The $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2]^+$ Cation: Synthesis and *X*-Ray Crystal Structure of $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$ †

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The clusters $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ react with acids HX (X = BF_4 or PF_6) to form the cationic derivatives $[Os_3(\mu\text{-}H)(CO)_{11}(MeCN)]X$ and $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2]X$, respectively. The cluster $[Os_3(CO)_{10}(MeCN)_2]$ also reacts with dry HCl to form the salt $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$. *X*-Ray analysis of this salt shows that the Os atoms in the cation lie at the vertices of an isosceles triangle. A hydride bridges the long Os–Os edge, and the two acetonitrile ligands occupy *trans* axial sites. Reaction of $[Os_3(\mu\text{-}H)(\mu\text{-}OH)(CO)_{10}]$ with HBF_4 in MeCN also produces $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2]^+$. In this reaction direct attack of H^+ on the co-ordinated OH^- ligand is considered to occur with the resultant liberation of H_2O. Treatment of $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2]^+$ with $[Os(CO)_4]^{2-}$ leads to the formation of the neutral complex $[Os_4H_2(CO)_{14}(MeCN)]$. The bridging hydride of the cation may also be replaced by a bridging nitrosyl ligand by reaction with NO^+.

Relatively few cationic clusters species have been fully characterised.[1] However, these species have considerable potential for reaction with mononuclear and cluster anions to produce larger clusters. The inclusion in cluster cations of labile ligands, such as MeCN, which may be displaced easily to create vacant co-ordination sites, also enhances their reactivity. Previously, neutral clusters, such as $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$, have been shown to undergo substitution reactions with a wide variety of molecules under mild conditions, by loss of the MeCN group.[2] The tetraosmium cation $[Os_4H_3(CO)_{12}(MeCN)_2]^+$ reacts readily with halide ions to give neutral cluster species, and with NO_2^- to give the anion $[Os_4H(CO)_{12}(MeCN)_2]^-$.[3] We now report on the synthesis of the related triosmium cations, $[Os_3H(CO)_{11}(MeCN)]^+$ and $[Os_3H(CO)_{10}(MeCN)_2]^+$, formed by the reaction of $[Os_3(CO)_{11}(MeCN)]$ or $[Os_3(CO)_{10}(MeCN)_2]$ with acids HX (X = BF_4 or PF_6), and the formation of the neutral cluster $[Os_4H_2(CO)_{14}(MeCN)]$ by the reaction of $[Os_3H(CO)_{10}(MeCN)_2]^+$ with $[Os(CO)_4]^{2-}$. The hydride ligand on the cationic cluster is also readily replaced by a nitrosyl group.

Results and Discussion

The mono-acetonitrile complex $[Os_3(CO)_{11}(MeCN)]$, in MeCN, reacts with HPF_6, in diethyl ether, to produce the PF_6^- salt of the cation $[Os_3H(CO)_{11}(MeCN)]^+$ quantitatively. Similarly, reaction of the bis-acetonitrile complex $[Os_3(CO)_{10}(MeCN)_2]$ with HX (X = PF_6^- or BF_4^-) produces the corresponding bis-acetonitrile cation $[Os_3H(CO)_{10}(MeCN)_2]^+$. In these reactions proton addition occurs directly on the central *triangulo*-osmium cluster. This behaviour is similar to that observed with the parent carbonyl, $[Os_3(CO)_{12}]$, and its related substituted derivatives.[4]

The same cation $[Os_3H(CO)_{10}(MeCN)_2]^+$ is the product of the reaction of the hydroxy-bridged cluster $[Os_3H(OH)(CO)_{10}]$ with HBF_4 [equation (1)]. In this case electrophilic attack of H^+ clearly occurs at the bridging OH group which leads to the elimination of the cation $[Os_3H(CO)_{10}(MeCN)_2]^+$. In contrast, addition to $[Os_3H(OH)(CO)_{10}]$ of strongly co-ordinating anions, X, such as Cl^- or $MeCO_2^-$ leads to derivatives of the type $[Os_3H(CO)_{10}X]$, equation (2).[5]

$$[Os_3H(OH)(CO)_{10}] + HBF_4 \xrightarrow{MeCN} [Os_3H(CO)_{10}(MeCN)_2]BF_4 + H_2O \quad (1)$$

$$[Os_3H(OH)(CO)_{10}] + HX \longrightarrow [Os_3H(CO)_{10}X] + H_2O \quad (2)$$
$$(X = Cl^- \text{ or } MeCO_2^-)$$

