Synthesis, Reactivity, and *X*-Ray Crystal Structure of the Cationic Cluster Complex $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ †

Brian F. G. Johnson, Jack Lewis,* William J. H. Nelson, José Puga, Paul R. Raithby, and Kenton H. Whitmire
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The anion $[Os_4H_3(CO)_{12}]^-$ reacts with NOX (X = BF_4 or PF_6) in MeCN to give the salt $[Os_4H_3(CO)_{12}(NCMe)_2]X$ in moderate yield. The fluoroborate salt crystallises in space group $P2_1/c$ with a = 17.555(7), b = 9.252(4), c = 17.767(8) Å, β = 108.93(3)°, and Z = 4. The structure was solved by a combination of direct methods and Fourier-difference techniques, and refined to a converged R = 0.049 for 3 454 diffractometer data. The four Os atoms in the cation adopt a 'butterfly' arrangement with 4.338(2) Å between the two 'wingtip' Os atoms. Each of these two metal atoms is co-ordinated to three carbonyl ligands and an axial acetonitrile ligand oriented away from the centre of the cluster. Each of the two 'hinge' Os atoms has three terminal carbonyl groups associated with it. The $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ cation reacts with X^- (X = Cl or I) to give the neutral complex $[Os_4H_3(CO)_{12}X]$, and with NO_2^- to give the cluster anion $[Os_4H(CO)_{12}(NCMe)_2]^-$. Protonation of this anion regenerates the title cation. The anion reacts with $Au(PPh_3)Cl$ to produce the neutral mixed-metal cluster $[Os_4H(CO)_{12}(NCMe)_2\{Au(PPh_3)\}]$, a derivative of the unobserved neutral molecule $[Os_4H_2(CO)_{12}(NCMe)_2]$.

The nitrosyl cation, NO^+, can react with mononuclear metal carbonyl derivatives in either of two ways, to give the corresponding nitrosyl derivative or an oxidation product.[1] Similar behaviour has been observed in the reaction of NO^+ with metal carbonyl clusters. For example, the anions $[M_3H(CO)_{11}]^-$ (M = Ru or Os) react with NO^+ to produce the nitrosyl derivatives $[M_3H(CO)_{10}(NO)]$,[2] but with $[Os_4H_4(CO)_{12}]$ the cationic complex $[Os_4H_4(CO)_{12}(OH)]^+$ is obtained.[3] In the latter case the nitrosyl cation is acting as an oxidising agent. A mechanism involving the formation of a nitrosyl intermediate has been proposed to account for the oxidation of some mononuclear metal carbonyl complexes with NO^+.[1] However, no evidence to support the presence of a nitrosyl intermediate has been found to account for the oxidation of $[Os_4H_4(CO)_{12}]$ with NO^+ in acetonitrile. In this paper we continue our studies of the oxidative properties of NO^+ in its reaction with $[Os_4H_3(CO)_{12}]^-$ in MeCN and report some of the chemistry of the major product.[4]

Results and Discussion

The reaction of the anion $[Os_4H_3(CO)_{12}]^-$ with NOX (X = BF_4 or PF_6) in acetonitrile does not give a nitrosyl-containing product, but leads to the cationic cluster species $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1) according to equation (i). The

$$[Os_4H_3(CO)_{12}]^- + 2NO^+ \xrightarrow{MeCN} [Os_4H_3(CO)_{12}(NCMe)_2]^+ + 2NO\uparrow \quad (i)$$

cation was isolated as its BF_4^- salt, and was obtained as yellow, air-stable crystals from dichloromethane. The i.r. spectrum of the cluster cation, in CH_2Cl_2, exhibits carbonyl absorptions at 2 115w, 2 093ms, 2 072s, 2 019s, and 2 004 (sh) cm^{-1}, all of which may be assigned to terminal carbonyl groups. The ^1H n.m.r. spectrum, at 30 °C in CD_2Cl_2, showed peaks at δ 2.73, −17.27, and −18.22 with intensity ratios 6 : 1 : 2, respectively. The signal at lowest field was assigned to two equivalent acetonitrile ligands, and the other peaks to the three bridging hydrides. The lability of the acetonitrile ligands has been demonstrated by the addition of CD_3CN, which causes a decrease in intensity of the signal at δ 2.73 and the appearance of a new peak at δ 1.96 due to unco-ordinated acetonitrile. After *ca.* 1 h the exchange is complete: only the signal at δ 1.96 and the peaks in the hydrido-region are observed.

To date only four cationic cluster species have been structurally characterised, and there are no examples of cationic carbonyl clusters containing more than four metal atoms that have been investigated by *X*-ray diffraction. Their formation may be disfavoured because the presence of the positive charge requires additional ligands to maintain the electronic balance. This results in increased steric congestion, and since the ligand-to-metal ratio drops as the size of cluster increases the formation of positive species becomes less probable. Alternatively, the positive charge affects the strength of the metal–metal bonds within the cluster framework by reducing the orbital overlap between the metal centres *via* the orbital contraction resulting from the positive charge. In the Os_4 cationic clusters that have been isolated,[3] the metal geometry is more open than that of the idealised regular polyhedron. For example, the cation $[Os_4H_4(CO)_{12}(OH)]^+$ has an 'open-butterfly' metal geometry[3] rather than the 'closed' tetrahedral metal framework observed in $[Os_4H_4(CO)_{12}]$.[5] An 'open' structure will more readily accommodate additional ligands.

