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THE FIRST NITROSYL DERIVATIVES OF HIGH NUCLEARITY CARBONYL CLUSTERS: SYNTHESIS AND X-RAY ANALYSIS OF THE $[(Ph_3P)_2N]^+$ SALTS OF THE ANIONS $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ AND $[Os_{10}C(CO)_{23}(NO)]^-$

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Summary

The carbido dianion $[Os_{10}C(CO)_{24}]^{2-}$ reacts with $NOBF_4$ in MeCN to give $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ (**1**) in which the nitrosyl ligand adopts a novel bonding mode bridging the wingtips of a "butterfly" indentation of metal atoms. The anion **1** undergoes rearrangement and CO loss in solution to give $[Os_{10}C(CO)_{23}(NO)]^-$ (**2**); the overall molecular geometry of **2** is close to that previously found for the dianion $[Os_{10}C(CO)_{24}]^{2-}$ with the nitrosyl ligand bonded in a terminal fashion to the tetrahedral Os_{10} metal skeleton. Crystals of the $[(Ph_3P)_2N]^+$ salt of **1** are triclinic, space group $P\bar{1}$, with *a* 20.389(4), *b* 14.670(3), *c* 12.333(3) Å, α 99.55(3), β 94.43(3), γ 103.03(3)°, $Z = 2$, refinement of atomic parameters using 2699 absorption corrected data converged at $R = 0.0952$. The $[(Ph_3P)_2N]^+$ salt of **2** crystallises with one molecule of CH_2Cl_2 in the triclinic space group $P\bar{1}$, with *a* 19.374(3), *b* 16.813(3), *c* 11.791(2) Å, α 85.00(3), β 101.81(3), γ 99.43(3)°, $Z = 2$, refinement of atomic parameters using 8736 absorption corrected data converged at $R = 0.0943$.

Introduction

The presence of nitrosyl ligands in metal carbonyl cluster compounds has been shown to produce enhanced reactivity [1]. Although a number of trinuclear [1–3] and tetranuclear [4–5] carbonyl clusters have recently been prepared which contain the NO ligand, the only higher nuclearity examples known are the hexaruthenium species $[Ru_6C(CO)_{15}(NO)]^-$, $Ru_6C(CO)_{14}(NO)_2$, $Ru_6C(CO)_{15}(NO)AuPPh_3$ [7], and $HRu_6C(CO)_{15}(NO)$ [8]. In these Ru_6 systems the NO ligand is bonded in a terminal linear manner. We now report the reaction of the carbido dianion $[Os_{10}C(CO)_{24}]^{2-}$ with $NOBF_4$ in MeCN which has yielded the first high nuclearity osmium nitrosyl clusters, $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ (**1**) [1] and $[Os_{10}C(CO)_{23}(NO)]^-$ (**2**).

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Results and discussion

Two methods are commonly used to introduce a nitrosyl ligand into a carbonyl cluster: (i) reaction of a neutral carbonyl species with $[(Ph_3P)_2N][NO_2]$ [3,7] and (ii) reaction of an anionic carbonyl cluster with NO^+. We have successfully used the latter method to prepare several trinuclear [2] and tetranuclear [4,9] nitrosyl (and nitrido) clusters of ruthenium and osmium. However, to avoid the formation of undesirable products it is important to use freshly sublimed nitrosonium salts and well dried solvents [10]. Another aspect of NO^+ that makes it a less than ideal reagent for nitrosylation is the fact that it is often more effective as an oxidant so that no nitrosyl containing product is formed [11]. This limitation has prompted Gladfelter to explore methods of reducing the likelihood of oxidation, while still allowing nitrosylations to occur at lower temperature, by stabilising NO^+ with an electron pair donor [12].

As part of our studies of the reactions of NO^+ with osmium carbonyl cluster anions, we have investigated the reaction of NO^+ with $[Os_{10}C(CO)_{24}]^{2-}$, which has previously been shown to react with a range of electrophiles [13]. Addition of 1 equivalent of $NOBF_4$ to a solution of $[X]_2[Os_{10}C(CO)_{24}]$ ($X = (Ph_3P)_2N$, Ph_3MeP or Ph_4As) in MeCN gives the $[X]^+$ salt of the new anion $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ (**1**), which was characterised on the basis of its analytical and spectroscopic properties (Table 1). The IR spectrum of **1** in the region 2070–2000 cm^{-1} is very similar to that reported for the iodo monoanion $[Os_{10}C(CO)_{24}(\mu_2\text{-}I)]^-$ [14], in addition a weak broad absorption is present at 1603 cm^{-1} also consistent with the presence of a bridging NO ligand. After much experimental difficulty (vide infra) crystals of the $[(Ph_3P)_2N]^+$ salt of **1** suitable for X-ray analysis were grown overnight at 25°C from CH_2Cl_2/hexane using the slow evaporation technique; the structure of the anion **1** is shown in Fig. 1 and some important bond distances and angles are given in Tables 2 and 3 respectively.

The structure of the monoanion **1** closely resembles that observed for the iodo monoanion $[Os_{10}C(CO)_{24}I]^-$ formed by electrophilic attack by "I^+" on the dianion $[Os_{10}C(CO)_{24}]^{2-}$ [14]. Both structures have 'butterfly' indentations on the cluster surface bridged by the formally cationic NO^+ or I^+ ligands (both 2e donors) and formed by the breaking of an Os–Os bond of a capping tetrahedron. The 'wingtip' Os–Os distances in **2** and $[Os_{10}C(CO)_{24}I]^-$ are 3.517 and 3.907 Å respectively, reflecting the difference in metal–ligand bond lengths for NO and I.

Over a period of ca. ten days the anion **1** undergoes rearrangement and CO loss in solution to give a new anion **2**. The IR spectrum changes (Table 1) and its overall

(Continued on p. 178)

TABLE 1

INFRARED DATA FOR COMPOUNDS 1 AND 2

Compound [a]	$\nu(CO)$ (ν(N–O)) (cm^{-1}) [b]
$[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ (**1**)	2066s, 2056vs, 2031w, 2013s, 2005 ssh (1603wbr)
$[Os_0C(CO)_{24}(\mu_2\text{-}I)]^-$	2065s, 2057vs, 2017m, 2004s
$[Os_{10}C(CO)_{23}(NO)]^-$ (**2**)	2054s, 2046ssh, 2006s (1760m)
$[Os_{10}C(CO)_{24}]^{2-}$	2035s, 1987s [15]

[a] $[(Ph_3P)_2N]^+$ salts. [b] In CH_2Cl_2.

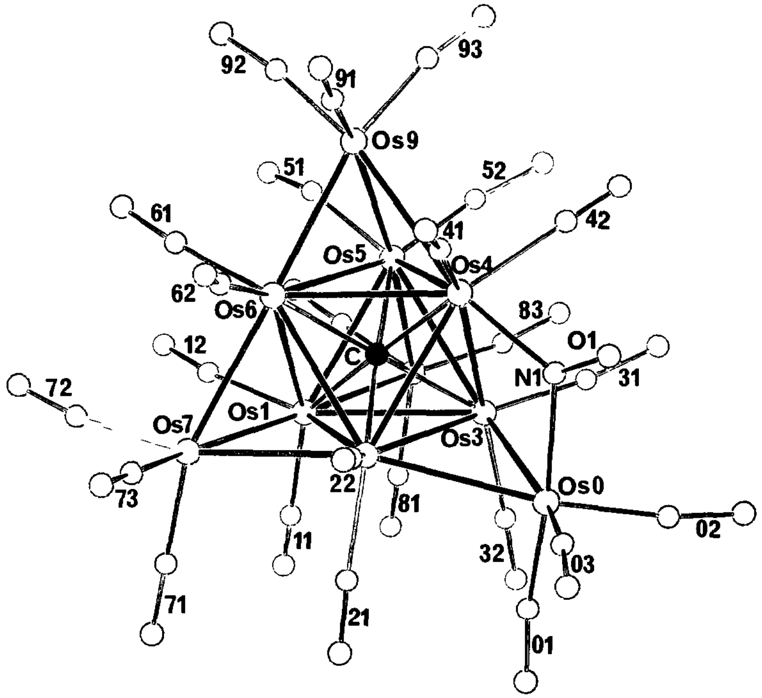

Fig. 1. The structure of the $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ anion (**1**) and the numbering scheme; the first digit of the carbonyl ligands is the number of the osmium atom to which it is attached.