A surprising reaction occurred when $[Os_3(CO)_{10}(MeCN)_2]$ was treated with gaseous HCl, giving the salt $[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$ in good yield [equation (3)]. The route by which this reaction occurs is unclear; however, this type of reaction is not unique. When $[Os_4H_4(CO)_{12}]$ is treated similarly with NO^+ the salt $[Os_4H_4(OH)(CO)_{12}][Os(CO)_3(NO_3)_3]$ is obtained in good yield.[6] The reaction of $[Os_3(CO)_{11}(MeCN)]$ with gaseous HCl appears to be simpler. In this case the salt $[Os_3H(CO)_{11}(MeCN)]Cl$ is produced, and there is no evidence for the formation of the $[Os(CO)_3Cl_3]^-$ anion.

$$[Os_3(CO)_{10}(MeCN)_2] + HCl \longrightarrow [Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3] \quad (3)$$

Prolonged exposure of $[Os_3H(CO)_{10}(MeCN)_2]^+$ to gaseous HCl results in the formation of the known cluster $[Os_3H(CO)_{10}Cl]$.[7]

Treatment of the cation $[Os_3H(CO)_{10}(MeCN)_2]^+$ with the osmium carbonyl dianion $[Os(CO)_4]^{2-}$, which may contain significant quantities of $[OsH(CO)_4]^-$,[8] produces as one of the major products the neutral cluster $[Os_4H_2(CO)_{14}(MeCN)]$ [equation (4)], which has previously been obtained from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $[OsH_2(CO)_4]$.[9] The formation of the tetranuclear osmium cluster from the triosmium cation by the addition of a mononuclear anion under mild conditions, in a manner similar to that observed previously for the reactions of a number of neutral osmium clusters with osmium anions,[9] illustrates the potential for systematic cluster build up of the trinuclear cationic species.

$$[Os_3H(CO)_{10}(MeCN)_2]^+ + [Os(CO)_4]^{2-} \longrightarrow [Os_4H_2(CO)_{14}(MeCN)] \quad (4)$$

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† 2,3-Bis(acetonitrile)-1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-μ-hydrido-*triangulo*-triosmium tricarbonyltrichloro-osmate(1−).

Supplementary data available (No. SUP 56015, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Spectroscopic data for the cluster complexes

Complex	ν(CO)/cm^{-1}	^{1}H N.m.r. (τ)
$[Os_3H(CO)_{11}(MeCN)]PF_6$	[a] 2 150w, 2 108s, 2 087s, 2 062s, 2 019m, 2 007vw	[b] 26.85 (s, 1 H), 7.28 (s, 3 H)
$[Os_3H(CO)_{10}(MeCN)_2]BF_4$	[c] 2 120w, 2 087s, 2 071s, 2 029s	[d] 20.09 (s, 1 H), 7.23(s, 6 H)
$[Os_3H(CO)_{10}(MeCN)_2]PF_6$	[a] 2 119w, 2 105w, 2 089s, 2 073s, 2 025br	[b] 24.25 (s, 1 H), 7.37 (s, 6 H)
$[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$	[a] 2 120s, 2 090vs, 2 074vs, 2 028vs	[b] 24.27 (s, 1 H), 7.32 (s, 6 H)
$[Os_3H(CO)_{10}(PMe_3)_2][Os(CO)_3Cl_3]$	[a] 2 121m, 2 078s, 2 063s, 2 035vs, 2 020s, 1 995m	[b] 30.17 [d, 1 H, *J*(P–H) = 20 Hz], 8.21 (q, 18 H)
$[Os_3(NO)(CO)_{10}(MeCN)_2]BF_4$	[a] 2 124m, 2 090vs, 2 072vs, 2 028vs 1 646m [e]	
$[Os_3H(CO)_{10}Cl]$	[a] 2 117w, 2 078vs, 2 069s, 2 029vs, 2 016s, 2 002w, 1 992m	[b] 20.5 (s, 1 H)

[a] CH_2Cl_2 solvent. [b] CD_2Cl_2 solvent. [c] MeCN solvent. [d] $(CD_3)_2CO$ solvent. [e] ν(NO).