In order to determine the metal arrangement and the ligand distribution in the cation $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1) a single-crystal *X*-ray analysis was undertaken. The unit-cell contents, showing the relative positions of the cations and anions, are presented in Figure 1. The shortest anion–cation contact is 2.102 Å, between F(1) and the methyl hydrogen atom, H(4c), related by the symmetry transformation $2 - x$, $-y$, $1 - z$. This short distance, coupled with the fact that the BF_4^- group shows only a slight tendency towards disorder [relatively low F temperature factors, particularly for F(1)], suggests a weak anion–cation interaction.

The molecular geometry of the cation is illustrated in Figure 2, which includes the atom numbering scheme. The final bond

† 1,3-Bis(acetonitrile)trihydridotetrakis[tricarbonylosmium(I)]-(5 *Os–Os*) tetrafluoroborate.

Supplementary data available (No. SUP 23579, 27 pp.): structure factors, thermal parameters, hydrogen co-ordinates, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

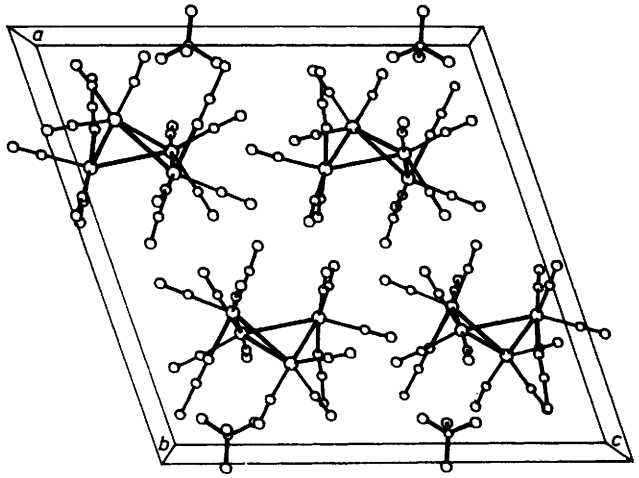


Figure 1. The unit-cell contents for $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ viewed down the crystallographic *b* axis

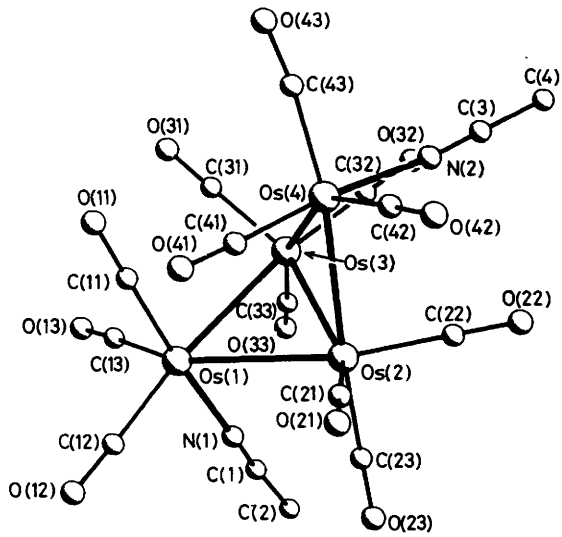


Figure 2. The molecular geometry of the cation $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1); methyl hydrogen atoms have been omitted for clarity

lengths and interbond angles for the structure are listed in Tables 1 and 2, respectively. The two Os_3 triangles share the common Os(2)–Os(3) 'hinge' bond, and the torsion angle between the Os(1)Os(2)Os(3) and the Os(2)Os(3)Os(4) planes is 112.2(1)°. The four metal atoms in (1) adopt the *arachno*-octahedral structure, consistent with Wade theory[6] for a cluster having seven skeletal electron pairs (sixty-two valence electrons) and four skeletal atoms. However this configuration, with no ligand bridging the two 'wingtip' atoms [Os(1) and Os(4)], has not been observed previously in tetra-osmium systems. In the related cationic cluster $[Os_4H_4(CO)_{12}(OH)]^+$, where the 'butterfly' is supported by the OH group, the torsion angle between the two Os_3 triangles is significantly narrower, at 97.7°. Carty *et al.*[7] have discussed large differences in torsion angle in a number of Ru_4 'butterfly' systems in terms of metal–metal bond lengths and the number of electrons in the cluster. However, the difference of 14.5° in torsion angle between $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1) and $[Os_4H_4(CO)_{12}(OH)]^+$ is somewhat smaller than observed in the Ru complexes under discussion, and since both these cations are

Table 1. Bond lengths (Å)