TABLE 2

SELECTED BOND LENGTHS (Å) FOR $[(Ph_3P)_2N][Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]$ (**1**)

Os(1)–Os(2)	2.889(6)	Os(1)–Os(3)	2.876(6)
Os(1)–Os(5)	2.847(7)	Os(1)–Os(6)	2.912(6)
Os(1)–Os(7)	2.789(6)	Os(1)–Os(8)	2.795(6)
Os(1)–C	2.07(8)		
		Os(2)–Os(3)	2.957(6)
Os(2)–Os(4)	2.906(7)	Os(2)–Os(6)	2.907(6)
Os(2)–Os(7)	2.830(6)	Os(2)–Os(0)	2.887(7)
Os(2)–C	2.01(7)		
		Os(3)–Os(4)	2.984(6)
Os(3)–Os(5)	2.897(6)	Os(3)–Os(8)	2.831(6)
Os(3)–Os(0)	2.859(7)	Os(3)–C	2.18(6)
Os(4)–Os(5)	2.919(6)	Os(4)–Os(6)	2.928(7)
Os(4)–Os(9)	2.960(6)	Os(4)–C	2.03(8)
Os(4)–N(1)	2.09(7)		
		Os(5)–Os(6)	2.907(6)
Os(5)–Os(8)	2.839(6)	Os(5)–Os(9)	2.813(6)
Os(5)–C	2.07(7)		
		Os(6)–Os(7)	2.794(7)
Os(6)–Os(9)	2.730(7)	Os(6)–C	2.00(6)
Os(0)–N(1)	2.11(7)	N(1)–O(1)	1.23(9)
	Os–C(carbonyl)	2.12–1.77	
	Os–C(mean)	1.92	
	C–O	0.98–1.34	
	C–O(mean)	1.18	

TABLE 3

SELECTED BOND ANGLES (°) FOR $[(Ph_3P)_2N][Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]$ (**1**)

Os(3)–Os(1)–Os(2)	61.7(1)	Os(5)–Os(1)–Os(2)	90.6(2)
Os(5)–Os(1)–Os(3)	60.8(2)	Os(6)–Os(1)–Os(2)	60.1(1)
Os(6)–Os(1)–Os(3)	92.3(2)	Os(6)–Os(1)–Os(5)	60.6(2)
Os(7)–Os(1)–Os(2)	59.8(2)	Os(7)–Os(1)–Os(3)	121.5(2)
Os(7)–Os(1)–Os(5)	119 3(2)	Os(7)–Os(1)–Os(6)	58.6(2)
Os(8)–Os(1)–Os(2)	121.6(2)	Os(8)–Os(1)–Os(3)	59 9(2)
Os(8)–Os(1)–Os(5)	60.4(2)	Os(8)–Os(1)–Os(6)	121.1(2)
Os(8)–Os(1)–Os(7)	178 4(2)		
C(11)–Os(1)–Os(3)	102(3)	C(11)–Os(1)–Os(2)	101(3)
C(11)–Os(1)–Os(6)	147(3)	C(11)–Os(1)–Os(5)	152(3)
C(11)–Os(1)–Os(8)	92(3)	C(11)–Os(1)–Os(7)	89(3)
C(12)–Os(1)–Os(2)	142(3)	C(12)–Os(1)–Os(3)	150(4)
C(12)–Os(1)–Os(5)	96(4)	C(12)–Os(1)–Os(6)	91(3)
C(12)–Os(1)–Os(7)	85(3)	C(12)–Os(1)–Os(8)	94(3)
Os(3)–Os(2)–Os(1)	58.9(1)	Os(4)–Os(2)–Os(1)	90.0(2)
Os(4)–Os(2)–Os(3)	61.2(2)	Os(6)–Os(2)–Os(1)	60.3(1)
Os(6)–Os(2)–Os(3)	90.8(2)	Os(6)–Os(2)–Os(4)	60.5(2)
Os(7)–Os(2)–Os(1)	58.4(1)	Os(7)–Os(2)–Os(3)	117.3(2)
Os(7)–Os(2)–Os(4)	118.7(2)	Os(7)–Os(2)–Os(6)	58.3(2)
Os(0)–Os(2)–Os(1)	115.1(2)	Os(0)–Os(2)–Os(3)	58.6(2)
Os(0)–Os(2)–Os(4)	74.8(2)	Os(0)–Os(2)–Os(6)	134 5(2)
Os(0)–Os(2)–Os(7)	163.3(2)		
C(21)–Os(2)–Os(3)	105(2)	C(21)–Os(2)–Os(1)	95(2)
C(21)–Os(2)–Os(6)	139(2)	C(21)–Os(2)–Os(4)	159(2)
C(21)–Os(2)–Os(0)	85(2)	C(21)–Os(2)–Os(7)	81(2)
C(22)–Os(2)–Os(1)	157(1)	C(22)–Os(2)–Os(3)	141(2)
C(22)–Os(2)–Os(4)	95(3)	C(22)–Os(2)–Os(6)	103(3)
C(22)–Os(2)–Os(7)	100(1)	C(22)–Os(2)–Os(0)	87(1)
Os(2)–Os(3)–Os(1)	59.4(1)	Os(4)–Os(3)–Os(1)	88.7(2)
Os(4)–Os(3)–Os(2)	58.6(1)	Os(5)–Os(3)–Os(1)	59.1(2)
Os(5)–Os(3)–Os(2)	88.2(2)	Os(5)–Os(3)–Os(4)	59.5(1)
Os(8)–Os(3)–Os(1)	58.6(2)	Os(8)–Os(3)–Os(2)	118.0(2)
Os(8)–Os(3)–Os(4)	118.9(2)	Os(8)–Os(3)–Os(5)	59.4(1)
Os(0)–Os(3)–Os(1)	116.4(2)	Os(0)–Os(3)–Os(2)	59.5(2)
Os(0)–Os(3)–Os(4)	74.0(2)	Os(0)–Os(3)–Os(5)	132.9(2)
Os(0)–Os(3)–Os(8)	164.5(2)		
C(31)–Os(3)–Os(2)	143(4)	C(31)–Os(3)–Os(1)	152(4)
C(31)–Os(3)–Os(5)	99(4)	C(31)–Os(3)–Os(4)	94(3)
C(31)–Os(3)–Os(0)	91(4)	C(31)–Os(3)–Os(8)	96(4)
C(32)–Os(3)–Os(1)	95(3)	C(32)–Os(3)–Os(2)	106(3)
C(32)–Os(3)–Os(4)	159(2)	C(32)–Os(3)–Os(5)	139(3)
C(32)–Os(3)–Os(8)	80(2)	C(32)–Os(3)–Os(0)	86(2)
Os(3)–Os(4)–Os(2)	60.3(1)	Os(5)–Os(4)–Os(2)	88.8(2)
Os(5)–Os(4)–Os(3)	58.8(1)	Os(6)–Os(4)–Os(2)	59.8(2)
Os(6)–Os(4)–Os(3)	89.8(2)	Os(6)–Os(4)–Os(5)	59.6(1)
Os(9)–Os(4)–Os(2)	115.0(2)	Os(9)–Os(4)–Os(3)	115.9(2)
Os(9)–Os(4)–Os(5)	57 2(1)	Os(9)–Os(4)–Os(6)	55.2(2)
N(1)–Os(4)–Os(3)	78(2)	N(1)–Os(4)–Os(2)	81(2)
N(1)–Os(4)–Os(6)	140(2)	N(1)–Os(4)–Os(5)	134(2)
C(41)–Os(4)–Os(3)	162(4)	N(1)–Os(4)–Os(9)	162(2)
C(41)–Os(4)–Os(6)	88(4)	C(41)–Os(4)–Os(2)	103(4)
C(42)–Os(4)–Os(2)	155(2)	C(41)–Os(4)–Os(5)	134(3)

TABLE 3 (continued)