The bridging hydrido-ligand in $[Os_3H(CO)_{10}(MeCN)_2]^+$ can be replaced by a nitrosyl group by its reaction with NO^+ [equation (5)]. The ^{1}H n.m.r. spectrum of the reaction mixture shows the loss of the hydride signal, while the i.r. spectrum exhibits a signal at 1 646 cm^{-1} which is indicative of a bridging NO group co-ordinated to a cationic species.

$$[Os_3H(CO)_{10}(MeCN)_2]^+ \xrightarrow{NOBF_4} [Os_3(NO)(CO)_{10}(MeCN)_2]^+ \quad (5)$$

The neutral cluster $[Os_3(CO)_{10}(MeCN)_2]$ readily undergoes substitution with PMe_3, in tetrahydrofuran (thf), by loss of acetonitrile to give $[Os_3(CO)_{10}(PMe_3)_2]$ as the major product; a small amount of the trisubstituted product $[Os_3(CO)_9(PMe_3)_3]$ is also obtained. $[Os_3(CO)_{10}(PMe_3)_2]$, like $[Os_3(CO)_{10}(MeCN)_2]$, undergoes reaction with gaseous HCl to give a salt, namely $[Os_3H(CO)_{10}(PMe_3)_2][Os(CO)_3Cl_3]$.

The cationic species have been characterised by spectroscopic techniques (Table 1). The i.r. spectrum of $[Os_3H(CO)_{11}(MeCN)]PF_6$ exhibits six bands in the region 2 150—2 000 cm^{-1}. The ^{1}H n.m.r. spectrum (in $CDCl_3$) shows resonances at τ 26.85 (s, 1 H) and 7.28 (s, 3 H) corresponding to the hydride and the co-ordinated MeCN ligand respectively. For $[Os_3H(CO)_{10}(MeCN)_2]PF_6$ the i.r. spectrum is comparatively simple exhibiting two strong and three weak absorptions in the 2 150—2 000 cm^{-1} region. The ^{1}H n.m.r. spectrum (CD_2Cl_2, 30 °C) shows a singlet at τ 7.37 which may be assigned to two equivalent MeCN ligands and a singlet at τ 24.25 attributable to the hydrido-ligand.

In order to establish the molecular geometry of the cationic species and to confirm the nature of the anion in the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with gaseous HCl an *X*-ray crystal-structure analysis of the reaction product was undertaken. The Figure shows the discrete $[Os_3H(CO)_{10}(MeCN)_2]^+$ and $[Os(CO)_3Cl_3]^-$ units together with the atom-labelling scheme adopted. There are no abnormally short intermolecular contacts between the cations and anions. The final bond lengths and interbond angles are presented in Tables 2 and 3, respectively.

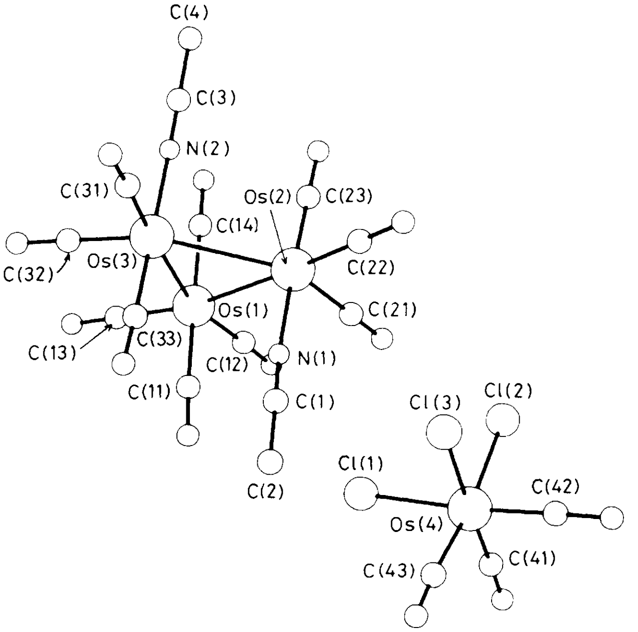

Figure. The molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$ showing the atom-numbering scheme