Os(1)–Os(2)	3.130(2)	Os(1)–Os(3)	2.828(2)
Os(1)–N(1)	2.100(16)	Os(1)–C(11)	1.848(19)
Os(1)–C(12)	1.931(20)	Os(1)–C(13)	1.924(25)
Os(2)–Os(3)	2.937(2)	Os(2)–Os(4)	2.847(2)
Os(2)–C(21)	1.893(24)	Os(2)–C(22)	1.882(19)
Os(2)–C(23)	1.928(18)	Os(3)–Os(4)	3.145(2)
Os(3)–C(31)	1.885(20)	Os(3)–C(32)	1.901(16)
Os(3)–C(33)	1.888(21)	Os(4)–N(2)	2.130(13)
Os(4)–C(41)	1.899(16)	Os(4)–C(42)	1.886(27)
Os(4)–C(43)	1.923(21)	N(1)–C(1)	1.150(26)
C(1)–C(2)	1.432(30)	N(2)–C(3)	1.114(22)
C(3)–C(4)	1.432(29)	C(11)–Os(1)	1.848(19)
C(12)–O(12)	1.157(26)	C(13)–O(13)	1.096(33)
C(21)–O(21)	1.138(30)	C(22)–O(22)	1.144(23)
C(31)–O(31)	1.125(25)	C(32)–O(32)	1.148(21)
C(33)–O(33)	1.137(27)	C(41)–O(41)	1.125(20)
C(42)–O(42)	1.174(34)	C(43)–O(43)	1.152(26)
B(1)–F(1)	1.366(32)	B(1)–F(2)	1.294(43)
B(1)–F(3)	1.367(45)	B(1)–F(4)	1.381(42)

Table 2. Bond angles (°)

Os(2)–Os(1)–Os(3)	58.8(1)	Os(2)–Os(1)–N(1)	81.8(4)
Os(3)–Os(1)–N(1)	89.7(4)	Os(2)–Os(1)–C(11)	101.2(6)
Os(3)–Os(1)–C(11)	83.3(5)	N(1)–Os(1)–C(11)	169.4(8)
Os(2)–Os(1)–C(12)	110.8(7)	Os(3)–Os(1)–C(12)	169.5(7)
N(1)–Os(1)–C(12)	89.9(7)	C(11)–Os(1)–C(12)	98.5(8)
Os(2)–Os(1)–C(13)	151.0(6)	Os(3)–Os(1)–C(13)	94.3(6)
N(1)–Os(1)–C(13)	87.8(8)	C(11)–Os(1)–C(13)	84.8(9)
C(12)–Os(1)–C(13)	96.1(9)	Os(1)–Os(2)–Os(3)	55.5(1)
Os(1)–Os(2)–Os(4)	93.0(1)	Os(3)–Os(2)–Os(4)	65.9(1)
Os(1)–Os(2)–C(21)	109.4(6)	Os(3)–Os(2)–C(21)	147.5(6)
Os(4)–Os(2)–C(21)	88.6(7)	Os(1)–Os(2)–C(22)	160.4(7)
Os(3)–Os(2)–C(22)	106.0(7)	Os(4)–Os(2)–C(22)	83.3(6)
C(21)–Os(2)–C(22)	89.8(9)	Os(1)–Os(2)–C(23)	88.7(5)
Os(3)–Os(2)–C(23)	112.1(6)	Os(4)–Os(2)–C(23)	175.7(5)
C(21)–Os(2)–C(23)	94.6(9)	C(22)–Os(2)–C(23)	93.8(8)
Os(1)–Os(3)–Os(2)	65.7(1)	Os(1)–Os(3)–Os(4)	93.0(1)
Os(2)–Os(3)–Os(4)	55.7(1)	Os(1)–Os(3)–C(31)	92.2(5)
Os(2)–Os(3)–C(31)	148.8(6)	Os(4)–Os(3)–C(31)	107.0(6)
Os(1)–Os(3)–C(32)	171.0(5)	Os(2)–Os(3)–C(32)	110.2(6)
Os(4)–Os(3)–C(32)	90.8(6)	C(31)–Os(3)–C(32)	94.5(8)
Os(1)–Os(3)–C(33)	84.9(5)	Os(2)–Os(3)–C(33)	107.4(6)
Os(4)–Os(3)–C(33)	161.7(6)	C(31)–Os(3)–C(33)	91.3(9)
C(32)–Os(3)–C(33)	88.9(8)	Os(2)–Os(4)–Os(3)	58.4(1)
Os(2)–Os(4)–N(2)	94.5(5)	Os(3)–Os(4)–N(2)	81.0(5)
Os(2)–Os(4)–C(41)	81.6(6)	Os(3)–Os(4)–C(41)	102.0(6)
N(2)–Os(4)–C(41)	172.7(7)	Os(2)–Os(4)–C(42)	95.5(7)
Os(3)–Os(4)–C(42)	150.2(7)	N(2)–Os(4)–C(42)	87.7(7)
C(41)–Os(4)–C(42)	86.5(9)	Os(2)–Os(4)–C(43)	169.2(6)
Os(3)–Os(4)–C(43)	113.5(7)	N(2)–Os(4)–C(43)	90.9(7)
C(41)–Os(4)–C(43)	93.9(8)	C(42)–Os(4)–C(43)	93.9(10)
Os(1)–N(1)–C(1)	169.4(18)	N(1)–C(1)–C(2)	174.9(24)
Os(4)–N(2)–C(3)	174.2(17)	N(2)–C(3)–C(4)	179.5(25)
Os(1)–C(11)–O(11)	179.1(18)	Os(1)–C(12)–O(12)	176.1(21)
Os(1)–C(13)–O(13)	176.9(20)	Os(2)–C(21)–O(21)	178.1(19)
Os(2)–C(22)–O(22)	175.9(19)	Os(3)–C(31)–O(31)	176.8(19)
Os(3)–C(32)–O(32)	174.4(18)	Os(3)–C(33)–O(33)	175.1(18)
Os(4)–C(41)–O(41)	175.6(19)	Os(4)–C(42)–O(42)	177.9(21)
Os(4)–C(43)–O(43)	173.2(17)	F(1)–B(1)–F(2)	111.5(30)
F(1)–B(1)–F(3)	111.0(24)	F(2)–B(1)–F(3)	107.6(28)
F(1)–B(1)–F(4)	112.1(26)	F(2)–B(1)–F(4)	107.3(27)
F(3)–B(1)–F(4)	107.0(29)		