C(42)–Os(4)–Os(5)	90(3)	C(41)–Os(4)–Os(9)	77(3)
C(42)–Os(4)–Os(9)	85(2)	C(41)–Os(4)–N(1)	92(4)
C(42)–Os(4)–N(1)	82(3)	C(42)–Os(4)–Os(3)	98(2)
		C(42)–Os(4)–Os(6)	138(3)
Os(3)–Os(5)–Os(1)	60.1(2)	Os(4)–Os(5)–Os(1)	90.6(2)
Os(4)–Os(5)–Os(4)	61.7(1)	Os(6)–Os(5)–Os(1)	60.8(2)
Os(6)–Os(5)–Os(3)	92.0(2)	Os(6)–Os(5)–Os(4)	60.3(2)
Os(8)–Os(5)–Os(1)	58.9(2)	Os(8)–Os(5)–Os(3)	59.1(1)
Os(8)–Os(5)–Os(4)	120.8(2)	Os(8)–Os(5)–Os(6)	119.7(2)
Os(9)–Os(5)–Os(1)	117.7(2)	Os(9)–Os(5)–Os(3)	123.8(2)
Os(9)–Os(5)–Os(4)	62.2(2)	Os(9)–Os(5)–Os(6)	57.0(2)
Os(9)–Os(5)–Os(8)	174.6(2)		
C(51)–Os(5)–Os(3)	150(3)	C(51)–Os(5)–Os(1)	99(3)
C(51)–Os(5)–Os(6)	95(3)	C(51)–Os(5)–Os(4)	145(3)
C(51)–Os(5)–Os(9)	84(3)	C(51)–Os(5)–Os(8)	93(3)
C(52)–Os(5)–Os(1)	144(2)	C(52)–Os(5)–Os(3)	98(3)
C(52)–Os(5)–Os(4)	104(4)	C(52)–Os(5)–Os(6)	154(2)
C(52)–Os(5)–Os(8)	86(2)	C(52)–Os(5)–Os(9)	98(2)
Os(2)–Os(6)–Os(1)	59.5(1)	Os(4)–Os(6)–Os(1)	89.1(2)
Os(4)–Os(6)–Os(2)	59.7(2)	Os(5)–Os(6)–Os(1)	58.6(1)
Os(5)–Os(6)–Os(2)	89.0(2)	Os(5)–Os(6)–Os(4)	60.0(2)
Os(7)–Os(6)–Os(1)	58.5(2)	Os(7)–Os(6)–Os(2)	59.5(2)
Os(7)–Os(6)–Os(4)	119.2(2)	Os(7)–Os(6)–Os(5)	117.0(2)
Os(9)–Os(6)–Os(1)	118.2(2)	Os(9)–Os(6)–Os(2)	122.7(2)
Os(9)–Os(6)–Os(4)	63.0(2)	Os(9)–Os(6)–Os(5)	59.8(2)
Os(9)–Os(6)–Os(7)	175.2(2)		
C(61)–Os(6)–Os(2)	148(3)	C(61)–Os(6)–Os(1)	98(2)
C(61)–Os(6)–Os(5)	99(2)	C(61)–Os(6)–Os(4)	149(3)
C(61)–Os(6)–Os(9)	87(3)	C(61)–Os(6)–Os(7)	90(3)
C(62)–Os(6)–Os(1)	142(3)	C(62)–Os(6)–Os(2)	97(3)
C(62)–Os(6)–Os(4)	105(3)	C(62)–Os(6)–Os(5)	157(3)
C(62)–Os(6)–Os(7)	84(3)	C(62)–Os(6)–Os(9)	99(3)
		C(62)–Os(6)–C(61)	88(4)
Os(2)–Os(7)–Os(1)	61.9(2)	Os(6)–Os(7)–Os(1)	62.9(2)
Os(6)–Os(7)–Os(2)	62.2(2)		
C(71)–Os(7)–Os(1)	98(3)	C(71)–Os(7)–Os(2)	101(3)
C(71)–Os(7)–Os(6)	159(3)		
C(72)–Os(7)–Os(1)	109(3)	C(72)–Os(7)–Os(2)	164(4)
C(72)–Os(7)–Os(6)	102(4)	C(73)–Os(7)–Os(1)	160(3)
C(73)–Os(7)–Os(2)	99(3)	C(73)–Os(7)–Os(6)	104(3)
Os(3)–Os(8)–Os(1)	61.5(2)	Os(5)–Os(8)–Os(1)	60.7(2)
Os(5)–Os(8)–Os(3)	61.5(2)	C(81)–Os(8)–Os(1)	97(2)
C(81)–Os(8)–Os(3)	105(3)	C(81)–Os(8)–Os(5)	157(2)
C(82)–Os(8)–Os(1)	106(2)	C(82)–Os(8)–Os(3)	163(2)
C(82)–Os(8)–Os(5)	103(2)	C(83)–Os(8)–Os(3)	102(3)
C(83)–Os(8)–Os(1)	163(3)	Os(5)–Os(9)–Os(4)	60.7(2)
C(83)–Os(8)–Os(5)	109(3)	Os(6)–Os(9)–Os(5)	63.2(2)
Os(6)–Os(9)–Os(4)	61.8(2)	C(91)–Os(9)–Os(5)	157(4)
C(91)–Os(9)–Os(4)	98(4)	C(92)–Os(9)–Os(4)	167(4)
C(91)–Os(9)–Os(6)	99(4)	C(92)–Os(9)–Os(6)	106(4)
C(92)–Os(9)–Os(5)	110(3)	C(93)–Os(9)–Os(4)	107(4)
C(93)–Os(9)–Os(5)	95(3)	C(93)–Os(9)–Os(6)	158(3)

(continued)

TABLE 3 (continued)

Os(3)–Os(0)–Os(2)	61.9(2)		
N(1)–Os(0)–Os(2)	81(2)		
N(1)–Os(0)–Os(3)	80(2)		
C(01)–Os(0)–Os(2)	94(3)	C(01)–Os(0)–Os(3)	93(3)
C(01)–Os(0)–N(1)	173(4)	C(02)–Os(0)–Os(3)	104(3)
C(02)–Os(0)–Os(2)	166(3)	C(03)–Os(0)–Os(2)	105(2)
C(02)–Os(0)–N(1)	95(4)		
C(03)–Os(0)–Os(3)	165(2)		
C(03)–Os(0)–N(1)	91(2)		
		Os(0)–N(1)–Os(4)	114(4)
O(1)–N(1)–Os(4)	124(6)	O(1)–N(1)–Os(0)	121(6)

appearance in the carbonyl region more closely resembles (in pattern) that of the parent dianion $[Os_{10}C(CO)_{24}]^{2-}$ (Table 1) [15]. The ν(N–O) band at 1603 cm^{-1} is also replaced by one of medium-weak intensity at 1760 cm^{-1} which may be attributed to a terminally bound nitrosyl group. Microanalytical and spectroscopic data, together with an X-ray analysis of the $[(Ph_3P)_2N]^+$ salt (as its CH_2Cl_2 solvate) have shown the anion **2** to be $[Os_{10}C(CO)_{23}(NO)]^-$ with a molecular geometry

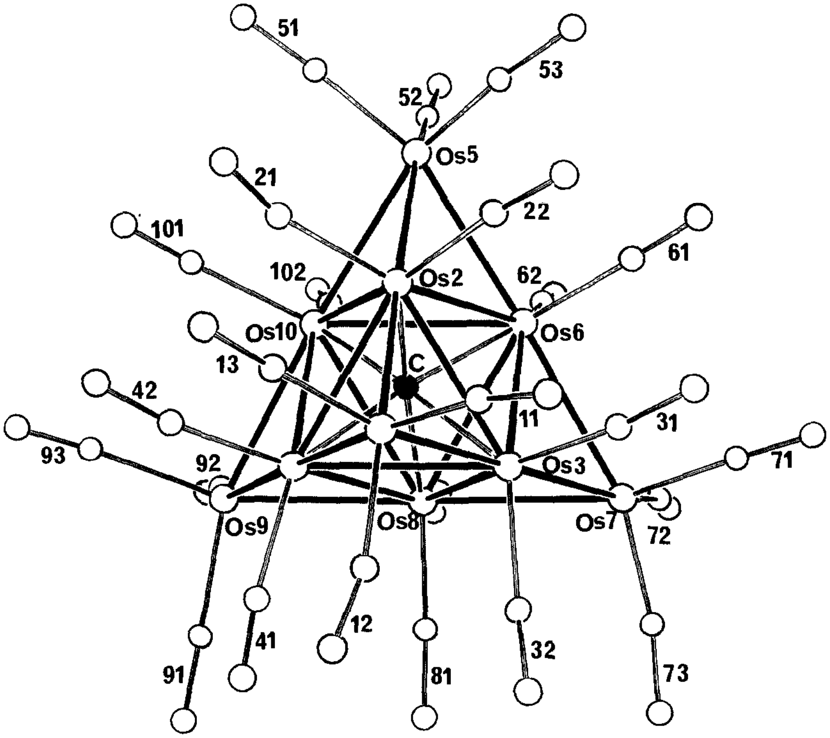

Fig. 2. The structure of the $[Os_{10}C(CO)_{23}(NO)]^-$ anion (**2**); the X-ray data did not allow distinction between the NO ligand and the CO ligands on the basis of thermal parameters. In the numbering scheme the first digit of the carbonyl ligand is the number of the osmium atom to which it is attached.

almost identical to that found for $[Os_{10}C(CO)_{24}]^{2-}$ [15]. The structure of **2** is shown in Fig. 2 and some important bond distances and angles are given in Tables 4 and 5 respectively. The terminal mode of NO bonding is clearly established although the X-ray data did not allow the nitrosyl ligand to be distinguished from the carbonyl ligands.

