Synthesis, Reactivity, and Spectroscopic Studies of Some Tetranuclear Osmium Clusters. Structural Characterization of $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ (M = Au or Cu) and $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$[‡]

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The interaction of $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (**1**) with $[N(PPh_3)_2][X]$ (X = NO_2, Cl, Br, or I) affords the species $[N(PPh_3)_2][Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]$ (**2**) (X = NO_2), $[Os_4H_3(CO)_{12}(\mu\text{-}X)]$ [X = Cl (**6**), Br (**7**), or I (**8**)], and $[N(PPh_3)_2][Os_4H_2(CO)_{12}X]$ [X = Cl (**9**), Br (**10**), or I (**11**)] which were characterized by i.r. and ^1H n.m.r. spectroscopy. The reaction of complex (**1**) with nitrite ion results in a novel interaction which involves oxygen transfer from the nitrite ion and conversion of a co-ordinated NCMe ligand into an amido group on the cluster surface. The anionic species (**2**) reacts with $[M(PPh_3)]^+$ to yield the neutral mixed-metal clusters $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ [M = Au (**3**) or Cu (**4**)] which have been structurally characterized by single-crystal *X*-ray diffractometry. This shows that they possess a butterfly metal framework capped by the heterometallic fragment and μ_3-bridged by the four-electron-donor amido group. Complexes (**3**) and (**4**) are isomorphous, monoclinic, with space group *C*2/*c* and *Z* = 8: (**3**), *a* = 25.681(7), *b* = 16.069(1), *c* = 18.265(2) Å, and β = 90.90(1)°; (**4**) *a* = 25.318(6), *b* = 15.964(5), *c* = 18.347(7) Å, and β = 91.80(2)°. Spectroscopic data suggest that compounds (**6**) and (**7**) also possess a butterfly metal framework with a bridging, three-electron-donor, halide ligand, while the anionic species (**11**) possesses a tetrahedral arrangement of metal atoms with a terminally co-ordinated iodide ligand, as shown by *X*-ray diffractometry: monoclinic, space group $P2_1/a$, *Z* = 8, *a* = 16.841(2), *b* = 20.699(1), *c* = 29.249(3), and β = 90.91(2)°. Protonation of (**11**) yields the neutral species $[Os_4H_3(CO)_{12}(\mu\text{-}I)]$, showing that facile reversible tetrahedral–butterfly interconversion is assisted by a change in co-ordination mode and electron donation of the I atom. The reaction of compound (**11**) with CF_3SO_3R (R = Me or Et) was monitored by ^1H n.m.r. spectroscopy and the results explained in terms of the formation of alkyl iodide derivatives.

Tetranuclear osmium clusters are efficient catalyst precursors for a number of processes in both the homogeneous[1] and heterogeneous[2] phases. Thus enhancement of metal cluster reactivity represents an important aspect in the study of these compounds from the synthetic and catalytic point of view. A variety of routes can be envisaged to favour cluster reactivity. Halide ligands for example are found both as doubly bridging, three-electron donor, or terminal one-electron donors.[3] Conversion from bridging into a terminal mode results in the formation of a vacant co-ordination site on the polynuclear metal framework. The reversibility of this process would be relevant to the reactivity of metal clusters particularly in reactions promoted by halides including catalytic processes.[4] Inclusion of substitution labile ligands within the cluster unit represents another way to prepare a number of derivatives.[5] Modification of the metal framework configuration involving interconversion between 'closed' and 'open' structures should play an important role in the chemistry and catalytic properties of metal clusters.

This article describes the interaction of $[N(PPh_3)_2][X]$ (X = Cl, Br, I, or NO_2) with the tetranuclear osmium cluster $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ as its $[BF_4]^-$ salt. A novel interaction between the NO_2^- ion and a co-ordinated acetonitrile ligand is reported. A reversible iodide-assisted tetrahedral–butterfly metal core rearrangement and a ^1H n.m.r. study of the interaction of the anionic species $[Os_4H_2(CO)_{12}I]^-$, as its $[N(PPh_3)_2]^+$ salt, with CF_3SO_3R (R = Me or Et) are also described. Complete descriptions of the *X*-ray structural characterization of the tetrahedral species $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$ and of the neutral derivatives $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ (M = Au or Cu) are included. Some aspects of this work have been published in the form of preliminary communications.[6]

Results and Discussion

Synthesis and Characterization of $[N(PPh_3)_2][Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]$ (**2**) *and Related Species*.—The reaction of $[Os_4H_3(CO)_{12}(NCMe)_2]^+$[7] (**1**), as its $[BF_4]^-$ salt, with $[N(PPh_3)_2][NO_2]$ results in a novel interaction involving oxygen transfer from the nitrite ion to an acetonitrile ligand, to yield the anionic complex $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]^-$ (**2**), as its $[N(PPh_3)_2]^+$ salt, which contains an amido group co-ordinated to the metal framework (see Scheme 1).

Although incorporation of an amido group into a triosmium cluster has been achieved by displacement of the acetonitrile

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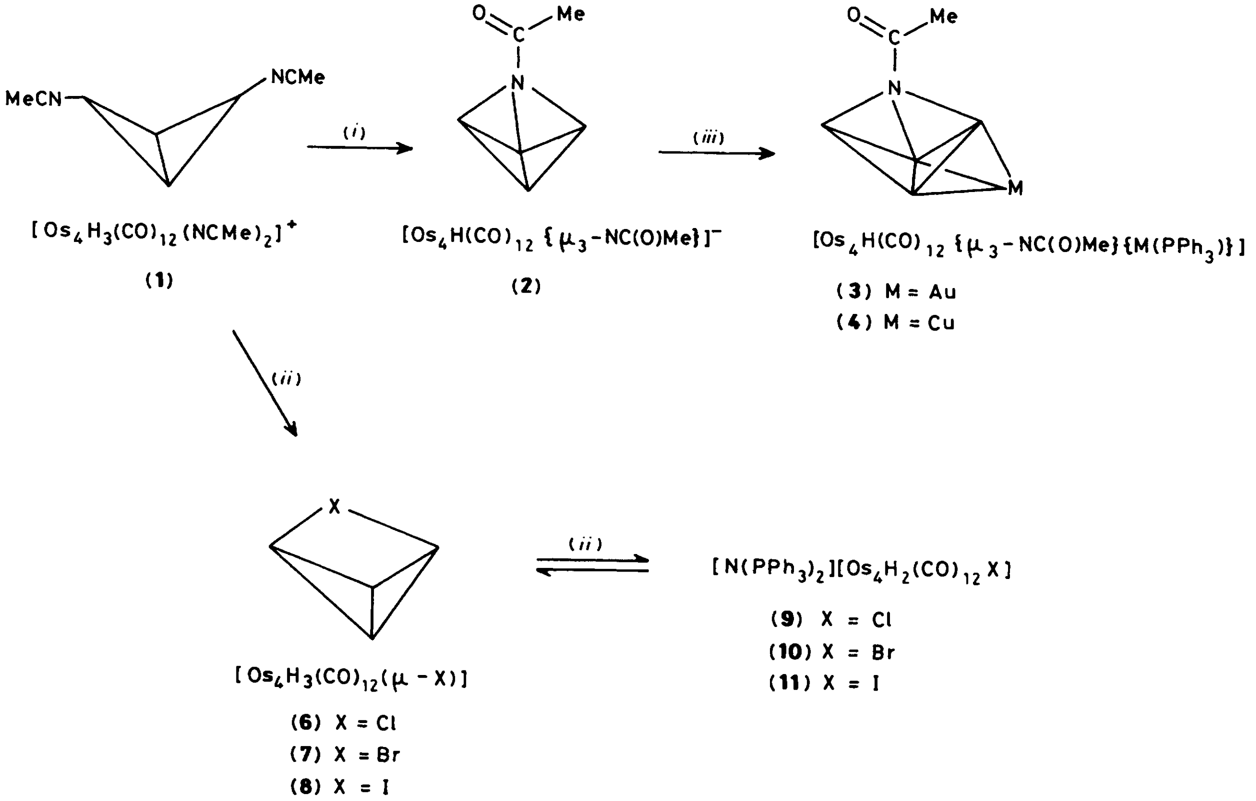
[‡] 1,2,3-μ_3-Acetylimido-1,4-μ-hydrido-1,2,4-μ_3-triphenylphosphineaurio-*cyclo*-tetrakis(tricarbonylosmium) (5*Os*–*Os*, 3*Os*–*Au*), 1,2,3-μ_3-acetylimido-1,4-μ-hydrido-1,2,4-μ_3-triphenylphosphinecuprio-*cyclo*-tetrakis(tricarbonylosmium) (5*Os*–*Os*, 3*Os*–*Cu*), and bis(triphenylphosphine)iminium 1,2;2,3-di-μ-hydrido-1-iodo-*tetrahedro*-tetrakis(tricarbonylosmate).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

ligands in $[Os_3(CO)_{10}(NCMe)_2]$ by the appropriate amide,[8] the reaction reported herein represents a unique example of the conversion of an acetonitrile ligand into an amido group on a cluster surface. The mechanism of this interaction is at present unknown, but the formation of (**2**) implies an oxygen-transfer capability of the nitrite ion besides its dual behaviour as a deprotonating and nitrosylating agent which we recently illustrated.[9]

Spectroscopic data for this compound, collected in Table 1, indicate a butterfly configuration of the metal cluster and clearly show the presence of the amido group.