sixty-two electron systems and the differences in Os–Os bond lengths are due to the different numbers of hydride ligands in the two clusters, it is probable that steric requirements are important in determining the geometries. In structure (1) two carbonyls, one on each 'wingtip' Os atom, point towards

each other and lie over the centre of the cluster. To reduce the interaction between them the 'butterfly' opens up and the ligands on the 'wingtip' metal atoms are staggered with respect to each other. In $[Os_4H_4(CO)_{12}(OH)]^+$ there is only one ligand over the centre of the cluster; the bridging OH group and the carbonyls on the two 'wingtip' atoms are eclipsed.[3]

The five metal–metal bonds in structure (1) may be split into three groups in terms of bond length. The Os(1)–Os(2) and Os(3)–Os(4) bonds are the longest [mean 3.138(7) Å]. The Os(2)–Os(3) 'hinge' bond is intermediate in length, at 2.937(2) Å, and the Os(1)–Os(3) and Os(2)–Os(4) bonds are shortest [mean 2.838(9) Å]. The same trends have been observed in the cluster $[Os_4H_3(CO)_{12}I]$, where the lengths of the three types of bond are 3.055(1), 2.927(2), and 2.877(1) Å, respectively.[8] The arrangement of the equivalent bonds in these two clusters is such that they are related by a two-fold axis (crystallographic in the case of the neutral complex) which passes through the midpoint of the Os–Os 'hinge' bond. For $[Os_4H_3(CO)_{12}I]$ a neutron diffraction study [8] has shown that the hydride ligands bridge the two Os–Os bonds of length 3.055(1) Å, and the 'hinge' bond of length 2.927(2) Å. The ligand arrangement in (1) is consistent with the hydrides bridging the same bonds; the carbonyl groups *cis* to the Os(1)–Os(2), Os(2)–Os(3), and Os(3)–Os(4) bonds bend away from them with an average *cis* Os–Os–C angle of 109° owing to the steric influence of the hydrides. This hydride arrangement is in agreement with the ^1H n.m.r. data: hydrides bridging the Os(1)–Os(2) and Os(2)–Os(4) bonds are equivalent (C_2 rotation). The differences between the similar types of bridged and unbridged Os–Os bonds in the two clusters may reflect the presence of the positive charge in $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1). The metal–metal distances in (1) are similar to the average hydride bridged Os(hinge)–Os(wingtip) distance of 3.038(5) Å, and the unbridged Os–Os 'hinge' bond length of 2.831(2) Å in $[Os_4H_4(CO)_{12}(OH)]^+$.[3]

None of the twelve carbonyl groups deviates significantly from linearity and the average Os–C–O angle is 176(3)°. The average C–O bond length is 1.15(3) Å. Ten of the carbonyl groups are approximately *trans* to Os–Os bonds and have an average Os–C distance of 1.90(2) Å. The two remaining carbonyls are *trans* to the two acetonitrile ligands and exhibit a somewhat shorter average Os–C distance of 1.87(2) Å. The average Os–N acetonitrile distance of 2.12(2) Å, on the other hand, is relatively long. This is consistent with the *trans* effect of the carbonyl group, which is a strong π-acceptor ligand. There is little competition between the carbonyl carbon and the acetonitrile nitrogen *trans* to it for back donation of electron density from the same metal orbital. Thus these two shorter Os–C carbonyl bonds exhibit strong multiple-bond character, whereas the Os–N(acetonitrile) bond is essentially single. Similar trends have been observed in the complex $[Ru_5C(CO)_{15}(NCMe)]$,[9] where the acetonitrile is co-ordinated to a Ru atom, which adopts a geometry similar to that of the 'wingtip' Os atoms in (1). In both these complexes the co-ordination of the acetonitrile may be considered as adduct formation with the solvent. The two terminal acetonitrile ligands, co-ordinated to the 'wingtip' metal atoms, show only slight deviations from linearity, with average Os–N–C and N–C–C angles of 172(3) and 177(3)°, respectively. The average N–C distance of 1.13(2) Å is short, and indicative of triple-bond character. The C–C(methyl) bonds, with an average length of 1.43(3) Å, must be single σ bonds; their lengths would be expected to be greater if librational corrections were applied. The dimensions of the BF_4^- anion are in good agreement with the expected values.