It is interesting to note that the nitrosyl species $H_3Os_4(CO)_{12}(\mu_2\text{-NO})$ [4,9] and $HOs_4(CO)_{13}(\mu_2\text{-NO})$ [9], which have "butterfly" metal arrangements, are apparently easily converted into the nitrido cluster $HOs_4(CO)_{11}N$, of similar metal geometry, via the loss of the elements of H_2O and CO_2 respectively. In contrast in the conversion of the anion **1** into **2** the nitrosyl ligand is retained, and closure of the "butterfly" indentation in the molecule occurs together with the concomitant loss of a CO ligand. A strong tendency for opened out derivatives of $[Os_{10}C(CO)_{24}]^{2-}$ to reform the tetrahedral symmetry $Os_{10}C$ metal skeleton has previously been noted, and for example the iodo monoanion $[Os_{10}C(CO)_{24}I]^-$ reacts with iodide to regenerate the closed structure of the $[Os_{10}C(CO)_{24}]^{2-}$ dianion [14].

The nitrosyl monoanion **2** has an almost identical overall geometry to that of the hydrido monoanion $[HOs_{10}C(CO)_{24}]^-$ [16]. As neither the hydrido ligand in $[HOs_{10}C(CO)_{24}]^-$ nor the nitrosyl ligand in **2** can be identified from X-ray data alone it is important to note that these two monoanions can clearly be distinguished from the relative sizes of the Os_4 capping groups. The monohydride (in the

(Continued on p. 182)

TABLE 4

BOND LENGTHS (Å) FOR $[(Ph_3P)_2N][Os_{10}C(CO)_{23}(NO)]$ (**2**)

Os(1)-Os(2)	2.779(2)	Os(1)-Os(3)	2.776(2)
Os(1)-Os(4)	2.794(2)		
Os(2)-Os(3)	2.872(2)	Os(2)-Os(4)	2.874(2)
Os(2)-Os(5)	2.789(2)	Os(2)-Os(6)	2.886(2)
Os(2)-Os(10)	2.892(2)	Os(2)-C	2.01(3)
Os(3)-Os(4)	2.892(2)	Os(3)-Os(6)	2.867(2)
Os(3)-Os(7)	2.784(2)	Os(3)-Os(8)	2.872(2)
Os(3)-C	2.05(3)		
Os(4)-Os(9)	2.781(2)	Os(4)-Os(8)	2.892(2)
Os(4)-C	2.07(4)	Os(4)-Os(10)	2.881(2)
Os(5)-Os(10)	2.796(2)	Os(5)-Os(6)	2.773(2)
Os(6)-Os(7)	2.784(2)	Os(6)-Os(8)	2.885(2)
Os(6)-Os(10)	2.896(2)	Os(6)-C	2.01(4)
Os(7)-Os(8)	2.777(2)		
Os(8)-Os(9)	2.767(2)	Os(8)-Os(10)	2.890(2)
Os(8)-C	2.07(3)		
Os(10)-C	2.03(3)	Os(9)-Os(10)	2.793(2)
	Os-C(carbonyl)	1.93-1.80	
	Os-C(mean)	1.84	
	C-O	1.12-1.30	
	C-O(mean)	1.18	

TABLE 5

BOND ANGLES (°) FOR $[(Ph_3P)_2N][Os_{10}C(CO)_{23}(NO)]$ (**2**)

Os(3)–Os(1)–Os(2)	62.3(1)	Os(4)–Os(1)–Os(2)	62.1(1)
Os(4)–Os(1)–Os(3)	62.6(1)	C(11)–Os(1)–Os(2)	95(2)
C(11)–Os(1)–Os(3)	156(1)	C(11)–Os(1)–Os(4)	101(1)
C(12)–Os(1)–Os(2)	107(2)	C(12)–Os(1)–Os(3)	96(2)
C(12)–Os(1)–Os(4)	159(2)		
C(13)–Os(1)–Os(2)	155(1)	C(13)–Os(1)–Os(3)	100(2)
C(13)–Os(1)–Os(4)	95(1)		
		Os(3)–Os(2)–Os(1)	58.8(1)
Os(4)–Os(2)–Os(1)	59.2(1)	Os(4)–Os(2)–Os(3)	60.4(1)
Os(5)–Os(2)–Os(1)	176.9(1)	Os(5)–Os(2)–Os(3)	118.2(1)
Os(5)–Os(2)–Os(4)	118.9(1)	Os(6)–Os(2)–Os(1)	118.5(1)
Os(6)–Os(2)–Os(3)	59.7(1)	Os(6)–Os(2)–Os(4)	90.3(1)
Os(6)–Os(2)–Os(5)	58.5(1)	Os(10)–Os(2)–Os(1)	119.2(1)
Os(10)–Os(2)–Os(3)	90.0(1)	Os(10)–Os(2)–Os(4)	60.0(1)
Os(10)–Os(2)–Os(5)	58.9(1)	Os(10)–Os(2)–Os(6)	60.2(1)
C(21)–Os(2)–Os(1)	92(2)	C(21)–Os(2)–Os(3)	148(2)
C(21)–Os(2)–Os(3)	94(2)	C(21)–Os(2)–Os(5)	90(2)
C(21)–Os(2)–Os(6)	146(1)	C(21)–Os(2)–Os(10)	93(1)
C(22)–Os(2)–Os(3)	95(2)	C(22)–Os(2)–Os(1)	89(2)
C(22)–Os(2)–Os(5)	93(2)	C(22)–Os(2)–Os(4)	146(2)
C(22)–Os(2)–Os(10)	150(2)	C(22)–Os(2)–Os(6)	97(2)
		Os(2)–Os(3)–Os(1)	58.8(1)
Os(4)–Os(3)–Os(1)	59.0(1)	Os(4)–Os(3)–Os(2)	59.8(1)
Os(6)–Os(3)–Os(1)	119.3(1)	Os(6)–Os(3)–Os(2)	60.4(1)
Os(6)–Os(3)–Os(4)	90.3(1)	Os(7)–Os(3)–Os(1)	177.7(1)
Os(7)–Os(3)–Os(2)	119.4(1)	Os(7)–Os(3)–Os(4)	119.0(1)
Os(7)–Os(3)–Os(6)	59.0(1)	Os(8)–Os(3)–Os(1)	119.2(1)
Os(8)–Os(3)–Os(2)	90.4(1)	Os(8)–Os(3)–Os(4)	60.2(1)
Os(8)–Os(3)–Os(6)	60.3(1)	Os(8)–Os(3)–Os(7)	58.8(1)
C(31)–Os(3)–Os(1)	91(2)	C(31)–Os(3)–Os(2)	96(1)
C(31)–Os(3)–Os(4)	147(1)	C(31)–Os(3)–Os(6)	95(2)
C(31)–Os(3)–Os(7)	91(2)	C(31)–Os(3)–Os(8)	147(2)
C(32)–Os(3)–Os(2)	147(1)	C(32)–Os(3)–Os(1)	91(1)
C(32)–Os(3)–Os(6)	147(1)	C(32)–Os(3)–Os(4)	95(1)
C(32)–Os(3)–Os(8)	94(1)	C(32)–Os(3)–Os(7)	90(1)
		Os(2)–Os(4)–Os(1)	58.7(4)
Os(3)–Os(4)–Os(1)	58.4(1)	Os(3)–Os(4)–Os(2)	59.7(1)
Os(8)–Os(4)–Os(1)	118.0(1)	Os(8)–Os(4)–Os(2)	90.0(1)
Os(8)–Os(4)–Os(3)	59.6(1)	Os(9)–Os(4)–Os(1)	176.3(1)
Os(9)–Os(4)–Os(2)	119.4(1)	Os(9)–Os(4)–Os(3)	117.9(1)
Os(9)–Os(4)–Os(8)	58.3(1)	Os(10)–Os(4)–Os(1)	119.0(1)
Os(10)–Os(4)–Os(2)	60.3(1)	Os(10)–Os(4)–Os(3)	89.8(1)
Os(10)–Os(4)–Os(8)	60.1(1)	Os(10)–Os(4)–Os(9)	59.1(1)
C(41)–Os(4)–Os(1)	90(2)	C(41)–Os(4)–Os(2)	148(2)
C(41)–Os(4)–Os(3)	101(2)	C(41)–Os(4)–Os(8)	101(2)
C(41)–Os(4)–Os(9)	91(2)	C(41)–Os(4)–Os(10)	150(2)
C(42)–Os(4)–Os(2)	93(2)	C(42)–Os(4)–Os(1)	88(1)
C(42)–Os(4)–Os(8)	151(1)	C(42)–Os(4)–Os(3)	144(1)
C(42)–Os(4)–Os(10)	97(2)	C(42)–Os(4)–Os(9)	96(1)
		Os(6)–Os(5)–Os(2)	62.5(1)
Os(10)–Os(5)–Os(2)	62.4(1)	Os(10)–Os(5)–Os(6)	62.7(1)
C(51)–Os(5)–Os(2)	101(2)	C(51)–Os(5)–Os(6)	99(1)