Complex (**2**) reacts with the cations $[M(PPh_3)]^+$ (M = Au



Scheme 1. (*i*) $[N(PPh_3)_2][NO_2]$, 25 °C; (*ii*) $[N(PPh_3)_2][X]$ (X = Cl, Br, or I), 25 °C; (*iii*) $[M(PPh_3)]^+$, $TlPF_6$

Table 1. Spectroscopic data for the new complexes

Compound	^1H N.m.r. (δ) in $CDCl_3$ at 253 K	I.r. [ν(CO)/cm^{-1}] in CH_2Cl_2
$[N(PPh_3)_2][Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]$	2.67 (Me, s) −16.02 (OsH, s)	2 045s, 2 010s, 1 992s, 1 968 (sh), 1 932 (sh), 1 658 (amide)
$[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{Au(PPh_3)\}]$	2.58 (Me, s) −18.57 (OsH, s)	2 095m, 2 066s, 2 029vs, 1 989s, 1 968 (sh), 1 949 (sh)
$[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{Cu(PPh_3)\}]$	2.58 (Me, s) −18.20 (OsH, s)	2 088m, 2 060s, 2 027vs, 1 990s
$[Os_4H_3(CO)_{12}Cl]$	−15.13 (2 H, s) −17.92 (1 H, s)	2 089s, 2 062s, 2 018s, 1 995 (sh), 1 970 (sh)
$[Os_4H_3(CO)_{12}Br]$	−15.87 (2 H, s) −17.68 (1 H, s)	2 087s, 2 073s, 2 023s, 2 010 (sh), 1 992 (sh)
$[Os_4H_3(CO)_{12}I]$	−17.35 (1 H, s) −17.70 (2 H, s)	2 109w, 2 084s, 2 066s, 2 018s, 2 008 (sh)
$[N(PPh_3)_2][Os_4H_2(CO)_{12}Cl]$	−12.69 (s)	2 072w, 2 043s, 2 016s, 1 996s, 1 964 (sh), 1 918 (sh)
$[N(PPh_3)_2][Os_4H_2(CO)_{12}Br]$	−13.50 (s)	2 063w, 2 039s, 2 012s, 1 994s, 1 962 (sh), 1 912 (sh)
$[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$	−19.74 (d) −21.66 (d) *J*(H–H) = 1.07 Hz	2 078m, 2 046s, 2 012s, 1 985 (sh)

or Cu) to yield the corresponding neutral mixed-metal species $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ [M = Au (**3**) or Cu (**4**)], Scheme 1, whose spectroscopic properties are also summarized in Table 1. The anionic species $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]^-$ (**2**) also reacts with $[Cu(NCMe)_4]^+$, as its $[BF_4]^-$ salt, to form compound (**5**) (green in colour) which shows an i.r. spectrum very similar to that observed for the neutral derivatives (**3**) and (**4**). Thin-layer chromatography of (**5**), using a hexane–dichloromethane mixture as eluant, showed that slow disproportionation takes place on the silica plate to regenerate the red anionic complex (**2**). When acetonitrile was added to the eluant mixture disproportionation was practically instantaneous upon contact to give (**2**). This behaviour can be explained according to equation (1).

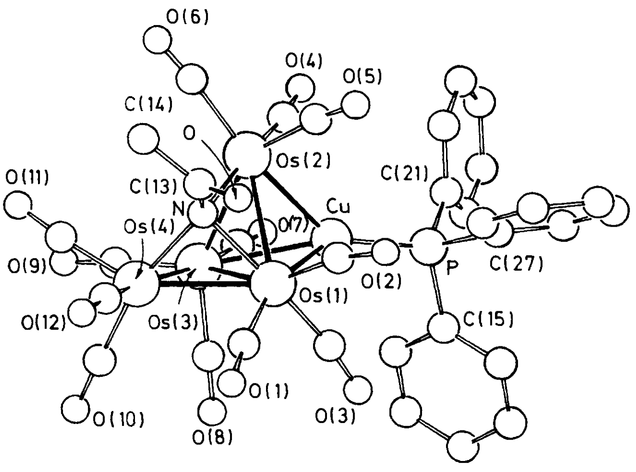


Figure 1. The structure of $[Os_4H(CO)_{12}\{\mu_3\text{-}N(CO)Me\}\{M(PPh_3)\}]$ shown in the case of M = Cu. The C atoms of the CO groups are labelled according to the corresponding O atoms

$$\underset{\text{(red)}}{[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]^-} + [Cu(NCMe)_4]^+ \underset{NCMe}{\overset{CH_2Cl_2}{\rightleftharpoons}}$$
$$\underset{\text{(green)}}{[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{Cu(NCMe)\}]} + 3NCMe \quad (1)$$

Structural Characterization of $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ [M = Au (**3**) *or* Cu (**4**)].—Compounds (**3**) and (**4**) are strictly isostructural and their crystals are isomorphous (see Experimental section) so that the molecular structures of the two species are best illustrated together. Relevant bond distances and angles are listed in Table 2, for direct comparison. The heterometallic polyhedra comprise a butterfly of Os atoms capped on one external triangular face by the $M(PPh_3)^+$ fragment as shown in Figure 1 for M = Cu. The NC(O)Me ligand lies on one side of the Os_4 butterfly with the N atom μ_3-co-ordinated to one atom of the butterfly hinge and to both wing tips. The four Os atoms each bear three terminal CO groups, while the H(hydride) atom is believed to bridge one of the butterfly edges not involved in the amido ligand bridging (see below). Considering that electron-precise butterfly species possess 62 valence electrons, the amido ligand is required to supply four electrons to the cluster orbitals, while the heterometallic fragments, seen as $M(PPh_3)^{\bullet}$, formally donate one electron to the cluster [alternatively, $M(PPh_3)^+$ fragments can

Table 2. Relevant bond distances (Å) and angles (°) for compounds (**3**) and (**4**)

	M = Au	M = Cu		M = Au	M = Cu
Os(1)–Os(2)	2.955(1)	2.864(1)	Os(3)–C(7)	1.92(2)	1.82(3)
Os(1)–Os(3)	2.939(1)	2.885(1)	Os(3)–C(8)	1.87(2)	1.89(3)
Os(2)–Os(3)	2.908(1)	2.891(1)	Os(3)–C(9)	1.87(2)	1.85(3)
Os(1)–Os(4)	2.759(1)	2.768(1)	Os(4)–C(10)	1.94(2)	1.86(2)
Os(3)–Os(4)	2.785(1)	2.775(1)	Os(4)–C(11)	1.88(2)	1.86(2)
Os(1)–M	2.762(1)	2.646(3)	Os(4)–C(12)	1.92(2)	1.88(3)
Os(2)–M	2.814(1)	2.709(3)	C(1)–O(1)	1.17(2)	1.22(3)
Os(3)–M	2.940(1)	2.745(3)	C(2)–O(2)	1.11(3)	1.21(4)
Os(1)–N	2.12(1)	2.10(2)	C(3)–O(3)	1.11(2)	1.18(3)
Os(2)–N	2.11(1)	2.14(2)	C(4)–O(4)	1.16(3)	1.23(4)
Os(4)–N	2.12(1)	2.06(2)	C(5)–O(5)	1.20(3)	1.09(4)
M–P	2.303(4)	2.250(6)	C(6)–O(6)	1.17(3)	1.08(4)
N–C(13)	1.37(2)	1.41(3)	C(7)–O(7)	1.18(3)	1.23(4)
C(13)–C(14)	1.47(3)	1.50(4)	C(8)–O(8)	1.13(2)	1.16(3)
C(13)–O	1.21(3)	1.19(3)	C(9)–O(9)	1.15(3)	1.17(3)
Os(1)–C(1)	1.85(2)	1.83(2)	C(10)–O(10)	1.10(2)	1.18(3)
Os(1)–C(2)	1.91(2)	1.85(3)	C(11)–O(11)	1.14(2)	1.15(3)
Os(1)–C(3)	1.93(2)	1.91(2)	C(12)–O(12)	1.12(2)	1.16(3)
Os(2)–C(4)	1.91(2)	1.81(3)	P–C(15)	1.83(1)	1.82(2)
Os(2)–C(5)	1.87(2)	1.94(3)	P–C(21)	1.81(1)	1.83(2)
Os(2)–C(6)	1.85(2)	1.95(4)	P–C(27)	1.81(1)	1.83(2)
Os(1)–N–Os(2)	88(1)	85(1)	Os(2)–C(6)–O(6)	179(2)	174(3)
Os(1)–N–Os(4)	81(1)	83(1)	Os(3)–C(7)–O(7)	170(2)	178(3)
Os(2)–N–Os(4)	118(1)	119(1)	Os(3)–C(8)–O(8)	179(2)	175(2)
N–C(13)–C(14)	117(2)	117(2)	Os(3)–C(9)–O(9)	177(2)	177(2)
N–C(13)–O	122(2)	122(2)	Os(4)–C(10)–O(10)	176(2)	179(2)
O–C(13)–C(14)	121(2)	121(2)	Os(4)–C(11)–O(11)	176(2)	174(2)
Os(1)–C(1)–O(1)	167(2)	173(2)	Os(4)–C(12)–O(12)	178(2)	172(2)
Os(1)–C(2)–O(2)	176(2)	168(2)	M–P–C(15)	113(1)	113(1)
Os(1)–C(3)–O(3)	176(2)	170(2)	M–P–C(21)	117(1)	119(1)
Os(2)–C(4)–O(4)	178(2)	173(2)	M–P–C(27)	111(1)	111(1)
Os(2)–C(5)–O(5)	175(2)	174(3)			

be regarded as interacting with an anionic cluster with no electron contribution].