The change in the ^1H n.m.r. spectrum of $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1) upon addition of CD_3CN at 30 °C clearly demonstrates the lability of the co-ordinated acetonitriles towards ligand substitution. The mechanism for the exchange of MeCN by CD_3CN has not been established, but it probably involves an initial dissociation. The cation (1) could, in principle, react in a similar fashion to $[Os_3(CO)_{10}(NCMe)_2]$, which is of considerable importance as a starting material in substitution reactions of triosmium clusters.[10,11] However, the loss of one or more protons could provide an alternative reaction path, depending on experimental conditions. Both of these possible processes have been observed. Thus the cation (1) reacts with X^- (X = Cl or I) according to equation (ii), to give the known neutral halogeno-derivative (2); [12] this reacts further with an excess of X^- to give the anion (3).

$$[Os_4H_3(CO)_{12}(NCMe)_2]^+ + X^- \xrightarrow{MeCN}$$
(1)

$$[Os_4H_3(CO)_{12}X] \underset{H^+}{\overset{X^-}{\rightleftharpoons}} [Os_4H_2(CO)_{12}X]^- \quad \text{(ii)}$$
(2) (3)

X = Cl or I

Table 3. Infrared spectral data of Os_4 complexes in dichloromethane solution

Complex	ν(C–O)/cm^{-1}
$[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$	2 115w, 2 093s, 2 072s, 2 019s, 2 004 (sh)
$[Os_4H_3(CO)_{12}I]$	2 109w, 2 084s, 2 066s, 2 018s, 2 008 (sh)
$[Os_4H_3(CO)_{12}Cl]$	2 088s, 2 069s, 2 020s, 2 010 (sh)
$[Os_4H_2(CO)_{12}I]^-$	2 081m, 2 049s, 2 020s, 1 997 (sh)
$[Os_4H_2(CO)_{12}Cl]^-$	2 050s, 2 022s, 2 002s, 1 976 (sh)
$[Os_4H(CO)_{12}(NCMe)_2]^-$	2 045s, 2 016s, 1 995s, 1 971 (sh), 1 957 (sh)
$[Os_4H(CO)_{12}(NCMe)_2\{Au(PPh_3)\}]$	2 097m, 2 068s, 2 031s, 2 005m, 1 990m, 1 970 (sh), 1 954 (sh)

The neutral species (2) were identified on the basis of their i.r. and mass spectra (Table 3), and by comparison with the data for the iodine complex reported previously.[12] Protonation of the anions (3) regenerates the neutral molecules. Although $[Os_4H_3(CO)_{12}I]$ has been obtained as the product of the reaction of $[Os_4H_3(CO)_{12}]^-$ with I_2,[12] the cation (1) may be a more suitable precursor for obtaining a wide range of such bridged 'butterfly' clusters by reaction with the appropriate nucleophile.

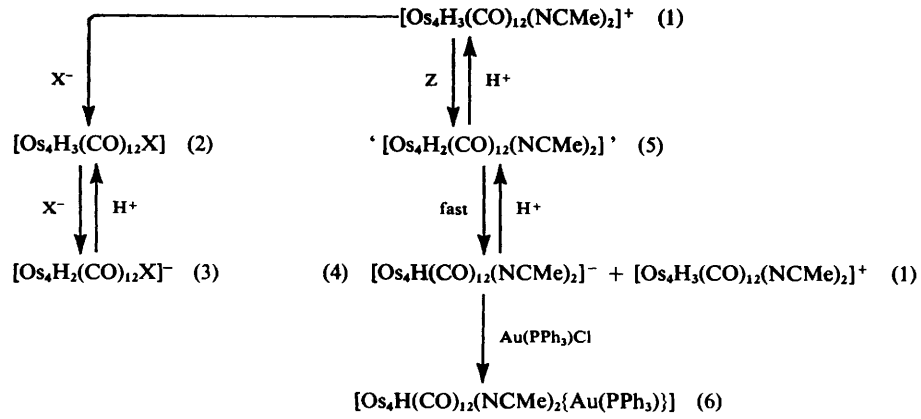
The reaction of the complex (1) with NO_2^- was therefore undertaken in an attempt to prepare a cluster containing a bridging NO_2 ligand. However, the reaction was found to proceed according to equation (iii), the alternative deproton-

$$[Os_4H_3(CO)_{12}(NCMe)_2][BF_4] + [N(PPh_3)_2][NO_2]$$
(1)

$$\underset{(MeCN)}{\overset{H^+}{\rightleftharpoons}}$$

$$[N(PPh_3)_2][Os_4H(CO)_{12}(NCMe)_2] + HNO_2 + HBF_4 \quad \text{(iii)}$$
(4)

ation pathway. When reaction (iii) was carried out using equimolecular quantities of (1) and $[N(PPh_3)_2][NO_2]$, it did not