TABLE 5 (continued)

C(51)–Os(5)–Os(10)	159(1)	C(52)–Os(5)–Os(2)	157(2)
C(52)–Os(5)–Os(6)	100(2)	C(52)–Os(5)–Os(10)	98(2)
C(53)–Os(5)–Os(6)	159(22)	C(53)–Os(5)–Os(2)	99(2)
		C(53)–Os(5)–Os(10)	101(2)
Os(3)–Os(6)–Os(2)	59.9(1)	Os(5)–Os(6)–Os(2)	59.0(1)
Os(5)–Os(6)–Os(3)	118.9(1)	Os(7)–Os(6)–Os(2)	118.9(1)
Os(7)–Os(6)–Os(3)	59.0(1)	Os(7)–Os(6)–Os(5)	177.3(1)
Os(8)–Os(6)–Os(2)	89.8(1)	Os(8)–Os(6)–Os(3)	59.9(1)
Os(8)–Os(6)–Os(5)	119.0(1)	Os(8)–Os(6)–Os(7)	58.6(1)
Os(10)–Os(6)–Os(2)	60.0(1)	Os(10)–Os(6)–Os(3)	90.0(1)
Os(10)–Os(6)–Os(5)	59.1(1)	Os(10)–Os(6)–Os(7)	118.6(1)
Os(10)–Os(6)–Os(8)	60.0(1)		
		C(61)–Os(6)–Os(2)	97(1)
C(61)–Os(6)–Os(3)	96(1)	C(61)–Os(6)–Os(5)	91(1)
C(61)–Os(6)–Os(7)	91(1)	C(61)–Os(6)–Os(8)	148(1)
C(61)–Os(6)–Os(10)	148(1)		
C(62)–Os(6)–Os(2)	147(1)	C(62)–Os(6)–Os(3)	148(2)
C(62)–Os(6)–Os(5)	91(1)	C(62)–Os(6)–Os(7)	91(1)
C(62)–Os(6)–Os(8)	95(2)	C(62)–Os(6)–Os(10)	95(2)
Os(6)–Os(7)–Os(3)	62.0(1)	Os(8)–Os(7)–Os(3)	62.2(1)
Os(8)–Os(7)–Os(6)	62.5(1)	C(71)–Os(7)–Os(3)	97(1)
C(71)–Os(7)–Os(6)	97(1)	C(71)–Os(7)–Os(8)	155(1)
C(72)–Os(7)–Os(3)	156(1)	C(72)–Os(7)–Os(6)	98(1)
C(72)–Os(7)–Os(8)	97(1)		
C(73)–Os(7)–Os(3)	104(2)	C(73)–Os(7)–Os(6)	162(2)
C(73)–Os(7)–Os(8)	102(2)		
		Os(4)–Os(8)–Os(3)	60.2(1)
Os(6)–Os(8)–Os(3)	59.7(1)	Os(6)–Os(8)–Os(4)	89.9(1)
Os(7)–Os(8)–Os(3)	59.0(1)	Os(7)–Os(8)–Os(4)	119.2(1)
Os(7)–Os(8)–Os(6)	58.9(1)	Os(9)–Os(8)–Os(3)	119.1(1)
Os(9)–Os(8)–Os(4)	58.8(1)	Os(9)–Os(8)–Os(6)	119.3(1)
Os(9)–Os(8)–Os(7)	177.7(1)	Os(10)–Os(8)–Os(3)	90.0(1)
Os(10)–Os(8)–Os(4)	59.8(1)	Os(10)–Os(8)–Os(6)	60.2(1)
Os(10)–Os(8)–Os(7)	119.1(1)	Os(10)–Os(8)–Os(9)	59.1(1)
C(81)–Os(8)–Os(3)	150(1)	C(81)–Os(8)–Os(4)	148(1)
C(81)–Os(8)–Os(6)	100(1)	C(81)–Os(8)–Os(7)	92(1)
C(81)–Os(8)–Os(9)	90(1)	C(81)–Os(8)–Os(10)	99(1)
		C(82)–Os(8)–Os(3)	97(1)
C(82)–Os(8)–Os(4)	98(1)	C(82)–Os(8)–Os(6)	147(1)
C(82)–Os(8)–Os(7)	90(1)	C(82)–Os(8)–Os(9)	91(1)
C(82)–Os(8)–Os(10)	149(1)		
		Os(8)–Os(9)–Os(4)	62.8(1)
Os(10)–Os(9)–Os(4)	62.2(1)	Os(10)–Os(9)–Os(8)	62.6(1)
C(91)–Os(9)–Os(4)	156(1)	C(91)–Os(9)–Os(8)	100(1)
C(91)–Os(9)–Os(10)	99(1)	C(92)–Os(9)–Os(4)	99(2)
C(92)–Os(9)–Os(8)	99(2)	C(92)–Os(9)–Os(10)	158(2)
C(93)–Os(9)–Os(8)	156(2)	C(93)–Os(9)–Os(4)	97(2)
		C(93)–Os(9)–Os(10)	97(2)
Os(4)–Os(10)–Os(2)	59.7(1)	Os(5)–Os(10)–Os(2)	58.7(1)
Os(5)–Os(10)–Os(4)	118.4(1)	Os(6)–Os(10)–Os(2)	59.8(1)
Os(6)–Os(10)–Os(4)	89.9(1)	Os(6)–Os(10)–Os(5)	58.3(1)
Os(8)–Os(10)–Os(2)	89.6(1)	Os(8)–Os(10)–Os(4)	60.1(1)
Os(8)–Os(10)–Os(5)	118.1(1)	Os(8)–Os(10)–Os(6)	59.8(1)

(continued)

TABLE 5 (continued)

Os(9)–Os(10)–Os(2)	118.3(1)	Os(9)–Os(10)–Os(4)	58.7(1)
Os(9)–Os(10)–Os(5)	175.9(1)	Os(9)–Os(10)–Os(6)	118.0(1)
Os(9)–Os(10)–Os(8)	58.2(1)		
C(01)–Os(10)–Os(4)	96(1)	C(01)–Os(10)–Os(2)	96(1)
C(01)–Os(10)–Os(6)	147(1)	C(01)–Os(10)–Os(5)	91(1)
C(01)–Os(10)–Os(9)	92(1)	C(01)–Os(10)–Os(8)	148(1)
C(02)–Os(10)–Os(2)	145(2)	C(02)–Os(10)–Os(4)	149(1)
C(02)–Os(10)–Os(5)	89(2)	C(02)–Os(10)–Os(6)	94(1)
C(02)–Os(10)–Os(8)	96(1)	C(02)–Os(10)–Os(9)	93(2)

$[Ph_4As]^+$ salt) has one slightly enlarged capping group (mean Os–Os 2.856 Å) thought to incorporate the interstitial hydrogen ligand, and three equivalent smaller capping groups (mean Os–Os 2.838 Å) [16]. The nitrosyl monoanion **2** has slightly smaller capping groups with a mean Os–Os bond length for four capping groups in the range 2.823 to 2.837 Å giving a overall of mean 2.380 Å. As the maximum e.s.d. for the Os–Os bonds in these two structures is 0.002 Å the differences between the capping groups in the two monoanions are significant.

The site (or sites) of electrophilic addition of reagents such as NO^+ has not been established with certainty. It might be expected that the position of attack will be at the metal atom with the highest connectivity. However, it is also possible that attack may occur on a metal–metal bond to produce a μ_2-NO species. The observations reported here of initial formation of μ_2-NO complex in **1** tend to support this suggestion since attack directly at a metal atom would be expected to bring about CO ejection and the immediate formation of the terminal NO complex **2**, which is the normal behaviour of the nitrosyl ligand. The fact that the compound initially produced, **1**, and then undergoes further reaction to displace CO and form a terminal NO ligand indicates a balance between a μ_2-NO group with no M–M bond and a terminal NO ligand together with a M–M bond. In this connection it is interesting to note that treatment of the monoanions $[Fe_4N(CO)_{12}]^-$ and $[Ru_6C(CO)_{15}(NO)]^-$ with NO^+ gives the species $Fe_4N(CO)_{11}(NO)$ [5] and $Ru_6C(CO)_{14}(NO)_2$ [7], respectively, in which the nitrosyl ligands are coordinated in a terminal fashion. In these cases it is possible that the reactions proceed via the intermediate formation of compounds related to $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ which contain bridging NO ligands.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 257 instrument using carbon monoxide gas calibrant (central position 2143 cm^{-1}). Thin layer chromatography plates were brought from Merck and consisted of 20 × 20 cm glass plates coated with a 0.25 mm layer of silica gel. Acetonitrile (A.R. grade) was distilled from P_2O_5 prior to use. All reactions were carried out under an atmosphere of nitrogen.

