermal parameters, observed and calculated structure factors, and details of least-squares planes have been deposited as Supplementary Publication No. SUP 22625 (30 pp.).*

All operations were carried out with rigorous exclusion of air. Solvents were distilled over drying agents and saturated with purified nitrogen.

Preparations.—The salts $Na[Ru_3(CO)_{11}H]$ and $Na[Os_3(CO)_{11}H]$ were prepared according to the previously published method.[2]

$[Ru_3(CO)_{10}H(NO)]$.—A solution of $Na[Ru_3(CO)_{11}H]$ (100 mg) and $[NO][PF_6]$ (30 mg) in methyl cyanide (20 cm^3) was stirred for 1 h. The solution was filtered through filter floc and taken to small volume under vacuum. After separation on silica (t.l.c.) the product was eluted with CH_2Cl_2–C_6H_{12} (1 : 10). The product was crystallised from hexane, yield 58 mg (*ca.* 60%) (Found: C, 19.5; H, 0.15; N, 2.30. Calc. for $C_{10}HNO_{11}Ru_3$: C, 20.0; H, 0.40; N, 2.20%); *M* (mass spectroscopic) 615.

The complex $[Os_3(CO)_{10}H(NO)]$ was prepared similarly from $Na[Os_3(CO)_{11}H]$ and was identified on the basis of its mass ($m/e = 883$) and i.r. spectra (Table 1).

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Reactions.—[$Ru_4(CO)_{13}H_2$) *and* [NO][PF_6]. A solution of [$Ru_4(CO)_{13}H_2$] (100 mg) and [NO][PF_6] (26 mg) in MeCN (50 cm^3) was stirred for 1 h. After filtration, the solvent was removed and the product crystallised from hexane.

[$Ru_3(CO)_{10}H(NO)$] *with* $P(OMe)_3$. A solution of [Ru_3-(CO)H(NO)] (50 mg) and $P(OMe)_3$ (50 mg) in cyclohexane (20 cm^3) was heated under reflux for 1.5 h. The solution was reduced under vacuum and then chromatographed (t.l.c.) on silica. One band was observed which on elution gave the product [$Ru_3(CO)_7H(NO)\{P(OMe)_3\}_3$] which was crystallised from hexane.

[$Ru_3(CO)_{10}H(NO)$] *with* PPh_3. A solution of [Ru_3-$(CO)_{10}H(NO)$] (50 mg) and PPh_3 (22 mg) in cyclohexane (30 cm^3) was stirred for 10 h. The resulting reddish solution was reduced in volume and chromatographed on silica (t.l.c.). Three bands were obtained. On elution the first band gave [$Ru_3(CO)_9H(NO)(PPh_3)$] (55 mg, 80%) which was crystallised from hexane (Found: C, 38.2; H, 2.15; N, 1.40. Calc. for $C_{27}H_{16}NO_{10}Ru_3$: C, 38.3; H, 1.90; N, 1.65%); *M* (mass spectropic) 849. The second band gave [$Ru_3(CO)_8H(NO)(PPh_3)_2$] (4 mg, 5%) (Found: C, 48.8; H, 3.20; N, 1.25. Calc. for $C_{44}H_{31}NO_9Ru_3$: C, 48.7; H, 2.85; N, 1.30%). The third band gave [Ru_3-$(CO)_7H(NO)(PPh_3)_3$] (2 mg, 3%) (Found: C, 55.6; H, 3.70; N, 0.35. Calc. for $C_{61}H_{46}NO_8Ru_3$: C, 55.5; H, 3.50; N, 1.05%).

The complex [$Os_3(CO)_7H(NO)\{P(OMe)_3\}_3$] was prepared in a manner similar to that reported for the ruthenium analogue and characterised on the basis of its spectroscopic data.

Variable-temperature ^{13}C *N.M.R. Study.*—The measurements were carried out on a Varian XL-100-15 spectrometer using *ca.* 70% ^{13}CO-enriched samples. For the low-temperature measurements a 1 : 3 mixture of CD_2Cl_2 and $CHCl_2F$ was used; for higher temperatures CD_2Cl_2 was employed. Tris(acetylacetonato)chromium(III) was added as relaxation reagent. Chemical shifts were recorded relative to the CD_2Cl_2 signal and related to the standard $SiMe_4$ using the conversion $\delta(SiMe_4) = \delta(CD_2Cl_2) + 53.9$ p.p.m.

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