Scheme. Reactivity of the cluster cation $[Os_4H_3(CO)_{12}(NCMe)_2]^+$. X = Cl or I; Z = NO_2^-, OH^-, or ' proton sponge '

proceed to completion, but when a 1 : 2 ratio of the starting materials (respectively) was used only the bands attributable to (4) were observed in the i.r. spectrum (Table 3). Formation of (4) was also observed when (1) was treated with tetrabutylammonium hydroxide (dissolved in toluene–methanol) with acetonitrile as solvent. The product of reaction of (1) with ' proton sponge ' [1,8-bis(dimethylamino)naphthalene] and equimolecular amounts of reagents also showed the presence of only (1) and (4) in the i.r. spectrum. It is probable that the species ' $[Os_4H_2(CO)_{12}(NCME)_2]$ ' (5) is formed but is rapidly decomposed according to the equilibrium in equation (iv).

$$2\ \underset{(5)}{'\ [Os_4H_2(CO)_{12}(NCMe)_2]\ '} \rightleftharpoons \underset{(1)}{[Os_4H_3(CO)_{12}(NCMe)_2]^+} + \underset{(4)}{[Os_4H(CO)_{12}(NCMe)_2]^-} \quad \text{(iv)}$$

Addition of an excess of ' proton sponge ' gives the anionic species as the main product. The rapid decomposition of the neutral complex (5) makes its characterisation difficult. However, the reaction of the anionic complex (4) with triphenylphosphinegold chloride in the presence of thallium hexafluorophosphate, with acetonitrile as solvent, yields the neutral derivative $[Os_4H(CO)_{12}(NCMe)_2\{Au(PPh_3)\}]$ (6), characterised by i.r. (Table 3) and ^1H n.m.r. spectroscopy. The ^1H n.m.r. spectrum showed a multiplet at δ 7.53 assigned to the phenyl rings, a singlet at δ 2.62 attributed to two equivalent acetonitrile ligands, and a singlet at δ −18.97 assigned to a bridging hydride. This complex also probably displays an ' unsupported-butterfly ' Os_4 geometry with the two acetonitrile ligands bonded to the ' wingtip ' Os atoms. The reactions of (1) are summarised in the Scheme.

These studies suggest that the cluster cation $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ (1) is potentially a useful reagent which may undergo substitution (*via* loss of NCMe ligands) or deprotonation reactions to yield a range of new cluster compounds. It may prove possible to produce larger cluster complexes by treating the cation (1) with cluster anions, and work in this area is proceeding. It is apparent that the products depend on the relative basicity and nucleophilicity of the reagents used; with more basic reagents deprotonation occurs.

Experimental

All reactions were carried out under nitrogen, although the products were air-stable in the solid state at 25 °C. Acetonitrile and dichloromethane were distilled over calcium hydride and deoxygenated before use. Tetrabutylammonium hydroxide (in toluene–methanol) was purchased from B.D.H. Laboratory Reagents, and bis(triphenylphosphoranylidene)ammonium chloride from Alfa Products. Bis(triphenylphosphoranylidene)ammonium nitrite was prepared according to the method of Martinsen and Songstad.[13] Nitrosyl tetrafluoroborate was sublimed before use, and ' proton sponge ' [1,8-bis(dimethylamino)naphthalene] was recrystallised before use; both compounds were purchased from Aldrich Chemical Company. 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 spectrometer.

Preparation of $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (1).—The salt $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ (780 mg, 0.47 mmol) was dissolved in acetonitrile (100 cm^3), and $NOBF_4$ (165 mg, 1.41 mmol) was added. The solution was stirred for *ca.* 1 h, filtered through Kieselguhr, and evaporated to dryness under vacuum. Yellow crystals (200 mg, 33%) were obtained by crystallisation from dichloromethane at 0 °C (Found: C, 15.3; H, 0.8; N, 2.25. $C_{16}H_9BF_4N_2O_{12}Os_4$ requires C, 15.15; H, 0.7; N, 2.2%).

Preparation of $[Os_4H_3(CO)_{12}Cl]$ (2; X = Cl).—The salt $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (20 mg, 0.017 mmol) was dissolved in acetonitrile (10 cm^3) and $[N(PPh_3)_2]Cl$ (9.8 mg, 0.017 mmol) was added. The solution was stirred for *ca.* 5 min, during which time the originally yellow solution became orange. The yield of $[Os_4H_3(CO)_{12}Cl]$ is quantitative. Addition of an excess of $[N(PPh_3)_2]Cl$ yielded the anionic derivative $[Os_4H_2(CO)_{12}Cl]^-$, protonation of which in acetonitrile regenerates the neutral species.