In the cation the Os atoms lie at the vertices of an isosceles triangle with the two MeCN ligands occupying *trans* axial sites on two of the three metal atoms. The metal–metal distance [Os(2)–Os(3)] between the two Os atoms bonded to the MeCN ligands is relatively long, being *ca.* 0.12 Å longer than the average value of 2.884(3) Å for the other two Os–Os distances. The Os(2)–Os(3) bond is also *ca.* 0.13 Å longer than the average Os–Os bond length of 2.877(3) Å in the parent binary carbonyl, $[Os_3(CO)_{12}]$.[10] Long Os–Os distances are associated with the presence of bridging hydrido-ligands when no other bridging groups span the same metal–metal bond,[11] and in this case the presence of a hydride bridging the Os(2)–Os(3) edge is confirmed by an analysis of the ligand distribution round the cluster. The equatorial carbonyl groups [C(22)-O(22) and C(31)O(31)] adjacent to the Os(2)–Os(3) edge bend away from it, as shown by the average Os–Os–C angle of 118(2)° when compared to the average *cis* Os–Os–C angle of 93(2)° for the other two Os–Os bonds. The Os(1)–Os(2) and Os(1)–Os(3) bond lengths are slightly longer than the similar Os–Os bonds [average 2.877(3) Å], between the Os atoms bonded to the MeCN groups and the tetracarbonyl-co-ordinated Os atom, in the related neutral cluster $[Os_3(CO)_{10}$-

Table 2. Bond lengths (Å) for $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$

Os(1)–Os(2)	2.886(2)	Os(1)–Os(3)	2.882(2)
Os(1)–C(11)	1.957(22)	Os(1)–C(12)	1.869(29)
Os(1)–C(13)	1.902(23)	Os(1)–C(14)	1.946(22)
Os(2)–Os(3)	3.002(2)	Os(2)–C(21)	1.939(26)
Os(2)–C(22)	1.853(22)	Os(2)–C(23)	1.802(24)
Os(2)–N(1)	2.071(17)	N(1)–C(1)	1.145(28)
C(1)–C(2)	1.475(32)	Os(3)–C(31)	1.893(32)
Os(3)–C(32)	1.809(23)	Os(3)–C(33)	1.873(22)
Os(3)–N(2)	2.072(19)	N(2)–C(3)	1.145(31)
C(3)–C(4)	1.528(36)	C(11)–O(11)	1.134(27)
C(12)–O(12)	1.161(37)	C(13)–O(13)	1.154(29)
C(14)–O(14)	1.141(28)	C(21)–O(21)	1.076(32)
C(22)–O(22)	1.190(28)	C(23)–O(23)	1.193(29)
C(31)–O(31)	1.159(40)	C(32)–O(32)	1.202(29)
C(33)–O(33)	1.157(27)	Os(4)–Cl(1)	2.414(7)
Os(4)–Cl(2)	2.360(9)	Os(4)–Cl(3)	2.385(10)
Os(4)–C(41)	2.012(95)	Os(4)–C(42)	1.872(26)
Os(4)–C(43)	1.973(37)	C(41)–O(41)	0.905(102)
C(42)–O(42)	1.180(100)	C(43)–O(43)	0.949(52)

$(MeCN)_2]$,[12] which may reflect the positive charge on the former complex.