Homometallic bonding interactions within the butterfly core can be grouped in two distinct sets: the Os–Os bonds belonging to the capped face are longer than those of the uncapped face. Moreover while the latter have identical values in compounds (**3**) and (**4**) [2.772(1) Å], the Os–Os distances within the capped face are longer in (**3**) than in (**4**) [2.934(1) and 2.880(1) Å, respectively], suggesting that the heteroatoms exhibit fairly different interactions with the osmium butterfly. While Cu [mainly as the Cu(NCMe) ligand] is usually found μ_3-bridging cluster triangular faces,[10] Au [mainly as the $Au(PPh_3)$ ligand] tends to give μ co-ordination,[10a,11] although asymmetric μ_3 co-ordination has also been observed.[12] However in all cases the presence of an $Au(PPh_3)$ ligand, whether μ- or μ_3-co-ordinated, results in an appreciable lengthening of the bridged metal–metal bonds. Good examples are the structures of $[Os_{10}C(CO)_{24}\{Au(PPh_3)\}]^-$ [10a] where the μ-bridged Os–Os bond is 2.962(1) Å compared with an average of 2.840(1) Å for the other bonds, and $[Ru_6C(CO)_{15}(NO)\{Au(PPh_3)\}]$[12] where the Ru–Ru bonds involved in the asymmetric μ_3 bridge average 2.971(2) Å [longest 3.053(2) Å] compared with an average of 2.910(2) Å for the other Ru–Ru bonds.

A similar effect is caused by Cu(NCMe), as in $[Os_{10}C(CO)_{24}\{Cu(NCMe)\}]^-$ [10a] and in $[Os_{11}C(CO)_{27}\{Cu(NCMe)\}]^-$ [10b] where the μ_3-bridged Os–Os bonds are longer [mean 2.900(1) and 2.825(2) Å, respectively] than the other Os–Os bonds in the two frameworks [2.850(1) and 2.801(2) Å respectively].

However the absence of other isostructural species containing these two fragments makes difficult a rationalization of the larger lengthening effect exerted by the $Au(PPh_3)$ group with respect to $Cu(PPh_3)$ on the bridged Os–Os bonds in (**3**) and (**4**). It is interesting that both sets of Os–M (M = Au or Cu) heteroatomic interactions show marked asymmetry with values ranging from 2.762(1) to 2.940(1) Å in (**3**) and from 2.646(3) to 2.745(3) Å in (**4**), the longest distances being always from Os(3) which is not involved in the amido-bridge (see Table 2).

The most remarkable aspect of the structures of compounds (**3**) and (**4**) is the unprecedented bonding mode of the μ_3-NC(O)Me ligand. This group is strictly planar and the C atom [C(13)] is sp^2 hybridized as demonstrated by the angles in Table 2. The C–O distances are in accord with expected values for double-bonded C–O pairs [1.21(3) and 1.19(3) Å, in (**3**) and (**4**) respectively], while both the C–N and C–C bond lengths are within the ranges for single $C(sp^2)$–N and $C(sp^2)$–C interactions. All differences between corresponding values in (**3**) and (**4**) appear to have little significance, being well within experimental errors. The Os–N distances also show good agreement between the two compounds [mean 2.12(1) Å in (**3**) and 2.10(2) Å in (**4**)] and compare well with those in other species containing Os–N bonds such as $[Os_3(CO)_{10}(NCMe)_2]$ [2.13(1) Å],[13] $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ [2.12(1) Å],[14] and $[Os_4H_3(CO)_{12}(\mu\text{-}NO)]$ [2.10(2) Å].[15]

The whole ligand system is placed on one side of the Os_4 butterfly with the O atom pointing outwards and the CH_3 group inwards, with respect to the open edge, probably in order to reduce contacts with neighbouring CO groups.

The H(hydride) atom location poses some problems: the simple criterion based on M–M bond lengthening commonly used for recognizing μ-H bridge formation fails to give trustworthy information in the cases of compounds (**3**) and (**4**) because of the presence of the heterometallic ligands which also cause longer metal–metal interactions as discussed above. However space-filling diagrams [16] proved to be very helpful, clearly showing the existence of a large 'niche' in the ligand coverage above the Os(2)–Os(3) edge which can be confidently assigned to the H atom (see Figure 2).[17] It is worth noting that the steric requirements of the hydride atom may be responsible for the location of the N(CO)Me group on one side of the Os_4 butterfly.

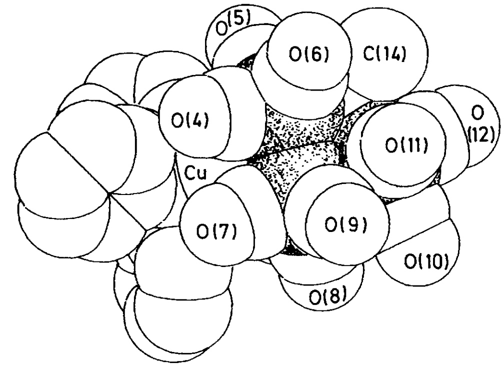


Figure 2. Space-filling diagram of $[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ showing the H-bridged edge

The presence of the NC(O)Me ligand causes an appreciable decrease in the angle between the butterfly wings [mean Os(2)–Os(*N*)–Os(4) (*N* = 1 or 3) 79.3(1) and 79.5(1)° for (**3**) and (**4**), respectively] with respect to the unsupported metal core of the parent $[Os_4H_3(CO)_{12}(NCMe)_2]^+$ [mean 93.0(1)°]. This observation allows some speculation on the reaction mechanism: the intermediacy of a tetrahedral species formed upon loss of one NCMe ligand and dehydrogenation can be thought to assist 'closure' of the N-atom lone pairs on neighbouring Os atoms, accompanied by metal–metal bond breaking and butterfly formation. Some support to this hypothesis comes from the reversible interconversion of the butterfly cluster species (**8**) and the tetrahedral species (**11**) upon deprotonation, assisted by a change in the electron donation of the halogen ligand, as discussed below.

Synthesis and Characterization of $[Os_4H_3(CO)_{12}(\mu\text{-}X)]$ *and* $[N(PPh_3)_2][Os_4H_2(CO)_{12}X]$ (X = Cl, Br, *or* I).—The reaction of compound (**1**) with $[N(PPh_3)_2][X]$ (X = Cl or I) has previously been reported to yield $[Os_4H_3(CO)_{12}X]$ and $[N(PPh_3)_2][Os_4H_2(CO)_{12}X]$, only characterized by i.r. spectroscopy.[7] We now report the synthesis, i.r., and ^1H n.m.r. data for the complete series $[Os_4H_3(CO)_{12}X]$ [X = Cl (**6**), Br (**7**), or I (**8**)] and $[N(PPh_3)_2]$ $[Os_4H_2(CO)_{12}X]$ [X = Cl (**9**), Br (**10**), or I (**11**)]. The complexes were prepared by interaction of (**1**) with $[N(PPh_3)_2][X]$, and the spectroscopic data are collected in Table 1. Formation of the neutral species (**6**)—(**8**) is achieved by using stoicheiometric amounts of the corresponding halide salts. The presence of an excess of the latter salts affords the anionic compounds (**9**)—(**11**) (Scheme 1).

Structural Characterization of $[Os_4H_2(CO)_{12}I]^-$, (**11**).—Crystals of compound (**11**) contain two isostructural independent $[Os_4H_2(CO)_{12}I]^-$ anions and two $[N(PPh_3)_2]^+$ cations separated by normal van der Waals interactions. The structural parameters are averaged on corresponding values in the two anions, although relevant distances and bond angles for (**11**) are listed separately in Table 3 to allow direct comparison. The structure is shown in Figure 3.

The metal atom polyhedron comprises a distorted tetrahedron of Os atoms. Two sets of Os–Os interactions are present: four 'short' Os–Os bonds [mean 2.799(1) Å] and two 'long' consecutive edges [mean 2.951(1) Å] which are believed to be bridged by two hydride atoms as can be deduced on the basis of both metal–metal bond lengthening and displacement of the CO ligands.

However it should be noted that the two metal atom polyhedra, though isostructural, show appreciable differences: while