Preparation of $[Os_4H_3(CO)_{12}I]$ (2; X = I).—A procedure similar to that used for the preparation of the chlorine analogue gave the iodine derivative in quantitative yield. However, the reaction time was much longer: the formation of the anionic species required *ca.* 72 h stirring at 25 °C.

Preparation of $[N(PPh_3)_2][Os_4H(CO)_{12}(NCMe)_2]$ (4).—The salt $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (20 mg, 0.017 mmol) was dissolved in acetonitrile (20 cm^3), and ' proton sponge ' [1,8-bis(dimethylamino)naphthalene] (9.1 mg, 0.46 mmol) was added. The solution was stirred for *ca.* 24 h while the originally yellow solution became orange in colour. Protonation with sulphuric acid regenerated the cationic species.

A similar procedure using either tetrabutylammonium

Table 4. Atomic co-ordinates ($\times 10^4$)

Atom	X/a	Y/b	Z/c
Os(1)	6 779(1)	−1 284(1)	646(1)
Os(2)	7 149(1)	−1 182(1)	2 491(1)
Os(3)	7 834(1)	809(1)	1 594(1)
Os(4)	6 601(1)	1 722(1)	2 455(1)
N(1)	7 715(10)	−2 811(18)	968(9)
C(1)	8 265(11)	−3 546(22)	1 056(12)
C(2)	8 965(12)	−4 447(27)	1 239(19)
N(2)	7 682(9)	2 480(19)	3 314(8)
C(3)	8 224(12)	2 989(26)	3 744(10)
C(4)	8 926(15)	3 632(32)	4 297(15)
C(11)	6 096(11)	279(22)	324(11)
O(11)	5 660(8)	1 304(15)	113(8)
C(12)	6 019(12)	−2 802(23)	175(12)
O(12)	5 529(10)	−3 660(21)	−104(12)
C(13)	7 071(12)	−884(23)	−288(13)
O(13)	7 255(11)	−711(24)	−814(11)
C(21)	6 228(12)	−1 786(24)	2 739(12)
O(21)	5 679(9)	−2 188(19)	2 883(11)
C(22)	7 677(11)	−773(22)	3 573(12)
O(22)	7 955(10)	−536(18)	4 238(8)
C(23)	7 600(10)	−3 096(20)	2 556(10)
O(23)	7 812(8)	5 745(17)	2 634(10)
C(31)	7 674(11)	2 065(22)	721(11)
O(31)	7 546(9)	2 833(18)	204(9)
C(32)	8 650(10)	1 965(20)	2 305(10)
O(32)	9 185(8)	2 615(20)	2 706(9)
C(33)	8 644(11)	−205(22)	1 326(11)
O(33)	9 134(9)	−734(17)	1 131(10)
C(41)	5 630(11)	876(20)	1 792(11)
O(41)	5 028(7)	437(17)	1 418(9)
C(42)	6 175(13)	1 498(25)	3 296(14)
O(42)	5 914(10)	1 312(22)	3 819(10)
C(43)	6 213(12)	3 670(23)	2 224(12)
O(43)	5 940(9)	4 788(18)	2 010(12)
B(1)	9 664(19)	−2 275(39)	3 631(20)
F(1)	10 476(7)	−2 483(16)	3 943(8)
F(2)	9 374(15)	−2 847(31)	2 931(17)
F(3)	9 272(10)	−2 885(21)	4 103(11)
F(4)	9 462(12)	−827(24)	3 558(13)

hydroxide (dissolved in toluene–methanol) or $[N(PPh_3)_2][NO_2]$ as the deprotonating agent also gives the $[Os_4H(CO)_{12}(NCMe)_2]^-$ anion.

Preparation of $[Os_4H(CO)_{12}(NCMe)_2\{Au(PPh_3)\}]$ (6).—The anion $[Os_4H(CO)_{12}(NCMe)_2]^-$ was prepared *in situ* by the reaction of $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ with $[N(PPh_3)_2][NO_2]$ in acetonitrile. Addition of triphenylphosphinegold chloride in the presence of thallium hexafluorophosphate produced a precipitate of thallium chloride and the originally orange-red solution became red-green in colour. The solution was stirred for *ca.* 1 h, filtered through Kieselguhr, and evaporated to dryness. Thin-layer chromatography using dichloromethane as eluant gave a main green band, which was extracted with the same solvent. Crystallisation from dichloromethane–hexane produced dark green crystals of $[Os_4H(CO)_{12}(NCMe)_2\{Au(PPh_3)\}]$, characterised by i.r. and ^1H n.m.r. spectroscopy.

Molecular Structure Determination.—A single, yellow crystal with dimensions *ca.* 0.35 × 0.27 × 0.23 mm was mounted on a glass fibre with epoxy-resin adhesive, and the unit-cell dimensions and space group were determined *via* Weissenberg (Cu) *X*-ray photography.