The average Os–N distance of 2.07(2) Å for the two axially co-ordinated MeCN groups is shorter than the average Os–N distance of 2.13(2) Å for the bis-acetonitrile complex $[Os_3(CO)_{10}(MeCN)_2]$, but similar to the value of 2.07(2) Å for the single axially-co-ordinated MeCN ligand in the mono-acetonitrile complex $[Os_3(CO)_{11}(MeCN)]$.[12] The Os–N bonds in $[Os_3H(CO)_{10}(MeCN)_2]^+$ are also shorter than the two values of 2.10(2) and 2.13(1) Å for the Os–N bonds in the tetraosmium cation $[Os_4H_3(CO)_{12}(MeCN)_2]^+$.[3]

The acetonitrile and carbonyl ligands in $[Os_3H(CO)_{10}(MeCN)_2]^+$ are all essentially linear and do not deviate from precise linearity by more than 4σ. The Os–C(carbonyl) bond lengths in $[Os_3H(CO)_{10}(MeCN)_2]^+$ show similar trends to those observed in $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$.[12] The Os–C lengths *trans* to the axial acetonitrile groups are relatively short, reflecting the inability of the acetonitrile to accept back-donated density from the metals. By contrast, the Os–C lengths of the *trans* axial carbonyls on Os(1) are relatively long because both CO groups are competing for back donation from the metal. The Os–C distances for the equatorial carbonyls, which are *trans* to Os–Os bonds, are intermediate in length.

The $[Os(CO)_3Cl_3]^-$ anion adopts the *fac* configuration similar to that observed for the anion in the salt $[Os_4H_4(OH)(CO)_{12}][Os(CO)_3(NO_3)_3]$.[7] The anion shows some thermal disorder, but the co-ordination geometry about the Os atom is close to idealised octahedral. The average Os–Cl bond length of 2.39(2) Å is not significantly different from the value of 2.38 Å reported for the Os–Cl bonds in the $[OsO_2Cl_4]^{2-}$ anion,[13] where each Cl atom is *trans* to another. The Os–C(carbonyl) bonds [average 1.95(5) Å] are somewhat longer than the equivalent bonds in the $[Os(CO)_3(NO_3)_3]^-$ anion [average 1.87(2) Å] where each carbonyl is *trans* to a monodentate nitrate group.

Experimental

Solvents were distilled over calcium hydride and deoxygenated before use. The clusters $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ were prepared by literature methods.[2] I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer using carbon monoxide as calibrant. ^1H N.m.r. spectra were obtained on a Varian CFT-20 spectrophotometer.

Table 3. Bond angles (°) in $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$