Preparation of $[X][Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]$ *(X =* $(Ph_3P)_2N$, Ph_3MeP, *or* Ph_4As*)*

The dark red salt $[X]_2[Os_{10}C(CO)_{24}]$ (70 mg) was dissolved in MeCN (60 cm^3) and 1 equivalent of freshly sublimed $NOBF_4$ was added as a solid. Removal of the solvent under vacuum followed by TLC of the residue using CH_2Cl_2 as eluent gave a red band as the only product. Crystals were obtained overnight in 85–90% yield from CH_2Cl_2/hexane at 25°C using the slow evaporation technique; these were characterised as the salt $[X][Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]$ on the basis of spectroscopic (Table 1) and microanalytical data ($[Ph_3MeP]^+$ salt, Found: C, 18.16; H, 0.62; N, 0.46. $C_{44}H_{18}NO_{25}Os_{10}P$ calcd.: C, 18.26; H, 0.63; N, 0.48%), and by a full single crystal X-ray structure analysis of the $[(Ph_3P)_2N]^+$ salt. The anion $[Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]^-$ rearranges and loses CO on standing in solution (vide infra). Addition of excess $NOBF_4$ to solutions of $[X]_2[Os_{10}C(CO)_{24}]$ in MeCN gives an insoluble purple-brown solid which is tentatively formulated as $Os_{10}C(CO)_{24}(\mu_2\text{-}NO)_2$ on the basis of microanalytical data.

Synthesis of $[X][Os_{10}C(CO)_{23})(NO)]$ *(*$X = (Ph_3P)_2N$*,* Ph_3MeP *or* Ph_4As*)*

Allowing solutions of $[X][Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]$ in CH_2Cl_2/hexane to evaporate slowly over a period of ca. ten days at ~ 0°C gives dark red crystals of $[X][Os_{10}C(CO)_{23}(NO)]$ in moderate (~ 30%) yield. These were characterised on the basis of spectroscopic (Table 1) and microanalytical data ($[(Ph_3P)_2N]^+$ salt, CH_2Cl_2 solvate, Found: C, 23.21; H, 0.89; N, 0.87. $C_{60}H_{30}N_2O_{24}Os_{10}P_2 \cdot CH_2Cl_2$ calcd.: C, 22.81; H, 1.00; N, 0.87%) and by a full single crystal X-ray structure analysis of the $[(Ph_3P)_2N]^+$ salt (as its CH_2Cl_2 solvate).

Crystal data

For 1. $C_{36}H_{30}NP_2 \cdot C_{25}NO_{25}Os_{10}$, $M = 3154.86$, Triclinic, space group $P\bar{1}$, a 20.389(4), b 14.670(3), c 12.333(3) Å, α 99.55(3), β 94.43(3), γ 103.03(3)°, V 3518.77 Å^3, $Z = 2$, $F(000) = 2800$, D_c 2.977 g cm^{-3}, μ(Mo-K_α) 173.85 cm^{-1}, Mo-K_α radiation, λ 0.71069 Å.

For 2. $C_{36}H_{30}NP_2 \cdot C_{24}NO_{24}Os_{10} \cdot CH_2Cl_2$, $M = 3211.85$, Triclinic, space group $P\bar{1}$, a 19.374(3), b 16.813(3), c 11.791(2) Å, α 85.00(3), β 101.81(3), γ 99.43(3)°, V 3702.91 Å^3, $Z = 2$, $F(000) = 2902$, D_c 2.879 g cm^{-3}, μ(Mo-K_α) 166.24 cm^{-1}, Mo-K_α radiation, λ 0.71069 Å.

The methods of data collection, data processing, and absorption correction used for the salts **1** and **2** were similar to those described previously [15]. The crystals selected for data collection had dimensions $0.24 \times 0.20 \times 0.17$ mm for **1** and $0.33 \times 0.22 \times 0.19$ mm for **2**. A scan width of 0.80° was used to collect data in the θ range 3–25.0° for both crystals. 213 Azimuthal scan data for **1** and 386 for **2** were used in absorption correction and relative transmission factors varied from 1.00 to 0.63 for **1** and 1.00 to 0.43 for **2**. Equivalent reflections were averaged to give 2699 and 8736 data with $I/\sigma(I) > 3.0$ for **1** and **2** respectively. The crystals of **1**, which were obtained with great difficulty, diffracted rather poorly and the crystals of both compounds decomposed slightly in and the X-ray beam (ca. 10%).

Structure solution and refinement [17]

For both **1** and **2** the position of six osmium atoms (defining an octahedron) were found from Patterson syntheses. The remaining osmium atoms together with the other non-hydrogen atoms were found from subsequent difference-Fourier syntheses. Blocked full matrix refinement of the atomic positional and thermal parameters converged at final R and R_w values of 0.0952 and 0.0914 for **1** and 0.0943 and 0.0943 for **2**. The phenyl groups were treated as rigid hexagons (d(C–C) 1.395 Å)

(Continued on p. 188)

TABLE 6

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS (Å^2) FOR $[(Ph_3P)_2N][Os_{10}C(CO)_{24}(\mu_2\text{-}NO)]$ (**1**)

Atom	x	y	z	U_{iso} or U_{eq}
Os(1)	0.1151(2)	−0.0964(3)	0.1059(3)	0.031(3)
Os(2)	0.1039(2)	−0.1106(3)	0.3349(3)	0.033(3)
Os(3)	0.1009(2)	−0.2805(3)	0.1660(3)	0.035(3)
Os(4)	0.2193(2)	−0.1961(3)	0.3393(4)	0.037(2)
Os(5)	0.2287(2)	−0.1790(3)	0.1083(3)	0.032(3)
Os(6)	0.2314(2)	−0.0110(3)	0.2728(3)	0.033(3)
Os(7)	0.1178(2)	0.0654(3)	0.2628(3)	0.026(3)
Os(8)	0.1146(2)	−0.2553(3)	−0.0546(3)	0.035(3)
Os(9)	0.3421(2)	−0.0864(3)	0.2641(4)	0.042(3)
Os(0)	0.0509(3)	−0.3009(4)	0.3731(4)	0.037(3)
P(1)	0.5482(14)	0.6202(18)	0.3167(21)	0.039(18)
P(2)	0.6758(13)	0.5492(18)	0.3190(21)	0.037(18)
Os(7A) [a]	0.1283(4)	0.0890(4)	0.3268(6)	0.045(8)
Os(0A) [a]	0.0910(6)	−0.2952(43)	0.3833(51)	0.045(8)
C	0.1689(37)	−0.1408(48)	0.2282(55)	0.000(17)
N(1)	0.1549(37)	−0.2891(50)	0.4186(57)	0.032(22)
O(1)	0.1742(38)	−0.3220(52)	0.4977(60)	0.073(25)
C(11)	0.0300(56)	−0.0984(72)	0.0581(81)	0.052(32)
O(11)	−0.0329(33)	−0.1252(43)	0.0337(48)	0.041(18)
C(12)	0.1489(61)	−0.0057(82)	0.0112(96)	0.064(39)
O(12)	0.1670(42)	0.0265(57)	−0.0605(67)	0.080(27)
C(21)	0.0083(12)	−0.1011(61)	0.3307(48)	0.051(30)
O(21)	−0.0490(11)	−0.1027(56)	0.3250(55)	0.096(27)
C(22)	0.1134(58)	−0.0666(29)	0.4981(7)	0.064(35)
O(22)	0.1346(39)	−0.0266(40)	0.5899(11)	0.075(24)
C(31)	0.1152(59)	−0.3961(84)	0.1481(91)	0.068(37)
O(31)	0.1303(37)	−0.4795(52)	0.1338(57)	0.067(22)
C(32)	0.0052(13)	−0.3302(78)	0.1003(64)	0.087(40)
O(32)	−0.0513(12)	−0.3595(59)	0.0634(60)	0.109(32)
C(41)	0.2726(56)	−0.1312(76)	0.4753(90)	0.057(33)
O(41)	0.2963(41)	−0.0954(57)	0.5701(66)	0.086(26)
C(42)	0.2645(44)	−0.3029(44)	0.3191(79)	0.092(41)
O(42)	0.2946(32)	−0.3612(35)	0.3012(54)	0.080(24)
C(51)	0.2805(33)	−0.1084(73)	0.0077(86)	0.043(32)
O(51)	0.2961(39)	−0.0744(53)	−0.0542(61)	0.067(24)
C(52)	0.2593(43)	−0.2804(59)	0.0513(65)	0.021(24)
O(52)	0.2793(36)	−0.3618(50)	0.0322(55)	0.066(22)
C(61)	0.2768(44)	0.0826(59)	0.1991(67)	0.018(23)
O(61)	0.3060(33)	0.1304(45)	0.1414(50)	0.048(19)
C(62)	0.2606(53)	0.0819(73)	0.4104(85)	0.050(32)
O(62)	0.2815(37)	0.1192(51)	0.5083(60)	0.066(22)
C(71)	0.0288(57)	0.0696(73)	0.2355(83)	0.053(32)
O(71)	−0.0285(34)	0.0751(44)	0.2079(50)	0.048(19)
C(72)	0.1496(61)	0.1773(85)	0.1996(95)	0.064(38)
O(72)	0.1755(40)	0.2309(56)	0.1538(62)	0.073(25)
C(73)	0.1284(50)	0.1570(7)	0.4186(82)	0.040(29)
O(73)	0.1402(40)	0.1877(56)	0.4971(65)	0.073(25)
C(81)	0.0204(19)	−0.2763(31)	−0.1249(81)	0.061(34)
O(81)	−0.0347(14)	−0.2962(45)	−0.1694(59)	0.089(27)
C(82)	0.1457(49)	−0.2042(40)	−0.1864(54)	0.059(35)
O(82)	0.1794(38)	−0.1573(48)	−0.2418(46)	0.104(29)