The crystal was transferred to a Syntex $P2_1$ four-circle diffractometer, and accurate cell dimensions were obtained by centering 15 strong reflections ($20 < 2\theta < 25°$). 4 049 Intensities were measured in the range $3.0 < 2\theta < 55.0°$, using graphite-monochromated Mo-K_α radiation ($\lambda_{\alpha1} = 0.709\,26$, $\lambda_{\alpha2} = 0.713\,54$ Å) and a 96-step ω–2θ scan procedure; peaks were scanned from 1.0° below $K_{\alpha1}$ to 1.0° above $K_{\alpha2}$ at rates between 2.5 and 29.3° min^{-1}, dependent on an initial 2-s peak count; reflections with intensities ≤ 5 counts s^{-1} were not measured. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

The data were profile-fitted according to the method of Clegg.[14] A semi-empirical absorption correction based on a pseudo-ellipsoidal model and 433 azimuthal scan data from 14 independent reflections was applied. Transmission factors ranged from 0.435 to 0.976 for the full data set. Lorentz polarisation corrections were also applied and equivalent reflections were averaged to give 3 454 unique observed data [$F > 3\sigma(F)$].

Crystal data. $C_{16}H_9BF_4N_2O_{12}Os_4$, $M = 1\,268.86$, monoclinic, $a = 17.555(7)$, $b = 9.252(4)$, $c = 17.767(8)$ Å, $\beta = 108.93(3)°$, $U = 2\,729.6$ Å^3, D_m not measured, $Z = 4$, $D_c = 3.087$ g cm^{-3}, $F(000) = 2\,240$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 186.3 cm^{-1}, space group $P2_1/c$ from systematic absences.

The four osmium-atom positions were located by multi-solution Σ_2 sign expansion. These atoms were assigned anisotropic thermal parameters, and subjected to three cycles of least-squares refinement. The refined parameters for these atoms were used to calculate a difference electron-density synthesis from which all the non-hydrogen atoms were located. The methyl groups were refined as rigid bodies with the hydrogen atoms placed in idealised positions (C–H 1.08 Å; H–C–H 109.5°) and constrained to 'ride' on the relevant C atom; the H atoms were assigned a common isotropic temperature factor. The structure was refined by blocked-cascade least-squares methods with anisotropic thermal parameters assigned to the Os, O, N, and acetonitrile C atoms, and isotropic thermal parameters to the B, F, and carbonyl C atoms. In the final cycles of refinement a weighting scheme of the form $w = [\sigma^2(F) + 0.0016|F|^2]^{-1}$ was introduced, since this reduced the dependence of $\omega\Delta^2$ on F_o and $\sin\theta$. The final converged residuals were $R = 0.049$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0.051$, and a difference map calculated at this stage showed ripples of *ca.* 2 e Å^{-3} close to the Os atom positions but no other regions of significant electron density. The hydride ligands were not located.

Complex neutral-atom scattering factors were employed throughout.[15] All computations were performed on the University of Cambridge IBM 370/165 computer, using programs written by Professor G. M. Sheldrick.[16] The atomic fractional co-ordinates for the non-hydrogen atoms are listed in Table 4.

Acknowledgements

We thank the S.E.R.C., I.C.I. (W. J. H. N.), and N.A.T.O. (K. H. W.) for financial support, and we are grateful to Consejo Nacional de Investigaciones Cientificas y Tecnologica for a grant (to J. P.).

References

1 P. K. Ashford, P. K. Baker, N. G. Connelly, R. L. Kelly, and V. A. Woodley, *J. Chem. Soc., Dalton Trans.*, 1982, 477.
2 B. F. G. Johnson, P. R. Raithby, and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1980, 99.
3 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1980, 716.
4 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, J. Puga, P. R. Raithby, M. Schröder, and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1982, 610.

5 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1981, **37**, 1728.
6 K. Wade, *Chem. Br.*, 1975, **11**, 177.
7 A. J. Carty, S. A. MacLaughlin, J. Van Wagner, and N. J. Taylor, *Organometallics*, 1982, **1**, 1013.
8 B. F. G. Johnson, J. Lewis, P. R. Raithby, K. Wong, and K. D. Rouse, *J. Chem. Soc., Dalton Trans.*, 1980, 1248.
9 B. F. G. Johnson, J. Lewis, J. N. Nicholls, I. A. Oxton, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Chem. Commun.*, 1982, 289.
10 B. F. G. Johnson, J. Lewis, and D. A. Pippard, *J. Chem. Soc., Dalton Trans.*, 1981, 407.
11 P. A. Dawson, B. F. G. Johnson, J. Lewis, J. Puga, P. R. Raithby, and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1982, 233.
12 B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, K. Wong, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1978, 673.
13 A. Martinsen and J. Songstad, *Acta Chem. Scand., Ser. A*, 1977, **31**, 645.
14 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
16 SHELX 76, Crystal Structure Solving Package, G. M. Sheldrick, Cambridge, 1976.

Received 1*st November* 1982; *Paper* 2/1840