Os(2)–Os(1)–Os(3)	62.7(1)	Os(2)–Os(1)–C(11)	86.4(7)
Os(3)–Os(1)–C(11)	90.5(7)	Os(2)–Os(1)–C(12)	98.2(9)
Os(3)–Os(1)–C(12)	160.7(9)	C(11)–Os(1)–C(12)	90.9(11)
Os(2)–Os(1)–C(13)	161.2(7)	Os(3)–Os(1)–C(13)	98.5(7)
C(11)–Os(1)–C(13)	93.4(9)	C(12)–Os(1)–C(13)	100.6(11)
Os(2)–Os(1)–C(14)	89.9(7)	Os(3)–Os(1)–C(14)	85.8(7)
C(11)–Os(1)–C(14)	175.7(10)	C(12)–Os(1)–C(14)	91.8(11)
C(13)–Os(1)–C(14)	89.3(9)	Os(1)–Os(2)–Os(3)	58.6(1)
Os(1)–Os(2)–C(21)	86.4(7)	Os(3)–Os(2)–C(21)	144.9(7)
Os(1)–Os(2)–N(1)	91.8(5)	Os(3)–Os(2)–N(1)	87.4(5)
C(21)–Os(2)–N(1)	92.1(9)	Os(1)–Os(2)–C(22)	176.6(6)
Os(3)–Os(2)–C(22)	118.4(7)	C(21)–Os(2)–C(22)	96.7(10)
N(1)–Os(2)–C(22)	89.7(8)	Os(1)–Os(2)–C(23)	89.3(8)
Os(3)–Os(2)–C(23)	91.4(7)	C(21)–Os(2)–C(23)	90.1(11)
N(1)–Os(2)–C(23)	177.7(10)	C(22)–Os(2)–C(23)	89.2(10)
Os(1)–Os(3)–Os(2)	58.7(1)	Os(1)–Os(3)–C(31)	176.3(9)
Os(2)–Os(3)–C(31)	117.6(9)	Os(1)–Os(3)–N(2)	90.4(6)
Os(2)–Os(3)–N(2)	87.8(5)	C(31)–Os(3)–N(2)	88.9(11)
Os(1)–Os(3)–C(32)	87.3(8)	Os(2)–Os(3)–C(32)	145.9(8)
C(31)–Os(3)–C(32)	96.4(12)	N(2)–Os(3)–C(32)	92.3(9)
Os(1)–Os(3)–C(33)	91.1(7)	Os(2)–Os(3)–C(33)	92.5(7)
C(31)–Os(3)–C(33)	89.6(12)	N(2)–Os(3)–C(33)	178.4(9)
C(32)–Os(3)–C(33)	88.4(10)	Os(1)–C(11)–O(11)	175.5(21)
Os(1)–C(12)–O(12)	175.4(21)	Os(1)–C(13)–O(13)	174.0(21)
Os(1)–C(14)–O(14)	177.3(22)	Os(2)–C(21)–O(21)	179.1(25)
Os(2)–N(1)–C(1)	175.0(16)	N(1)–C(1)–C(2)	177.4(22)
Os(2)–C(22)–O(22)	177.9(19)	Os(2)–C(23)–O(23)	173.3(21)
Os(3)–C(31)–O(31)	176.1(23)	Os(3)–N(2)–C(3)	171.2(20)
N(2)–C(3)–C(4)	177.9(24)	Os(3)–C(32)–O(32)	177.1(22)
Os(3)–C(33)–O(33)	178.5(19)	Cl(1)–Os(4)–Cl(2)	88.1(3)
Cl(1)–Os(4)–Cl(3)	89.2(1)	Cl(2)–Os(4)–Cl(3)	87.0(5)
Cl(1)–Os(4)–C(41)	87.2(27)	Cl(2)–Os(4)–C(41)	82.1(26)
Cl(3)–Os(4)–C(41)	168.6(26)	Cl(1)–Os(4)–C(42)	175.7(8)
Cl(2)–Os(4)–C(42)	88.0(8)	Cl(3)–Os(4)–C(42)	89.1(9)
C(41)–Os(4)–C(42)	93.7(28)	Cl(1)–Os(4)–C(43)	87.8(11)
Cl(2)–Os(4)–C(43)	170.0(11)	Cl(3)–Os(4)–C(43)	83.8(12)
C(41)–Os(4)–C(43)	106.8(28)	C(42)–Os(4)–C(43)	95.9(13)
O(41)–C(41)–Os(4)	145.8(90)	O(43)–C(43)–Os(4)	155.8(40)
Cl(1)–Os(4)–Cl(2)	88.1(3)	Cl(1)–Os(4)–Cl(3)	89.2(3)
Cl(2)–Os(4)–Cl(3)	87.0(5)	Cl(1)–Os(4)–C(41)	87.2(27)
Cl(2)–Os(4)–C(41)	82.1(26)	Cl(3)–Os(4)–C(41)	168.6(26)
Cl(1)–Os(4)–C(42)	175.7(8)	Cl(2)–Os(4)–C(42)	88.0(8)
Cl(3)–Os(4)–C(42)	89.1(9)	C(41)–Os(4)–C(42)	93.7(28)
Cl(1)–Os(4)–C(43)	87.8(11)	Cl(2)–Os(4)–C(43)	170.0(11)
Cl(3)–Os(4)–C(43)	83.8(12)	C(41)–Os(4)–C(43)	106.8(28)
C(42)–Os(4)–C(43)	95.9(13)		

Preparation of $[Os_3H(CO)_{10}(MeCN)_2]BF_4$.—The cluster $[Os_3(CO)_{10}(MeCN)_2]$ (42.0 mg, 0.045 mmol) was dissolved in acetonitrile (10 cm^3) and 3–4 drops of HBF_4 in diethyl ether solution were added. The reaction was instantaneous with the solution changing from dark to light yellow. The acetonitrile was removed under vacuum and the residue washed with hexane and ether. The compound was recrystallised from hot chloroform (yield 85%) (Found: C, 15.60; H, 0.95; N, 2.35. Calc. for $C_{14}H_7BF_4N_2O_{10}Os_3$: C, 15.80; H, 0.70; N, 2.45%).