Table 3. Relevant bond distances (Å) and angles (°) for compound **(11)**

Os(1)–Os(2)	2.938(1)	Os(5)–Os(6)	2.990(1)	Os(3)–C(8)	1.85(2)	Os(7)–C(20)	1.86(2)
Os(1)–Os(3)	2.830(1)	Os(5)–Os(7)	2.810(1)	Os(3)–C(9)	1.86(2)	Os(7)–C(21)	1.86(2)
Os(2)–Os(3)	2.952(1)	Os(6)–Os(7)	2.924(1)	Os(4)–C(10)	1.85(2)	Os(8)–C(22)	1.90(2)
Os(3)–Os(4)	2.764(1)	Os(7)–Os(8)	2.783(1)	Os(4)–C(11)	1.89(2)	Os(8)–C(23)	1.87(2)
Os(2)–Os(4)	2.797(1)	Os(6)–Os(8)	2.810(1)	Os(4)–C(12)	1.86(2)	Os(8)–C(24)	1.87(2)
Os(1)–Os(4)	2.801(1)	Os(5)–Os(8)	2.796(1)	Os(4) ··· C(2)	2.53(2)	Os(8) ··· C(13)	2.50(2)
Os(1)–I(1)	2.738(2)	Os(5)–I(2)	2.725(2)	Os(3) ··· C(1)	2.75(1)	Os(7) ··· C(14)	2.78(2)
Os(1)–C(1)	1.86(2)	Os(5)–C(13)	1.82(3)	P(1)–C(111)	1.79(1)	P(3)–C(312)	1.78(1)
Os(1)–C(2)	1.83(2)	Os(5)–C(14)	1.88(2)	P(1)–C(121)	1.76(1)	P(3)–C(321)	1.80(1)
Os(1)–C(3)	1.87(2)	Os(5)–C(15)	1.82(2)	P(1)–C(131)	1.80(1)	P(3)–C(331)	1.79(1)
Os(2)–C(4)	1.89(2)	Os(6)–C(16)	1.85(2)	P(2)–C(211)	1.80(1)	P(4)–C(411)	1.79(2)
Os(2)–C(3)	1.89(3)	Os(6)–C(17)	1.85(2)	P(2)–C(221)	1.80(1)	P(4)–C(421)	1.78(1)
Os(2)–C(6)	1.86(2)	Os(6)–C(18)	1.90(2)	P(2)–C(231)	1.77(1)	P(4)–C(431)	1.81(1)
Os(3)–C(7)	1.85(2)	Os(7)–C(19)	1.86(2)				
I(1)–Os(1)–Os(2)	112.6(1)	I(2)–Os(5)–Os(6)	112.2(1)	Os(3)–C(7)–O(7)	177(2)	Os(7)–C(19)–O(19)	176(2)
Os(1)–C(1)–O(1)	165(2)	Os(3)–C(13)–O(13)	159(2)	Os(3)–C(8)–O(8)	174(2)	Os(7)–C(20)–O(20)	178(2)
Os(1)–C(2)–O(2)	161(2)	Os(5)–C(14)–C(14)	167(2)	Os(3)–C(9)–O(9)	178(2)	Os(7)–C(21)–O(21)	176(2)
Os(1)–C(3)–O(3)	178(2)	Os(5)–C(15)–O(15)	171(2)	Os(4)–C(10)–O(10)	171(2)	Os(8)–C(22)–O(22)	179(2)
Os(2)–C(4)–O(4)	178(2)	Os(6)–C(16)–O(16)	178(2)	Os(4)–C(11)–O(11)	176(2)	Os(8)–C(23)–O(23)	172(2)
Os(2)–C(5)–O(5)	172(3)	Os(6)–C(17)–O(17)	176(2)	Os(4)–C(12)–O(12)	170(3)	Os(8)–C(24)–O(24)	177(2)
Os(2)–C(6)–O(6)	175(3)	Os(6)–C(18)–O(18)	176(2)				

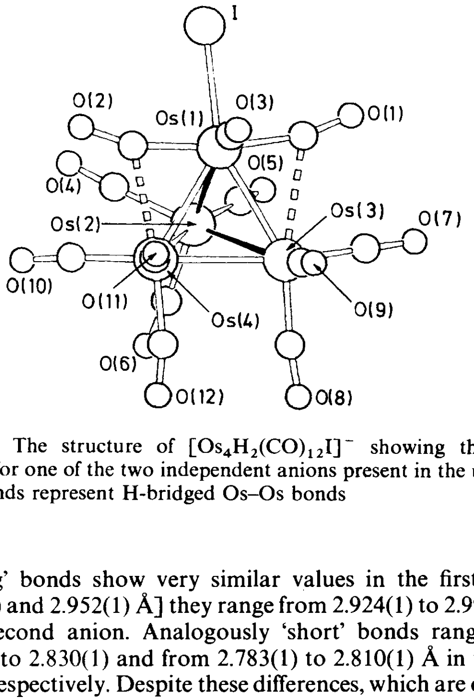


Figure 3. The structure of $[Os_4H_2(CO)_{12}I]^-$ showing the atom labelling for one of the two independent anions present in the unit cell. Filled bonds represent H-bridged Os–Os bonds

the 'long' bonds show very similar values in the first anion [2.938(1) and 2.952(1) Å] they range from 2.924(1) to 2.990(1) Å in the second anion. Analogously 'short' bonds range from 2.764(1) to 2.830(1) and from 2.783(1) to 2.810(1) Å in the two anions, respectively. Despite these differences, which are difficult to attribute *only* to the packing environment of the two anions, the average values show much better agreement [2.945(1), 2.798(1) and 2.957(1), 2.800(1) Å for 'long' and 'short' bonds in the two anions, respectively]. These values can be compared with other hydride-bridged and unbridged Os–Os bond lengths found in isoelectronic species such as $[Os_4H_2(CO)_{12}]^{2-}$ [2.934(4) and 2.798(4)],[18] $[Os_4H_3(CO)_{12}]^-$ [2.949(2) and 2.798(2)],[19] and $[Os_4H_3(CO)_{11}(NO)]$ [2.925(2) and 2.799(2) Å],[9] showing substantial agreement. However, as previously reported,[6] tetrahedral species usually show shorter M–M bonds, regardless of the presence of hydride bridges, than the corresponding butterfly species as can be deduced from a comparison of the bridged and unbridged Os–Os bond lengths in the cluster pairs: $[Os_4H_2(CO)_{12}I]^-$ and $[Os_4H_3(CO)_{12}I]$ [2.951(2), 2.799(1) and 3.010(1), 2.877(1) Å]; $[Os_4H_3(CO)_{11}(NO)]$[9] mentioned above and $[Os_4H_3(CO)_{12}(NO)]$ [2.997(5), 2.853(5) Å].[15]

Each Os atom bears three terminally bound CO groups. The I ligand is also terminally bound to one metal atom at a distance of 2.732(1) Å. Interestingly, no appreciable difference in the Os–I bond length can be detected whether the I atom is bound in a terminal (one-electron donor) or bridging (three-electron donor) fashion. The value of 2.732(1) Å is in good agreement not only with the Os–I(terminal) bond lengths observed in $[Os_5(CO)_{15}I]^-$[20] [2.740(5) Å] and $[Os_{10}C(CO)_{22}(NO)I]^{2-}$ [2.75(1) Å],[21] but also with the values reported for Os–I(bridge) in $[Os_{10}C(CO)_{24}(\mu\text{-}I)_n]^{2-n}$[21] [2.724(4) and 2.736(5) for $n = 1$ and 2, respectively].

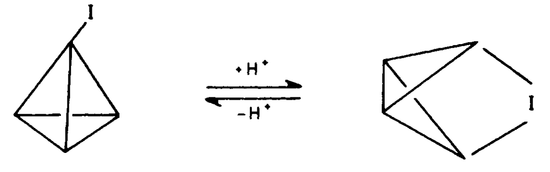
The Os–C and C–O distances average 1.87(2) and 1.14(1) Å, respectively and appear to be within the range expected for terminal CO bound to anionic clusters.[22] It is worth noting that the Os atom bearing the I ligand is also involved in three Os–CO and one Os–H interactions; the resulting steric crowding is partially alleviated by pushing two radial CO groups towards semibridging positions with respect to the neighbouring Os atoms [mean Os ··· C 2.64(2) Å]. However electronic factors also play a role: both the slight bending of the CO groups coplanar with the I atom [mean Os–C–O 163(2)°] and the short contacts mentioned above indicate that weak bonding interactions between the bent CO groups and the contiguous Os atoms are established in order to facilitate an even electronic distribution among all metal atoms. Short Os ··· C interactions (mean 2.70 Å) were also observed in $[Os_5(CO)_{15}I]^-$[20] where a similar 'Os(CO)$_3$I' unit is present.

As discussed already,[6] the fact that a more symmetric C_s-*m* distribution of the H atoms is not adopted in compound **(11)** can be explained only by assuming that one H atom coordinates to the Os atom bearing the I ligand which is electron rich, so that two non-equivalent sites are available for the second H atom. Two of these sites [Os(2)–Os(3) and Os(2)–Os(4) for the anion depicted in Figure 3] are twice as probable as the third one [Os(3)–Os(4)] and are probably favoured when the molecule is frozen in the crystal.

Proton N.M.R. Spectroscopy and Structural Configuration.— The ^1H n.m.r. patterns observed for a number of structurally

Table 4. Proton n.m.r. data in $CDCl_3$ at 253 K. Data for CH_3SO_3R are included for comparison

Compound	CH_2	CH_3	Os–H	$J_{\alpha\beta}$/Hz	$J_{\psi\omega}$/Hz
$[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$	—	—	−19.74 (d), −21.66 (d)	—	1.07
$[Os_4H_2(CO)_{12}(IMe)]$	—	2.12 (s)	−19.88 (d), −21.22 (d) −20.04 (d), −20.31 (d)	—	1.07
$[Os_4H_2(CO)_{12}(IEt)]$	3.16 (q)	1.79 (t)	−19.89 (d), −21.22 (d) −20.04 (d), −20.31 (d)	7.4	1.07
CF_3SO_3Et	4.61 (q)	1.49 (t)	—	7.0	—
CF_3SO_3Me	—	4.22 (s)	—	—	—



$[Os_4H_2(CO)_{12}I]^-$ $[Os_4H_3(CO)_{12}I]$

Scheme 2.

characterized Os_4 'butterfly' clusters may be useful in the assignment of the metal framework configuration present in closely related species. For instance, two signals with a 1:2 intensity ratio are observed for $[Os_4H_3(CO)_{12}(\mu\text{-}I)]$,[23] $[Os_4H_3(CO)_{12}(NCMe)_2]^+$,[14] and $[Os_4H_3(CO)_{12}(\mu\text{-}NO)]$.[15] A similar ^1H n.m.r. pattern has been found for the neutral derivatives (**6**) and (**7**) thus suggesting the presence of a 'butterfly' metal core arrangement in these complexes.