TABLE 6 (continued)

Atom	x	y	z	U_{iso} or U_{eq}
C(83)	0.1176(50)	−0.3745(71)	−0.1230(78)	0.044(29)
O(83)	0.1335(45)	−0.4451(64)	−0.1582(69)	0.105(30)
C(91)	0.3872(60)	−0.0273(83)	0.3981(97)	0.064(37)
O(91)	0.4204(44)	0.0086(60)	0.4831(71)	0.095(29)
C(92)	0.4027(52)	−0.0093(71)	0.2012(82)	0.047(31)
O(92)	0.4286(36)	0.0355(48)	0.1363(56)	0.064(23)
C(93)	0.3955(64)	−0.1738(90)	0.2165(97)	0.077(41)
O(93)	0.4190(39)	−0.2287(54)	0.2173(59)	0.070(24)
C(01)	−0.0398(51)	−0.3061(65)	0.3153(73)	0.036(27)
O(01)	−0.1012(49)	−0.3219(63)	0.2868(71)	0.109(31)
C(02)	0.0234(59)	−0.4400(87)	0.3645(90)	0.077(38)
O(02)	0.0153(46)	−0.5299(68)	0.3494(71)	0.107(31)
C(03)	0.0343(25)	−0.2846(56)	0.5307(10)	0.011(23)
O(03)	0.0215(34)	−0.2597(59)	0.6204(18)	0.104(29)
N(2)	0.6133(38)	0.5740(50)	0.3510(56)	0.046(22)
C(112)	0.6076(35)	0.7578(55)	0.0653(41)	0.136(56)
C(113)	0.6235(35)	0.8546(55)	0.1121(41)	0.073(36)
C(114)	0.6140(35)	0.8838(55)	0.2221(41)	0.085(38)
C(115)	0.5886(35)	0.8162(55)	0.2853(41)	0.153(56)
C(116)	0.5728(35)	0.7194(55)	0.2385(41)	0.013(20)
C(111)	0.5823(35)	0.6902(55)	0.1286(41)	0.056(30)
C(122)	0.4611(32)	0.4459(49)	0.2709(46)	0.075(37)
C(123)	0.4005(32)	0.3811(49)	0.2233(46)	0.058(32)
C(124)	0.3585(32)	0.4041(49)	0.1427(46)	0.106(45)
C(125)	0.3771(32)	0.4919(49)	0.1096(46)	0.065(33)
C(126)	0.4377(32)	0.5567(49)	0.1572(46)	0.065(32)
C(121)	0.4797(32)	0.5337(49)	0.2378(46)	0.050(29)
C(132)	0.4566(26)	0.6792(37)	0.4422(41)	0.041(26)
C(133)	0.4350(26)	0.7276(37)	0.5345(41)	0.057(31)
C(134)	0.4816(26)	0.7758(37)	0.6261(41)	0.062(31)
C(135)	0.5500(26)	0.7755(37)	0.6254(41)	0.050(30)
C(136)	0.5716(26)	0.7270(37)	0.5331(41)	0.021(22)
C(131)	0.5250(26)	0.6789(37)	0.4415(41)	0.030(23)
C(212)	0.7492(29)	0.5866(30)	0.1375(48)	0.043(26)
C(213)	0.7897(29)	0.6479(30)	0.0806(48)	0.052(29)
C(214)	0.8048(29)	0.7462(30)	0.1189(48)	0.064(32)
C(215)	0.7794(29)	0.7831(30)	0.2139(48)	0.041(27)
C(216)	0.7389(29)	0.7218(30)	0.2707(48)	0.075(35)
C(211)	0.7238(29)	0.6235(30)	0.2325(48)	0.033(24)
C(222)	0.6883(27)	0.3501(43)	0.2665(44)	0.082(38)
C(223)	0.6650(27)	0.2562(43)	0.2098(44)	0.033(24)
C(224)	0.6090(27)	0.2317(43)	0.1291(44)	0.073(35)
C(225)	0.5763(27)	0.3011(43)	0.1050(44)	0.087(40)
C(226)	0.5996(27)	0.3950(43)	0.1617(44)	0.077(37)
C(221)	0.6556(27)	0.4195(43)	0.2425(44)	0.031(24)
C(232)	0.7989(31)	0.5577(40)	0.4254(38)	0.045(26)
C(233)	0.8448(31)	0.5625(40)	0.5172(38)	0.068(34)
C(234)	0.8235(31)	0.5675(40)	0.6224(38)	0.053(29)
C(235)	0.7562(31)	0.5679(40)	0.6356(38)	0.079(36)
C(236)	0.7103(31)	0.5631(40)	0.5437(38)	0.061(31)
C(231)	0.7316(31)	0.5580(40)	0.4386(38)	0.030(24)

[a] The osmium atoms labelled Os(7A) and Os(0A) correspond to a 10% disorder of the site of attachment of the μ-NO ligand (see Experimental).

TABLE 7

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS (Å^2) FOR $[(Ph_3P)_2N][Os_{10}C(CO)_{23}(NO)]$ (**2**)

Atom	x	y	z	U_{iso} or U_{eq}
Os(1)	0.50876(8)	0.09895(9)	0.76631(13)	0.0305(8)
Os(2)	0.36510(8)	0.11284(8)	0.73665(13)	0.0278(7)
Os(3)	0.47324(8)	0.25236(9)	0.76598(13)	0.0276(7)
Os(4)	0.44338(8)	0.16678(9)	0.55487(13)	0.0308(8)
Os(5)	0.22283(8)	0.13579(10)	0.70362(15)	0.0370(9)
Os(6)	0.32606(8)	0.27151(9)	0.73416(14)	0.0323(8)
Os(7)	0.43322(8)	0.40467(8)	0.75836(13)	0.0295(8)
Os(8)	0.40515(8)	0.32620(8)	0.55247(13)	0.0279(7)
Os(9)	0.37637(9)	0.24219(10)	0.35238(13)	0.0345(8)
Os(10)	0.29552(8)	0.18659(10)	0.52200(14)	0.0319(8)
P(1)	0.8981(5)	0.3016(5)	0.0492(8)	0.024(4)
P(2)	0.8630(5)	0.3655(6)	0.2525(8)	0.029(5)
C	0.3829(71)	0.2184(19)	0.6457(27)	0.019(6)
C(11)	0.4937(26)	−0.0088(29)	0.7358(42)	0.038(11)
O(11)	0.4909(23)	−0.0822(26)	0.7290(38)	0.064(11)
C(12)	0.5419(31)	0.0874(34)	0.9213(52)	0.048(14)
O(12)	0.5616(30)	0.0829(33)	1.0212(50)	0.074(16)
C(13)	0.6003(27)	0.1246(30)	0.7372(44)	0.039(11)
O(13)	0.6570(31)	0.1315(34)	0.7043(50)	0.097(17)
C(21)	0.3368(26)	0.0073(30)	0.6853(43)	0.044(11)
O(21)	0.3162(32)	−0.0614(37)	0.6688(52)	0.090(18)
C(22)	0.3705(36)	0.0865(40)	0.8957(61)	0.050(17)
O(22)	0.3748(23)	0.0784(26)	0.9942(38)	0.058(11)
C(31)	0.4892(26)	0.2464(29)	0.9271(43)	0.038(11)
O(31)	0.4923(22)	0.2411(25)	1.0269(37)	0.057(11)
C(32)	0.5681(25)	0.3012(27)	0.7490(40)	0.031(10)
O(32)	0.6266(30)	0.3227(33)	0.7515(47)	0.075(16)
C(41)	0.5307(29)	0.1908(32)	0.5084(47)	0.046(12)
O(41)	0.5857(32)	0.2159(35)	0.4803(51)	0.080(17)
C(42)	0.4286(27)	0.0645(31)	0.4966(44)	0.036(12)
O(42)	0.4139(19)	0.0011(21)	0.4611(30)	0.052(9)
C(51)	0.2062(27)	0.1187(30)	0.8517(45)	0.046(12)
O(51)	0.2008(23)	0.1099(26)	0.9487(39)	0.070(11)
C(52)	0.1450(32)	0.1835(36)	0.6483(52)	0.066(15)
O(52)	0.0857(22)	0.2130(24)	0.6106(36)	0.072(10)
C(53)	0.1795(37)	0.0337(43)	0.6607(60)	0.081(18)
O(53)	0.1537(31)	−0.0299(36)	0.6341(50)	0.090(17)
C(61)	0.3225(23)	0.2693(26)	0.8899(38)	0.040(10)
O(61)	0.3171(17)	0.2648(19)	0.9853(29)	0.063(8)
C(62)	0.2637(26)	0.3314(29)	0.6891(41)	0.048(12)
O(62)	0.2172(20)	0.3779(23)	0.6531(33)	0.070(11)
C(71)	0.4422(21)	0.4109(24)	0.9140(35)	0.034(9)
O(71)	0.4457(20)	0.4241(22)	1.0118(32)	0.069(10)
C(72)	0.3760(22)	0.4861(24)	0.7060(35)	0.033(9)
O(72)	0.3487(21)	0.5426(24)	0.6693(34)	0.088(11)
C(73)	0.5133(29)	0.4733(32)	0.7454(47)	0.070(14)
O(73)	0.5706(19)	0.5105(21)	0.7381(31)	0.060(10)
C(81)	0.3529(22)	0.4033(25)	0.4757(36)	0.042(10)
O(81)	0.3109(24)	0.4463(27)	0.4321(39)	0.075(13)
C(82)	0.4864(24)	0.3844(27)	0.5117(39)	0.050(11)
O(82)	0.5394(19)	0.4165(21)	0.4905(30)	0.055(9)
C(91)	0.3156(20)	0.3030(22)	0.2589(32)	0.036(8)