Preparation of $[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$.—Into a suspension of $[Os_3(CO)_{10}(MeCN)_2]$ (200 mg, 0.21 mmol) in dry hexane at 40—50 °C, was bubbled a stream of gaseous HCl. After 30 min the yellow-brown solid had changed to yellow crystals. After removal of the solvent and recrystallisation from acetone–dichloromethane, the salt was obtained in quantitative yield (Found: C, 15.55; N, 2.10; H, 0.55. Calc. for $C_{17}H_7Cl_3N_2O_{13}Os_4$: C, 15.50; N, 2.15; N, 0.55%).

Preparation of $[Os_4H_2(CO)_{14}(MeCN)]$.—The salt $[Os_3H(CO)_{10}(MeCN)_2]BF_4$ (60 mg, 0.052 mmol) was dissolved in thf

(35 cm^3). Excess $[Os(CO)_4]^{2-}$ was added and the mixture stirred for 30 min. The reaction was followed by i.r. spectroscopy and spot t.l.c. until the i.r. bands due to the cation had disappeared. The solution was filtered through a sinter to remove the undissolved $[Os(CO)_4]^{2-}$ and stirring continued for 15 min. The solvent was removed under vacuum. The mixture was separated by t.l.c. using dichloromethane–hexane (30 : 70) as eluant. The compound with the highest R_f value was obtained in 25% yield and identified as the known compound $[Os_4H_2(CO)_{14}(MeCN)]$.

Addition of PMe_3 *to* $[Os_3(CO)_{10}(MeCN)_2]$.—Trimethylphosphine (0.05 cm^3) was added to a thf solution of $[Os_3(CO)_{10}(MeCN)_2]$. The mixture was stirred at room temperature and after 30 min a yellow-orange solution was obtained. The solvent was removed under a flow of N_2, the residue dissolved in a minimum quantity of dichloromethane, and the mixture separated by t.l.c. using light petroleum–dichloromethane (1 : 1). Two main bands were obtained, the first (80% yield) was characterised as $[Os_3(CO)_{10}(PMe_3)_2]$ (m/e^+ 1 008) and the second (10% yield) as $[Os_3(CO)_9(PMe_3)_3]$ (m/e^+ 1 056).

Preparation of $[Os_3H(CO)_{10}(PMe_3)_2][Os(CO)_3Cl_3]$.—A current of HCl gas was bubbled through a hexane solution of $[Os_3(CO)_{10}(PMe_3)_2]$ (200 mg) at room temperature. The solution turned cloudy and a light yellow precipitate was obtained by solvent decantation. The solid was dried under vacuum (yield 100%) (Found: C, 16.45; H, 1.40. Calc. for $C_{19}H_{19}Cl_3O_{13}Os_4P_2$: C, 16.50; H, 1.45%).

Reaction of $[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$ *with* HCl.—When gaseous HCl was bubbled through a freshly prepared hexane solution of $[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$ and the mixture heated to reflux for 4 h, a yellow solution was obtained. The solvent was removed under a flow of nitrogen and the residue recrystallised from dichloromethane–hexane. The complex was identified as $[Os_3H(CO)_{10}Cl]$.

Preparation of $[Os_3(NO)(CO)_{10}(MeCN)_2]BF_4$.—A mixture of $[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$ (100 mg, 0.07 mmol) and freshly sublimed $NOBF_4$ (12.2 mg, 0.10 mmol) was stirred in dry thf for 8 h at room temperature, during which time the solution changed from yellow to orange-red. The solvent was removed under a fast stream of nitrogen, and the residue recrystallised from dichloromethane to give the product (yield 60%).

Crystal Structure Determination of $[Os_3H(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$.—Suitable single crystals were obtained as orange blocks and a crystal with dimensions *ca.* 0.40 × 0.25 × 0.25 mm was sealed in a 0.5-mm Lindemann capillary.