For the anionic species we note that compounds (**9**) and (**10**) showed only a singlet in the ^1H n.m.r. spectra, Table 1, whereas complex (**11**) shows two doublets [J(H–H) = 1.07 Hz]. The structure of (**11**) consists of a tetrahedral arrangement of metal atoms (see above) with inequivalent hydride ligands. The situation for (**9**) and (**10**), in the absence of X-ray data, is not conclusive, since at least one tetrahedral and one butterfly metal core arrangement possessing two equivalent hydride ligands can be envisaged; furthermore, these compounds could also be isostructural with (**11**) in the solid state, but fluxional in solution, giving rise to the observed differences in the ^1H n.m.r. spectra.

Preliminary data on the catalytic properties of (**9**) in the hydrogenation of styrene indicate that the behaviour of this complex is similar to that of the tetrahedral clusters $[Os_4H_4(CO)_{12}]$ and (**11**), and considerably different from that of the butterfly species (**8**). Interestingly, protonation of the anionic species $[Os_4H_2(CO)_{12}I]^-$ regenerates the neutral compound $[Os_4H_3(CO)_{12}(\mu\text{-}I)]$, clearly showing the facile reversible tetrahedral–butterfly metal framework rearrangement (see Scheme 2).

The study of the reactivity of the anionic compound (**11**) toward electrophilic reagents indicates that its behaviour is considerably different from that of the isoelectronic $[Os_4H_3(CO)_{12}]^-$; thus, interaction with the nitrosonium ion $[NO]^+$, using diethyl ether, CH_2Cl_2, or tetrahydrofuran as solvent, affords unidentified anionic species. Attempts to prepare the neutral mixed-metal derivatives by treating (**11**) with $[M(PPh_3)]^+$ (M = Au or Cu), using CH_2Cl_2 as solvent, have been unsuccessful, probably due to the steric hindrance imposed by the presence of the iodide ligand (see above).

Reaction of $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$ *with* CF_3SO_3R (R = Me *or* Et).—Interaction of the anionic species (**11**), as its $[N(PPh_3)_2]^+$ salt, with CF_3SO_3R, using $CDCl_3$ as solvent, was monitored by ^1H n.m.r. spectroscopy. On addition of CF_3SO_3R the two doublets observed in the hydride region for (**11**) (Table 1) are replaced by two pairs of doublets [J(H–H) = 1.07 Hz] as depicted in Figures 4 and 5. Addition of $[N(PPh_3)_2][BH_4]$ to a solution of this species at room temperature induces evolution of a gas with reformation of (**11**). This information is consistent with formation of alkyl iodide derivatives according to equation (2). Addition of $[BH_4]^-$, as its $[N(PPh_3)_2]^+$ salt, would induce

$$[N(PPh_3)_2][Os_4H_2(CO)_{12}I] + CF_3SO_3R \longrightarrow [Os_4H_2(CO)_{12}(IR)] + [N(PPh_3)_2][CF_3SO_3] \quad (2)$$

$$[Os_4H_2(CO)_{12}(IR)] + [N(PPh_3)_2][BH_4] \longrightarrow [N(PPh_3)_2][Os_4H_2(CO)_{12}I] + R\text{–}H + BH_3 \quad (3)$$

alkane evolution regenerating the anionic species (**11**) according to equation (3). The process is completely reproducible and the two pairs of doublets always maintain an integration ratio close to 3:1 (Figures 4 and 5), thus suggesting an equilibrium between two isomers as shown in Scheme 3. Additionally the ^1H n.m.r. spectra of the compounds RI (R = Me or Et), obtained in $CDCl_3$, showed that the chemical shifts of the alkyl groups present in these complexes were practically identical to those found for the species (**12**) and (**13**) (Scheme 3, Table 4). Formation of alkyl iodide species is also supported by i.r. data: $[Os_4H_2(CO)_{12}(IMe)]$ in CH_2Cl_2 solution, 2 068s, 2 042s, 1 990s, 1 978 (sh), and 1 956 (sh) cm^{-1}.

Adduct formation involving species with co-ordinated iodide ligands has been previously reported. For instance $[Mo(\eta\text{-}C_5H_5)(NO)I]$[24] and $[Os_5(CO)_{15}I]^-$[25] interact with $AgBF_4$. Formation of $[Mo(\eta\text{-}C_5H_5)(NO)I{\cdot}AgBF_4]$ is observed in CH_2Cl_2, while iodide abstraction takes place in more polar solvents.

Electrophilic attack of the R^+ group at a metal atom (or at a metal–metal bond) was ruled out on the basis of the chemical shifts shown by the alkyl groups (Table 1). Electrophilic attack at a carbonyl ligand (probably *via* metal–alkyl interaction) was also excluded since no carbonyl band attributable to the presence of an acyl group was detected in the i.r. spectrum after addition of CF_3SO_3R. Attempts to isolate the reported alkyl iodide species by evaporating the solvent under vacuum and extraction of the residue with diethyl ether failed due to disproportionation to $[Os_4H_3(CO)_{12}I]$ and $[Os_4H_4(CO)_{12}]$ which were characterized by ^1H n.m.r. spectroscopy.

Experimental

All reactions were carried out under purified nitrogen, unless otherwise specified. Acetonitrile was distilled twice over P_2O_5

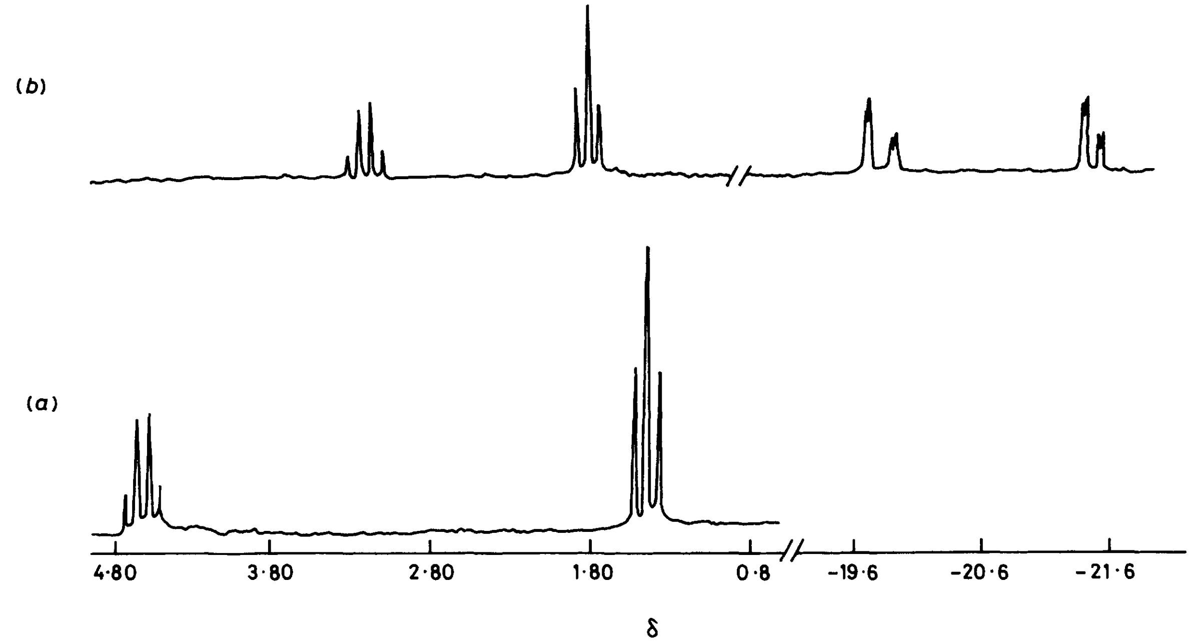


Figure 4. Proton n.m.r. spectra of CF_3SO_3Et (*a*) and $[Os_4H_2(CO)_{12}(IEt)]$ (*b*) in $CDCl_3$ at 253 K

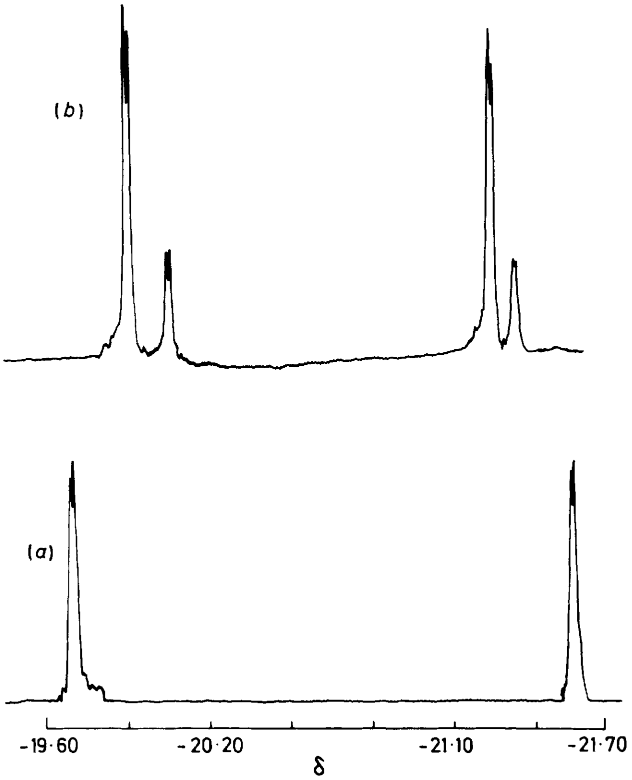
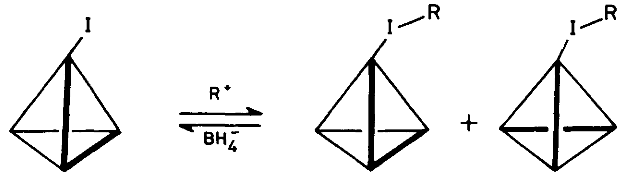


Figure 5. Proton n.m.r. spectra of $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$ (*a*) and $[Os_4H_2(CO)_{12}(IEt)]$ (*b*) in the hydride region at 253 K using $CDCl_3$ as solvent

and analysed by gas chromatography prior to use. All other solvents were distilled under nitrogen using appropriate drying reagents. I.r. spectra were recorded on a Perkin-Elmer 1320 spectrophotometer, ^1H n.m.r. spectra on a Varian XL-100 spectrometer. The compounds $[N(PPh_3)_2][X]$ (X = Cl, Br, I, or NO_2), CF_3SO_3R (R = Me or Et) and $[Fe(\eta-C_5H_5)_2][BF_4]$ were prepared according to literature procedures.[26-28]



$[Os_4H_2(CO)_{12}I]^-$ **(11)** **(12)** **(13)**

Scheme 3.