TABLE 7 (continued)

Atom	x	y	z	U_{iso} or U_{eq}
O(91)	0.2790(20)	0.3428(22)	0.1921(33)	0.072(10)
C(92)	0.4572(33)	0.2859(36)	0.2910(52)	0.066(16)
O(92)	0.5029(25)	0.3144(27)	0.2497(39)	0.080(13)
C(93)	0.3515(31)	0.1532(36)	0.2674(50)	0.097(15)
O(93)	0.3329(24)	0.0913(28)	0.2175(40)	0.100(14)
C(01)	0.2583(21)	0.0889(24)	0.4488(34)	0.043(9)
O(01)	0.2371(20)	0.0273(23)	0.4070(33)	0.075(10)
C(02)	0.2236(25)	0.2423(27)	0.4535(41)	0.042(11)
O(02)	0.1757(24)	0.2737(27)	0.3967(39)	0.086(13)
N(1)	0.9025(14)	0.3168(16)	0.1810(24)	0.031(6)
C(111)	0.8648(10)	0.3775(10)	−0.0515(16)	0.014(5)
C(112)	0.8037(10)	0.3635(10)	−0.1378(16)	0.045(10)
C(113)	0.7795(10)	0.4278(10)	−0.2094(16)	0.044(10)
C(114)	0.8162(10)	0.5059(10)	−0.1949(16)	0.043(9)
C(115)	0.8773(10)	0.5198(10)	−0.1086(15)	0.043(12)
C(116)	0.9016(10)	0.4556(10)	−0.0370(16)	0.017(6)
C(121)	0.9850(9)	0.2948(14)	0.0268(19)	0.022(7)
C(122)	1.0353(9)	0.2666(14)	0.1171(19)	0.037(8)
C(123)	1.1023(9)	0.2579(14)	0.0978(19)	0.050(9)
C(124)	1.1190(9)	0.2774(14)	−0.0118(19)	0.044(10)
C(125)	1.0687(9)	0.3056(14)	−0.1021(19)	0.057(12)
C(126)	1.0017(9)	0.3143(14)	−0.0828(19)	0.054(11)
C(131)	0.8442(14)	0.2054(13)	0.0119(22)	0.036(14)
C(132)	0.8449(14)	0.1749(13)	−0.0941(22)	0.036(8)
C(133)	0.8013(14)	0.1031(13)	−0.1279(22)	0.044(9)
C(134)	0.7569(14)	0.0617(13)	−0.0557(22)	0.052(10)
C(135)	0.7562(14)	0.0921(13)	0.0502(22)	0.059(10)
C(136)	0.7998(14)	0.1640(13)	0.0841(22)	0.041(9)
C(211)	0.9223(13)	0.4539(12)	0.3051(22)	0.044(11)
C(212)	0.8994(12)	0.5109(12)	0.3625(22)	0.038(9)
C(213)	0.9463(12)	0.5797(12)	0.4006(22)	0.056(11)
C(214)	1.0160(12)	0.5916(12)	0.3814(22)	0.038(8)
C(215)	1.0389(12)	0.5346(12)	0.3240(22)	0.060(12)
C(216)	0.9920(12)	0.4657(12)	0.2859(22)	0.034(8)
C(221)	0.7798(14)	0.3960(18)	0.1830(26)	0.069(11)
C(222)	0.7767(14)	0.4719(18)	0.1256(26)	0.056(11)
C(223)	0.7144(14)	0.4875(18)	0.0498(26)	0.062(15)
C(224)	0.6552(14)	0.4272(18)	0.0313(26)	0.083(22)
C(225)	0.6583(14)	0.3513(18)	0.0887(26)	0.087(17)
C(226)	0.7206(14)	0.3357(18)	0.1646(26)	0.072(16)
C(231)	0.8420(20)	0.3009(21)	0.3770(28)	0.070(13)
C(232)	0.8701(20)	0.2292(21)	0.4095(28)	0.088(17)
C(233)	0.8540(20)	0.1826(21)	0.5071(28)	0.122(19)
C(234)	0.8098(20)	0.2076(21)	0.5722(28)	0.084(16)
C(235)	0.7817(20)	0.2793(21)	0.5398(28)	0.095(19)
C(236)	0.7978(20)	0.3260(21)	0.4422(28)	0.125(21)
C(1s)[a]	0.0177(51)	0.0093(57)	0.1852(88)	0.065(23)
Cl(1s)	−0.0502(9)	0.0555(10)	0.1448(15)	0.063(4)
Cl(2s)	0.0953(11)	0.0469(12)	0.1555(18)	0.067(5)
Cl(3s)	0.0004(12)	−0.0941(14)	0.1881(20)	0.082(5)
Cl(2s)	0.0300(51)	0.0245(57)	0.2519(88)	0.082(23)
Cl(4s)	0.0354(27)	−0.0049(30)	0.3536(44)	0.077(12)
Cl(5s)	0.0505(25)	0.0881(28)	0.3523(40)	0.069(11)

[a] Atoms labelled with s refer to the solvate molecule of CH_2Cl_2 which is disordered over two sites.

and the hydrogen atoms were included in the structure factor calculations at calculated positions with d(C–H) 1.08 Å. Anisotropic thermal parameters were assigned to the Os and P atoms in the final cycles of refinement for both **1** and **2**. For **1** there is a slight disorder corresponding to 10% of a second orientation of the cluster in which the μ-NO bridged 'butterfly' group interchanges with a capping Os_4 tetrahedron in such a way that the metal atom positions are virtually the same in both orientations except for Os(7) and Os(0). The light atoms of the minor component of the disorder were not located. For **2** there was a disorder of the CH_2Cl_2 solvate molecule. The poor diffraction by the crystals of the $[(Ph_3P)_2N]^+$ salt of **1**, the slight decomposition in the X-ray beam and the disorder of the cluster all contribute to the relatively high e.s.d.'s obtained for the parameters of this structure. The principal features of this unusual cluster are however well established by this analysis. The data for the salt of **2** was much better than that for **1** but even so, in the presence of ten osmium atoms, it proved impossible to distinguish the N atom of the nitrosyl ligand from the C atom of the carbonyls on the basis of thermal parameters or bond lengths, but the important point that the NO ligand has adopted a terminal mode of bonding is clearly established.

Selected bond lengths for **1** and **2** are given in Tables 2 and 4 and the corresponding interbond angles in Tables 3 and 5 respectively. The final atomic coordinates for the anions in **1** and **2** are listed in Tables 6 and 7 respectively.

Supplementary data. Observed and calculated structure factors, thermal parameters, complete lists of bond lengths and angles, and full list of atomic coordinates for both **1** and **2**, are available from the authors (K.H.) *.

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* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, (Great Britain). Any request should be accompanied by the full literature citation for this paper.

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