Crystal data. $C_{17}H_7Cl_3N_2O_{13}Os_4$, $M = 1\,314.40$, monoclinic, $a = 9.825(7)$, $b = 21.751(12)$, $c = 13.715(10)$ Å, $\beta = 90.72(6)°$, $U = 2\,930.9(10)$ Å^3 (by least-squares refinement for 60 automatically-centred reflections in the range $20 < 2\theta < 25°$), space group $P2_1/n$ (alternative $P2_1/c$, no. 14), $Z = 4$, $D_c = 2.98$ g cm^{-3}, D_m not measured, $F(000) = 2\,208$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 175.85 cm^{-1}.

Data collection and processing. For details of data collection techniques see ref. 14: Stoe four-circle diffractometer, $\omega/2\theta$ scan mode with ω scan width 1.2°, scan speed 0.025—0.1° s^{-1}, graphite-monochromated Mo-K_α radiation; 5 652 reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $+h$, $+k$, $\pm l$), 5 167 unique [merging $R = 0.042$ after absorption correction (max., min. transmission factors = 0.071, 0.018], giving 5 167 with $F > 3\sigma(F)$. No significant crystal deterioration occurred during data collection.

Table 4. Atom co-ordinates (× 10^4) for $[Os_3(\mu\text{-}H)(CO)_{10}(MeCN)_2][Os(CO)_3Cl_3]$

Atom	*X/a*	*Y/b*	*Z/c*
Os(1)	1 968(1)	1 921(1)	2 127(1)
Os(2)	4 133(1)	1 791(1)	3 553(1)
Os(3)	1 223(1)	1 938(1)	4 152(1)
C(11)	1 885(22)	1 022(10)	2 117(18)
O(11)	1 866(16)	503(7)	2 050(13)
C(12)	3 032(27)	1 920(13)	1 006(22)
O(12)	3 641(21)	1 886(10)	289(17)
C(13)	200(23)	2 009(11)	1 563(18)
O(13)	−818(17)	2 084(8)	1 152(13)
C(14)	2 091(22)	2 811(10)	2 239(18)
O(14)	2 163(17)	3 335(8)	2 266(14)
C(21)	5 342(25)	1 705(12)	2 455(19)
O(21)	6 026(18)	1 655(8)	1 854(14)
N(1)	3 835(16)	850(8)	3 637(13)
C(2)	3 640(23)	−346(11)	3 792(18)
C(1)	3 772(21)	326(10)	3 691(17)
C(22)	5 462(21)	1 736(10)	4 520(17)
O(22)	6 345(17)	1 695(8)	5 119(13)
C(23)	4 374(23)	2 612(11)	3 531(19)
O(23)	4 660(16)	3 145(8)	3 559(12)
C(31)	855(30)	1 952(14)	5 504(23)
O(31)	558(22)	1 947(10)	6 319(17)
N(2)	1 563(18)	2 878(9)	4 209(15)
C(3)	1 743(24)	3 388(11)	4 368(19)
C(4)	1 931(26)	4 071(12)	4 599(21)
C(32)	−518(23)	2 043(10)	3 741(18)
O(32)	−1 681(18)	2 133(8)	3 497(14)
C(33)	921(21)	1 088(10)	4 138(17)
O(33)	716(16)	564(7)	4 147(13)
Os(4)	7 294(1)	4 653(1)	2 749(1)
Cl(1)	5 503(7)	−8(4)	1 666(6)
Cl(2)	8 496(9)	667(4)	2 028(8)
Cl(3)	7 092(9)	−43(8)	3 857(7)
C(41)	8 242(95)	−423(42)	845(69)
O(41)	8 465(46)	−684(21)	358(33)
C(42)	9 445(27)	−549(12)	2 725(21)
O(42)	479(21)	−698(10)	3 097(17)
C(43)	6 842(36)	−1 132(17)	2 614(28)
O(43)	6 599(36)	−1 551(16)	2 535(28)

Structure analysis and refinement. Centrosymmetric direct methods (Os atoms) were used followed by Fourier-difference techniques. Refinement was by blocked-cascade least squares with Os and Cl anisotropic. The weighting scheme $w = 1/\sigma^2F$ gave satisfactory agreement analyses. Final R and R' values are 0.070 and 0.055. Complex neutral-atom scattering factors were employed,[15] and all computations were performed on the University of Cambridge IBM 3081 computer using a modified version of SHELX.[16] The final atomic fractional co-ordinates are listed in Table 4.

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