Preparations.—$[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$. The salt $[Fe(\eta-C_5H_5)_2][BF_4]$ (144 mg, 0.53 mmol) was slowly added to a solution of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ (450 mg, 0.27 mmol) in acetonitrile (125 cm^3). The originally yellow solution became blue upon addition of $[Fe(\eta-C_5H_5)_2]^+$. The solution was stirred at room temperature for *ca.* 1 h, after which time a yellow colour was again observed. The solvent was evacuated to dryness and the residue washed several times with hexane. The required compound was obtained as a yellow solid. Yield: 306 mg, 90%.

$[N(PPh_3)_2][Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]$. The compound $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (100 mg, 78 × 10^{-3} mmol) was dissolved in freshly distilled acetonitrile (80 cm^3) and $[N(PPh_3)_2][NO_2]$ (46 mg, 78 × 10^{-3} mmol) was slowly added over 0.5 h. The originally yellow solution became red. The solution was stirred for *ca.* 3 h at room temperature, evaporated to dryness, and the compound extracted with diethyl ether. Thin-layer chromatography using hexane–dichloromethane

Table 5. Crystal data and details of measurements for compounds (**3**), (**4**), and (**11**)[a]

	(**3**)	(**4**)	(**11**)
Formula	$C_{32}H_{19}AuNO_{13}Os_4P$	$C_{32}H_{19}CuNO_{13}Os_4P$	$C_{48}H_{32}INO_{12}Os_4P_2$
M	1 614.2	1 480.7	1 764.4
a/Å	25.681(7)	25.318(6)	16.841(2)
b/Å	16.069(1)	15.964(5)	20.699(1)
c/Å	18.265(2)	18.347(7)	29.249(3)
β/°	90.90(1)	91.80(2)	90.91(2)
U/Å^3	7 536.5	7 411.9	10 194.7
D_c/g cm^{-3}	2.84	2.65	2.30
Space group	$C2/c$	$C2/c$	$P2_1/a$
F(000)	5 760	5 360	6 480
Crystal size (mm)	0.1 × 0.1 × 0.2	0.02 × 0.1 × 0.15	0.1 × 0.15 × 0.05
Colour	Green	Green	Orange
μ(Mo-K_α)/cm^{-1}	168	138	106.7
Scan range/°	2.5—25	1.5—25	2.5—23
Scan interval/°	0.8 + 0.35 tan θ	0.85 + 0.35 tan θ	0.7 + 0.35 tan θ
Prescan acceptance, $\sigma(I)/I$	0.5	0.5	0.3
Max. time for data collection/s	120	120	100
No. of data collected (at room temperature)	7 088	6 989	14 665
No. of data used [$F_o > 5\sigma(F_o)$]	4 332	2 391	6 002
Equivalent reflections merging	0.06	0.02	0.07
No. of azimuthal reflections used for absorption correction	432	296	370
Min. and max. transmission	29—100	44—100	37—100
Average correction factor	0.86	0.93	0.71
R	0.052	0.035	0.043
R'[b]	0.057	0.036	0.034
K	0.68	0.99	1.64
g	0.014	0.000 89	0.000 1

[a] Details common to all three complexes: monoclinic; $Z = 8$; graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\ 69$ Å; ω—2θ scans; prescan speed, 5° min^{-1}; required final $\sigma(I)/I = 0.02$; background measurements, equal to half peak scanning time; collected octants, $\pm h$, $+k$, $+l$. [b] Where $w = K/[\sigma^2(F) + |g|F^2]$.

Table 6. Fractional atomic co-ordinates for compound (**3**)

Atom	x	y	z
Os(1)	0.189 54(2)	0.550 42(4)	0.175 16(3)
Os(2)	0.203 90(3)	0.455 62(4)	0.038 34(4)
Os(3)	0.183 67(2)	0.367 77(4)	0.174 16(3)
Os(4)	0.095 52(2)	0.468 14(4)	0.162 36(3)
Au	0.279 98(2)	0.462 36(4)	0.150 80(4)
P	0.366 9(2)	0.464 6(2)	0.184 0(2)
C(1)	0.138 2(7)	0.612 1(11)	0.220 5(9)
O(1)	0.113 1(6)	0.662 9(9)	0.249 8(7)
C(2)	0.223 8(9)	0.648 7(14)	0.142 2(11)
O(2)	0.241 5(7)	0.708 1(12)	0.124 7(9)
C(3)	0.230 3(7)	0.549 2(9)	0.264 9(9)
O(3)	0.251 7(6)	0.552 1(9)	0.318 5(8)
C(4)	0.259 0(10)	0.385 0(15)	0.007 3(13)
O(4)	0.291 5(7)	0.340 8(13)	−0.012 1(10)
C(5)	0.235 2(9)	0.546 7(12)	−0.006 8(12)
O(5)	0.256 7(7)	0.606 4(11)	−0.030 9(9)
C(6)	0.167 6(8)	0.425 1(15)	−0.045 6(11)
O(6)	0.144 8(8)	0.404 2(13)	−0.098 4(11)
C(7)	0.244 2(8)	0.298 0(14)	0.171 6(11)
O(7)	0.276 4(7)	0.245 9(13)	0.170 2(10)
C(8)	0.182 5(6)	0.374 7(11)	0.276 4(9)
O(8)	0.182 0(6)	0.380 3(9)	0.337 9(8)
C(9)	0.137 7(8)	0.277 7(13)	0.172 8(10)
O(9)	0.110 8(6)	0.220 9(10)	0.174 7(8)
C(10)	0.070 3(7)	0.421 9(12)	0.253 2(9)
O(10)	0.055 4(6)	0.400 2(9)	0.306 2(7)
C(11)	0.057 9(8)	0.390 3(12)	0.106 0(10)
O(11)	0.037 3(6)	0.340 7(10)	0.072 0(8)
C(12)	0.038 8(7)	0.545 8(11)	0.157 4(10)
O(12)	0.004 4(7)	0.589 1(11)	0.156 0(9)
N	0.142 0(5)	0.525 6(8)	0.081 7(7)
O	0.132 2(6)	0.659 0(11)	0.044 9(9)
C(13)	0.120 9(7)	0.586 6(13)	0.037 9(10)
C(14)	0.081 8(11)	0.560 7(18)	−0.017 1(15)
C(16)	0.360 3(5)	0.377 2(7)	0.313 6(6)
C(17)	0.368 6(5)	0.362 3(7)	0.388 2(6)
C(18)	0.394 0(5)	0.421 6(7)	0.431 5(6)
C(19)	0.411 2(5)	0.495 8(7)	0.400 3(6)
C(20)	0.402 9(5)	0.510 6(7)	0.325 8(6)
C(15)	0.377 4(5)	0.451 3(7)	0.282 5(6)
C(22)	0.449 0(5)	0.347 5(8)	0.181 9(5)
C(23)	0.483 1(5)	0.294 7(8)	0.145 4(5)
C(24)	0.477 2(5)	0.281 9(8)	0.070 2(5)
C(25)	0.437 1(5)	0.321 8(8)	0.031 5(5)
C(26)	0.403 0(5)	0.374 5(8)	0.067 9(5)
C(21)	0.409 0(5)	0.387 4(8)	0.143 1(5)
C(28)	0.450 6(4)	0.573 0(8)	0.164 0(8)
C(29)	0.472 7(4)	0.648 4(8)	0.142 8(8)
C(32)	0.441 0(4)	0.713 1(8)	0.117 7(8)
C(33)	0.387 1(4)	0.702 6(8)	0.113 9(8)
C(34)	0.364 9(4)	0.627 2(8)	0.135 1(8)
C(27)	0.396 7(4)	0.562 5(8)	0.160 2(8)

(2:8) gave a red band which was extracted with CH_2Cl_2. Orange crystals were obtained upon crystallization from diethyl ether. Yield: 60 mg, 45%.

$[Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}\{M(PPh_3)\}]$ (M = Au *or* Cu).

The compound $[Au(PPh_3)]Cl$ (74 mg, 0.15 mmol) was added to a solution of $[N(PPh_3)_2][Os_4H(CO)_{12}\{\mu_3\text{-}NC(O)Me\}]$ [200 mg, 0.12 mmol in CH_2Cl_2 (100 cm^3)]. After addition of $TlPF_6$ (70 mg, 0.20 mmol) the originally orange solution became green.

Table 7. Fractional atomic co-ordinates for compound (**4**)

Atom	*x*	*y*	*z*
Os(1)	0.190 04(3)	0.545 39(6)	0.171 01(4)
Os(2)	0.206 12(4)	0.450 10(7)	0.041 34(5)
Os(3)	0.186 05(4)	0.364 91(6)	0.176 73(5)
Os(4)	0.094 88(3)	0.460 34(6)	0.159 59(4)
Cu	0.276 61(9)	0.455 08(18)	0.155 42(13)
P	0.363 3(2)	0.460 5(4)	0.186 2(3)
C(1)	0.139 8(9)	0.605 8(14)	0.218 2(12)
O(1)	0.110 0(7)	0.653 0(11)	0.249 6(9)
C(2)	0.216 3(11)	0.643 8(18)	0.133 1(15)
O(2)	0.236 8(8)	0.710 7(13)	0.121 4(11)
C(3)	0.237 4(9)	0.548 7(15)	0.253 9(12)
O(3)	0.259 9(7)	0.551 6(11)	0.311 3(10)
C(4)	0.262 7(12)	0.385 8(17)	0.021 2(15)
O(4)	0.297 1(10)	0.335 9(15)	0.004 3(13)
C(5)	0.236 5(12)	0.545 9(22)	−0.006 5(16)
O(5)	0.254 1(8)	0.602 6(14)	−0.027 8(11)
C(6)	0.172 7(15)	0.411 4(22)	−0.049 6(21)
O(6)	0.150 8(10)	0.387 2(16)	−0.096 6(15)
C(7)	0.245 0(12)	0.300 0(19)	0.178 2(16)
O(7)	0.284 0(9)	0.253 9(13)	0.180 1(12)
C(8)	0.186 8(10)	0.375 2(16)	0.279 4(15)
O(8)	0.183 9(7)	0.386 0(12)	0.341 7(11)
C(9)	0.141 6(10)	0.272 8(17)	0.175 8(14)
O(9)	0.115 4(8)	0.212 7(13)	0.176 5(11)
C(10)	0.070 9(9)	0.421 7(14)	0.248 1(12)
O(10)	0.055 4(7)	0.395 8(11)	0.303 9(9)
C(11)	0.056 5(9)	0.378 7(14)	0.108 3(12)
O(11)	0.036 7(7)	0.326 8(11)	0.073 8(10)
C(12)	0.039 1(10)	0.537 6(16)	0.150 2(13)
O(12)	0.001 9(8)	0.579 9(12)	0.150 7(10)
N	0.139 7(7)	0.516 4(10)	0.081 3(9)
O	0.126 5(8)	0.649 3(12)	0.039 9(11)
C(13)	0.117 3(9)	0.576 8(14)	0.033 3(13)
C(14)	0.078 4(11)	0.545 7(19)	−0.024 0(15)
C(16)	0.356 6(6)	0.378 4(9)	0.317 4(8)
C(17)	0.367 6(6)	0.363 9(9)	0.391 4(8)
C(18)	0.398 3(6)	0.420 8(9)	0.431 9(8)
C(19)	0.418 1(6)	0.492 2(9)	0.398 4(8)
C(20)	0.407 2(6)	0.506 7(9)	0.324 5(8)
C(15)	0.376 4(6)	0.449 8(9)	0.284 0(8)
C(22)	0.442 4(6)	0.334 0(9)	0.186 4(6)
C(23)	0.477 7(6)	0.281 6(9)	0.151 4(6)
C(24)	0.478 8(6)	0.280 5(9)	0.075 5(6)
C(25)	0.444 6(6)	0.331 9(9)	0.034 5(6)
C(26)	0.409 3(6)	0.384 3(9)	0.069 4(6)
C(21)	0.408 2(6)	0.385 3(9)	0.145 4(6)
C(28)	0.446 4(5)	0.576 3(8)	0.165 5(8)
C(29)	0.466 3(5)	0.652 8(8)	0.141 7(8)
C(32)	0.431 8(5)	0.713 7(8)	0.113 4(8)
C(33)	0.377 6(5)	0.698 1(8)	0.108 8(8)
C(34)	0.357 8(5)	0.621 6(8)	0.132 6(8)
C(27)	0.392 2(5)	0.560 8(8)	0.160 9(8)

The solution was stirred for *ca.* 3 h at room temperature and the volume reduced under vacuum. Thin-layer chromatography using hexane–dichloromethane (1:1) gave a green band which was extracted with CH_2Cl_2. Green crystals were obtained upon crystallization from a hexane–dichloromethane mixture. Yield: 77 mg, 40%.

$[Os_4H_3(CO)_{12}X]$ (X = Cl, Br, *or* I). In a typical experiment $[N(PPh_3)_2][I]$ (42 mg, 63 × 10^{-3} mmol) was slowly added over a period of *ca.* 0.5 h to a solution of $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (80 mg, 63 × 10^{-3} mmol) in acetonitrile (80 cm^3). The solution was stirred for *ca.* 2 h at room temperature. Reduction of the volume under vacuum results in precipitation of yellow microcrystals of the required compound. Yield: 69 mg, 90%. Shorter reaction times are required for X = Br. The reaction for X = Cl only takes a few minutes. The complexes can also be purified by t.l.c. using hexane–dichloromethane (8:2) as eluant.

$[N(PPh_3)_2][Os_4H_2(CO)_{12}X]$ (X = Cl, Br, *or* I). In a typical experiment $[N(PPh_3)_2][Cl]$ (72 mg, 126 × 10^{-3} mmol) was slowly added over *ca.* 10 min to a solution of $[Os_4H_3(CO)_{12}(NCMe)_2][BF_4]$ (80 mg, 63 × 10^{-3} mmol) in acetonitrile (80 cm^3). The originally yellow solution became orange. The solution was stirred for *ca.* 0.5 h at room temperature. The solvent was evaporated to dryness and the compound extracted with diethyl ether. Thin-layer chromatography using hexane–dichloromethane (3:7) gave a red band which was extracted with CH_2Cl_2. Orange crystals were obtained upon crystallization from diethyl ether. Yield: 29 mg, 40%. The complexes are obtained as oily materials which are sometimes difficult to crystallize.

Interaction of $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$ *with* CF_3SO_3R (R = Me *or* Et).—In a typical experiment CF_3SO_3Et (8 μl) was added to a solution of $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$ (80 mg, 44 × 10^{-3} mmol) in $CDCl_3$ (*ca.* 1 cm^3). The reaction was carried out at 273 K and monitored by ^1H n.m.r. spectroscopy. The originally orange solution became dark red. After *ca.* 3 h the pair of doublets attributed to compound (**11**) were replaced by two pairs of doublets assigned to species (**12**) and (**13**). The reaction was also carried out at 300 K with similar results, however a shorter time (*ca.* 1 h) is required at this temperature. Preparation of the sample either in a dry-box or in the presence of air yielded the same result.

Addition of $[N(PPh_3)_2][BH_4]$ (48 mg, 80 × 10^{-3} mmol) at room temperature resulted in evolution of a gas with concomitant regeneration of $[N(PPh_3)_2][Os_4H_2(CO)_{12}I]$. All ^1H n.m.r. spectra were recorded at 253 K.

Crystallography.—Crystal data and details of measurements for compounds (**3**), (**4**), and (**11**) are reported in Table 5. The diffraction experiments were carried out on an Enraf-Nonius CAD4 diffractometer equipped with Mo-K_α radiation, at room temperature. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 well centred high-θ reflections. Diffraction intensities were corrected for Lorentz and polarization factors. An empirical absorption correction was applied by measuring azimuthal reflections ($\chi > 80°$).

The structures of compounds (**3**) and (**11**) were solved by Patterson and direct methods which afforded the positions of a metal triangle. The remaining heavy atoms and the light atoms were located by subsequent Fourier and Fourier-difference maps. Crystals of (**4**) were found to be isomorphous with those of (**3**) so that co-ordinates from the latter could be used as preliminary input in the refinement of (**4**). For all calculations the SHELX[29] package of crystallographic programs was used. Metal atoms and P atoms were allowed to vibrate anisotropically, all light atoms isotropically. Phenyl groups of the PPh_3 ligands and of the $[N(PPh_3)_2]^+$ cations were treated as rigid bodies [C–C–C 120°, C–C 1.40 Å]. Hydrogen atoms were added in calculated positions and not refined, though their contributions to the structure factors were taken into account. Residual peaks occurred at *ca.* 3, 1, and 1.5 e Å^{-3} for (**3**), (**4**), and (**11**), and were located in the vicinity of the metal atoms. In the

Table 8. Fractional atomic co-ordinates for compound (**11**)

Atom	*x*	*y*	*z*
Os(1)	0.568 86(6)	0.0629 1(4)	0.858 18(4)
Os(2)	0.431 38(5)	0.149 41(4)	0.865 91(4)
Os(3)	0.426 80(6)	0.030 00(4)	0.810 75(4)
Os(4)	0.432 50(6)	0.0262 3(4)	0.905 21(4)
I(1)	0.710 51(10)	0.127 40(8)	0.864 98(7)
Os(5)	0.346 32(6)	0.153 32(4)	0.402 56(4)
Os(6)	0.473 03(5)	0.145 82(4)	0.332 29(4)
Os(7)	0.506 25(6)	0.167 45(4)	0.429 53(4)
Os(8)	0.450 83(6)	0.048 64(4)	0.397 93(4)
I(2)	0.207 93(10)	0.202 46(9)	0.367 69(8)
P(1)	0.943 6(3)	0.175 0(2)	0.113 7(2)
P(2)	1.039 4(3)	0.058 7(2)	0.126 0(2)
P(3)	0.072 7(3)	0.200 7(2)	0.635 0(2)
P(4)	0.007 1(3)	0.069 9(2)	0.626 6(2)
C(1)	0.578 7(13)	0.073 2(10)	0.795 5(6)
O(1)	0.600 0(9)	0.087 4(7)	0.758 9(6)
C(2)	0.572 6(13)	0.064 7(10)	0.920 9(6)
O(2)	0.597 3(9)	0.070 4(7)	0.959 2(6)
C(3)	0.616 2(12)	−0.018 8(8)	0.858 6(9)
O(3)	0.642 5(9)	−0.068 3(7)	0.858 8(6)
C(4)	0.469 0(13)	0.189 2(10)	0.920 4(7)
O(4)	0.493 6(10)	0.213 1(7)	0.952 3(6)
C(5)	0.435 5(17)	0.219 9(12)	0.825 1(10)
O(5)	0.432 5(12)	0.265 3(9)	0.803 8(8)
C(6)	0.326 1(12)	0.156 6(11)	0.882 5(9)
O(6)	0.264 0(11)	0.160 1(8)	0.895 6(7)
C(7)	0.435 1(13)	0.045 8(10)	0.748 9(7)
O(7)	0.438 5(10)	0.058 0(8)	0.710 5(6)
C(8)	0.319 8(11)	0.009 9(10)	0.806 8(9)
O(8)	0.254 5(10)	−0.005 7(8)	0.800 8(7)
C(9)	0.456 3(12)	−0.056 5(8)	0.807 1(8)
O(9)	0.475 8(9)	−0.109 4(7)	0.803 6(6)
C(10)	0.427 0(14)	0.052 7(11)	0.965 3(7)
O(10)	0.416 6(11)	0.074 3(8)	1.000 3(7)
C(11)	0.466 8(14)	−0.059 8(9)	0.915 0(9)
O(11)	0.492 3(9)	−0.111 2(7)	0.919 7(6)
C(12)	0.326 2(12)	0.002 8(12)	0.900 4(11)
O(12)	0.261 4(11)	−0.009 8(9)	0.904 0(7)
C(13)	0.308 3(14)	0.072 3(10)	0.379 2(9)
O(13)	0.263 4(9)	0.033 2(7)	0.366 1(6)
C(14)	0.366 7(14)	0.238 6(9)	0.421 5(9)
O(14)	0.364 2(10)	0.291 6(8)	0.432 7(7)
C(15)	0.308 3(14)	0.137 9(10)	0.459 4(7)
O(15)	0.289 7(9)	0.120 3(7)	0.494 8(6)
C(16)	0.571 8(11)	0.111 9(10)	0.319 8(9)
O(16)	0.632 2(9)	0.091 7(7)	0.310 5(6)
C(17)	0.423 6(11)	0.092 4(9)	0.289 8(7)
O(17)	0.389 7(8)	0.059 1(6)	0.265 3(6)
C(18)	0.482 9(13)	0.216 9(9)	0.291 1(8)
O(18)	0.493 5(9)	0.257 4(7)	0.267 4(6)
C(19)	0.528 3(14)	0.252 3(9)	0.446 6(9)
O(19)	0.538 4(9)	0.304 5(7)	0.459 0(6)
C(20)	0.489 8(14)	0.138 2(10)	0.488 6(7)
O(20)	0.479 7(10)	0.118 1(7)	0.524 9(6)
C(21)	0.612 7(11)	0.143 8(10)	0.429 5(9)
O(21)	0.677 7(9)	0.130 5(7)	0.432 5(6)
C(22)	0.555 7(11)	0.014 2(10)	0.400 9(9)
O(22)	0.618 6(9)	−0.005 4(7)	0.403 0(6)
C(23)	0.421 9(13)	0.011 6(10)	0.453 4(7)
O(23)	0.396 4(9)	−0.012 8(7)	0.484 2(6)
C(24)	0.415 8(13)	−0.019 8(10)	0.361 1(8)
O(24)	0.398 3(9)	−0.062 6(7)	0.338 8(6)
N(1)	0.964 6(8)	0.102 4(6)	0.125 2(6)
C(111)	0.884 0(7)	0.178 2(7)	0.062 6(4)
C(112)	0.852 6(7)	0.121 6(7)	0.003 6(4)
C(113)	0.806 9(7)	0.124 3(7)	−0.017 7(4)
C(114)	0.792 6(7)	0.183 6(7)	0.043 8(4)
C(115)	0.824 0(7)	0.240 2(7)	0.001 2(4)
C(116)	0.869 7(7)	0.237 5(7)	0.041 3(4)
C(121)	1.025 3(6)	0.226 8(5)	0.106 2(6)
C(122)	1.056 9(6)	0.233 5(5)	0.062 6(6)
C(123)	1.128 0(6)	0.267 0(5)	0.056 9(6)
C(124)	1.167 4(6)	0.293 7(5)	0.094 6(6)
C(125)	1.135 9(6)	0.286 9(5)	0.138 2(6)
C(126)	1.064 8(6)	0.253 5(5)	0.144 0(6)
C(131)	0.882 8(7)	0.206 0(6)	0.159 0(4)
C(132)	0.848 3(7)	0.162 8(6)	0.189 4(4)
C(133)	0.801 0(7)	0.185 8(6)	0.224 6(4)
C(134)	0.788 1(7)	0.252 0(6)	0.229 3(4)
C(135)	0.822 6(7)	0.295 2(6)	0.198 9(4)
C(136)	0.870 0(7)	0.272 2(6)	0.163 8(4)
C(211)	1.104 0(8)	0.070 8(6)	0.078 1(5)
C(212)	1.182 1(8)	0.092 4(6)	0.083 5(5)
C(213)	1.228 7(8)	0.102 7(6)	0.045 2(5)
C(214)	1.197 3(8)	0.091 5(6)	0.001 5(5)
C(215)	1.119 2(8)	0.070 0(6)	−0.003 9(5)
C(216)	1.072 5(8)	0.059 6(6)	0.034 4(5)
C(221)	1.098 5(7)	0.065 2(6)	0.177 6(4)
C(222)	1.167 1(7)	0.028 3(6)	0.184 3(4)
C(223)	1.211 3(7)	0.034 3(6)	0.224 8(4)
C(224)	1.187 0(7)	0.077 2(6)	0.258 6(4)
C(225)	1.118 5(7)	0.114 0(6)	0.251 9(4)
C(226)	1.074 2(7)	0.108 0(6)	0.211 4(4)
C(231)	1.007 9(8)	−0.022 7(4)	0.121 9(5)
C(232)	1.054 1(8)	−0.070 6(4)	0.101 9(5)
C(233)	1.027 3(8)	−0.134 4(4)	0.100 8(5)
C(234)	0.954 2(8)	−0.150 2(4)	0.119 7(5)
C(235)	0.908 1(8)	−0.012 3(4)	0.139 7(5)
C(236)	0.934 9(8)	−0.038 5(4)	0.140 8(5)
N(2)	0.063 5(9)	0.129 3(7)	0.616 6(6)
C(311)	0.132 7(8)	0.244 6(6)	0.596 3(5)
C(312)	0.153 5(8)	0.308 1(6)	0.606 9(5)
C(313)	0.196 6(8)	0.344 9(6)	0.576 0(5)
C(314)	0.219 0(8)	0.318 0(6)	0.534 4(5)
C(315)	0.198 2(8)	0.254 5(6)	0.523 7(5)
C(316)	0.155 1(8)	0.217 8(6)	0.554 7(5)
C(321)	0.121 2(8)	0.203 0(7)	0.690 4(4)
C(322)	0.122 4(8)	0.258 3(7)	0.717 7(4)
C(323)	0.164 0(8)	0.258 2(7)	0.759 3(4)
C(324)	0.204 4(8)	0.202 8(7)	0.773 7(4)
C(325)	0.203 3(8)	0.147 5(7)	0.746 4(4)
C(326)	0.161 7(8)	0.147 6(7)	0.704 8(4)
C(331)	−0.018 3(7)	0.244 5(6)	0.639 5(7)
C(332)	−0.059 1(7)	0.249 7(6)	0.680 4(7)
C(333)	−0.130 9(7)	0.283 3(6)	0.681 7(7)
C(334)	−0.161 8(7)	0.311 8(6)	0.642 0(7)
C(335)	−0.121 0(7)	0.306 6(6)	0.601 1(7)
C(336)	−0.049 3(7)	0.273 0(6)	0.599 8(7)
C(411)	−0.047 1(9)	0.048 3(9)	0.575 9(5)
C(412)	−0.050 0(9)	0.088 1(9)	0.537 4(5)
C(413)	−0.096 8(9)	0.070 7(9)	0.499 5(5)
C(414)	−0.140 6(9)	0.013 5(9)	0.500 2(5)
C(415)	−0.137 6(9)	−0.026 3(9)	0.538 6(5)
C(416)	−0.090 9(9)	−0.008 9(9)	0.576 5(5)
C(421)	0.067 1(8)	0.001 9(6)	0.641 6(5)
C(422)	0.145 3(8)	0.001 1(6)	0.626 7(5)
C(423)	0.193 0(8)	−0.053 0(6)	0.634 9(5)
C(424)	0.162 3(8)	−0.106 2(6)	0.657 9(5)
C(425)	0.084 0(8)	−0.105 4(6)	0.672 8(5)
C(426)	0.036 4(8)	−0.051 3(6)	0.664 6(5)
C(431)	−0.061 6(8)	0.080 5(5)	0.672 8(5)
C(432)	−0.140 3(8)	0.097 6(5)	0.663 5(5)
C(433)	−0.190 1(8)	0.114 8(5)	0.699 2(5)
C(434)	−0.161 2(8)	0.114 8(5)	0.744 1(5)
C(435)	−0.082 5(8)	0.097 7(5)	0.753 4(5)
C(436)	−0.032 7(8)	0.805 5(5)	0.717 8(5)

case of (**3**) they were attributed to a not completely satisfactory absorption correction.

The co-ordinates of all non-hydrogen atoms for (**3**), (**4**), and (**11**) are reported in Tables 6—8. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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